

What happened in the Neoproterozoic? Investigations using a simplified Earth system model

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Basing our work on a Phanerozoic earth system model [1], we derive a stripped down, simplified system that can be used to investigate the events of the late Proterozoic. In a feedback-based approach, the model links the cycling of carbon, nutrients and oxygen to global biotic and tectonic processes. Using a parameterised ice-albedo feedback [2], we examine the conditions required for the initiation of self-sustained glacial oscillations. Hypothesised triggers [3, 4] for the Neoproterozoic snowball glaciations are simulated in the model and the resulting changes in atmospheric composition, nutrient deposition and stable isotope records are compared to geochemical proxies [5-7]. This allows us to make qualitative, falsifiable predictions based on these theories. For example, the balance between silicate weathering rate and volcanic degassing determines the long term concentration of carbon dioxide in the atmosphere [8]. We can initiate a glacial cycle either by enhancement of silicate weathering (due to early colonization of the land or tectonic processes associated with continental breakup), or by weakening of degassing. Some of these processes also increase atmospheric oxygen, broadly in line with the idea that oxygen increases at this time. The model geochemical record implied by scenarios such as these, together with evidence from the literature, constitutes a useful tool for examining this period and deciding which hypotheses are in most agreement with observations.

[1] Bergman *et al.* (2004) *Am J Sci*, **304**, 397–437. [2] Boyle. R. (2008) *PhD thesis*. University of East Anglia. [3] Lenton & Watson. (2004) *GRL*, **31**, L05202. [4] Stern. (2008) *Gondwana Research*, **14**, 33–50. [5] Halverson *et al.* (2005) *Geological Society of America Bulletin*. **117**, 1181–1207. [6] Canfield *et al.* (2008) *Science*. **321**, 949. [7] Fike *et al.* (2006) *Nature*. **444**, 744–747. [8] Kump *et al.* (2000) *Annu. Rev. Earth planet Sci.* **28**, 611–667.

Controls on the Formation of Geogenic Cr(VI) in Soils of the Sacramento Valley, California

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Chromium (III) is relatively non-toxic and immobile while Cr (VI) is a known carcinogen and highly soluble. Oxidation of Cr (III) derived from ultramafic rocks is a suspected source of Cr (VI) in ground waters in several parts of the world including the Sacramento Valley. Concentrations of Cr (VI) in some valley ground waters exceeds the California maximum contaminant level for drinking water (50 $\mu\text{g L}^{-1}$). A positive correlation between Cr (VI) and nitrate concentrations in some ground waters suggests that geogenic Cr oxidation processes may be exacerbated by agricultural activities. Our published geochemical survey of valley surface soils indicates their enrichment in total Cr (30-1420 mg kg^{-1}) relative to the U.S. geometric mean (37 mg kg^{-1}) due to transport of ultramafic material from surrounding mountains. Much of the Cr in valley soils is still bound as Cr (III) in refractory spinels, but a portion occurs as Cr (III) associated with iron oxide and clay particles. Manganese oxides, the major oxidant of Cr (III) in soil environments, are also abundant in both surface and vadose zone soils of the valley. Valley surface soils have undetectable Cr (VI), likely due to an abundance of organic carbon which can reduce Cr (VI) through both biotic and abiotic mechanisms. Up to 42 $\mu\text{g kg}^{-1}$ of Cr (VI) were detected in vadose zone soils, but Cr oxidation rates are likely limited by the mobility of Cr (III) in the pH range (7 to 9) of the soils. We performed a series of incubations with valley subsoil to investigate the controls on the oxidation of geogenic Cr in the valley and the potential influence of constituents in irrigation return water. The rate of Cr (VI) generation (24 $\mu\text{g kg}^{-1} \text{yr}^{-1}$) in control incubations was linear with time over 130 days. Chromium (VI) generation was much faster in soils amended with varying amounts of HCl. Increased mobility of Cr (III) due to proton exchange appeared to be the main driver of enhanced Cr (VI) generation, although increased solubility of chromite may have also contributed. Soils amended with ammonium sulfate initially exhibited enhanced Cr (VI) production due to proton exchange. However, increased carbon cycling as a result of the growth of autotrophic nitrifying bacteria resulted in reduction of the generated Cr (VI) later in the incubations. Our results suggest that agricultural practices have the potential to impact the generation rates and stability of geogenic Cr (VI) in the valley soils.