$(Zn/Si)_{opal}$ 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 Zn^{2+} 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 O_2 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 O_2 in subsurface environments, having a constant $\delta^{18}O$ value of +23.5‰ (VSMOW). In the subsurface, this O_2 can be consumed by processes including organic matter decay, respiration, and oxidation of reduced metals. Although the stable isotopic composition of O_2 can reveal detailed information on processes influencing O_2, published $\delta^{18}O$ data for soil and vadose zone O_2 are few and overwhelmingly collected within a meter of ground surface. Even fewer studies exist on dissolved O_2 and its $\delta^{18}O$ in groundwater systems. This study was conducted to investigate processes controlling the concentration and $\delta^{18}O$ of O_2 in unsaturated zones and near-surface phreatic aquifers. O_2 and $\delta^{18}O$ samples were collected from vadose zones at nine field sites (n=92) and four phreatic aquifers (n=77). The range in O_2 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 $\delta^{18}O$ of the O_2 was great and mostly positive, ranging from +20 to +39‰ in vadose zones and +4.4 to +46‰ in groundwaters. Biogeochemical O_2 consumption reactions preferentially consume the ^{16}O over ^{18}O, and as a result the isotopic composition of O_2 in the subsurface is usually enriched in ^{18}O and the resulting $\delta^{18}O$ values were greater than +23.5‰ with the O_2 isotope fractionation by consumption (α_k) 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 α_k ranging from 1.000 to 1.300) resulting in $\delta^{18}O$ values less than atmospheric values. Experimental data showed that natural subsurface radiolysis could produce anomalous ^{18}O depletion observed at some sites. Circumstantial evidence implies that O_2 consumed during sulfide oxidation and precipitation of Fe-oxyhydroxides (or other unidentified processes) could also result in the ^{18}O depletions. No definitive explanation for ^{18}O depletions has yet been identified.