

FAST TRACK PAPER

SEO3: A new model of olivine electrical conductivity

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Accepted 2006 April 13. Received 2006 April 13; in original form 2006 February 24

SUMMARY

Standard Electrical Olivine 3 (SEO3) is a new model of electrical conductivity for olivine as a function of temperature and oxygen fugacity, and is based on a previous study of point defect behaviour in a dunite. That study produced quantitative estimates of mobility and concentration for small polarons and magnesium vacancies as a function of temperature and oxygen fugacity. Unlike earlier SO1 and SO2 models of olivine conductivity, the dunite sample was buffered by pyroxene, and avoided alteration at high temperature. The low-temperature extrapolation produced by SEO3 is in good agreement with SO2, while the high-temperature extrapolation is significantly more conductive, which is in general agreement with many field studies that show the Earth's upper mantle to be more conductive than predicted by SO2 for reasonable temperatures. Plausible variations in mantle oxygen fugacity correspond to about half an order of magnitude variation in electrical conductivity, equivalent to about 100 degrees in temperature.

Key words: electrical conductivity, hydrogen, mantle, olivine, oxygen fugacity.

1 INTRODUCTION

Models of dry olivine electrical conductivity as a function of temperature, such as the SO1 model of Shankland & Duba (1990) and the SO2 model of Constable *et al.* (1992), appear to underestimate the electrical conductivity of the Earth's mantle (e.g. Gatzemeier & Moorkamp 2005), leading to proposals for increased conductivity through other conduction mechanisms. Particularly, Karato's (1990) suggestion that hydrogen enhances olivine conductivity has gained widespread support. Because the hydrogen diffusivity data upon which this hypothesis is based (Mackwell & Kohlstedt 1990) predicts much greater conduction along the olivine a-axis, evidence of electrical anisotropy in the mantle has been interpreted as support of hydrogen conduction (e.g. Simpson & Tommasi 2005). However, direct laboratory evidence for such a conduction process has been slow to appear and initial reports are in poor agreement (e.g. Shankland & Duba 1997; Poe *et al.* 2005; Wang *et al.* 2005).

As successful as the SO2 model has been as a broadly understood yardstick, it is perhaps time to reconsider its accuracy, especially at high temperature (greater than 1200°C). There are two potential problems with the high-temperature behaviour of SO2. First is that it is based on single crystals that have no silica buffering, while it is known that buffering by pyroxene has a significant effect on olivine conductivity (Wanamaker & Duba 1993). Second, extrapolation to high temperature is based on a purely parametric fit to conductivity data collected over a temperature range in which conduction is thought to be a mixture of small polarons (charge ex-

change between Fe³⁺ and Fe²⁺) and magnesium vacancies. Given that the high-temperature conduction mechanism (vacancies) is not fully expressed, and that measurements at high temperature are susceptible to melting of the sample (Al Duba, private communication, 1993) and iron loss to electrodes (Du Frane *et al.* 2005), there are reasons to doubt the reliability of the SO2 model in the geophysically important temperature range of 1300°–1500°C.

2 THE NEW MODEL

The change in conduction mechanism from polarons to magnesium vacancies occurs around 1300°C (Schock *et al.* 1989), but the addition of a pyroxene buffer to olivine lowers the melting point to about this temperature. There seems little one can do short of relinquishing the fine control on oxygen fugacity (f_{O_2}) obtainable in one-atmosphere gas mixing furnaces by resorting to high-pressure measurements to inhibit melting. However, since f_{O_2} exerts a significant effect on olivine conductivity, that also presents some problems. The solution perhaps lies in a conduction model developed by Constable & Roberts (1997). By simultaneously modelling thermopower and conductivity data collected on a naturally occurring olivine aggregate (a dunite) that included small amounts of pyroxene, they were able to independently model both the concentration and mobilities of polarons and magnesium vacancies. To summarize their results, olivine conductivity σ is given by

$$\sigma = [\text{Fe}_{\text{Mg}}^{\bullet}] \mu_{\text{Fe}} e + 2[V_{\text{Mg}}^{\prime\prime}] \mu_{\text{Mg}} e, \quad (1)$$

for mobilities

$$\mu_{\text{Fe}} = 12.2 \times 10^{-6} e^{-1.05 eV/kT}, \quad (2)$$

$$\mu_{\text{Mg}} = 2.72 \times 10^{-6} e^{-1.09 eV/kT}, \quad (3)$$

and concentrations

$$[\text{Fe}_{\text{Mg}}^{\bullet}] = b_{\text{Fe}}(T) + 3.33 \times 10^{24} e^{-0.02 eV/kT} f_{\text{O}_2}^{1/6}, \quad (4)$$

$$[V_{\text{Mg}}^{\prime\prime}] = b_{\text{Mg}}(T) + 6.21 \times 10^{30} e^{-1.83 eV/kT} f_{\text{O}_2}^{1/6}, \quad (5)$$

where e is electronic charge, T is temperature and k is Boltzmann's constant. The only *ad hoc* parameters in this model are the constant defect concentration terms b_{Fe} and b_{Mg} , observed by most authors (e.g. Du Frane *et al.* 2005) and representing an f_{O_2} -independent defect population.

Although based on data at only 1000°, 1100° and 1200°C, the above model is closely tied to the physics of conduction and correctly predicts equal contributions of polarons and vacancies at 1300°C. The data set upon which the model is based has advantages over the single crystal measurements; the low temperatures provide some insurance against sample alteration, the natural polycrystal averages over the three axes of olivine (dry olivine conductivity is weakly anisotropic), and the sample is naturally buffered for silicon. We only need a way to extrapolate the b_{Fe} and b_{Mg} terms to generate a new olivine $\sigma - T$ relationship, which is done by fitting a linear relationship in $\log[\] - 1/T$ space to the original b at the three temperatures, yielding

$$b_{\text{Fe}}(T) = 5.06 \times 10^{24} e^{-0.357 eV/kT}, \quad (6)$$

$$b_{\text{Mg}}(T) = 4.58 \times 10^{26} e^{-0.752 eV/kT}. \quad (7)$$

Finally, we need to specify an $f_{\text{O}_2}(T)$ model; the quartz–fayalite–magnetite buffer is often used for the mantle, but for comparison we also make calculations for the iron–wüstite equilibrium. The results are shown in Fig. 1 (SEO3-QFM and SEO3-IW). To make it easy to relate the calculations to field observations, resistivity versus temperature is presented, but a plot of conductivity versus reciprocal temperature is also given to show the effective activation energies.

Table 1. MATLAB script to compute electrical conductivity from temperature (C) and oxygen fugacity (Pa).

```
function sT = SO3(T, fO2);
e = 1.602e-19;
k = 8.617e-5;
kT = k*(T+273);
bfe = (5.06e24)*exp((-0.357)/kT);
bmg = (4.58e26)*exp((-0.752)/kT);
ufe = (12.2e-6)*exp((-1.05)/kT);
umg = (2.72e-6)*exp((-1.09)/kT);
concFe = bfe + (3.33e24)*exp((-0.02)/kT).*fO2.^(1/6);
concMg = bmg + (6.21e30)*exp((-1.83)/kT).*fO2.^(1/6);
sT = concFe.*ufe.*e + 2.*concMg.*umg.*e;
return
end
```

Table 1 presents a short MATLAB script that was used to make the calculations.

We see a reasonable agreement between SEO3 and SO2 below 1000°C, with the new model about a factor of 2 less conductive; the agreement in activation energy supports the validity of extrapolating the new model a considerable distance in $1/T$. Above 1200°C the SEO3-QFM model is significantly more conductive than SO2, addressing the concerns that motivated this work. The model is also significantly more conductive at high temperature than the recent results of Du Frane *et al.* (2005), which, like SO2, are based on single crystal olivine measurements lacking a pyroxene buffer (shown as GM-QFM in Fig. 1). Du Frane *et al.* used iron-doped electrodes to avoid iron loss from the sample to the electrodes, and observed that this may account for a $10^{0.15}$ increase in conductivity over previous measurements. Iron loss to electrodes could well have been a problem with the high-temperature data upon which SO2 was based. It is not clear whether this effect is important at the lower temperatures of the dunite measurements, but the new model could be made slightly more conductive by the suggested amount. At temperatures below about 1300°C the Du Frane *et al.* data and model are up to one order of magnitude more conductive than most other observations

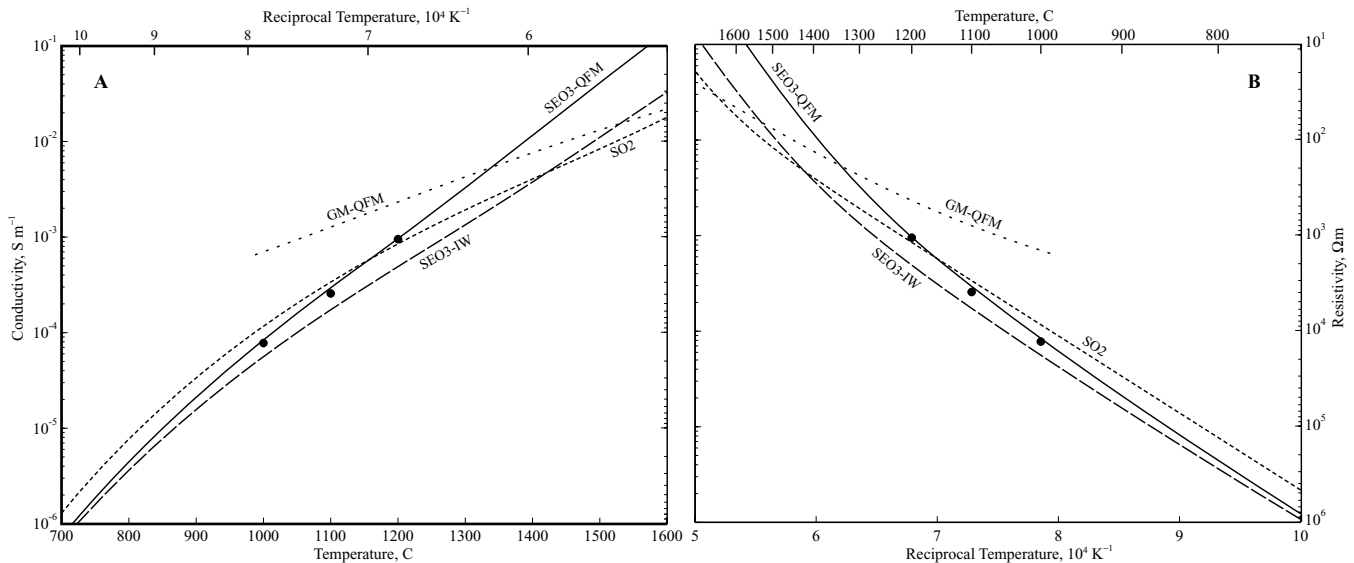


Figure 1. Olivine conductivity versus temperature (A) and reciprocal temperature (B) for two different f_{O_2} conditions, quartz–fayalite–magnetite (SEO3-QFM) and iron–wüstite (SEO3-IW). For comparison the SO2 model of Constable *et al.* (1992) is shown, along with the geometric mean of Du Frane *et al.* (2005) computed for QFM (GM-QFM). The SEO3 model is based on actual data between 1000°C and 1200°C at various f_{O_2} , of which three data points closest to the QFM buffer are shown here as filled circles.

made on olivine. They attribute this to a larger b_{Fe} term at lower temperatures; why this should be so requires further study.

At transition zone temperatures of around 1400°C, SEO3 predicts a significant dependence of conductivity on f_{O_2} (a factor of 3 for the two buffers shown in Fig. 1). Since mantle f_{O_2} may decrease towards the transition zone (e.g. McCammon 2005), this could be an important and observable effect, resulting in a decrease in conductivity with depth if the temperature gradient is small, or an uncertainty of about 100 K in temperature if f_{O_2} is not taken into consideration.

3 CONCLUSIONS

A new model of olivine conductivity, SEO3, has been derived and is based on a physical model of electrical conduction by point defects. The model agrees well with an earlier model (SO2) at temperatures below 1200°C, but is significantly more conductive at higher temperatures. This addresses a widespread concern that for temperatures expected in the Earth's upper mantle, electrical conductivities observed by field measurements are generally more conductive than SO2. There are several reasons why a high-temperature extrapolation of SO2 could be problematic, while the new model should be much more robust in this regard. The only *ad hoc* parameter, an f_{O_2} -independent concentration of vacancies, is unimportant at high temperatures where thermally activated conduction by magnesium vacancies dominates. The effect of pressure on olivine conductivity is small (Xu *et al.* 2000), while we see that the effect of oxygen fugacity is more than half an order of magnitude at high temperature. The new model should lessen the requirement to invoke enhanced conduction in olivine by means of dissolved hydrogen, trace carbon on grain boundaries or partial melt, although these materials are all known to be present in some mantle rocks and may play a role in electrical conduction in some circumstances.

ACKNOWLEDGMENTS

The author would like to thank Tom Shankland, Al Duba and Jeff Roberts for discussions pertaining to this paper, and Tom and an

anonymous reviewer. Support was provided by NASA and NSF through grants NAG5-13747 and EAR 00-87391.

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