

Graphitisation of carbon - a p,T-laboratory experiment

Georg Nover & Johannes Stoll*

Mineralogisch-Petrologisches Institut, Universität Bonn

* BGR, Hannover

Graphitisation of organic matter was studied under in-situ pressure and temperature conditions by means of X-ray diffraction and electrical conductivity measurements. Samples were an anthracite, a black shale and a synthetic calcite/anthracite mixture. The anthracite revealed a broad amorphous 002 reflection in energy dispersive X-ray diffraction experiments (EDX) before, while nearly perfect crystallised graphitic carbon was detected after the p-,T-treatment (pressure up to 0.6 GPa, temperature up to 500° C and reaction times of more than one month). The complex electrical conductivity was measured under in-situ p,T-conditions in the frequency range 0.7 up to 100 kHz. The bulk resistivity was decreased by about three orders in magnitude, and the complex response indicated "quasi-metallic" charge transport, as typical for well ordered and interconnected carbon planes. This result was improved by X-ray analysis of the sample, showing that the formerly random oriented carbon sheets were interconnected by application of pressure, stress, temperature and time.

Introduction

The effect of pressure and temperature on coalification and graphitisation.

Coalification is a maturation process of organic material by which randomly oriented aromatic lamella of the carbon network lost adsorbed volatiles. At the same time the degree of molecular ordering and of interconnection of the carbon-sheets is increased. Temperature accelerated chemical reactions during coalification, whereas pressure promotes a physico-structural organisation of the carbon network (Teichmüller&Teichmüller, 1982). Natural graphite is formed at temperatures as low as 300°-500° C and pressures of 0.4-0.5 GPa, that means upper green schist metamorphism, whereas graphitisation of high rank coal required in laboratory experiments much higher pressure and temperature conditions: Bituminous coal ("hard" coal) required temperatures around 2200° C if no pressure is applied, lignite or sub-bituminous coal, do not show graphitisation even at temperatures of up to 3000° C (Oberlin, 1984). Consequently, temperature alone could not be the only driving force causing graphitisation of organic matter (Bonijoly et al., 1982).

Application of pressure (0.5 GPa) allowed the formation of semi-graphite at temperatures of 1000° C, in contrast to temperatures of 2000° C without pressure. A further reduction in the required transformation pressure was observed by Wilks et al., (1993) when shear stress was applied (900° C, 1.0 GPa). An enhanced ordering of the graphite crystallinity was detected by an increase of the 002 graphite reflection intensity. This finding was improved by transmission electron microscopy (TEM) of tectonally deformed anthracite showing that stress/pressure beside temperature is required to align the "aromatic" lamella. Fonton et al., (1980) found that graphitisation develops discontinuously with sudden improvements in the degree of molecular ordering. The turbostratic structure of the anthracite disappears by partial graphitization. This first jump of graphitization requires high temperatures and pressures and is enhanced by shearing and stretching. Finally true graphite is formed through the attainment of three-dimensional arrangement of the layers, combined with the rapid increase of layer diameter to 5000 µm and more.

High electrical conductivity caused by graphite.

Electromagnetic surveys in central Europe have revealed deep seated crustal zones of regional extend high in electrical conductivity. These high conductive layers correlate with former sites of continent-continent collisions (ERCEUGT,1992; Volbers et al., 1990, Cazes et al., 1986; Haak et al., 1985; Ritter et al., 1999). They are typical for the Variscan crust that is formed by extensive

metamorphic blocks, which partly comprise reactivated pre-Variscan basement. The German Continental Deep-Drilling KTB is located in this area and revealed interconnected conductive graphitic veins and shear zones that were formed during retrograde metamorphism of high grade rocks containing disconnected graphite crystals (Zulauf, 1992; Kontny et al., 1997). In the cataclasites of these fault zones, graphite is associated with mineral assemblages suggesting deposition temperatures of graphite in the temperature range 250°-340° C and $p < 200$ MPa. This reconnected graphite extends over distances of at least some kilometres. This finding was confirmed in different scales by plug-, borehole measurements and the "mise-a-la-masse experiment" (ELEKTB, 1997; Stoll et al., 1992, 1995, 2000). Complex conductivity measurements performed on plus samples from the SE1 fault zones confirmed that an interconnected network of graphite is the cause for the high electrical conductivity of these samples (Nover et al., 1998).

Graphite in meta sedimentary strata is generally assumed to originate from progressive metamorphism of kerogen. This *biogenic* process of graphitisation is fairly well understood, but the crucial point of *abiotic* graphite precipitation is how the reduction or oxidation process of carbon rich fluids or gases worked in detail. Fluid inclusions in KTB showed coexistence of N₂, CH₄ and CO₂, whereas graphite exists only on shear planes. Thus Walther & Althaus (1993) concluded that graphite was precipitated from a methane-carbon-dioxide fluid. The activation energy for the reduction of CO₂ and the oxidation of CH₄ should be provided by heat generation during tectonic movement (mechanical-tribochemical-mechanism).

In this study we consider the problem of the formation of natural graphite and attempt to understand the manner in which pressure, shear stress or strain facilitates graphitization at lower temperatures. Using high confining pressures (up to 1 GPa), graphite has been formed at temperatures as low as 300-500° C.

Experimental

Sample description

The samples used in this study were an anthracite from the Ruhr mining area, Germany, a carbon rich black shale from the Konzen drilling V 21, Hohes Venn, Germany and a synthetic sample being a mixture of marble and anthracite (80/20 vol %). The black shale consists of approximately 55 % quartz, albite (30%), pyrite (10%) and less ordered graphite (5%). Differential Thermo Analysis (DTA) and Thermo Gravimetry (TG) were used to measure the loss of volatiles in the temperature range from 107° C up to 850° C.

Ex-situ analysis and in-situ energy dispersive x-ray diffraction (EDX) of HPHT experiments

Graphitisation of anthracite was performed in the pressure range 0.5 - 1.5 GPa at temperatures of 450° C - 1500° C in a piston-cylinder and a multi-anvil-device of hexaeder geometry. The reaction times were varied from minutes up to some hours to get an estimate for reaction kinetics for the transformation anthracite into graphite. The yield of the experiments was analysed by angle dispersive X-ray diffraction (Siemens D5000) of the recovered samples.

In-situ energy dispersive x-ray diffraction experiments were performed at the synchrotron radiation source at DESY, HASYLAB, Hamburg, Germany. A multi anvil device of MAX80 geometry was used. Energy dispersive X-ray diffraction experiments were done at 600° C and 0.7 GPa. Dispersion spectra were measured every 10 minutes for a period of 8 hours due to limitations in beam time and heating up of the device. In total we could measure and analyse more than 50 spectra.

Frequency dependent complex conductivity measurements at 0.7 GPa and 450° C

The electrical conductivity was measured on crushed powder samples in a piston cylinder apparatus (Fig. 3). The samples were pre compressed into pellets of 10 mm in diameter and about 4 mm high and placed in a high pressure cell assembly designed for electrical conductivity measurements. Pressure was increased up to 0.7 GPa and temperatures were raised stepwise (50° C) up to 450°-500° C. Heating of the sample was done with a graphite resistance furnace. The oxygen fugacity was defined by the graphite heater that acts a C-CO buffer. The temperature was measured by a NiCr-thermocouple and was kept constant using a computer controlled Eurotherm device. For each step in temperature and time the complex response of the sample was recorded in the frequency range 0.6 up to 100 kHz using a computer controlled lock-in-analyzer (PARC, EG&G). In semiconducting materials the electrical field is separated into a real part (conduction) and an imaginary part (dissipation), both being a function of frequency. Both components were measured and were interpreted on the basis of equivalent circuit models, namely RC-elements in series. This allowed to distinguish between electrolytic and metallic charge transport. Any variation in the degree of interconnection of the carbon network thus could be detected by a variation of the phase shift.

Results

Differential Thermo Analysis, Thermo Gravimetry (DTA/TG)

Volatiles like CO₂, CH₄ and hydrocarbons were removed from the carbon network in the temperature range 107° C up to 450° C. At lower temperatures light volatiles were removed, while higher temperatures were required to remove heavier hydrocarbons. The total weight loss was 9.9 weight % at 450° C, leaving back a less ordered network of carbon as detected by X-ray analysis. A low electrical conductivity was measured on the residual carbon of the DTA experiment and is confirmed by the X-ray analysis that did not show a sharp 002 graphite reflection.

X-ray Diffraction Analysis: ex-situ and in-situ

The ex-situ x-ray analysis of the starting materials revealed a broad 002 reflection for anthracite, thus indicating a low degree of ordering of the carbon layers. Graphitisation of anthracite was studied in the temperature and pressure range 1500° C - 450° C, 1.5 - 0.5 GPa. Reaction times required to complete the transformation were roughly one hour at temperatures above 900° C at a pressure of 1 GPa, whereas below 600° C reaction times can exceed some 100 hours without being completed. Thus a rough estimate for the reaction kinetics was derived by means of ex-situ x-ray diffraction analysis. A significant increase in the intensity of the 002 graphite reflection was detected when temperature and stress were applied. Consequently graphitisation has to be considered as a time-temperature-pressure dependent reaction. The in-situ energy dispersive x-ray diffraction experiments focussed on the detection of graphitisation under p,T-conditions of 650° C and 0.6 GPa. Within a time period of only 8 hours the analysis of the 002 reflection showed that the FWHM (full-width-half-maximum) decreased from 0.99 to 0.84, indicating that the parallel orientation of the hexagonal carbon rings and the degree of interconnection and was enhanced. This result encouraged us to perform electrical conductivity measurements at reduced temperatures >450° C and <500° C and pressures < 1 GPa.

Complex Electrical conductivity

Three samples different in carbon content were used for the graphitisation experiments. Thus we could check whether a reduced carbon concentration would impede the formation of an interconnected conductive network. In Figure 1 we have displayed the decrease of the bulk impedance (that was derived from the least-squares-refinement of model data to the measured data) as a function of time for the 100% anthracite sample. At ambient conditions the impedance exceeds 10⁵ ohm*m and decreases down to about 400 ohm*m when pressure and temperature of 450° C and 0.7 GPa were applied. This decrease is due to sintering of the powder sample. Pressure and temperature were then kept constant for approximately 200 hours and a continuous decrease of the impedance of more than one order in magnitude was detected. Stress was applied to the sample by cycling the uniaxial load and this caused a significant decrease of the impedance. An increase of the uniaxial load up to 0.75 GPa caused a reduction of the bulk impedance down to 2 ohm*m. A decrease of the bulk impedance by more than one order in magnitude down to 0.1 ohm*m could be detected (450° C, 1 GPa) when pressures were cycled from 0.7 up to 1 GPa. Temperature release increased the impedance up to 1 ohm*m, thus showing that temperature induced semiconduction still contributes to the total conductivity. In total the impedance of the sample was decreased by more than 3 orders in magnitude from 400 ohm*m down to 0.1 ohm*m for 450° C and 0.7 GPa pressure. Graphitisation of anthracite was evident from X-ray analysis of the recovered sample that exhibited well ordered graphite (Fig. 2) and thus confirmed the findings of the conductivity measurements where a change in charge transport from "semi"-conducting carbon into "metallic" conducting graphite was detected.

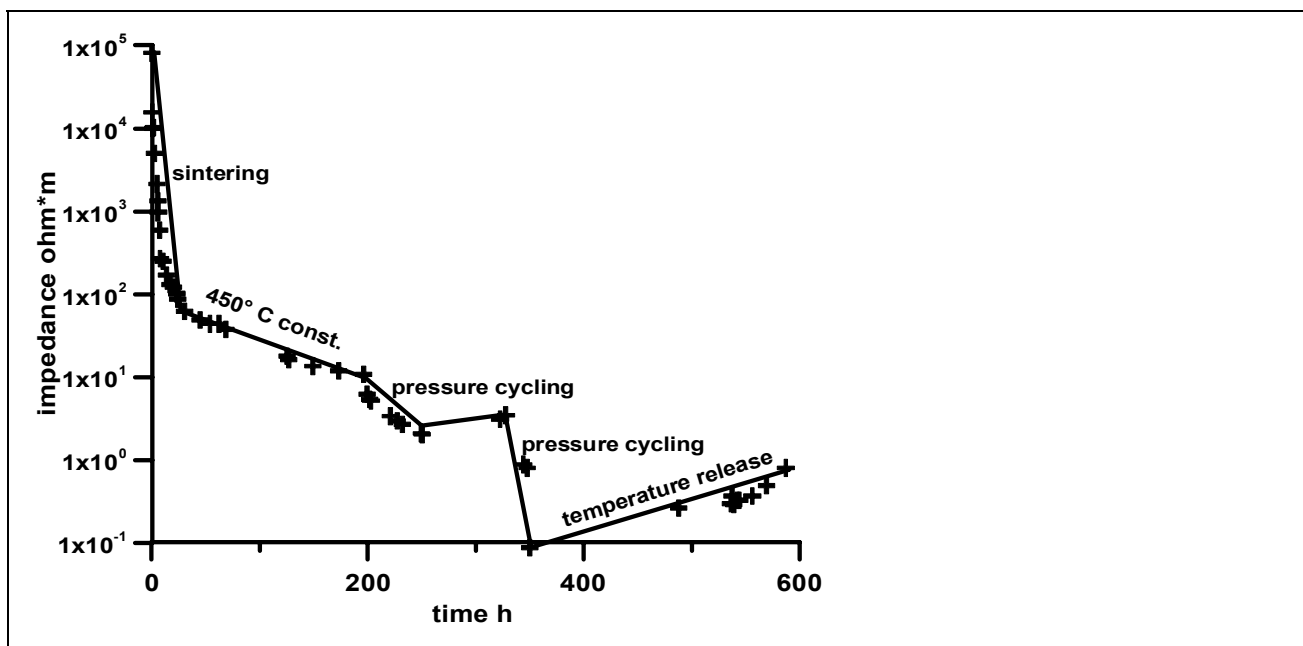


Fig. 1 Impedance of the pure anthracite versus time. The first sharp decrease of the impedance is due sintering at 450° C and 0.7 GPa pressure. Temperature alone decreases the impedance moderately, but stress causes a significant decrease. For further details see text.

The frequency dependence of the complex conductivity was measured in the frequency range 700 Hz up to 100 kHz for each step in time and as a result the charge transport varied from "electrolytic" to "metallic" conduction. This was derived from an least squares refinement of an equivalent circuit that was fitted to the measured data. The model consisted of an RC-parallel element (R2,C1) in series with the resistor R1, considering the cable impedance. R1 is constant within the error limits, while R2/C2 are related to the complex response of the sample. Figure 2 displays the X-ray diffraction diagram of the recovered sample: upper curve, broad 002 reflection, unprocessed; lower curve, sharp 002 graphite reflection as detected after the p,T treatment.

In the "synthetic sample" (80% calcite, 20% anthracite) the carbon concentration was reduced, but was still sufficient to form an interconnected highly conductive network. The overall result is comparable to that of the anthracite measurement. Again we could detect a decreases of the bulk impedance in the range of three orders in magnitude as a function of time, temperature, pressure and stress. Due to the higher experimental temperatures of 500° C reaction kinetics were faster.

The Konzen black-shale sample finally exhibited less than 10% carbon, but the bulk-impedance exhibits a similar time dependence as detected in the anthracite. It decreased by more than one order in magnitude for 400 hours experimental reaction time and fixed p,T conditions. Again, stress being induced by pressure cycling caused a further decrease of the impedance by one order in magnitude. At the same time the shape of the Cole-Cole-semicircles indicate a change of the charge transport to "quasi metallic" conduction.

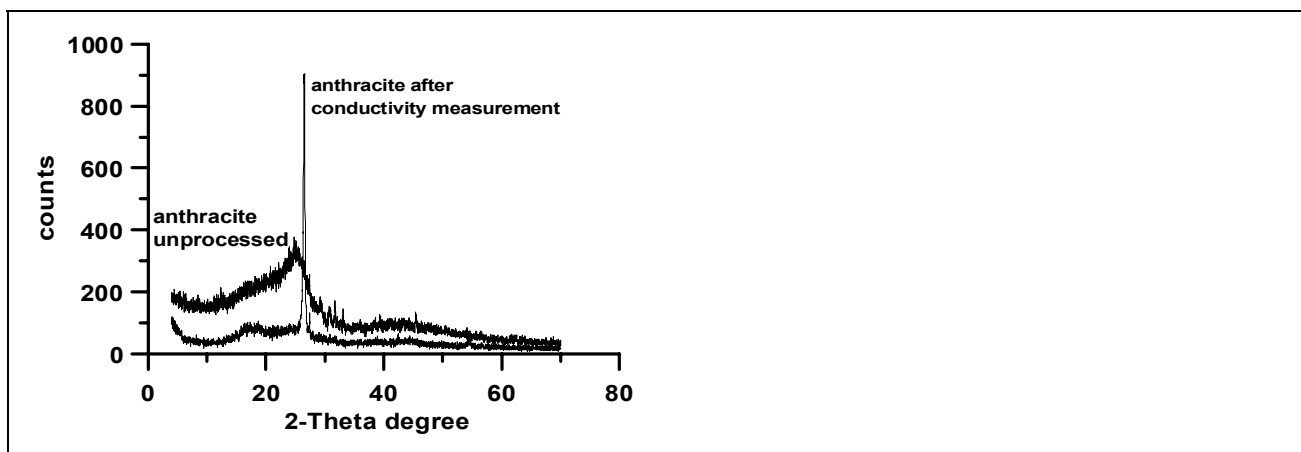


Fig. 2 X-ray diffraction diagram of the unprocessed anthracite and the diffraction diagram as recorded from the recovered sample after having finished the conductivity measurements.

Discussion

Graphitic conductors of up to tens of kilometres in length were detected in crustal rocks. These conductors are assumed to have remained in former collision zones, but the physical and chemical causes for transportation, precipitation and interconnection over distances of some km are not well understood in view of pressure-, temperature- and dynamic conditions during metamorphism in the past. Knowledge about graphite in the deep crust is based on a few deep drillings, e.g. the Münsterland I borehole and the German Deep Continental Drilling (KTB). Graphite found on shear planes indicated a formation of graphite through shear movement. Petrologists indirectly confirmed such ideas by using the different stages of graphitisation as an indicator for the grade of metamorphism (Diessel et al., 1978; Teichmüller, 1987). Bustin et al. (1995) showed that graphite formation is facilitated to a considerable degree by strain energy. Although low-grade metamorphism of rocks commonly corresponds to the rank stages of meta-anthracite and semi-graphite, temperatures of 350° C - 600° C may lead to the transformation of organic matter from the stage of meta-anthracite into graphite, especially under high pressure (Teichmüller, 1987). Basing on these ideas we have performed the above described graphitisation experiments. As starting material a poorly conducting anthracite coal was used as a carbon source (Fig. 1) and by p,T treatment carbon was transformed into graphite and thus the conductivity, connectivity and the crystallinity were enhanced. This result even holds for those samples where the carbon concentration was reduced down to 10 % carbon content. Thus these small scale laboratory experiments allowed to understand the transformation processes of poorly conducting carbon into highly conducting and well interconnected graphite in view of the thermodynamic parameters that were varied during the experiments:

- Graphitisation of organic material (anthracite) is possible at temperature and pressure conditions of 450° C and 0.7 GPa.
- In-situ X-ray analysis improved that the crystallinity of the carbon network is enhanced by the time-pressure-temperature treatment.
- The electrical conductivity increased by orders in magnitude when graphitisation takes place.
- Pressure (stress) acts as an ordering parameter to align and to interconnect the carbon network.
- Temperature accelerates chemical reactions.

If conductive carbon films are already present in rock sample, these films can be disrupted mechanically due to pressure and temperature release, but a reconnection is possible if pressure is

applied. This was studied by Glover&Vine, (1992) who measured the electrical conductivity on carbon bearing granulites under lower crustal p,T-conditions and detected evidence for a higher degree of interconnection of the carbon-film present on open shear plane surfaces when pressures were raised and fractures closed. A similar finding was published by Nover et al. (1998) on KTB core samples. They reported an increase in conductivity when less interconnected graphite-films were reconnected by application of pressure. Jödicke et al. (1990) and Duba et al. (1988) measured a high conductivity on black shales from the Münsterland drilling and clued from impedance spectroscopy that metallic conduction dominates the charge transport. But these experiments do not offer ideas for graphite mobilisation and precipitation.

Walther et al., 1990 reported that solid carbon coexisted with CO₂, CH₄, H₂O and N₂ in fluid inclusion in KTB rocks and they clued that carbon was transported as a gas within a fluid phase and was precipitated as graphite + water. The required (high) activation energy for the oxidation, reduction reaction of CH₄/CO₂ should be provided from frictional sliding along cataclastic shear zones. But thermodynamic details of this abiotic carbon precipitation are still under question. Roberts et al. (1999) were the first that report on abiotic carbon precipitation in laboratory experiments. They measured carbon enhanced electrical conductivity during fracture of rocks on Nugget sandstone and Westerly granite. Samples were exposed to a carbonaceous CO gas-atmosphere and they assume carbon precipitation from the gas-phase on chemical reactive, fresh surfaces being formed during shear experiments at pressures of 100 to 170 MPa and temperatures of 354° to 502° C. Carbon was detected by TOF-SIMS (time of flight-secondary ion mass spectroscopy) on these surfaces, but it is still uncertain if carbon was precipitated from the gas phase, or if it was already present in the sample. Mogk & Mathez (2000) analysed carbon of KTB samples by means of TOF-SIMS. They found coexistence of carbon and heavier hydrocarbons and proposed that the graphite precipitation started from hydrocarbons. Thus they escaped the problem to explain how the required activation energy for the formation of graphite from a gas-phase was provided. But up to now there are still open questions about the carbon source (biogenic or abiotic), the mode of carbon precipitation and its thermodynamics, transportation and mobilisation of carbon under crustal conditions.

To resolve the role of strain (Ross et al., 1990, 1991), pressure and temperature in the transformation of carbon into graphite, the above described experiments were performed. We could show by simple shear experiments that anthracite is transformed into graphite under upper greenschist p,T-conditions. It is essential to notice that shear triggers the graphitisation of less ordered carbon.

Acknowledgement

I wish to thank Dr. von der Gönna for EDX measurements and helpful discussions, Dr. S. Heikamp for helpful comments and Mr. Meurer for technical help in all stages of the experiments, but especially throughout the electrical conductivity measurements.

References

- Bonijoly, M., Oberlin M., Oberlin A., (1982) A possible mechanism for natural graphite formation. *Int. J. Coal Geol.* 1, 283-313
- Bustin RM, Ross JV, Rouzaud JN (1995) Mechanism of Graphite formation from kerogen: experimental evidence. *Int. J. Coal Geol.*, 28, 1-36
- ELEKTG Group, (1997) KTB and the electrical conductivity of the crust. *J. Geophys. Res.* 102, 18,289-18,305
- ERCEUGT-Group, 1992. An electrical resistivity crustal section from the Alps to the Baltic Sea (central segment of the EGT), *Tectonophysics*, Vol.207, pp.123-139.
- Cazes M, Mascle A, Torreilles X, Bois Ch, Damotte X, Matte X, Raoult Ph, Pham VH, Hirn A, Duba A, Huenges E, Nover G, Will G, Jödicke H, (1988) Impedance of blackshale from Münsterland 1 borehole: An anomalous good conductor? *Geophys. J.* 94, 413-419

- Diessel CFK, Brothers RN, Black PM, (1978) Coalification and graphitisation in high-pressure schists in New Caledonia. *Contrib. Mineral. Petrol.* 68, 63-78
- de Fonton S., Oberlin A., Inagaki M. (1980) Characterisation by electron microscopy of carbon phases (intermediate turbustratic phase and graphite) in hard carbons when heattreated under pressure. *J. Mater. Sci.*, 15, 909-917
- Glover PWJ, Vine FJ, (1992) Electrical conductivity of carbon bearing granulite at raised temperatures and pressures. *Nature*, 360, 723-726
- Haak, V, Blümecke, Th, Fischer, G, Schnegg, P and Rath, V, 1985. Electrical conductivity studies, Oberpfalz, Abstract in 2nd International Symposium on Observation of the Continental Crust through Drilling, 55, Seeheim.
- Jödicke H, (1990) Zonen hoher elektrischer Krustenleitfähigkeit im Rhenoharzynikum und seinem nördlichen Vorland. PhD Thesis, Hochshulschriften Bd. 24, Lit Verlag, Münster
- Kontny A, Friedrich H, Behr HJ, DeWall H, Horn E, Möller P, Zulauf G, (1997) Formation of ore minerals in metamorphic rocks of the German continental deep drilling site (KTB). *J. Geophys. Res.* 102, 18,323-18,336
- Mogk DW., Mathez EA., (2000) Carbonaceous films in midcrustal rocks from the KTB borehole, Germany, as characterized by time-of-flight secondary ion mass spectroscopy. *G3*, Vol 1,
- Nover G, Heikamp S, Meurer HJ, Freund D, (1998) In-situ electrical conductivity and permeability of mid-crustal rocks from the KTB drilling: Consequences for high conductive layers in the Earth crust. *Surveys in Geophysics*, 19, 73-85
- Oberlin A., (1984) Carbonisation and graphitisation. *Carbon*, 22, 521-541 Oh JH.,
- Rouzaud J, Oberlin A, Deurbergue A, Kwak YH, (1990) Structural study of graphitisation in the Moongyeong coalfield South Korea. *Bull. Soc. Geol. Fr. Spec. Congr. Coal Formation, Occurence and Related Properties*, Orleans
- Ritter, O, Haak., V, Rath, V, Stein, E and Stiller, M, 1999. Very high electrical conductivity beneath the Münchberg Gneiss area in Southern Germany: Implications for horizontal transport along shear planes. *Journ. Geophy. Int.*, 139, pp. 161-170.
- Ross JV, Bustin RM, (1990) The role of strain energy in creep graphitisation of anthracite. *Nature*, 343, 58-60
- Ross JV, Bustin RM, Rouzaud JN, (1991) Graphitisation of high rank coals - the role of shear strain: experimental considerations. *Organ. Geochem.* 17, 585-596
- Stoll J, (1992) A Mise-a-la-Masse Experiment for detecting an electronic network of cataclastic zones of the KTB site. *Proceedings of the colloquium Elektromagnetische Tiefenforschung Vol. 14*, 323-338
- Stoll J, Bigalke J, Grabner EW, (1995) Electrochemical Modelling of Self Potential Anomalies. *Surveys in Geophysics*, 16, 107-120
- Stoll J, Haak V, Spitzer K, (2000) The electrical double dipole experiment in the KTB deep borehole. *JGR*, 105, B9, 21319-21331
- Teichmüller M, (1982) The geological basis of coal formation. In: E. Stach, MT. Mackowsky, M. Teichmüller, GH Taylor, D. Chandra and R. Teichmüller (eds.) *Stachs Textbook of coal petrology*. Bornträger, Berlin, pp. 5-86
- Volbers R, Jödicke H, Untiedt J, (1990) Magnetotelluric study of the earth's crust along the deep seismic reflection profile DEKORP 2-N. *Geol. Rundschau*, 79, 581-601
- Walther J, Althaus E, (1993) Graphite deposition in tectonally mobilised fault planes of the KTB pilot drill hole. *KTB Report 93-2*, 497-497
- Wilks, KR, Mastalerz, M, Ross JV, Bustin RM, (1993) The effect of experimental deformation on the graphitisation of Pennsylvania anthracite. *Int. J. of Coal Geology*, 24, 347-369
- Zulauf G, (1992) Late to post Variscian deformation phases and paleostresses in the KTB pilot research well (Bohemian Massif, Germany). *Tectonophysics*, 202, 1-21