Universität Basel

Research Project

Isotope Fractionation of O2 Associated with Enzymatic and Photochemical Reactions in Aquatic Environments

Third-party funded project

Project title Isotope Fractionation of O2 Associated with Enzymatic and Photochemical Reactions in Aquatic Environments
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Molecular oxygen (O_2) is one of the most important electron acceptors for enzymatic and abiotic redox reactions in the environment. Enzymes that utilize O_2as the terminal electron acceptor catalyze a large number of biological reactions involved in processes of metabolic activity, cellular detoxification, and biosynthesis. Many of these reactions are essential for life, but some of them also contribute to the metabolic and co-metabolic removal of anthropogenic organic contaminants in natural aquatic environments and during wastewater treatment. Abiotic reduction of $O_2$is important for the biogeochemical cycling of elements, such as iron or other trace metals, as well as the photomineralization of organic compounds in sunlit surface water. Measuring systematic changes in the stable isotopic composition (i.e., isotope fractionation) of dissolved O_2during enzymatic reactions has been shown to enable the identification of underlying O_2reduction mechanisms. Consequently, measuring isotope fractionation of $O_2$is a promising tool for investigating environmentally relevant redox reactions. However, to ultimately apply this approach to reactions with unknown O_2reduction mechanisms, it is important to systematically extend the current knowledge of reaction-specific ^{18}O-kinetic isotope effects (^{18}O-KIEs), which ultimately determine observable isotope fractionation of enzymatic and abiotic reactions of O_2 in aquatic environments.The overall objective of this project is to experimentally determine reaction-specific ^{18}O-KIEs associated with selected enzymatic and abiotic O_2 reduction reactions and, in turn, to evaluate the potential of O_2 isotope analysis as a tool to study environmental redox reactions. The central part of this project will entail the systematic investigation of well-known enzymatic reactions in laboratory experiments to determine the dependence of O_2 consumption-associated ^{18}O-KIEs on the type of enzyme, substrate, and catalyzed reaction. Different O_2 reduction reactions will be studied in headspace-free reactors containing an oxidase or oxygenase enzyme, native or non-native substrates, and required cofactors and/or co-substrates. Reaction-specific ^{18}O-KIEs will be determined in replicate experiments, where O_2 concentrations will be monitored continuously, and the isotopic composition of dissolved O_2 will be measured at different time-points. Comparison of these ^{18}O-KIEs with isotope fractionation of O_2 during enzymatic oxidations of anthropogenic contaminants with unknown reaction mechanisms will represent the first step in our efforts to evaluate the suitability of this approach to study O_2 reduction mechanisms in anthropogenically impacted ecosystems. Similarly, ^{18}O-KIEs will be studied for photochemical reactions involving O_2 , including singlet oxygen and superoxide radical formation. The gas chromatography isotope ratio mass spectrometry (GC/IRMS) method used for these experiments will be optimized regarding sample size and the O_2 extraction procedure at the beginning of the proposed project.It is expected that results from this project will enable the routine use of isotope analysis of O_2

to study environmentally relevant redox reactions in laboratory-scale experiments and provide valuable mechanistic insights into specific enzymatic and abiotic redox reactions. The comprehensive set of ^{18}O-KIEs determined in this work will establish benchmarks for various abiotic and microbial O_2 consumption processes in the aquatic environment, which can be used in future studies applying isotope analysis of dissolved O_2 , or of organic products containing O-atoms derived from O_2, in natural systems.

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