

Paleoclimatic changes across the Cretaceous-Paleogene boundary: Geochemical reconstructions from Seymour Island, Antarctica

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The Cretaceous-Paleogene (K-Pg) boundary, ~66.0 Ma, marks the most catastrophic global extinction event of the past 100 Myr and is well documented in both terrestrial and marine biotic records. Although the K-Pg mass extinction occurred at a time when the Earth's climate operated under greenhouse conditions, the specific climatic and environmental changes associated with this event remain poorly understood. Shallow marine sediments exposed on Seymour Island, Antarctica (paleolatitude ~65°S) provide one of the most expanded K-Pg successions known. Moreover, the high latitudes represent areas of significant climatic importance due to polar amplification of global warming.

We first present a low resolution MBT/CBT (methylation of branched tetraethers/cyclisation of branched tetraethers) continental temperature reconstruction that indicates a persistent cool temperate climate (11.4 ± 5 °C) on the Antarctic Peninsula during the latest Cretaceous to early Paleogene. The addition of a higher resolution study across the K-Pg boundary is then used to investigate short-term paleoclimatic and paleoenvironmental perturbations, using MBT/CBT, BIT indices and biomarker abundances. Integration of these data with paleontological and paleobotanical datasets allows us to reconstruct the response and recovery of high latitude terrestrial and marine environments to the K-Pg global extinction event.

Reaction mechanisms, pathways, and transport in anaerobic abiotic and microbial U(IV)-oxide dissolution studies

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Applications of combined thermodynamic-kinetic descriptions to mineral-water interface processes that include chemical reactivity, microbial metabolism, and physical transport are challenged by the need to bridge differences in spatial and temporal scales for multiple, competing reactions. Even in simplified systems, formulation of reactive-transport model descriptions requires parameterization that must aggregate the details of molecular-scale reactions and microbial catalysis to some extent. Investigations of the oxidative dissolution of biogenic U(IV)-oxide (nominally $\text{UO}_2(\text{s})$) under anaerobic conditions by either chemical oxidants (nitrate or nitrite) or by *Thiobacillus denitrificans*, a chemolithoautotrophic bacterium that catalyzes anaerobic, nitrate-dependent U(IV) and Fe(II) oxidation, are used to examine coupled and competing oxidation-reduction processes in flow-through column experiments. Abiotic oxidation of $\text{UO}_2(\text{s})$ in the presence of nitrate under anaerobic conditions is slow but faster than control experiments of non-oxidative dissolution. Abiotic $\text{UO}_2(\text{s})$ oxidation by nitrite is significantly faster by several orders of magnitude. In the presence of *T. denitrificans* and dissolved nitrate, higher rates of dissolved U release were observed compared with abiotic controls, suggesting that *T. denitrificans* catalyzed the oxidative dissolution of $\text{UO}_2(\text{s})$ in addition to the abiotic oxidation pathways. X-ray spectroscopic characterization of reaction products indicates solid-associated oxidized U(VI) that is retained in the column. Analysis of local atomic structures shows formation of U-oxo molecular moieties within or on particle surfaces that are similar but not identical to aqueous or sorbed uranyl species, suggesting mostly surface particle oxidation rather than detachment and re-adsorption of uranyl in the column. Reactive transport modeling incorporating thermodynamic solubility, irreversible overall abiotic and biotic kinetic reactions, and uranyl sorption can simulate effluent U concentrations for a small amount of $\text{UO}_2(\text{s})$ oxidation relative to total mass, but calculations are sensitive to particle surface area.