Mobilizing Molybdenum: Interpreting Archean Oxidative Weathering Signatures

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Prior to the Great Oxidation Event (GOE) at ~2.45 Ga, several lines of evidence suggest small-scale, transient episodes of oxygenation in Earth's surface environment. Among these lines of evidence are the variations in abundance of redox-sensitive transition metals in Archean black shales, such as the Mo enrichment observed in the Mount McRae shale (2.5 Ga) from Western Australia. The interpretation of Mo enrichments as an oxidative weathering signature relies on the assumption that Mo is hosted in mineral phases sensitive to local O_2 concentrations, which are rapidly weathered upon the onset of oxidative weathering. If this assumption is correct, the mineral phase hosting Mo can be calibrated as a paleo-oxybarometer and inform us about the initial rise of O_2 in the surface environment.

Here we present a weathering model that approximates the minimum pO_2 required to mobilize sulfide-hosted Mo, using newly constrained rates of sulfide oxidation at Archean levels of O_2 ($<10^{-5}$ PAL pO_2). Rate measurements were made using highly sensitive O_2 sensors to monitor the rates at which powdered minerals consumed dissolved O_2 in pH-buffered solutions. We then used these rates to calculate the minimum pO_2 required to oxidize the minerals, mobilize redox-sensitive metals, and enrich nearby euxinic marine sediments to produce continental weathering signatures. Our results suggest that for short intervals prior to the GOE, dissolved O_2 in terrestrial waters exceeded nanomolar concentrations (equivalent to equilibrium with $>10^{-5}$ PAL pO_2).