## ARE LABORATORY ELECTRICAL CONDUCTIVITY DATA RELEVANT TO THE EARTH?

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Before using laboratory data on the  $\sigma$  of rocks and minerals to interpret field electromagnetic data, one must be aware that the laboratory data may not be truly representative of conditions which generally prevail in the earth. Important conditions are oxidation state and time for solid-solid reactions to approach equilibrium. Data on the electrical conductivity ( $\sigma$ ) of rocks and minerals relevant to the crust and upper mantle of the earth are considered. Recent investigations which treat the time dependence of  $\sigma$  at high temperatures and the effect of oxidizing environments on  $\sigma$  are applied to the earth's upper mantle. The  $\sigma$  change at the olivine to spinel transition is unknown because of the effect of oxidation and contamination under the conditions of measurement. The  $\sigma$  of albite and basalt is observed to be time dependent below melting; thus, the assumption that  $\sigma$  increases with partial melting is questionable.

## 1. Introduction

The electrical conductivity ( $\sigma$ ) of silicates has been studied extensively as a means for determining temperature vs. depth in the earth. In a recent review, SHANKLAND [41] has pointed out that  $\sigma$  is most affected by temperature, oxygen fugacity ( $f_{O_2}$ ), and transition-metal ion content. He indicates that the effects of orientation, twinning, and order-disorder have also been observed. The present review will discuss  $f_{O_2}$  effects, the importance of orderdisorder phenomena, and the measurement of  $\sigma$  in polycrystalline materials.

When considering laboratory experiments on geological systems, an obvious question to ask is, "Do the experimental conditions differ significantly from those that prevail in the geological system of interest?" The point "differ significantly" is often missed. If one were asked to enumerate the important variables for the outer 400 km of the earth's mantle, he would probably respond that there are two whose limits are as follows: temperature up to about 2000 K, and pressure up to about 15 GPa. Perhaps he would enumerate  $f_{O_2}$ , but he most assuredly would not consider time as an important variable. In the real sense, time and  $f_{O_2}$  are probably not important variables in the mantle since time is usually sufficient for most chemical reactions to attain equilibrium, and  $f_{O_2}$  is controlled within fairly narrow limits by the phases present. However, in the laboratory experiment, these two variables can be much more important than either temperature or pressure. This situation arises because the  $f_{O_2}$  imposed in the laboratory is usually not controlled by the same phases

present in the mantle, and most experiments are performed in a time-frame of hours with little attention paid to kinetic effects. This paper will attempt to show where these two variables have led us astray regarding electrical conductivity measurements in the laboratory and their interpretation in terms of observations within the earth.

Electrical conductivity of silicate minerals is a thermally activated process which fits an equation of the form  $\sigma = \sigma_i \exp(-A_i/kT)$ . Here,  $\sigma_i$  is a constant depending on conduction mechanism,  $A_i$  is an "activation energy" which is the sum of the energy required to produce and to move a charge carrier in the structure. The term in the energy related to production vanishes at lower temperature where charge carrier concentration is extrinsically controlled. Despite much time and effort, no conduction mechanism has been satisfactorily defined for silicates likely to exist in the mantle. This arises from the difficulty of the measurement as in Hall effect studies [40], or from failure to control oxidation effects in thermoelectric measurements [6]. The  $\sigma$ of silicates shows a large dependence on temperature, and activation energies of 2 to 4 eV are common. However, the dependence of  $\sigma$  on pressure is small at least for olivine single crystals [14].

Studies of the variation of  $\sigma$  as a function of  $f_{O_2}$  have had a good deal of success in determining conduction mechanisms in simple oxides [29] and have been applied to very magnesian olivines with some success [34]. The  $\sigma$  of natural single crystals of olivine [15] containing about 10 weight% iron and pyroxene of about the same composition [13] cannot easily be interpreted in terms of the oxygen defect model. The large effect of oxidizing  $f_{O_2}$  on  $\sigma$ outside the olivine stability field [11], for example, shows that heed must be given to chemical stability when one attempts to use these simple oxygen defect models to explain conduction mechanisms in olivine of mantle composition. However, studies in the oxidizing regime of  $\sigma$  as a function of time and  $f_{O_2}$  may help in understanding the conduction mechanism within the stability field.

The other major effect to be discussed here is that of time. Studies in olivine below 1500 °C have indicated no time dependence of  $\sigma$  except where  $f_{O_4}$  was changed. However, there is some indication that time may be a factor above 1500° C [14]. The  $\sigma$  of orthopyroxene also shows no rate effects so long as no phase transformations are induced by the pressure – temperature regime [17]. Once pyroxene is outside its P-T stability field, it undergoes large, irreversible, time-dependent  $\sigma$  changes [13, 17].

Another phenomenon involving time is that of order-disorder in silicates. Plagioclase is a ubiquitous phase in crustal rocks such as granites and basalts and many comprise almost half the mineral fraction of rocks in the intermediate compositional ranges. The  $\sigma$  of albite, the sodic end-member of the plagioclase series increases with time and becomes equal to the  $\sigma$  of molten albite [33].