Estimating isotope fractionation driven by nuclear size

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Mass-independent fractionation (MIF), where isotope abundance variations are disproportionate in mass, can have several causes. The nuclear field shift effect, proposed by Jacob Bigeleisen to explain mass independent uranium isotope signatures observed in chemical exchange experiments, stems from slight perturbations in chemical bond strengths caused by variation the volume and shape of nuclei[1]. It is unique in being a thermodynamically driven MIF mechanism that persists at conditions of equilibrium isotope exchange, and is truly independent of isotopic mass. Theoretical calculations have so far been limited to fairly small molecules, atoms and ions, in part because relativity becomes important for electrons interacting closely with nuclei, necessitating an approximate solution of the Dirac equation for electronic structure modeling. Methods for estimating isotopic fractionation factors in more complex materials are needed in order to understand recent detections of nuclear volume signatures in evaporating liquid metals, ores, and sediment, and to guide future studies. In this study we have developed procedures for cross-calibrating calculations made with relativistic electronic structure theory against less computationally intensive models.

Our initial goal was to calculate the equilibrium fractionation between liquid mercury liquid and mercury vapor to compare with experiment[2]. We observed a strong correlation ($R^2 \approx 0.9$) between a) relativistically estimated nuclear volume fractionation and b) the Mulliken population of 6s electrons in Hg-bearing species calculated with methods that incorporate relativistic effects only in the generation of a mercury pseudopotential. This is consistent with the strong correlation between atomic polar tensor charges and fractionation observed previously[3]. Based on the slope of the correlation (~1.5‰ in ^{202}Hg/^{198}Hg per 6s electron at 295 K), and estimated ~70-80% occupation of 6s orbitals in liquid mercury[4], we estimate 0.5-0.9‰ nuclear volume fractionation of ^{202}Hg/^{198}Hg between liquid and vapor, liquid being enriched in neutron-rich isotopes, and a positive Δ^{199}Hg signature of 0.1-0.2‰ in vapor. Including mass dependent fractionation effects, a total liquid-vapor ^{202}Hg/^{198}Hg fractionation of 0.7-1.3‰ is calculated, in good agreement with experimental results.

Plane-wave density functional theory methods, which can be applied to crystalline solids and liquids (within a periodic boundary condition approximation), appear to similarly show strong correlation with relativistic estimates of nuclear-volume fractionation. This suggests that it may be possible to estimate equilibrium MIF signatures in a wide variety of complex, geochemically interesting materials.

[1] Bigeleisen, 1996, JACS 118:3676. [2] Estrade et al. 2009, GCA 73: 2693; Ghosh et al, in press, Chem. Geol. [3] Wiederhold et al. 2010, Env. Sci. Tech. 44:4191. [4] Mattheiss et al. 1977, Phys. Rev. B 16:624.

The Rofna Porphyry Complex: Combining LA-ICPMS and CA-TIMS U-Pb ages on zircons.

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The Rofna Porphyry Complex (RPC) in the northern part of the Suretta nappe of the Penninic zone in eastern Switzerland, is mainly composed of two different lithologies: porphyritic rock types and augengneisses (Fig. 1). The augengneisses are cross-cut by porphyritic rocks and have been traditionally interpreted as Ordovician intrusives [1] without having any radiometric age control. Our field observations indicate that (a) the augengneisses show homogenous penetrative deformation whereas the porphyritic rocks reveal variable degrees of Alpine deformation, and (b) the augengneisses occur structurally above the porphyritic rocks (Fig. 1).

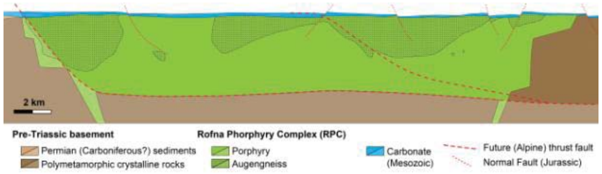

Figure 1: Restored section of the frontal part of the Suretta nappe - a feasible pre-Alpine constellation at the time of Jurassic rifting.

The magmatic event emplacing the porphyry has already been dated by ID-TIMS at 268.3 ± 0.6 Ma, which is a mean ^{206}Pb/^{238}U age of two nearly concordant multigrain fractions [2]. In order to constrain the age relationship between the different RPC rock types, we performed U-Pb LA-ICPMS measurements on zircons. In the augengneiss two age populations can be observed: One showing little spread at 311 Ma, and another younger one with a larger spread from 250 to 288 Ma. For the porphyritic rocks there is only one cluster of LA-ICPMS ages yielding an age range from 260 to 278 Ma.

Our new data suggest that the augengneisses are not the result of Ordovician magmatism, but may be related to the Variscian orogeny. The younger population in the augengneisses overlaps with the intrusion age of the porphyry and could either be the result of zircon neoformation or partial resetting of the U-Pb system.We therefore interpret the RPC as a composite late-Variscan and post-Variscan intrusive complex, where the pophyritic rocks followed pre-existing magma conduits, replenishing and disrupting the older augengneiss body at a shallow crustal level. High precision CA-TIMS data will provide further control of the emplacement relationships between these metamorphosed magmatic rocks.

[1] Spicher (1980) *Geological map of Switzerland*, 1:500.000. [2] Marquer, Challandes & Schaltegger (1998) *Schweiz. Mineral. Petrogr. Mitt.* **78**, 397-414.