

Three methods for the calculation of equilibrium fractionation factors from isotopic exchange experiments.

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Three methods, based on a newly derived exact mass-balance equation for isotopes in a system containing multiple phases, have been used for the calculation of equilibrium fractionation factors (α) from isotopic exchange experiments. The first method is valid for pseudo first-order rate kinetics, similar to [1,2], the second for isotopic fractionation due to volume diffusion in a mineral phase with a restricted amount of fluid surrounding the mineral [3], and the third for net-isotopic fractionation due to dissolution-precipitation of a single phase, similar to [4]. The second and the third method both are forward calculating models, which allow the calculation of a final isotopic composition of the bulk mineral and water phases from their initial isotopic compositions. An algorithm is then used to minimize the difference between the final calculated isotopic compositions and the final measured isotopic compositions. In these methods the α values (mineral-fluid) and in the case of the second method the average diffusion coefficient of the diffusing element in the mineral, and in the case of the third method, the extent of the dissolution-precipitation reaction are simultaneously determined. All three new methods yield similar α values from a given experiment, which are in most cases also similar to previously determined values. Different α values for the same pair of phases calculated from different types of isotope exchange experiments done by different research groups are in most cases not related to the method of calculation.

These new derivations and methods also show that 1) The exact mass balance equation for isotopes of an element present in different phases is mathematically the same as for multiple elements substituting on sites in different phases (e.g. Mg-Fe in pyroxene and olivine). 2) During volume diffusion in a mineral, which is in contact with a fluid, only in the final stages towards equilibrium is the reaction of first order, with a constant rate constant. 3) The isotopic composition of phases at equilibrium is independent of the process, when local equilibrium is maintained at one point in the system during the process.

[1] Northrop D.A. and Clayton R.N. (1966) *J. of Geology* **74**, 174-196. [2] Criss R.E. (1999) *University press*, Oxford. [3] Crank J. (1975) *University press*, Oxford. [4] Dubinina E.O. and Lakshtanov L.Z. (1997) *GCA* **61**, **11**, 2265-2273.

Traces of a fossil deep biosphere in fracture fillings of the Äspö Diorite (Sweden)

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Organic biomarkers are widely used as molecular fingerprints for the characterization of recent and ancient microbially driven ecosystems. We here report on ToF-SIMS experiments aiming on organic remains of a fossil deep biosphere in fracture fillings within the 1.8 Ga old Äspö Diorite, Sweden. The fracture fillings consist of fluorite and calcite formed at low temperature conditions [1]. Samples were taken from a 50mm drill core obtained at 450 m depth in the Tunnel of Äspö (Äspö Hard Rock Laboratory). ToF-SIMS molecular mappings were performed on thick sections along the phase boundaries of fluorite and calcite. The measurements reproducibly revealed numerous organic compounds producing ions at e.g. m/z 44.05 (C₂H₆N), 55.06 (C₄H₇), 57.04 (C₃H₅O), 81.07 (C₆H₁₁). In addition, ions of complex organic molecules showing masses as high as 339 Da were observed within the fracture fillings. These substances are considered indigenous as they show a very specific distribution confined to the boundary between calcite and fluorite. Subsequent La-ICP-MS measurements on the same target areas revealed a concomitant, significant accumulation of the light rare earth elements (Lanthanum – Samarium) along mineral phase boundaries, most likely induced by biologically driven element fractionation. Additional investigations are underway to further elucidate these organic biosignatures in the ancient deep biosphere ecosystem.

[1] Drake, H., Tullborg, E.-V., (2004). SKB P-04-250.