Electrical Conductivity of Rocks and Dominant Charge Carriers

Part I: Thermally Activated Positive Holes

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Abstract

The prevailing view in the geophysics community is that the electrical conductivity structure of the Earth’s continental crust over the 5-35 km depth range can best be understood by assuming the presence of intergranular fluids and/or of intergranular carbon films. Based on single crystal studies of melt-grown MgO, magma-derived sanidine and anorthosite feldspars and upper mantle olivine we present evidence for the presence of electronic charge carriers, which derive from peroxy defects that are introduced during cooling, under non-equilibrium conditions, through a redox conversion of pairs of solute hydroxyl arising from dissolution of H₂O. The peroxy defects become thermally activated in a 2-step process, leading to the release of defect electrons in the oxygen anion sublattice. Known as positive holes and symbolized by h⁺, these electronic charge carriers are highly mobile. Chemically equivalent to O− in a matrix of O²− they are highly oxidizing. Being metastable they can exist in the matrix of minerals, which crystallized in highly reduced environments. The h⁺ are highly mobile. They appear to control the electrical conductivity of crustal rocks in much of the 5-35 km depth range.

Keywords

Electrical conductivity, igneous rocks, non-equilibrium conditions, peroxy defects, positive holes, metastable electronic charge carriers, dc conductivity, dielectric polarization.

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I Introduction

For many geophysical processes in the Earth’s crust it is crucially important to understand the nature of the charge carriers, which control the electrical properties of rocks. In this report we focus on conditions in the Earth’s continental crust over the 5-35 km depth range, where most major crustal earthquakes occur. Our goal is to identify the electric charge carriers that are present or can be activated in this depth range.

Any cursory inspection of geological maps reveals how heterogeneous the crust can be. Magneto-telluric (MT) soundings have provided ample evidence for the electrical heterogeneity as a function of depth. However, they have also identified high conductivity zones that seem to consistently exist at certain crustal depth levels, as well as large-scale inhomogeneities in the upper mantle.

The two most widely quoted causes for variations in the electrical properties of rocks are interconnected networks of aqueous fluids and/or of intergranular carbon or graphite films [Glover 1996]. In this report we point to the presence of electronic charge carriers in minerals and rocks, which have not been fully recognized in the past.

Any electrical charge transport in rocks can be attributed to one or more of the following three contributing causes: (i) electrolytic conduction, (ii) electronic conduction, or (iii) ionic conduction. Electrolytic conduction will occur in rocks where aqueous fluids fill pores and the intergranular space, forming an interconnected network. Ionic transport is negligible at the temperatures most relevant for the crustal depth range of interest here but surely becomes important at high temperatures, both in the solid state and with the on-set of partial melting. Electronic conduction can occur over the entire temperature range of interest here, either through intergranular networks or through the bulk.

I.1 Emphasis on Intergranular Fluids and on Carbonaceous Films

Aqueous fluids certainly exist in the shallow crust in the form of saline solutions filling the omnipresent pore space in rocks. Open pores can form a communicating network through which fluids are able to flow under the influence of tectonic pressure gradients. Such forced fluid flow through narrow pores will produce electrical signals, known as streaming potentials. They arise when cations are preferentially retained along the walls of narrow conduits while anions are swept along with the fluids [Dobrovolsky et al., 1989]. Streaming potentials are the foundation of the electrokinetic effect, widely used in prospecting of the shallow crust by magneto-telluric and other techniques as well in attempts to understand pre-earthquake electrical or electromagnetic signals [Merzer and Klemperer, 1997; Mizutani et al., 1976; Takahashi et al., 2007; Teisseyre, 1983; Yoshida et al., 1998].

Deeper into the crust, as the overload of the rock column increases, pores that communicate with the surface must close as the difference between lithostatic and hydrostatic pressures becomes too large. Closing occurs around 3-5 km. Below this cap, fluids are at lithostatic pressures. They can either be trapped in situ in sediment-derived formations, which had been transported downward through tectonic processes such as faulting [Yardley et al., 2000], or be supplied from below through degassing of magmas during crystallization or through mineral dehydration above a mantle plume [Vanyan and Gliko, 1999] or above a subducting slab [Hyndman, 1988]. The presence of an electrolytically conductive intergranular phase should have a profound effect on the electrical conductivity structure.

Two views emerged in the literature regarding the nature of intergranular films. One view emphasizes the presence of “water”. The other view emphasizes the presence of carbon films precipitated in the
intergranular space out of CO/CO$_2$–bearing fluids within the stability field of graphite [Constable and Duba, 1990; Nover et al., 2005; Shankland et al., 1997].

The inferred presence of water has been widely invoked as an explanation for increased electrical conductivities in the crust and the upper mantle [Frost and Bucher, 1994; Fuji-ta et al., 2004; lio et al., 2002; Karato, 2011; Khan and Shankland, 2011b; Nekut et al., 1977; Qin et al., 1992; Wannamaker, 1994] or to explain high conductivity layers in the crust at a certain depth ranges, around 20 km [Chen and Chen, 2002; Fuji-ta et al., 2004; Lee et al., 1983; Patro et al., 2005; Qin et al., 1992]. The zones of high electrical conductivity seem to correlate with zones of low velocity for seismic waves, though this correlation has been called into question [Bai et al., 2002]. The presence of water has also been invoked to account for high electrical conductivity along seismically active faults such as the Parkfield section of the San Andreas Fault in California [Unsworth et al., 1999].

Intergranular carbon, carbonaceous or graphite films have been considered as an alternative to water [Nover et al., 2005; Olhoeft, 1981; Shankland et al., 1997]. Carbon films have been invoked in the context of zones of high crustal conductivity around 20 km, the presence of which suggests conduction mechanisms that are not activated in at shallower depth and disappear at greater depth [Glover, 1996; Haak and Hutton, 1986; Hyndman et al., 1993].

Surface analytical techniques such as x-ray photoelectron spectroscopy (XPS), secondary ion mass spectrometry (SIMS) or ion probes have indeed provided evidence for carbonaceous surface films a few atomic layers thick after rocks had been fractured in 95% CO$_2$ +5% CO or 5% CH$_4$ gas mixtures at temperatures between 350–500°C [Roberts et al., 1999]. Such films are assumed to have been deposited in situ from fluids containing reduced carbon species such as CO or CH$_4$ that would have percolated through the rocks. Experiments with thin carbon films along the contact between two quartz crystals at 1 GPa have demonstrated that, when the temperature was raised to about 630°C, the graphite films disintegrate and disappear [Yoshino and Noritake, 2011].

In the petrological literature a strong case has been made that the stable lower crust should be “dry” and devoid of percolating or stagnant fluid phases [Yardley and Valley, 1997]. The argument is that, given the prevailing high temperatures, any “water” in these deep environments will be consumed rapidly – on a geological time scale – by metamorphic reactions leading to hydroxyl-bearing minerals such as amphiboles and mica, both of which are characterized by low electrical conductivities [Litovchenko and Mazykin, 1984; Meunier et al., 1983; Wang et al., 2012]. The case for a “dry” lower crust has sparked an insightful discussion about alternative views [Wannamaker, 1999; Yardley and Valley, 2000].

### 1.2 AC versus DC

Numerous laboratory studies have been conducted to characterize the electrical properties of minerals and rocks. Most often the electrical conductivity was measured using ac methods. The reason for preferring is that ac measurements can (i) provide more parameters than dc techniques and (ii) are better suited for experiments under the high temperatures and high pressures needed to explore the electrical properties of minerals and rocks under lower crust and upper mantle conditions [Fuji-ta et al., 2004; Liu et al., 1999; Nover, 2005; Wang et al., 2012; Yang, 2011].

When an ac electric field is applied, a marked frequency dependence is often observed, which is caused by the complex interplay between conduction and displacement currents. Displacement currents from the polarization of electrons, bonds, mobile ions, defects that either have a dipole or develop a dipole in the alternating electric field, charges accumulated along grain boundaries or
charges trapped and detrapped at the interfaces between the sample and the electrodes.

To appreciate the complexity of the situation we look at the resistivity $\rho$ [\(\Omega\text{ cm}\)] or its reciprocal, the conductivity $\sigma$ [\(\Omega^{-1}\text{ cm}^{-1}\)], and at the dielectric permittivity $\varepsilon$ [\(\text{F cm}^{-1}\)]. For a linear system we can write the conduction current density $\mathbf{J}_{\text{total}}$ at time $t$ and the electric displacement $\mathbf{D}$ caused by an electric field $\mathbf{E}$:

$$\mathbf{J}_{\text{total}} = \sigma \mathbf{E} + \varepsilon \varepsilon_0 \frac{\partial \mathbf{E}}{\partial t}$$  \[1\]

and

$$\mathbf{D} = \varepsilon \mathbf{E}$$  \[2\]

The relative dielectric constant $\varepsilon_r$ of the medium is defined as

$$\varepsilon_r = \varepsilon / \varepsilon_0$$  \[3\]

where $\varepsilon_0 = 8.854 \times 10^{-12}$ [\(\text{F/m}\)] is the dielectric permittivity of free space. Conduction currents and displacement currents will be out of phase with each other.

The parameters that are actually measured are not the true values but the effective values given by

$$\varepsilon_{\text{eff}}(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega)$$  \[4\]

and

$$\varepsilon_{\text{eff}}(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega)/\omega$$  \[5\]

The ratio of the imaginary part to its real part defines the phase angle $\Psi$ given as:

$$\tan \delta = \frac{\varepsilon''(\omega)}{\varepsilon'(\omega)}$$  \[6\]

**Figure 1a:** Resistivity $\rho$, loss tangent, $\tan \delta$, and dielectric constant $\varepsilon$ as a function of frequency $\omega$. The “true” conductivity $\sigma$ defined for $\omega = 0$.

**Figure 1b:** Example of the conductivity $\sigma$ of a pyroxene as a function of temperature from 25 to 400°C and 0 to 10^6 Hz [Olhoeft, 1976].

**Figure 1a** illustrates how the resistivity $\rho$, the loss angle $\tan \delta$, and the effective dielectric constant $\varepsilon_{\text{eff}}$ depend upon the frequency $\omega$. The “true” conductivity $\sigma$ is defined only at 0 Hz. **Figure 1b** shows the
conductivity $\sigma$ of a pyroxene between 25$^\circ$C to 400$^\circ$C at frequencies $\omega$ between 0 Hz and 10$^6$ Hz [Olhoeft, 1976]. A frequency-dependent loss feature is seen, which shifts to higher temperatures with increasing frequencies but also becomes increasingly indistinct.

Data as depicted in Figure 1b have diagnostic value for the interpretation of laboratory experiments. However, they are not directly useful in the analysis of many sets of field data collected by MT techniques. The reason is that, while the first few hundred meters below the surface with EM waves in the 1-5 kHz range, low to ultralow frequencies in the Hz, mHz and $\mu$Hz ranges are needed to penetrate deep enough into the Earth to send back information about the electrical structure of the deeper regions of the Earth [Cagniard, 1953].

In order to build the case for dc measurements, it is opportune to take a step back and look at the electronic conductivity of materials from a broader perspective.

Electronic Charge Carriers

Materials can be broadly classified into three groups: metals, semiconductors, and insulators. The three groups differ in the position of their valence bands (VB) and conduction bands (CB) relative to each other on the energy scale.

In metals, VB overlaps with CB allowing electrons from the VB to flow over into the CB. The CB electrons are not bound to any particular atom, meaning that their wavefunctions are delocalized.

Semiconductors have a modestly wide band gap, $E_g$ on the order of 1 eV. Such gaps allow some electrons from the VB to become thermally activated to the CB, where they act as negative charge carriers $e^-$. Around 300 K the thermal energy $kT$ is $\sim$25 meV, where $k$ is the Boltzmann constant, $8.618 \times 10^{-5}$ eV/deg, and $T$ the absolute temperature. Assuming a Boltzmann distribution, the probability for VB electrons to be thermally activated across $E_g$ is $e^{-E_g/kT}$. For a 1 eV band gap this means $e^{-40} \sim 4 \times 10^{-18}$ at 300 K. Electrons that make the transition to the CB leave behind defect electrons in the VB. The defect electrons are called holes, designated by $h^+$. They carry a +1 charge.

Holes in the VB are less mobile than electrons on the CB.

In insulators, $E_g$ is wide to very wide, often 5 eV or more. Thus the probability for electrons to be thermally activated from VB to CB becomes vanishingly small. Numerically, for $e^{-E_g/kT} \sim 5$ eV, the probability at 300 K or room temperature is on the order of $10^{-87}$ and still as low as $10^{-29}$ for 900 K or $\sim$630$^\circ$C. Thus, the electronic conductivity of insulators should be zero. Any observed conductivity has to arise from the presence of defects and/or impurities.

Eq. [7] links conductivity to the number density of charge-carrying species $n$ and their mobility $\mu$:

$$\sigma = n \mu \frac{z^2}{e^2} (kT)$$  \[7\]

where $z$ is the valence of the conducting species, $e$ the unit charge, $k$ the Boltzmann constant, and $T$ the absolute temperature.

If the conductivity is thermally activated with an activation energy $E_{act}$, we have:

$$\sigma = \sigma_0 \exp \left[ -\frac{E_{act}}{kT} \right]$$  \[8\]

where the pre-exponential factor $\sigma_0$ is the product of several contributions including $\mu$, $z$ and $e$. If more than one process control the conductivity, each with an activation energy $E_1$, $E_2$ ..., we have:

$$\sigma = \sigma_1 \exp \left[ -\frac{E_1}{kT} \right] + \sigma_2 \exp \left[ -\frac{E_2}{kT} \right] + ...$$  \[9\]

Plotting $\sigma$ versus $1/T$ eq. [8] will give a straight line, called an Arrhenius plot, with the slope $E_{act}$.

Eq. [9] will give two or more straight sections corresponding to $E_1$, $E_2$ ...

In semiconductors electrons in the CB, $e^-$, always compete with holes in the VB, $h^+$. The overall
conductivity behavior depends on at the number densities of e' and h', designated as n' and n', and the mobilities, designated as \( \mu' \) and \( \mu' \). If the product \( n'\mu' \) is larger than \( n'\mu' \), electrons control the overall conductivity and the semiconductor is said to be n-type. Conversely, if the product \( n'\mu' \) is smaller than \( n'\mu' \), holes control the conductivity and the semiconductor is said to be p-type.

\[
\begin{align*}
\text{n'-type} & : n'\mu' > n'\mu' \\
\text{p-type} & : n'\mu' < n'\mu'
\end{align*}
\]

Any semiconductor that is chemically pure is said to be intrinsic. In the intrinsic case, when electrons are thermally promoted across \( E_g \), the number of electrons on the CB will be equal to the number of holes in the VB: \( n' = n' \). Since the mobility of electrons on the CB is always higher than the mobility of holes in the VB, any intrinsic semiconductor will be n-type. While \( n' \) and \( n' \) depend exponentially on the temperature, the temperature dependence of the mobilities, \( \mu' \) and \( \mu' \) is weak.

If a semiconductor is doped with aloivalent impurities, it can be made more n-type or p-type depending on the nature and concentrations of the dopants. Alovalent dopants mean impurities with valencies other than those of the regular lattice constituents of the semiconductor material. However, alovalency can also involve native lattice constituents of the semiconductor in a different valence state. This aspect will play an important role in the discussion below.

The electrical conductivity of a material is the sum of the conduction of each type of charge carriers or each type of defects, all acting in parallel:

\[
\sigma = \sum \sigma_i = \sum n_i z_i \mu_i
\]

where \( n_i \) is the concentration of the \( i \)th type of charge carrier, \( z_i \) is the charge, and \( \mu_i \) the mobility.

Minerals and rocks are “dirty” systems with complex chemistries and defects of many different kinds always present over a range of number densities or concentrations. Each type of impurity or defect contributes to \( \sigma \), though usually not more than two types will dominate in any given temperature window under a given set of thermodynamic conditions.

Activation Energies, Charge Carrier Concentrations and Mobilities

Figures 2a/b show Arrhenius plots for mafic and ultramafic igneous rocks samples that have been conditioned by cycling them through the temperature interval of interest under controlled redox conditions, using a variety of heating and cooling rates [Parkhomenko, 1967; Parkhomenko, 1982].

From below 100°C to about 600-700°C, \( \sigma \) for all rocks under study is consistent with eq. [8], i.e. with a single conductivity mechanism characterized by a single value of \( E_{\text{act}} \). Remarkably \( E_{\text{act}} \) is closely the same for all rocks, ~1 eV. This suggests that, irrespective of the type of rock and in spite of mineralogical and chemical differences, the conductivity of these rocks appears to be controlled by the same conductivity mechanism over the low temperature region (LT), from below 100°C to 600-700°C.

Different samples of the same rock produce straight sections of the Arrhenius plots that can be shifted parallel to each other on the log \( \sigma \) scale by a significant amount. Hence, in the \( \Delta T \) window shown here, the only difference is the numerical value of \( \sigma_0 \). According to eq. [7] the only T-dependent contributions to \( \sigma_0 \) are \( n \) and \( \mu \), the number density of charge carriers and their mobilities, respectively. Since the temperature dependence of the mobility is weak, we can treat \( \mu' \) and \( \mu' \) as approximately constant across the temperature interval of interest here, Hence our focus can center on \( n' \) and \( n' \).
Figure 2a/b: Electrical conductivity of mafic and ultramafic rocks after [Parkhomenko, 1982].

Figure 2b shows that, when the rock samples were heated beyond 550-600°C, up to about 1000°C, straight sections with different slopes are obtained, suggesting different $E_{\text{act}}$ values for the high temperature (HT) region.

The two linear sections point to two conduction mechanisms, endowed with activation energies, $E_1$ in the LT range and $E_2$, $E_3$, $E_4$ ... in the HT range, as suggested by eq. [9]. At HT ionic conductivity sets in, exhibiting different slopes for different rock types, suggesting different ionic conduction with different $E_{\text{act}}$ values. At the same time $E_{\text{act}}$ in the LT range is closely the same for all rocks, although the $\sigma_0$ values may vary over orders of magnitude, even for the same rock type. For instance, the Arrhenius plot for peridotite in Figure 2a shows a conductivity over the 50-300°C window that is 6 orders of magnitude higher than the conductivity of the peridotite shown in Figure 2b over the 100-500°C window.

The constancy of the activation energy $E_{\text{act}} \sim 1$ eV across different rock types in the LT range is as remarkable as the widely different $\sigma_0$ values within one rock type.

Nature of the Charge Carriers

MgO, a II-VI material, is not a semiconductor. It has a very wide band gap of about 8 eV, MgO is the most ionic among all alkaline earth oxides with mostly Coulombic interaction between $\text{Mg}^{2+}$ and $\text{O}^{2-}$ [Pacchioni et al., 1993]. As a main-group element with the electronic configuration $1s^2 2s^2$, Mg has only one stable oxidation state, $2^+$. Therefore, pure MgO should be a model insulator.

Large MgO single crystals can be melt-grown by the carbon arc fusion technique [Abraham et al., 1971]. Crystals are available at nominal 99.9% purity grades, designated as 3N, either undoped or doped with various levels with divalent 3d transition elements Mn, Fe, Co, or Ni. Purer MgO crystals, up to purity grade 99.99%, designated as 4N, are also available in sizes up to several cm$^3$.

If MgO single crystals are well-annealed, their electrical conductivity at room temperature can be
below $10^{-16} \text{[} \Omega^{-1} \text{cm}^{-1}]$. However, when heated, MgO single crystals display a striking dc conductivity behavior as illustrated in Figures 3a-d for a high purity 4N-MgO crystal measured under the most stringent clean conditions and with a guard electrode to remove contributions from surface conductivity [Kathrein and Freund, 1983].

**Figure 3.** Sequence of dc conductivity measurements of a highest purity grade MgO single crystal under the most stringent clean conditions. (a) shows an anomalous increase in conductivity during the first heating, which is not observed as shown in (b) when the crystal is reheated immediately after cooling. However, if the crystal is annealed for several hours, the anomalous conductivity reappears as shown in (c). Panel (d) shows that this anomalously high conductivity is due to the activation of charge carriers that conduct electricity with an activation energy $\sim 1 \text{eV}$ [Kathrein and Freund, 1983].
Upon first heating, starting around 350-400°C, the conductivity of the MgO crystal increases by about 6 orders of magnitude as shown in Figure 3a. At the heating rate used in this experiment, 10° min⁻¹, the conductivity reaches a maximum around 600-650°C and then decreases, only to increase again above 700°C. Around 850-900°C the conductivity joins an Arrhenius straight section that describes the reversible HT conductivity, which is endowed with an activation energy of 2.4 eV. At very slow cooling rates the HT mechanism can be followed downward to below 500°C [Lempicki, 1953]. At any cooling rate the HT mechanism is eventually replaced by an LT mechanism, endowed with an activation energy of ~1 eV. The transition from HT to LT occurs around 650-700°C. In the HT regime the electrical conductivity of MgO is controlled by Mg²⁺ diffusion via an Mg²⁺ vacancy hopping mechanism [Sempolinski and Kingery, 1980], possibly augmented by O²⁻ diffusion [Wuensch et al., 1973]. The nature of the LT 1 eV mechanism has long remained undetermined.

If the MgO crystal is reheated immediately after cooling as in the run depicted in Figure 3b, the conductivity curve “2nd up” closely follows the LT conductivity behavior observed during first cooling “1st down” and also during second cooling “2nd down”. If, however, the MgO crystal is not reheated immediately after cooling but allowed to anneal for several hours or overnight at temperatures below ~150°C, Figure 3c shows a conductivity pattern, “3rd up”, similar to that of the first heating, “1st up” in Figure 3a. This conductivity pattern is reproducible except that, during repetitive heating-cooling cycles, the highest conductivity achieved around 650°C slowly decreases with the number of cycles and with the holding time at the highest temperature. Another subtle but reproducible feature is that, during cooling, the transition from the HT section to LT section shifts to ever lower temperatures the more often the MgO crystal has been cycled through HT and the longer it has been kept at temperatures >900°C.

A similar conductivity pattern has been observed in studies with natural samples, both single crystal minerals and rocks [Constable and Duba, 1990; Duba and Constable, 1993; Roberts et al., 1999]. In those cases the high conductivity recorded during first heating in the LT range has been blamed on adventitious surface contamination by carbonaceous films. Surface contamination can never be totally ruled out during conductivity measurements, even under very well controlled conditions. However, conductivity measurements can be performed in such a way that surface contamination as a reason for the anomalous electrical conductivity behavior can be ruled out [Kathrein and Freund, 1983].

Figure 3d shows what happens when the heating of the 4-N MgO crystal is intermittently reversed three times within the range of the anomalously rapid conductivity increase, at 540°C, 555°C, and 590°C. After each intermediate cooling, the MgO crystal was immediately reheated. For every cycle, Arrhenius straight sections are obtained, all with the same slope corresponding to an activation energy of ~1 eV. Each time, during reheating, the conductivity eventually rejoins the main branch, marked by solid red circles. The main branch is characterized by an Eₘ value around 3.2 eV.

Because this particular experiment was conducted at heating and cooling rates of 20°C min⁻¹, the main branch in Figure 3d is shifted towards higher temperatures relative to the curves in Figures 3a-c, which were conducted at 10° min⁻¹. Except for this experimental effect, which due to the thermal inertia of the system, the conductivity patterns are very similar.

A conductivity pattern as depicted in Figure 3d is not consistent with surface contamination. It points to two processes working in tandem.

Process (i) involves the activation of defects in the MgO structure, which are electrically inactive but release mobile charge carriers as the temperature increases. These charge carriers must be electronic. The activation begins at a threshold temperature, ~350°C at the 10° min⁻¹ heating rate or ~450°C at the 20° min⁻¹ heating rate, and has an apparent activation energy barrier (E₁ + E₂) ~3.2 eV. Process (i) is
consistent with the number n of mobile charge carriers increasing exponentially as the MgO crystal is 
heated. Process (i) takes place only after the MgO crystal has been annealed for some time, operating 
between 350-600°C during the 10° min⁻¹ runs or 450-650°C during the 20° min⁻¹ run. Around 600- 
650°C process (i) comes to an end, suggesting that all available charge carriers have been activated. 
Above 700°C the conductivity decreases, indicating that charge carriers are being destroyed. This is 
consistent with the aforementioned decrease in maximum conductivity value obtained during 
consecutive heating-cooling cycles. 
Once the charge carriers are activated, they remain active for a sufficiently long time to immediately 
conduct successive cooling-reheating cycles. If the MgO crystal is allowed to anneal, the charge 
carriers return to an inactive state, from which they can be reactivated by reheating to 350-450°C. 
Process (ii) relates to how much current is carried by n mobile charge carriers, where n is the number 
of charge carriers activated through process (i). The charge carriers require an activation energy E₂ to 
jump from one site to the next. Both processes, (i) with the combined activation energy (E₁ + E₂) ~ 
3.2 eV, and (ii) with the activation energy E₂ ~ 1 eV, follow Arrhenius relations. To describe the 
system under study we can use a relation very similar to eq. [9]: 
\[ \alpha = \alpha_0 \exp\left[-\frac{(E_1+E_2)}{kT}\right] \] 
The sum (E₁ + E₂), ~3.2 eV, applies to the main heating branch in Figure 3d. E₂ ~ 1 eV applies to the 
cooling-reheating straight sections in Figures 3a-d. The value for E₁ is ~2.2 eV, that for E₂ is ~1 eV. 
In summarizing this section we can state with confidence that highest purity-grade 4N-MgO single 
crystals exhibit a complex dc conductivity behavior in the temperature window between ambient and 
800-900°C. The conductivity increase by at least 6 orders of magnitude between 300°C and 600- 
700°C is clearly at odds with the presumed model insulator nature of MgO. It points to either the 
presence of impurities that are not included in the chemical purity grade or to the presence of defects, 
which had not been identified in prior work. 
There is one more important observation: MgO crystals doped with divalent 3d transition metal 
cations, Mn²⁺, Fe²⁺, Co²⁺ or Ne²⁺ at various, even high concentration levels exhibit the same electrical 
conductivity pattern as described here for 4N-grade MgO [Freund et al., 1993; Kathrein and Freund, 
1983]. This suggests that the anomalous conductivity behavior is not caused by transition metal 
impurities nor by charge carriers that would propagate via the metal cation sublattice. 
Furthermore we can state with confidence that the observed conductivity behavior of the MgO single 
crystals and their 1 eV conductivity mechanism cannot be due to surface contamination. MgO crystals 
that were temperature-cycled in pure O₂ show the same conductivity pattern, ruling out that the 
increased conductivity would be caused by carbonaceous surface films [Kathrein and Freund, 1983].

**Valence Changes in the Oxygen Anion Sublattice**

MgO was the first oxide material for which evidence was obtained that the valence of oxygen anions is 
not fixed at 2-, as is widely assumed, but can change to the higher oxidation state 1-. When ultrahigh 
purity Mg(OH)₂ was thermally decomposed to MgO + H₂O, forming a dilute MgO–H₂O solid 
solution, Mg₁₋ₓ(OH)₂₋ₓO₁₋ₓ, it released copious amounts of H₂, 10,000 ppm, even though the 
transition metal impurity level was <5 ppm, equivalent to a purity grade >99.999% [Martens et al., 
1976b]. Since Mg cations are fixed in their 2⁺ valence state, the only possibility for H⁺ to be reduced 
to H₂ was to concomitantly oxidize oxygen anions from valence 2- to valence 1-. 
Follow-on studies with MgO single crystals revealed that the redox conversion takes place in the MgO
matrix involving OH\(^-\) pairs associated with and chargewise compensated by Mg\(^{2+}\) vacancies. During
the redox conversion two hydroxyl protons are reduced to H, forming H\(_2\), while two hydroxyl oxygen
are oxidized to O\(^-\), forming a peroxy anion, O\(_2\)^\(-2\) [Baltto et al., 1991; Freund and Wengeler, 1982].
Using the Kröger-Vink point defect designation\(^1\) we can write this reaction as:

\[ \text{[OH}^\cdot \text{V}_{\text{Mg}} \text{HO}^\cdot \text{]}^\text{x} \Leftrightarrow [\text{O}^\cdot \text{V}_{\text{Mg}} \text{H}^\cdot \text{]}^\text{x} \]  [13]

The defect on the right hand side can release its H\(_2\) molecule into an interstitial site:

\[ [\text{O}^\cdot \text{V}_{\text{Mg}} \text{H}^\cdot \text{]}^\text{x} \Leftrightarrow [\text{O}^\cdot \text{V}_{\text{Mg}} \text{]}^\text{x} + (\text{H}_2)^x \]  [14]

where the right side now describes an Mg\(^{2+}\) vacancy chargewise compensated by a peroxy anion, O\(_2\)^\(-2\).
If the MgO crystals are small [Martens et al., 1976] or if the time for outdiffusion is long, the H\(_2\) can
ecape from the solid matrix. Such loss of H\(_2\) would change M\(_{1-e}\)(OH)\(_{2-e}\)O\(_{1-2e}\) into M\(_{1-e}\)-O. If e\(\leq\)1,
cation-deficient M\(_{1-e}\)-O may also be written as MgO with excess of oxygen, MgO\(_{1+e}\).

MgO is intrinsically diamagnetic. Peroxy anions are diamagnetic, because the two O\(^-\) are tightly
coupled and spin-paired. Upon heating, the spin pairing loosens up and eventually breaks, causing a
transition from a diamagnetic to a paramagnetic state and dissociation. Magnetic susceptibility studies
have provided information about this transition [Baltto et al., 1991]. Peroxy spin decoupling and
dissociation take place in two distinct steps: (i) the peroxy bond loosens up, (ii) full dissociation takes
place. Designating as I the peroxy defect as I and as II the transition state, where spins associated with
the two O\(^-\) begin to decouple, we have:

\[ \text{[O}^\cdot \text{V}_{\text{Mg}} \text{]}^\text{x} \Leftrightarrow [\text{O}^\cdot \text{V}_{\text{Mg}} \text{O}^\cdot \text{]}^\text{x} \]  [15]

During stage II, the wave functions associated with the two O\(^-\) delocalize over many neighboring
oxygen anion positions, causing anomalies in fundamental physical properties such as in the thermal
expansion and in the refractive index [Freund et al., 1994]. However, at this decoupling stage, there is
no significant increase in the electrical conductivity.

During stage II, the two O\(^-\) dissociate. Dissociation involves an electron transfer from a neighboring
O\(^2-\) donates into the [O\(^\cdot\) V\(_{\text{Mg}}\) O\(^\cdot\)]\(^x\) defect. The neighboring O\(^2-\), which had donated the electron,
thereby turns into an O\(^-\), which is no longer bound to the Mg\(^{2+}\) vacancy. It becomes an unbound defect
electron on the oxygen anion sublattice. The Mg\(^{2+}\) vacancy retains one O\(^-\), forming a V\(^-\) center, a
point defect widely studied by electron paramagnetic resonance spectroscopy [Henderson and Wertz,
1977; Marfunin, 1979]. Designating the dissociated state with III we have:

\[ [\text{O}^\cdot \text{V}_{\text{Mg}} \text{O}^\cdot \text{]}^\text{x} \Leftrightarrow [\text{O}^\cdot \text{V}_{\text{Mg}} \text{]}^+ + \text{O}^\cdot \]  [16]

**Figure 4** outlines the temperature windows for the transitions between defects I, II, and III. It
summarizes the insight gained from a wide range of studies aimed at understanding the electrical
conductivity of nominally high purity MgO single crystals. These studies have positively identified
peroxy defects in the MgO matrix as the cause for this anomalous conductivity behavior.

\(^1\) V stands for vacancy; subscripts identify the site (except for oxygen sites, where subscripts are omitted);
superscript prime, dot, and x designate single negative, positive and neutral charges, respectively, double prime
and double dot designate double negative and positive charges; subscript i means interstitial; square brackets
outline the essential parts of any given point defect.
Unbound $O^-$ constitute defect electrons in the $O^{2-}$ sublattice to be designated h' [Griscom, 1990]. The h' are free to roam – as electronic charge carriers – through the oxygen anion sublattice. Therefore, when the peroxy defects break up, releasing h' charge carriers, the electrical conductivity increases sharply as demonstrated in Figure 3d, rising by 6-7 orders of magnitude over a 250°C wide interval, from about 450°C to about 700°C.

Close to 700°C the release of h' charge carriers comes to completion, marking the end of dissociation of defect II. Above 700°C the conductivity drops. The reason is that another process sets in, namely Mg$^{2+}$ diffusion, which becomes thermally activated above ~600°C [Lempicki, 1953]. Mg$^{2+}$ diffusion is essential for non-stoichiometric Mg$_{1-x}$O to return to equilibrium. It requires annihilation of the excess Mg$^{2+}$ vacancies at the crystal surface, a process that proceeds by way of cation vacancy hopping [Conrad and Yang, 2010; Sempolinski and Kingery, 1980; Wuensch et al., 1991].

**Figure 4:** Interpretative representation of the anomalous electrical conductivity pattern of highest purity MgO single crystals, supposedly a model insulator. Three temperature windows are identified, below 250°C, between 250-450°C and 450-700°C, each associated with different states of peroxy defects in the MgO matrix, designated as I, II and III. The dissociation of the defect III uniquely controls the electric conductivity of MgO through the release of positive hole charge carriers, h’, here shown as $O^+$ states.

**Thermodynamic Equilibrium and Non-Equilibrium Conditions**

If $O^-$ is to be introduced into MgO under thermodynamic equilibrium conditions, highly oxidizing conditions are required [Wuensch et al., 1991]. No MgO crystal grown from the melt of a carbon arc fusion furnace under highly reducing conditions should contain oxygen in the valence state 1-.

Therefore, the presence of peroxy defects appears to be in disagreement with thermodynamics.

However, the reaction described by eq. [8], the loss of H$_2$ as described by eq. [9], and the presence of oxygen in the valence 1− are not in conflict with thermodynamics. Nor is the presence of excess Mg$^{2+}$ vacancies in the non-stoichiometric Mg$_{1-x}$O. The number of Mg$^{2+}$ vacancies in the MgO matrix is not a reflection of the O$_2$ fugacity at the time of crystallization but a consequence (i) of the concentration of H$_2$O dissolved in the MgO matrix under thermodynamic equilibrium conditions and (ii) of the solid state reactions described by eqs. [8] and [9], which occurred at temperatures too low for equilibrium to be maintained.

When nanocrystalline Mg$_{1-x}$O produced by the outdiffusion of H$_2$ according to eq. [14] was heated above 600°C, atomic O started to evolve, indicating disproportionation [Martens et al., 1976b]:

$$O_2^{2−} \rightarrow O^{2−} + O$$  \[17\]

Through this reaction Mg$_{1-x}$O evolves toward the 1:1 stoichiometry that a material like MgO with Schottky defects is supposed to have at thermodynamic equilibrium [Alfé and Gillan, 2005]:

$$Mg_{1-x}O \rightarrow MgO + \frac{3}{2}O_2$$  \[18\]
Confirmation of Positive Holes by Dielectric Polarization

Electrical conductivity measurements do not provide the sign of the majority charge carriers. If we want to learn more about the nature of the charge carriers, it is advisable to supplement conductivity measurements with corroborating techniques.

One option is to conduct Hall effect measurements, widely used to study semiconductors [Clayhold and B. M. Kerns, 2008], which provide information about the sign of the majority charge carriers and their mobilities. Another option is to measure the dielectric polarization $\mathbf{P}$, a fundamental property of materials, given by $\mathbf{P} = \varepsilon_0(\varepsilon - 1)/4\pi \mathbf{E}_{\text{ext}}$, where $\varepsilon_0$ and $\varepsilon$ are the permittivity of vacuum and dielectric constant, respectively, and $\mathbf{E}_{\text{ext}}$ is the externally applied electric field [Freund et al., 1989].

![Dielectric Polarization](image)

**Figure 5:** Schematic representation of the dielectric polarization of insulators, giving rise to the effective dielectric constant $\varepsilon_{\text{eff}}$ a fundamental bulk property. Different contributions are identified. The first three on the right, at high frequencies, are characteristic of perfect crystals. The 4th and 5th arise from defects, which either increase the local polarizability or create mobile charges that can move as a space charge in the externally applied $E$ field.

As illustrated in Figure 5 the dielectric polarization $\mathbf{P}_{\text{total}}$ is composed of several contributions in different frequency ranges. Five contributions are characteristic of the bulk, $\mathbf{P}_{\text{el}}, \mathbf{P}_{\text{bond}}, \mathbf{P}_{\text{dipole}}, \mathbf{P}_{\text{local}},$ and $\mathbf{P}_{\text{space}}$, plus a sixth contribution, $\mathbf{P}_{\text{surface}}$, which arises from the surface [Kittel, 1980]. At high frequencies, in the visible (VIS) region, $10^{15}$–$10^{13}$ Hz, only electrons can respond to the rapidly alternating $E$ field. Their contribution $\mathbf{P}_{\text{el}}$ defines the refractive index $n$. In the infrared (IR) region, below $10^{13}$ Hz, atoms linked by bonds or forming dipoles can follow the $\mathbf{E}_{\text{ext}}$ field, converting energy into atomic vibrations. The sum ($\mathbf{P}_{\text{el}} + \mathbf{P}_{\text{bond}} + \mathbf{P}_{\text{dipole}}$) defines the dielectric constant, $\varepsilon$, linked to the refractive index $n$ by the Lorentz-Lorenz relation $n = \sqrt{\varepsilon}$. In perfect dielectrics $\mathbf{P}_{\text{total}}$ will not increase further with decreasing frequency. In practice defects are always present, some of which may have dipoles that can align in the $\mathbf{E}_{\text{ext}}$ field, possess a local polarizability that is different from that of the surrounding matrix. Their contributions are combined in $\mathbf{P}_{\text{local}}$. When mobile charge carriers appear, they can form space charges that respond to the external $\mathbf{E}_{\text{ext}}$ field. Their contribution is designated as $\mathbf{P}_{\text{space}}$. In the context of this paper only $\mathbf{P}_{\text{local}}$ and $\mathbf{P}_{\text{space}}$ are of interest.

The sixth contribution, $\mathbf{P}_{\text{surface}}$, arises uniquely from the surface. When a dielectric generates mobile charge carriers, these charge carriers repel each other in the bulk and are driven toward the surface. The sign of the surface charge is determined by the majority charge carriers, their number density $n$. 

13
and mobility $\mu$. According to eqs. [5a/b] the surface charge is positive if $n' \mu' < n' \mu^+$, indicating p-type, and negative, if $n' \mu' > n' \mu^+$ indicating n-type characteristics [King, 1984 #102].

Figure 6 illustrates the principle of the measurement, the protocol and representative results [Freund et al., 1989]. Figure 6a shows the sample placed between a small gold sphere and an annular gold electrode. Connecting the annular electrode to ground and applying a voltage to the small electrode, generates a divergent electric field, which produces a force $F_z$ acting on the sample. In practice the sample is suspended from a microbalance into a small, cup-shaped furnace, which contains both electrodes. Figure 6b shows a temperature-time program with temperature steps, $\Delta T$, typically in 5° or 10°C increments/decrements. During each $\Delta T$ step, at constant $T$, a voltage-time program is applied as shown in Figure 6c with typical $\pm \Delta V$ steps of $\pm 5$, $\pm 10$, $\pm 20$ or $\pm 50$ V.

![Diagram](image)

Figure 6: Principle and execution of a dielectric polarization measurement in a divergent electric field gradient (see text).

In the case of a dielectric with contributions from $P_{el}$, $P_{bond}$, $P_{dipole}$, $P_{local}$, and $P_{space}$, $F_z$ is proportional to the square of the applied voltage leading to parabolas as in Figure 6d. In the case of a dielectric with mobile positive charges in the bulk, which make a $P_{surface}$ contribution, the parabolas are skewed by the addition of a linear term, proportional to the density of the surface charge, as illustrated in Figure 6e.

Bulk and surface contributions can be separated by forming linear combinations $F_\Sigma = \frac{1}{2} (F_z^- + F_z^+)$ and $F_A = \frac{1}{2} (F_z^- - F_z^+)$, where $F_z^+$ and $F_z^-$ are the forces measured with $+$ and $-$ bias, respectively. $F_\Sigma$ depends quadratically on the bias voltage and is given by:
\[ F_\Sigma = - \int_{\text{vol}} \left[ \phi_{\text{vol}} + \phi_{\text{bond}} + \phi_{\text{dipole}} + \phi_{\text{local}} + \phi_{\text{space}} |\nabla| E_{\text{int}} \right] dV \]  

\[ F_\Delta = - \int |P_{\text{surf}}| \nabla E_{\text{int}} dV \]  

\( F_\Delta \) depends linearly on the bias voltage and is a unique function of the surface charge density:

**Figures 7a/b** show \( F_\Sigma(T) \) and \( F_\Delta(T) \) plots of an MgO single crystal, here a 3N-MgO crystal, 99.9% basic purity grade doped with 200 ppm Co\(^{2+}\). \( F_\Sigma(T) \) and \( F_\Delta(T) \) graphs of undoped 4N-MgO or of moderately doped 3N-MgO crystals with divalent 3d-transition metal cations are practically indistinguishable. The data were obtained during stepwise heating to \( T_{\text{max}} = 600^\circ\text{C} \) in \( \text{N}_2 \) atmosphere following the protocol depicted in **Figure 6b** with 15 sec polarization time at each \( \Delta T \) step during each \( \Delta T \) step. The dotted line in **Figure 7a** indicates how \( F_\Sigma(T) \) changes, if the polarization time is 15 min at each \( \Delta T \) step. The 15 min polarization data were obtained in a separate run over this narrow \( T \) interval. **Figure 7b** indicate the evolution of \( F_\Delta(T) \). The black triangles show \( F_\Delta \) going negative, if heating is continued above 600\(^\circ\)C. These data were obtained in a separate run.

**Figure 7a/b:** Bulk polarization \( F_\Sigma \) and surface charge \( F_\Delta \) show the evolution of the effective dielectric constant and the thermal activation of positive charge carriers in MgO during heating to 600\(^\circ\)C, which is consistent with the 2-step activation process as described by eqs. [15/16].

In **Figure 7a** the \( F_\Sigma(T) \) data are fitted to the dielectric constant \( \varepsilon \) of MgO, 9.6 at room temperature [Young and Frederikse, 1973]. At the limit of 0 Hz \( \varepsilon \) begins to increase around 250\(^\circ\)C at 15 sec polarization time or already around 200\(^\circ\)C at 15 min polarization time. \( \varepsilon \) reaches a plateau around 350\(^\circ\)C but exhibits a second stepwise increase beginning around 450\(^\circ\)C. The \( F_\Delta(T) \) data in **Figure 7b** indicate a slightly negative surface charge of the MgO up to about 350\(^\circ\)C, followed by a pronounced positive surface charge, indicating the onset of p-type behavior. The positive surface charge reaches a maximum about 450\(^\circ\)C, then decreases and turns negative above 600\(^\circ\)C, indicating n-type behavior.

According to eq. [14] \( F_\Sigma(T) \) is the sum of the five bulk contributions to \( \mathbf{P}_{\text{total}} \). Only the last two, \( \mathbf{P}_{\text{local}} \) and \( \mathbf{P}_{\text{space}} \), depend on the presence of defects. The stepwise increase in \( F_\Sigma(T) \) indicates that these defects are thermally activated. During the first increase, there is no change in \( F_\Delta(T) \), i.e. no activation of mobile charge carriers. This means that the first \( F_\Sigma(T) \) increase, which begins at 250\(^\circ\)C or 200\(^\circ\)C, is due to the thermal activation of defects, which only affect the local polarizability, \( \mathbf{P}_{\text{local}} \).
This is fully consistent with the transition of the tightly bound, spin-coupled peroxo defect \( \text{[O} \cdot \cdot \cdot \text{V}^\text{II}_\text{Mg}]\), designated state I, to state II, the spin-decoupled state \( \text{[O} \cdot \cdot \cdot \text{V}^\text{II}_\text{Mg} \cdot \cdot \cdot \text{O}^\text{II}]\) as described by eq. [10]. It is consistent with the absence of any significant increase in the electrical conductivity of the MgO in the temperature range below approximately 350°C as evidenced in Figure 3a.

By contrast, above 350°C, the electrical conductivity of the MgO starts to increase as shown in Figure 3a, indicating the activation of mobile charge carriers. This is consistent with the increase in \( F_2(T) \), due to a contribution of \( P_{\text{space}} \) and simultaneous \( P_{\text{surface}} \) contribution as reflected in the change in \( F_\Delta(T) \) in Figure 7b. This is consistent with the break-up of the peroxo bond as described by eq. [11], i.e. with the transition of the spin-decoupled state \( \text{[O} \cdot \cdot \cdot \text{V}^\text{II}_\text{Mg} \cdot \cdot \cdot \text{O}^\text{II}]\) to the dissociated state \( \text{[O} \cdot \cdot \cdot \text{V}^\text{II}_\text{Mg} \cdot \cdot \cdot + \text{O}^\text{II}] \) and the activation of mobile positive hole charge carriers \( h^+ \).

Dielectric polarization measurements during cooling show that \( F_2(T) \) is fully reversible under the conditions of the experiments, i.e. under slow stepwise cooling over many hours. The high temperature portion of \( F_\Delta(T) \), the trend from the high positive values around \( T_{\text{max}} \sim 500°C \) toward negative values at \( \sim 600°C \), is also reversible. Below \( \sim 500°C \), however, the surface charge lingers on, causing \( F_\Delta(T) \) to remain positive down to ambient temperatures. At room temperature the surface charge dissipates over the course of hours with about the same time constant with which the electrical conductivity \( \sigma(T) \) recovered during annealing as discussed in the context of Figures 3a-c.

### Positive Hole Charge Carrier Activation in Feldspars

MgO is not the only material that contains peroxo defects and activates positive hole charge carriers at distinct temperature steps upon heating. Silicates also contain peroxo defects, probably in the form of peroxo bridges, \( \text{O}_3\text{Si}^{\text{OO}}\text{SiO}_3 \) or \( \text{O}_3\text{Si}^{\text{OO}}\text{AlO}_3 \), replacing \( \text{O}_3\text{Si}^{\text{O}}\text{SiO}_3 \) or \( \text{O}_3\text{Si}^{\text{O}}\text{AlO}_3 \) bonds respectively, or linking [Si-O-Si] groups.

In the case of MgO the introduction of peroxo defects was linked to the dissolution of \( \text{H}_2\text{O} \) and formation of hydroxyl pairs associated with \( \text{Mg}^{2+} \) vacancies, \( \text{OH}^- \), followed by the redox conversion described by eqs. [13/14]. Feldspars are tectosilicates the structures of which consist of [Si,AlO₄] tetrahedra 3-dimensionally connected by \( \text{O}_3\text{Si}^{\text{O}}\text{SiO}_3 \) and/or \( \text{O}_3\text{Si}^{\text{O}}\text{AlO}_3 \) bonds. If \( \text{H}_2\text{O} \) is dissolved, it will most likely hydrolyze the bonds forming as primary product hydroxyl pairs:

\[
\text{O}_3\text{Si}^{\text{O}}\text{SiO}_3 + \text{H}_2\text{O} \stackrel{\text{H}_2\text{O}}{\rightleftharpoons} \text{O}_3\text{Si}^{\text{OH}}\text{SiO}_3
\]

The hydroxyl pair on the right hand side of eq. [21] could undergo the same type of redox conversion as \( \text{OH}^- \) pairs in MgO, leading to

\[
\text{O}_3\text{Si}^{\text{OH}}\text{SiO}_3 \rightleftharpoons \text{O}_3\text{Si}^{\text{OO}}\text{SiO}_3 + \text{H}_2
\]

Feldspars indeed exhibit the same \( F_2(T) \) and \( F_\Delta(T) \) behavior when heated. This is exemplified in Figure 8a/b for \( F_2(T) \) of a sanidine single crystal from Volkesfeld, Eifel volcanic district, Germany [Bertelmann et al., 1985], and for \( F_2(T) \) of an anorthosite from Larvik, Norway [Wanvik, 2000]. The sanidine, \( \text{K}_{0.96}\text{Na}_{0.14}\text{AlSi}_{2.5}\text{O}_8 \), was cut from a very large (40 cm) single crystal extracted from a leucite phonolite tuff [Bank, 1967]. The anorthosite sample consisted of an 8 mm diameter disk, 2 mm thick, cut of the coarsely polycrystalline Larvik anorthosite rock. The sanidine and anorthosite were transparent or translucent and smoky gray due to the presence of unbound positive holes, which localize at low temperatures at \( \text{O}_3\text{Si}^{\text{O}}\text{AlO}_3 \) or \( \text{O}_3\text{Al}^{\text{O}}\text{AlO}_3 \) [Speit and Ehmann, 1982]. Both bleached
upon heating beyond 500°C to a light gray color.

In both cases $F_\Sigma(T)$ increases in 2 steps, at 200-250°C and 400-500°C for the sanidine and at 100-150°C and 400-500°C for the anorthosite. The $F_\Delta(T)$ response, which is not shown, is somewhat complicated by the fact that the unbound positive holes anneal out during first heating. Therefore a stable $F_\Delta(T)$ response can be obtained only after careful annealing during second and subsequent heating cycles [unpubl. results].

**Figure 8a:** $F_\Sigma(T)$ of a sanidine single crystal from Volkesfeld, Eifel volcanic field, brought up by an explosive eruption producing a leucite phonolite tuff [Bank, 1967]. The $F_\Sigma(T)$ response as measured at different voltages is shown. **Figure 8b:** $F_\Sigma(T)$ of a coarsely crystalline anorthosite from Larvik, Norway [Wanvik, 2000]. Both feldspar specimens exhibit the characteristic $F_\Sigma(T)$ behavior that points to the presence of peroxo defects and their 2-step activation, leading to the release of positive hole charge carriers.

The similarity of the $F_\Sigma(T)$ response of sanidine and anorthosite to the $F_\Sigma(T)$ response of MgO is striking. Since we know for certain that, in the case of MgO, the 2-step increase in $F_\Sigma(T)$ is due to the 2-step break-up of peroxo defects in the MgO matrix and activation of positive hole charge carriers, we take the results presented in **Figure 8a/b** as indication that these feldspars also contain peroxo defects.

If this is so, the question arises whether there are other materials, compositionally similar to feldspars, which are produced under conditions that are not conducive to the introduction of “water” in form of solute O$_2$Si-OH. Normal plate glass, produced from the melt at relatively low temperature and low relative humidity levels, is such a material. Typical compositional ranges of clear glasses in mol-% are SiO$_2$ 63-81, Al$_2$O$_3$ 0-2, MgO 0-6, CaO 7-14, Na$_2$O 9-15, K$_2$O 0-1.5 with most others below 0.5%.

**Figure 9a/b** show the $F_\Sigma(T)$ and $F_\Delta(T)$ responses of plate glass heated to 500°C. $F_\Sigma(T)$ exhibits a increasing trend consistent with the increase in the overall polarizability as a function of temperature. At the glass transition temperature $T_g$ $F_\Sigma(T)$ increases more sharply, due to an increase in $P_{\text{local}}$ as a result of the softening of the glass structure and increase in diffusivity of Na$^+$ and other alkali cations. $F_\Sigma(T)$ is mostly reversible under the conditions of the experiment with some hysteresis during cooling below $T_g$. The reason for the slight deviation from a linear $F_\Sigma(T)$ increase/decrease around 200°C is
unknown. However, the overall $F_{\Sigma}(T)$ response of the glass is distinctly different from the $F_{\Sigma}(T)$ behavior of either feldspar minerals shown in Figure 8a/b. There is no evidence for the characteristic $F_{\Sigma}(T)$ response linked to the 2-step activation of peroxy defects.

**Figure 9a/b:** Dielectric polarization response of common plate glass provides no evidence for peroxy defects and the thermal activation of positive hole charge carriers.

This conclusion is supported by the $F_{\Delta}(T)$ response shown in Figure 9b. During heating a slight negative surface charge develops, which changes abruptly to a positive surface charge above $T_g$. The evolution of $F_{\Delta}(T)$ towards positive values is due to the high diffusivity of Na$^+$ and other alkali cations in the externally applied divergent E field. The Na$^+$ segregation is irreversible during cooling down to room temperature as demonstrated by the persistence of the positive $F_{\Delta}(T)$ values in Figure 9b.

The absence of evidence for peroxy defects in the dielectric polarization response of normal plate glass is consistent with the overall theme of this study: Peroxy defects are formed metastably out of solute OH$^-$, O$_2$Si-OH, or O$_3$Al-OH, presumably hydroxyl pairs, which undergo a redox conversion during cooling. This reaction takes place in glasses as well as in crystalline materials. For instance, fused silica, which dissolves traces of H$_2$O at a much higher temperature than ordinary plate glass, has been shown to contain peroxy defects and activated positive hole charge carriers in much the same way as melt-grown MgO [Freund and Masuda, 1991].

**Peroxy Defects and Positive Hole Charge Carrier Activation in Olivine**

The dielectric polarization behavior described in the preceding section indicates the thermal activation of mobile positive hole charge carriers in MgO and feldspar crystals but not in regular plate glass. It provides unambiguous support for the presence of peroxy defects in MgO grown from the melt under the extremely reducing conditions of a carbon-arc fusion furnace [Abraham et al., 1971] and in feldspar specimens that crystallized in a magma under reducing lower crustal conditions. The dielectric polarization response is fully consistent with the electrical conductivity behavior of the melt-grown MgO and magma-grown feldspar crystals. It is fully consistent with our conclusion from the
first part of this paper that positive hole are the controlling charge carriers that define the electrical conductivity in the LT region, up to about 600°C, of MgO and of mafic and ultramafic rocks.

This study points to a mechanism by which crystals grown under reducing, even extremely reducing conditions, can acquire excess oxygen in the form of peroxy defects. The peroxy defects are introduced via the dissolution of H₂O. The dissolution of H₂O, however, is a process that is very common in nature. It takes place whenever minerals and rocks crystallize from an H₂O-laden magma.

The electrical conductivity of dunite, an olivine-rich peridotite, is illustrated in Figure 10, adapted from work by Constable and Duba [Constable and Duba, 1990]. During heating in a 1:1 CO:CO₂ atmosphere, the conductivity increases rapidly between ~350°C and 670°C. At 670°C, as T was held constant for an unspecified length of time, the conductivity decreased precipitously. During further heating the conductivity increased again, merging into a high temperature branch similar to the HT branch observed with MgO. During cooling the beginning of an Arrhenius straight section can be seen with an activation energy of ~1 eV characteristic of the LT conductivity response of MgO.

The interpretation given by Constable and Duba [Constable and Duba, 1990] is based on the assumption that, during heating, carbon was depositing out of the vapor phase onto the sample surface, providing a low resistivity pathway. The carbon deposition is assumed to have ended at 670°C when, according to thermodynamic calculations, the 1:1 CO:CO₂ mixture was leaving the stability field of graphite, creating oxidizing conditions, which caused the surface carbon film to “burn off”.

Figure 10: Electrical conductivity measured on a sample of Jackson County peridotite, 99% olivine, in a 1:1 CO:CO₂ atmosphere showing an anomalously high conductivity in the LT region, thought to be due to vapor-phase deposited surface carbon (after [Duba and Constable, 1993]).

The comparison between electrical conductivity and dielectric polarization shows that \( P_{\text{total}} \) and its separation into \( P_{\text{bulk}} \) and \( P_{\text{surface}} \) can provide unique information about the nature of the charge carriers responsible for the conductivity response. We therefore present next the dielectric polarization response of an olivine single crystal. To circumvent complications arising from carbon precipitation in the graphite stability field we chose to conduct the first set of experiments in high purity N₂. The choice of an inert gas atmosphere is justified on the basis of the observation that the CO:CO₂ = 1:1 mixture remained unequilibrated up to at least 500°C, possibly higher [Constable and Duba, 1990].

The sample was prepared by cutting a 1 mm thick slice, 8 mm diameter, from a randomly oriented cylinder of a gem-quality San Carlos olivine single crystal, 7 mm thick, polished on both sides. Before the slice was cut off, the IR spectrum was recorded.

As shown in Figure 11 the broad absorption in the spectral range of the \( \nu_{OH} \) stretching vibrations, 3150-3700 cm⁻¹, lacks distinct features except for a weak band at 3600 cm⁻¹. The absence of \( \nu_{OH} \)
bands is conventionally interpreted to mean that such an olivine crystal without OH\(^-\) has a very low solute “water” content and may have come from a “dry” of the upper mantle [Khan and Shankland, 2011a]. However, there is also the possibility that, similar to OH\(^-\) pairs in MgO, solute OH\(^-\) in olivine may have converted to H\(_2\) plus peroxo defects. In this case the near-absence of \(\nu_{OH}\) bands may mean that an olivine crystal with an IR spectrum as exemplified in Figure 11 may have lost most of its solute OH\(^-\) content due to this redox conversion. If the solute OH\(^-\) content was originally high, the olivine should have a high concentration of peroxo defects. Measuring the dielectric polarization would then be the technique of choice [Freund et al., 1989].

Figure 11: Infrared spectrum of a 7 mm thick section of a gem-quality olivine single crystal in the range of the O–H stretching frequencies indicates an extremely low solute OH\(^-\) content.

Figures 12a/b show \(F_\Sigma(T)\) and \(F_\Delta(T)\) of this olivine crystal, recorded according to the protocol outlined in Figure 5 with 15 sec polarization time at each \(\Delta T\) and \(\Delta V\) step. \(F_\Sigma(T)\) is fitted at room temperature to a dielectric constant \(\varepsilon\) scale. Because the orientation of the olivine single crystal disk is not known, we chose for the one-point fit the average of the three components of the dielectric constant along the crystallographic axes a, b, and c of forsterite [Cygan and Lasaga, 1986].

Figure 12a/b: Bulk polarization \(F_\Sigma\) and surface charge \(F_\Delta\) parameters of a San Carlos olivine single crystal, which show that, despite the chemical complexity of this mineral, its effective dielectric constant increases upon heating in the same way as that of high purity MgO, in two distinct steps, and a positive charge appears around 400°C.

\(F_\Sigma(T)\) of this olivine crystal is strikingly similar to \(F_\Sigma(T)\) of MgO and of the two feldspar specimens. During heating the bulk polarization increases in a stepwise fashion at 100-250°C and 450-500°C. During cooling \(F_\Sigma(T)\) follows closely the heating curve down to at least 100°C.
FΔ(T) recorded is also strikingly similar to FΔ(T) of MgO and the feldspars. The curves labeled +/- and +/- correspond to FΔ values obtained during heating taking the data from the sections going in ΔV steps from +500 V to −500 V and from −500 V to +500 V, respectively. The differences between the two FΔ(T) curves provides information about the time-dependent polarization during the 15 sec time steps. FΔ(T) remains close to zero from 100°C to almost 400°C, while FΣ(T) goes through its first stepwise increase. Thus the first FΣ(T) increase is due to a Plocal contribution to Pbuls without activation of mobile charge carriers. Mobile charge carriers only appear upon approaching 400°C. At first their number is small, insufficient to cause a noticeable increase in FΣ(T). By about 450-500°C their number has increases enough so that FΣ(T) also increases, due to a Pspace contribution to Pbulk.

The sign of the mobile charges in the olivine is unambiguously positive, as in MgO and the feldspar specimens, providing firm evidence that positive holes are the active charge carriers.

Metastability and Thermodynamic Equilibrium

The very weak IR absorption of a 7 mm thick olivine crystal in the range of νOH stretching vibrations as evidenced by Figure 11 indicate a near-complete absence of solute OH−. The same olivine crystal however provides evidence for positive hole charge carriers that become thermally activated at about the same temperature at which positive holes are activated in MgO, suggesting that they derive from peroxy defects in the olivine matrix, formed by the same type of redox conversion that turned OH− in MgO into O2− + H2 as given by eq. [13]. For olivine we have:

\[
\text{O}_3\text{Si}^\text{OH}_2^\text{SiO}_3 \rightleftharpoons \text{O}_3\text{Si}^\text{HO}_2^\text{SiO}_3 + \text{H}_2 \quad [23]
\]

where the # sign is used to indicate a divalent cation vacancy, Mg2+ or Fe2+. By analogy to the dilute solid solution MgO–H2O, we formulate a dilute olivine–H2O solid solution as:

\[
(\text{Mg},\text{Fe}^{2+})_2\text{SiO}_4 + \delta \text{H}_2O \rightleftharpoons (\text{Mg},\text{Fe}^{2+})_2\gamma\text{SiO}_4\gamma_2\gamma\text{OH}_2\delta \quad [24]
\]

If the OH− in this olivine–H2O solid solution undergo a redox conversion according to eq. [23] and if some or all of the molecular H2 is lost from the crystal matrix by outdiffusion, we have:

\[
(\text{Mg},\text{Fe}^{2+})_2\gamma\text{SiO}_4\gamma_2\gamma\text{OH}_2\delta \rightleftharpoons (\text{Mg},\text{Fe}^{2+})_2\gamma\text{SiO}_4 + \delta \text{H}_2 \quad [25]
\]

where we do not separately indicate on the right hand side the fraction of oxygen in the valence 1−. We specify, however, that the iron continues to be ferrous, Fe2+. In order for the cation-deficient olivine on the right hand side to be balanced, a 2δ fraction of the oxygens have to be in the valence 1−.

Low solute OH− concentrations are usually interpreted to mean that such crystals come from “dry” regions of the upper mantle [Bell and Rossman, 1992; Miller et al., 1987; Rossman, 1996]. Eq. [25] suggests instead that solute OH− may have “disappeared” from the IR spectra by converting to H2 plus peroxy. Molecular H2, if present, has an extremely weak νH–H absorption [Kriegler and Welch, 1968]. Other techniques such as SIMS or nuclear reaction profiling, which measure the total H concentration, often yield higher H values than those obtained by IR measurements of νOH [Bell et al., 2003].

“Burning off” Positive Holes in Olivine

If the enhanced electrical conductivity observed during initial heating were due to carbonaceous films precipitated within the stability field of graphite [Constable and Duba, 1990], such films should “burn
off under oxidizing conditions. If the enhanced electrical conductivity is due to h', i.e. highly oxidizing O' in a matrix of O^2-, the best way to annihilate them is to use reducing conditions.

We therefore conducted a dielectric polarization experiment with a San Carlos olivine single crystal, heating it first in pure N_2 atmosphere in 20 temperature steps from 50°C to 600°C, cooled it back in the same steps, and let it sit overnight in the pure N_2. F_2(T) as recorded during this first heating is shown by the top curve labeled with squares in Figure 13a.

Next we replaced the N_2 with a 9:1 N_2–CH_4 gas mixture and reheated the same olivine crystal five times. The 1st heating in N_2–CH_4, up to 575°C, produced the F_2(T) curve marked by open circles in Figure 13a. After stepwise cooling the olivine crystal was reheated in the same N_2–CH_4 gas mixture four more times. The 3rd heating up to 550°C produced the F_2(T) curve shown in Figure 13a by open triangles. The 5th heating up to 600°C produced the F_2(T) curve in Figure 13a marked by diamonds.

Figure 13b shows F_Δ(T) curves recorded during the 1st heating in the N_2–CH_4 gas mixture with ± bias voltages of 20V, 40V, 60V and 80V. The F_Δ(T) response displays the same overall pattern as observed for MgO and the feldspar specimens. The dashed lines present the F_Δ(T) response during stepwise cooling: fully reversible from 600°C to about 500°C, followed by elevated F_Δ(T) values below 400°C due to the fact that, after heating in the N_2–CH_4 mixture, the positive surface charge no longer dissipates after cooling.

Comparing the F_2(T) response during the 1st run in pure N_2 and the subsequent runs in the N_2–CH_4 gas mixture provides insight into the reactions at the olivine surface. Figure 13a shows that, during heating in the presence of CH_4, the F_2(T) response is similar up to about 450°C, though the values are slightly lower. This overall decrease of F_2(T) is due to the fact that the 1st heating in pure N_2 had already caused changes in the polarization response of the olivine, presumably due to oxidation of Fe^{2+} to Fe^{3+} in the olivine matrix, equivalent to the annihilation of mobile h’ charge carriers.

Above 450°C the F_2(T) curve drops during heating in the N_2–CH_4 gas mixture, indicating that h’ charge carriers are being consumed. Above 530°C F_2(T) increases again, indicating that the surface reaction, which consumes h’ charge carriers, has stopped and new h’ are able to flood the surface. This behavior, in particular the dip of F_2(T) above 450°C, repeats itself during the 3rd heating cycle. By the time of the 5th heating, however, the dip has essentially disappeared, indicating that the reaction between the olivine and CH_4 has reached some form of endpoint.

Of further interest is the fact that, in the ΔT range marked in pale yellow in Figures 13a/b, F_2(T) continues to increase even though the F_Δ(T) curves show that h’ charge carriers have already begun to flood the olivine surface. F_2(T) begins to dip in the ΔT range marked in yellow, i.e. only after the F_Δ(T) values have reached their maxima. The area marked in red outlines the ΔT range, where F_2(T) recovers, rising in spite of the presence of CH_4.
Figure 13a: Bulk dielectric polarization of an olivine crystal subjected to 6 heating/cooling cycles, the 1st in pure N₂, the others in N₂–CH₄ gas mixtures. The colors indicate temperature regions at which h⁺ become activated but do not yet react with the CH₄ (light yellow), start to react with the CH₄ (yellow), and overwhelm the reaction with CH₄ (red).

Figure 13b: Surface charge developing on an olivine crystal during the 1st heating/cooling in the N₂–CH₄ gas mixture. In contrast to the first heating in pure N₂, when the positive surface dissipates after cooling, heating in the N₂–CH₄ gas mixture leaves a positive surface charge. The colors correlate with ΔT ranges at which the bulk polarization of the olivine crystal is affected by the reaction with CH₄.

Summarizing this last set of experiments we can say with additional confidence that, though the olivine crystals under study have originated in the upper mantle and crystallized in a highly reducing environment, they release highly oxidizing h⁺ charge carriers upon heating. From this we infer that they contain per oxy defects, presumably formed during cooling by way of a redox conversion of OH⁻ pairs that had been incorporated into the olivine structure at upper mantle temperature through dissolution of traces of “water”. Consistent with our earlier conclusion that h⁺ are highly oxidizing O⁻, they are consumed by a reaction with CH₄, presumably through oxidative coupling, which produces OH⁻ and methyl as an intermediate, •CH₃ [Asame et al., 1988].

Discussion

In this paper we have focused on fundamental processes that are important for understanding the electrical properties of materials, both laboratory-grown and from natural environments, both single crystal minerals and igneous rocks. We make the extraordinary claim that MgO crystals, grown from the melt under the viciously reducing conditions of a carbon arc fusion furnace, contain per oxy defects in their crystal structure, hence oxygen in the oxidized valence state 1⁻. When the per oxy defects break up, they release positive hole charge carriers, formally defect electron in the oxygen anion sublattice, equivalent to O⁻ in a matrix of O₂⁻. These positive holes have two outstanding properties: they are highly mobile and highly oxidizing.

We make the even more extraordinary additional claim that olivine crystals, which have been brought up from the upper mantle, feldspar crystals, which have been brought up from the lower crustal depth,
and – more generally – mafic/ultramafic rocks such as basalts, gabbro and peridotite produce the same
type of mobile positive hole charge carriers and, hence, must also contain peroxy defects. This claim
seems to run counter to the well-established fact that upper mantle and lower crustal environments are
highly reduced and highly reducing. Thermodynamically, oxygen in the oxidized valence state 1– can
never be introduced under these in situ conditions.

In fact there is no contradiction with thermodynamics. The reason is that the process, which occurs
under in situ conditions, is the dissolution of H₂O into the matrix of MgO grown from the carbon arc
fusion melt and into the matrix of silicates crystallizing from a magma. The dissolution of H₂O and
formation of solute OH⁻ or O₃Si-OH are redox insensitive. They can occur irrespective of the redox
state of the system. According to our results O⁻ is introduced through a follow-on process, the redox
conversion of hydroxyl pairs to peroxy defects plus H₂. This process only occurs under metastable
conditions, namely during cooling when the systems have drifted out of thermodynamic equilibrium.

Depending upon the rate at which a rock or a crystal is cooled, thermodynamic equilibrium can only
be maintained as long as diffusional processes remain thermally activated. Diffusional processes are
necessary for the adjustment of the oxidations states of transition metal cations and the adjustment of
the cation vacancy concentration, both dictated by the oxygen fugacity of the system. Without these
continuous adjustments any system will be out of thermodynamic equilibrium. Even at very slow
cooling rates these diffusional processes become so slow around 600°C that they can be considered
frozen. At faster cooling rates the freezing temperatures tend to be higher, more in the 700°C range.

The in situ redox conversion, which turns solute hydroxyl pairs into peroxy defects plus molecular H₂,
takes place below 600°C, in the 600-400°C window, when the systems under consideration – MgO,
feldspar, olivine crystals and igneous rocks – have already drifted out of thermodynamic equilibrium.
Since the redox conversion as outlined by eqs. [13] and [23/25] operate outside equilibrium, oxygen in
the valence 1– can exist metastably in an otherwise reduced environment and can co-exist with
reduced cations such as Fe²⁺. Since O⁻ form highly mobile electronic charge carriers, the electrical
conductivity behavior is affected.

Therefore, the claim of oxygen in the valence state 1– is not as extraordinary as it may first appear.
The presence of O⁻ does not contradict thermodynamics because, by the time O⁻ is introduced,
equilibrium thermodynamics is no longer in control. The work presented here casts doubts on the
validity of the widely offered explanation of thin carbonaceous films deposited from CO/CO₂-laden
fluids in the crust [Glover and Vine, 1992; Shankland et al., 1997] and upper mantle [Constable and
Duba, 1990; Duba and Constable, 1993; Mathez, 1987; Roberts et al., 1999]. Maybe electrolytically
conductive, intergranular fluids and/or intergranular carbonaceous films are not needed to explain the
origin of zones of high electrical conductivity in the lower continental crust, which have been called
“a long-standing mystery” [Frost et al., 1989]. Those high conductivity zones, which have been
identified by magneto-telluric sounding techniques, appear to be an almost universal feature of the
Earth’s crust at a depth range of about 20 km [Glover, 1996; Lee et al., 1983; Qin et al., 1992].

If peroxy defects and thermally activated positive hole charge carriers can be metastably present, we
can tie the high conductivity zones to the geotherm [Freund, 2003]. If temperatures along the
gerotherm reach values sufficiently high to thermally dissociate peroxy defects and release positive
hole charge carriers, we can envision a depth range, where the peroxy defects would be in a
permanently dissociated state. With reference to eq. [7] this means an increase in the number density
n of mobile charge carriers and, hence, an increase in the conductivity ø. Deeper into the crust, at

² This statement holds for “dry” systems. In environments with free supercritical fluids and other fluid-
dominated systems equilibrium can be established down to lower temperatures.
higher temperatures, the positive holes will be consumed by equilibrium oxidation reactions, for instance Fe$^{2+}$ to Fe$^{3+}$, concomitant with structural rearrangements that require cation and cation vacancy diffusion to be thermally activated.

An analogous situation is seen in the experimental conductivity curves obtained during heating of MgO single crystals as depicted in Figures 3a, 3c, and 3d: at temperatures above 500-700°C the electrical conductivity decreased precipitously because the $h^+$ charge carriers begin to be consumed by reactions linked to the return of the MgO crystals toward equilibrium. The same behavior is reflected in the conductivity curve recorded during heating of an olivine single crystal as depicted in Figure 9, even though the authors of this graph base their interpretation of the conductivity decrease at 630°C on the assumption that vapor-phase deposited carbon films on the sample surface where “burning away” as the system moved out of the stability field of graphite in the CO:CO$_2$ gas mixture [Constable and Duda, 1990]. Finally, the dielectric polarization behavior of the olivine single crystal heated in a CO:CH$_4$ gas mixture as depicted in Figure 13a/b indicates as well that $h^+$ charge carriers are being consumed under highly reducing conditions – in this case by reacting with CH$_4$ by way of an oxidative coupling that produces OH$^-$ and methyl as an intermediate, •CH$_3$ [Asame et al., 1988].

References


Cagniard, L. (1953), Basic Theory of the Magneto-Telluric Method of Geophysical Prospecting, Geophysics, 18(3), 603-635.

Bozovic (2008), Combinatorial measurements of Hall effect and resistivity in oxide films, Rev. Sci.
Instrum., 79, 033908
Conrad, H., and D. Yang (2010), Influence of an applied dc electric field on the plastic deformation
kinetics of oxide ceramics, Philosophical Magazine, 90(9), 1141-1157.
Constable, S., and A. Duba (1990), Electrical conductivity of olivine, a dunite and the mantle, J.
Cygan, R. T., and A. C. Lasaga (1986), Dielectric and polarization behavior of forsterite at elevated
temperatures, Amer. Mineral., 71, 758-766.
Dobrovolsky, I. P., et al. (1989), Theory of electrokinetic effects occurring at the final stage in the
preparation of a tectonic earthquake, Pys. Earth Planet. Int., 57, 144-156.
11885-11899.
Freund, F., and H. Wengeler (1982), The infrared spectrum of OH--compensated defect sites in C-
Freund, F., and M. M. Masuda (1991), Highly mobile oxygen hole-type charge carriers in fused silica,
Freund, F., et al. (1993), Critical review of electrical conductivity measurements and charge
Freund, F., et al. (1994), Positive hole–type charge carriers in oxide materials, in Grain Boundaries
and Interfacial Phenomena in Electronic Ceramics, edited by L. M. Levinson, pp. 263-278, Amer.
Ceram. Soc., Cincinnati, OH.
Freund, F. T. (2003), On the electrical conductivity structure of the stable continental crust, J.
Geodynamics, 35, 353-388.
63(Nov. 6, 1989), 2096-2099.
Frost, B. R., et al. (1989), Grain boundary graphite in rocks and impolcation for high electric
continental crust?, Tectonophysics, 231, 293-309.
Fuji-ta, K., et al. (2004), Electrical conductivity measurement of granulite under mid- to lower crustal
pressure-temperature conditions, Geophys. J. Inter., 157, 79-86.
Glover, P. W. J., and F. J. Vine (1992), Electrical conductivity of carbon-bearing granulite at raised
temperatures and pressures, Nature, 360(24), 723-726.
Glover, P. W. J. (1996), Graphite and electrical conductivity in the lower continental crust: A review,
Physics and Chemistry of The Earth, 21(4), 279-287.
Haak, V., and R. Hutton (1986), Electrical resistivity in continental lower crust, in Nature of Lower


