

Simultaneous Modeling of Thermopower and Electrical Conduction in Olivine

Steven Constable¹ and Jeffery J. Roberts²

¹Institute of Geophysics and Planetary Physics, University of California San Diego, La Jolla, CA 92093-0225, USA

²Lawrence Livermore National Laboratory, L201, Livermore, CA 94550, USA

Abstract. Measurements of conductivity and thermopower as a function of oxygen fugacity (f_{O_2}) are used to derive a model for conduction in olivine. Thermopower at 1000–1200°C is between 50 and 400 $\mu\text{V}/\text{K}$ and has a positive f_{O_2} dependence, and electrical conductivity exhibits approximately a $1/11$ power dependence on f_{O_2} . However, small polarons, considered to be the conducting defect in olivine at these temperatures, would produce a larger thermopower than observed, with a negative f_{O_2} dependence, as well as a $1/6$ power dependence of conductivity on f_{O_2} . At least one other conducting defect species must be invoked to explain the observed magnitude and f_{O_2} dependence of thermopower. An electron/polaron model cannot be made to fit the conductivity and thermopower data well, but a polaron/magnesium vacancy model fits the data if a constant polaron or magnesium vacancy term is included. Concentrations from our fits are consistent with predictions from theoretical models, and our analysis predicts a transition from polaron dominance in conduction to magnesium vacancy dominance at around 1300°C, as has been previously inferred from other data.

Introduction

An understanding of defect chemistry is important in the study of the electrical conductivity, rheology, and diffusion in Earth’s mantle, and there have been several recent attempts to model the point defect structure in olivine. Typically, these efforts have been based on laboratory measurements of either the temperature dependence or the oxygen fugacity (f_{O_2}) dependence of electrical conductivity (*e.g.* Schock *et al.*, 1989; Constable and Duba, 1990; Roberts and Tyburczy, 1991, 1993; Duba and Constable, 1993; Wanamaker and Duba, 1993). Thermopower, on the other hand, is determined by the sign and concentration of the dominant charge carrier, resulting from the migration of the conducting species from the hotter electrode of a sample in a temperature gradient. Using thermopower sign and electrical conductivity measured as functions of f_{O_2} , Schock *et al.* (1989) conclude that

conduction in olivine over the temperature range 1000 to 1300°C is probably dominated by small polarons of positive charge, that is Fe_{Mg}^{\bullet} .

Quantitative defect models have been formulated that are based on a set of defect reactions and available thermodynamic data to produce an internally consistent model of defect populations (Hirsch and Shankland, 1993; and Hirsch *et al.*, 1993), and these models also support polaron dominated conduction in olivine, although they include contributions to conduction from magnesium vacancies (V_{Mg}'') and electrons. Hirsch and Shankland (1993) modeled an ‘effective charge carrier’ population of electrons, polarons and magnesium vacancies. Several workers have proposed a mixed electron and polaron conduction in olivine (Schock *et al.*, 1989; Hirsch and Shankland, 1993; Wanamaker, 1994; Roberts and Duba, 1995), although Duba and Constable (1993) showed that the mixed electron/polaron conduction model does not fit the electrical conductivity data as well as a threshold plus f_{O_2} -dependent polaron model, especially for pyroxene-buffered samples. Schock *et al.* (1989) favoured mixed V_{Mg}'' and polaron conduction. V_{Mg}'' is an abundant defect, and electrons are very mobile, so both are candidates for a second charge carrier.

The defect models of Hirsch and co-workers are largely theoretical, and electrical conduction provides one of the few strong physical constraints used. In this paper we take the first steps towards developing a quantitative model using thermopower in olivine in order to supplement the conductivity constraints on the defect models. Because conductivity is a product of defect concentration and mobility, while thermopower is dependent only on concentration, a simultaneous model of conductivity and thermopower offers the possibility of estimating defect concentrations and mobilities independently.

Our primary data for interpretation (Figure 1) comprise thermopower and conductivity measurements published by Roberts and Duba (1995). The measurements were performed on a dunite from the San Quintin volcanic field, Baja California, Mexico. The sample was fine-grained ($\approx 300 \mu\text{m}$ grain size) and contains approximately 95% olivine (Fo90.5), 3% clinopyroxene, and 2% spinel. Optical and scanning electron microscopy revealed no alteration. The thermopower and conductivity data were collected at temperatures of 1000, 1100, and 1200°C, over a range of oxygen fugacities that span the olivine stability field, in the furnace design described by Duba *et al.* (1990). Thermopower, also referred to as the thermoelectric effect or the Seebeck coefficient, is the voltage generated across a sample in a thermal gradient:

$$Q = - \lim_{\Delta T \rightarrow 0} \frac{\Delta V}{\Delta T} \quad (1)$$

where ΔV and ΔT are the voltage and temperature differences between the hot and cold ends of the sample (Mason, 1987). Thermopower was determined using the method described by Schock *et al.* (1989); at a given temperature and oxygen fugacity, the sample was moved into an area of the furnace with a known temperature gradient. The emf that results from charge-carrier migration from the hotter electrode is measured by a digital voltmeter with an accuracy of $10 \mu V$. This was done for several temperature gradients at each temperature and gas mixture. The thermopower was then calculated using the slope of the $\Delta V/\Delta T$ plot and corrected for the thermopower of the Pt leads (Cusack and Kendall, 1958).

Building the Model

The relationship between the major defect population and f_{O_2} is thought to be described by



(Nakamura and Schmalzreid, 1983; Schock *et al.*, 1989). For samples buffered by pyroxene, this model predicts that $[Fe_{Mg}^{\bullet}]$ and $[V_{Mg}'']$ will each have a dependence on f_{O_2} of the form

$$[Fe_{Mg}^{\bullet}] = a_{Fe} f_{O_2}^{1/6} \quad ; \quad [V_{Mg}''] = a_{Mg} f_{O_2}^{1/6} \quad (3)$$

where the preexponential terms a are constant and $[]$ denotes concentration (Stocker and Smyth, 1978). Electron concentration is tied to polaron concentration to maintain charge balance, and will have an inverse dependence on f_{O_2} ;

$$n_e = a_e f_{O_2}^{-1/6} \quad (4)$$

and so if we consider the general case of mixed conduction, total conductivity is given by

$$\begin{aligned} \sigma &= \sigma_{Fe} + \sigma_e + \sigma_{Mg} \\ &= [Fe_{Mg}^{\bullet}] \mu_{Fe} e + n_e \mu_e e + 2[V_{Mg}''] \mu_{Mg} e \end{aligned} \quad (5)$$

where the μ are the respective mobilities for the charge carriers and e is the charge on the electron or hole.

Thermoelectric power is inversely proportional to the concentration of charge carriers, and is equivalent to the entropy per charge carrier (Ioffe, 1960, p293ff). Tuller and Nowick

(1977) provide an expression for thermoelectric power of electron hopping based on the entropy transported by the charge carriers:

$$Q = -\frac{k}{e} \left[\ln \beta \frac{(1-c)}{c} + \frac{S}{k} \right] \quad (6)$$

where c is the fraction of sites which contain an electron, β is a degeneracy factor (usually taken to be equal to 2 for the two possible spin states), S is the vibrational entropy associated with the ions around the polaron (usually considered negligible) and k is Boltzmann's constant. We can adapt this formula for polaron hopping in olivine if we neglect the Mg sites and take $[Fe_{Mg}^{\times}]$ to be the total available sites for the purposes of estimating entropy and change the sign of the charge carrier:

$$Q_{Fe} = \frac{k}{e} \ln 2 \frac{(1 - [Fe_{Mg}^{\bullet}]/[Fe_{Mg}^{\times}])}{[Fe_{Mg}^{\bullet}]/[Fe_{Mg}^{\times}]} \approx \frac{k}{e} \ln 2 \frac{[Fe_{Mg}^{\times}]}{[Fe_{Mg}^{\bullet}]} \quad (7)$$

(the approximation is for charge carrier fractions much less than one). This equation is easily inverted to obtain an expression for $[Fe_{Mg}^{\bullet}]$ given Q_{Fe} .

For an electronic semiconductor, thermoelectric power is given by

$$Q_e = -\frac{k}{e} \left(\frac{E_c - \mu}{kT} + \frac{3}{2} \right) \quad (8)$$

(Kittel, 1986, p212) where $E_c - \mu$ is the difference between the conduction band energy and the chemical potential (sometimes called the Fermi level). In order to relate the thermoelectric power to an f_{O_2} -driven concentration of electrons, n_e , we relate the band gap to n_e using

$$n_e = 2 \left(\frac{2\pi m^* kT}{h^2} \right)^{3/2} e^{(\mu - E_c)/kT} \quad (9)$$

(Kittel, 1986, p202), which can be inverted and substituted into (8) to obtain

$$Q_e = \frac{k}{e} \left\{ \ln \left[\frac{n_e}{2} \left(\frac{h^2}{2\pi m^* kT} \right)^{3/2} \right] - \frac{3}{2} \right\} \quad (10)$$

where h is Plank's constant and m^* is the effective mass of the conduction electron. If one assumes the effective mass is equal to the electronic mass, then this expression can be evaluated for a given n_e .

Following the entropy model for polarons, we take thermopower for magnesium vacancies as

$$Q_{Mg} = \frac{k}{e} \ln \frac{(1 - [V_{Mg}'']/[Mg_{Mg}^{\times}])}{[V_{Mg}'']/[Mg_{Mg}^{\times}]} \quad (11)$$

For mixed conduction with contributions from polaron, magnesium vacancy, and electronic conduction, total thermoelectric power is given by the thermopowers of the individual charge carriers weighted by the contribution to the total conductivity (Hannay, 1959, p375):

$$Q = Q_{Fe} \frac{\sigma_{Fe}}{\sigma} + Q_e \frac{\sigma_e}{\sigma} + Q_{Mg} \frac{\sigma_{Mg}}{\sigma} \quad (12)$$

where σ_{Fe} , σ_e and σ_{Mg} are the contributions to conductivity from polarons, electrons and V''_{Mg} respectively and σ is the total conductivity.

Modeling the Data

The positive sign of the thermopower is consistent with the polaron model, and indeed was an important part of the basis for the polaron hypothesis (Schock *et al.*, 1989). Thermoelectric power is also inversely proportional to the concentration of charge carriers, and so the observed decrease with temperature (Figure 1) is consistent with a thermally activated defect population. However, thermopower increases with f_{O_2} , but this is not what would be predicted by an increased polaron population at high f_{O_2} implied by the increased conductivity and eq. (2). Furthermore, if the magnitudes of observed thermoelectric data are interpreted in terms of polaron conduction only, large $[Fe^{\bullet}_{Mg}]/[Fe^{\times}_{Mg}]$ ratios of 0.73 to 0.18 are implied. The largest $[Fe^{\bullet}_{Mg}]/[Fe^{\times}_{Mg}]$ ratios estimated by Hirsch and Shankland (1993) at 1200°C are about 10^{-3} (at an f_{O_2} of 10 Pa) which would predict a thermoelectric power of about 650 $\mu\text{V}/\text{K}$. This would be even higher at lower temperatures and f_{O_2} . In contrast, we observe thermopowers of about 100 $\mu\text{V}/\text{K}$ at 1200°C and even at 1000°C thermopower does not exceed 500 $\mu\text{V}/\text{K}$.

It was noted by Shock *et al.* (1989) that the Fo90 conductivity- f_{O_2} data did not always follow the predicted $1/6$ slope, but often displayed much lower slopes. This was found to be true for observations of $\sigma(f_{O_2})$ in single crystals, pyroxene-buffered olivines (Constable and Duba, 1990), dunites (Roberts and Tyburczy, 1993), and lherzolites (Duba and Constable, 1993). This behaviour is also evident in the conductivity data considered here (Figure 1). Duba and Constable (1993) suggest a model of threshold and f_{O_2} -dependent conduction:

$$\sigma = \sigma_0 + \sigma_1(f_{O_2})^{1/6}, \quad (13)$$

which allows one to fit the expected slope to the data by the inclusion of the constant term. However, this term is not well explained; it varies by over an order of magnitude between samples and is smaller for olivines of metamorphic origin than of igneous origin. Duba and Constable (1993) speculate that buffering by pyroxene limits the ability to lower the

f_{O_2} state of the sample beyond the threshold value. That is, equilibrium with pyroxene ensures a minimum population of Fe_{Mg}^\bullet . Electrical conductivity data on self-buffered and pyroxene-buffered San Carlos Olivine collected by Wanamaker and Duba (1993) support this hypothesis, with the self-buffered sample having a lower conductivity at low f_{O_2} .

Neither the slope of the conductivity- f_{O_2} relationship nor the slope of the thermoelectric power- f_{O_2} relationship support the simple polaron paradigm, and the data clearly suggest either a different conduction mechanism than polarons or mixed conduction. However, we must assume that polarons are responsible for the positive thermoelectric power because the only other positive charge carriers are cation interstitials of low abundance and low mobility. Even if electronic conduction or V_{Mg}'' conduction does not contribute greatly to conductivity, a comparatively low concentration implies a large thermoelectric power of opposite sign to the polaron component. So, for example, an increasing contribution of σ_{Fe} with increasing f_{O_2} might well account for the positive slope of the thermopower- f_{O_2} relationship.

We can use Marquardt inversion (Marquardt, 1963) to solve equations (3) through (12) for a_{Fe} , a_e , a_{Mg} , μ_{Fe} , μ_e , and μ_{Mg} , using the conductivity and thermopower data at 1000, 1100, and 1200°C as constraints. We compute the cation and vacancy ratios by taking the total metal ion concentration as $2.638 \times 10^{28} \text{ m}^{-3}$, with Fe and Mg site densities as 10% and 90% of this respectively (a typical Fe concentration for this and other olivines). The convention used in previous papers has been to report the oxygen fugacity produced by a particular gas mixture as that which was measured at 1200°C using a calcia-stabilized zirconia tube as described in Duba *et al.* (1990). Oxygen fugacity at any temperature can be calculated from the 1200°C data from the following equation:

$$\log_{10}(f_{\text{O}_2})_T = \log_{10}(f_{\text{O}_2})_{1200^\circ\text{C}} + 29530\left(\frac{1}{1473} - \frac{1}{T}\right) \quad (14)$$

where T is the new temperature in kelvins. For our quantitative model and figures in this paper this relationship was used to compute the actual f_{O_2} at the temperature of measurement, in order to decouple the effect of increased f_{O_2} of the stability field and gas mixes with temperature from thermally activated mobility.

Even with 27 parameters (three concentrations and mobilities at each of three temperatures) for a relatively small number (60) of data, we are not able to fit the conductivity/thermopower data well. The $1/6$ power forces the slope to be steeper than observed, and the $-1/6$ power associated with electronic conduction cannot combine with this to produce

an adequate fit. If we resort to the two-component model of Duba and Constable (1993) for the polarons :

$$[Fe_{Mg}^{\bullet}] = b_{Fe} + a_{Fe} f_{O_2}^{1/6} \quad (15)$$

we are able to fit the conductivity data well. For the sake of generality, and because a constant term seems to be strongly implied by the levelling of the conductivity at low f_{O_2} , we include a constant term for $[V_{Mg}'']$ and n_e as well, for a total of 30 parameters.

We stress that we do not expect all 30 parameters to be significant and many, such as mobility and density for a given defect, are highly correlated. Nor are we claiming that three charge carriers are all contributing in a significant way to conductivity at a given temperature. However, we wish to maintain this generality in our quantitative model of thermopower so that we can explore the acceptable parameter space. We will attempt to determine which combinations are consistent with the data. In order to stabilize the large number of correlated parameters, we add preferred values of the parameters themselves (often taken from Hirsch and Shankland (1993)) to the data set, and manipulate the tendency to achieve these preferred values by the size of the error assigned to these extra data constraints.

Although we do not claim to have searched all of model space, on the order of 200 inversions were run from different starting models and with various constraints on model parameters. We rejected as inadequate any model that did not approach the estimated data error of about 5%, although inadequate models were usually evident immediately as a consequence of slopes of opposite sign or grossly incorrect conductivities and thermopowers. The following observations are made based on these inversions:

a) A second, negative charge carrier must exist alongside Fe_{Mg}^{\bullet} both to drop the magnitude of the thermopower and produce a positive thermopower- f_{O_2} slope. This can be accomplished to first approximation using electrons, but the negative f_{O_2} dependence of n_e produces models in which thermopower plunges steeply at low f_{O_2} . We cannot find any fits using a polaron-electron model that we consider adequate, and all acceptable models consist of polarons and magnesium vacancies. Duba and Constable (1993) also discounted the polaron-electron model based on fitting conductivity- f_{O_2} data, because the change of slope at low f_{O_2} for this model was too sharp. This is not to say that electrons cannot be included in the quantitative model, but rather they appear not to play a dominant role in either conduction or thermopower.

b) The low slope of the conductivity– f_{O_2} and thermopower– f_{O_2} data requires that constant terms are included for both $[Fe_{Mg}^\bullet]$ and $[V_{Mg}'']$. Surprisingly, the same effect cannot be achieved by an ad hoc change of the $1/6$ power to $1/11$ in the f_{O_2} dependency, nor even by allowing the power to be variable for both $[V_{Mg}'']$ and $[Fe_{Mg}^\bullet]$. On the other hand, the defect model of Hirsch and Shankland (1993) produced an exponent of $1/5.6$ for the f_{O_2} dependence of the major defects, but our model cannot distinguish the difference between this and $1/6$, as minor changes occur in the free parameters to accommodate the small change in power.

c) After eliminating electrons as a significant defect, but including constant terms for $[V_{Mg}'']$ and $[Fe_{Mg}^\bullet]$, there are still 18 parameters in our model. With such a large number of free parameters there are inevitably correlations, and an individual parameter cannot necessarily be determined uniquely. However, we expect at least some of the parameters to be thermally activated, and we attempted to fit the data using a Boltzmann relationship for all concentrations and mobilities. This was not successful. However, we determined that all but the constant terms b_{Fe} and b_{Mg} could be expressed as thermally activated processes without degrading the fit. This not only reduces the number of parameters but makes the model somewhat more physical. Thus, mobilities were parameterized by

$$\mu_{Fe} = c_{Fe} e^{-A_h/kT} \quad ; \quad \mu_{Mg} = c_{Mg} e^{-A_{Mg}/kT} \quad (16)$$

where c are constants and the A are activation energies. The f_{O_2} concentration terms a_{Fe} and a_{Mg} for the three temperatures were related exponentially in a similar fashion.

We were able to fit the data well using this model, with a root-mean-square misfit of 6%, which is about the accuracy of the data. Figure 1 shows the fits of our model to the data. The numerical model is

$$\mu_{Fe} = 12.2 \times 10^{-6} e^{-1.05 \text{ eV}/kT} \quad (17)$$

$$\mu_{Mg} = 2.72 \times 10^{-6} e^{-1.09 \text{ eV}/kT} \quad (18)$$

$$[Fe_{Mg}^\bullet] = b_{Fe}(T) + 3.33 \times 10^{24} e^{-0.02 \text{ eV}/kT} f_{\text{O}_2}^{1/6} \quad (19)$$

$$[V_{Mg}''] = b_{Mg}(T) + 6.21 \times 10^{30} e^{-1.83 \text{ eV}/kT} f_{\text{O}_2}^{1/6} \quad , \quad (20)$$

where the temperature dependent concentration terms are given in Table 1 and shown graphically in Figure 2 (all units are SI except the activation energies).

The activation energy for the Fe_{Mg}^\bullet term is very low, essentially zero. However, it is not constrained to be zero and can be forced as high as about 0.4 eV before the fit degrades (to

9.4%). This exercise forces the activation energy for V''_{Mg} term to decrease; it appears that the sum of the two activation energies is constrained to be 1.8 eV.

The constant terms (b_{Fe} and b_{Mg}) seem to have a similar slope to the magnesium vacancy f_{O_2} term between 1100 and 1200°C (≈ 1.8 eV), but the 1000° values are about the same as the 1100°C values. We again attempted to fit a model in which all terms were thermally activated, using the coefficients shown in Figure 2 as a guide to the starting values, and although the general features of the data were represented, the fits were not adequate (18% misfit). Some non-Boltzmann temperature behaviour of the coefficients seems to be required, although not a great deal. This prompts us to speculate on the physical interpretation of the constant terms. At some level there will exist a thermally activated population of defects, independent of f_{O_2} , but one would expect this to follow the Boltzmann relationship. A chemical doping behaviour, perhaps associated with Cr^{+++} or Al^{+++} impurities, could maintain a minimum population of defects. We would expect doping to produce a temperature-independent defect population, and perhaps this is indeed consistent with the data (it certainly is below 1200°C). We are able to obtain a somewhat acceptable fit (9% average misfit) whilst holding the threshold polaron term (b_{Fe}) constant at 2.8×10^{23} , but cannot hold the Mg vacancy term (b_{Mg}) constant as well. We noted above that the threshold term seems to be related to pyroxene buffering; the pyroxene could be supplying a dopant or some other chemical equilibration could be affecting the defect population. In the latter case, levelling of the constant term below 1100°C could be associated with slower kinetics of the chemical equilibrium at the lower temperature.

Discussion

Our modeling demonstrates that mixed conduction can explain the behaviour of both conductivity and thermopower. The defect concentrations we obtain are similar enough to those of Hirsch and Shankland (1993) that we are confident the assumptions and approximations we have made are valid. On the other hand, our results can be used to refine the theoretical model. For example, Hirsch and Shankland arbitrarily assigned a mobility to V''_{Mg} that was 10% of the polaron mobility. Our model indicates that $\mu_{V''_{Mg}}$ is closer to 20% of the polaron mobility. Electrons do not appear to play a significant role in conduction at these temperatures.

There are a few direct measurements we can compare our results with. Sato estimated polaron mobility at 1400°C as $6.3 \times 10^{-8} \text{ m}^2\text{V}^{-1}\text{s}^{-1}$ for [001] and $2.0 \times 10^{-7} \text{ m}^2\text{V}^{-1}\text{s}^{-1}$ for

[010]. Extrapolating our polaron mobility to 1400°C provides a value that is significantly smaller than these ($8.4 \times 10^{-9} \text{ m}^2 \text{V}^{-1} \text{s}^{-1}$). This does draw attention to the fact that by using a polycrystalline rock with no preferred crystallographic orientation, our values are averages over the three crystal axes (Shankland and Duba (1990) discuss various mathematical models of such averages).

Using the Nernst-Einstein relationship, we can compute diffusivities from mobility by

$$D = \frac{\mu kT}{q} \quad (21)$$

where q is the charge of the defect. Our model thus predicts a V''_{Mg} diffusivity of $3.2 \times 10^{-11} \text{ m}^2 \text{s}^{-1}$ at 1200°C, which compares well with estimates at this temperature by Mackwell *et al.* (1988) ($3.5\text{--}9.8 \times 10^{-11} \text{ m}^2 \text{s}^{-1}$), Nakamura and Schmalzreid (1984) ($1.9 \times 10^{-11} \text{ m}^2 \text{s}^{-1}$), Wanamaker (1986) ($4.8 \times 10^{-11} \text{ m}^2 \text{s}^{-1}$), and Duba and Constable (1993) ($7.0 \times 10^{-11} \text{ m}^2 \text{s}^{-1}$).

It is instructive to plot the contributions of V''_{Mg} and Fe^{\bullet}_{Mg} to conductivity and thermopower as a function of temperature and f_{O_2} (Figure 3). In this figure we have predicted the behaviour at 1300°C based on an extrapolation of the b_{Fe} and b_{Mg} coefficients from their values at 1100 and 1200°C. We see that V''_{Mg} play a more significant role at low f_{O_2} , and that as temperature increases the V''_{Mg} contribution also increases, until at 1300°C the contributions of V''_{Mg} and Fe^{\bullet}_{Mg} are about equal and the thermopower changes sign, as observed by Schock *et al.* (1989). The ability to predict an independent observation not used as a data constraint in our modeling provides further support for our basic approach.

This defect model will provide the basis for further understanding of the electrical properties and point defect diffusivity in olivine. For example, observations of an f_{O_2} -dependent diffusivity (Constable, Duba, and Roberts, manuscript in preparation) can be readily understood as due to the changing relative contribution of the various defects as a function of f_{O_2} . The change in activation energy of conductivity-temperature measurements at around 1300°C has proved somewhat difficult to model because at these temperatures iron loss to electrodes and sample metamorphism becomes a problem (Shankland and Duba, 1990; Constable *et al.*, 1992). Roberts and Tyburczy (1991) also observed a change in activation energy at 1344°C and interpreted the cause as a change from polaron to V''_{Mg} dominated conduction. The present model indicates near equal contributions to conduction from Fe^{\bullet}_{Mg} to V''_{Mg} at 1300°C, strengthening these conclusions. Finally, the effect of pyroxene buffering on the low- f_{O_2} behaviour of conduction (Duba and Constable, 1993;

Wanamaker and Duba, 1993) is likely associated with the threshold V''_{Mg} term.

Acknowledgements. The authors wish to thank Al Duba, who has been closely involved in our work over the years and provided many discussions relevant to this work, and Tom Shankland, who critically read the manuscript. Comments by the associate editor, Steve Mackwell, and an anonymous reviewer led to significant improvements in the manuscript. We thank Bob Parker for Plotxy, which was used to create the figures in this paper. This work was supported by the Institute of Geophysics and Planetary Physics under their mini-grant program, and was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under contract W-7405-ENG-48.

References

- Constable, S.C. and Duba, A. (1990) The electrical conductivity of olivine, a dunite, and the mantle. *J. Geophys. Res.* 95:6967–6978
- Constable, S.C., Shankland, T.J. and Duba, A. (1992) The electrical conductivity of an isotropic olivine mantle. *J. Geophys. Res.* 97:3397–3404
- Cusack, N., and P. Kendall (1958) The absolute scale of thermoelectric power at high temperature. *Proc. Phys. Soc. London.* 72:898–901
- Duba, A, and S. Constable (1993) The electrical conductivity of a lherzolite. *J. Geophys. Res.* 98:11885–11900
- Duba, A.G., R.N. Schock, E. Arnold, and T.J. Shankland (1990) An apparatus for measurement of electrical conductivity to 1500°C at known oxygen fugacity. In: *The Brittle-Ductile Transitions in Rocks, The Heard Volume, Geophys. Monogr. Ser., vol. 56* (ed) A.G. Duba, W.B. Durham, J.W. Handin and H.F. Wang, AGU, Washington, D.C., pp 207–210
- Hannay, N.B. (1959) *Semiconductors*. Reinhold, New York
- Hirsch, L.M., and T.J. Shankland (1993) Quantitative olivine-defect chemical model: insights on electrical conduction, diffusion, and the role of Fe content. *Geophys. J. Int.* 114:21–35
- Hirsch, L.M., A.G. Duba, and T.J. Shankland (1993) Electrical conduction and polaron

- mobility in Fe-bearing olivine. *Geophys. J. Int.* 114:36–44
- Ioffe, A.F. (1960) *Physics of Semiconductors*. Academic Press, New York
- Kittel, C (1986) *Introduction to Solid State Physics* (sixth edition). Wiley, New York
- Mackwell, S.J., D. Dimos, and D.L. Kohlstedt (1988) Transient creep of olivine: Point-defect relaxation times. *Phil. Mag. A* 57:779–789
- Marquardt, D.W. (1963) An algorithm for least-squares estimation of non-linear parameters. *J. Soc. Ind. Appl. Math.* 11:431–441
- Mason, T.O. (1987) Cation intersite distributions in iron-bearing minerals via electrical conductivity/seebeck effect. *Phys. Chem. Minerals* 14:156–162
- Nakamura, A., and H. Schmalzried (1983) On the nonstoichiometry and point defects of olivine. *Phys. Chem. Min.* 10:27–37
- Nakamura, A., and H. Schmalzried (1984) On the Fe^{2+} - Mg^{2+} interdiffusion in olivine (II). *Ber. Bunsenges. Phys. Chem.* 88:140–145
- Roberts, J.J., and A.G. Duba (1995) Transient electrical response of San Quintin dunite as a function of oxygen fugacity changes: information about charge carriers. *Geophys. Res. Lett.* 22:453–456
- Roberts, J.J. and J.A. Tyburczy (1991) Frequency dependent electrical properties of polycrystalline olivine compacts. *J. Geophys. Res.* 96:16205–16222
- Roberts, J.J. and J.A. Tyburczy (1993) Frequency dependent electrical properties of dunite as functions of temperature and oxygen fugacity. *Phys. Chem. Minerals* 19:545–561
- Shankland, T.J., and A.G. Duba (1990) Standard electrical conductivity of isotropic, homogeneous olivine in the temperature range 1100–1500°C. *Geophys. J. Int.* 103:25–31
- Schock, R.N., A. Duba, and T.J. Shankland (1989) Electrical conduction in olivine. *J. Geophys. Res.* 94:5829–5839
- Stocker, R.L., and D.M. Smyth (1978) Effect of enstatite activity and oxygen partial

pressure on the point-defect chemistry of olivine. *Phys. Earth Planet. Inter.* 16:145–156

Tuller, H.L. and A.S. Norwick (1977) Small polaron electron transport in reduced CeO_2 single crystals. *J. Phys. Chem. Solids* 38:859–867

Wanamaker, B.J. (1986) The kinetics of crack healing and the chemical and mechanical reequilibrium of fluid inclusions in San Carlos olivine. PhD thesis, Princeton University

Wanamaker, B.J. (1994) Point defect diffusivities in San Carlos olivine derived from reequilibration of electrical conductivity following changes in oxygen fugacity. *Geophys. Res. Lett.* 21:21–24

Wanamaker, B.J., and A.G. Duba (1993) Electrical conductivity of San Carlos olivine along [100] under oxygen- and pyroxene-buffered conditions and implications for defect equilibria. *J. Geophys. Res.* 98:489–500

TABLE 1. Parametric Fits to Conductivity and Thermopower Data

Parameter	1000°C	1100°C	1200°C
b_{Mg}	5.28×10^{23}	6.46×10^{23}	1.36×10^{24}
b_{Fe}	2.32×10^{23}	1.70×10^{23}	3.71×10^{23}

The table presents numerical values for the parameters shown in Figure 2. Units are m^{-3} .

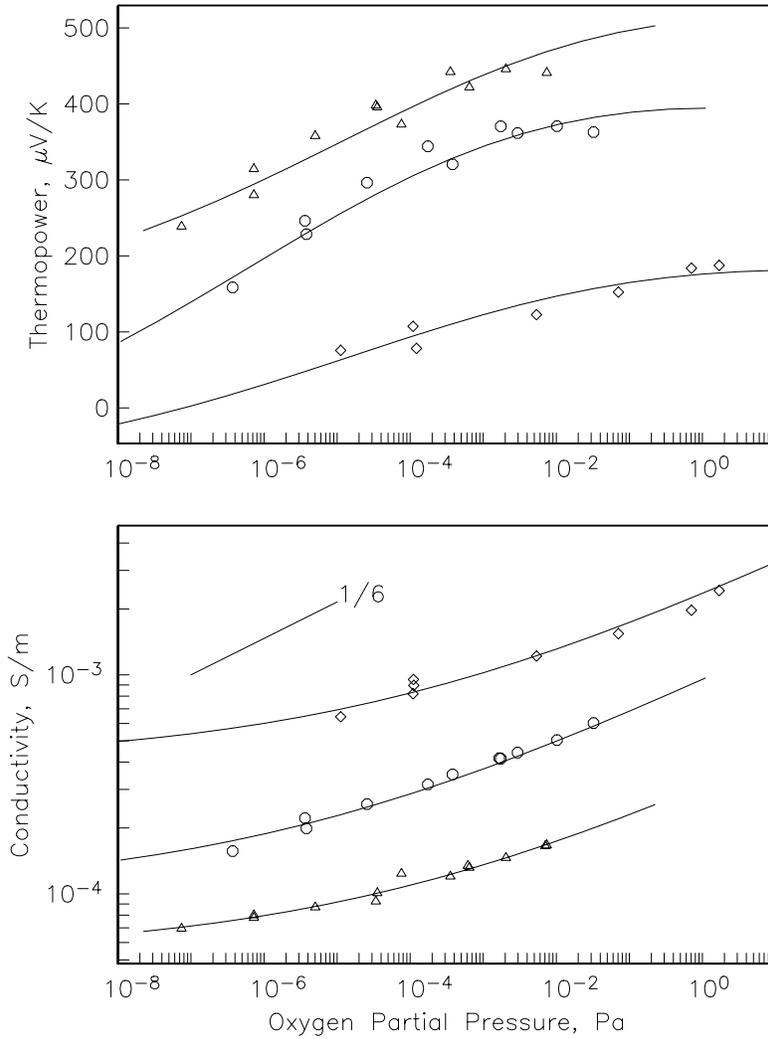


Fig. 1. Electrical conductivity data and thermopower data (symbols), along with model fits (solid lines) as described in the text. Data are collected at 1000°C (triangles), 1100°C (octagons), and 1200°C (diamonds).

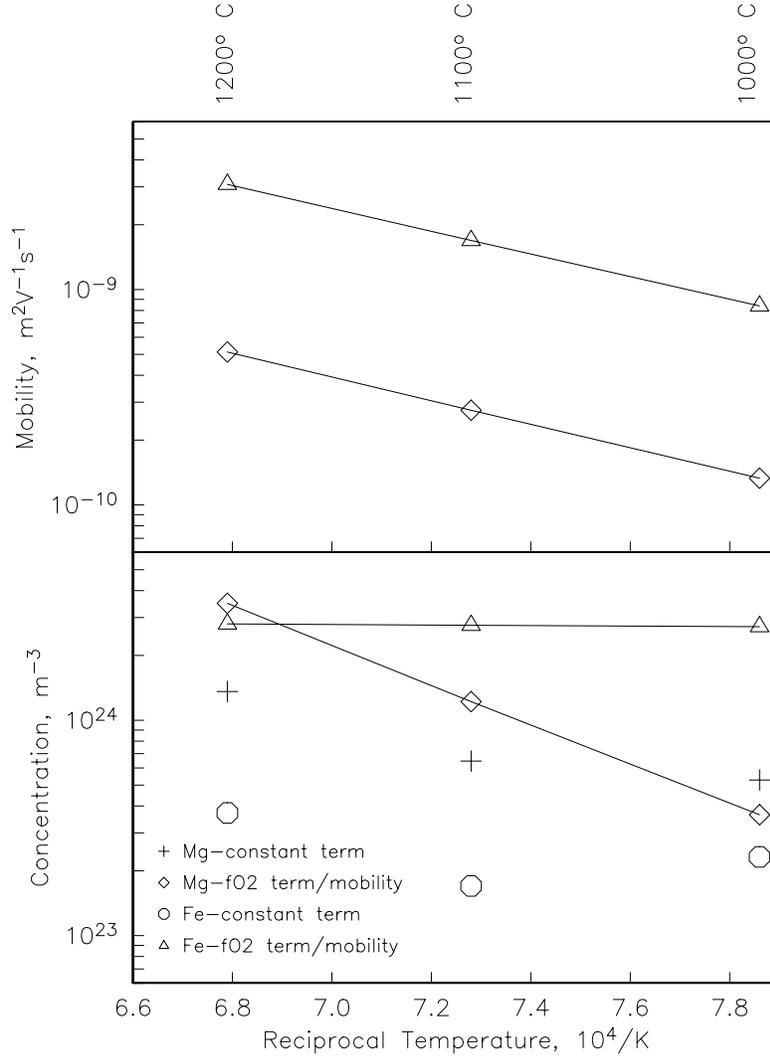


Fig. 2. Values of the model coefficients found by inverting the data in Figure 1. With reference to the description in the text, triangles are a_{Fe} , octagons are b_{Fe} , diamonds are a_{Mg} , and plusses are b_{Mg} . Symbols connected by solid lines have been defined in the model as thermally activated parameters.

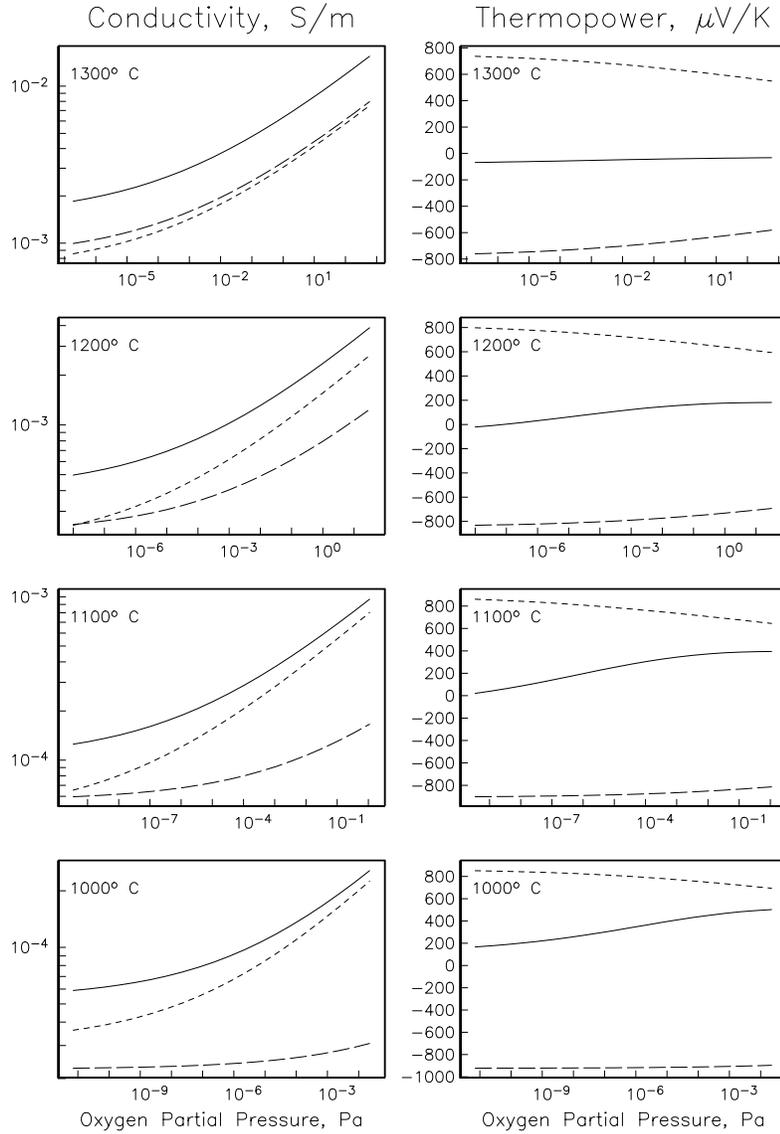


Fig. 3. Contributions from magnesium vacancies (coarsely broken lines), polarons (finely broken lines) to total conductivity or thermopower (solid lines). Between 1000°C and 1200°C the model is as fit to the data in Figure 1; 1300°C is an extrapolation which predicts a transition to conduction dominated by magnesium vacancies and a change of sign in the thermopower.