Chromium mobilization from the unsaturated zone

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Recent work has shown that natural Cr(VI) concentrations in oxic, alkaline aquifers, especially those in mafic terrains, occasionally exceed the California Maximum Contaminant Level for chromium of 50 μg/L. δ^{53}Cr data in the western Mojave Desert intended to define the margin of a chromium contamination plume in an area having high natural background Cr(VI) concentrations revealed high Cr(VI) concentrations having near-zero δ^{53}Cr compositions at the top of the water table upgradient from obvious point sources of contamination. These values may be related to overlying land uses, especially land uses associated with large concentrations of animals. In the study area, high-sulphate concentrations, exceeding 2,000 mg/L, that are associated with animal-waste discharges appear to have mobilized Cr(VI) sorbed on iron and manganese oxides. This may occur because sulphate is an oxyanion having sorptive properties similar to those of Cr(VI). Oxic conditions in the unsaturated zone limit the reduction of Cr(VI) to Cr(III) despite the obvious presence of organic reductants. The reduction of Cr(VI) to Cr(III) is further limited by high-nitrate concentrations, exceeding 200 mg/L as N, that provide a more thermodynamically favourable electron donor—thereby partly inhibiting the reduction of Cr(VI) to Cr(III). As long as high-nitrate concentrations persist, Cr(VI) can persist in both the unsaturated and saturated zones at the site, even if anoxic conditions develop. Although these processes are probably more important in unsaturated zones in mafic terrains they also may occur in other geologic settings.

Evolution of deglacial North Pacific abyssal circulation based on $\Delta^{14}C$, $\delta^{13}C_{benthic}$ and $^{231}Pa/^{230}Th$

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Recent $\Delta^{14}C$ results from the Gulf of Alaska clearly show that the deep North Pacific was more poorly ventilated during the LGM when compared to today and that ventilation improved during the last glacial termination. During the last deglaciation, export production increased dramatically *ca.* 14.5 – 15 kybp across the entire subarctic Pacific, while the oxygenation of bottom waters increased as indicated by a decrease in redox-sensitive trace metal accumulation in the sediments. The remarkable temporal coincidence of changes in the deep and surface oceans suggests that the arrival of better-oxygenated deep waters was mechanistically linked to an increase in the upward flux of nutrients to the surface thus fuelling primary productivity. The close coincidence of this with the start of the Bolling warm period in the North Atlantic hints that a tight physical relationship linked the North Pacific circulation and the reinvigoration of the Atlantic meridional overturning at this time.

On the other hand, sedimentary $^{231}Pa/^{230}Th$ measured at ODP sites 882 (Emperor Seamount region) & 887 (Gulf of Alaska) show a sustained, parallel increase starting at around 17.5 kyr – significantly before any regional increase in particle flux. This signal is tentatively interpreted as illustrating the dissipation of a large ^{231}Pa pool accumulated in a relatively stagnant glacial abyssal Pacific Ocean at the onset of deglaciation.

In this contribution we will test the applicability of $^{231}Pa/^{230}Th$ as a proxy for relative changes in deep Pacific circulation across the last glacial termination. In addition, the apparent timing discrepancy between $\Delta^{14}C$ and $^{231}Pa/^{230}Th$ and its potential implication for the carbon cycle will be discussed.