The Electrical Conductivity of an Isotropic Olivine Mantle

STEVEN CONSTABLE
Scripps Institution of Oceanography, La Jolla, California

THOMAS J. SHANKLAND
Los Alamos National Laboratory, Los Alamos, New Mexico

AL DUBA
Lawrence Livermore National Laboratory, Livermore, California

INTRODUCTION

Electrical conductivity is one of the few mantle properties that can be sensed from Earth’s surface, and laboratory studies of olivine and olivine-rich rocks are extremely important in the interpretation of field and observatory studies of mantle conductivity. Recently, Shankland and Duba [1990] presented data for the three principal axes of a single crystal of San Carlos olivine (SCO), between 1200°C and 1500°C. These data were collected as part of a more general study by Schock et al. [1989]. The SCO data show an anisotropy of about a factor of 2 for the most resistive and most conductive axes, [010] and [001], respectively. Shankland and Duba [1990] used various mixing laws to infer the conductivity of an isotropic, polycrystalline olivine rock from the three axis data; upper and lower bounds, which differ by 15%, were obtained by parallel and series mixing laws to infer the conductivity of an isotropic, polycrystalline olivine rock (a dunite from Jackson County, North Carolina, or JCD) between 640°C and 1100°C, and Tyburczy and Roberts [1990] examined a sintered, polycrystalline San Carlos olivine between 800 and 1300°C (Figure 1).

Although low-temperature extrapolation of SO1 also diverges from earlier data for the [010] direction of Red Sea peridot (or RSP, Figure 1 [Duba et al., 1974]), the SCO data of Shankland and Duba [1990] are more applicable to mantle conditions in their temperature range than any other current data set. SCO is a mantle olivine, unlike JCD and RSP which are metamorphic in origin and systematically of lower conductivity, and the experiments were done with as little modification or alteration of the sample as possible. Data above 1200°C cannot be collected at atmospheric pressures from tholeiites without melting of samples. The SCO data are also complete in that they are available for all three principal axes. However, with the exception of sparse data in the [100] direction (Figure 1), there are no three-axis low-temperature data for SCO currently available.

The purpose of this paper is to combine the high-temperature, anisotropic SCO data with activation energies inferred from the lower-temperature data in order to provide a single σ - T curve appropriate for an extended temperature range in the mantle. We also make improvements in the methodology used to fit the standard olivine model to the SCO data and introduce some preliminary data from a mantle tholeiite in support of our model.

EXPERIMENTAL METHOD AND CONDUCTIVITY DATA

An understanding of the experimental method and fO2 dependences in olivine are important in understanding the limitations of the parameter fitting and our treatment of the various data sets. All the measurements discussed in this paper were collected using a furnace in which fO2 is controlled by pass-
Fig. 1. Conductivity versus temperature for various olivine samples and fits. The higher-temperature SCO data (three short dashed lines) are represented by the fits shown in Figure 2. The lower-temperature single crystal data for Red Sea peridot [010] (squares, [Duba et al., 1974]) and SCO [010] (diamonds) are shown. Jackson County dunite (triangles) is represented by every second datum from Constable and Duba [1990], and a lherzolite (circles) is represented by every fourth datum from the original experiment (A. Duba and S. Constable, work in progress, 1991). Stars are grain interior conduction estimates for crushed and sintered SCO [Tyburczy and Roberts, 1990]. The similarity in activation energies for all data below 1200°C strongly suggests that a single activation energy is sufficient to describe all three crystallographic axes. It is notable that the metamorphic olivines (JCD and RSP) are significantly less conductive than the mantle olivines SCO and the lherzolite and that all measurements made on mantle materials group into a relatively tight band with less than 1/3 decade dispersion below 1200°C. Shankland and Duba's [1990] SO1 model is shown (long dashed line), as well as SO2 for the low temperature activation energy fixed at 1.4, 1.5, and 1.6 eV (solid lines). We see that for 1.4 eV, SO2 is comparable to SO1 but that SO2 for 1.6 eV provides a much better match to the activation energies of the lower temperature data.
Fig. 2. Conductivity versus temperature for the three crystallographic directions of San Carlos olivine (triangles, data from Shankland and Duba, [1990]). The dashed lines are the fits according to the parameters of Table 2 with a low-temperature activation energy of 1.6 eV. The 10 highest temperature data in the [010] direction have been excluded from the fitting. The solid lines show the fits decomposed into high- (subscript 2) and low- (subscript 1) temperature components for the three directions. It is clear that conduction is dominated by the low-temperature component and that anisotropy is greater for the high-temperature component.

Another systematic effect that is expected to bias the parameter fitting is the unusually rapid change in slope in data for the [010] direction above 1450°C (Figure 2). The model given in equation (1) produces a poor fit to these data, and yields an activation energy greater than the band gap [Shankland and Duba, 1990]. Given the ease with which the sample can be metamorphosed at high temperatures we speculate that the sudden change in slope is anomalous and results from alteration, perhaps from a furnace contaminant during this run. Although upon examination the sample does not appear to be melted or oxidized, our speculation is supported by the unpublished cooling data for this run, which follow a path that is much more conductive and has a lower activation energy than the heating data. If this alteration were an actual property of San Carlos olivine, we would expect all three directions to show the effect. We have consequently removed the 10 highest-temperature data in the [010] direction from the analysis. Shankland and Duba retained these data because their aim was to fit the data as they were for the purpose of the spatial averaging, on which they had little effect.
Mount Porndon lherzolite is their narrow band of variation under all circumstances of study. This agreement strengthens the hypothesis that a useful relationship between temperature and conductivity can be derived for mantle materials based on laboratory studies.

PARAMETRIC FITS TO OLIVINE CONDUCTIVITY DATA

Both data and theory for conduction in minerals support the use of an Arrhenius relationship between conductivity and temperature, which for two conduction mechanisms with activation energies $A_1$ and $A_2$ is

$$\sigma = \sigma_1 e^{-A_1/kT} + \sigma_2 e^{-A_2/kT}$$

(1)

where $k$ is Boltzmann's constant and $T$ is absolute temperature. Constable and Duba [1990] demonstrated the use of the non-linear, least squares parameter estimation method of Marquardt [1963] to recover the coefficients $\sigma_1$, $\sigma_2$ and activation energies $A_{1,2}$ from a set of conductivity–temperature data. Shankland and Duba [1990] applied this method to conductivity data measured along each axis of SCO and also to one of the binary averaging schemes to obtain coefficients and activation energies for an isotropic olivine rock. They adopted the general model in which the activation energies $A_{1,2}$ for the different axes were different and independent; after spatial averaging the six activation energies were reduced to two. When the polycrystal data are considered, it becomes clear that this fitting can be revised and simplified, for the following reasons.

First, the low-temperature activation energies modeled for SCO (0.97–1.52 eV) are significantly lower than the activation energies of the polycrystals (Table 1), which are 1.49, 1.60, and 1.92 eV. When the SCO fits are extrapolated to 700°C, there is up to an order of magnitude mismatch between the SCO conductivities and those of the polycrystals.

Second, data from the polycrystals exhibit extremely little curvature on an Arrhenius plot between 700º and 1200ºC, implying that any variation in activation energy between axes is too small to be measured. For the data of Constable and Duba [1990] one activation energy of 1.60 eV is maintained over 480ºC (Figure 1). Furthermore, the only low-temperature data available for the SCO experiments, collected on heating a SCO [100] sample from room temperature [Shankland and Duba, 1990], also have an activation energy close to 1.6 eV (Figure 1), rather than the 1.11 eV obtained using the high temperature data alone. (Unfortunately, heating data for the other two axes are not available.) Tyburczy and Roberts [1990] obtained 1.49 eV for grain interior conductivity in a sintered, polycrystalline SCO; this result agrees well with JCD, especially after considering the different sample preparation (sintering) and the different origin of the olivine.

Third, it is well known that in fitting exponentials there can be a great deal of correlation between the preexponential terms and the activation energies. This is particularly true if the fitting is done over a relatively limited temperature range, as by Shankland and Duba. This explains why $A_1$ can be essentially the same for the three axes and still be consistent with Shankland and Duba’s data over a limited temperature range. The errors in Table 1 were derived from the diagonal elements of the parameter covariance matrix, but in many cases the off-diagonal terms will also be large. The parameter correlation matrix illustrates this problem. If $c_{ij}$ are the elements of the covariance matrix, the symmetric matrix of linear correlation coefficients is given by

$$\text{corr}_{ij} = \frac{c_{ij}}{c_{ii}^{1/2}c_{jj}^{1/2}}.$$

For example, the fit of (1) to the [010] data of San Carlos olivine has the correlation matrix

$$\begin{bmatrix}
\log_{10}(\sigma_1) & A_1 & \log_{10}(\sigma_2) & A_2 \\
1 & 1.00 & 1.00 & 1.00 \\
1 & 0.782 & 0.783 & 1.00 \\
1 & 0.792 & 1.00 & 1.00 \\
\end{bmatrix}.$$

We see that $\sigma_1$ is highly correlated with $A_1$ and $\sigma_2$ is highly correlated with $A_2$. This means that an increase in activation energy can be offset by an increase in the corresponding coefficient, trade-off that is not reflected when selecting errors from the diagonal elements of the covariance matrix, which makes the implicit assumption that the parameters are independent. Covariance is not a problem for a purely parametric description of the data, as used by Shankland and Duba, but is a problem if an interpretation is placed on the $A_i$ and $\sigma_i$, or if an extrapolation is required. Quantitative interpretation of the correlation coefficients is difficult. Normally, one would test the coefficients against the maximum value one would get from an uncorrelated population, say, 95% of the time. This depends on the number of degrees of freedom, which for this example appears to be 63 data - 4 parameters = 59, implying

<table>
<thead>
<tr>
<th>Material and Reference</th>
<th>$A_1$, eV</th>
<th>$f_{O_2}$, Pa</th>
<th>Fe/(Fe+Mg)</th>
<th>Temperature, C</th>
</tr>
</thead>
<tbody>
<tr>
<td>San Carlos olivine (Shankland and Duba, 1990) [100]</td>
<td>1.11 ± 0.10</td>
<td>$10^{-4}$</td>
<td>0.087</td>
<td>1200–1500</td>
</tr>
<tr>
<td>[010]</td>
<td>1.52 ± 0.02</td>
<td>$10^{-4}$</td>
<td>0.087</td>
<td>1200–1500</td>
</tr>
<tr>
<td>[001]</td>
<td>0.97 ± 0.11</td>
<td>$10^{-4}$</td>
<td>0.087</td>
<td>1200–1500</td>
</tr>
<tr>
<td>SO1</td>
<td>1.38 ± 0.04</td>
<td>$10^{-4}$</td>
<td>0.087</td>
<td>1200–1500</td>
</tr>
<tr>
<td>San Carlos olivine [100] heating (this paper)</td>
<td>1.66 ± 0.01</td>
<td>$10^{-4}$</td>
<td>0.087</td>
<td>900–1500</td>
</tr>
<tr>
<td>Jackson County dunite [Constable and Duba, 1990]</td>
<td>1.60 ± 0.01</td>
<td>$10^{-4}$</td>
<td>0.073</td>
<td>650–1200</td>
</tr>
<tr>
<td>Red Sea peridot (fit from Constable and Duba [1990])</td>
<td>1.53 ± 0.02</td>
<td>$10^{-3}$</td>
<td>0.096</td>
<td>900–1450</td>
</tr>
<tr>
<td>Sintered SCO [Tyburczy and Roberts, 1990]</td>
<td>1.49 ± 0.04</td>
<td>$10^{-3}$</td>
<td>0.09</td>
<td>800–1400</td>
</tr>
<tr>
<td>Lherzolite (A. Duba and S. Constable, manuscript in preparation, 1991)</td>
<td>1.92 ± 0.01</td>
<td>$10^{-4}$</td>
<td>0.09</td>
<td>605–1010</td>
</tr>
</tbody>
</table>

Low-temperature activation energies for various olivines. $f_{O_2}$ refers to oxygen fugacity at 1200°C.
that 95% of the time the correlation coefficient would be 0.254 or less in uncorrelated series [Bevington, 1969]. However, if one examines the residuals (data minus the model predictions) versus \( T^{-1} \), one finds that the sign of the residuals form only five runs (a run is an unbroken sequence of residuals with one sign), indicating the data are not independent of each other (see a description of the runs test given by Crow et al. [1960, pp. 83-85]) and that the number of degrees of freedom is much smaller than 59. The reduction in degrees of freedom arises from the close sampling of the data in time and temperature, and the systematic departures from equilibrium discussed above. For 6 degrees of freedom the 95% level would be 0.811.

Another approach to examining parameter independence is to perform a singular value decomposition of the linearized system [Lanczos, 1960] (for a geophysical application, see Jupp and Vozoff [1975]). From this we learn that the resolved parameter eigenvectors, or orthogonal linear combinations of physical parameters, are approximately 0.95\( A_1 \) -0.30\( \log_{10}(\sigma_1) \), 0.94\( +0.32\log_{10}(\sigma_2) \), and 0.29\( +0.95\log_{10}(\sigma_1) \). While it is clear that significant correlation between \( A_1 \) and \( \sigma_1 \) exists, it is probably not any worse than the correlation coefficient of 0.9996 implies because the first and third eigenelements are dominated by \( A_1 \) and \( \sigma_1 \). Finally, one must caution that the above considerations only hold in the linear approximation, while the true problem is nonlinear.

Considering the evidence from the polycrystal data that the activation energies \( A_1 \) are essentially the same in all three directions and having justified trading off variations in \( A_1 \) with variations in \( \sigma_1 \) during the parametric fitting, we will consider the less general case of a single pair of high- and low-temperature activation energies, \( A_1 \) and \( A_2 \), for all three axes. We use a fixed \( A_1 \) obtained from polycrystal data collected at lower temperature. We can impose a low-temperature activation energy on the SCO data because the limited temperature range of the SCO data provides ability to trade off \( A_1 \) and \( \sigma_1 \). We include only the slope from the lower-temperature data directly in the parameter estimation because variations in sample preparation, sample origin, iron content, and \( f_{02} \) will all alter \( \sigma_1 \) [Schock et al., 1989; Constable and Duba, 1990]. Thus the low-temperature intercepts \( \sigma_1 \) are determined by the lower-temperature portions of SCO, and the new fit will lie above JCD and parallel to it. A dependence of \( A_1 \) on \( f_{02} \) and iron content might be expected, but inspection of Table 1 indicates that variations between samples and experiments obscure any such effects. We have performed the reduced parameter set fitting for \( A_1 \) equal to 1.4, 1.5, and 1.6 eV to reflect the small variations in activation energy for the low-temperature data sets and to indicate the dependence of the other parameters on the chosen \( A_1 \). Pending further work, we give less weight to the larger activation energy of the lherzolite because of the small temperature range of the measurements and the unknown complicating effects of secondary minerals in this rock. Our preferred value for \( A_1 \) is 1.6 eV, a prejudice based on the extended temperature range and data quality of the JCD experiment. Although there is less reason to believe that \( A_2 \) is identical for the three directions, we shall see that our ability to resolve this parameter is very poor, and so we keep the parameterization as simple as possible.

We fit the following model to data from all three axes of SCO: \( A_1 \), a low-temperature activation energy for all three axes; \( A_2 \), a high-temperature activation energy for all three axes; \( \sigma_{1a} \), \( \sigma_{2a} \), low- and high-temperature coefficients for [100]; \( \sigma_{1b} \), \( \sigma_{2b} \), low- and high-temperature coefficients for [010]; and \( \sigma_{1c} \), \( \sigma_{2c} \), low- and high-temperature coefficients for [001]. Results are tabulated in Table 2 and the response for \( A_1 = 1.6 \) eV is shown in Figure 2. Fixing the activation energies also has the advantage that the average conductivity model is estimated from all three data sets simultaneously, rather than estimating SO1 (which has a single \( A_1 \) also) from three independent fits.

The reduced number of parameters (7 free parameters compared with Shankland and Duba's 12) produces a slightly worse fit, but the misfit is still reasonable for these data. In fact, the removal of the 10 [010] points allows us to fit the conductivities better than Shankland and Duba for an \( A_1 \) of 1.1 eV. However, because the misfit applies to the high-temperature data only, it does not reflect our requirement that the low-temperature extrapolation fit the slope of the polycrystal data. That is, we are including outside constraints when fitting this data set, rather than taking a simple least squares fit for all parameters.

Our higher-temperature activation energies of 3.56-4.23 eV are comparable to 3.90 eV for SO1 and 3.33 eV of Tyburczy and Roberts [1990]. However, imposition of a uniform low-temperature activation energy results in values for the individual coefficients that differ from those obtained by Shankland and Duba [1990], even though the fit to the data is not very different, because of the high correlation among the fitting parameters, mentioned above. The three \( \sigma_{1a} \) in the new model, which have been forced to follow the observed anisotropy in the data at these temperatures, vary by a factor of about 2, while Shankland and Duba's original values varied by a factor of 50.

The correlation matrix for the \( A_1 = 1.6 \) eV model is

\[
\begin{pmatrix}
\sigma_{1a} & \sigma_{1b} & \sigma_{1c} & \sigma_{2a} & \sigma_{2b} & \sigma_{2c} & A_2
\end{pmatrix}
\]

\[
\begin{pmatrix}
1.00 \\
0.02 1.00 \\
0.11 0.16 1.00 \\
0.09 0.18 0.82 1.00 \\
0.13 0.03 0.84 0.94 1.00 \\
0.13 0.19 0.85 0.96 0.98 1.00 \\
0.13 0.19 0.86 0.96 0.98 1.00 1.00
\end{pmatrix}
\]

(the logarithms of conductivity are implied here).

Fixing \( A_1 \) has, of course, removed what would otherwise be a strong correlation between that parameter and almost all others. Inspection of the residuals suggests that there are perhaps of the order of 10-20 degrees of freedom for this model, implying that a correlation coefficient above about 0.5 is sig-

### Table 2. Parametric Fits to Conductivity–Temperature Data

<table>
<thead>
<tr>
<th>Parameter</th>
<th>( A_1=1.4 )</th>
<th>( A_1=1.5 )</th>
<th>( A_1=1.6 ) eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \log_{10}(\sigma_{1a}) ) S/m</td>
<td>1.672</td>
<td>2.011</td>
<td>2.345 ± 0.003</td>
</tr>
<tr>
<td>( \log_{10}(\sigma_{1b}) ) S/m</td>
<td>1.613</td>
<td>1.956</td>
<td>2.291 ± 0.003</td>
</tr>
<tr>
<td>( \log_{10}(\sigma_{1c}) ) S/m</td>
<td>1.871</td>
<td>2.225</td>
<td>2.571 ± 0.004</td>
</tr>
<tr>
<td>( \log_{10}(\sigma_{2a}) ) S/m</td>
<td>7.46</td>
<td>8.22</td>
<td>8.68 ± 0.51</td>
</tr>
<tr>
<td>( \log_{10}(\sigma_{2b}) ) S/m</td>
<td>7.48</td>
<td>8.26</td>
<td>8.86 ± 0.50</td>
</tr>
<tr>
<td>( \log_{10}(\sigma_{2c}) ) S/m</td>
<td>8.14</td>
<td>9.05</td>
<td>9.97 ± 0.49</td>
</tr>
<tr>
<td>( A_2 ) eV</td>
<td>3.35</td>
<td>3.90</td>
<td>4.25 ± 0.17</td>
</tr>
<tr>
<td>RMS misfit</td>
<td>1.52%</td>
<td>2.00%</td>
<td>2.69%</td>
</tr>
<tr>
<td>( \log_{10}(\beta) ) S/m</td>
<td>1.719</td>
<td>2.064</td>
<td>2.402</td>
</tr>
<tr>
<td>( \log_{10}(\delta) ) S/m</td>
<td>7.69</td>
<td>8.51</td>
<td>9.17</td>
</tr>
</tbody>
</table>

Values for least squares fits to SCO data constrained by various values for \( A_1 \). The errors only apply for \( A_1 = 1.6 \) eV, but are similar for the other fits.
significant. The first three eigenparameters are \( \log(\sigma_{1i}) \), \( \log(\sigma_{1b}) \), and \( \log(\sigma_{1c}) \) unmixed with other parameters, while the fourth is \( \sigma_2 \) mixed partially with \( \log(\sigma_{1i}) \) and less with \( \log(\sigma_{1b}) \). The \( \log(\sigma_{1c}) \) are in unresolved eigenparameters and mixed together. Thus, if we accept 1.60 eV as a good value for \( \sigma_1 \) then the errors given in Table 2 for the \( \sigma_1 \) are fairly reliably, the error for \( \sigma_2 \) approximate and the errors on the \( \sigma_2 \) unreliable.

It is instructive to present the two components \( \sigma_1 e^{-A_1/kT} \) and \( \sigma_2 e^{-A_2/kT} \) of the fits graphically (Figure 2), which demonstrates several things. First, conductivity across the entire experimental range is dominated by the low-temperature \( \sigma_1 e^{-A_1/kT} \). Second, the pattern of [001] being very much more conductive than [100] and [010] is maintained by the high-temperature mechanism. The reversed ordering of [100] and [010] in the high-temperature mechanism is not significant, as may be seen by the errors presented in Table 2, the lack of independence indicated by the correlation matrix, and its absence in the Shankland and Duba fits. Third, the higher-temperature mechanism exhibits more anisotropy than the lower-temperature mechanism. Similar examination of the individual fits presented by Shankland and Duba indicates that anisotropy exists even if the activation energies are not fixed and the [010] data are not truncated.

**A MODEL FOR ISOTROPIC OLIVINE**

Shankland and Duba [1990] demonstrated that with the exception of the parallel and series bounds (which are not isotropic), all the other mixing laws considered gave similar results, to within about 3%. The geometric mean has the advantage that it averages the three axes directly; the other mixing laws considered by Shankland and Duba are binary mixing laws that need to be applied to the parallel and series bounds. The geometric mean has the additional advantage that in this case, because of the fixed activation energy for the three axes, it preserves the underlying physical model for high and low temperature extrapolations. For example, for the low temperature extrapolation the geometric mean is given by

\[
\frac{(\sigma_{1a} e^{-A_1/kT} \cdot \sigma_{1b} e^{-A_1/kT} \cdot \sigma_{1c} e^{-A_1/kT})^{1/3}}{v/[(a/2)^2 + (b/4)^2 + (c/4)^2]} (\text{long hop}) = \frac{(\sigma_{1a} \cdot \sigma_{1b} \cdot \sigma_{1c})^{1/3} e^{-A_1/kT}}{v/[(a/2)^2 + (b/4)^2]} (\text{short hop}),
\]

where \( \sigma_1 \) is \( \sigma_1 e^{-A_1/kT} \). Second, the pattern of [001] being very much more conductive than [100] and [010] is maintained by the high-temperature mechanism. The lowered-temperature mechanism exhibits more anisotropy than the lower-temperature mechanism. Similar examination of the individual fits presented by Shankland and Duba indicates that anisotropy exists even if the activation energies are not fixed and the [010] data are not truncated.

**ANISOTROPY AND CRYSTAL STRUCTURE**

When activation energies are the same for all three directions, the relative magnitudes of the coefficients \( \sigma_1 \) then contain the measure of anisotropy, which we would like to relate to crystal structure. Normalizing to the [100] direction yields the conductivity ratios \( \sigma_{1a}/\sigma_{1a} : \sigma_{1b}/\sigma_{1a} : \sigma_{1c}/\sigma_{1a} \), which when evaluated are 1.000 : 0.883 : 1.683. These ratios are virtually independent of the choice of \( \sigma_1 \) and simply reflect the anisotropy that may be observed in the data. The dominant conduction mechanism inferred by Schock et al. [1989] in the better determined, low-temperature regime that we discuss here is the "small polaron" \( \text{Fe}^{3+} \) (\( \text{Fe}^{3+} \) in Kröger-Vink notation) produced by oxidation of \( \text{Fe}^{2+} \) \( \text{Fe}^{2+} \). The problem of analyzing anisotropy for an electronic mechanism differs from that of ionic transport in which cations or their vacancies must move past the hexagonal close packed oxygen sublattice [e.g., Condit, 1985]. Another consideration for the polaron mechanism is the fact that only about 1 out of 11 Mg sites contain \( \text{Fe}^{3+} \), and of these only a small fraction are \( \text{Fe}^{3+} \).

Support for the polaron mechanism is provided by the positive thermoelectric coefficient below 1390°C [Schock et al., 1989], dielectric measurements [Sato, 1986], and the increase of \( \sigma \) with iron content [Hinze et al., 1982; Hirsch et al., 1989; Constable and Duba, 1990]. Support is also provided by the positive dependence of conductivity on oxygen fugacity [Schock et al., 1989; Constable and Duba, 1990]. Changing the oxidation state of Fe does not require migration of oxygen defects. As noted by Schock et al., reequilibration of conductivity after a change in \( f_{O_2} \) is accomplished on time scales of 10^3 s, much too rapid for the diffusion of oxygen into the samples, which occurs on time scales of 10^6 s. Several other physical and chemical changes are also observed to reequilibrate with changes in \( f_{O_2} \) on similar time scales [e.g. Boland and Duba, 1985; Mackwell et al., 1988; Kohlstedt and Vander Sande, 1975], but the most direct evidence that the oxidation state (rather than some other property) of the interior of olivine grains can be rapidly influenced by changes in external \( f_{O_2} \) is provided by Pasteris and Wanamaker [1988], who produced CO and graphite in CO2 inclusions in SCO on time scales a short as 1 hour after changing the \( f_{O_2} \) of the experimental atmosphere. Metal ion vacancies [Pasteris and Wanamaker, 1988] and electronic transport [Boland and Duba, 1985] have both been suggested as mechanisms by which the internal oxidation state of olivine is rapidly changed.
be normalized to the ratios 1.000 : 0.919 (or 1.000 for long hop) : 0.788. The relation between diffusion and hopping mobility [e.g., Honig, 1966] predicts that conductivity should be proportional to the square of the hopping distance, which in this case would give the ratios 1.000 : 0.845 (or 1.000) : 0.621. However, none of these ratios are in the order of the conductivity anisotropy ratios given above.

A hypothesis that accounts for the conductivity anisotropy ratios comes from observing that the olivine structure contains two different crystallographic sites that Mg and Fe can occupy, M1 and M2. Fe$^+$ is a smaller ion than Fe$^{2+}$, and if it prefers the smaller M1 site, then the hopping distances would be the M1-M1 distances closest to the three principal axes. Their ratios are $a : (a/2)^2 + (b/2)^2 : c/2$ or 1.000 : 1.184 : 0.629. More significantly, reciprocals of these ratios are 1.000 : 0.845 : 1.590; the latter are not only in the proper order for the conductivity anisotropy ratios but match them to within about 5%. The inference from this agreement is intuitively favorable, namely, that hopping probability is inversely proportional to hopping distance. Such a dependence is often given as a qualitative explanation of conductivity anisotropy [Schock et al., 1989; Ottonello et al., 1990] despite the presumed dependence on the square of the hopping distance. We see then that placing all the low-temperature anisotropy in the $\sigma_{ij}$ term by fixing $A_i$ permits hypothesizing both a crystallographic ordering of Fe$^+$ and a polaron hopping parameterization.

Crystallographic studies have some ambiguous implications for this picture. Experiments [Aikawa et al., 1985; Ottonello et al., 1990] and theory [Ottonello et al., 1990] indicate a moderate preference of Fe$^{2+}$ for the M1 site, principally an effect of crystal field stabilization. This distribution increases with temperature, but may not be substantial enough to account for the low-temperature anisotropy in $\sigma_{ij}$. A more difficult problem comes from theoretical models [Ottonello et al., 1990] that imply Fe$^{2+}_{M2}$ should be strongly stabilized on M2. (For comparison, M2-M2 shortest distances are $\sqrt{(a/2)^2 + (c/2)^2}$ : $\sqrt{(a/2)^2 + (b/2)^2}$ : $\sqrt{(a/2)^2 + (c/2)^2}$, which yield the ratios 1.000 : 1.473 : 1.000, again in the wrong order.) Another issue that cannot presently be addressed is that of second nearest-neighbor hopping when nearest-neighbor sites are too few to interact.

The variation in coefficients for the high-temperature conduction mechanism is much larger, having an order of magnitude variation between the most conductive [001] direction and the other two. The strong variation adds to the arguments of Schock et al. [1989] for an ionic mechanism (magnesium vacancies) at high temperature; thus the considerations discussed by Condit [1985] for ionic diffusion are relevant to the interpretation of anisotropy. Ottonello et al. [1990] argue that the anisotropy is enhanced by a preference of $V_{M2}$ for M1 whose shortest jump distances are along [100]. It is interesting that for the ionic case the ordering of conductivity anisotropy, although not the quantitative values, is again of the order of the reciprocals of jump distances, which is in this case the nearest-neighbor distances above. However, in view of untreated geometrical factors (the jump vectors are not parallel to the principal axes) and the errors and strong covariances in the high temperature $\sigma_{ij}$, it would be reckless to attempt a quantitative interpretation. The strong anisotropy for the high-temperature mechanism is consistent with its being ionic (Mg vacancies) and the low-temperature mechanism being electronic (polarons) as hypothesised by Hughes [1955], Sato [1986], and Schock et al. [1989].

**SUMMARY AND CONCLUSIONS**

Because high-temperature conductivity measurements are difficult to make on polycrystalline material, the most reliable measurements above 1100°C have been made on single-crystal specimens. Olivine conductivity is anisotropic, and so the conductivity in the three crystal directions must be averaged in some way if an estimate of conductivity for an isotropic olivine mantle is desired. The geometric mean of the parameter fit to the three-axis data is, to good approximation, given by $\bar{\sigma} = 10^{2.40} e^{-1.60eV/kT} + 10^{9.17} e^{-4.25eV/kT}$. Between 720°C and 1500°C, uncertainties in this model are likely to be less than those discussed by Shankland and Duba [1990] and, in principle, provide a means of obtaining temperature from conductivity under lithospheric (subsolidus) conditions. Alternatively, if one has a thermal model for the lithosphere, conductivities can be predicted and compared with field data, as done by Heinson and Constable [1991].

The accepted model for electrical conduction in silicate minerals by means of thermally activated point defects is described by the sum $\sum \sigma_i e^ {-A_i/kt}$ (k is Boltzmann's constant and $T$ absolute temperature). $\sigma_i$ and $A_i$ are a coefficient and activation energy particular to conduction mechanism i. A conclusion from electrical conductivity versus temperature data from both single-crystal and polycrystal olivines is that below about 1400°C one activation energy is satisfactory for all three crystallographic axes. The strong correlation between activation energies and coefficients makes it difficult to reach this conclusion by examination of three-axis, high-temperature (1200°-1500°C) data independently of lower-temperature data. The dominant activation energy for temperatures between 720° and 1500°C is about 1.6 eV, in accordance with the relatively low temperature experiments of Duba et al. [1974], Constable and Duba [1990], and Tyburczy and Roberts [1990]. Parametric fits to high-temperature single crystal data of Shankland and Duba [1990] in which the low temperature activation energy is held constant at this value yield precise estimates of the preexponential coefficients in each crystallographic direction, with little covariance between parameters. It is observed that anisotropy in conduction, as represented by the ratios of these coefficients, is the same as the interionic distances for the M1 magnesium sites, implying both that interionic spacing determines the efficiency of conduction and that Fe$^{2+}$ substitues preferentially at M1 sites at temperatures above 1200°C.

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S. Constable, Institute of Geophysics and Planetary Physics, 0225, Scripps Institution of Oceanography, La Jolla, CA 92093-0225.

A. Duba, Lawrence Livermore National Laboratory, L201, Livermore, CA 94550.

T.J. Shankland, Los Alamos National Laboratory, MS C335, Geophysics Group, Los Alamos, NM 87545.

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