

Potential significance of sulfide mineral oxidation for the Cenozoic carbon cycle

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A climatic control on the rate of CO₂ consumption by silicate weathering is thought to stabilize Earth's climate over geologic timescales. At the same time, the observation that tectonic uplift accelerates weathering rates suggests that mountain building can profoundly affect the carbon cycle and global climate. Extensive uplift of mountain ranges during the Cenozoic is thought to have increased silicate weathering rates as evidenced by the marine isotopic records of Sr, Os, and Li, which all show dramatic changes from ~40 Ma to present. Without a corresponding input of CO₂, increased silicate weathering fluxes would deplete the atmosphere of all CO₂ within a few million years, a clearly unreasonable scenario. While a variety of hypotheses have been put forward in order to balance the Cenozoic C cycle, none of them appear to adequately describe the observations. As such, reconciling this "Cenozoic carbon-weathering paradox" has been a major and as yet unresolved challenge in geochemistry and Earth history. We hypothesize that Cenozoic uplift, in addition to increasing rates of CO₂ drawdown by silicate weathering, increased rates of sulfide oxidation coupled to carbonate dissolution. This provided a transient source of CO₂ that contributed, at least in part, to the relative stability of Cenozoic atmospheric pCO₂. The feasibility of this hypothesis is tested in two ways: (1) a simplified mass balance model that constrains the duration of transient CO₂ release in response to increased rates of sulfide oxidation and (2) an inverse isotope mass balance model that uses the Cenozoic isotope records of Sr and Os to reconstruct changes in silicate weathering and sulfide oxidation rates. Together, these models show that the contrasting residence times of DIC and SO₄²⁻ is sufficient to allow for CO₂ release over 40 Myr timescales and that modeled rates of silicate weathering and sulfide oxidation are consistent with independent proxy records of paleo-pCO₂.

On-site porewater measurements of Lake Baikal sediments

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The extraction and analysis of sediment porewater is crucial to investigate the unique early diagenetic processes in Lake Baikal, the world's largest and deepest freshwater source. Investigation of the intricate sedimentary Fe/Mn layers requires porewater sampling and analysis with high spatial resolution and high yield of chemical parameters. Transporting the sediment samples from the field to the laboratory is logically laborious, and prone to contamination, temperature changes, outgassing, mixing, diffusion and redox changes. Therefore, on-site methods are to be preferred.

Here we present an on-site application of a high spatial resolution porewater sampling and analysing method. The facility, combining filter tube sampler and a portable capillary electrophoresis instrument, was set up in a container on the shore of Lake Baikal for the immediate porewater sampling and analysis after coring from the ice.

The extraction of one porewater sample and the detection of its major inorganic cations and anions including the nutrients P and N could be accomplished in less than 15 minutes. The disturbance of the sediment was minimal and oxygen-sensitive reduced iron (Fe(II)) was detected within the set of cations, including Li⁺, Na⁺, K⁺, Mg²⁺, Ca²⁺, NH₄⁺, and Mn(II) without splitting, acidification or dilution of the sample. The equipment is inexpensive, easy to handle and to transport.

