Speciation of iron regenerated through grazing

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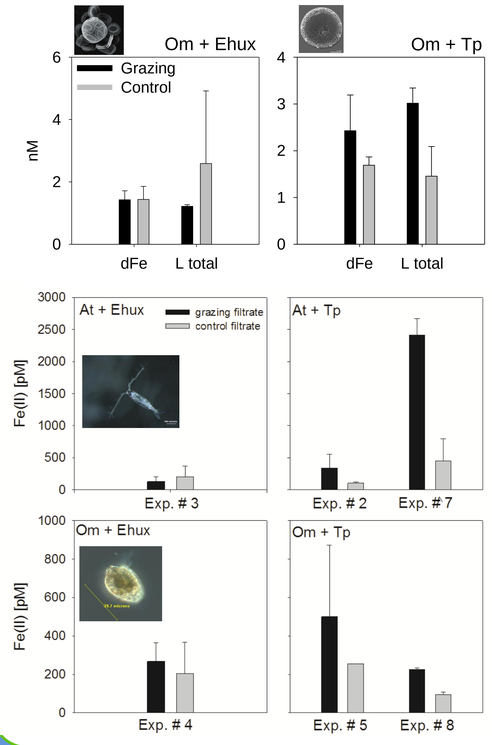
Abstract

Iron availability controls primary production and community composition in large regions of the global ocean. Like nitrogen, iron is readily regenerated following ingestion of phytoplankton by protistan and mesozooplankton grazers. In fact, in most systems a majority of the iron taken-up by phytoplankton has been regenerated, passing through a grazer digestive system en route to the phytoplankton. Laboratory and field studies have shown regenerated iron to be highly bioavailable. Despite this importance, only a handful of studies have documented the chemical speciation of iron regenerated by grazing. We conducted laboratory grazing incubations with the heterotrophic dinoflagellate *Oxyrrhis marina* and the calanoid copepod *Acartia tonsa*. Phytoplankton prey used were the diatom *Thalassiosira pseudonana*, the coccolithophore *Emiliania huxleyii*, or the cyanobacterium *Synechococcus*. Ingestion of diatoms by either the protist or copepod, or *Synechococcus* by the protist, resulted in higher Fe(II) concentrations compared to prey-free controls. In contrast, ingestion of *E. huxleyii* by either grazer did not produce elevated Fe(II). Regenerated Fe(II) was more stable than inorganic Fe(II), suggesting stabilization by Fe(II)-binding ligands. Increased concentrations of dFe and Fe(III)-binding organic ligands (FeL) were also measured in grazing experiments. Observations of vacuole pH in protist grazers suggest that *E. huxleyii* buffered pH changes, resulting in reduced acidification. Protist grazing experiments with natural plankton communities in the southern Indian Ocean also demonstrated elevated FeL and Fe(II) production via grazing. These results demonstrate the important impact of grazing processes on Fe speciation in the surface ocean.

Research questions

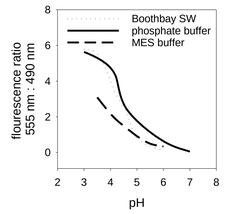
- Does protist and mesozooplankton grazing generate dFe, FeL, and Fe(II)?
- Does prey type affect regeneration of Fe?
- Is regenerated Fe(II) oxidized at a similar rate as inorganic Fe(II)?
- Can grazer digestive physiology explain Fe(II) production?
- Is Fe(II) generated during protist grazing in a natural ocean ecosystem?

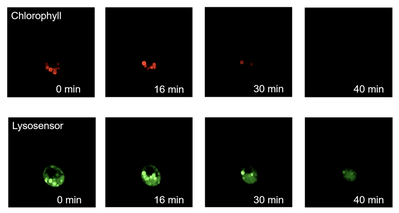
dFe, Fe(II) and FeL are produced during grazing of some prey



- Upper two panels: protist grazers (Om) produce dFe and Fe ligands when consuming diatoms (Tp) but not coccolithophores (Ehux)
- Mid and lower panels: both grazers produce Fe(II) from diatoms and cyanobacteria (Syn) but not coccolithophores
- This matches measurements of regenerated Fe bioavailability made in parallel experiments (Nuester et al. 2014. *L&O*. 59)

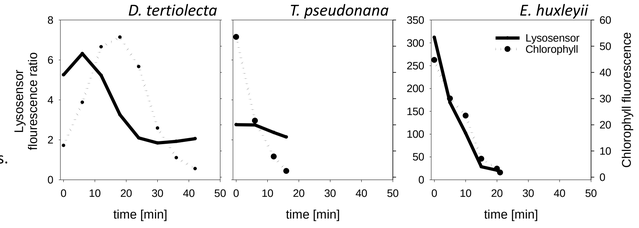
pH and redox conditions within grazer guts

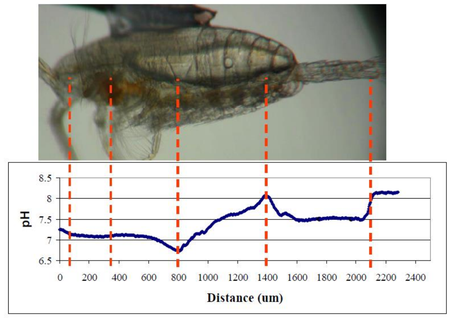




Left: *Oxyrrhis* gut pH measured with Lysosensor Yellow/Blue DND 160 fluorescent dye. Chl from algal prey is degraded with time.

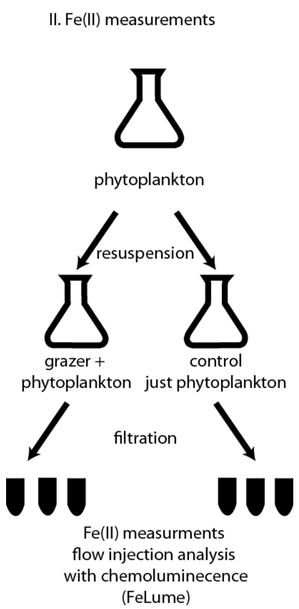
Right: *Oxyrrhis* gut pH and Chl during digestion of algal prey. pH dropped most rapidly following ingestion of coccolithophores.



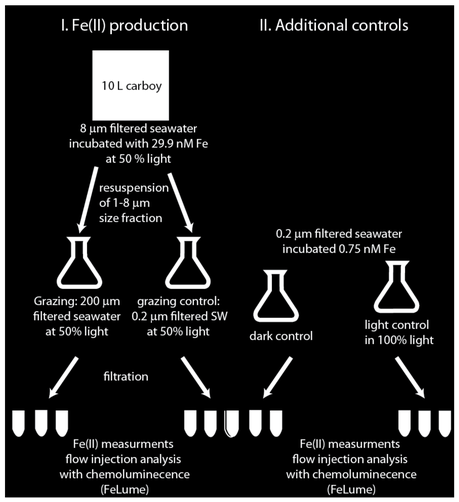


- Microsensor measurements of gut pH along live *Calanus* sp. show relatively minor reductions in pH compared to protists
- Published measurements of dissolved O_2 in copepod gut (Tang et al. 2011. *L&O*. 56) show reducing conditions in mid gut
- Recent work shows ingested coccolithophores buffer pH reductions in copepod guts (White et al. 2018. *Sci. Reports*).

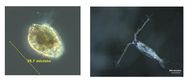
Lab experiments



Field experiments



Grazers



Oxyrrhis marina

Acartia tonsa

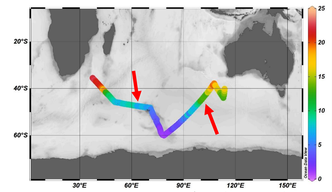
Prey

Thalassiosira pseudonana

Synechococcus

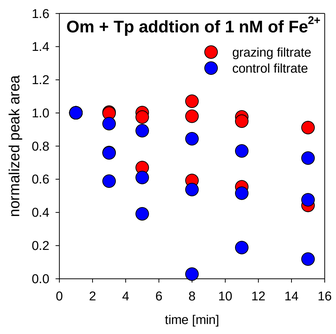
Emiliania huxleyii

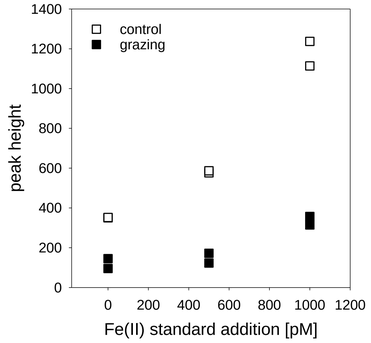
Site of field experiments



sea surface temperature

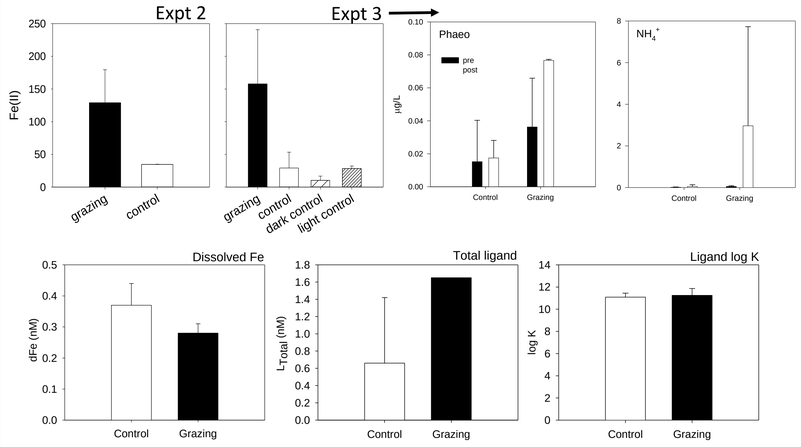
Fe(II) may be stabilized by ligands following regeneration





- Left: Fe(II) added to grazing filtrate oxidized more slowly than Fe(II) added to control filtrate, suggesting production of Fe(II) stabilizing ligands
- Right: Chemiluminescence instrument response to added Fe(II) was also reduced in grazing filtrate compared to control filtrate, indicating binding by ligands

Fe(II) and Fe(III)-ligands are produced in a natural system



- Two experiments with natural protist communities from Indian Ocean show Fe(II) production through grazing
- Fe(III)-binding ligands were produced by grazing, but total dFe was not higher, potentially due to rapid uptake by ambient phytoplankton in mixed community

Conclusions

- dFe, Fe(II), and FeL are regenerated via protist and mesozooplankton grazing
- Differences in instrument response and Fe(II) half-life between grazing treatments and controls suggest that Fe(II)-stabilizing ligands are produced in grazing treatments
- Fe(II) and FeL do not appear to be generated when grazing on calcified coccolithophores
- Coccolithophores appear to alter pH in digestive vacuoles, likely affecting Fe speciation
- Fe(II) and FeL are shown to be produced by natural communities of protist grazers

Acknowledgements

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