Sulfide weathering may have sustained methanogenesis across the Great Oxidation Event

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The Great Oxidation Event (~2.4 Ga), when free O_2 first accumulated in the atmosphere, was arguably one of the most profound turning points in the history of Earth and life. The causes and exact timing of this transformation are difficult to determine, but [1] argued persuasively that the transition from an anoxic, Archean atmosphere to a slightly oxygenated, Paleoproterozoic atmosphere required a dramatic decrease in the flux of biogenic methane to the atmosphere. The drop in methane production is thought to have resulted from either unsuccessful ecological competition of methanogens with sulfate-reducing bacteria [1] or a "nickel famine" [2,3], resulting from greatly reduced fluxes to seawater of this critical trace nutrient for methanogens. In an effort to piece together how the controls on the Ni supply to the oceans may have changed in the Latest Archean Eon, we have measured Ni isotope signatures in several suites of terrestrial and marine rocks. Our results indicate that the biogeochemical cycle of Ni underwent a transformation at ~2.7 Ga. The continental crust became much poorer in Ni, so Ni flux to the ocean fell. Ni isotope systematics indicate, however, that release of Ni from sulfide minerals likely sustained a small, but crucial flux of dissolved Ni. We hypothesize that, although methanogens likely became Ni-limited, they were able to continue producing enough methane to prevent the Earth from completely freezing over as the rise of oxygen took place.

[1] Zahnle et al., 2006, *Geobiology* 4, 271; [2] Konhauser et al., 2009, *Nature* 458, 750; [3] Konhauser et al., 2015, *Astrobiology* 15, 804.