

## Speciation of phosphorus in soils peripheral to meltwater ponds in Victoria Land, Antarctica

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Meltwater ponds are the most common habitat for terrestrial biota on continental Antarctica. The productivity of benthic cyanobacteria (the dominant biomass) is considered to be limited by phosphorus (P) availability in inland areas, but sources of P and factors limiting its bioavailability are poorly understood. Consequently it is difficult to predict how productivity will be affected by climate change-induced increases in pond size and volume. As part of a larger research programme to determine the P biogeochemical cycle for meltwater ponds, this study has explored P concentration and speciation in the soils near the ponds to identify additional potential sources of P to the pond water during periods of increased temperature and meltwater volume.

Over three years (2011 – 2013), soils were collected (together with sediments, waters and biological material) from 15 ponds from 3 areas of the Dry Valleys, and from 7 ponds in the McMurdo Ice Shelf /Ross Island region in Victoria Land, representing inland and coastal meltwater environments respectively. Concentrations of P were up to an order of magnitude higher in the soils of coastal ponds (mean = 2.2 g/kg), compared to inland pond soils (mean = 0.32 g/kg). P speciation, determined using standard sequential extraction methods indicated that <3% of the P in the soils was in a form that might be readily released during flooding or during the seasonal anoxia that develops in meltwater ponds. However, up to 10% was in a form that could be released under alkaline conditions (pH>10), as can occur during period of intense photosynthesis during summer months in the ponds.

The remaining P (70 to 99%) is refractory and less likely to be readily dissolved during soil flooding, though weathering of apatite and/or dissolution of refractory oxide phases may release P in the longer term, particularly from the relatively P-enriched coastal soils. In coastal ponds on the McMurdo Ice Shelf, pond sediments had <25% of the readily exchangeable P concentration in adjacent soils, and <80% total P, confirming immediate *and* longer term release of soil P into pond water.

## Green rust sulphate - making space for interlayer cations

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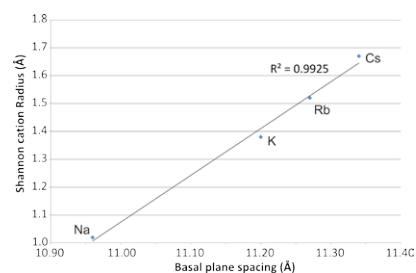
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Green rusts (GR) are layered double hydroxides with brucite like Fe(II),Fe(III) hydroxide layers. The surplus charge from Fe(III) is balanced by incorporation of anions and in some cases also cations. GR can reduce a range of redox sensitive compounds, e.g. nitrate, chromate and chlorinated solvents. GR forms readily in the laboratory at ambient temperatures, neutral pH and slightly reducing conditions, can be stable under groundwater conditions, making it a good candidate for contaminant remediation

Although GR has been the subject of numerous studies, several structural aspects are poorly understood. Interlayer ions for example, define the interlayer spacing, which in turn impacts interlayer accessibility for redox sensitive compounds and thereby the reactivity of GR. We have investigated interlayer incorporation of a range of monovalent cations (Na<sup>+</sup>, K<sup>+</sup>, Rb<sup>+</sup> and Cs<sup>+</sup>) in GR<sub>SO4</sub>. Synchrotron X-ray diffraction demonstrated that the interlayer spacing correlates with radius of the cations, showing that they intercalate.

X-ray photoelectron spectroscopy showed that interlayer incorporation differs greatly among cations and is correlated with the stability constant for the X<sup>+</sup>-SO<sub>4</sub><sup>-</sup> ion pairs. Infrared spectroscopy showed that sulfate symmetry was affected differently by the incorporated cations. If interlayer spacing limits anion or cation availability for reaction, our results indicate that the identity of the incorporated monovalent cation would also affect reaction rates.



**Figure 1.** Correlation between GR<sub>SO4</sub> basal plane spacing and ionic radius of cations in solution during formation.