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**Zn/Si** opal as a paleoproxy: Insight into Southern Ocean processes

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Diatoms dominate ecosystems in large areas of the modern oceans including climatically important regions such as coastal upwelling zones and ice-edge blooms [1]. In particular, diatoms are abundant in the carbonate-poor sedimentary record around Antarctica, and the development of opal based proxies is essential for investigating past Southern Ocean processes. Here, we review some recent developments in the use of opal trace metal proxies and paleoceanographic applications.

Laboratory cultures show the zinc content of diatom opal, expressed as (Zn/Si)opal, relates to the concentration of free Zn²⁺ in ambient seawater [2]. Furthermore, modern diatoms from coastal Antarctica, collected in sediment traps, show a seasonal variation in (Zn/Si)opal relating to changes in production and water stratification. Comparison of these results and core top data indicates the (Zn/Si)opal signal is faithfully transferred to the sediments and records an empirical relationship with salinity. This calibration has been used downcore to investigate recent changes in the freshwater budget of coastal regions as a result of enhanced glacier and iceberg melting. The (Zn/Si)opal proxy has also been taken back further in time to investigate low resolution glacial-interglacial changes in micronutrient availability in the Southern Ocean.


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**Stable isotope composition of gaseous and dissolved oxygen in the subsurface**

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The presence or absence of O₂ is a crucial factor in biological and geologic processes and in defining the oxidation state of transitional metals. The atmosphere is the main source for molecular O₂ in subsurface environments, having a constant δ¹⁸O value of +23.5‰ (VSMOW). In the subsurface, this O₂ can be consumed by processes including organic matter decay, respiration, and oxidation of reduced metals. Although the stable isotopic composition of O₂ can reveal detailed information on processes influencing O₂, published δ¹⁸O data for soil and vadose zone O₂ are few and overwhelmingly collected within a meter of ground surface. Even fewer studies exist on dissolved O₂ and its δ¹⁸O in groundwater systems. This study was conducted to investigate processes controlling the concentration and δ¹⁸O of O₂ in unsaturated zones and near-surface phreatic aquifers. O₂ and δ¹⁸O samples were collected from vadose zones at nine field sites (n=92) and four phreatic aquifers (n=77). The range in O₂ concentrations ranged from atmospheric (20.9%) to 2.1% in the vadose zones and 12 to 1 mg/L in the groundwaters. The range in δ¹⁸O of the O₂ was great and mostly positive, ranging from +20 to +39‰ in vadose zones and +4.4 to +46‰ in groundwaters. Biogeochemical O₂ consumption reactions preferentially consume the ¹⁶O over ¹⁸O, and as a result the isotopic composition of O₂ in the subsurface is usually enriched in ¹⁸O and the resulting δ¹⁸O values were greater than +23.5‰ with the O₂ isotope fractionation by consumption (αₑ) ranging from 0.975 to 1.000. However, a confounding observation was that some vadose zones and groundwaters appeared to undergo an inverse oxygen isotope fractionating processes (apparent αₑ ranging from 1.000 to 1.300) resulting in δ¹⁸O values less than atmospheric values. Experimental data showed that natural subsurface radiolysis could produce anomalous ¹⁸O depletion observed at some sites. Circumstantial evidence implies that O₂ consumed during sulfide oxidation and precipitation of Fe-oxyhydroxides (or other unidentified processes) could also result in the ¹⁸O depletions. No definitive explanation for ¹⁸O depletions has yet been identified.