

A High-Temperature Electrical Conduction Mechanism in the Lower Mantle Phase (Mg,Fe)_{1-x}O

David P. Dobson,* Nicola C. Richmond, John P. Brodholt

Measurements of electrical conductivity at high pressure and temperature were taken on the lower mantle phase magnesiowüstite with varying Fe³⁺ content. Although previous measurements at atmospheric pressure suggest Fe²⁺-Fe³⁺ hopping (small polaron) as the dominant conductivity mechanism, the present experiments show a change in charge transport mechanism with temperature. The lower temperature measurements are consistent with small polaron conduction, but at higher temperatures, which are more applicable to the lower mantle, a large polaron mechanism is suggested. Because these mechanisms have different temperature and compositional dependencies, this transition has important implications for extrapolation to mantle conditions.

Field measurements of electrical conductivity provide important information about lower mantle chemistry that cannot be obtained by other means. The electrical conductivity of most minerals is sensitive to subtle changes in defect chemistry, iron and water content, and oxygen fugacity. Experimental determination of the effect of these chemical components on conductivity might therefore provide important constraints on the chemical environment of the lower mantle.

Magnesiowüstite samples with no initial ferric iron were sintered from oxide mixtures at 1573 K and at a controlled partial pressure of O₂ (pO₂) as in (1). Pellets 0.6 mm long and 1.6 mm in diameter were loaded into a multianvil cell similar to that used by Omura (2) for use in our Walker-type multianvil press. A four-lead method using two R-type thermocouples as terminals allowed resistance of the measuring circuit to be filtered out. Iron loss to the terminals was less than 0.4% during the experiments. A Keithley DMM197 and a Hewlett-Packard 4284LCA measured the dc and ac sample resistance. Current leakage was minimized by use of an alumina cylinder between the sample and furnace. Tests with insulating blanks in place of the sample gave conductivities of <1% of the original value, showing that leakage within our experimental setup is minimal. Errors in measured conductivity, due to uncertainties in sample geometry, are 20%. Temperature was measured to ±1% using the terminal thermocouples.

In order to perform experiments on samples containing different ferric/ferrous ratios [Fe³⁺] = Fe³⁺/(Fe³⁺ + Fe²⁺), we used ei-

ther normal ceramic pressure media or ones doped with either 10% iron or 10% nickel. The metals consumed some of the available free oxygen, initially contained in pore spaces, that would have otherwise oxidized the sample. Although this procedure is not true buffering, we suggest that local equilibrium is reached, imposing some [Fe³⁺] on the sample, by consumption of all of the free oxygen during initial heating, and thereafter redox does not occur (3). The increase in electrical conductivity (EC) seen between 1000 and 1300 K during initial heating was probably the result of sample annealing, which may have also been related to redox as vacancies re-equilibrated. The EC measurements are, therefore, presented at fixed [Fe³⁺] rather than for oxygen fugacity (fO₂) buffer curves.

All experimental samples were examined by x-ray diffraction (XRD) and electron probe microanalysis (EPMA) and show absolutely no evidence for any minor phases. Additionally, Mössbauer experiments were performed on the most oxidized samples, and there was no evidence of magnesioferrite or other Fe-spinel phases.

Discussion will be confined to dc conductivity as this could be accurately measured to 200 megohms, whereas ac (1 to 100 kHz) measurements broke down at resistances above 10 kilohms because of inductive coupling with the furnace circuit. Samples with resistances below 10 kilohms produced identical dc and ac values. Two separate Arrhenius regions can be identified in each experiment (Fig. 1).

Electrical conduction in nonmetals is thermally activated with energy barriers for the production and motion of charge carriers: The conductivity is $\sigma = ne\mu$, where the charge-carrier density $n = n_0 \exp(E_f/kT)$, e is the charge on each carrier, the carrier mobility $\mu = \mu_0 \exp(E_m/kT)$, E_f and E_m are the activation energies of formation and

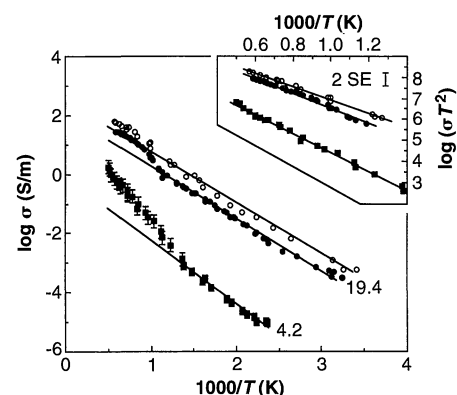


Fig. 1. Electrical conductivity (σ) plotted against absolute reciprocal temperature for samples containing 4.2 and 19.4% wüstite. Open symbols are for experiments at 10 GPa and [Fe³⁺] ~ 0.1, and closed symbols are for 5 GPa and [Fe³⁺] ~ 0. The two standard error bars for 4.2% wüstite are typical of all experiments. The two separate conductivity regions are evident from the deviation of the high-temperature measurements from the low-temperature, small polaron curve (solid line). (**Inset**) Plot of $\log(\sigma T^2)$ against reciprocal temperature for the portions of the curves that deviate from small polaron behavior. The linear relation supports a large polaron transport mechanism.

migration, k is Boltzmann's constant, and T is temperature. Possible EC mechanisms in magnesiowüstites include ionic conductivity with V_{Mg} [each dot denotes single electron deficiency (or vacancy); the subscript refers to the lattice site occupied by the species] charge carriers, large polaron electronic conductivity involving donor (Fe_{Mg}) or acceptor (Fe_{Mg}) impurities, and electronic hopping between Fe²⁺ and Fe³⁺ (small polaron).

There are several lines of evidence that suggest that the low-temperature conduction mechanism is in fact small polaron, as

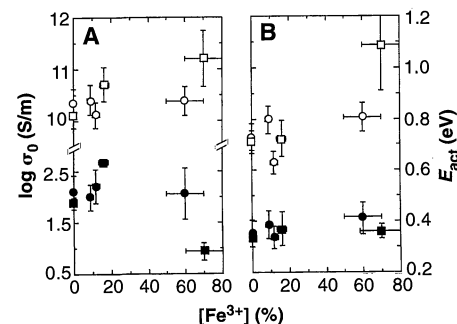


Fig. 2. (A) Pre-exponentials $\log(\sigma_0)_{SP}$ and $\log(\sigma_0 T^2)_{LP}$ and (B) activation energies E_{act} for 19.4% wüstite plotted against [Fe³⁺] at 5 and 10 GPa (circles and squares, respectively). The two standard error bars include the uncertainties in measuring T , σ , and sample dimensions as well as the error in fitting the data. Open and closed symbols are for large (LP) and small (SP) polarons, respectively.

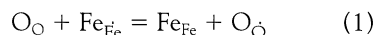
Department of Geological Sciences, University College London, London WC1E 6BT, UK.

*To whom correspondence should be addressed. E-mail: d.dobson@ucl.ac.uk

previously suggested (4, 5): (i) for Fe^{2+} - Fe^{3+} hopping, the maximum carrier concentration occurs at intermediate $[\text{Fe}^{3+}]$, as predicted by the low-temperature pre-exponentials (Fig. 2A), (ii) the low-temperature E_{act} of 0.3 to 0.4 eV, independent of $[\text{Fe}^{3+}]$, is consistent with small polaron conduction (1, 5–7), and (iii) the small activation volume of $-0.6 \pm 0.5 \text{ cm}^3 \text{ mol}^{-1}$, derived from experiments on 5 and 19.4% wüstite (all measurements are in mole percent) at 5 and 10 GPa, is as expected for small polaron processes.

Additional independent support comes from optical absorption spectra: The presence of a strong optical absorption around $15,000 \text{ cm}^{-1}$ is interpreted as Fe^{2+} - Fe^{3+} charge transfer (8, 9), consistent with small polaron conduction. Also, percolation theory for NaCl-structure, small polaron conductors predicts that there should be a large increase in activation energy below an iron content of 17.5% as hopping changes from nearest-neighbor to next-nearest-neighbor mode. This change is seen in measurements below 1000 K (7) but not at higher temperatures (5, 6). Therefore, at low temperatures, all experimental data point to a small polaron conduction mechanism.

At high temperatures, activation energies of 0.6 to 1 eV are too low for ionic conductivity, where estimated E_m falls around 2 eV (10). Processes with lower activation energies include ligand-metal charge transfer (LMCT), which is our preferred mechanism. The iron-oxygen bond is strongly covalent in character, facilitating charge transfer: for example



The mobility of holes in the $\text{O}(2p)$ valence band is large (11), and their extrinsic formation by the process described by Eq. 1 would cause large polaron conduction where carriers are not bound to lattice sites

(12). The mobility of large polaron charge carriers takes the form (13) $\mu = \mu_0 T^{-1/2}$. The excellent fit of the high-temperature data to a modified Arrhenius plot of $\log(\sigma T^2)$ against $1/T$ (Fig. 1, inset) is consistent with large polaron conduction. Additionally, the positive dependence of σ_0 and E_{act} on $[\text{Fe}^{3+}]$ (Fig. 2) is consistent with Eq. 1 as the carrier production process; carrier density increases with $[\text{Fe}^{3+}]$, and lattice distortion related to $\text{O}(2p)$ vacancies may cause an increase in E_{act} near vacancy saturation.

Additional support for a large polaron mechanism comes from optical absorption spectra, which suggest an activation energy for LMCT two to three times higher than that for small polaron transfer (8), in agreement with our measured E_{act} . The pressure intensification of LMCT optical absorption bands (14) supports the observed increasing importance of large polaron conduction with pressure. It is possible that phase changes in iron oxide spinels will significantly reduce ferric iron solubility in magnesiowüstite at higher pressures, but 0.1% or less ferric iron will cause extrinsic electronic conductivity to predominate. Optical absorption spectra demonstrate that there is sufficient ferric iron in magnesiowüstite at lower mantle pressures to cause significant LMCT.

All of our data and data from other studies (Fig. 3) can be reconciled through a change between large and small polaron mechanisms. The agreement between studies at low temperature is remarkably good; however, most studies terminate at temperatures below the onset of large polaron conduction. The existing high-temperature studies all show values of σ_0 and E_{act} higher than the equivalent low-temperature measurements. The measurements of Li and Jeanloz (5) made in an externally laser-heated diamond anvil cell show a different

temperature dependence for experiments on identical samples using identical preparation techniques for both sets of measurements. The combination of data from (1) and (15) for the same 17% wüstite at a similar $p\text{O}_2$ are also consistent with two conductivity regimes. Wood and Nell (1) interpreted their measurements at various values of $p\text{O}_2$ and atmospheric pressure to show small polaron conduction at mantle temperatures. However, experiments on the same sample (15) show a definite increase in E_{act} with temperature. At 1273 K, no maximum in EC was observed, but rather conductivity continually increased with increasing $p\text{O}_2$ across the stability field of the sample (15).

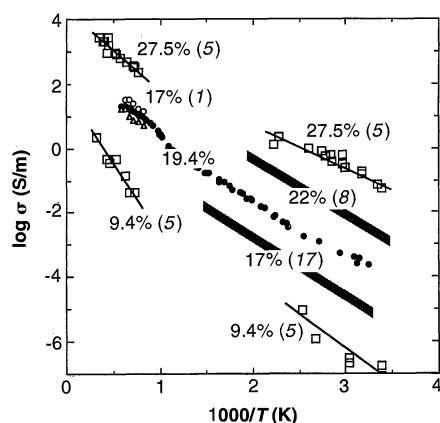
Wood and Nell (1) have demonstrated that the electrical conductivity of the lower mantle can be interpreted in terms of a network of conductive magnesiowüstite between an insulating matrix of perovskite. Our results for magnesiowüstite conductivity at high temperature, however, necessitate caution. Regardless of the aptness of the assumption that perovskite is essentially an insulator, temperature extrapolations of measured magnesiowüstite conductivity must use the large polaron temperature dependence; otherwise, they will be incorrect. Any attempt to apply low-temperature experiments to the lower mantle will yield conductivities as much as two orders of magnitude lower than they should be.

An additional factor in applying experimental measurements to the lower mantle is the weaker compositional dependence of large polaron conduction. In light of recent experimental studies of iron partitioning between magnesiowüstite and perovskite (16–18), which suggest that aluminum causes a partition coefficient close to unity, estimates of iron content in lower mantle magnesiowüstite should be revised from approximately 17% to around 10%. Although small polaron conductivity is reduced by at least three orders of magnitude between 20 and 10% total iron, large polaron mechanisms are not so strongly dependent on composition (Fig. 3). If magnesiowüstite is the main conductive phase, then a large polaron conduction mechanism means that EC does not place a particularly strong constraint on the iron content of the lower mantle, which is in sharp contrast to previous assumptions.

REFERENCES AND NOTES

1. B. J. Wood and J. Nell, *Nature* **351**, 309 (1991).
2. K. Omura, *Phys. Earth Planet. Inter.* **65**, 292 (1991).
3. Samples were analyzed by EPMA, powder XRD, and for those with maximum $[\text{Fe}^{3+}]$, Mössbauer spectroscopy. Samples quenched from high temperature and those cooled slowly were indistinguishable. Repeated cooling and heating cycles produced identical EC measurements, and there was no discernible

Fig. 3. Electrical conductivity of magnesiowüstites. Our data for 19.4% wüstite ($[\text{Fe}^{3+}] \sim 0$; 5 GPa) agrees well with other studies; numbers show mole % wüstite, followed by a reference. Open circles are for f_{O_2} equal to that of a fayalite-magnetite-quartz buffer ($[\text{Fe}^{3+}] \sim 0.2$), and triangles are for two log units more reduced ($[\text{Fe}^{3+}] \sim 0.01$), both at atmospheric pressure (1). These data are sufficiently higher than the Lawrence Livermore National Laboratory measurements (15) at 17% on the same sample [at an oxygen fugacity intermediate to that in (1) and at atmospheric pressure] to suggest a possible change in mechanism with temperature. Roberts *et al.* (15) state that an increase in activation energy was observed with temperature (2 eV at 1473 K), but only the low-temperature portion of the curve was considered accurate. Data from (5) and (8) are for samples in a diamond anvil cell at 30 GPa and unknown $[\text{Fe}^{3+}]$. The data of Li and Jeanloz (5) are consistent with a conduction mechanism that changes with temperature.



drift in conductivity for experiments where maximum temperature was maintained for 30 min. Given the demonstrably slow re-equilibration of magnesiowüstite with changing f_{O_2} (15), this evidence suggests that once the free oxygen was consumed by the pressure medium, $[Fe^{3+}]$ remained constant. We measured $[Fe^{3+}]$ in samples equilibrated under more reducing conditions using the change in unit cell parameter resulting from the incorporation of vacancies. A calibration curve of $[Fe^{3+}]$ against cell parameter was produced for large samples with the same total iron content equilibrated under gas mixtures using Mössbauer spectroscopy and XRD. The close agreement between predicted and measured $[Fe^{3+}]$ in samples equilibrated at given f_{O_2} demonstrated that the recoil-free fraction is equal in ferric and ferrous sites.

4. A. G. Duba and B. J. Wanamaker, *Geophys. Res. Lett.* **21**, 1643 (1994).
5. X. Li and R. Jeanloz, *J. Geophys. Res.* **95**, 21609 (1990).
6. H. K. Mao, *Carnegie Inst. Washington Yearb.* **72**, 554 (1973).
7. K. W. Hansen and I. B. Cutler, *J. Am. Ceram. Soc.* **49**, 100 (1966).
8. H. K. Mao, in *The Physics and Chemistry of Minerals and Rocks*, R. G. J. Strens, Ed. (Wiley, New York, 1976), pp. 573–582.
9. D. M. Sherman, *J. Geophys. Res.* **96**, 14299 (1991).
10. L. Volcador, A. Wall, S. C. Parker, G. D. Price, *Phys. Earth Planet. Inter.* **88**, 193 (1995).
11. Y. Xu and W. Y. Ching, *Phys. Rev. B* **43**, 4461 (1991).
12. Electronic charge carriers in ionic crystals cause sig-

nificant strain on the lattice around the excess charge. This combination of the carrier and its associated strain field is the polaron. The mobility of the polaron depends on the mean drift between formation and trapping and the ease of accelerating the carrier in an electric field. Small polarons are bound to lattice sites and can only move by jumps between nearest or next-nearest neighbors, whereas large polarons are free to move in the conduction or valence band of the crystal and consequently have far higher mobilities.

13. H. L. Tuller, in *Point Defects in Minerals*, R. N. Shock, Ed. (American Geophysical Union, Washington, DC, 1985), pp. 47–68.
14. T. Goto, T. J. Ahrens, G. R. Rossman, Y. Syono, *Phys. Earth Planet. Inter.* **22**, 277 (1980); D. M. Sherman, *Phys. Chem. Miner.* **12**, 161 (1985).
15. J. Roberts *et al.*, *Eos* **76**, S156 (1995).
16. T. Katsura and E. Ito, *Geophys. Res. Lett.* **23**, 2005 (1996).
17. T. Irifune, *Nature* **370**, 131 (1994).
18. F. Guyot, M. Madon, J. Peyronneau, J. P. Poirier, *Earth Planet. Sci. Lett.* **90**, 52 (1990); B. J. Wood and D. C. Rubie, *Science* **273**, 1522 (1996).
19. We wish to thank N. Cohen and the University of London Intercollegiate Research Service in Mössbauer Spectroscopy for their assistance in Mössbauer analysis of samples and H. O'Neill for useful discussion in an early stage of this project. This work was supported by the Natural Environment Research Council.

22 October 1996; accepted 22 January 1997

SBF Cell Cycle Regulator as a Target of the Yeast PKC–MAP Kinase Pathway

Kevin Madden, Yi-Jun Sheu, Kristin Baetz, Brenda Andrews, Michael Snyder*

Protein kinase C (PKC) signaling is highly conserved among eukaryotes and has been implicated in the regulation of cellular processes such as cell proliferation and growth. In the budding yeast, *PKC1* functions to activate the *SLT2(MPK1)* mitogen-activated protein (MAP) kinase cascade, which is required for the maintenance of cell integrity during asymmetric cell growth. Genetic studies, coimmunoprecipitation experiments, and analysis of protein phosphorylation in vivo and in vitro indicate that the SBF transcription factor (composed of Swi4p and Swi6p), an important regulator of gene expression at the G₁ to S phase cell cycle transition, is a target of the Slk2p(Mpk1p) MAP kinase. These studies provide evidence for a direct role of the *PKC1* pathway in the regulation of the yeast cell cycle and cell growth and indicate that conserved signaling pathways can act to control key regulators of cell division.

The coordination of polarized growth and cell proliferation is a critical process in many cell types. In yeast, the *PKC1* MAP kinase cascade functions to maintain the integrity of the cytoskeleton and cell wall (1, 2) and is a candidate regulatory system for coupling cell growth and proliferation. The PKC pathway contains Pkc1p, which activates a MAP kinase cascade that consists of sequentially activated protein ki-

nases: Bck1p(Slk1p), a MAP kinase extracellular signal-regulated kinase (MEK) kinase (MEKK), the redundant Mkk1 and Mkk2 MEKs, and Slk2p(Mpk1p), a MAP kinase (3). Genetic evidence has implicated this pathway in the regulation of cell cycle progression (4–6). In addition, the Slk2p MAP kinase is specifically activated during bud emergence and mating projection formation, periods of the cell cycle during which cell growth is highly polarized (7, 8).

The SBF transcription factor also regulates both the yeast cell cycle and polarized growth (9). SBF is a heterodimeric complex composed of the Swi4p and Swi6p proteins (10). SBF regulates the transition from G₁ into S phase by activating the expression of

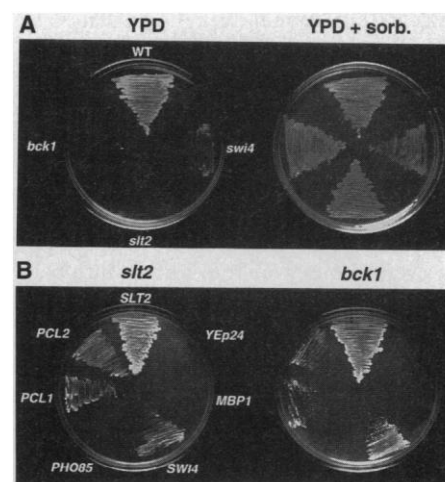


Fig. 1. Growth phenotypes of *SLT2* pathway and *swi4Δ* mutants, and suppression of the *slt2Δ* mutant by cell cycle regulatory components. (A) Growth of WT, *bck1Δ*, *slt2Δ*, and *swi4Δ* strains at 37°C on either rich YPD (yeast extract, peptone, dextrose) plates (left) or YPD plates containing 1 M sorbitol (right). (B) Assay for the suppression of the *slt2Δ* (left) and *bck1Δ* (right) growth defect at 37°C by either YEP24 vector alone or high-copy number plasmids containing either *SLT2*, *SWI4*, *PCL1*, *PCL2*, *PHO85*, or *MBP1* (22).

the G₁ cyclin genes *CLN1*, *CLN2*, *PCL1*, and *PCL2* (11–13). Cln and Pcl proteins associate with the Cdc28 (14) and Pho85 (13) cyclin-dependent kinases, respectively, to promote entry into S phase; Cln-Cdc28p complexes also promote polarized growth (15). Thus, both SBF and PKC function to mediate cell cycle progression and polarized growth.

We used a genetic screen (16, 17) to identify a mutation in the *SWI4* gene, *swi4-100*, that requires *SPA2* for growth (18). The Spa2 protein localizes to sites of polarized growth in yeast and is required for mating projection formation and proper bud site selection (19). Mutation of *SLT2* or *BCK1* is also lethal in the absence of *SPA2* (16). Moreover, other similarities are observed between *swi4Δ* and *SLT2* pathway mutants. Deletion of each kinase in the *SLT2* cascade results in temperature-sensitive growth, and at 37°C cells die by lysis; this temperature-sensitive growth defect is suppressed by the osmotic stabilizer 1 M sorbitol (3, 16) (Fig. 1A). Haploid *swi4Δ* mutants are also temperature-sensitive for growth at 37°C in some backgrounds (11), and like *SLT2* pathway mutants, this temperature sensitivity is suppressed by the presence of 1 M sorbitol (Fig. 1A). Also, *swi4Δ* mutants exhibit a defect in projection formation upon exposure to mating pheromone, as do *SLT2* pathway mutants (5, 8, 16, 18).

The phenotypic similarities between

K. Madden, Y.-J. Sheu, M. Snyder, Department of Biology, Yale University, Post Office Box 208103, New Haven, CT 06520–8103, USA.

K. Baetz and B. Andrews, Department of Molecular and Medical Genetics, University of Toronto, 1 King's College Circle, Toronto, Ontario M5S 1A8, Canada.

*To whom correspondence should be addressed.