

FREQUENCY DEPENDENT ELECTRICAL PROPERTIES OF MINERALS AND PARTIAL-MELTS

JEFFERY J. ROBERTS¹ and JAMES A. TYBURCZY²

¹*Lawrence Livermore National Laboratory, PO Box 808, L-201, Livermore, CA 94551, U.S.A.*

²*Dept. of Geology Arizona State University Tempe, AZ 85287-1404, U.S.A.*

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Abstract. The resistance to current flow of minerals and partial-melts is a frequency dependent electrical property. Measurements of the frequency dependent electrical impedance of single crystal olivine, polycrystalline olivine, dunites, metapelites, and partial-melts, between 10^{-4} and 10^5 Hz, when plotted in the complex impedance plane, reveal arcs that correspond to different conduction mechanisms in the material being studied. In polycrystalline materials, two impedance arcs related to material properties (as opposed to electrode properties or electrode-sample interactions) are observed. Each impedance arc is activated over a distinct range of frequency, that is, the mechanisms occur in series. Based on experiments comparing single and polycrystalline impedance spectra, experiments on samples with different electrode configurations, and on samples of varying dimension, the mechanisms responsible for these impedance arcs are interpreted as grain interior conduction (σ_{gi}), grain boundary conduction (in polycrystalline materials; σ_{gb}), and sample-electrode interface effects, from highest to lowest frequency, respectively. Impedance spectra of natural dunitic rocks reveal analogous behavior, that is, σ_{gb} and σ_{gi} add in series. The grain boundaries do not enhance the conductivity of any of the materials studied (a direct result of the observed series electrical behavior) and, under certain conditions, limit the total conductivity of the grain interior-grain boundary system. By examining the frequency dependence of the electrical properties of partial-melts, it is possible to gain information about microstructure and the distribution of the melt phase and to determine the conditions under which the presence of melt enhances the total conductivity. Impedance spectra of olivine-basalt partial-melts indicate that at least two conduction mechanisms occur in series over the frequency range 10^{-4} – 10^5 Hz, similar to the observed electrical response of melt-absent polycrystalline materials. In a sample containing isolated melt pockets the intermediate frequency grain boundary impedance arc is modified by the presence of melt indicating series conduction behavior. In a sample with an interconnected melt phase the high frequency grain interior impedance arc is modified by the melt phase, indicating the initiation of parallel conduction behavior. Because field EM response versus frequency curves are used to derive conductivity versus depth profiles, it is important to perform laboratory experiments to understand the frequency-dependent electrical behavior of Earth materials. Activation energies determined from studies that measure conductivity at a single frequency may be erroneous because of the shift of the dominant conduction mechanism with frequency as temperature is varied.

Introduction

Methods have been developed that utilize the electrical and magnetic properties of rocks and their response to either naturally occurring or artificially induced electromagnetic (EM) stimuli to explore the interior of the Earth. Profiles of conductivity versus depth derived from field observations add to our understanding of the composition, state, and dynamics of the crust and mantle. The usefulness of field based EM methods is dependent on accurate laboratory measurements of the electrical properties of relevant Earth materials and the interpretation of those

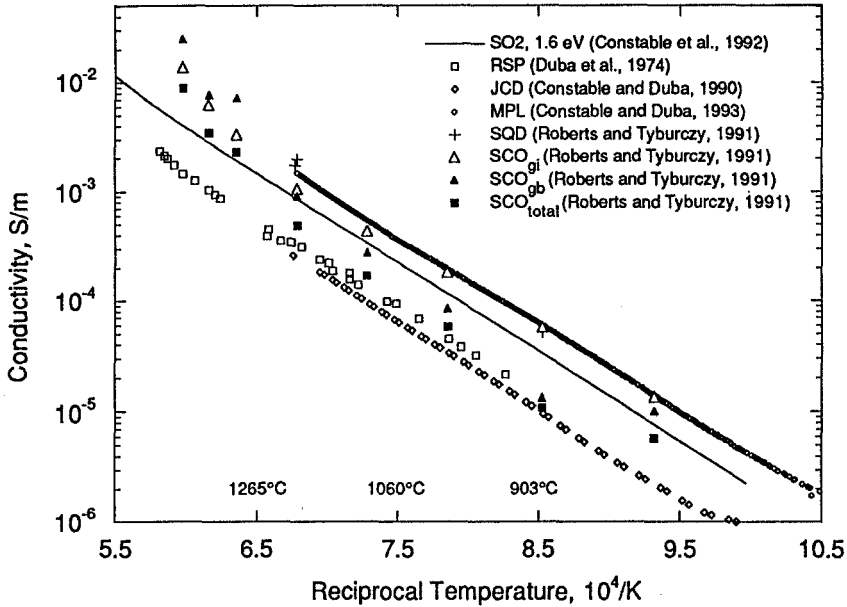


Fig. 1. Log conductivity versus reciprocal temperature for several single crystal olivine and olivine dominated rocks measured at 10^5 Pa total pressure. Symbols represent the conductivity of Red Sea peridot (RSP, [010], $f_{O_2} = 10^{-3}$ Pa, cgm; Duba *et al.*, 1974), 'standard' San Carlos single crystal olivine (SO2, 10^{-4} Pa, cgm; Constable *et al.*, 1991), Jackson County dunite (JCD, $f_{O_2} = 10^{-4.5}$ Pa, cgm; Constable and Duba, 1990), San Quintin dunite (SQD, $f_{O_2} = 10^{-5}$ Pa, wustite-magnetite; Roberts and Tyburczy, 1991), San Carlos sintered olivine compacts (SCO, $f_{O_2} = 10^{-5}$ Pa, wustite-magnetite; Tyburczy and Roberts, 1990), and Mount Porndon lherzolite (MPL, $f_{O_2} = 10^{-4}$ Pa, cgm; Constable and Duba, 1993). The oxygen fugacities listed above are the f_{O_2} for each experiment at 1200 °C using a constant gas mix (cgm) or corresponding to a specific buffer assemblage (assemblage given). The line SO2 is a model of the conductivity of an isotropic material based on single crystal olivine measurements made in each of the principle crystallographic directions. The SCO data represent the DC conductivity of the grain interior (open triangles) and grain boundary (solid triangles) mechanisms of the polycrystalline olivine compact as determined by a frequency dependent analysis. The SCO_{total} data (solid squares) represent the total conductivity of the sintered San Carlos olivine compact according to the series mixing model. Between 1200 and 800 °C the activation energy for all samples is within the range 1.45–1.6 eV.

measurements. The electrical properties of minerals are strongly dependent on temperature, composition, and point defect chemistry, and are also dependent on the frequency at which the measurements are made. Complex impedance measurements aid our understanding and interpretation of single frequency electrical properties measurements. In this paper the frequency dependent nature of the electrical response of minerals and partial-melts is reviewed with particular attention to the mineral olivine, an important mineral in the lower crust and upper mantle.

A number of recent laboratory studies reporting the conductivity of single crystal olivine, polycrystalline olivine sintered compacts, and natural dunites and lherzolites as a function of temperature are shown in Figure 1. All of the data

were taken under conditions of controlled f_{O_2} at 10^5 Pa (1 bar) total pressure. The Fe content for these samples ranges from $\sim\text{Fo}_{90}$ to Fo_{93} .

The difference in absolute conductivity at any given temperature most likely is a result of the differing Fe contents, the f_{O_2} of the experiment, minor element chemistry, and sample history. As noted by Duba and Constable (1993), the metamorphic or recrystallized olivines from the Red Sea (RSP) and Jackson County, North Carolina (JCD) have a lower conductivity than the igneous olivines from San Carlos (Arizona; SC), San Quintin dunite (Baja California; SQD), and Mount Porndon lherzolite (Australia; MPL). Overall, the agreement between these different samples and laboratories is quite good; the determined activation energies for all the samples fall between the range of 1.45 and 1.6 eV. It is important to note that the data reported in Figure 1 were taken at a single frequency with the exception of SQD and SCO. The results for these two experiments are the dc conductivity of the grain interior conduction mechanism as determined by measurements taken over a range of frequency (Roberts and Tyburczy, 1991).

Single frequency measurements of the electrical conductivity of single crystal olivine have led to an increased understanding of point defect chemistry and defect mobility in these materials (e.g., Sato, 1986; Schock *et al.*, 1989; Hirsch *et al.*, 1993). Conductivity studies as a function of temperature and f_{O_2} and thermopower studies of Fe bearing olivine indicate that below 1390 °C the dominant defect species responsible for electrical conduction is the small polaron ($\text{Fe}_{\text{Mg}}^{\cdot}$; standard Kroger–Vink defect notation), and above 1390 °C Mg vacancies (V_{Mg}') are the dominant charge carriers (Schock *et al.*, 1989). In polycrystalline materials grain boundaries are also known to play an important role in the diffusive and electrical properties of polycrystalline materials. Small amounts of melt have a potentially large effect on the overall electrical properties of a material. An understanding of how grain boundaries and the presence of melt affect the electrical properties of polycrystalline olivine is also important to our interpretation of the lower crust and upper mantle. One purpose of this study is to demonstrate that information about individual conduction mechanisms and microstructure can be determined by examining the frequency dependent electrical response of minerals and partial-melts. Another important factor is that parameters such as resistivity and conductivity determined at a single frequency may differ significantly from parameters determined by examining the frequency dependent electrical behavior. This can be especially important for the determination of activation energies at relatively low temperatures (e.g., below 1000 °C for olivine).

Nomenclature

Impedance is the total opposition to current flow in response to an AC signal and is a complex quantity, generally expressed as a magnitude and a phase ($|Z|$, ϕ), as a real component and an imaginary component (Z' , Z''), or as a resistance and

a capacitance (R, C). In rocks impedance normally contains both resistive and capacitive components. The complex impedance Z^* is given by

$$Z^* = Z' - jZ'' \quad (1)$$

where the asterisk denotes a complex quantity, a single prime indicates a real quantity, the double prime indicates an imaginary quantity, and j is $\sqrt{-1}$. The real and imaginary parts of the impedance are obtained from the measured quantities $|Z|$ and ϕ determined at a given frequency by

$$Z' = |Z| \cos \phi, \quad (2)$$

$$Z'' = |Z| \sin \phi. \quad (3)$$

The complex resistivity ρ^* is obtained by multiplying the impedance by the geometric factor which is the area to thickness ratio of the sample, $gf = A/l$. The complex conductivity ψ^* is equal to the inverse of ρ^* . The complex conductivity is also represented as

$$\psi^* = \sigma + j\omega\epsilon', \quad (4)$$

where the conductivity $\sigma = \omega\epsilon''$, ω is the angular frequency, and ϵ' and ϵ'' are the real and imaginary parts of the dielectric permittivity. ϵ^* is related to the complex impedance through

$$\epsilon^* = (j\omega C_0 Z^*)^{-1} = Y^*/j\omega C_0 = (M^*)^{-1} \quad (5)$$

where C_0 is the capacitance of the empty cell ($C_0 = \epsilon_0 A/l$). The relative permittivity κ^* is the dielectric permittivity divided by the permittivity of free space $\epsilon_0 = 8.854 \times 10^{-12} \text{ F/m}$. The complex admittance Y^* and modulus M^* are related to the complex impedance through

$$Y^* = (Z^*)^{-1} = \psi^* l/A \quad (6)$$

$$M^* = j\omega C_0 Z^* = (\epsilon^*)^{-1}. \quad (7)$$

Each of the above formalisms emphasize different aspects of the AC response, and we find that plots in the complex impedance plane are the most illustrative and useful in terms of modeling our data. The permittivity and modulus formalisms refer to properties of the material, while the impedance and admittance formalisms involve the measured response of the sample with dimensions A and l . In this work we will differentiate between conductivities determined by single frequency measurements as 'apparent' conductivities (σ_{app}) and conductivities determined by analysis of the frequency dependent electrical response (σ_{DC}). The true 'DC' conductivity or resistivity of a given mechanism is the real value of the complex impedance at zero frequency (uninfluenced by overlap of other mechanisms or processes).

Experimental data

A set of impedance measurements typical for polycrystalline olivine is shown in Figure 2. The data shown in this figure are the results of an experiment at 1200 °C, one atmosphere total pressure, and an f_{O_2} of $10^{-5.2}$ Pa on a dunite from Jackson County, North Carolina (Roberts and Tyburczy, 1993a). The measured parameters $|Z|$ and ϕ are plotted against frequency in Figure 2a. In Figure 2b, the imaginary part of the complex impedance Z'' is plotted against the real part Z' . The complex impedance plane plot displays parts of three impedance arcs, which are circular arcs approximately centered on the real axis. Each impedance arc has a different characteristic relaxation time ($\tau = R \cdot C$) and corresponds to a separate conduction process that is dominant over a distinct frequency range. Impedance arcs will be distinct in the complex impedance plane if the time constants differ by a factor of 100 or more. An arc can be partial or incomplete if it extends past the range of measurement and adjacent impedance arcs can overlap.

Modeling the data with equivalent circuits

Impedance spectra can be modeled using circuits of resistors, capacitors, and other more specialized circuit elements (Bauerle, 1969). A complex non-linear least squares (CNLS) fitting routine is commonly used to find the best fit. By fitting the data in this way, accurate values for individual resistors and capacitors are obtained that are then related to specific conduction and polarization mechanisms within the material (Macdonald, 1985; Roberts and Tyburczy, 1991). Because we observe impedance arcs that have different time constants, i.e., the impedance arcs occur over different ranges of frequency and are distinct on complex impedance plane plots, the equivalent circuit generally consists of two or more parallel RC circuit elements connected in series. A parallel RC element produces a semi-circle in the complex impedance plane, having a center that falls on the real axis (Figure 3). Because in real materials the electrical response often exhibits impedance arcs with centers that lie below the real axis, a constant phase element (CPE) is used in the equivalent circuit in place of the capacitor to empirically account for the depressed impedance arcs (Figure 3c). With the use of the CPE an additional parameter α is introduced to the fit corresponding to the angle of depression of the impedance arc. The equation describing the complex impedance of the parallel circuit element containing a CPE (also referred to as a distributed circuit element) is

$$Z_{\text{ARC}}^* = \frac{R}{1 + (j\omega\tau)^\alpha} \quad (8)$$

where $\alpha = 1 - 2\theta/\pi$. The exponent α varies between 0 and 1, and θ is the angle of depression of the center of the impedance arc below the real axis. For $\alpha = 1$, the CPE is an ideal capacitor. Distributed elements and their responses represent

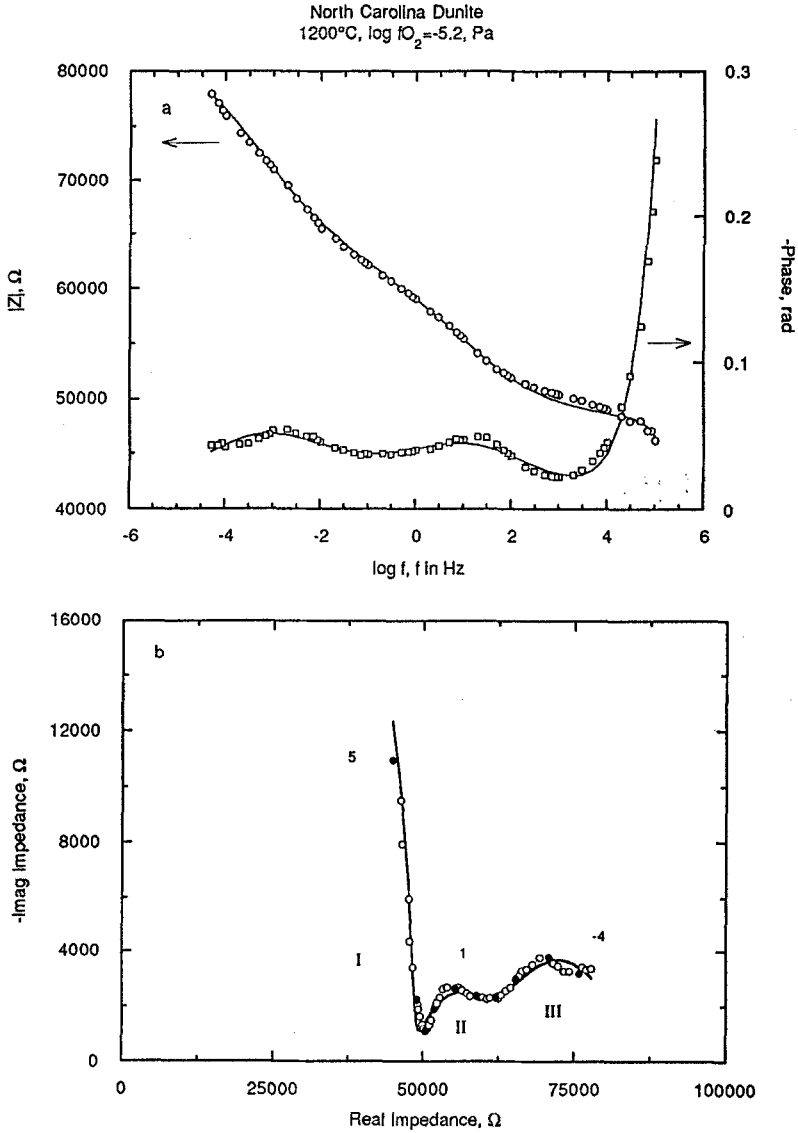


Fig. 2. Impedance data at 1200 °C and an f_{O_2} of $10^{-5.2}$ Pa for the North Carolina Dunite (Roberts and Tyburczy, 1993a). (a) Impedance magnitude and phase angle versus log frequency in Hz. Figure b is the complex impedance plane plot of the data. The impedance spectra of polycrystalline olivine display three impedance arcs, referred to as arcs I, II, and III from high to low frequency as indicated on the diagram. A filled circle occurs every decade of frequency; numerals are log frequency of the corresponding filled data point. The lines through the data are model responses obtained from CNLS fitting with an equivalent circuit.

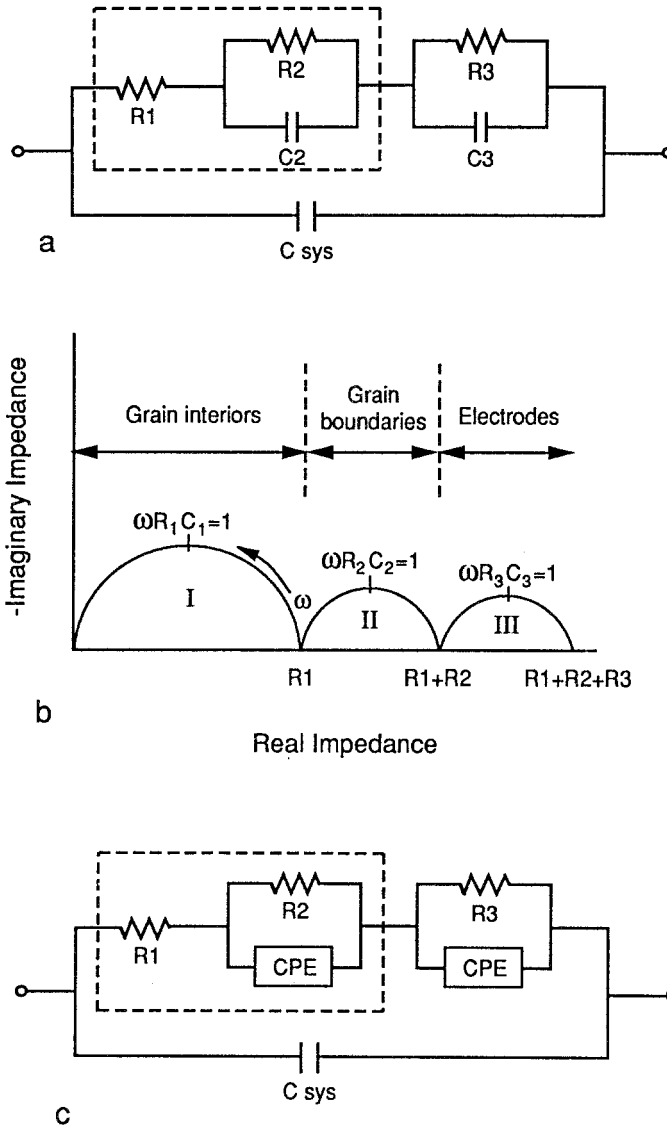


Fig. 3. (a) The general form of the equivalent circuit used to model the overall response observed in single, polycrystalline, and partially-molten samples. This circuit produces three impedance arcs in the complex plane, schematically represented in (b). If only two impedance arcs are observed as in the single crystal experiments, the second element is removed from the circuit. The portion of the circuit enclosed by the dashed box indicates the parts of the circuit that correspond solely to properties of the material. The system capacitance masks the smaller C_1 capacitance and is in parallel with the entire circuit. (c) To account for impedance arcs having centers that fall below the real axis, constant phase elements are substituted for the capacitors in (a). See text for discussion.

deviations from perfect Debye relaxation in materials and are discussed by many authors (e.g., Macdonald, 1985; Raistrick, 1987).

Previous impedance studies

It has been amply demonstrated that rocks that exist in the crust (wet, dry, and partially molten rocks) display frequency dependent electrical behavior (e.g., Knight, 1984; Lockner and Byerlee, 1985; Will and Nover, 1986; Sato *et al.*, 1986; Roberts and Tyburczy, 1991). While there has been much study of the electrical properties of olivine (e.g., Hughes, 1955; Duba, 1972; Duba *et al.*, 1974; Cemř *et al.*, 1980; Lacam, 1983; Schock *et al.*, 1989; Constable and Duba, 1990), few experiments have been performed investigating the frequency dependence of electrical properties. The earliest study of this nature concerning olivine is that by Abelard and Baumard (1980), who investigated the AC properties of sintered polycrystalline forsterite between 400 and 900 °C. They observed a strong frequency dependence over the range 10^{-1} to 10^5 Hz. They suggest that the electrical response they observe at frequencies under 1 Hz may be caused by microstructure or electrode processes. Sato (1986) measured the high-temperature (1000–1400 °C) AC electrical properties of San Carlos olivine single crystals between 10^{-1} and 10^4 Hz to find conductivities and dielectric constants as a function of oxygen partial pressure. Sato concluded that between 1200 and 1400 °C and at relatively high oxygen partial pressures ($f_{O_2} \geq 10^{-5}$ Pa), real dielectric constants are proportional to $P_{O_2}^{1/6}$ and the major defect species contributing to conduction are Mg vacancies and Fe^{3+} on Fe^{2+} sites (electron holes). At lower oxygen partial pressures, Sato observed a weaker P_{O_2} dependence and suggested that Mg interstitials and electrons contribute to the electrical conductivity in addition to Mg vacancies and electron holes.

A study of the electrical conductivity of diopside single crystals from 800 to 1300 °C over the frequency range 10^{-3} to 10^5 Hz revealed frequency dependent behavior (Huebner and Voight, 1988). The DC conductivity values of the crystal interiors were taken at the frequencies where the phase angle was closest to zero (no imaginary component in $|Z|$), usually between 10 and 100 Hz, corresponding to the width of the first (grain interior) impedance arc.

Determination of conduction mechanisms in polycrystalline materials: Observations of grain boundary conductivity

There are many studies in the ceramics literature that utilize electrical measurements as a function of frequency to separate the contributions of the crystals (grain interior) and the grain boundaries of polycrystalline materials to the overall electrical properties of the material (e.g., Bauerle, 1969; Chu and Seitz, 1978; Lilley and Strutt, 1979; van Dijk and Burggraaf, 1981; Verkerk *et al.*, 1982; Tanaka

et al., 1987) The study by Bauerle (1969) reported the electrical response of polycrystalline yttria stabilized zirconia (YSZ). Bauerle used an equivalent circuit of resistors and capacitors to describe the experimentally observed response. By comparing measurements made with two- and four-electrode configurations, and by examining the variation of the individual circuit parameters with sample dimensions, he concluded that the high, intermediate, and low frequency responses are due to grain interior, grain boundary, and electrode processes, respectively.

Most work involving grain boundary transport in geologic materials has come from studies of intergranular diffusion (Naughton and Fujikawa, 1959; Brady, 1983; Watson, 1986; Jurewicz and Watson, 1989), rather than electrical measurements. Grain boundaries are known to play an important role in many physical properties of rock including diffusion, creep, and electrical conduction. It has previously been suggested that grain boundaries may be responsible for enhanced conduction in olivine-rich rock (e.g., Shankland and Waff, 1977; Shankland, 1981; Kariya and Shankland, 1983). Schock *et al.* (1977) studied the single frequency conductivity of ground-and-pressed polycrystalline olivine and concluded that grain boundaries have only a small effect on the overall conductivity. Haak (1982) compared conductivity results of single and polycrystalline olivine samples and concluded that between 560 and 1150 °C polycrystalline samples exhibit higher conductivity than single crystal samples. Because single crystal samples have higher activation energies than polycrystalline samples, the conductivities become equal at approximately 1400 °C.

Will and Nover (1986) employed frequency dependent electrical measurements on wet and dry metapelite samples at pressures of 1 to 20 MPa and 1 GPa from the Konzen, Germany borehole to determine the individual resistances caused by the grain interior, grain boundary and electrode conduction mechanisms, which occurred from high to low frequencies, respectively. Tyburczy and Roberts (1990) and Roberts and Tyburczy (1991) applied impedance spectroscopy to polycrystalline olivine compacts and natural dunite samples in a one atmosphere total pressure gas mixing furnace. By examining the change in resistance of the two highest frequency mechanisms with changing sample dimensions (Figure 4) and by utilizing different electrode configurations (Figure 5), they determined that the grain interior and grain boundary mechanisms add in a series manner leading to increased resistance and decreased conductivity for a polycrystalline material as compared to a single crystal sample.

The most basic and direct evidence for grain boundary conduction is the direct comparison of the impedance spectra of a single crystal, a polycrystalline compact, and a dunite (Figure 6; Roberts and Tyburczy, 1993b). These three experiments were performed using the two electrode technique at a temperature of approximately 1200 °C and similar f_{O_2} 's. In the single crystal experiment two impedance arcs are observed, while the polycrystalline compact and natural dunite display portions of three impedance arcs. Thus we infer that the additional impedance

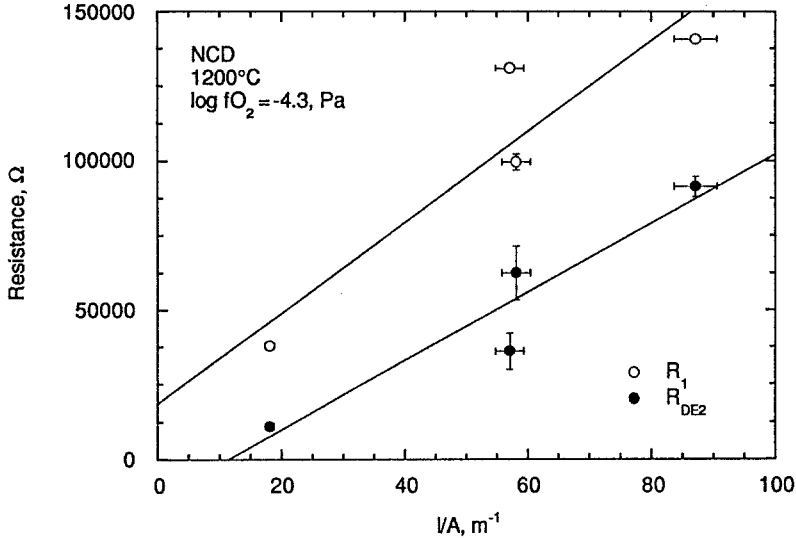


Fig. 4. Resistances of the two highest frequency mechanisms plotted against the inverse of the geometric factor, l/A (Roberts and Tyburczy, 1993a). Open circles, mechanism I (highest frequency, grain interior); filled circles mechanism II (intermediate frequency, grain boundaries). Data are from CNLS fitting to impedance data for a dunite from Jackson County, North Carolina, 1200 °C, $f_{O_2} = 10^{-4.3}$. The resistance is dependent on sample size indicating that the two high frequency mechanisms are properties of the material rather than electrodes or system effects.

arc in the polycrystalline spectra is caused by the presence of grain boundaries, and that the highest frequency impedance arc represents grain interior conduction through the crystal.

There is some question about whether or not the observed grain boundary response (that is, relatively resistive grain boundaries acting in series with grain interiors) is the result of grain boundary microcracking from thermal expansion anisotropy and grain boundaries that are not intact. Roberts and Tyburczy (1991) performed experiments on polycrystalline olivine compacts at 1200 °C as a function of grain size (7–180 μm) and report no effect on the electrical response of the grain interior and grain boundary mechanisms. An especially important aspect of Will and Nover's (1986) work is that they performed measurements at 1 MPa and 1 GPa pressure, and still observed impedance spectra characteristic of resistive (series) grain boundary behavior. Electrical measurements on fine grained dry rocks at these pressures indicate portions of three impedance arcs, similar to the response observed for polycrystalline materials at one atmosphere total pressure.

Sato and coworkers (Sato and Ida, 1984; Sato *et al.*, 1986) observed the frequency dependent electrical response of partially molten gabbro that they attributed to physical constriction of the interconnections between melt pockets, but did not find grain boundaries to be resistive at temperatures below T_{solidus} . Pro-

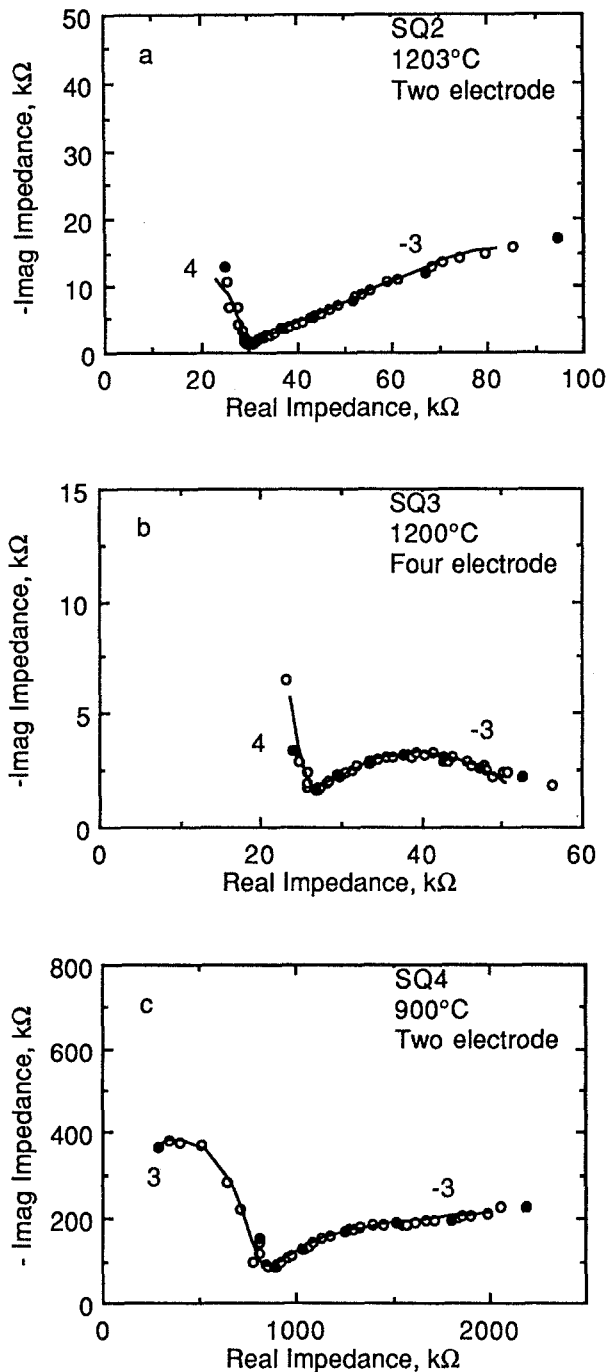


Fig. 5. Complex plane plots of impedance for San Quintin dunite using two- and four-electrode methods (Roberts and Tyburczy, 1991). Solid lines are fits to experimental data using equivalent circuits. (a) 1203 °C, two-electrode, $f_{O_2} = 10^{-5}$ Pa. (b) 1200 °C, four-electrode, $f_{O_2} = 10^{-5}$ Pa. (c) 900 °C two-electrode, $f_{O_2} = 10^{-10.4}$ Pa. Two-electrode results show low-frequency, high impedance behavior characteristic of electrode effects. The four-electrode method eliminates electrode effects from the measurement and reveals low-frequency behavior of the sample. In the 1203 °C case (a), the low frequency response of the sample is obscured by the electrode effects in the two-electrode measurement.

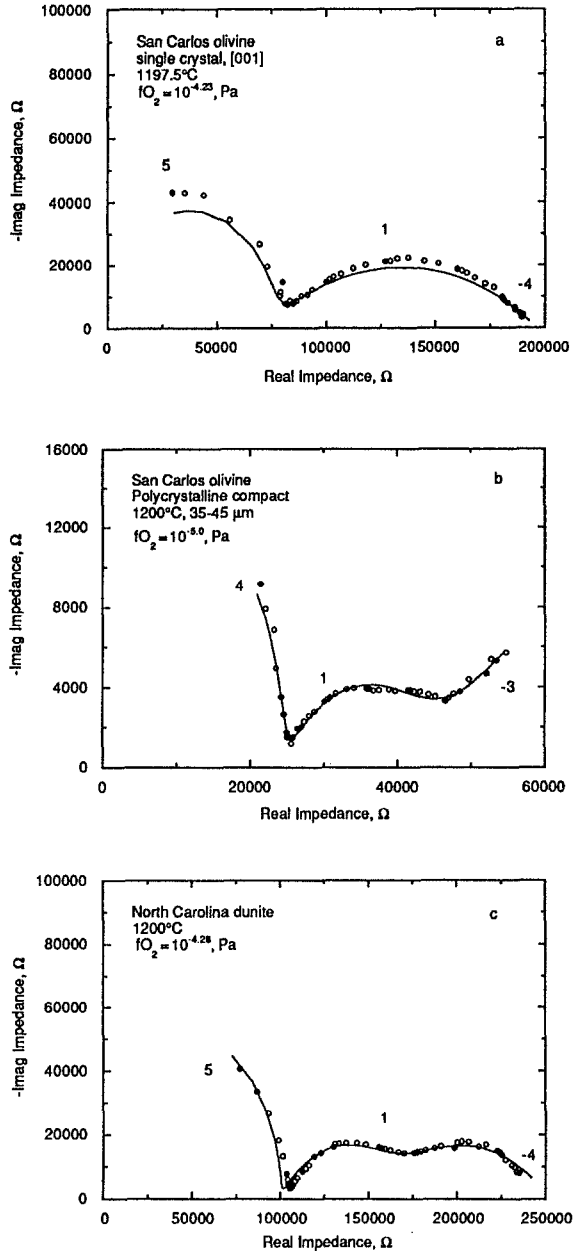


Fig. 6. Complex impedance spectra, two-electrode method (Roberts and Tyburczy, 1993a). (a) Single crystal San Carlos olivine, 1197.5 °C, $f_{O_2} = 10^{-4.23}$ Pa, [001] orientation, Pt electrodes. (b) Polycrystalline San Carlos olivine compact, 1200 °C, $f_{O_2} = 10^{-5.0}$ Pa, 35–45 μm average grain size, Pt electrodes. (c) Dunite from Jackson County, North Carolina, 1200 °C, $f_{O_2} = 10^{-4.28}$ Pa, Ir electrodes. The minor differences in temperature and f_{O_2} do not significantly alter the general response of these materials, and they are suitable for comparison. The most obvious difference in the impedance spectra of these materials is the number of impedance arcs; two for the single crystal, three for the polycrystalline specimens. The lines through the data are models obtained by CNLS fitting with equivalent circuits.

posed causes of low grain boundary conductivity that have been discussed in the literature include impurity or phase segregation along grain boundaries and static space-charge polarized regions that exist at equilibrium on grain boundaries (Kingery *et al.*, 1976; Chu and Seitz, 1978). Identification and characterization of the grain boundary structures and processes that control grain boundary conductivity are important problems that remain for future work. It is likely that in natural materials there exists extreme variability in the composition of grain boundaries and in their transport properties.

A contrasting view of the frequency dependence of electrical properties and the role of grain boundaries on the overall electrical properties of a material is presented by Constable and Duba (1990) who measured the electrical conductivity of polycrystalline dunite from Jackson County, North Carolina. Between 0.1 and 10 kHz they reported no significant dependence of conductivity on frequency with dispersion of conductivity less than 2 hundredths of a log unit over this frequency range. Their lowest frequency of measurement roughly coincides with the frequency of maximum phase angle (minimum negative phase angle) commonly observed in other frequency dependent measurements (Huebner and Voight, 1988; Roberts and Tyburczy, 1991). This could mean that they did not measure the electrical properties at low enough frequencies to observe additional conduction mechanisms that may have a low frequency response. Another important factor is that they measured the impedance magnitude, and did not report a phase angle measurement. The frequency variation of electrical measurements is commonly most pronounced in the phase angle versus frequency, the real and imaginary impedances plotted against frequency, and the imaginary impedance plotted against the real impedance in the complex plane.

Olivine-basalt partial-melts

With the background knowledge that grain boundaries act electrically in series with the grain interiors, a useful set of experiments is the observation of the effect of a small amount of melt on the electrical properties of a polycrystalline material such as olivine. These measurements have direct relevance to the interpretation of areas identified by field EM surveys that display relatively high apparent conductivity such as the high conductivity layer (HCL) that exists beneath the oceanic crust near mid ocean ridges (Filloux, 1980; Oldenburg, 1981) and other areas where a melt phase might coexist with the solid minerals.

As mentioned above, Sato and coworkers investigated the frequency dependent electrical response of partially molten gabbro between 3.2×10^{-2} and 10^4 Hz from 780 to 1200 °C (Sato and Ida, 1984; Sato *et al.*, 1986). This important work related the observed frequency response to the microstructural distribution of the melt phase and diffusion of ions within the melt (Sato and Ida, 1984). Another important aspect of this work is the conclusion that the observed frequency dispersion

in partial-melt samples may have an effect on the interpretation of magnetotelluric (MT) sounding curves and that conductivities of partially-molten rocks determined at frequencies above 10 Hz are not directly applicable in the interpretation of geomagnetic results. Sato and Ida demonstrate that apparent conductivities determined from MT models differ from experimentally determined conductivities, and that the difference is dependent on the degree of frequency dispersion. It is possible that this effect will cause the mis-estimation of temperature as determined by the comparison of laboratory measurements and MT sounding curves and is judged important if melt pockets are larger than 1 mm.

Recent measurements of the frequency dependence of conductivity of polycrystalline olivine in a Na-silicate glass matrix show significant frequency dispersion between 10^2 and 10^4 Hz at temperatures above 900 °C (Wanamaker and Duba, 1991). They suggest that the measured conductivity is a sensitive indicator of melt fraction, melt distribution, and melt structure.

We report here results of preliminary impedance spectroscopy experiments on olivine-basalt partial-melts. Two different types of partial-melts were examined. The first sample consisted of Fo₈₀ olivine grains mixed with 5% powdered basalt (a mid-ocean ridge basalt from the Juan de Fuca Ridge; composition given by Fine and Stolper, 1985) by weight in the starting material (PM03). The mixture was placed in Fe doped Pt capsules and prepared in an internally heated Ar gas pressure vessel at 350 MPa and 1130 °C for a period of 284 hours. Post-run ion microprobe analyses indicated that some water was present in the melt (on the order of 1%), but quantitative measurement was not possible. At these conditions the sample was above the solidus temperature. The relatively long run time served to ensure that the sample reached an equilibrium distribution of the melt phase (Figure 7a). The second partial-melt sample consisted of San Carlos olivine grains and a melt phase that was created during the sintering of a polycrystalline compact in a one atm gas mixing furnace at 1450 °C (PC07, grain size 50–90 μm). This sample did not reach textural equilibrium as evidenced by post-run SEM (Figure 7b). It is useful to compare the impedance spectra of these two types of samples and observe the effect of the melt phase on the previously described grain interior and grain boundary conduction mechanisms.

The impedance spectra for the interconnected partial-melt (PM03) are reported in Figure 8. Measurements were taken at 684, 812, 1004, and 1200 °C in a one atmosphere gas mixing furnace (CO/CO₂ gas mixture) at an f_{O_2} approximately corresponding to the FMQ buffer assemblage minus two log units (FMQ-2; at 1200 °C, FMQ-1.6). An interesting observation is that at the lower temperatures (684 and 812 °C) portions of three impedance arcs are clearly observed, similar to the dry polycrystalline response, while at higher temperatures (1004 and 1200 °C), only two impedance arcs are clearly observed. At the higher temperatures one less conduction mechanism appears to be in effect. Another important point is illustrated in Figure 9, a plot of $\log \sigma_{\text{gr-DC}}$ versus reciprocal temperature for the

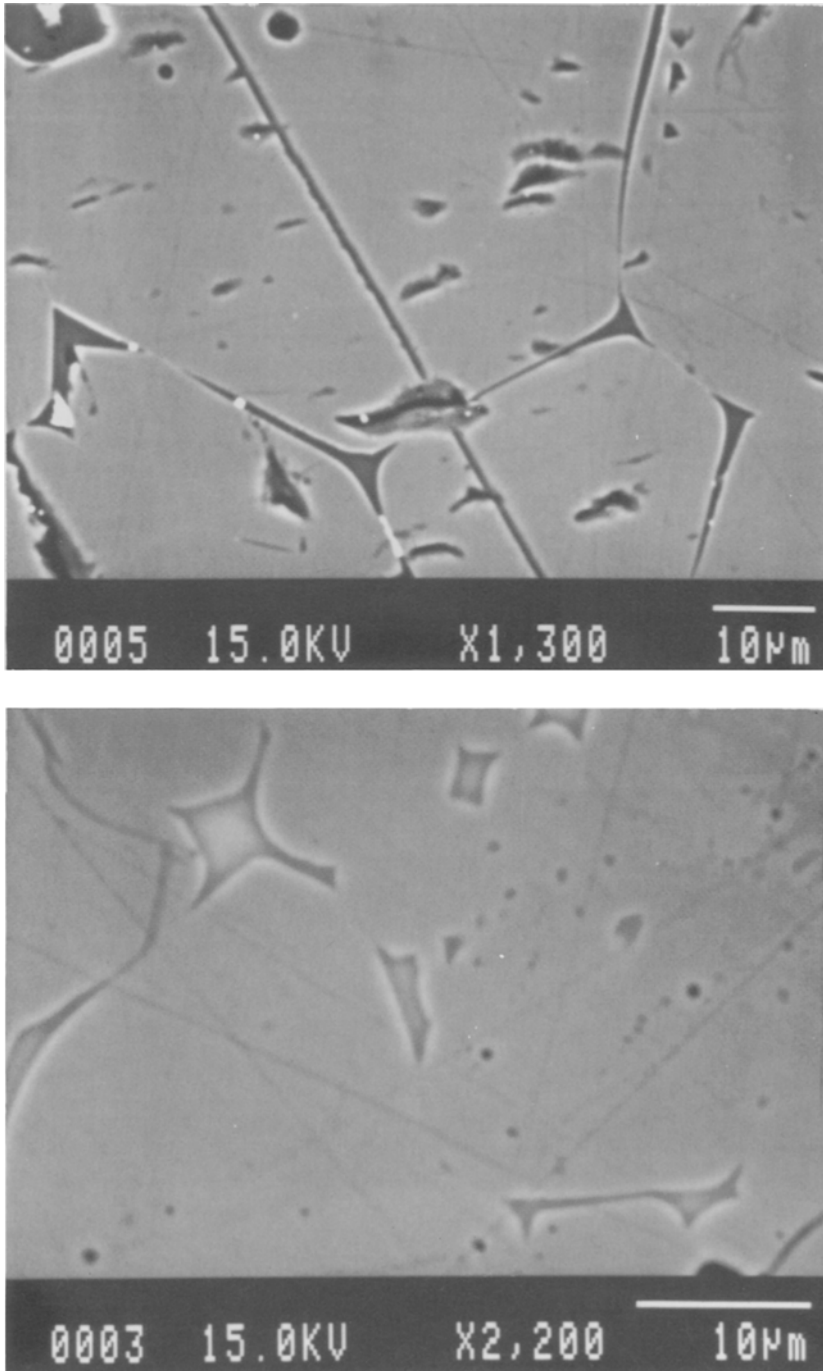


Fig. 7. (a) Backscatter SEM image of the texturally equilibrated partial-melt (PM03). The melt regions (dark gray) form an interconnected melt network. (b) Backscatter SEM image of the non-texturally equilibrated partial-melt (PC07).

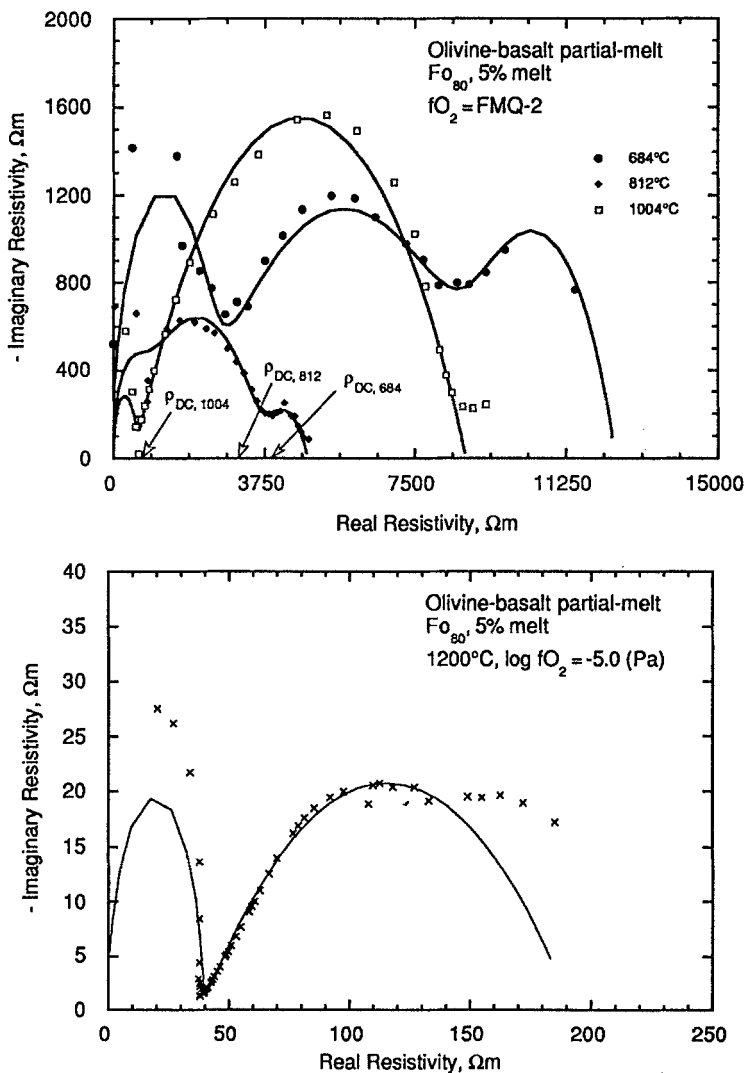


Fig. 8. Impedance spectra of the interconnected partial-melt system (PM03) at 684, 812, 1004, and 1200°C. At the two lowest temperatures three impedance arcs appear, at 1004 and 1200°C only two impedance arcs are clearly observed. Lines through the data are models of the data obtained using CNLS analysis and an equivalent circuit.

high frequency mechanism only. In this diagram it can be seen that the high frequency mechanism, which corresponds to grain interior conductivity in melt-absent studies of polycrystalline olivine, increases dramatically at 1200°C. Our interpretation is that at the higher temperatures parallel conduction behavior

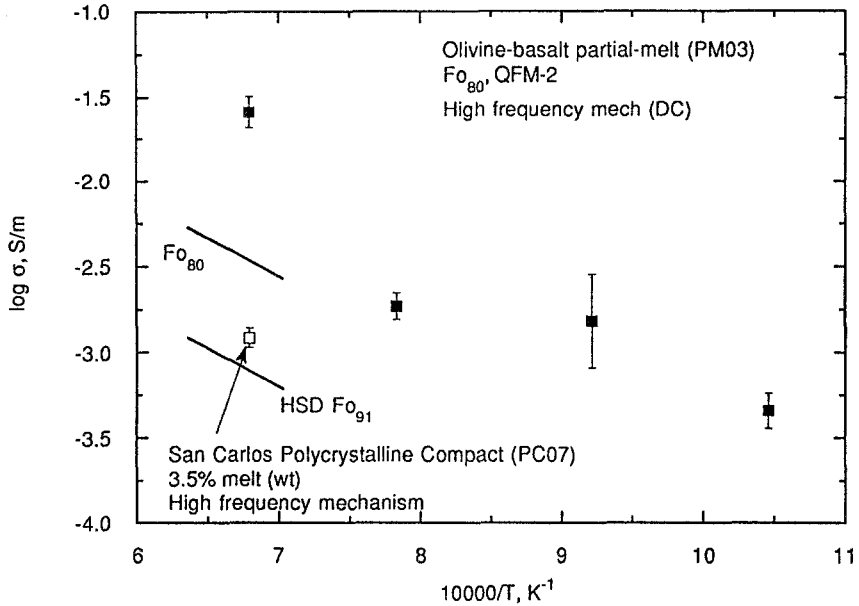


Fig. 9. Log DC conductivity versus $1/T$ diagram showing the high frequency mechanism conductivities for the interconnected (PM03) and non-interconnected (PC07) partial-melt. Lines are orientationally averaged conductivity for single crystal olivine (Fo_{80} and Fo_{91}) as calculated by Hirsch *et al.* (1993). The interconnected melt system data plot near the predicted conductivity of a single crystal, except for the data point at 1200°C . This data point displays an increased high frequency mechanism conductivity attributed to parallel conduction through the melt phase.

between the crystal and melt phases is initiated. This would also account for the apparent decrease in the number of observed impedance arcs at 1004 and 1200°C .

In contrast, the non-interconnected partial-melt (PC07) displays portions of three impedance arcs at 1200°C (Figure 10a). The interpretation of the observed electrical response is that the sample did not achieve textural equilibrium and an interconnected melt conduction path does not exist, therefore series electrical behavior is observed. Shown in Figure 10b is the impedance spectrum of a polycrystalline olivine sample (San Carlos olivine, $35\text{--}45\ \mu\text{m}$ grain size), prepared in the same manner as PC07, that does not have a melt phase present. Comparison of the high frequency (grain interior) and intermediate frequency (grain boundary/grain boundary-melt) conductivities (Figure 11) reveals that the grain interior conductivities for these samples are nearly the same within experimental error, whereas the grain boundary conductivity (conductance corrected for overall sample dimensions rather than volume of grain boundary 'phase') of PC07 displays a conductivity approximately 4 times higher than that of the dry samples. This is further evidence that in the case of material with a non-connected conductive (melt) phase, series electrical behavior occurs, and the grain boundary conduction mechanism is modi-

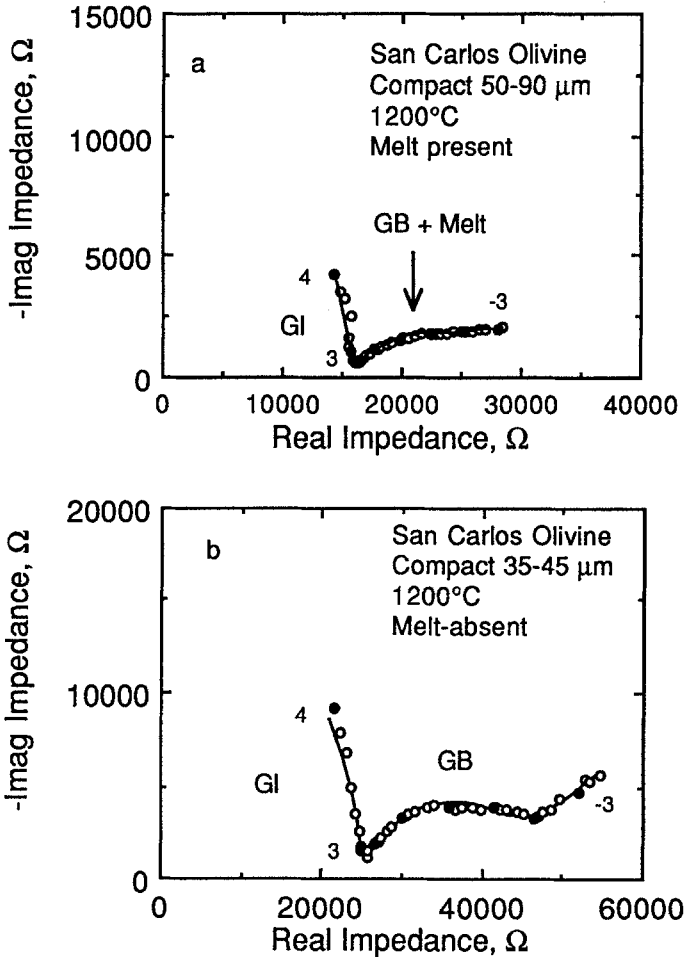


Fig. 10. Impedance spectra of two polycrystalline olivine compacts, one with non-texturally equilibrated melt present (a; PC07), the other melt absent (PC06). Both samples display grain interior and grain boundary arcs. The grain boundary impedance arc is modified in the melt present sample. See text for discussion.

fied by the presence of the melt. Only by measuring and analyzing the frequency response of these materials was it possible to determine the individual mechanisms responsible for conduction and assess the effect of melt on the electrical properties of the material being studied.

Frequency bias in the determination of activation energies

A common method of determining activation energies for conduction in minerals is to make resistance (or impedance) measurements at a single frequency while varying temperature along a trajectory of constant gas mixing ratio (typically CO-

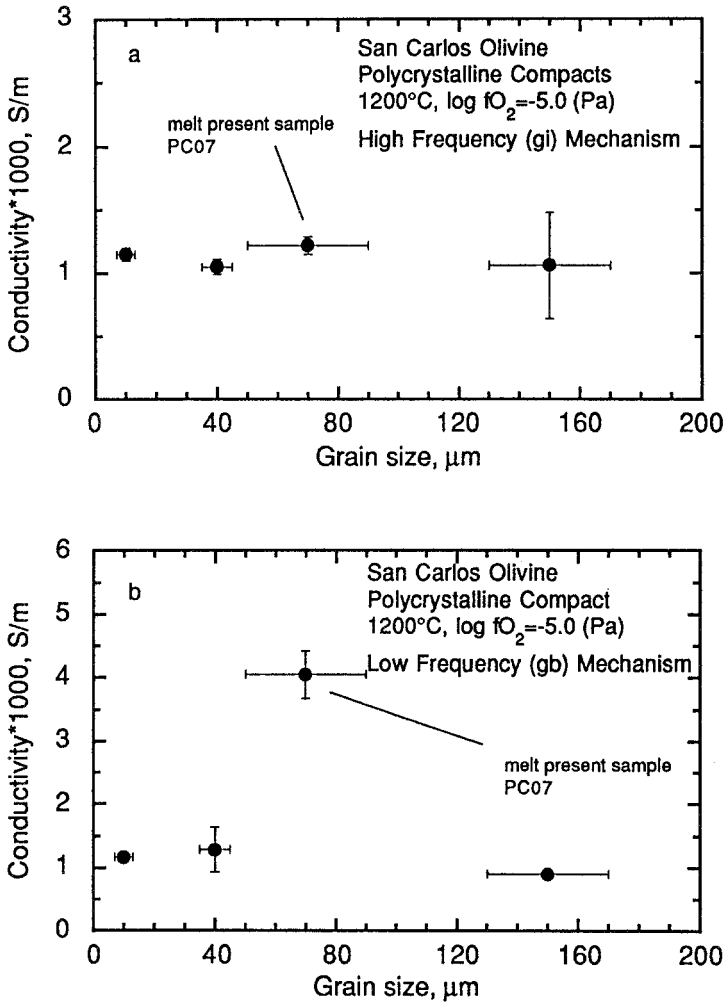


Fig. 11. Conductivity versus grain size for several polycrystalline San Carlos olivine compacts. The DC conductivity of the grain interior mechanism (a) is nearly constant for all the samples, including the melt present sample. The grain boundary conductivity (see text) of the melt present sample (PC07, non-interconnected melt) is approximately four times that of the dry samples (b). That the presence of melt does not appear to have an effect on the grain interior mechanism and does affect the grain boundary mechanism is an indication that a material without an interconnected melt phase conducts according to the series model.

CO₂). For olivine, this method has been shown to yield fairly reproducible results (Schock *et al.*, 1989; Constable and Duba, 1990), however, the neglect of the effect of frequency on measurements made at different temperatures creates a possible source of error in this method. Because the resistance and capacitance of a material has been shown to vary with temperature (e.g., Roberts and Tyburczy, 1991), the characteristic relaxation frequency, as well as the frequency at which

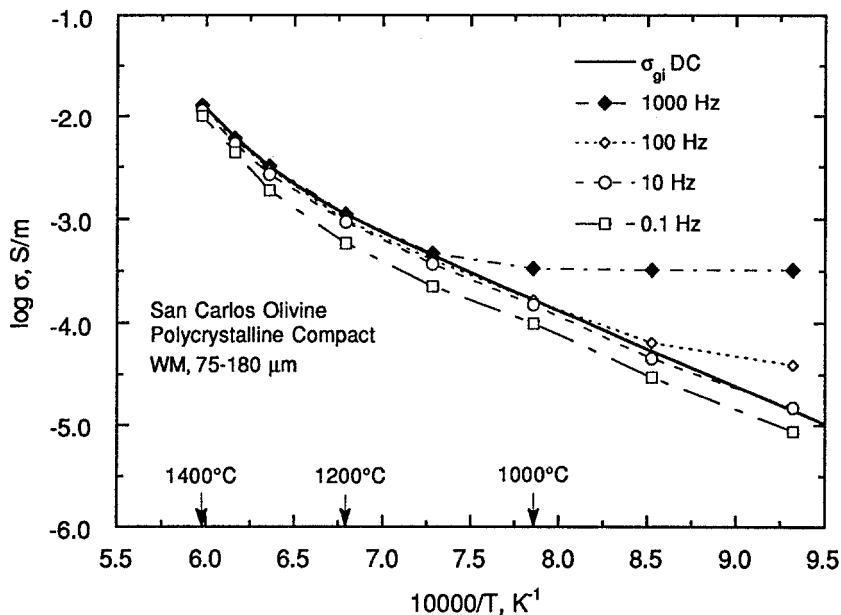


Fig. 12. Log conductivity calculated from the impedance magnitude versus reciprocal temperature for a polycrystalline San Carlos olivine compact for several frequencies (f_{O_2} held to that of the wustite-magnetite buffer). The solid line labeled 'gi DC' is a fit to the grain interior conductivities as determined by equivalent circuit analysis (see text). The 1000 Hz conductivities are nearly coincident with the gi DC line above 1100 °C. Below 1100 °C the 10 Hz conductivities coincide with the gi DC conductivity curve. Activation energies determined by measurements made at only one frequency may be in error because of this effect.

the impedance arc intersects the real axis, changes with the frequency of measurement. The point on the real axis intersected by the impedance arc (at frequency f_0) is the value for the DC resistance of the conduction mechanism. A measurement taken at a higher frequency will have a shorter (lower) impedance magnitude than the measurement taken at f_0 . This problem is compounded at relatively low temperatures (500–1000 °C) where sample resistances are significantly higher, and capacitive coupling of measurement leads results in a lower measured impedance magnitude. The effect of the leads can be corrected for by utilizing a mathematical cable correction algorithm or impedance analyzers with built-in correction circuitry.

Figure 12 is a log conductivity versus $1/T$ plot and demonstrates this effect. The frequency dependent data are for a San Carlos olivine polycrystalline compact (data are taken from Roberts, 1992). Plotted on this diagram are the conductivities determined from $\sigma_{app,f} \pm (|Z|A/l)^{-1}$ at the frequencies 1000, 100, 10, and 0.1 Hz (connected data points) and the best fit line to the DC conductivity of the grain interior mechanism as determined by equivalent circuit analysis (Roberts and Tyburczy, 1991). It is quite clear that below 1100 °C the σ_{app} , 1000 Hz data are

significantly different than the true DC conductivities. The 100 Hz conductivity data are better, but not in very good agreement below 1000 °C. Materials commonly display a reduced slope at lower temperatures on log conductivity versus reciprocal temperature plots. The lowest frequency data shown (0.1 Hz) closely represent the total conductivity (DC) for the grain interiors in series with the grain boundaries.

As an example, the activation energies determined between 800 and 1100 °C for the 100 and 10 Hz data are 0.99 and 1.37 eV, respectively. The activation energy over this temperature range for the grain interior mechanism determined by analysis of the DC conductivities is 1.45 eV (Roberts and Tyburczy, 1991). The higher frequency data (100 Hz) yield an artificially low activation energy. To eliminate this possible source of error from conductivity measurements it is necessary to determine the true DC conductivity of a conduction mechanism by examining the frequency dependence of the electrical properties to <1 Hz, or alternatively, to make the measurement at the frequency with the lowest phase angle at each temperature.

Conclusions

A variety of materials important in the study of the crust and mantle exhibit frequency dependent electrical behavior at relatively low frequencies, between 10^{-4} and 10^5 Hz. Because geophysical methods used to construct electrical conductivity versus depth profiles employ measurements in this low-frequency range, it is necessary to consider the effect of dispersion on these results. Phase angles as high as 75–90 mrad at frequencies as low as 10^{-2} Hz that are not a result of processes occurring at the electrodes have been observed. This dispersion may be important in the inversion of field electromagnetic measurements and is deserving of further study.

Information about individual conduction mechanisms such as crystal interior and grain boundary conductivities can be obtained through the analysis of the electrical response over a wide range of frequency. In the case of partially molten materials and materials containing a relatively conducting phase, information about the microstructure and distribution of the conducting phase can be determined. The idea that grain boundaries in polycrystalline materials representative of the upper mantle will enhance the electrical conductivity of those materials has not been supported by laboratory measurements that consider the frequency dependence of the electrical properties. In natural dunites, metapelites, and in polycrystalline olivine compacts it has been found that the grain boundary resistivity adds in series with the grain interior resistivity, resulting in a higher resistivity (lower conductivity) for the material. The two conduction mechanisms are distinguishable by making complex impedance measurements over a range of frequencies extending to as low as 10^{-3} to 10^{-4} Hz. The grain interior and grain boundary

resistances add in series; the resulting total conductivity is 2–5 times lower than that of grain interior measurements.

The electrical conductivity of olivine displays a strong dependence on temperature and has been used to infer temperatures in the upper mantle and lower crust from conductivity versus depth profiles. Temperature estimates based on single-crystal conductivity values or measurements of polycrystalline samples that do not consider grain boundary transport can be lower than temperatures calculated from rocks that display series behavior of grain interiors and grain boundaries. These differences are important to our understanding and interpretation of the conditions and processes occurring in the lower crust and upper mantle.

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References

- Abelard, P., Baumard, J. F.: 1980, 'Electric and Dielectric Properties of Forsterite between 400 and 900°C', *Phys. Earth Planet Inter.* **23**, 98–102.
- Bauerle, J. E. 1969, 'Study of Solid Electrolyte Polarization by a Complex Admittance Method', *J. Phys. Chem. Solids* **30**, 2657–2670.
- Brady, J. B.: 1983, 'Intergranular Diffusion in Metamorphic Rocks', *Am. J. Sci.* **283-A**, 181–200.
- Cemř, L., Will, G. and Hinze, E.: 1980, 'Electrical Conductivity Measurements on Olivines Mg_2SiO_4 – Fe_2SiO_4 under Defined Thermodynamic Conditions', *Phys. Chem. Minerals* **6**, 95–107.
- Chu, S. H., Seitz, M. A.: 1978, 'The ac Electrical Behavior of Polycrystalline ZrO_2 – CaO ', *J. Sol. St. Chem.* **23**, 297–314.
- Constable, S. C. and Duba, A. G.: 1990, 'The Electrical Conductivity of Olivine, a Dunite and the Mantle', *J. Geophys. Res.* **95**, 6967–6978.
- Constable, S. C., Shankland, T. J. and Duba, A. G.: 1992, 'The Electrical Conductivity of an Isotropic Olivine Mantle', *J. Geophys. Res.* **97**, 3397–3402.
- Duba, A.G.: 1972, 'Electrical Conductivity of Olivine', *J. Geophys. Res.* **77**, 2483–2495.
- Duba, A. G. and Constable, S. C.: 1993, 'The Electrical Conductivity of Lherzolite', *J. Geophys. Res.* submitted.
- Duba, A. G., Heard, H. C., Schock, R. N.: 1974, 'Electrical Conductivity of Olivine at High Pressure and under Controlled Oxygen Fugacity', *J. Geophys. Res.* **79**, 1667–1673.
- Filloux, J. H.: 1980, 'Magnetelluric Soundings over the North-East Pacific may Reveal Spatial Dependence of Depth and Conductance of the Asthenosphere', *Earth Planet Sci. Lett.* **46**, 244–252.
- Fine, G. and Stolper, E.: 1985, 'Dissolved Carbon Dioxide in Basaltic Glasses: Concentrations and Speciation', *Earth Planet Sci. Lett.* **76**, 263–278.
- Haak, V.: 1982, 'A Comparison of the Electrical Conductivity of Natural Mono- and Polycrystalline Olivines – A Case to Decide', in Schreyer, W. (ed.), *High-Pressure Researches in Geoscience*. E Schweizerbart'sche Verlagsbuchhandlung, Stuttgart, pp. 407–417.

- Hirsch, L. M., Shankland, T. J. and Duba, A. G.: 1993, 'Electrical Conduction and Mobility in Fe-Bearing Olivine', *Geophys. J. Int.* in press.
- Huebner, J. S. and Voight, D. E.: 1988, 'Electrical Conductivity of Diopside: Evidence for Oxygen Vacancies', *American Mineralogist* **73**, 1235–1254.
- Hughes, H.: 1955, 'The Pressure Effect on the Electrical Conductivity of Peridot', *J. Geophys. Res.* **60**, 187–191.
- Jurewicz, A. J. G. and Watson, E. B.: 1989, 'Cations in Olivine, Part 2: Diffusion in Olivine Xenocrysts, with Applications to Petrology and Mineral Physics', *Contrib. Mineral Petrol.* **99**, 186–201.
- Kariya, K. A. and Shankland, T.J.: 1983, 'Electrical Conductivity of Dry Crustal Rocks'. *Geophysics* **48**, 52–61.
- Kingery, W. D., Bowen, H. K. and Uhlmann, D. R.: 1976, *Introduction to Ceramics*, John Wiley, New York.
- Knight, R. J.: 1984, *The Dielectric Constant of Sandstones, 5 Hz to 13 MHz*, Ph.D. dissertation, Stanford Univ., Stanford, Calif., 119 pp.
- Lacam, A.: 1983, 'Pressure and Composition Dependence of the Electrical Conductivity of Iron-rich Synthetic Olivines to 200 kbar', *Phys. Chem. Minerals* **9**, 127–132.
- Lilley, E and Strutt, J. E.: 1979, 'Bulk and Grain Boundary Ionic Conductivity in Polycrystalline β -alumina', *Phys. Stat. Solidi* **54**, 639–650.
- Lockner, D. A. and Byerlee, J. D.: 1985, 'Complex Resistivity Measurements of Confined Rock', *J. Geophys. Res.* **90**, 7837–7847.
- Macdonald, J.R.: 1985, 'Generalizations of "Universal Dielectric Response" and a General Distribution-of-Activation-Energies Model for Dielectric and Conducting Systems', *J. Appl. Phys.* **58**, 1971–1978.
- Naughton, J. J. and Fujikawa, U.: 1959, 'Measurement of Intergranular Diffusion in a Silicate System: Iron in Forsterite', *Nature* **184**, 54–56.
- Oldenburg, D. W.: 1981, 'Conductivity Structure of Oceanic Upper Mantle Beneath the Pacific Plate', *Geophys. J. R. astr. Soc.* **65**, 359–394.
- Raistrick, I. D.: 1987, 'The Electrical Analogs of Physical and Chemical Processes', in Macdonald, J. R. (ed.), *Impedance Spectroscopy*, Wiley & Sons, New York, pp. 27–84.
- Roberts, J. J.: 1992, *Frequency Dependent Electrical Properties of Olivine and Dunite as a Function of Temperature and Oxygen Fugacity*, Ph.D. dissertation, Arizona State University, 223 pp.
- Roberts, J. J. and Tyburczy, J.A.: 1991, 'Frequency Dependent Electrical Properties of Polycrystalline Olivine Compacts', *J. Geophys. Res.* **96**, 16,205–16,222.
- Roberts, J. J. and Tyburczy, J. A.: 1993a, 'Impedance Spectroscopy of Single and Polycrystalline Olivine: Evidence for Grain Boundary Transport', *Phys. Chem. Minerals* in press.
- Roberts, J. J. and Tyburczy, J. A.: 1993b, 'The Frequency Dependent Electrical Properties of Dunite as Functions of Temperature and Oxygen Fugacity', *Phys. Chem. Minerals* in press.
- Sato, H.: 1986, 'High Temperature a.c. Electrical Properties of Olivine Single Crystal with Varying Oxygen Partial Pressure: Implications for the Point Defect Chemistry', *Phys. Earth Planet Inter.* **41**, 269–282.
- Sato, H., Ida, Y.: 1984, 'Low Frequency Electrical Impedance of Partially Molten Gabbro: The Effect of Melt Geometry on Electrical Properties', *Tectonophysics* **107**, 105–134.
- Sato, H., Manghnani, M. H., Lienert, B. R. and Weiner, A.T.: 1986, 'Effects of Electrode Polarization on the Electrical Properties of Partially Molten Rock', *J. Geophys. Res.* **91**, 9325–9332.
- Schock, R. N., Duba, A. G., Heard, H. C., Stromberg, H. D.: 1977, 'The Electrical Conductivity of Polycrystalline Olivine and Pyroxene under Pressure', in Manghnani, M., Akimoto, S. (eds.), *High Pressure Research: Applications in Geophysics*, Academic, San Diego, Calif., pp. 39–51.
- Schock, R. N., Duba, A. G. and Shankland, T. J.: 1989, 'Electrical Conduction in Olivine', *J. Geophys. Res.* **94**, 5829–5839.
- Shankland, T. J.: 1981, 'Electrical Conduction in Mantle Materials, in O'Connell, R. J. and Fyfe, W. S. (eds.), *Evolution of the Earth*, Geodyn. Ser., vol. 5, AGU, Washington DC, pp. 256–263.
- Shankland, T. J. and Waff, H.S.: 1977, 'Partial Melting and Electrical Conductivity Anomalies in the Upper Mantle', *J. Geophys. Res.* **82**, 5409–5417.
- Tanaka, J., Baumard, J., Abelard, P.: 1987, 'Nonlinear Electrical Properties of Grain Boundaries in an Oxygen-Ion Conductor (CeO₂-Y₂O₃)', *J. Am. Ceram. Soc.* **70**, 637–643.

- Tyburczy, J. A. and Roberts, J. J.: 1990, 'Low Frequency Electrical Response of Polycrystalline Olivine Compacts: Grain Boundary Transport', *Geophys. Res. Lett.* **17**, 1985–1988.
- van Dijk, T. and Burggraaf, A.J.: 1981, 'Grain Boundary Effects on Ionic Conductivity in Ceramic $Gd_xZr_{1-x}O_{2-(x/2)}$ Solid Solutions', *Phys. Stat. Sol.* **63**, 229–240.
- Verkerk, M. J., Middelhuis, B.J., Burggraaf, A.J.: 1982, 'Effect of Grain Boundaries on the Conductivity of High-Purity ZrO_2 - Y_2O_3 Ceramics', *Solid State Ionics* **6**, 159–170.
- Wanamaker, B.J. and Duba, A.G.: 1991, 'The Electrical Conductivity of San Carlos Olivine in a Nasilicate Glass Matrix (abstract)', *Trans Am. Geophys. Union* **72**, 529.
- Watson, E.B.: 1986, 'An Experimental Study of Oxygen Transport in Dry Rocks, and Related Kinetic Phenomena', *J. Geophys. Res.* **91**, 14,117–14,131.
- Will, G. and Nover, G.: 1986, 'Measurement of the Frequency Dependence of the Electrical Conductivity and Some Other Petro-Physical Parameters of Core Samples from the Konzen (West Germany) Drill Hole', *Ann. Geophys. Ser.* **B2**, 173–182.