diffusion-fundamentals.org

The Open-Access Journal for the Basic Principles of Diffusion Theory, Experiment and Application

# Absolute Diffusion Rates in Minerals of the Earth Lower Mantle from First Principles

*Michael W. Ammann, John P. Brodholt, Andrew J. Walker and David P. Dobson*

University College Department of Earth Sciences, Gower Street,
London, WC1 6BT, United Kingdom, E-Mail: m.ammann@ucl.ac.uk

## 1. Introduction

Diffusion controls most physical and chemical processes in the solid Earth. While experiments are limited to conditions of the shallow lower mantle, ab initio calculations allow us to probe conditions at any pressure and temperature. By applying harmonic transition state theory (Vineyard-theory [1]), we have calculated self-diffusion coefficients of $Mg^{2+}$, $Si^{4+}$ and $O^{2-}$ in MgO and MgSiO3 perovskite and post-perovskite at conditions of Earth's lower mantle from first principles. This is, to best of our knowledge, the first time that diffusion coefficients of complex materials such as MgSiO3 perovskite and post-perovskite have been calculated from first principles. Our approach relies on determining exact migration pathways using the climbing-image nudged elastic band method [2] and computing phonon frequencies using the small displacement method [3]. All quantities required by Vineyard-theory have been obtained from density functional calculations [4] (VASP [5]).

## 2. Active Diffusion Mechanisms

Our analysis shows that magnesium and oxygen in MgSiO3 perovskite migrate via simple single jumps to nearest neighbour sites. For silicon we propose diffusion via a six-jump cycle on the silicon-magnesium-B2 sublattice. In this mechanism, silicon diffuses by making use of vacated magnesium sites and magnesium uses vacated silicon sites. We investigated the rate of this mechanism using mean first passage theory [6] and the kinetic Monte-Carlo method [7]. The six-jump cycle mechanism works also in MgSiO3 post-perovskite allowing both cations to cross the octahedra-layers. Another interesting finding is that diffusion in post-perovskite is very anisotropic. Additionally, antistructure-bridge jumps could enhance magnesium diffusion across the octahedra-layers, depending on the degree of inversion, i.e. magnesia ions occupying silicon vacancies.

## 3. Comparison with Experiments

We compared our absolute diffusion rates with experimental data of magnesium and oxygen diffusion in MgO at temperatures between 1873 K and 2273 K and at pressures ranging from 7 GPa to 35 GPa. Our calculated diffusion rates of magnesium, silicon and oxygen in MgSiO3 perovskite have also been compared with experiments at 25 GPa with temperatures ranging from 1259 K to 2273K. All our diffusion rates are in excellent agreement with all the available experimental data.

## 3. Conclusions

We demonstrate that it is possible to calculate absolute diffusion rates from first principles, even for complex materials such as MgSiO3 perovskite where non-trivial diffusion mechanisms are at work. The excellent agreement between experiments and our calculated diffusion rates provides us with confidence that our diffusion rates in post-perovskite are correct despite that there is no experimental data yet available. Our results strongly support the idea that deformation within the lower mantle occurs via diffusion creep as we can readily reproduce viscosity profiles obtained from inversion modelling by assuming diffusion creep. The large anisotropy in post-perovskite suggests that the viscosity of post-perovskite strongly depends on the alignment of the grains and that it might be as weak as periclase. This would have important consequences for current convection models. Moreover, our results show that lattice diffusion in the Earth's lower mantle is too slow to assimilate even small chemical heterogeneities over the age of the Earth. Nevertheless, chemical assimilation may occur via grain-boundary diffusion. Lastly, oxygen ionic conduction can only explain inversion models of electrical conductivity in the shallow lower mantle, while towards the core-mantle boundary other mechanisms must be responsible for electrical conduction.

## References

[1] G. H. Vineyard (1957), *J. Phys. Chem. Solids* **3** 121-127

[2] G. Henkelman, B. P Uberuaga and H. Jonsson (2000), *J. Chem. Phys.* **113** 9901-9904

[3] D. Alfe. PHON - A Program to Calculate Phonons Using the Small Displacement Method. http://chianti.geol.ucl.ac.uk/ dario/, 2005

[4] P. Hohenberg, W. Kohn (1964), *Phys. Rev.* **136** B864-B871

[5] G. Kresse, J. Furthmueller (1996), *Phys. Rev. B* **54**, 11169-11186

[6] M. Arita, M Koiwa & S. Ishioka (1988), *Acta Metall.* **37** 1363-1374

[7] A. F. Voter (2005), *Radiation Effects in Solids* edited by K. E. Sickafus and E. A. Kotomin, Springer, NATO Publishing Unit