

The stable H and O isotope analysis of small highly saline water samples: A methodological study

A. DE HALLER¹, J. E. SPANGENBERG^{2*}, J. SMUDA²
AND M. KOROLEVA¹

¹RWI, Institute of Geological Sciences, University of Bern,
Switzerland (DeHaller@geo.unibe.ch)

²Institute of Mineralogy and Geochemistry, Univ. of
Lausanne, Switzerland

(*correspondence: Jorge.Spangenberg@unil.ch)

The isotope diffusive exchange technique is used to determine isotopic composition of pore water and the water content of low permeability rocks [1]. In the case of highly saline pore water, salt (NaCl or CaCl₂) has to be added (up to 6 molal) to the test water (≤5 ml) to avoid water transfer during equilibration with rock samples having low water activity. Quantitative distillation of the solution prior to analysis is the only way to eliminate the salt-induced isotopic fractionation [2] when using usual analytical methods (Cr or Zn reduction for δ²H, CO₂ equilibration for δ¹⁸O).

Here we report the results of a methodological study exploring different synthetic salt (NaCl, CaCl₂, Na₂SO₄ and NaF) solutions prepared at different concentrations (0 to near saturation) with five waters of known isotopic composition (δ²H = -275.6 to 3.4 ‰, δ¹⁸O = -35.3 to 0.4‰). Two distillation procedures were tested. Low-temperature distillation (LTD) was performed in closed system by heating at 90°C for >4 h followed by 1 h at 130°C. For high temperature distillation (HTD), the sample was heated in a closed system to 500°C for 1 h, and the residual salt to ~600°C for 10 min. The water sample was recovered cryogenically. The δ²H and δ¹⁸O values of all the water samples were determined using Cr-reduction in a ThermoFisher H-Device and CO₂-equilibration in a GasBench II, respectively.

For the moderately-hygroscopic salt solutions (NaCl, NaF and Na₂SO₄), the LTD gave results undistinguishable within the analytical error (±0.3‰ δ²H, ±0.1‰ δ¹⁸O) for pure water. The HTD gave good δ²H but inaccurate δ¹⁸O values for CaCl₂ solutions and is not suited for routine analysis. The addition of NaF to CaCl₂ solutions scavenges the Ca by CaF₂ (fluorite) precipitation, thus allowing the routine use of LTD on CaCl₂ solutions with results as good as for pure water.

[1] Rübél *et al.* (2002) *GCA* **66**, 1311-1321. [2] Horita (1989) *Chem. Geol.* **79**, 107-112.

Thermal conductivity of MgO periclase from equilibrium first principles molecular dynamics

NICO DE KOKER

Bayerisches Geoinstitut, Universität Bayreuth, D-95440
Bayreuth, Germany (nico.dekoker@uni-bayreuth.de)

Conductive transport of heat in an anisotropic medium in response to a thermal gradient ∇T is described by Fourier's equation:

$$\mathbf{Q} = -K_{ij} \nabla T$$

where \mathbf{Q} is the heat flux vector and K_{ij} is the thermal conductivity tensor, which reduces to a scalar of K in an isotropic medium. Finite lattice thermal conductivity is the result of anharmonicity, expressed as interaction among vibrational quanta (phonons). In the relaxation time approximation, this process is described as elastic collisions among otherwise independent phonons, and the thermal conductivity follows as an integration over the Brillouin zone:

$$K_{ij} = \sum_s \int_{\mathbf{q}} v_i v_j c \tau d\mathbf{q}$$

where v_i is the i -th component of the group velocity, c is the mode heat capacity, τ is the phonon lifetime, and N is the number of atoms per primitive unit cell.

We compute the phonon spectra and relaxation times by combining first principles molecular dynamics and first principles lattice dynamics computational methods. As a first implementation of the method, K_{ij} is computed for MgO periclase at pressures and temperatures relevant to Earth's entire mantle.

At ambient pressure we find very good correlation between vibrational frequencies computed using molecular dynamics, and those from lattice dynamics, indicating the validity of the assumption of weak anharmonicity embodied in the relaxation time approximation. Preliminary results for K_{ij} at ambient pressure show good agreement with experimental values, with relaxation times proportional to $1/T\omega^2$, in agreement with theoretical predictions of the temperature and frequency dependence of phonon-phonon scattering relaxation times.