

## Biogeochemical characterization of contaminant Mn sequestration

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Manganese contamination in soils is prevalent in industrialized regions. Over the past few centuries, large quantities of Mn have been extracted from the lithosphere, emitted to the air via anthropogenic activities, and redeposited to the Earth's surface. In order to evaluate environmental impacts of Mn deposition, we must better understand the biogeochemical behaviours of Mn in soils. Vegetation can act as an element "capacitor", storing large quantities of Mn and releasing it slowly into the environment over time. Here, we quantify mass fluxes of Mn amongst soil, vegetation, and pore fluid reservoirs in field and greenhouse experiments. We find that much greater quantities of Mn are taken up by vegetation than leached into pore fluids each year, preventing Mn loss from the soil system.

Characterization of Mn-compounds in the environment is often limited by their high reactivity and poor crystallinity; however, synchrotron source radiation can be used to map the microscale distribution of Mn (X-Ray Fluorescence) and identify its chemical state (X-ray Absorption Spectroscopy) in environmental samples. We use XRF and XAS to characterize the spatial abundance and chemical forms of Mn in mineral soil, organic soil, and tree leaf samples from both the field and a controlled greenhouse experiment. XRF analysis of leaves from trees exposed to high Mn reveals that the Mn is concentrated in visible dark spots, the key indicator of Mn toxicity in vegetation. XAS results indicate that Mn is present as an organically-complexed Mn<sup>+3</sup> compound in vegetation and as mixed-valence oxides (Mn<sup>+3/+4</sup>) in organic and mineral soils. Vegetation has previously been thought to contain primarily Mn<sup>+2</sup> due to the instability of the trivalent ion. The dominance of Mn<sup>+3</sup> in foliage would change current perceptions of biogeochemical Mn cycling and has implications for litter decomposition, a process that often uses Mn<sup>+3</sup> as a catalyst. The presence of Mn-oxides in soil organic matter is consistent with the rapid oxidation of Mn released from foliage during decomposition. High rates of Mn uptake into vegetation, combined with accumulation of solid-phase Mn in the soil, effectively increases the residence time of Mn in contaminated systems.

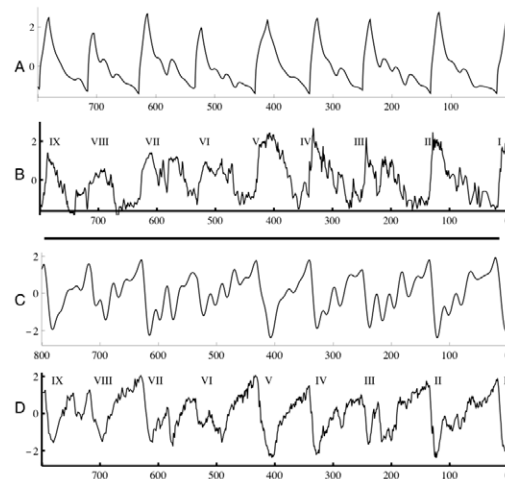
## Simulations of glacial/interglacial cycles with simple box-models: Key triggers for deglaciations

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García-Olivares *et al.* [1] have calibrated Paillard's model [2] to obtain a best fit with experimental time-series of  $\delta^{18}\text{O}$  and  $\text{CO}_2$  available for the last 800 kyr.



**Figure 1.**  $\text{CO}_2$  predicted by the model (A) and experimental time-series [3] (B). Ice Volume V predicted by the model (C) and  $\delta^{18}\text{O}$  experimental time-series [4] (D).

We discuss how the physical pump and, to some extent, the density of Antarctic deep water, may be important factors controlling the oceanic pulse that triggers deglaciations. Specifically, an increase of sea ice coverage during a glaciation may modulate the annual net heat gain of the Southern Ocean surface, and a reduction of the deep mixing rate would limit the upwelling of  $\text{CO}_2$  enriched deep water, thus being key factors for triggering deglaciations.

[1] García-Olivares & Herrero (2011). Submitted to *Scientia Marina*. [2] Paillard & Parrenin (2004) *Earth Planet. Sci. Lett.* **227**, 263–271. [3] Lüthi *et al.* (2008). *Nature* **453**, 379–382. [4] Lisiecki & Raymo (2005) *Paleoceanography* **Vol. 20**, PA1003, doi:10.1029/2004PA001071.