Detection of non-stoichiometric silicate mineral dissolution in rivers draining alpine glaciers using $\delta^{44/40}$Ca

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Rivers draining glaciers frequently have high Ca concentrations, which have been attributed to the dissolution of carbonate minerals, even in predominantly silicate watersheds. Apportioning riverine Ca between silicate and carbonate weathering is typically done with the "Ca/Na method," which assumes that plagioclase is the dominant source of silicate Ca and that Ca and Na are released in stoichiometric proportions. Here, we tested whether high-precision Ca isotope measurements ($\delta^{44/40}$Ca by MC-TIMS, $2\sigma_{SD}=\pm0.07‰$) could track Ca sources to non-glacial and glacial rivers draining the Southern Alps of New Zealand. The mountain range consists of schist and greywacke containing trace hydrothermal calcite (1-3%). Hydrothermal calcite and silicate rocks are isotopically distinct. The Ca isotope composition of rivers is consistent with mixing between calcite and silicate sources. Glacial rivers are statistically different than non-glacial rivers ($p < 0.001$) and have more negative $\delta^{44/40}$Ca values. The glacial rivers plot closer to the silicate end-member. We observe no evidence for isotopic fractionation as a factor controlling the variability in stream water $\delta^{44/40}$Ca values. For non-glacial rivers, carbonate weathering provides ~50 – 90% of the riverine Ca, and more importantly, the Ca/Na and Ca-isotope source apportionment methods yield the same results within 2%. However, for glacial rivers, the Ca-isotope method yields 25% more Ca from silicate weathering compared to the Ca/Na method. Taken together, the data point to the enhanced release of silicate Ca in glacial watersheds. We attribute the effect to non-stoichiometric release of Ca from silicate mineral surfaces damaged by glacial grinding. One implication is that alpine glacial watersheds may consume atmospheric CO_2 at higher rates than previously realized.

Recent Changes in Coastal Aquifers: Local effects expressed globally

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Coastal populations are increasing rapidly, while potable water supplies are decreasing due to over-pumping and sea water intrusion into coastal aquifers. This problem has affected almost all coastlines during the past century. Here I focus on biogeochemical consequences of sea water intrusion into coastal aquifers, systems we call subterranean estuaries.

Oxygen is the most powerful oxidizing agent in most waters. However, its oxidizing capacity is limited by solubility (maximum ~0.28 mmol/L). Once dissolved oxygen is depleted, sulfate ion (~29 mmol/L in seawater) becomes the electron acceptor of choice to facilitate carbon oxidation. Thus seawater has a great deal more oxidizing capacity than fresh water. The reaction products of sulfate oxidation of organic matter include both inorganic and organic forms of dissolved N, P, and C as well as sulfide. Additionally, reducing conditions in the aquifer lead to reduction of iron and manganese oxides. This increases concentrations of Fe^{2+} and Mn^{2+} as well as other metals, plus ions that were absorbed onto the oxides. As this chemically-altered seawater exchanges into coastal waters as submarine groundwater discharge, it carries high nutrient, carbon, metal, and sulfide concentrations.

Continued seawater intrusion will lead to greater inland expansions of subterranean estuaries. This expansion may produce greater total SGD fluxes of nutrients, carbon, and metals because the biogeochemical reactions that affect their concentrations will operate over larger spatial scales and affect portions of aquifers that have not been in contact with seawater for thousands of years.

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