

Testing the ‘post-glacial weathering peak’ hypothesis – A lacustrine record of $^{87}\text{Sr}/^{86}\text{Sr}$

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Chemical weathering of the continents regulates levels of atmospheric CO₂, thereby acting as a primary control on Earth’s climate [1]. The effect of continental ice sheets, as observed during the Pleistocene, on this regulation of global climate is not clear. It has been suggested that repeated transitions between glacial (high physical weathering) and interglacial (high chemical weathering) states may have enhanced CO₂ drawdown during the Quaternary [2].

[2] argue that present riverine inputs to the oceans are still distorted by the last glaciation and are above the long-term average. During the incipient stages of chemical weathering the Sr released is more radiogenic than the bulk rock [3, 4]. Therefore, associated with the landscape rejuvenation caused by each Pleistocene glaciation one might expect a peak in radiogenic Sr in continental runoff. Such a ‘post-glacial weathering peak’ is required to explain the modern marine Sr budget [2, 5].

We attempt to test the ‘weathering peak’ hypothesis by constructing a record of Sr isotope composition of waters draining the Sierra Nevada through the last glaciation using ostracods in previously studied sediment cores from Owens Lake, California (e.g. [6]). Preliminary data from ostracods in Holocene sediments show elevated $^{87}\text{Sr}/^{86}\text{Sr}$ relative to the modern flow-weighted mean $^{87}\text{Sr}/^{86}\text{Sr}$ of streams in the Owens Lake drainage (0.70911) [7]. Further analyses will complete a record of the Owens Lake Sr isotope composition from ~40ka to the present day and will allow for a comparison to the contemporaneous extent of glaciers in the Sierra Nevada [6] thus allowing us to test the ‘post-glacial weathering peak’ hypothesis.

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[2] Vance *et al.* (2009) *Nature* **458**, 493–496. [3] Blum *et al.* (1997) *GCA* **61**, 3193–3204. [4] Keech *et al.* (2009) *GCA* **73**, 13 S1 A632. [5] Krabbenhoft *et al.* (2010) *GCA* **74**, 4097–4109. [6] Benson *et al.* (1996) *Science* **274**, 746–749.

[7] Pretti & Stewart (2002) *Water Resour. Res.* **38**, 10.1029/2001 WR000370

As, Fe and S cycling during reductive biomineralisation of pedogenic jarosite

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Jarosite (KFe₃(SO₄)₂(OH)₆) is an abundant Fe (III) mineral phase and important contaminant sorbent in coastal acid sulfate soils (ASS) [1]. Jarosite in these environments can be prone to reductive dissolution as a result of changes in local hydrology (e.g. sea-level rise and tidal seawater reflooding) [2]. However, very few studies have examined the reductive dissolution and transformation of K-jarosite, and the associated effects on contaminant mobility following seawater inundation of a jarosite-rich soil. Here we investigate the reductive biomineralisation of a natural As (V)-bearing pedogenic K-jarosite and explore the effects of a seawater gradient on the cycling of As, Fe and S. Solid and aqueous phase partitioning and speciation of As, Fe and S were determined using a wide variety of techniques including As- and S- K-edge XAS, TEM-SAED, SEM and XRD.

Whilst the rate and magnitude of fermentation processes were initially similar across the seawater gradient (100%, 10%, 1%), reductive dissolution of jarosite proceeded faster under 100% seawater conditions. Concentrations of Fe²⁺_(aq) were ~4-fold higher in 100% seawater and Fe²⁺:K⁺ ratios were initially congruent with respect to solid-phase jarosite. Evidence suggests both dissimilatory reduction of jarosite-Fe (III) and abiotic reduction of Fe (III) by sulfide produced via sulfate-reducing bacteria. Residual jarosite became increasingly polycrystalline and developed hollow cores. Disordered nano-particulate mackinawite was a primary mineralisation product after 140 days in 100% seawater.

While As mobilisation was generally correlated with Fe²⁺_(aq) production, As displayed highly contrasting kinetics across the seawater gradient. Initial release of As_(aq) was most rapid in low seawater treatments. Although As mobilisation in 100% seawater eventually exceeded the low seawater treatments, it was not substantially attenuated by the formation of mackinawite. The proportion of solid-phase As (III) increased over time and was greatest in 100% seawater. Findings provide important insights into the reductive dissolution of pedogenic jarosite following seawater inundation in coastal ASS environments.

[1] Keene *et al.* (2011) *Biogeochemistry* **103**, 263–279.

[2] Johnston *et al.* (2011) *Chemical Geology* **2**, 257–280.