# Isotope fractionation due to temperature gradients: Molecular dynamics simulation

GAURAV GOEL[1,2], DANIEL J. LACKS[2], JAMES A. VAN ORMAN[1,2], CRAIG C. LUNDSTROM[3], CHARLES E. LESHER[4]

[1]Department of Geological Sciences, Case Western Reserve University, Cleveland, OH 44106
[2]Department of Chemical Engineering, Case Western Reserve University, Cleveland, OH 44106
[3]Department of Geology, University of Illinois, Urbana, IL 61801
[4]Department of Geology, University of California, Davis, CA 95616

Experimental studies show that large isotope fractionation can occur along temperature gradients in silicate melts [1-3]. This thermally induced isotope fractionation can be much larger than the equilibrium fractionation between minerals and melts, In particular, lighter isotopes are found to be enriched in the hotter regions, and heavier isotopes are enriched in the colder regions of experimental charges, with the magnitude of the fractionation depending on the type of atom. The effect may be important in places such as at the edges of magma chambers and in other regions with sustained thermal gradients.

We have carried out molecular dynamics simulations to determine the factors that control the thermal fractionation of isotopes. The simulations are run for magnesium silicate melts (50-70% $SiO_2$), with non-equilibrium molecular dynamics techniques used to produce the temperature gradient. The results of the simulations are in good agreement with experimental observations [e.g. 2, 3], both in terms of the absolute magnitude of the fractionation and the relative magnitudes for different types of atoms.

The simulations are carried out as a function of pressure, to predict the behavior under conditions deep inside the earth, which experiments have not yet addressed. Increasing pressure change the magnitude of the isotope fractionation per temperature change for atoms that form part of the network structure (Si, O), but its effects are insignificant for atoms that are not part of the network (Mg).

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# Pb and Zn distribution in stalagmites

J. GÖTTLICHER[1]*, S. MARKS[2], R. SIMON[1], R. STEININGER[1] A. PLATTE [3] AND S. NIGGEMANN[4]

[1]Karlsruhe Institute of Technology, Institute for Synchrotron Radiation, Eggenstein-Leopoldshafen, Germany (*correspondence: joerg.goettlicher@iss.fzk.de)
[2]Münster, Germany
[3]Letmathe, Germany
[3]Dechenhöhle, Letmathe, Germany

The impact of atmospheric emission on carstwaters and carst bedrocks is investigated by analyzing speleothems (here: stalagmites of $CaCO_3$) for metals that have been set free during the early years of industrialization. Letmathe in the Sauerland (one of the low mountain ranges in Germany) was chosen as a suitable area because two caves (Dechenhöhle and Hüttenbläser) are located in the main wind direction about 1 km away from a Pb and Zn smelter operating from 1862 to 1925. Additionally, slices from beech trees (≈155-165 y old) close to the cave were available for measuring their metal contents. Evidence for airborne Pb and Zn in this area came from analyses of gypsum encrustations at a nearby rock formation [1] and from deer antlers [2].

The young zone of the stalagmites is grey colored compared to the beige inner and therefore older part. X-ray fluorescence (XRF) spectra of the stalagmites measured at the SUL-X and FLUO beamline of the synchrotron radiation source ANKA show discrete peaks for Pb and Zn in the gray zone, highest contents at the boundary grey/beige and almost no Pb and Zn in beige zone. Pb and Zn are partly correlated. XRF spectra of beech trees exhibit a few spikes of Pb but they are not concentrated in the older part as expected. Zn is represented by a large number of peaks of different heights and frequencies with time. In both types of samples (stalagmite, wood) a discrete occurrence of Pb and Zn have been found rather than a homogeneous elevation during the time when atmospheric emission was most intensive. For the stalagmites the Pb and Zn pattern could be explained by particular entry or by enrichments at grain boundaries of crystallites which has to be proven. For the nature of metal distribution in trees no explanation has been found so far

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