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Nanoparticulate bioavailable iron minerals in icebergs and glaciers

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ABSTRACT

Ice-hosted sediments in glaciers and icebergs from Antarctica and Svalbard contain authigenic nanoparticulates of schwertmannite, ferrihydrite and goethite that formed during sulphide oxidation. These phases indicate the existence of subglacial biogeochemical hotspots containing fluids of low pH (2–4), rich in dissolved Fe(III) and sulphate. Nanophase Fe is partially bioavailable and potentially important to global biogeochemical cycles, since the flux delivered by icebergs to the Southern Ocean is comparable to the flux of soluble, bioavailable Fe from aeolian dust.

Introduction

GLACIAL comminution and the production of water in subglacial environments, either through geothermal heating or regelation during ice flow over irregularities at the bed, promote the production of authigenic Fe oxyhydr(oxides) that form by sulphide oxidation:

$$2FeS_2 + 7H_2O + 7/2O_2 \rightarrow 2Fe(OH)_3 + 4SO_4^{2-} + 8H^+$$

Raiswell *et al*. (2006, 2008) used high-resolution microscopy, combined with chemical extraction methods, to show that sediments hosted in icebergs and glaciers from Antarctica contain significant amounts of Fe oxyhydr(oxide) nanoparticulates. Here, we present further high resolution microscopy studies of Fe-bearing nanoparticulates in iceberg and subglacial sediments from Antarctica and Svalbard to show that they provide an important mineral signature for the chemistry of the subglacial environment, and that they are significant in global biogeochemical cycles due to their high reactivity and bioavailablity.

Sampling and methodology

Sediment samples were collected from icebergs in the Southern Ocean and subglacial ice (both sediment-rich and sediment-poor) from Taylor and Canada Glaciers (Antarctica) and the Monaco Glacier (Svalbard) (see Raiswell *et al*. (2008) for further details). All ice samples were melted onto coarse filter papers to collect the sediments, which were subsequently stored at 4ºC and air-dried when required for chemical analysis. Each sediment sample was treated with an ascorbate solution buffered at pH 7.5. The extractant was a deoxygenated solution of 50 g l^{-1} sodium citrate, 50 g l^{-1} sodium bicarbonate and 10 g l^{-1} of ascorbic acid. Approximately 30 mg of sample were mixed with 10 ml of the ascorbate solution, shaken for 24 h at room temperature and filtered through a 0.45 μm membrane filter. The Fe removed by ascorbate is hereafter termed FeA, and was measured using atomic absorption spectroscopy (AAS). This extraction removes 75–90% of nano-ferrihydrite and 25–75% of nano-goethite, with negligible effects on other Fe minerals (Hyacinthe and Van Cappellen, 2004).

Air-dried samples for microscopic imaging, nano-diffraction and elemental analyses were analysed using a Philips CM200 field-emission gun transmission electron microscope (FEG-TEM) equipped with an Oxford Instrument UTW energy dispersive X-ray spectrometer (EDS) and selected area diffraction (SAED) capabilities. The dried samples were re-suspended in ethanol by ultrasonication and deposited on standard holey carbon support films on copper grids (Agar Scientific Ltd) and imaged at 197 keV.

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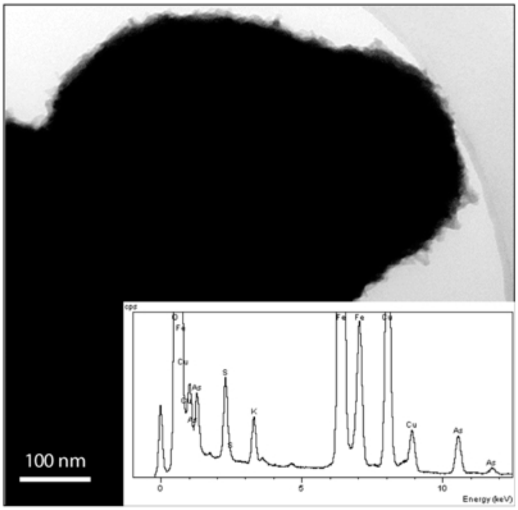

FIG. 1. TEM micrograph showing radially-oriented whiskers indicating As-rich schwertmannite. Inset shows the corresponding EDS pattern with S and As clearly shown. The SAED pattern revealed the two main SCH rings similar to those shown for ferrihydrite (see Fig. 2*a*).

Results and discussion

Chemical analyses of the sediments (Table 1) showed FeA ranging from 0.02−0.19%, with a mean and standard deviation of 0.06±0.05% for the Antarctic samples.

Various Fe phases were identified in the samples. Arsenic-rich schwertmannite (As-SCH) was identified in samples from Taylor, Canada and Monaco Glaciers as aggregates of 100 to 1000 nm in diameter (Fig. 1). These lacked the characteristic pin-cushion morphology of SCH (Bingham *et al*., 1990) but exhibited poorly-formed radially-oriented whiskers that are typical for As-SCH (e.g. Carlson *et al*., 2002). In addition, X-ray nano-diffraction and EDS analysis (inset Fig. 1) confirmed the phase as As-SCH.

Goethite (GT) occurred in all iceberg and glacial samples as laths typically <100 nm in length and 5−10 nm in diameter, assembled into bundles or star-shaped aggregates (Fig. 2*a*). Ferrihydrite (FH) occurred in all samples as nanoparticles (~5 nm diameter) in structureless aggregates and was identified by its morphology, nano-diffraction pattern (inset Fig. 2*b*) and EDS analysis, which showed an Fe-rich composition with As absent.

Origin of Fe nanophases

Schwertmannite is a poorly-ordered ferric (oxy)hydroxyl-sulphate nanophase with a variable composition, which commonly forms in acid mine drainage environments, where Fe(II) from Fe sulphides is oxidized to Fe(III) and SCH precipitates at pH 2−4 (Bigham *et al*., 1996).

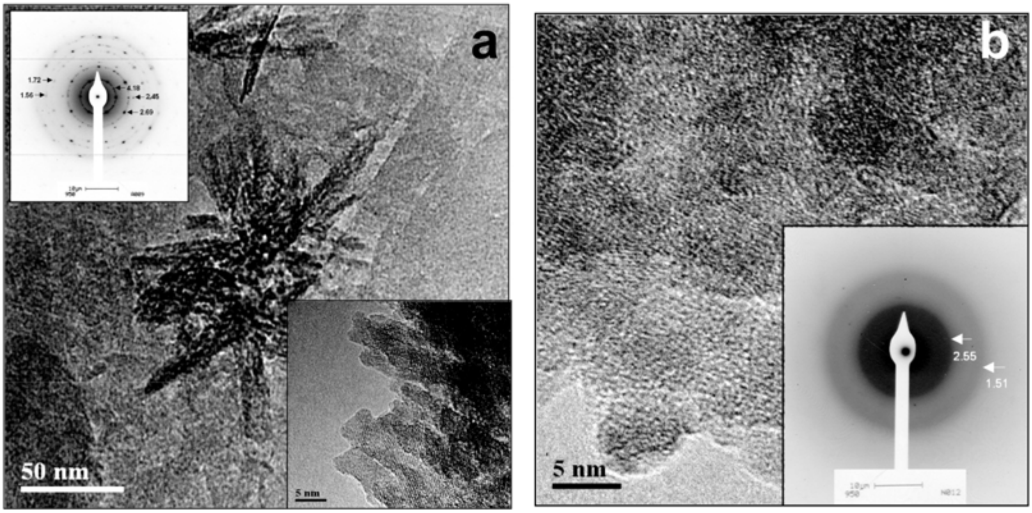

FIG. 2. (*a*) TEM micrograph of goethite laths. The insets show a high-resolution detail of the orientated attachment and the corresponding SAED pattern. (*b*) High-resolution TEM micrograph showing the nanoparticulate nature of 2-line ferrihydrite. The inset shows the two typical diffuse rings.

The surface energies of FH and SCH are small enough with respect to the bulk crystalline phases such that their nanoparticulate forms are metastable and their slow transformation kinetics enable them to persist in natural environments. Transformation of SCH to GT and hematite occurs via a FH intermediate (Davidson *et al*., 2008) with the transformation to GT being complete in 543 days at pH 3.9 and 100 days at pH 4–7.2 (Schwertmann and Carlson, 2005). Figure 2*a* suggests that continued GT crystal growth occurs by orientated attachment (Banfield *et al*., 2000), where nanoparticles of GT aggregate with their lattice fringes aligned.

It is unlikely that these Fe-bearing nanophases could have formed as a sample handling artefact because: (1) the pH of the icemelt was 6–7.5, dissolved Fe was 0.1–4 nm and these compositions are unsaturated with respect to FH (Raiswell *et al*., 2008); (2) the solubilities of SCH and FH increase with increasing temperature and contact with icemelt in the laboratory should result in dissolution and not precipitation; and (3) the As signal documented for SCH was confirmed in several samples. We conclude that the observed Fe nanophases are authigenic, although it is unclear whether FH and GT are original precipitates or represent products from the transformation of SCH and FH, respectively.

These iron nanophases indicate two significant features about the ice-rock interface. Firstly, SCH requires water for its formation, as do the transformations of SCH to FH, and FH to GT (Schwertmann and Murad, 1983; Davidson *et al*., 2008). Hence water must have been present at least transiently at the ice-rock interface of the Antarctic glaciers studied here, presumably during regelation and incorporation of sediment into the ice. Secondly, the abundance of FH suggests that fluids at the ice-rock interface were typically circum-neutral but biogeochemical hotspots with significantly lower pH (2–4), high dissolved Fe(III) and sulphate existed where SCH was stabilized by localized pyrite oxidation. The persistence of SCH and FH was additionally favoured by the low temperature (slow kinetics of transformation) and limited access to water.

Bioavailability

The solubility and reactivity of Fe nanophases in icebergs may play an important role in the biogeochemical cycling of Fe in the Southern Ocean (Raiswell *et al*., 2006, 2008; Smith *et al*., 2007), where productivity is Fe-limited. Bioavailable Fe can be supplied to surface waters in the Southern Ocean from a variety of sources (Lannuzel *et al*., 2007), but aeolian dust has usually been considered the most significant mineral source from outside the marine reservoir (Jickells *et al*., 2005).

However culture studies with marine diatoms (Wells *et al*., 1983; Rich and Morel, 1990) have shown that freshly-prepared, poorly-ordered Fe colloids can supply Fe for cell growth, but that more crystalline phases are not bioavailable. Chen *et al*. (2003) found intracellular uptake of 5–10% Fe from coastal and open-ocean colloids by marine diatoms over 12–24 h. These studies indicate that amorphous or poorly-crystalline FH are at least partially bioavailable, and this is the phase most readily extracted by ascorbate.

Raiswell *et al*. (2008) have estimated that iceberg calving from Antarctica produces 2.5 $\text{Tm}^3\ \text{yr}^{-1}$ of ice containing 0.5 kg m^{-3} of sediment. Table 1 indicates that such sediments have a mean FeA = 0.06% producing a potentially bioavailable Fe flux of 0.04–0.08 Tg yr^{-1}. By comparison, samples of aeolian dust have a mean FeA of 0.03%, but dust bioavailability is commonly estimated with respect to total Fe, 1–10% of which can be solubilized (the larger proportions requiring low pH cloud processing; Jickells *et al*., 2005). The aeolian dust flux to the Southern Ocean is 33 Tg yr^{-1} (Jickells *et al*., 2005) and thus the potentially bioavailable flux is 0.01–0.13 Tg yr^{-1} (Table 1). We conclude that nanoparticulate Fe in ice-hosted sediment is a

TABLE 1. Bioavailable Fe fluxes to the Southern Ocean.

Source	Mass Flux Tg yr^{-1}	Fe Content	Bioavailability	Fe Tg yr^{-1}
Ice-hosted sediment	1250	FeA = 0.06%	5–10%	0.04–0.08
Aeolian dust	33	Total Fe = 3.5%	1–10%	0.01–0.13

regionally significant source of potentially bioavailable Fe to the Southern Ocean, comparable to that from aeolian dust.

Conclusions

Sediment contained in icebergs and glaciers contain nanophases of schwertmannite, ferrihydrite and goethite that have originated from localized Fe sulphide oxidation. The existence of these phases clearly points to the presence of water, at least transiently at the bed of cold-based, polar glaciers. Sulphide oxidation generated chemical hotspots that produced low pH (2−4) fluids, which were rich in dissolved Fe(III) and sulphate, thus producing SCH. Nanophase Fe is partially bioavailable and the flux of ascorbate-extractable nanophase Fe delivered by icebergs to the Southern Ocean is comparable to the flux of soluble, bioavailable Fe delivered by aeolian dust.

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