Reverse Weathering in Antarctic Biosiliceous Oozes: Ge/Si$_{CLAY}$

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Ge is a trace element in the Earth's crust (~1 ppm). It has the same outer electronic structure and covalent Ge-O radii as Si, and thus substitutes for Si in tetrahedral silicate structures. Goldschmidt's phrase "Ge behaves like a super-heavy stable isotope of Si" resulted from his discovery that Ge/Si ratios in igneous minerals are all about one Ge per million Si atoms (10^{-6}). Azam later found that diatoms incorporate Ge into their frustules without discrimination using radioactive ^{68}Ge as a Si-pseudo-isotope to probe biochemical enzyme pathways during diatom Si uptake, transfer, and opal formation. He predicted that diatoms in surface ocean waters should incorporate Ge as a surrogate for Si and then fall into the deep sea and be dissolved or buried. Oceanic vertical profiles of Ge/Si ratios (0.7 pM/μM or 0.7 ppm) confirmed Azam's predictions. Frustules buried in Southern Ocean siliceous oozes are also 0.7 ppm. Thus diatoms faithfully record the oceanic ratio. Fluvial and MOR hydrothermal mass balances of Si and Ge fluxes to the sea revealed a "missing Ge-sink" which was found to be authigenic Ge-enriched phases formed during reverse weathering of Si. It was also discovered that the diatom Ge/Si ratio in downcore Antarctic sediments varied systematically over the past 400,000 years from 0.7 ppm (interglacials) to 0.4 ppm (glacials), indicating that the ocean Ge/Si ratio varies on 100,000 year glacial-interglacial cycles, perhaps due to variations in forward and reverse weathering reactions driving fast ocean changes in both Ge and Si. Here we will present high resolution pore water Ge/Si profiles extracted from cores and WHIMP samples across the biosiliceous oozes between New Zealand and McMurdo to demonstrate that during opal dissolution and diagenesis Ge is preferentially incorporated into authigenic clays, probably via substitution into aluminosilicate structures of poorly-crystallized phases. Modeling of these profiles provides equilibria and kinetic results that match the lab kinetic and solubility data of Dixit and Van Cappellen. Marine reverse weathering is now understood to be a globally important sink for Ge, Si and cations, which we suggest is dependent on a supply of reactive Al to the seabed in C-poor biosiliceous sediments and reactive biosilica in Al-, C- & Fe-rich settings.