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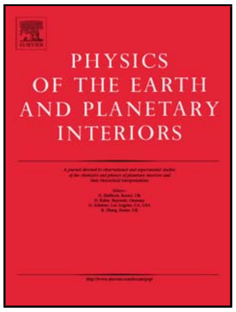

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Electrical Properties of a Graphite-rich Quartzite from a Former Lower Continental Crust exposed in the Serre San Bruno, Calabria (Southern Italy)

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Abstract

In this study electrical properties of a graphite-rich quartzite from the former lower crust exposed in the Serre San Bruno, Calabria (southern Italy) have been analysed by means of complex electrical conductivity measurements in the frequency range 10^{-3} up to 10^{6} Hz on plug samples of 25mm in diameter and 22mm high. The samples were identified as a former oil sandstones containing up to 12 to 15 % flake-like graphite, which present highly metamorphosed relics of its former hydrocarbon filling. Though high concentrations of graphite were detected, the graphite quartzite is highly resistive. The spatial ordering of isolated graphite grains like tiles prevent the generation of interconnected electrical pathways. These isolated good conductors are interconnected by electrolyte bridges, thus causing the high polarisability, indicating redox reactions at the electrolyte/graphite interfaces, that could be modelled using CPE elements. The type of graphite ordering was caused by the early formation of isolated oil droplets in the reservoir sandstone. After high-grade metamorphism and shearing, they appear as flat graphite grains in the foliation plane and were smeared together because of the rigidity of sillimanite and quartz, the main rock constituents. Thus this graphite quartzite is by no means a candidate to enhance the electrical conductivity of the deep continental crust.

Syngenetic graphite in former lower crustal rocks is largely resistant against varying geochemical conditions during prograde and retrograde metamorphism. This had also been shown for graphite that is contained in normal metapelites as accessory mineral, or enriched in former black shales where it may cause high conductivity (Jödicke et al., 2004, Nover, 2005).

Introduction

The debate about the electrical properties of the deep continental crust, in particular, about the origin of enhanced electrical conductivity as revealed by numerous magnetotelluric (MT) studies worldwide (e.g., Schwarz, 1990; Jones, 1992; Brown, 1994) is long lasting and controversial. Facing the dry conditions of the lower crust (Yardley and Valley, 1997) some kind of paradigma change may be occurring during the last few years. The long-lived concept of water as the conductive phase in a highly resistive rock matrix causing enhanced conductivity is more and more replaced by the concept of interconnected graphite, or, possibly, of other quasi-metallic minerals like ilmenite (Shankland et al., 1997, Nover et al., 1998, Duba et al, 2001). The existence of interconnected graphite has mostly been explained by graphite precipitation from C-O-H fluids covering faults and shear zones in the form of thin epigenetic films (e.g., Frost, 1979; Rumble and Hoering, 1986; Zulauf et al., 1990; Walther and Althaus, 1993). Alternatively, in a preceding study on electrical properties of former lower crustal rocks, exposed in the Serre San Bruno, Calabria (southern Italy), series of thin horizons rich in syngenetic graphite were described (Jödicke et al., 2004). These remarkable layers, most probably representing former C_{org}-rich black shales, exhibit extremely high, almost perfect quasi-metallic conductivity. The necessary interconnectivity of their graphite component was attained after enrichment during high-grade metamorphic processes and by later shearing without a major contribution of a fluid C-O-H phase.

The analysis of electrical properties of graphite-rich former lower crustal rocks will be accomplished in this second part of the Calabrian study. The focus is now laid on a graphite-rich quartzite layer, exposed in the Serre San Bruno in the direct neighbourhood of the thin highly conductive horizons mentioned above. In striking contrast to these conductive rocks, the graphitic inclusions of the quartzite mostly are not interconnected; the graphite quartzite is highly resistive, therefore. The investigation of such resistive rocks will provide additional information about graphite that has been exposed to high-grade metamorphic conditions and complete the knowledge about the variety of the specific electrical properties of graphite-rich rocks, in general.

Geological-geophysical background

In the north south trending mountain ridge of the Serre San Bruno in Calabria (southern Italy), a continuous, tilted section through a former lower continental crust is exposed (Schenk, 1984; 1990; Lüschen et al., 1992). It comprises a lower 2 to 3 km thick granulite-pyriclasite unit in the north (80 % metabasite, 20 % felsic granulite) that represents a former mafic intrusive body, and an upper 5 to 6 km thick metapelite unit in the south (76 % aluminous paragneisses, 14 % granofelses, 10 % metabasites and minor amounts of marbles, ultramafics etc.) (Figure 1).

Sr model ages of the metasediments range between 1000 and 600 Ma (Schenk, 1985; 1990). Peak granulite-facies metamorphism reached temperatures of about 800°C at the base and 670°C at the top of the lower crustal section, and lasted until the end of the Variscan orogeny (300 ± 10 Ma). Subsequently, at about 280 to 290 Ma, the lower crustal section was exhumed by around 7 km to a mid-crustal level. During subsequent isobaric cooling, the tectonic transport continued with the same direction and sense of shear (Kruhl, 1992). Consequently, numerous layer-parallel shear zones developed at amphibolite- and greenschist-facies temperatures (Altenberger and Kruhl, 2000). The final uplift of the lower crustal segment to the surface started at about 25 to 30 Ma, when the crustal segment had already cooled to around 250°C, and was completed at about 10 Ma (Görler, 1978; Schenk, 1985, 1990). The tilting produced a variety of brittle deformation structures as well as layer-parallel shear zones of sub-greenschist facies conditions. Despite all of these deformations at different temperatures, the lower crustal section was not overprinted penetratively (for details see Jödicke et al., 2004; and references therein).

The electrical rock properties of this section of a former lower continental crust were studied by means of geoelectric and electromagnetic field methods and impedance measurements on collected rock samples (Jödicke et al., 2004). Brievly summarized, they show that these high-grade metamorphic rocks are generally highly resistive as to be expected for crystalline, electrolytically conducting rocks of low porosity. In contrast to these general findings, the existence of a distinct elongated, stratiform self-potential (SP) anomaly within the metapelite series (Figure 1) helped to reveal a group of thin black, highly conductive layers exhibiting high, quasi-metallic bulk conductivities of up to 50 S/m (0.02 Ωm). This extremely high conductivity is caused by up to 20 % syngenetic graphite forming a network of interconnected streaks or crack fillings. A total thickness of a few meters of such highly conductive rocks would be adequate to explain magnetotelluric high conductivity anomalies in the deep crust.

It was shown, too, that the graphitic horizons most likely originate from former C_{org}-rich black shales (oil or gas source rocks) which may exhibit high conductivity after pre-graphitization of thin films of kerogen relics at the stage of very low-grade metamorphism. These films are thought to be destroyed at high metamorphic conditions because of grain coarsening and accretive crystallization processes favouring the formation of isolated graphite grains.

Consequently, also the high conductivity will be destroyed at this stage (Yardley and Valley, 1997). For the Calabrian black horizons, further analyses made conceivable that, in a final decisive step, isolated graphite grains were mechanically smeared to continuous pathways during uplift by shearing, producing hereby the observed high conductivity. This process was simulated in laboratory experiments that revealed an higher degree of interconnection of the hexagonal carbon rings in shear experiments by means of X-Ray diffraction and electrical impedance spectroscopy (Nover et al., 2005).

Rock sample description

Rock sample MR3, a graphite-rich quartzite, was collected at rock sampling site ③ from a quarry within the metapelite series northeast of the little town Monterosso (Figure 1), where the described series of highly conductive graphite horizons are exposed. Situated in between these series, the graphite quartzite forms several ‘massive’ 10 to 30 cm thick banks showing moderate weathering, indicated by a porosity of 4 to 5 % which is about five times larger compared to other rock samples presented in Figure 4 (below) and discussed at greater detail in Jödicke et al. (2004). In addition to its main component quartz, this rock type contains 12 to 15 % flake-like graphite of mm size lying well oriented in the foliation plane like tiles. Mostly these flakes are not interconnected (Figures 2, 3). Furthermore, 5 to 10 % of sillimanite are present. The strong foliation of the sample is formed by platy graphite, sillimanite, and the flat faces of strongly flattened and coarsely sutured quartz (Figure 3). The quartz grains of mm size clearly show an asymmetrically preferred crystallographic orientation with a high opening angle (roughly 90°) across the main flattening direction. This, together with the stability of the coarse sillimanite aligned in the foliation plane, indicates that the rock was sheared under amphibolite facies conditions. Consequently, the graphite flakes were aligned at high temperatures, too. A later deformation under lowermost greenschist to subgreenschist facies conditions is demonstrated by subgrains, strong wavy extinction, kinking and sub-basal deformation lamellae of quartz as well as by fine grain boundary suturing and beginning recrystallization (5 µm grain size and less) (Voll, 1969, 1976).

Due to the large portion of quartz clearly dominating its mineral composition, we may presume that this rock type represents a former oil sandstone (reservoir rock) which still after high-grade metamorphism kept part of its former hydrocarbon content, which may directly stem from the closely neighboured meta-black shales (source rocks). It is generally accepted that the thermal maturation of the organic substances and transformation to graphite at high temperatures is the same for hydrocarbons trapped in reservoir rocks as for the kerogen covering the grain surfaces of oil or gas source rocks (Stach et al., 1982). In contrast to source rocks, the generation of any interconnected pathways during beginning metamorphism is largely inhibited in oil sandstones, which usually contain their hydrocarbon content in the form of isolated oil droplets (Tissot and Welte, 1984). As described above, grain coarsening and accretive crystallization processes at high metamorphic conditions will further stabilize the existence of isolated graphite grains. In contrast to source rocks again, the generation of interconnected pathways during later uplift associated with shearing was most conceivably impeded because of the mechanical rigidity of the main components quartz and sillimanite of the quartzite.

The complex electrical conductivity measurements

The electrical properties of materials are characterised by the parameters resistivity $\rho(\Omega m)$, or its reciprocal, the conductivity $\sigma=1/\rho$ (S/m). These quantities define the conduction current density **J** **($J=\sigma E$)** being caused by an electric field **E** and the electric displacement **D** **($D=\varepsilon E$).** The dielectric constant ε_r of the medium is defined as $\varepsilon_r=\varepsilon/\varepsilon_o$, where $\varepsilon_o=8.854 \times 10^{-12}$ F/m is the dielectric permittivity of free space. Rock forming minerals thus exhibit conductivity and polarisability. An applied electric field causes both a conduction current and a displacement current being out of phase with each other (Fuller and Ward, 1970).

The frequency dependent electrical rock properties are described by the effective electrical conductivity or resistivity, respectively (e.g., Börner and Schön, 1995)

$$\sigma^*(\omega) = \sigma'(\omega) + i\sigma''(\omega) = 1/\rho^*(\omega)$$

with σ' and σ'' denoting the real and imaginary parts of conductivity, where ω is the angular frequency $\omega=2\pi f$, f being the frequency; $i=\sqrt{-1}$. Primed quantities are the real parts and double primed are the imaginary components, respectively. The ratio of the imaginary part of any complex quantity to its real part defines the phase angle Φ, e.g., for the effective conductivity, $\tan\Phi=[\omega\varepsilon''(\omega)]/\sigma'(\omega)$. A single relaxation process can be expanded using a distribution of relaxation times differing slightly in time constants, and thus represent a combination array of RC-circuits (Bauerle, 1969; Cole and Cole, 1941; Jonscher, 1975, 1978). Each RC-element describes one relaxation process with the time constant $\tau=RC$. The complex impedance of this circuit is $Z^*=Z'+iZ''$

To measure these properties on cylindrical rock samples (height about 22 mm, diameter about 25 mm), a 2-pole and a 4-pole cell were used, constructed on ideas of Olhoeft (1979), Vinegar and

Waxman (1984), and Lockner and Byerlee (1985). As a compromise, and to have access to low (4-pole-cell) and high frequency data (2-pole-cell), solid platinum electrodes with a diameter of 26 mm were used as current electrodes in the cell, while a platinum net was used to measure the voltage drop across the sample (for details, see Markfort and Jödicke, 1998; Jödicke et al., 2004). To prevent surface currents, the fluid saturated sample was enclosed in a shrink tubing. The system was calibrated using test resistors and electrolytes different in composition and concentration (NaCl, KCl). A Solartron SI 1260 (Schlumberger Ltd.) was used as an integrated frequency generator and measuring device. To enhance the input impedance of the system the voltage electrodes were connected to the Solartron using impedance converters for each voltage electrode. This limited the upper frequency to 1 MHz for the 4-pol-device. The standard frequency range was 1 mHz to 100 kHz, measured in the 4-pole cell, covering the frequency ranges of magnetotellurics/audiomagnetotellurics and typical induced polarisation methods used in applied geophysics. The accuracy of the results obtained in this frequency range is well within the 1 % error level of the measuring device. For special purposes of this study, the frequency range was extended to 1 MHz or 10 MHz using the 2-pole cell. In general, there was a very small misfit only between the two independent data sets in the overlapping frequency range, that could be easily concatenated. However, at the highest frequencies, the error increases to a 5 % level and beyond.

Results

The first results of impedance measurements on the graphite quartzite sample MR3-1 (oriented parallel to foliation) saturated with 0.01 M KCl solution (resistivity 7.8 Ωm, equivalent to many natural groundwaters) after air-drying and evacuation are displayed in Figure 4 in the form of a 'Bode' plot, i.e. for the (effective) resistivity magnitude

$$|\rho^*| = [(\sigma')^2 + (\sigma'')^2]^{-1/2}$$

and the phase

$$\varphi = \arctan(\sigma''/\sigma').$$

They show a highly resistive sample exhibiting a steady decrease of resistivity with increasing frequency in association with a very broad phase minimum (absolute minimum at -13.5° at 5.6 Hz). This high polarizability, in the context of applied geophysics called „induced polarization", is obviously due to redox reactions at the numerous electrolytic/quasi-metallic interfaces contained in this graphite-rich rock (Figures 2, 3). This type of dispersion differs strikingly from the frequency dispersion curves of other 'normal' resistive lower crustal rocks, displayed in Figure 4 for comparison. They include sample KR3502 (a graphite-free granulitic metabasite) as well as samples KR3360 and KR3436 which are thought to be representative of the regionally most common metapelites in the Serre San Bruno. As discussed at length in Jödicke et al. (2004), they contain about 1 % accessory graphite and show the typical behaviour of low porosity crystalline rocks characterized by a small, (almost) constant phase angle in the low frequency range, here below 1 Hz. The resistivity correspondingly increases towards low frequencies ('anomalous low frequency dispersion') (Börner and Schön, 1995, Nover and Will, 1991, Nover, 2005).

To further characterize the interaction between the electrolyte and the numerous quasi-metallic interfaces contained in the graphite quartzite, the sample MR3-1 was, in the next step, saturated with increasingly higher pore fluid concentrations (0.03, 0.1, 0.3, 1 M KCl), and measured again.

The results displayed in Figure 5a demonstrate the dominating effect of the pore filling, which lowers the effective resistivities and shifts the capacitive effects to higher frequencies with increasing salinity. In general, however, the shape of the dispersion curves remains almost unchanged. Except for the most resistive sample saturated with 0.01 M KCl, the resistivity levels tend to reach DC resistivity (constant resistivity, almost zero phase) at the lowest frequencies.

Some formal similarity is found, however, between the dispersion curves of sample MR3-1 and sample KR3244A that exhibits a strong phase effect with a maximum phase delay of -12.8° at 0.04 Hz and an increase of resistivity toward low frequencies that parallels the one of sample MR3-1. Like KR3360 and KR3436, sample KR3244A is a garnet-sillimanite gneiss with approximately 85% garnet and sillimanite, the rest is composed of coarse (up to 1 mm) plagioclase and K-feldspars ± biotite, ore and graphite, thus representing a typical metapelite again. In contrast to the ‘normal’ samples, KR3244 is strongly weathered. Repeated measurements within 6 weeks, leaving the system under constant conditions, generally reproduced its dispersion curves but random shifts of the maximum phase delay were observed. After saturation with 1M KCl solution, stable dispersion resulted, and, showing now the ‘anomalous low frequency dispersion’, the curves fit into the scheme of samples KR3360 and KR3436 (Figure 4). We may assume that chemical imbalance in the small pore space of only 0.6% causes the strong relaxation effect, probably due to retrograde formation, e.g., of clay minerals along inner surfaces caused by weathering.

Finally, it was tested how the spatial orientation of the graphite inclusions of the graphite quartzite may control the dispersion curves. In this context, strong anisotropy of resistivity may be presumed, considering its strictly gneissic layering. Based at numerous measurements on pairs of samples drilled parallel and perpendicular to foliation, the resistivity was on average larger by a moderate factor of 2 – 3 for measurements perpendicular to foliation than parallel to it, but factors up to 10 were also reached (Jödicke and Dreismickenbecker, 1994). Some typical examples are shown in Figures 6a-c. At first glance, the shapes of the resistivity curves do not differ much but the corresponding phases reveal that complex inner details may be inherent. In addition, the type of anisotropy may differ to some extent. The anisotropy of sample MR3-4 (Figure 6c) is almost frequency independent; accordingly, the phases are almost identical. The anisotropy of sample MR3-3 (Figure 6b) shows some variations which are expressed in larger deviations between the phases. In contrast, sample MR3-2 (Figure 6a) is characterized by a steady increase of anisotropy toward high frequencies.

Discussion

The graphite quartzite is best described as a highly resistive, highly polarizable, electrically moderately anisotropic rock. Its high resistivity fits into the typical range of low porous, medium to high-grade metamorphic rocks, thus giving no indication that the large amount of graphite inclusions may noticeably lower the bulk conductivity. This is supported by the values of anisotropy, which also fit into the typical range of gneisses (e.g., Rauen et al., 1991, Nover et al., 1995). Duba and Shankland (1982) used the upper bound formula (Hashin and Shtrikman ,1962) to calculate the absolute amount of well-ordered graphite required to enhance the conductivity of dry rocks and found that a volume fraction of carbon of only 5x10^{-6} % can cause a conductivity of 0.1 S/m if well interconnected. Obviously, through-going interconnections between the graphite grains do not exist, neither in the foliation plane, where they might be expected with somewhat higher probability. Otherwise, a much larger anisotropy factor would result. On the other hand, Shankland et al., (1997), Nover et al., 1998 and (Fowler et al., 2005) could show the a confining pressure increases the degree of interconnection of carbon rich phases in KTB and THTO rocks as well, thus causing a significant increase of the rock conductivity.

The high polarizability is explained as the effect of redox reactions at the numerous electrolyte/graphite interfaces varying widely in size and shape in this rock (Figure 2). In petrophysics this type of relaxation is called ‘Maxwell-Wagner’ (Wait, 1971), in electrochemistry ‘overvoltage’ effect (Collett, 1959). The resulting asymmetric broad dispersion curves extending over seven decades in the long period range (Figures 5, 6), give evidence of a complex system of superimposed series of Debye relaxation processes. As particularly a broad graphite grain size distribution will smear the phase minimum, any complicate phase behaviour may indicate distributional variations, for example, locally clustered instead of statistically distributed grain sizes (Figure 6b). It seems, however, that information that is more explicit may not be achieved from the dispersion curves. According to our experience, we even could not reveal any clear relation between phase behaviour and orientation of the measured sample parallel or perpendicular to foliation.

Polarization effects may be produced by other mechanisms, too. For example, clay minerals form anion barriers in small pore spaces instead of metallic interfaces. The resulting phase effect may look similar to the effect caused by the graphitic (quasi-metallic) interfaces, as sample KR3244A saturated with 0.01M KCl shows (Figure 4). However, in striking contrast to the graphite quartzite which keeps its type of dispersion independent of the salinity of the pore filling, the assumed ‘clay effect’ of sample KR3244A diminishes with increasing salinity. This can readily be explained by the restricted reach of the electrical inner surface potentials of the clay barriers in a concentrated electrolyte (Nover et al., 1995).

A definitely different type of polarization effect is observed in the frequency range above 10^2 Hz for all studied data sets of the metabasite, the metapelites, as well as of the graphite quartzite (Figure 4). The actual onset of the phase delay is shifted to higher frequencies with decreasing resistivity of the rock sample. It is also well known from more simple rock types like saturated porous sandstones or siltstones. Strikingly, the beginning phase-drop is documented at highest frequencies for the dispersion curve of the pure 0.01M KCl electrolyte, too (Figure 4). Therefore, it seems to be questionable that this relaxation is related to any fluid/rock interaction, for example, to the high-frequency capacitive effect of bound water (double-layer), depending on the pore space and on the salinity of the fluid (Nover and Will, 1991).

In order to test whether this effect may indicate electrical properties of the used measuring 2-pole measuring device instead, part of the data are displayed here again in the form of a Cole-Cole diagram, which allows to better recognize the contribution of specific electrical current circuit elements. Thus, the resistive samples KR3502 (graphite-free metabasite) and KR3360, KR3436 (metapelites with accessory graphite) clearly demonstrate their ‘anomalous low frequency dispersion’ behaviour by their long, almost real branches of low frequency data , which merge into an almost perfect single Debye relaxation process at high frequencies (Figure 7a). The same was tried for the samples, which are characterized by a strong long-period relaxation (Figure 7b). Again, the broadband polarization effect is followed by an almost perfect single relaxation process at high frequencies. Sample KR3244A (highly weathered metapelite with accessory graphite) is resistive enough to reach the minimum phase of that relaxation in the frequency range up to 1 MHz, so that an almost complete semicircle is formed. To show the same for the more porous and thus more conductive graphite samples MR3-1 (parallel and perpendicular to foliation), the measured frequency range of the 2-pole cell had to be extended up to 10 MHz. This was reached by the application of the 'quotient method' proposed by Pelster (1991) in which the sample signal is compared with a reference impedance (see also Markfort and Jödicke, 1998). At frequencies roughly above 1 MHz inductive coupling effects due to wiring and capacitive effects due to the geometry of the sample holder influence the the measured signal significantly with the consequence, that high frequency impedances reflect less significantly sample properties.

The test on sample MR3-1, that had shown that varying salinities of the pore filling do not principally change the type of the long-period relaxation process, also allows to estimate some important petrophysical parameters, e.g., the formation factor

$$F = \sigma_W/\sigma_0$$

(Sundberg, 1942), or, expanded to Archie's first law

$$F = a/\Phi^m$$

(Archie et al., 1942), where σ_0 denotes the bulk rock conductivity, σ_W the conductivity of the aqueous pore filling, and $0 \leq \Phi \leq 1$ the porosity. The free adjustment parameter a is for crystalline rocks often simply chosen to a=1; the exponent m ('cementation exponent' in sedimentary rocks) depends on the geometry of the open pore space, for crystalline rocks it may vary between 1.58 (Keller, 1967) and 2 (Brace, 1971).

Figure 5 makes clear that for sample MR3-1 all dispersion curves tend to reach DC resistivity towards lowest frequencies. To estimate the formation factor, the resistivity values were therefore picked from Figure 5 at the lowest measured frequency 0.001 Hz (≈ DC case) and are shown in Figure 8 as function of the conductivity/salinity of the pore filling. This presentation elucidates that the three most conductive samples (saturated with 1M, 0.3M, 0.1M KCl) follow a simple exponential law. For the low conductive pore fluids (0.03 M, 0.01 M KCl), the surface conduction clearly begins to dominate as shown in the classical experiments by Brace (1971). The bulk rock conductivity for the whole salinity range of the pore filling is best described by the exponential equation in the denotation by Schopper (1982)

$$\sigma_0 = 0.00304\ \sigma_w^{1.11} + \sigma_{q0},$$

with $\sigma_{q0} \approx 5 \cdot 10^{-4}$ S/m. The first term on the right side approximates Archie's first law (1942), which would require an exponent of exactly 1. The second, additive term, dominating the low salinity behaviour of the sample, describes the effective surface conductivity (Börner and Schön, 1995). Thus, surface conductivity dominates for conductivities of pore fluids that are about equal or less conductive than natural groundwaters. Ignoring the actual exponential behaviour and using Archie's law as an approximation, instead, the formation factor would reach the value of 329 with an exponent m varying between 1.8 and 1.9 for the given porosities between 4 and 5 % of the MR3 samples.

The over-proportional increase of the bulk rock conductivity with increasing salinity of the pore filling may be explained by the effect of numerous parallel resistance circuits in a system of two conductive components consisting of graphite grains and electrolytical bridges in-between, the embedded in a resistive matrix. To model such an electrical behaviour requires beside resistors and capacitors as circuit elements a constant phase element CPE being sensitive on electrochemical reactions that cause a distribution of active sites (different activation energies) on a surface. The electrolytical bridges connecting the metallic conducting graphite particles form such an interface that is best described by a broad distribution of relaxation times. The consequence of this can be seen in Fig. 7 a, b where depressed semicircles fit the measured data, but with a centre below the real axis. Mathematically a CPE impedance is given by

$$1/Z=Q^{o}(j\omega)^{n}$$

where Q^{o} has the numerical value of the admittance (1/|Z|) at ω=1rad/s. With n=1 its the equation for the impedance of a capacitor, where $Q^{o}=C$. In a Cole-Cole diagram, where the real part of the impedance is plotted versus the imaginary part, a parallel arrangement of a resistor and a CPE element will cause a depressed semicircle with its centre below the real axis. The centre of the semicircle is depressed by an angle of (1-n)*90°. Using an CPE in combination with RC-elements allowed to fit the measured data. Figure 7c shows as an example the result for sample 3502, data of the refinements of the other samples are listed in Table 1.

7. Conclusions

In this study, the electrical properties of a graphite-rich quartzite from the former lower crust exposed in the Serre San Bruno, Calabria (southern Italy) have been analysed by means of complex electrical measurements. Identified as a former oil sandstone (reservoir rock), this quartzite contains 12 to 15 % flake-like graphite, which is thought to present highly metamorphosed relics of its former hydrocarbon filling. The presence of syngenetic graphite in former lower crustal rocks makes evident that organic matter trapped in a reservoir rock, is largely resistant against the varying geochemical conditions during prograde and retrograde metamorphism. This had also been shown for graphite that is contained in normal metapelites as accessory mineral, or enriched in former black shales (source rocks) where it may cause high conductivity (Shankland et al., 1997, Nover et al., 1998; Jödicke et al., 2004; Fowler et al., 2005; Nover, 2005).

Despite the high portion of graphite in its rock composition, the graphite quartzite is highly resistive. This main result is mainly due to the spatial ordering of isolated graphite grains like tiles in the rock matrix, which prevents the generation of through-going electrical pathways. Instead, high polarizability is observed indicating redox reactions at the numerous electrolyte/graphite grain interfaces, causing high CPE values. Most conceivably, this ordering goes back to the early formation of isolated oil droplets in the reservoir sandstone. After high-grade metamorphism and shearing, they appear as flat graphite grains in the foliation plane. Obviously, they could not be smeared together because of the rigidity of sillimanite and quartz, the main rock constituents. We may conclude, therefore, that the analysed graphite quartzite is by no means a candidate that may significantly contribute to the electrical conductivity of the deep continental crust.

The effects of electrochemical relaxation processes observed on the Calabrian graphite quartzite proved to be remarkably large in the classical frequency range of magnetotellurics and audiomagnetotellurics ($< 10^4$ Hz, Figure 4). This may give some importance to the question whether the assumption to imply DC resistivities in magnetotelluric interpretation methods, is real and generally justified. Whereas the ‘anomalous low frequency dispersion’ effect typically observed on highly resistive rocks in this range is comparably small and may be hidden in the normal error level of the magnetotelluric data, MT measurements over occurrences of graphite-rich quartzites layers would pose a major problem. Such occurrences are known to form large parts of the upper crust, for example, in parts of Sri Lanka or South India. Beyond those examples, it may be generally useful to consider whether any frequency-dependent deviations between MT model responses and measured MT data might be related to electrochemical relaxation processes. Particularly, if such deviations can be assigned to deeper structures of unknown composition, the existence of larger series of graphite quartzites or similar rocks should not be excluded. In contrast, relaxations caused by ‘clay effects’ are restricted to the uppermost kilometres due to the increase of pore water salinity and the transformation of clay minerals to true micas with depth.

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Figure Captions

Figure 1: Former lower crustal metapelitic rocks, exposed in the Serre San Bruno, Calabria, southern Italy, showing the sampling site ③ within the course of a self potential anomaly; simplified after Jödicke et al. (2004).

Figure 2: Flake-like graphite in quartzite MR3, macroscopic photograph from thin section; long side of photograph ~ 16 mm.

Figure 3: Photomicrograph from strongly foliated graphite quartzite MR3. The foliation is formed by the flat faces of prismatic sillimanite (sil; with graphite inclusions) and coarsely sutured quartz grains with a preferred crystallographic orientation, and of well-aligned platy graphite. Oblique polarizer; long side of photograph = 7 mm.

Figure 4: Complex electrical measurements on graphite quartzite MR3-1 in comparison with lower crustal metabasites and metapelites, all samples oriented parallel to foliation and saturated with 0.01M KCl solution; 'Bode' plot.

Figure 5: Complex electrical measurements on graphite quartzite MR3-1, saturated with KCl solutions with increasing salinity.

Figures 6a-c: Complex electrical measurements of anisotropy on pairs of graphite quartzite samples MR3-2, MR3-2, and MR3-3, drilled parallel and perpendicular to foliation.

Figure 7a: Cole-Cole diagram of complex electrical measurements on metabasite KR3502 (upper and right scale axes), and on metapelites KR3360, KR3436 (lower and left scale axes).

Figure 7b: Cole-Cole diagram of complex electrical measurements on graphite quartzite samples MR3-1, measured parallel and perpendicular to foliation (lower and left scale axes); in comparison with strongly weathered metapelite KR3244A (upper and right scale axes).

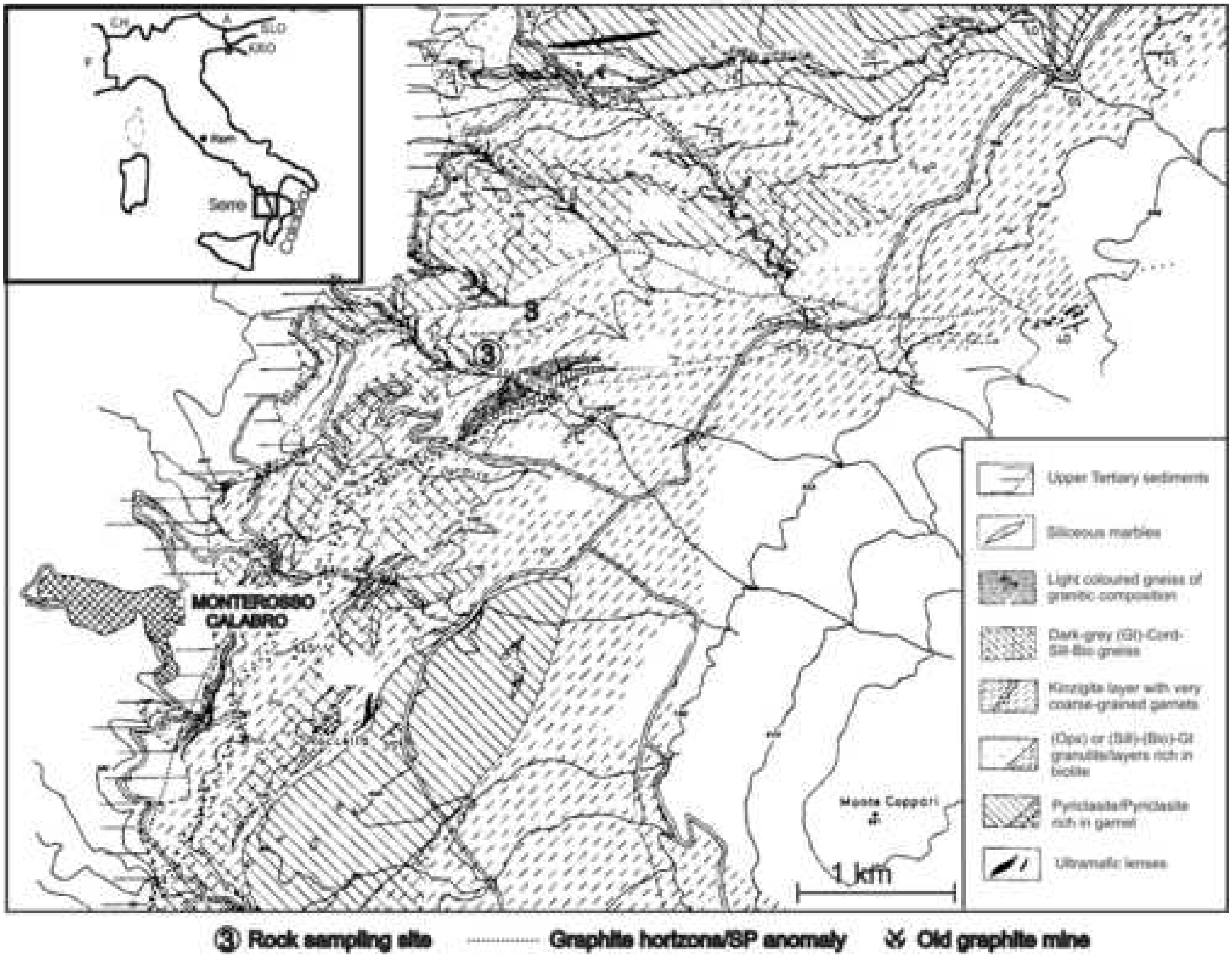
Figure 7c: Cole-Cole diagram of the complex resistivity of sample 3502. Squares represent model data, crosses represent measured data.

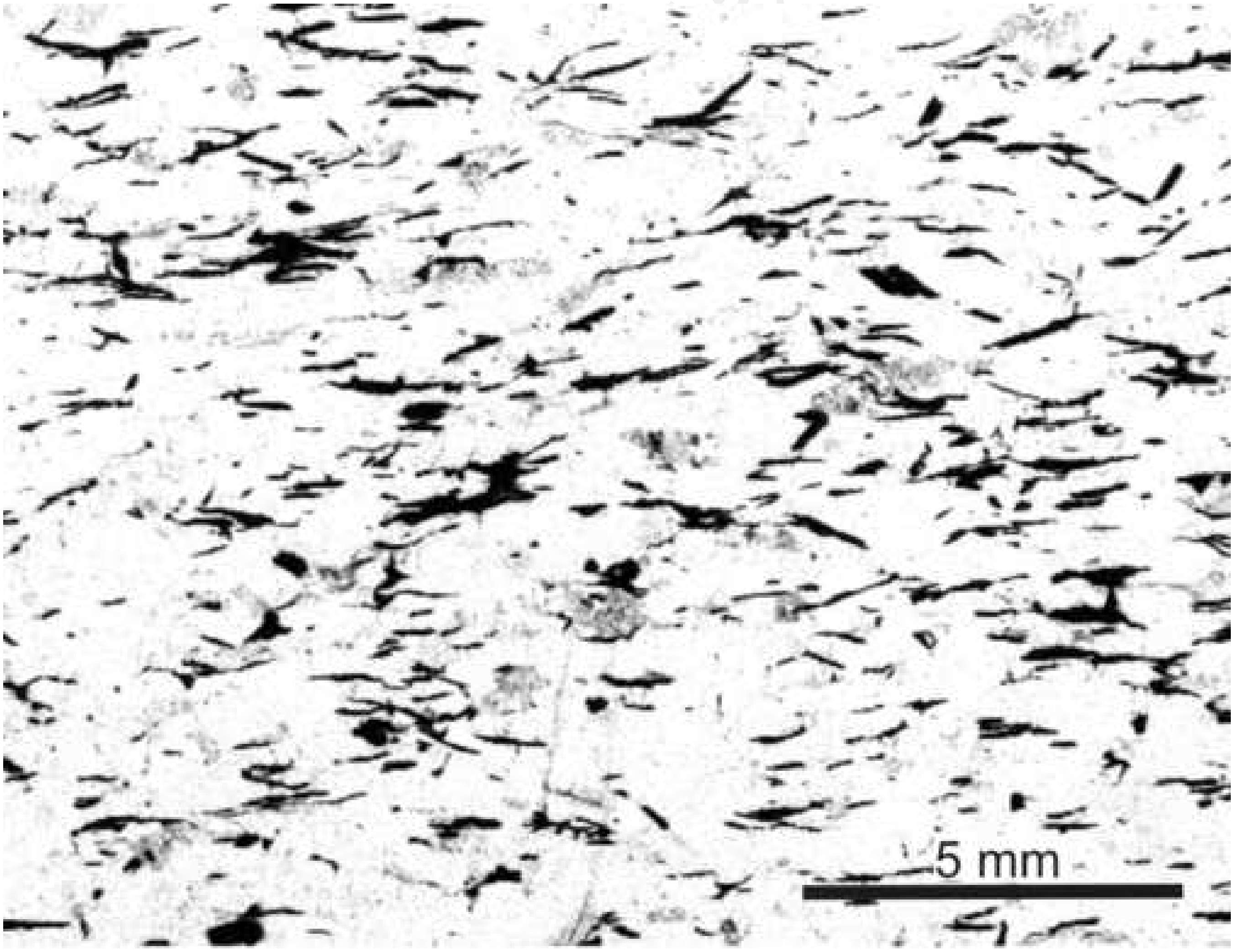
Figure 8: Relation between conductivity of aqueous pore filling and bulk rock conductivity for sample MR3-1.

Table 1 Compilation of petrological and electrical properties of the graphite free and graphite bearing samples. A qualitative description of the frequency effect is given in column 4, where the resistivity is marked as high or low, the second value describes the measured low frequency polarisation. The other columns list the refined model parameters of the equivalent circuit model. The equivalent circuit model considers conduction and polarisation. R and C are resistor and capacitor respectively. CPE is the constant phase element, it is a non-intuitive element found at the response of real systems. In Cole-Cole notation it is a semicircle with its center below the real axis, it describes the properties of non-homogenous systems. CPE has the dimensions of a admittance Y and n is the depression angle: $CPE=1/Z=Y=Q(i\omega)^n$, with Q=C for n=1.

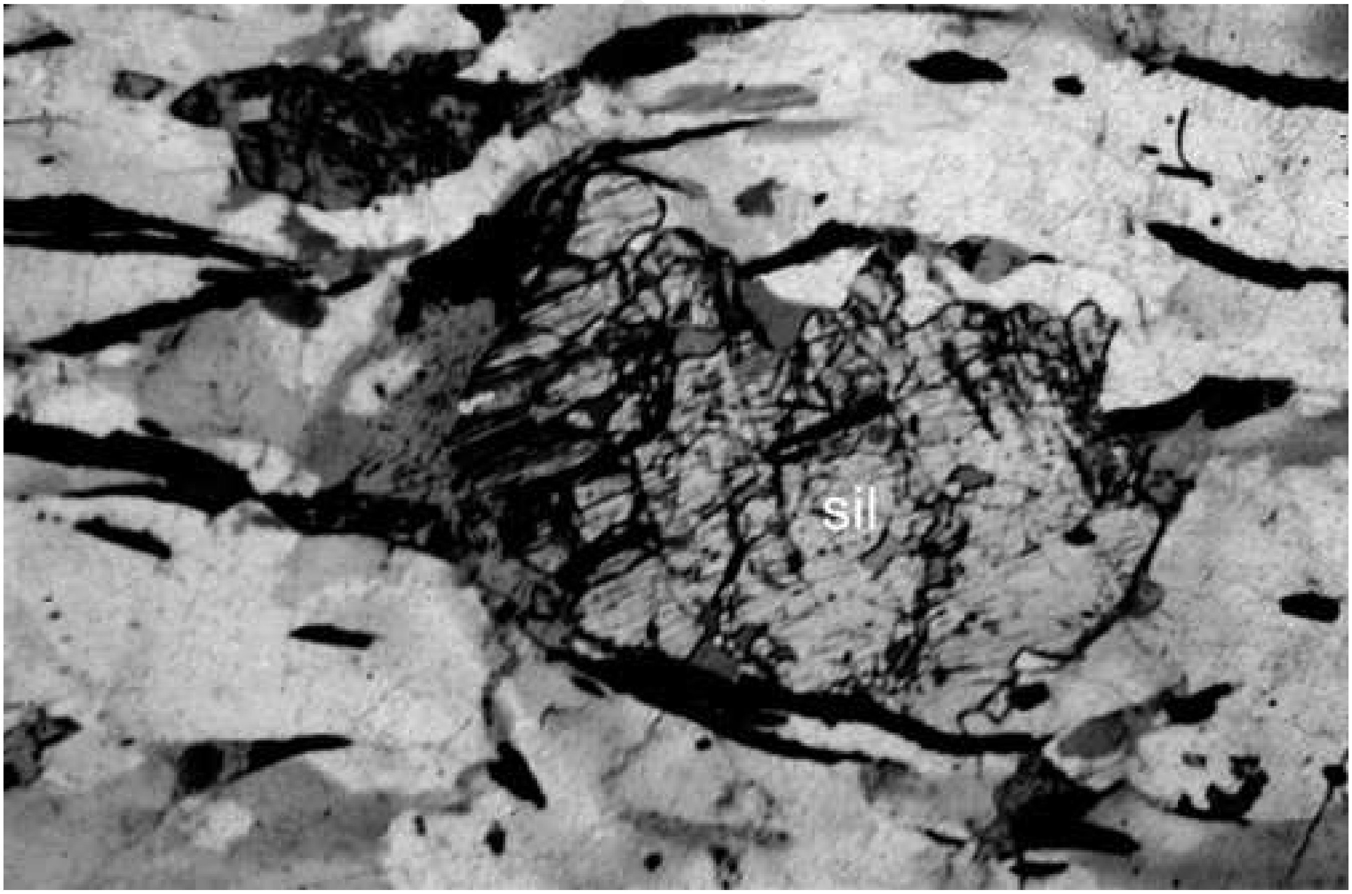
27

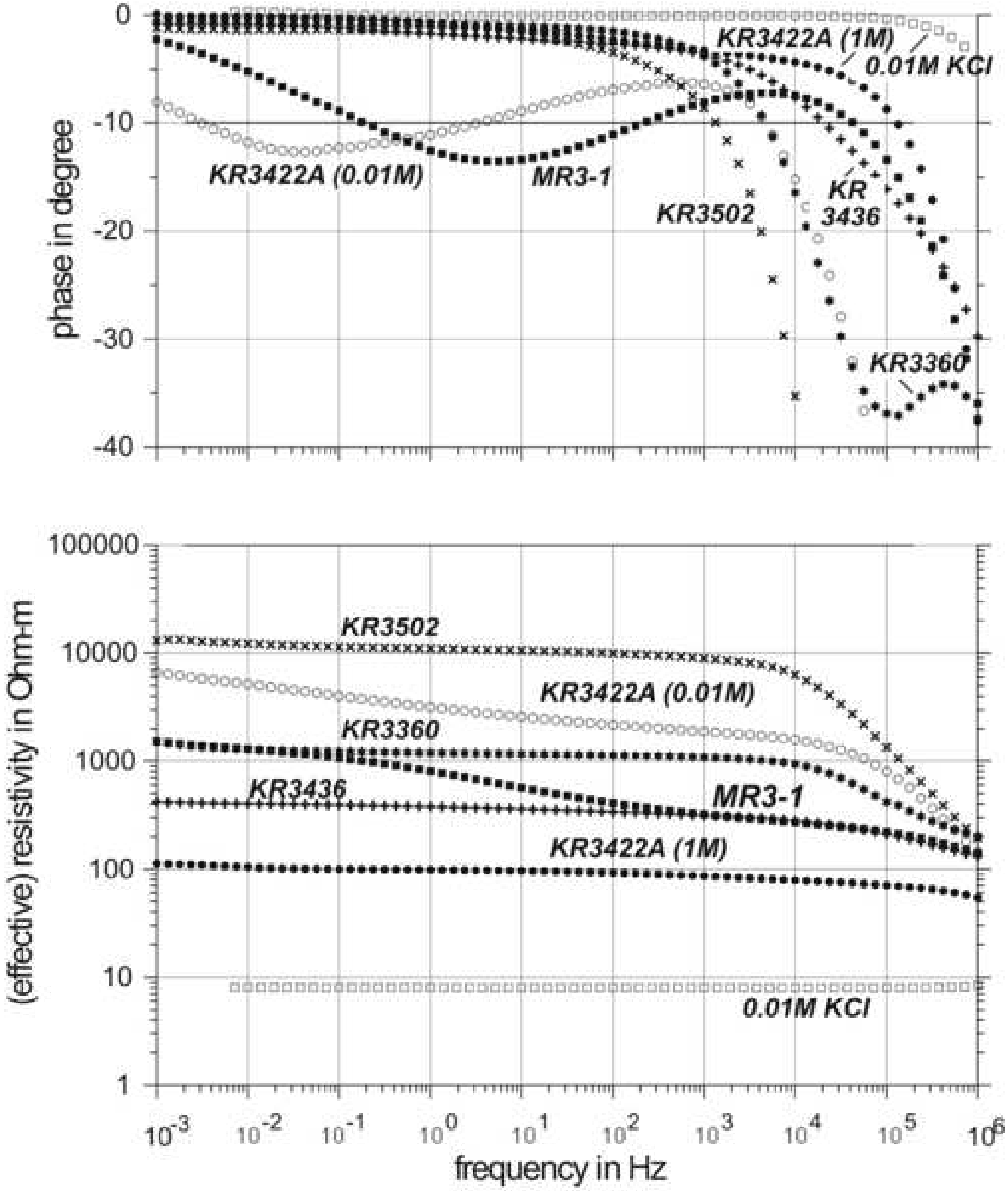
sample	*Petrology*	*Graphite*	*R / Polarisation*	*R ohm*	*C F*	*R ohm*	*n*	*CPE*
KR3244	metapelite	accessory	very high / low frequ.	7605	1.6e-9	1478	0,26	2,7e-4
KR3360	metapelite	accessory	high / low frequ.	1219	3.0e-10	209	0.68	2e-7
KR3436	metapelite	accessory	high / low frequ.	345	1.3e-9	59	0.24	1.3e-4
KR3502	pyriclasite	~0	very high / low frequ.	1.2e4	1e-9	53	0.26	3.3e-6
MR1	metapelite	24,7%	very low /~ zero	2322	6.6e-10	137	0.23	5.5e-4
MR3	metapelite	15%	high / low frequ.	4428	3.6e-10	277	0.22	3e-4

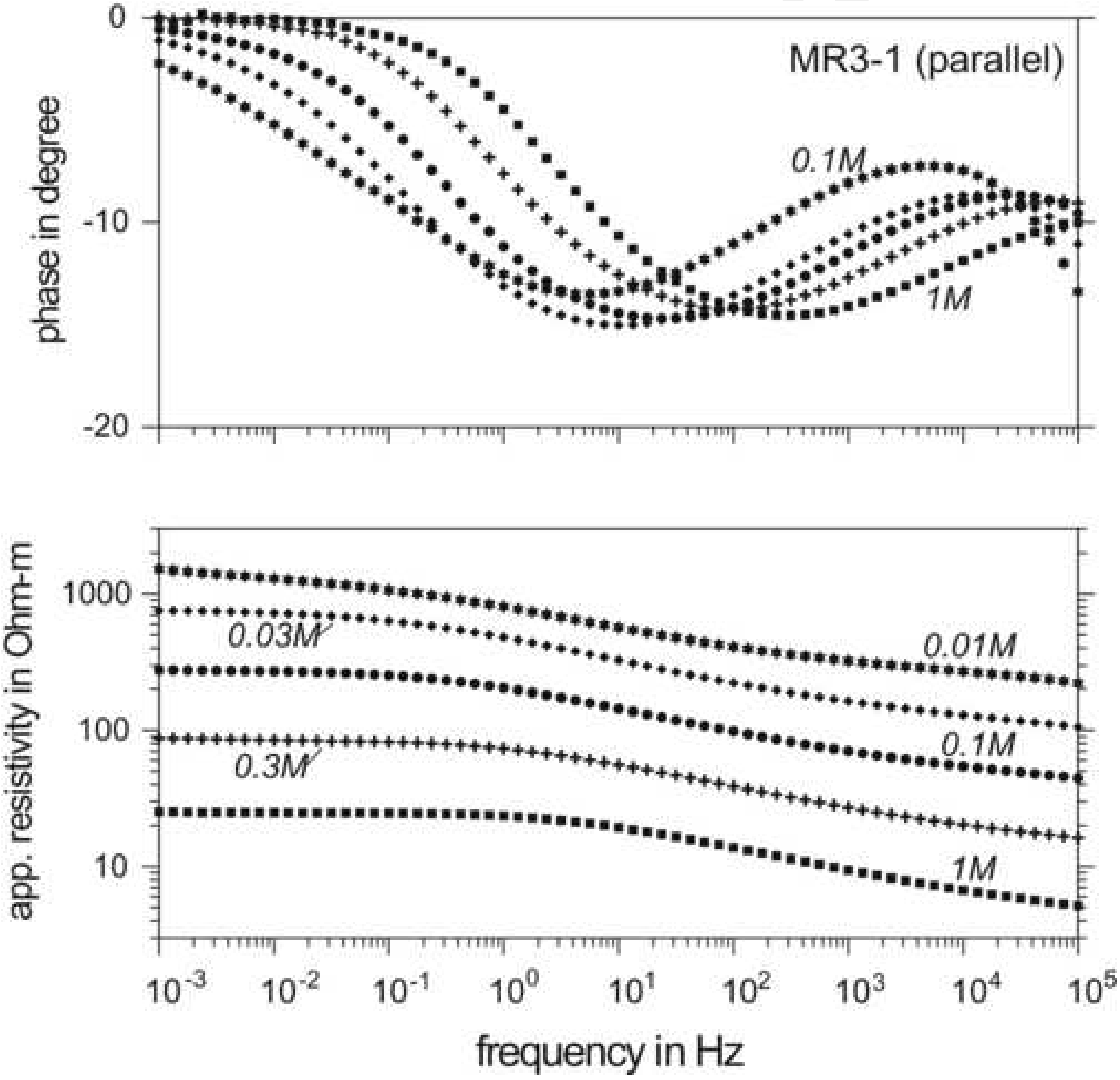

CH
A
SLO
CRO
F
Serre
Calabria
3
③
MONTEROSSO CALABRO
Monte Coppari
1 km
Upper Tertiary sediments
Siliceous marbles
Light coloured gneiss of granitic composition
Dark-grey (Gt)-Cord-Sill-Bio gneiss
Kinzigite layer with very coarse-grained garnets
(Opx) or (Sill)-(Bio)-Gt granulite/layers rich in biotite
Pyriclasite/Pyriclasite rich in garnet
Ultramafic lenses
③ Rock sampling site
Graphite horizons/SP anomaly
Old graphite mine

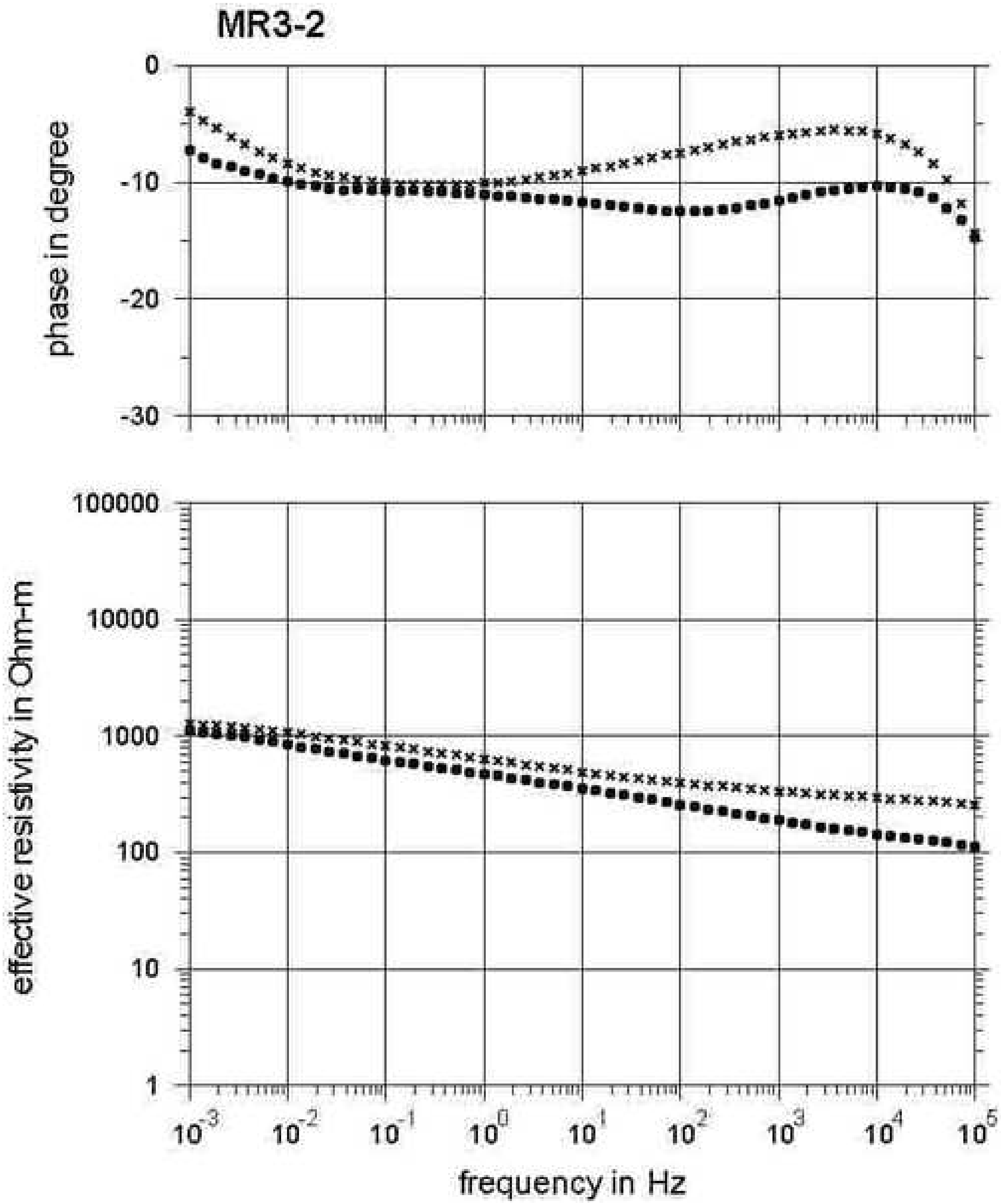


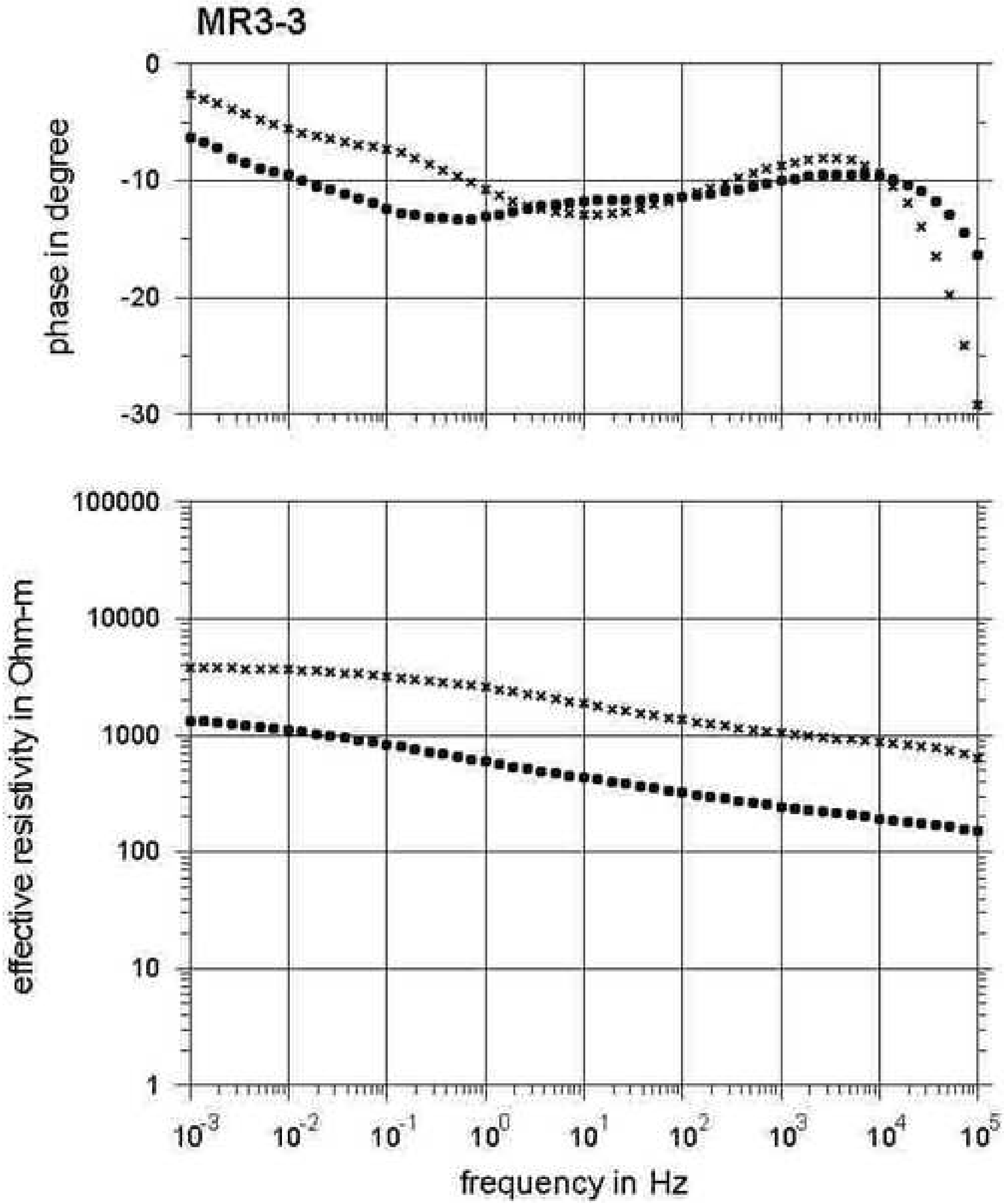
5 mm

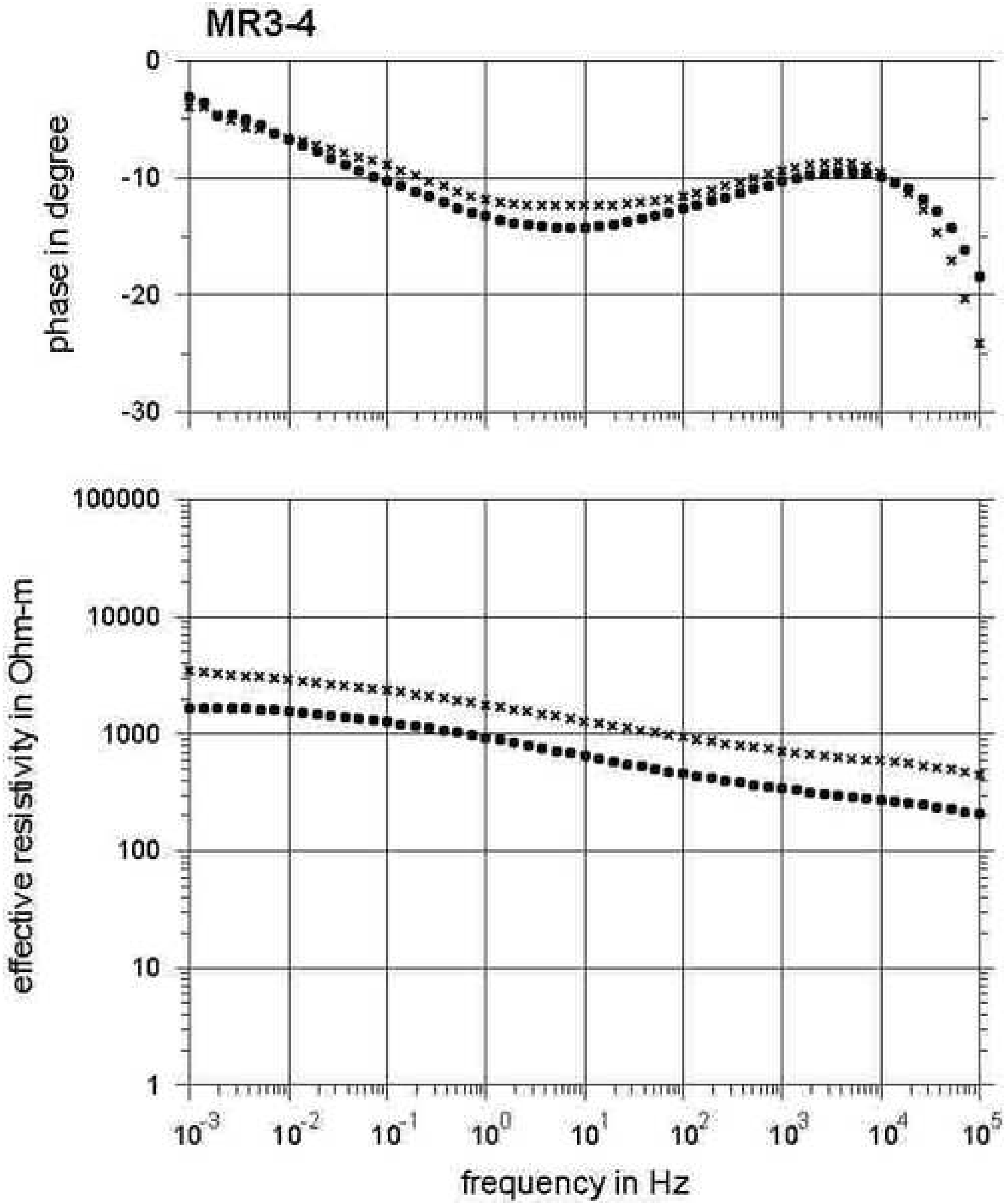

sil

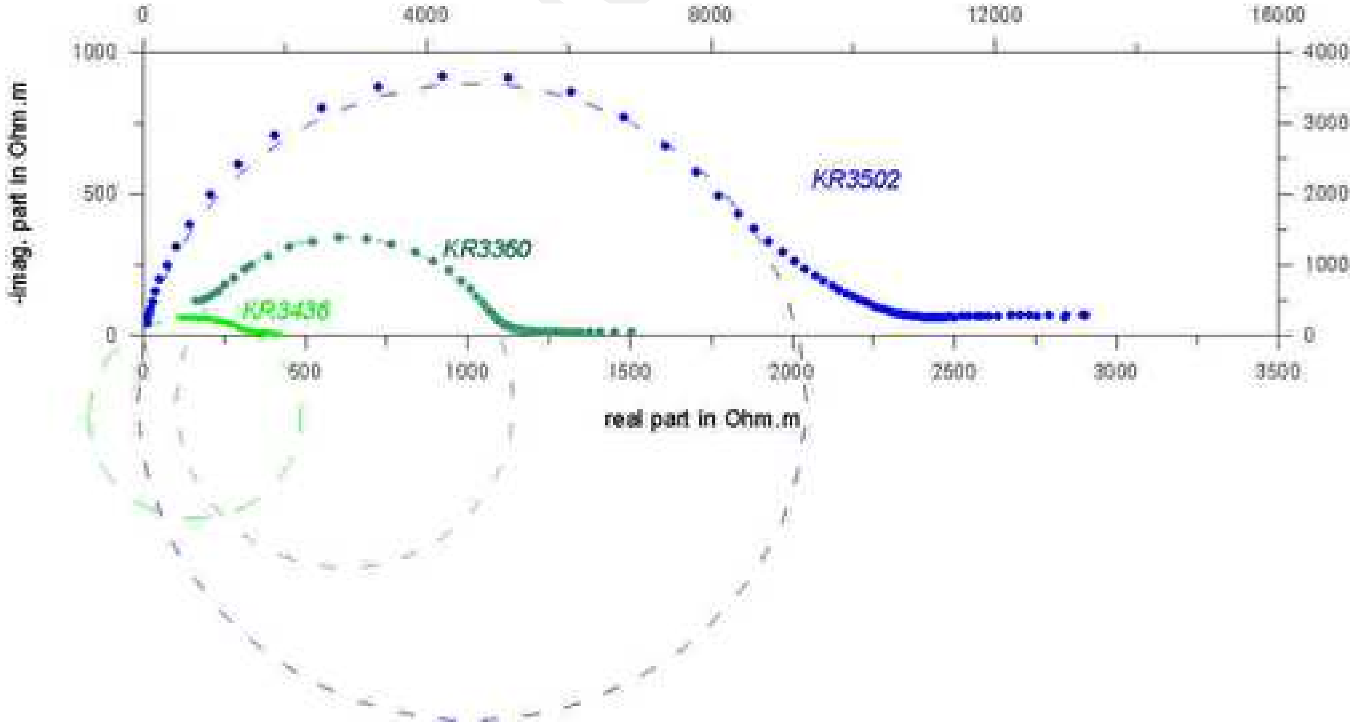

0
-10
-20
-30
-40
phase in degree
KR3422A (1M)
0.01M KCl
KR3422A (0.01M)
MR3-1
KR3502
KR 3436
KR3360
100000
10000
1000
100
10
1
(effective) resistivity in Ohm-m
KR3502
KR3422A (0.01M)
KR3360
KR3436
MR3-1
KR3422A (1M)
0.01M KCl
10^{-3}
10^{-2}
10^{-1}
10^{0}
10^{1}
10^{2}
10^{3}
10^{4}
10^{5}
10^{6}
frequency in Hz

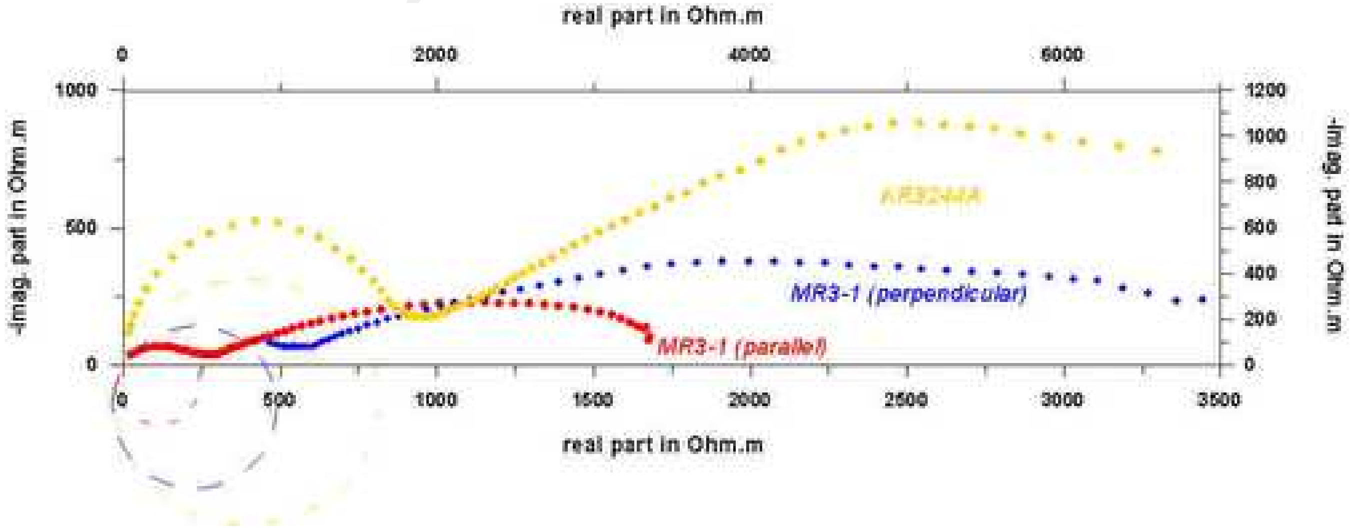

MR3-1 (parallel)
phase in degree
0
-10
-20
0.1M
1M
app. resistivity in Ohm-m
1000
100
10
0.03M
0.01M
0.3M
0.1M
1M
10^-3
10^-2
10^-1
10^0
10^1
10^2
10^3
10^4
10^5
frequency in Hz

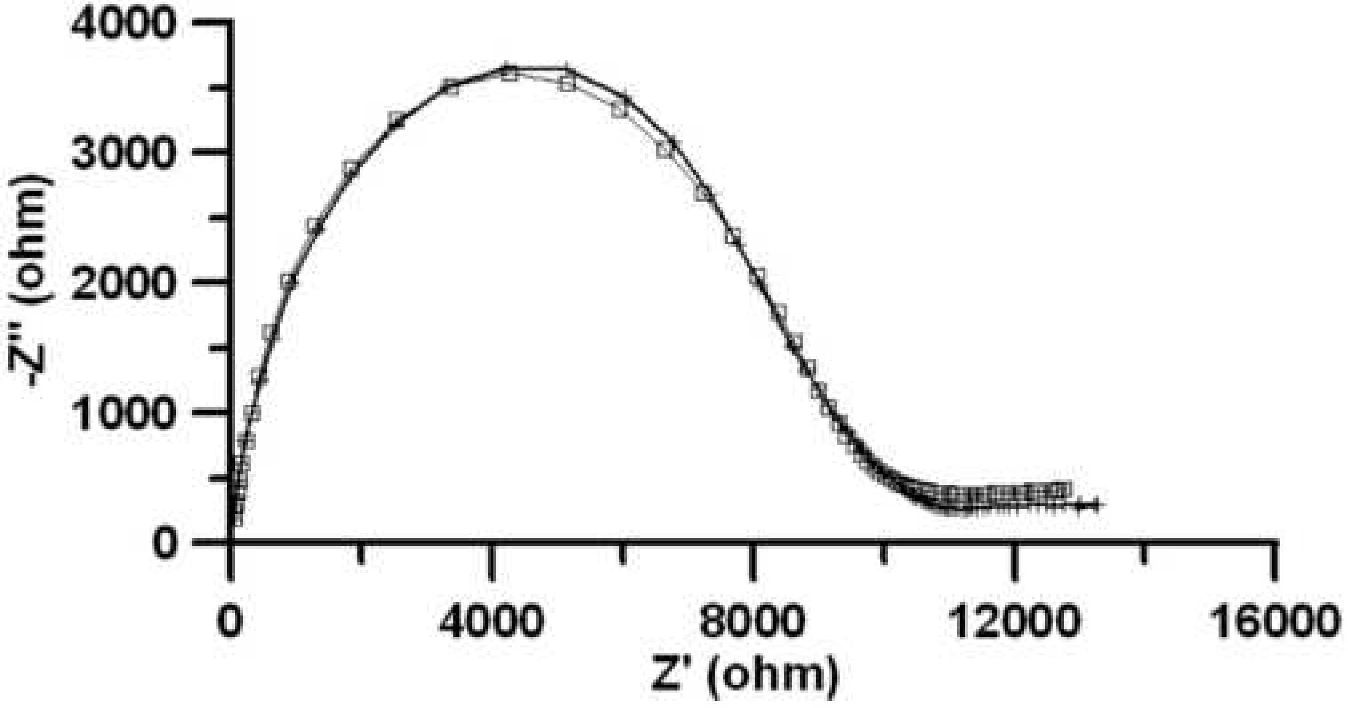

MR3-2
phase in degree
0
-10
-20
-30
effective resistivity in Ohm-m
100000
10000
1000
100
10
1
10^{-3}
10^{-2}
10^{-1}
10^{0}
10^{1}
10^{2}
10^{3}
10^{4}
10^{5}
frequency in Hz

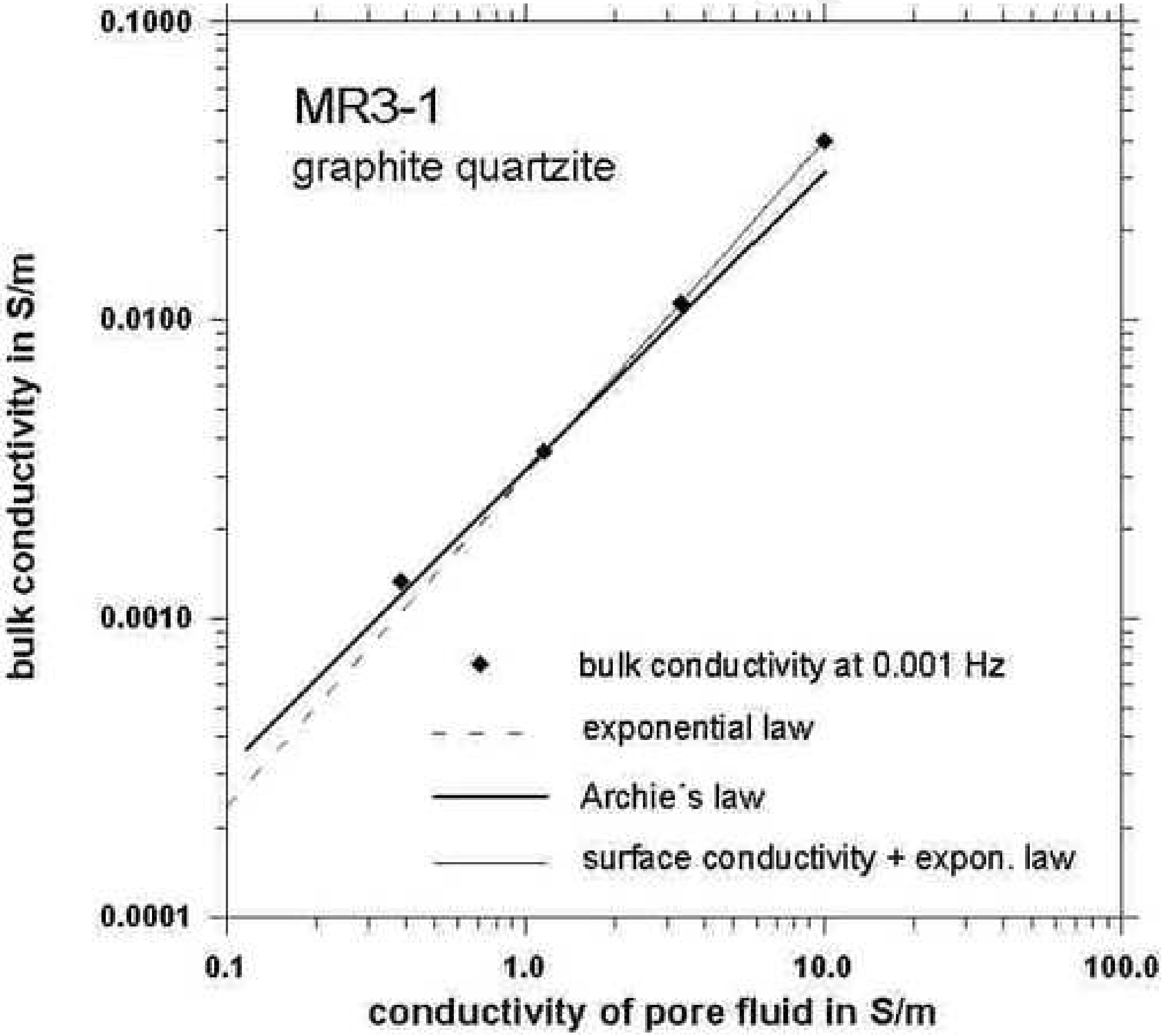

MR3-3
phase in degree
0
-10
-20
-30
effective resistivity in Ohm-m
100000
10000
1000
100
10
1
10^{-3}
10^{-2}
10^{-1}
10^{0}
10^{1}
10^{2}
10^{3}
10^{4}
10^{5}
frequency in Hz


MR3-4
phase in degree
0
-10
-20
-30
effective resistivity in Ohm-m
100000
10000
1000
100
10
1
10^-3
10^-2
10^-1
10^0
10^1
10^2
10^3
10^4
10^5
frequency in Hz


0
4000
8000
12000
16000
1000
500
0
4000
3000
2000
1000
0
-imag. part in Ohm.m
KR3502
KR3360
KR3436
0
500
1000
1500
2000
2500
3000
3500
real part in Ohm.m


real part in Ohm.m
0
2000
4000
6000
1000
500
0
-imag. part in Ohm.m
1200
1000
800
600
400
200
0
-imag. part in Ohm.m
KR3244A
MR3-1 (perpendicular)
MR3-1 (parallel)
0
500
1000
1500
2000
2500
3000
3500
real part in Ohm.m


4000
3000
2000
1000
0
-Z'' (ohm)
0
4000
8000
12000
16000
Z' (ohm)


MR3-1
graphite quartzite
0.1000
0.0100
0.0010
0.0001
bulk conductivity in S/m
0.1
1.0
10.0
100.0
conductivity of pore fluid in S/m
◆ bulk conductivity at 0.001 Hz
exponential law
Archie´s law
surface conductivity + expon. law