Selenium isotopes as a proxy for deep-ocean redox state during the Paleoproterozoic Lomagundi Event

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The onset of the Great Oxidation Event at ~2.45-2.32 Ga has been constrained with multiple, independent proxies [1]. However, the structure of ocean redox across this transition remains unclear. It has recently been proposed that during the Paleoproterozoic Lomagundi Event (LE; 2.22-2.06 Ga), atmospheric oxygen levels rose dramatically before plummeting to lower levels in the mid-Proterozoic [2]. This 'oxygen overshoot' may have been enabled by a positive feedback wherein enhanced oxidative weathering of sulfides reduced the pH of continental runoff, enhancing apatite dissolution and delivery of phosphorus to the oceans. Increased cyanobacterial primary productivity and subsequent organic burial may have caused as much as 12-22 times the amount of present atmospheric oxygen to be released [3].

To test some predictions of this hypothesis, we examine the behavior of selenium (Se) – a redox-sensitive trace element that is primarily delivered to the oceans via oxidative sulfide weathering. Here we present Se abundances and isotope ratios from kerogen-rich shales deposited in offshore environments across the LE. Se isotopes from shales ranging in age from 2.32 to 2.1 Ga consistently show more positive values ($\delta^{82/78}$Se = +0.98 ± 0.68‰) than those deposited during any other time in Earth's history. This signature may reflect a redox-stratified ocean in which partial reduction of Se oxyanions in coastal, suboxic water preferentially removed lighter isotopes, enriching the residual offshore Se reservoir in heavy isotopes. Such a scenario has been invoked to explain the positive excursion in Se isotopes across the ~2.5 Ga oxygen 'whiff' in the Mt. McRae shale [4]. Our results suggest enhanced oxidative continental weathering, resulting in a significant flux of selenium oxyanions to the ocean. Given the high redox potential of selenium, this is consistent with a dramatic increase in atmospheric pO_2 and a redox-stratified ocean during the LE.

[1] Bekker *et al.* (2004) *Nature* **427**, 117-120 [2] Bekker and Holland (2012) *EPSL* **317**, 295-304 [3] Karhu and Holland (1996) *Geology* **24**, 867-8870 [4] Stüeken *et al.* (2015) *Geology* **43**, 259-262