Iron nanoparticulates in icebergs: A source of bioavailable iron

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Ice-hosted sediments from Antarctica contain Fe nanoparticulates that are potentially bioavailable [1] and icebergs locally enhance productivity in the Southern Ocean [2]. Here we show that the rate of supply of potentially bioavailable, nanoparticulate Fe from melting icebergs is comparable to the soluble, bioavailable Fe from aeolian dust [5].

Antarctic glaciers and icebergs contain nano-phase schwertmannite, ferrihydrite and goethite. Concentrations (FeA) of nano-phase Fe estimated by ascorbate extractions removed 75-90% of ferrihydrite and 25-75% of nano-goethite with negligible effects on other Fe minerals [3]. Experimental evidence [4] suggests that this colloidal Fe is bioavailable with intracellular uptake rates of 15-20%.

Iceberg calving from Antarctica produces 2.5 Tm^3 yr^{-1} containing 0.5 kg m^{-3} of sediment [1] with a mean FeA = 0.06% (bioavailable Fe flux of 0.04-0.08 Tg yr^{-1}, Table 1). The flux of aeolian dust to the Southern Ocean is 33 Tg yr^{-1} and 1-10% of the total Fe believed to be soluble [5] and potentially bioavailable (Fe flux of 0.01 to 0.13 Tg yr^{-1}). We conclude that nanoparticulate Fe in ice-hosted sediment is a regionally significant source of potentially bioavailable Fe to the Southern Ocean.

Source	Mass Flux Tg yr^{-1}	Fe Content	Bio-availability	Fe Tg yr^{-1}
Ice	1250	FeA =0.06%	5-10%	0.11-0.15
Dust	33	Total Fe =3.5%	1-10%	0.01-0.13

Table 1: Bioavailable Fe Fluxes to the Southern Ocean.

[1] Raiswell *et al.* (2006) *GCA* **70**, 2765-2780. [2] Smith *et al.* (2007) *Science* **317**, 478-483. [3] Hyacinthe & Van Cappellen (2004) *Mar Chem* **91**, 227-252. [4] Chen *et al.* (2003) *Mar. Chem.* **81**, 177-189. [5] Jickells *et al.* (2005) *Science* **308**, 67-73.

Iron-nanoparticulates in ice-hosted sediments: A window into the subglacial environment

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The nature of the subglacial environment is poorly constrained and *in situ* sampling is difficult and does not necessarily reflect the range of chemical conditions resulting from the localised effects of regulation, microbial activity, and pressure gradients [1]. However sediments enclosed in icebergs and glaciers retain the mineralogical signatures of the subglacial environment [2].

High resolution transmission electron microscopy, selected area electron diffraction and energy dispersive X-ray analysis have identified Fe nanoparticulates in basal ice from glaciers in Antarctica (Taylor and Canada on granite, dolerite and sandstone bedrock) and Svalbard (Monaco on metasediments). All samples contained nanoparticulate iron phases (schwertmannite, 2-line ferrihydrite and goethite).

In surface terrestrial environments schwertmannite, ferrihydrite are unstable at ambient temperatures and near neutral pH and transform to geothite or hematite. Both schwertmannite and ferrihydrite can take months to years to fully transform to geothite, although goethite may initially appear after only a few days [3-4]. However, nanoparticulates enclosed in ice will be preserved for much longer by the low temperatures and limited water contact.

Schwertmannite has only been identified in acid mine drainage and its formation requires low pH (< 5) and high sulfate concentrations [4]. Its presence in basal ice from the Taylor and Canada Glaciers clearly indicates the existence of water at the base of these cold, polar glaciers. Furthermore the presence of schwertmannite in ice from a variety of bedorck suggests that site-specific factors do not control its formation. Instead it most likely forms where pyrite is oxidised in microenvironments containing thin films of oxygenated water, creating a low pH with rapid precipitation induced as water is removed by freezing.

[1] Tranter *et al.* (2002) *Hydrol. Proc*. **16**, 959-993.[2] Raiswell *et al*. (2006) *GCA* **70**, 2765-2780. [3] Regenspurg *et al.* (2004) *GCA* **68** 1185–1197. [4] Bingham *et al.* (1996) *GCA* **60**, 2111-2121.