Trace metal uptake and remineralization and their impact on upper ocean stoichiometry

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### Why worry about trace metal remineralization from sinking (biogenic) particulate matter?



<sup>(</sup>Kwon et al. 2009)

#### Outline

- Coupled element cycles and stoichiometry
- Trace element micronutrients and macronutrients: coupled or uncoupled?
- Pre-GEOTRACES and FeCycle II data
- Particle remineralization in GEOTRACES NAZT and EPZT datasets



#### Macronutrient stoichiometries

- •Redfield ratio
- •Correspondence of dissolved and particulate N:P ratios

 $\rightarrow$  similar chemical lability (?)



#### The extended Redfield ratio

- Morel & Hudson 1985
- Bruland et al. 1991
- Numerous Sunda studies



 $(C_{124}N_{16}P_{1}S_{1.3})_{1000}Fe_{7.5}Zn_{0.8}Cu_{0.38}Co_{0.19}Cd_{0.21}Mo_{0.03}$  (Ho et al. 2003)

#### The extended Redfield ratio

Table 3P-normalized metal stoichiometries for the North Atlantic, North Pacific, and Southern Oceans, as calculatedfrom regressions of dissolved concentrations in the upper water column (typically <800 m)</td>

Site	Fe <sup>b</sup>	Zn <sup>c</sup>	Ni <sup>d</sup>	Cu <sup>e</sup>	Cof	Cd <sup>g</sup>	References
North Atlantic Ocean	$1.1 \pm 0.4$	2.6 ± 1.0	1.6 ± 0.1	0.30	0.061	$0.24 \pm 0.12$	Bruland & Franks 1983, Yeats & Campbell 1983, Martin et al. 1993, Sunda 1997, Lane et al. 2009
North Pacific Ocean	$0.5 \pm 0.3$	3.9 ± 1.2	$1.0 \pm 0.1$	$0.41 \pm 0.08$	$0.038 \pm 0.002$	$0.40 \pm 0.11$	Sclater et al. 1976, Bruland 1980, Martin et al. 1989, Sunda 1997, Lane et al. 2009
Southern Ocean	$0.2 \pm 0.04$	6.0 ± 2.6	$1.8 \pm 0.1$	$0.53 \pm 0.13$	$0.041 \pm 0.005$	$0.65 \pm 0.30$	Sunda 1997, Löscher 1999, Ellwood 2008, Lane et al. 2009, Saito
Ca.	0.6	4	1.5	0.4	0.045	0.43	2011, Croot et al. 2011

(Twining & Baines 2013)

 $(C_{124}N_{16}P_{1}S_{1.3})_{1000}Fe_{7.5}Zn_{0.8}Cu_{0.38}Co_{0.19}Cd_{0.21}Mo_{0.03}$ 

(Ho et al. 2003)

### Contribution of lithogenic and scavenged fractions



(Twining et al. 2016)

# Correspondence of bulk plankton and dissolved remineralization ratios in pre-GEOTRACES field data



(Twining & Baines 2013)

#### Is there clear evidence for decoupling of TMs during remineralization?

#### Early estimates of TEI-nutrient decoupling

CARRIER MODEL



METAL/P (BULK) X  $\beta$  X NET P FLUX = METAL FLUX

(Collier & Edmond 1984)

#### Early estimates of TEI-nutrient decoupling

 $\beta$  = <u>residual metal fraction</u> residual P fraction

Element	β
Cd	0.5 – 0.9
Ni	2.4
Cu	3.4
Mn	2
Zn	?
Fe	6

 $\beta$  estimated from shipboard leaching / element loss experiments

(Collier & Edmond 1984)

#### Decoupled TEI remineralization during a GEOTRACES process cruise



#### Remineralization stoichiometries during FeCycle II spring bloom



(Twining et al. 2014)

#### Remineralization stoichiometries along North Atlantic Zonal Transect



(Boyd & Ellwood 2010)

### Comparison of remineralization stoichiometries for additional NAZT trace metals



Particulate data taken from pumps (Ohnemus and Lam) and corrected for lithogenic fraction



## Investigating decoupled remineralization through power curve fits



Martin et al. (1987): 
$$P(z) = P_0 \left(\frac{z}{z_0}\right)^{-b}$$

(Lam et al. 2011)



### Over what depth ranges can power curves be used to model remineralization?



#### Comparison of b values between ocean basins



<u>Caveats</u>: pumps vs. bottles; comparison restricted to offshore stations



#### **Eastern Pacific Zone Transect cruise**

#### **Outstanding questions**

- Can scavenging and the contribution of non-biogenic particle fractions be better constrained?
- Is trace metal remineralization from sinking biogenic matter truly decoupled? If so, what controls this decoupling?
- Do resulting vertical fluxes for nutrients match independent estimates?
- What spatial and temporal variability is there in these processes?

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