Why metabolic processes fractionate oxygen isotopes

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Metabolic fractionation of oxygen isotopes during photosynthesis was first established experimentally by Ruben and co-workers [1]. Later, Dole and co-workers observed fractionation of O_2 isotopologues during respiration by whole organisms [2]. Soon after, Feldman and co-workers showed that O_2 consumption in enzyme catalysis gives fractionation factors that are similar to those seen during respiration [3]. This was taken as indication that fractionation observed during respiration originates from activity of metalloenzymes [3]. Using Bigeleisen formalism [4], Klinman and co-workers made the first attempt to relate $^{18}O/^{16}O$ fractionation to the structures of reversibly formed enzyme-O_2 adducts [5]. More recently, studies in laboratories of Roth generated several important benchmarks and improved our understanding of the origin of isotope fractionation in biological and inorganic systems [6]. Roth confirmed that isotope effects on reactions of O_2, $O_2^{\bullet-}$ and H_2O_2 at natural abundance levels can be employed for elucidation of reaction mechanisms as well as structures of activated intermediates and products (from kinetic (KIE) and equilibrium (EIE) isotope effects, respectively) [6]. It is appropriate to note here that establishing: 1) the relationship between KIE and EIE on elementary step and 2) the influence of ΔG_{rxn} on transition state structure, remains a major challenge [6]. Advancement may come from studies of $^{18}O/^{16}O$ fractionation in reactions of $O_2^{\bullet-}$ forming O_2. Unlike O_2 or H_2O_2, $O_2^{\bullet-}$ is unstable in aqueous milieu and converts rapidly into O_2 and H_2O_2. To obtain individual isotope effects, fractionation is measured on forward and reverse reactions. We investigated Cu,Zn-superoxide dismutase [7] and tripodal Cu^{II} complexes [8]. Formation of Cu-O_2 intermediates was found in both systems showing that use of isotopic oxygen fractionation provides new ways of connecting O_2 and $O_2^{\bullet-}$ reactivity patterns in solution and biological environments.

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High-precision Lu-Hf and Sm-Nd dating of eclogites from the SW Scandinavian Caledonides reveals protracted or multi-stage HP metamorphism

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The Scandinavian Caledonides comprise a thrust stack that contains several non-cogenetic eclogite-bearing terranes [1]. To contribute to our knowledge on the geodynamic history of this orogenic belt, we have dated eclogites from the Jæren nappe, SW Norway, by Lu-Hf and Sm-Nd geochronology. Five out of the six studied samples were eclogitized during the Middle Ordovician, yielding a weighted mean Lu-Hf age of 469.9 ± 1.2 Ma (± 2σ). The sixth sample yielded a younger Lu-Hf age of 457.9 ± 2.4 Ma.

Major- and trace element analysis showed that garnet in the younger sample comprises one growth zone, whereas garnet in the other samples comprise core- and rim zones. Bulk-garnet Lu-Hf ages may be systematically weighed according to Lu-distribution and may therefore not be representative for individual zones [2]. Age estimates that take Lu-contributions of each zone into account suggest a core age of 471.0 ± 0.9 Ma and a rim age of ca. 455 Ma. The data indicate two stages of garnet growth during protracted or multi-stage HP metamorphism.

Garnet showed a wide grain size range (0.1-3.0 mm). However, age heterogeneity among the five older samples only resulted from a variable degree of age-mixing. This indicates that—in spite of a thermal overprint at $T > 750$°C—the Lu-Hf systematics in garnet were not reset. In contrast, the Sm-Nd system was disturbed in at least four samples, yielding ages as young as 430 Ma.

Our results provide the first Middle Ordovician HP age in the Scandinavian Caledonides. They either reveal a previously unidentified HP event or provide more-detailed insight into a HP event that is recorded in other segments of the orogenic belt.

[1] Brueckner & van Roermund (2004) *Tectonics* **23**, TC2004, 1-20. [2] Lapen *et al.* (2003) *Earth Planet. Sci. Lett.* **215**, 57-72.