

# PHOTO-INDUCED REDOX-CYCLING OF IRON IN SOUTHERN OCEAN WATERS

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**Iron (Fe) is a biological active element. The bio-availability of Fe is not simply a matter of concentration, but is especially depending on its chemical form. In order to better understand the limitation of iron on phytoplankton growth in high-nutrient-low-chlorophyll regions such as the Southern Ocean we investigated the effect of solar radiation on the chemistry and bioavailability of Fe. The project shows that light in concert with the chemical form of Fe plays an important role in the photoreduction and subsequent bio-availability of Fe. Moreover, the results suggest that diatoms can increase the photo-reduction of Fe(III).**

The redox-cycling of iron (i.e. the interconversion of  $\text{Fe}^{3+}$  (Fe(III)) and  $\text{Fe}^{2+}$  (Fe(II))) is supported by photochemical processes which potentially increases the bio-availability of Fe. To investigate the impact of enhanced ultraviolet B (UVB: 280-315 nm) on the photo-production of Fe(II) we determined the effect of the wavelength of light

( $\text{nm}^{-1}$ ). On board of the Polarstern (Fig. 1), deck-incubations already showed that UVB was the most effective wavelength region responsible for initiating the Fe redox-cycle (Fig. 2). Our results show that throughout the year, and even under ozone depleted conditions, the role of UVB in the photo induced redox-cycle of Fe is of

minor importance for the improvement of the bio-availability of Fe for phytoplankton in the Southern Ocean (Fig. 3).

Up to 99% of the dissolved Fe in the oceans is bound by dissolved organic molecules (ligands). Three of these naturally occurring molecules were found to influence the photo-production of Fe(II) (Fig. 4). Desferrioxamine B (a marine Fe binding molecule) decreased the photo-production of Fe(II). Moreover, it binds re-oxidized Fe(III) thus prevents the precipitation and transformation of Fe into a more reactive biological available fraction. In contrast, phytic acid (a metal complexing storage compound in terrestrial plants found in river run off) increased the photo-



Fig. 1. Research vessel "Polarstern".

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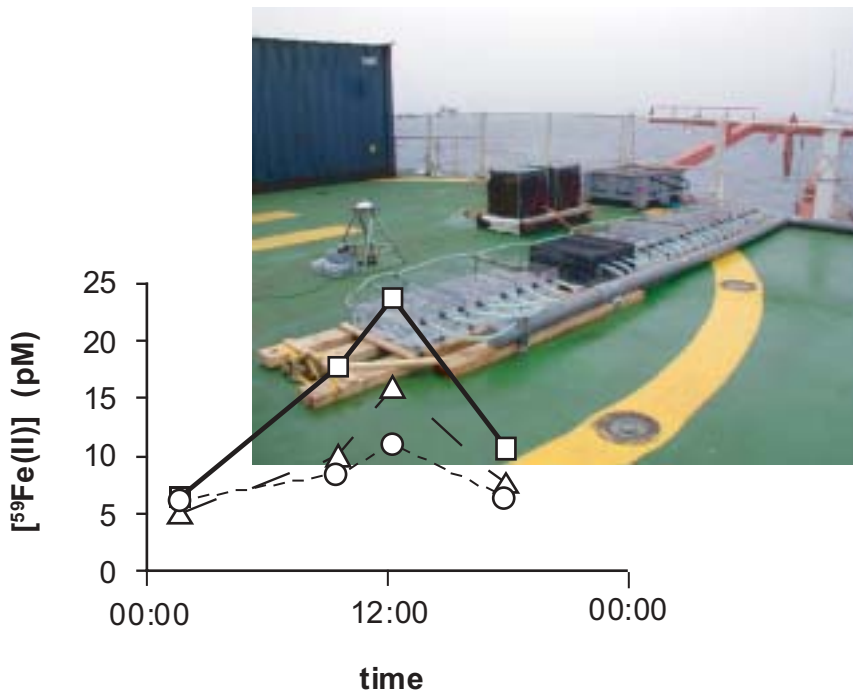


Fig. 2 The daily cycle of the concentration Fe(II) (pM) under three different light conditions, UVB+UVA+VIS ( $\square$ ), UVA+VIS ( $\triangle$ ) and VIS ( $\circ$ ) (UVA: 315-400 nm, VIS: 400-700 nm) as measured with deck-incubations in the Southern Ocean. The background shows the incubator on the helicopter deck of the German research vessel Polarstern.

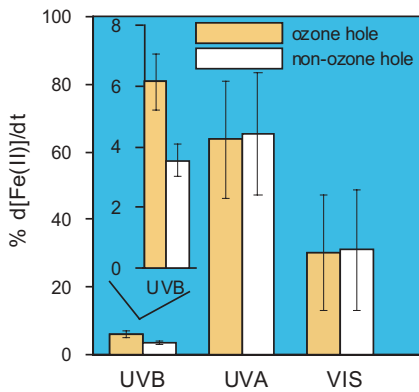


Fig. 3 The wavelength band dependent Fe(II) photo-production as percentage of the photo-production due to the total spectrum under ozone hole conditions (23 Sept. 2000) and under non-ozone hole conditions (9 Nov. 2000) at Palmer station.

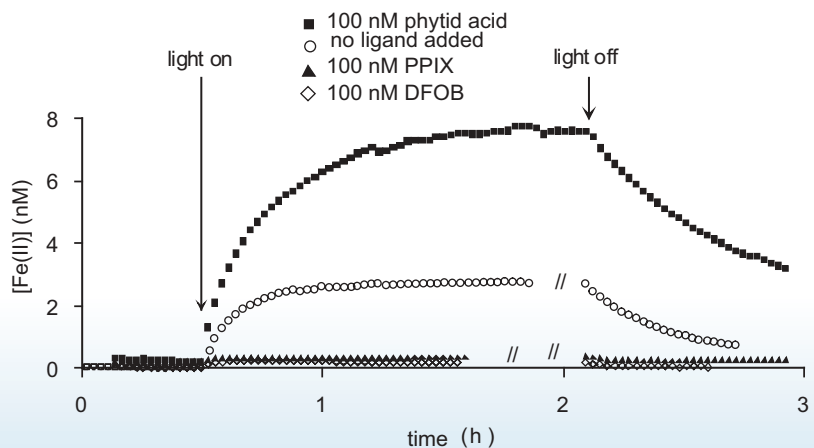


Fig. 4 The photo-production of Fe(II) without ligands added, and with 100 nM phytic acid, 100 nM protoporphyrin IX (PPIX) and 100 nM desferrioxamine B (DFOB) added. The Fe(III) (100 nM) was added to the Southern Ocean seawater before the experiments.

production of Fe(II). It increased the Fe fraction available for photo-reduction by influencing the precipitation of Fe. Protoporphyrin IX (PPIX) (representing ligands derived from the breakdown of phytoplankton photopigments, e.g. chlorophyll a) decreased the Fe(II) concentration by the binding of Fe(II). Yet, in a light driven catalytic process Fe(II)PPIX produced superoxide ( $O_2^-$ ) and free radical ligand species which reduced Fe(III) to Fe(II), even in the dark. The findings with PPIX are most relevant, because in open oceanic waters Fe is present bound to porphyrin-related molecules.

The natural organic Fe binding molecules in Dutch coastal seawater were insensitive for degradation due to UVA (315-400 nm) and

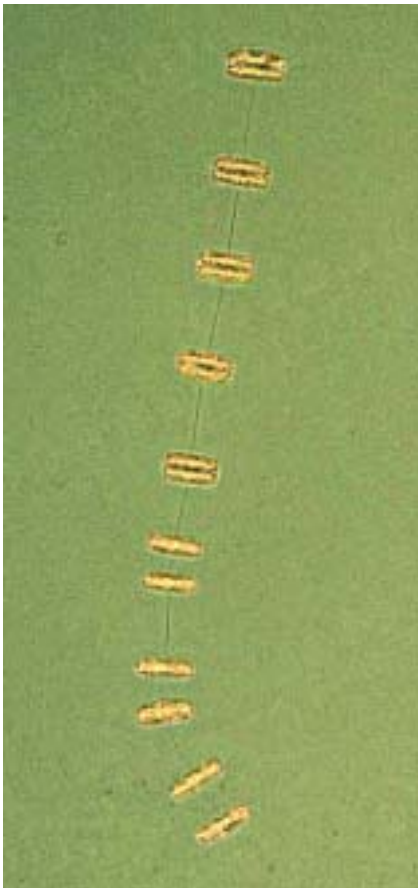


Fig. 5 *Thalassiosira* sp., an Antarctic open ocean and chain forming diatom with a cell length of ~ 70  $\mu\text{m}$ .

UVB. Although the organically complexed Fe concentration was high (24.4 nM), the Fe(II) concentrations upon irradiance stayed very low (< 240 pM Fe(II)). The Fe(II) production showed a similar pattern as the Fe(II) production from inorganic Fe colloids. These observations suggest that the Fe(II) originates mainly from the inorganic colloidal Fe fraction.

Photo-production of Fe(II) was also studied in the presence of two Southern Ocean diatoms, *Thalassiosira* sp. (Fig. 5) and *Chaetoceros brevis*. Both diatoms species increased the amount of photo-reducible Fe by releasing organic substances and thus

increasing the Fe(II) concentration. Moreover, *Chaetoceros brevis* transformed strong Fe binding molecules to weaker Fe binding molecules, thus also increasing the potential biological availability of Fe. Thus phytoplankton themselves influence the Fe chemistry. They can do that even with the use of light.