Paleo-ocean chemistry records in marine opal: Implications for fluxes of trace elements, cosmogenic nuclides ($^{10}$Be and $^{26}$Al), and biological productivity

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Abstract

Here, we provide evidence suggesting that marine (diatom) opal contains not only a high fidelity record of dissolved oceanic concentrations of cosmic ray-produced radionuclides, $^{10}$Be and $^{26}$Al, but also a record of temporal variations in a large number of trace elements such as Ti, Fe, Zn and Mn. This finding is derived from measurements in purified biogenic opal that can be separated from detrital materials using a newly developed technique based on surface charge characteristics. Initial results from a sediment core taken near the present-day position of the Antarctic Polar Front (ODP Site 1093) show dramatic changes in the intrinsic concentrations of, Be, Al, Ti, Fe, Mn and Zn in the opal assemblages during the past $\sim$140 kyr BP. The results imply appreciable climatically controlled fluctuations in the level of bioreactive trace elements. The time series of total Be, Al, Ti, Fe and $^{10}$Be in the sediment core are all well correlated with each other and with dust records in the polar ice cores. The observations suggest that a significant flux of these trace metals to oceans is contributed by the aeolian dust, in this case, presumably from the Patagonia. This observation also allows determination of fluxes of dust-contributed $^{10}$Be to the Antarctica ice sheets. However, our data show that the relationships among the various metals are not perfectly linear. During periods of higher dissolved concentrations of trace elements (indicated by Fe and Ti) the relative concentrations of bioreactive elements, Be, Al, Mn and Zn are decreased. By contrast, the Fe/Zn and Fe/Mn ratios decrease significantly during each transition from cold to warm periods. The relative behavior could be consistent with any of the following processes: (i) enhanced biological productivity due to greater supply of the bioreactive elements (e.g. Zn) during cold periods (ii) increased biological and inorganic scavenging of particle active elements (e.g. Be and Al) during early interglacial periods (iii) differential uptake/removal of the metals by the various diatom taxa whose relative productivity or growth rate changes with large scale climate. In any case, with one sedimentary phase and in single sedimentary sections, we now have the potential to compare directly a proxy for aeolian input of micronutrients (e.g. Fe or Ti), with a proxy for production (e.g. $^{26}$Al/Al ratios). We expect that studies of the temporal records of trace elements and cosmogenic nuclides in contrasting regions of upwelling and productivity, which exhibit different sensitivities to global climate fluctuations and micronutrient inputs, would lead to a direct and comprehensive test of ideas such as the hypothesis of iron control of atmospheric carbon dioxide [Martin, J.H., 1990. Glacial–interglacial CO$_2$ change: the iron hypothesis. Paleoceanography 5, 1–13]. Our present data from a single site do not show that increases in dissolved Fe concentrations, per se, were responsible for increased biological productivity. However, a much clearer picture of the effect of increased dust fluxes should emerge when we have data for trace elements and the cosmogenic nuclides, $^{10}$Be and $^{26}$Al from various oceanic provinces.

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