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Graphite and Electrical Conductivity in the Lower Continental Crust: A Review

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Abstract. Magneto-telluric measurements show that zones of high electrical conductivity commonly exist within the continental crust although their nature, depth and extent vary. The two most likely causes are the presence of highly inter-connected networks of aqueous fluids, and/or graphite. While the former has been well studied and reviewed, the latter is now becoming of greater interest since recent studies have observed thin graphite films which may be highly connected at depth. In addition recent high pressure/temperature experiments have shown that graphite-bearing rocks can provide sufficiently high electrical conductivities to fulfil the field observations. There are three major questions that need to be answered if graphite is to be considered as a major provider of crustal conductivity: (1) Is graphite present in the Earth's crust in sufficient quantity and with the necessary highly inter-connected distribution to cause large electrical conductivity anomalies, and if so, why has this not been observed hitherto? (2) Can laboratory experiments made upon rocks from the crust provide electrical conductivities similar to magneto-telluric field measurements? (3) What are the mechanisms whereby graphite films can be produced stably in the lower continental crust from mantle derived carbon-bearing fluids, and can these mechanisms operate on a scale sufficient to produce graphite films over the large volumes required?
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1 Introduction

It has been recognised that the electrical conductivity of parts of the Earth's crust are anomalously high for some years (Gough, 1986; Yardley, 1986; Hyndman and Shearer, 1989; Jones, 1992). Many mechanisms have been proposed to explain this, chief of which are the presence of an inter-connected network of aqueous fluids (e.g. Drury and Hyndman, 1979; Olhoeft, 1981; Lee et al., 1983; Shankland and Ander, 1983; Shankland, 1989; Marquis and Hyndman, 1992), and of a continuous network of grain boundary graphite (e.g. Alabi et al., 1975; Duba and Shankland, 1982; Duba et al., 1988; Frost et al., 1989; Mareshal et al., 1992; Glover and Vine, 1992; 1994; 1995; Mathez et al., 1995).

Other mechanisms that have been investigated include the presence of a highly conducting melt fraction (Hermance, 1979), solid state conduction through other accessory minerals such as magnetite (Parkhomenko, 1982; Duba et al., 1994), conduction through hydrous minerals in amphibolite facies rocks (Stesky and Brace, 1973), and conduction in the upper part of the lower crust through clay minerals (Toussaint-Jackson, 1984). Each of these may be important locally but cannot explain such a widespread distribution of highly conducting electrical anomalies as encountered in the middle and lower continental crust by magneto-telluric and other electro-magnetic field measurement techniques (Shankland and Ander, 1983; Hyndman and Shearer, 1989; Jones, 1992; Marquis and Hyndman, 1992).

The presence of brines in the crust has been examined in great detail and is well reviewed (Hyndman and Shearer, 1989; Jones, 1992). The evidence that graphite might play a more significant role in controlling the electrical conductivity of the middle and deep continental crust than has hitherto been realized is now growing (e.g. Frost et al., 1989; Mareschal et al., 1992; Glover and Vine, 1992; 1994; 1995; Mathez et al., 1995). The aim of this brief review is to amalgamate the information from papers such as these in order to synthesize the present state of knowledge

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concerning the role of graphite in the crust.

2 Graphite Recognition in Rocks

One of the greatest barriers to the awareness that graphite may be an important constituent of many crustal rocks has been its lack of recognition. Traditionally it has not been considered to be a cause of widespread high electrical conductivity in rocks because it was thought that natural deposits of graphite in rocks were rare, and certainly not distributed on a scale which would cause the large scale electrical conductivities observed by magneto-telluric techniques in many terrains around the world (Haak and Hutton, 1986; Jones, 1992). However, occassionally graphite is observed, for example in Scandinavia (Korja and Hjelt, 1993; Korja et al., 1996), in the KTB (Zulauf et al., 1990; Zulauf, 1992), and as a layer in the Grand St. Bernard nappe of the Central Valais penninic zone. In the last example the observed graphite coincides with a high conductivity layer observed using MT methods (Schnegg, pers. comm.).

In 1982 Duba and Shankland (1992) published a paper which set the ground rules concerning whether graphite could be a major source of upper mantle conductivity. Their paper was the first to discuss the abundance, stability, and electrical connectivity requirements for graphite in the mantle. They discovered that only a very small abundance of highly conducting graphite was required to be added to a matrix of negligibly conducting minerals (Red Sea Peridot) in order to make the conductivity of the rock similar to the observed conductivities of the upper mantle. In the case of an isolated distribution of graphite about 1000 ppm by volume was required, and if the graphite could be assumed to have a high electrical connectivity, this fell to less than 100 ppm by volume. There was also evidence from mantle derived rocks which had been analyzed for carbon that there was an ample amount of carbon to provide the 100 ppm required (Mathez and Delaney, 1981; Tingle et al., 1991). Furthermore, carbonaceous chondrites, which strongly mirror the Earth's bulk composition, have a chemical composition that commonly contains a few percent carbon (Taylor and McLennan, 1985).

The temperatures and pressures are much lower in the crust than in the mantle, but many of the points made by Duba and Shankland still apply. This is because graphite has a remarkably low activation energy, leading to a very weak temperature dependence, and in the massive form also has a weak dependence of electrical conductivity on confining pressure. It can also be assumed that the crust is composed of a relatively insulating matrix compared to graphite because the average conductivity of graphite is about ten orders of magnitude greater than that of common crustal rock forming minerals at crustal temperatures (e.g. Duba et al., 1994). The crust differs from the mantle in that it is reasonable to assume that the rocks have a greater porosity and contain a larger proportion of fractures and cracks formed by brittle failure, thereby increasing the potential for large scale connectivity of a conducting phase that occupies crack and pore surfaces as well as grain boundaries.

Graphite has been observed in xenoliths from the lower crust by Padovani and Carter (1977), and has also been cited as a possible contributor to crustal conductivity by Garland (1975) in, for example, the high conductivity zone that occupies western North America (Alabi et al., 1975). Watson and Brennan (1987) have surmised that regions of high conductivity in the continental crust may be caused by the presence of conducting phases on mineral grain and crack surfaces. Jödicke (1985) has also suggested that carbon coating grain boundaries was the cause of the high conductivities he measured in black shales. Until 1989, however, the only evidence for carbon in the continental crust was its presence in individual, often esoteric, rock types, or xenoliths which by their very nature could not be regarded as typical of the crust at depth. Solid evidence for widespread carbon in crustal rocks was not available.

However, in 1989 Frost et al. (1989) started reporting work using high definition Auger electron spectroscopy (AES) to look for graphite on grain boundaries where none was visible either by eye or with conventional light and scanning electron microscopic techniques. They discovered thin films of graphite (about 1000 Å thick) covering the surface of grains in rocks from the 1.4 Ga Laramie Anorthosite Complex, where none was visible by other methods. As others before them (cited previously), they realised that such films, if well connected, are the most efficient means of raising the electrical conductivity of a porous or cracked granular material using least mass of graphite. This particular rock type could hardly be considered as typical crustal material, but the observation was important in that it showed that thin graphite films were present in the rock, and had been overlooked previously.

A simple model designed to test the conductivity of a block of granular material of a given grain size, where each grain was covered by a film of graphite with such a thickness, showed that grain sizes in the range of 1 cm and smaller gave a sufficient increase in conductivity to explain the electrical conductivity anomalies in field measurements

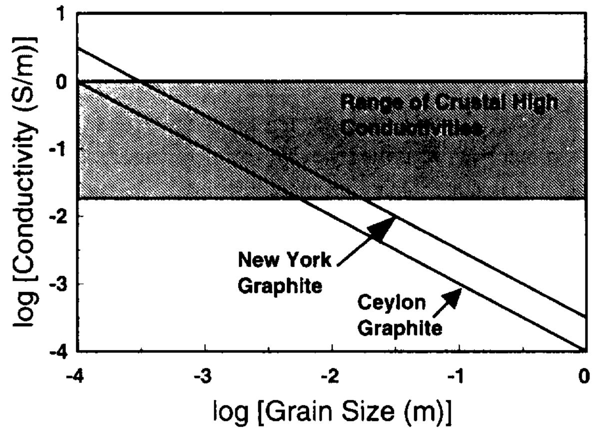

Fig. 1. Calculated conductivity for rocks that contain a 1000 Å thick graphite film on the grain boundaries, as a function of the average grain size of the rock, after Frost et al. (1989).

providing that the films retained a high degree of electrical connectivity (Fig. 1) (Frost et al., 1989). The grain size-conductivity relationship provided by Frost et al. was usefully summarised approximately by Jones (1992) as $\log(\sigma)=-4-\log(x)$ where x is the average grain size in metres and σ is the bulk rock electrical conductivity in Sm^{-1}. Such a grain size-conductivity relationship had also previously been noted by Kariya and Shankland (1983) in their review of the electrical conductivity data of dry crustal rocks.

Since 1989 work has continued probing rocks with no apparent graphite, and thin films of graphite continue to be discovered. In 1992 Mareschal et al. (1992) reported the use of Auger spectroscopy and showed that thin grain surface films of graphite existed in all but one of their samples from the Kapukasing uplift of the Canadian shield; rocks that are representative of those in the intermediate to lower crust. These films were approximately 30 Å to 300 Å thick. Furthermore, Raman spectroscopy also showed data consistent with the presence of ultra-thin films of graphite ~50 Å thick. Even more recently Mathez et al. (1995) have combined X-ray mapping with electrical conductivity measurements on rocks from the Yukon-Tanana Terrain, and again find that graphite is surprisingly common, even with the reduced film thickness resolution of this technique.

3 Disconnection and Reconnection

Unfortunately, when tested in the laboratory at atmospheric pressure, the unsaturated rocks that were known to contain carbon, typically showed low conductivities (e.g. Katsube et al., 1991; 1992; Glover and Vine, 1992). It was recognised that rocks tested in the laboratory had undergone stress relaxation and cooling with its attendant deformation in the form of crack growth concomitant upon the extraction of the rock from depth (Frost et al., 1989). It was proposed that these processes were sufficient to break the fine connected films of graphite in a rock sample, dramatically reducing its electrical conductivity (Katsube and Mareschal, 1993).

This hypothesis was supported by a study reported in Duba et al. (1988) and Duba (1992). Their initial tests showed high conductivities (1 Sm^{-1}) that were nearly frequency independent for frequencies between 17 Hz and 1 MHz, confirming that a highly inter-connected conducting phase was present in the rocks (Duba, 1992). This was consistent with Jödicke's earlier suggestion that the high electrical conductivity of black shales was due to grain boundary films of carbon (Jödicke, 1985). When the rock samples had been heated to 417°C the resulting conductivities were much lower ($<10^{-6}$ Sm^{-1}) and frequency dependant indicating that there had been widespread loss of inter-connectivity of the conducting phase Duba et al. (1988). This work had proved that disconnection of graphite films would occur and that their result was a loss of electrical conductivity.

It has since been suggested that the graphite network may be broken by a combination of crack growth and the alteration attendant upon retrograde metamorphism and oxidation (Duba, 1992; Duba et al., 1994). Either way, the electrical conductivity measured in the laboratory would not be expected to be as high as that predicted from a model that included highly connected thin films of graphite, as is indeed observed in laboratory electrical conductivity determinations (e.g. Glover, 1989; Katsube et al., 1991; 1992).

Perhaps the most striking example of the effects of disconnection of a network of graphite films occurs in graphitic pelites from northern Canada. These rocks contain such a large proportion of graphite that they are black in colour, yet laboratory measurements at atmospheric pressure yield electrical conductivity values of 10^{-5} Sm^{-1} and less (Camfield et al., 1989).

It was postulated that the disconnection of the graphite film would be irreversible even if the sample were taken to high confining pressures and thus closing the cracks that had originally disrupted the graphite films (Frost et al., 1989). This would make it impossible to measure in the laboratory the conductivity that a lower crustal rock had when it was present in the lower crust.

However, in 1992 Glover and Vine reported high pressure and temperature experiments on dry and brine saturated graphite-bearing rocks from the Beni Bouzere area of north Africa in which there was evidence for graphite film reconnection (Glover and Vine, 1992; 1994; 1995). They discovered that the electrical conductivity of their dry specimens increased when pressure was raised; the first rocks in which an increase in conductivity with confining pressure had been recorded. The increase in the conductivity due to reconnection was a factor of three or four for rocks measured parallel to the graphite foliation. There remained a decrease in the electrical conductivity of their brine saturated rocks with increased pressure but this was less than if there had been no graphite present.

Since then dramatic reconnection has been noted in rocks containing graphite and Fe-Ti oxides from the KTB Hauptbohrung (main bore-hole) in southern Germany (Duba et al., 1994). Here the authors chose to attribute the conductivity increase to reconnection between laths of ilmenite that were plainly present in thin sections. Unfortunately Duba et al. could not carry out an analysis for invisibly thin graphite films in these rocks. It is, of course, possible that the reconnection was due to such films as extensive macroscopic occurrences of graphite exist within the rocks from the KTB boreholes (Zulauf et al., 1990; Zulauf, 1992).

Infact most of the evidence in the KTB bore-holes points to graphite as the major source of electrical conductivity with other minerals such as pyrrhotite and ilmenite also making a contribution. Graphite exists along grain boundaries and in cracks throughout the majority of the depth of the Vorbohrung (pilot bore-hole) (about 4000 m), and also occurs throughout large sections of the Hauptbohrung. The graphite is usually associated with a gneiss host-rock (Zulauf et al., 1990; Zulauf, 1992). Electrical conductivity determinations in the Hauptbohrung often show low conductivities within graphite-free gneisses, but conductivities as high as 10 Sm^{-1} where the gneisses contain graphite deposits. It has also been pointed out by Haak et al., (1991) that the conductivities in the massive rock could be even higher if disconnection has occurred in the close-field of the borehole as a result of the stress reduction resulting from the presence of the bore-hole.

More recently reconnection has been discovered in graphite film bearing rocks of the Yukon-Tanana terrain in Alaska, that causes increases in electrical conductivity with increasing confining pressure even in rocks saturated with domestic tap water (Mathez et al., 1995). Recent experiments have also been completed on graphite-bearing rocks from the Grand St. Bernard Nappe (Losito, pers. comm.). These also show increasing conductivities as confining pressure is increased, indicating that reconnection is taking place.

The hypothesis of reconnection seems to be fairly well established, but we still do not know the extent to which reconnection occurs, although it seems reasonable to assume that it is not complete in the laboratory experiments. The observed increases in electrical conductivity must represent the lower bound for the ability of a graphite film network to reconnect.

Modelling by Katsube and Mareschal (1993), that takes into account the effect of graphite film disconnection based on the data of Mareschal et al. (1992), has shown that thin connected graphite films (50 Å to 200 Å thick) when lining the pores of a rock can produce bulk conductivities of 0.005 to 0.01 Sm^{-1}; a value typical of the conductivity found in the lower crust of shield areas (Shankland and Ander, 1983; Haak and Hutton, 1986; Marquis and Hyndman, 1992; Glover and Vine, 1994, 1995). Furthermore, according to the model, once uplifted to the surface, such rocks with graphite films would display conductivities a factor of ten smaller (0.0005 to 0.001 Sm^{-1}) due to film disconnection. Such values are the commonly observed for graphite-bearing unsaturated rocks measured in the laboratory at low confining pressures (Duba et al., 1988; Camfield et al., 1989; Glover and Vine, 1992; 1994; 1995). Yet these values are ten times or more higher than the electrical conductivity of typical dry graphite-free rocks measured in the laboratory (e.g. Kariya and Shankland, 1983; Čermák and Laštoviková, 1987).

The modelling of Katsube and Mareschal (1993) suggests that the effect upon electrical conductivity of 100% reconnection should be an increase of approximately one order of magnitude. In laboratory experiments on graphite-bearing saturated rocks Glover and Vine (1992) encountered an increase in electrical conductivity by a factor of about 3 to 4 resulting from raising the confining pressure to 400 MPa. According to the model of Katsube and Mareschal this represents only 30 to 40% of the potential recoverable conductivity if all graphite films present at depth were to reconnect.

4 Laboratory Measurements

Up until 1989 there were only a limited number of electrical measurements on continental crustal rocks known to contain graphite, and these were at laboratory temperatures and low confining pressures. As we have already stated, these studies very often provided surprisingly low conductivities (Duba et al., 1988; Camfield et al., 1989), which at the time were ascribed to disconnection (Frost et al., 1989).

From 1989 onwards a set of results were reported which measured the electrical conductivity of dry and saturated rocks some of which contained carbon and some of which were carbon-free (Glover, 1989; Glover and Ross, 1990; Glover et al., 1990a; 1990b). These were complex experiments in which the confining pressure (up to 400 MPa), pore-fluid pressure up to (200 MPa), and saturation state (0.5 M NaCl or distilled water) were all controlled up to temperatures of 900 °C. Experiments were done on a suite of highly foliated graphite-bearing garnetiferous granulites taken from the Beni Bouzere area of northern Africa as part of this work (Glover and Vine, 1992; 1994; 1995).

Experimental studies on rocks that had been freshly cored from the KTB Hauptbohrung in southern Germany had been found to contain significant abundances of highly conducting accessory mineral phases including graphite, ilmenite, magnetite, pyrite and pyrrhotite. Experimental measurement of the electrical conductivity of a range of these rocks, including amphibolites from four depth intervals, a gneiss from the Vorbohrung (KTB pilot well), and an amphibolite from a surface exposure, was carried out by Duba et al. (1994). These experiments measured the electrical conductivity from 1 kHz to 1 MHz during pressurization (up to 225 MPa) at laboratory temperatures of samples cored at various angles to the rock foliation and saturated with a 1 M NaCl solution.

Most recently a combination of carbon X-ray mapping and electrical conductivity measurements has been done on a suite of graphite-bearing greenschist and amphibolite grade metamorphic rocks of Palaeozoic age from the Yukon-Tanana terrain in Alaska (Mathez et al., 1995). Their electrical conductivity measurements were made in an oil pressure vessel operating up to 400 MPa and at ambient temperatures (25±3 °C). They were done at a single frequency (1 kHz) on samples cored parallel to the graphite foliation and saturated with distilled water.

Several of the studies mentioned above have also measured the conductivity of graphite-bearing rocks cored at different angles to the observed graphite foliation (Glover, 1989; Duba et al., 1994; Glover and Vine, 1992; 1995). In all cases a significant difference has been noted between the electrical conductivity behaviour of rocks cored parallel to the foliation and those perpendicular to it, with higher conductivities and reconnection occurring when the measurement direction is parallel to the foliation.

Almost no experiments have been done on the electrical conductivity of graphite-bearing crustal rocks as a function of temperature due to their extreme difficulty. However, the high temperatures within the crust make it necessary that we should have such information before we can make confident assessments of the role that graphite might play in the electrical conductivity of the lower and middle crust. Some measurements of the electrical conductivity of graphite-bearing rocks saturated with 0.5 M NaCl at raised confining pressures and pore fluid pressures, and temperatures up to 700 °C have been reported (Glover, 1989; Glover and Vine, 1992; 1995). These experiments showed anomalously large increases in electrical conductivity with temperature compared with the electrical conductivity measurements of similar but graphite-free saturated rocks. The very small temperature dependence of the electrical conductivity of graphite cannot explain this observation. It has been suggested by Glover and Vine (1992) that the answer might lie in the physics and chemistry of the carbon-electrolyte system at high pressures and temperatures. Carbon-sodium intercalation compounds, which have an electrical conductivity several orders of magnitude higher than graphite might be formed in the lower crust over geological timescales at the high temperatures and pressures present in the crust.

5 Comparing Field and Laboratory Data

The wide range of rock types, confining pressures, and temperatures studied by Glover and Vine (1994; 1995) has enabled them to use the results of their laboratory experimental studies to synthesise an electrical conductivity profile of the Earth's continental crust which can be compared directly with magneto-telluric electrical conductivity profiles. For this work they used the compilation of MT data by (Marquis and Hyndman, 1992) to provide the mean thicknesses of the upper, middle, and lower crusts, and assumed that each could be represented by their data from samples of granodiorite, amphibolite, and graphite-free granulite or graphite-bearing granulite respectively. Synthetic profiles (Fig. 2) were constructed for two geotherms that were taken to represent Phanerozoic (20.5 °C km^{-1}) and stable Precambrian (12.7 °C km^{-1}) crust based on electrical data that they had measured at the pressures and temperatures existing at depth. In all cases the rocks were saturated with 0.5 M NaCl solution. For comparison, in each part of Fig. 2 the shaded areas represent the mean bounds of MT conductivity calculated from over 65 magneto-telluric and controlled source determinations of

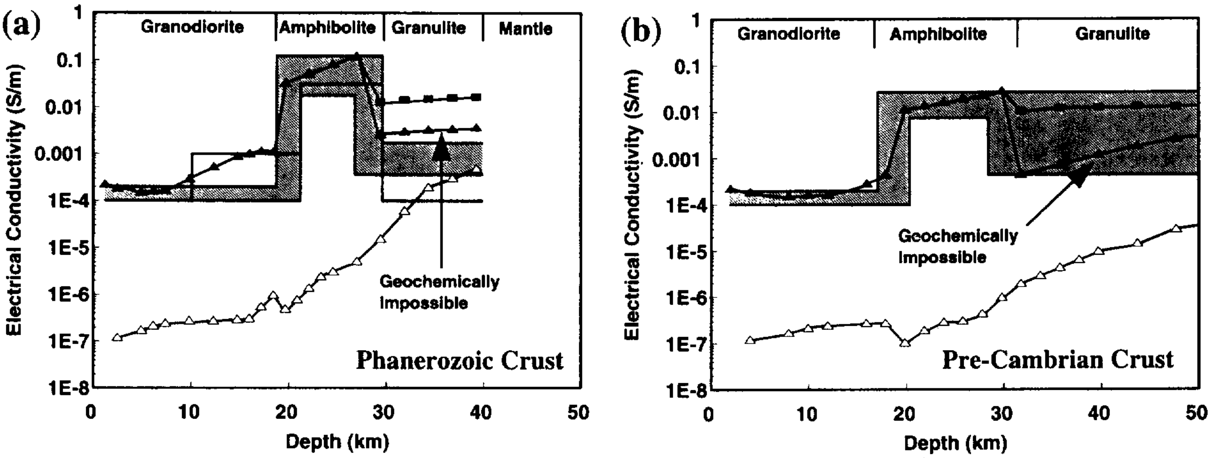

Fig. 2. Conductivity/depth profiles for the Phanerozoic (2a), and stable (2b) continental crust based on laboratory measurements of electrical conductivity of a range of crustal rock types of Glover (1989), Glover and Vine (1992; 1994; 1995) made at raised temperatures and pressures. Upper crust, granodiorite; middle crust, amphibolite: lower crust granulite. Interface depths from the mean of MT data in Marquis and Hyndman (1992). Filled symbols: 0.5 M NaCl saturated rock, triangles graphite-free granulites, squares graphite-bearing granulites; open symbols: dry rock, graphite-free, from Toussaint-Jackson (1984) and Čermák and Laštovičová (1987). The shaded area represents the mean of MT data from 65 studies reported in Marquis and Hyndman (1992) for comparison. The thick symbol-less line is the result of the MT study by Connerney et al. (1980).

crustal conductivity at 24 Phanerozoic and 11 Precambrian locations. The source of this data is Marquis and Hyndman (1992) and the references therein.

In both parts of Fig. 2 it is plain that the laboratory measurements agree with those made in the field indicating that perhaps we should not be labelling the high conductivity zones of the Earth's crust as 'anomalous' any longer. The question, of course, is whether the assumptions of depth and rock type made by Glover and Vine (1994; 1995) are applicable in the continental crust in general. Although their assumptions may be true on average, it does not preclude local conditions and local mechanisms from perturbing the local conductivity profile. The profile from unsaturated samples is also shown in Fig. 2, and plainly demonstrates that either the presence of graphite or that of brines (or both) is necessary if the profiles from the laboratory determinations are to match the observed MT data. It is particularly noteworthy that in both cases it can be seen that graphite-bearing rocks have more than sufficient conductivity at mid-crustal depths to account for the MT observations, but so do the rock samples saturated with a 0.5 M NaCl solution. The modelling demonstrates that instead of lacking a mechanism able to explain the high conductivities observed in the lower crust, we now have two that have the physical ability of providing this order of conductivity, at least when measured at laboratory scale. The question remains whether other geochemical and geophysical criteria allow them to continue as contenders. The debate continues about the geochemical and geophysical possibility of free fluids occupying pores and cracks in the rock at middle and lower crustal depths, and how fluids remain trapped at depth. In the case of graphite films these geochemical and geophysical criteria are discussed in the following section.

6 Carbon Formation and Stability

The deposition of graphite films in continental crustal rock depends essentially upon there being a source of carbon. This is usually considered to be in the form of carbon rich fluids emanating from the mantle, and is inferred from models for the formation of crustal granulites, reduction of water activity, the presence of orthopyroxene-bearing assemblages, dehydration, and the depletion of large ion lithophile (LIL) elements (Hoefs and Touret, 1975; Collerson and Freyer, 1978; Newton et al., 1980; Glassley, 1982; Janardhan et al., 1982; Lamb and Valley; 1984;

Harris, 1989). Additionally, fluid inclusions found in many highly metamorphosed rocks from the deep crust have fluid inclusions which are rich in CO_2 (Touret, 1971), and helium isotope studies have estimated the amount of CO_2 entering the crust from the mantle (O'Nions and Oxburgh, 1988; Harris, 1989).

What are the processes whereby graphite might be deposited from such a gaseous source in a stable way, and in a way that would form thin interconnected graphite films?

One possibility is that graphite films are deposited on cooling by reduction of the CO_2-rich fluid (Frost et al., 1989):

$$C + O_2 \rightarrow CO_2 \qquad (1)$$

Indeed it has been shown that the stable precipitation of graphite from a CO_2-rich fluid is a direct consequence of deep crustal metamorphism in the presence of a CO_2-rich fluid phase (Glassley, 1982). This mechanism is sufficient to explain the formation of stable films of graphite if the rock assemblage exists at or near to the graphite saturation surface, and requires only small amounts of cooling along the relevant buffering surface of the particular assemblage to precipitate graphite from the fluid phase (Frost et al., 1989).

If the rock exists at oxygen fugacities above the graphite saturation surface it is not immediately clear how graphite can precipitate on cooling. However, it has been reported that interoxide equilibrium during cooling can reduce the oxygen fugacity to that of the graphite saturation surface, and then further cooling precipitates graphite with accompanied oxyexsolution, whereby titanomagnetite removes itself of its titanium. The deposition of graphite then occurs by the reaction (Fuhrman et al., 1988; Frost et al., 1989):

$$6Fe_2TiO_4 + CO_2 \rightarrow 2Fe_3O_4 + 6FeTiO_3 + C \qquad (2)$$

Here the oxygen fugacity is decreased because the oxyexsolution process can only proceed when there is a donor of oxygen. This is provided by the fluid CO_2. The result of the reaction is the deposition of solid carbon on the nearest mineral surfaces and the removal of titanium from the magnetite in the form of ilmenite. This process begins when the temperature drops to between 600°C and 675°C depending on the composition of the rock. All of the solid minerals in Eq. (2) are common in the lower crust; indeed it is striking how often graphite, magnetite, and ilmenite occur together in mineral assemblages formed at lower crustal conditions. Once the graphite saturation surface is reached, further cooling causes processes (1) and (2) to occur concurrently.

Interestingly the exsolved and reconstituted oxide compositions from rocks studied by Fuhrman et al., (1988) and Frost et al. (1989), as well as almost all exsolved and reconstituted oxide compositions from granulites in general, plot on the graphite saturation surface (Frost et al., 1989). According to Frost et al. (1989), this is clear evidence that graphite precipitation is a common feature of lower crustal rocks containing two oxides if a CO_2-rich fluid is present, even if the rock did not have graphite as part of its primary assemblage.

A third mechanism for the production of graphite should also be considered. This is the possibility of graphite being generated along strike-slip faults (Walther and Althaus, 1993). The reaction here is:

$$CH_4 + CO_2 \rightarrow 2C + H_2O \qquad (3)$$

and takes place at temperatures about 280°C and pressures of 300 to 500 MPa. This mechanism is particularly relevant to crustal high conductivity zones of mid-crustal origin where the temperatures are 250°C to 450°C. The combination of mechanism (3) occuring during shearing, with redistribution and smearing out of the graphite within extended shear zones has the potential for creating mid-crustal high zones. This mechanism is a particularly good candidate for explaining the situation at both the KTB site and the Grand St Bernard nappe (Schnegg, pers.comm.). By comparison, the first two mechanisms are much more suited to explaining the conductivity of the lowermost parts of the crust as the temperatures encountered there render saline fluids relatively non-conductive unless their fluid pressure is high, which in turn would imply low interconnectivity and low bulk conductivity of the rock (Nesbitt, 1993).

The conclusion must be that graphite film deposition from a gaseous source is a common process in lower crustal rocks. Furthermore, deposition of carbon films in this way provides exactly the highly connected conductor required to raise the electrical conductivity of the rock significantly, while being present in minimal abundance. Now we know that graphite films can exist in rocks without being immediately obvious to conventional analysis, we must take special care to ensure that they are recognised when they do occur. The extent of their occurrence might very well be surprising.

7 Summary

To what extent can we now answer the questions posed at the start of this review:

Evidence is growing, but not yet conclusive, that carbon exists in crustal rocks in proportions much higher than it was once thought. In all the studies so far carried out the abundance of graphite is sufficient to allow it to play a significant role in the control of the electrical conductivity of each particular rock. The reason why this has remained unrecognised for so long lies in the extreme thinness of the graphite films that represent the greatest volume of graphite within the rocks. These films were unobserved by traditional methods of examining rocks. Indeed they were overlooked precisely because no one thought that they would be there. The distribution of graphite in this manner has great implications for the electrical conductivity of the rock because thin films on grain boundaries, pore and crack surfaces have, ipso facto, a high inter-connectivity. However, this connectivity can be easily disrupted by mechanical deformation when the rocks are brought to the surface by either natural processes operating over geological timescales, or by drilling.

We now know that the electrical conductivity of rocks known to contain graphite films is sufficient to explain the electrical conductivity of the lower crust, while in the mid-crust both fluids and graphite have the potential for causing high conductivities. Early measurements made at laboratory temperatures and pressures indicated that the electrical conductivity of such rocks was too low. However, a greater understanding of the processes of disconnection and reconnection, coupled with measurements made at in situ conditions provides conductivities that are more than sufficient to provide electrical conductivities matching those measured by large scale field determinations of deep high conductivity layers.

There are several geochemical processes which can lead to the deposition of graphite films in dry crustal rocks under the conditions of temperature and pressure encountered in the deep continental crust. In fact the deposition of graphite is the inescapable result of metamorphism or cooling of lower crustal rocks containing CO_2-rich fluids. These mechanisms depend only upon the presence of a fluid containing the gaseous oxides of carbon, and a flux of such gasses is recognised to emanate from the mantle in many areas.

The conclusions of this review must be that we still do not know the extent to which graphite films are responsible for the commonly observed high electrical conductivity of many parts of the continental lower crust. However, it does indicate that many of the arguments against graphite that have hitherto been aired are now not applicable, and what was seen as an unlikely mechanism, is now a strong contender in explaining high crustal electrical conductivity in many areas.

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