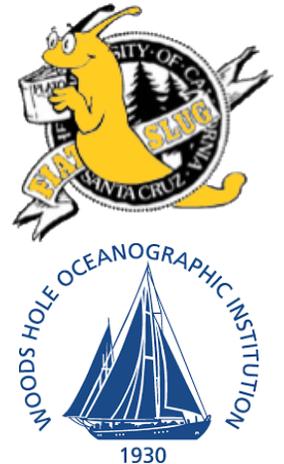


Marine particles: Distribution, composition, and role in scavenging of TEIs

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Joint OCB/GEOTRACES synthesis workshop on
Biogeochemical cycling of trace elements within the
ocean

August 1-4, 2016, LDEO

Many thanks to:



Daniel Ohnemus, pump team, many GEOTRACES collaborators

Particles are key to the biogeochemical cycling of most elements in the ocean

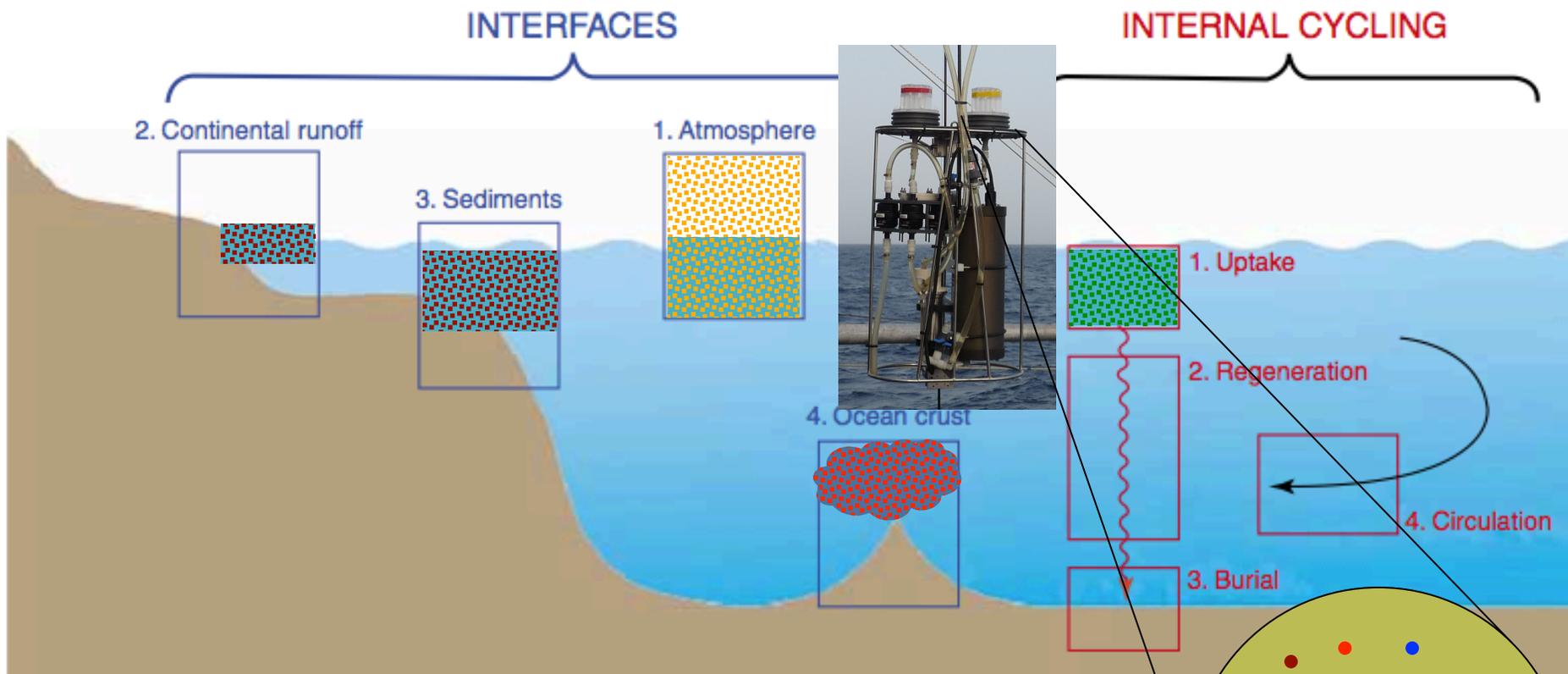
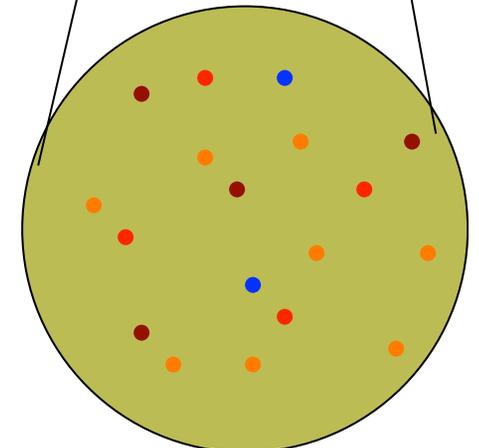
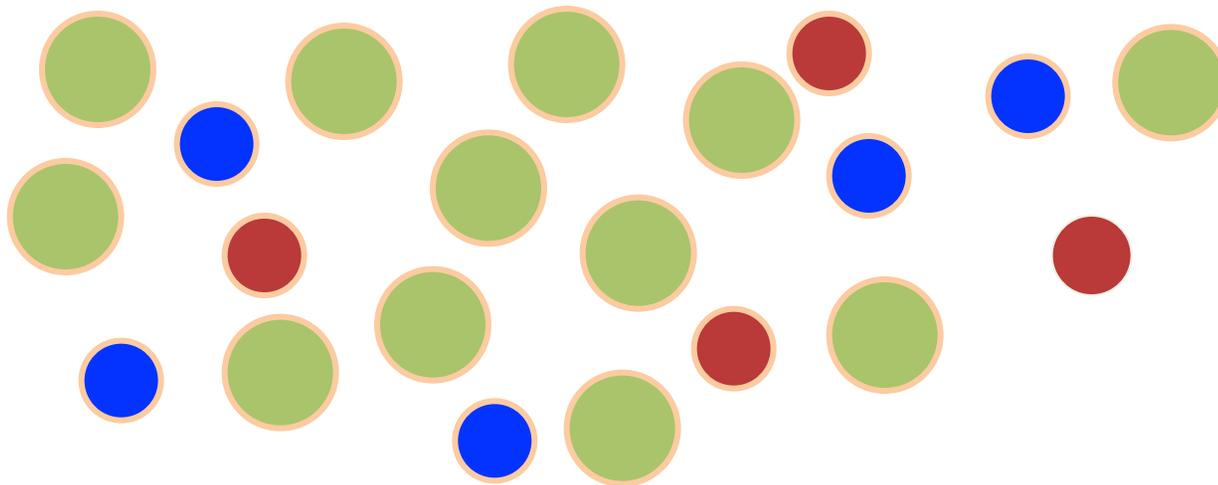


Figure 12. A schematic diagram illustrating the major influences on the distribution of TEIs. ocean interfaces (blue) and four major internal processes (red) are responsible for ocean TEI. GEOTRACES, interface processes form the basis of Theme 1, while internal cycling processes

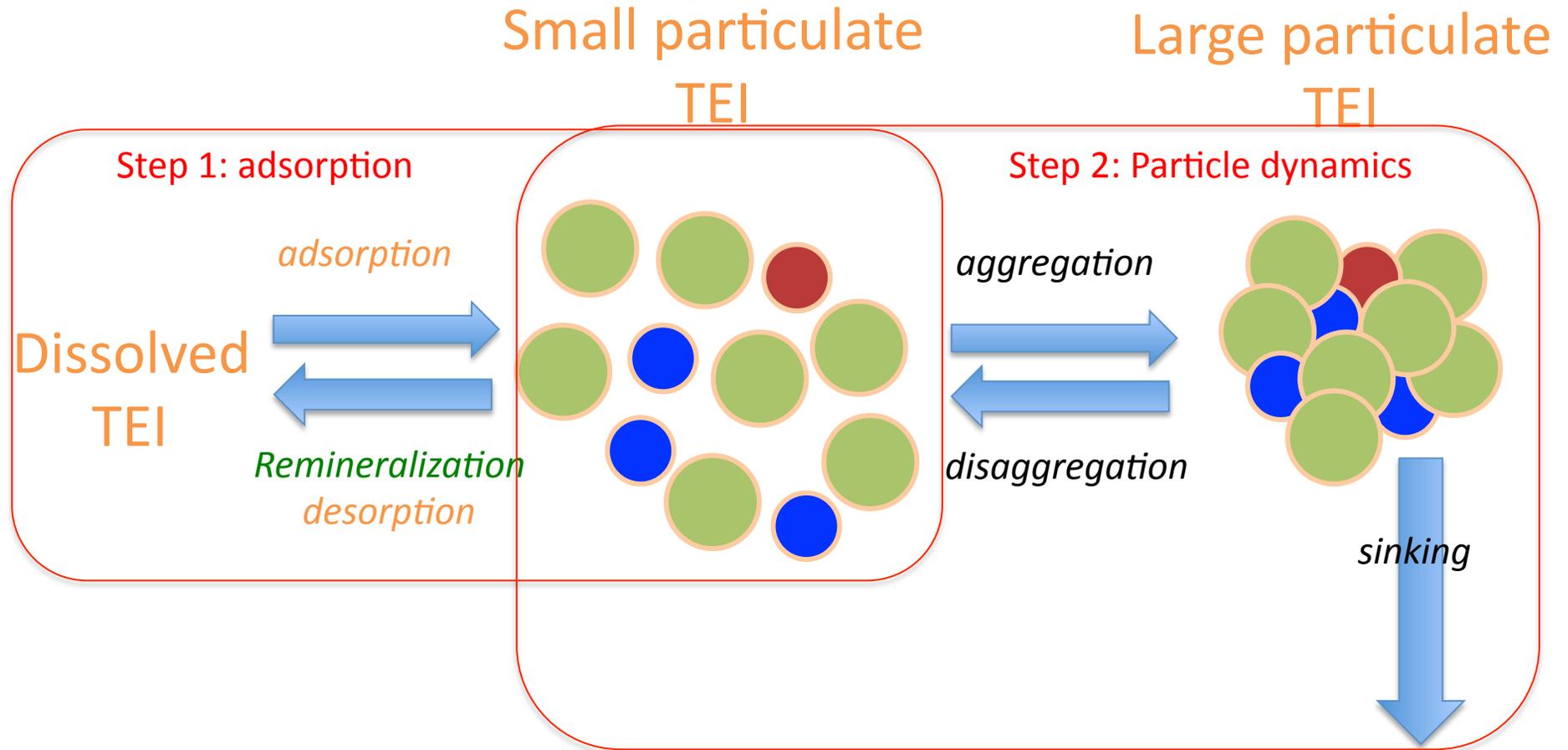
- Particles can be sources of TEIs
- Particles can be sinks of TEIs (biological uptake and abiotic scavenging)

What are particles made of?

- Biogenic particles (eg. particulate organic matter, CaCO_3 , biogenic Si)
- Lithogenic particles (eg. aluminosilicates)
- Authigenic particles (eg. Fe and Mn oxyhydroxides)
- Trace elements and isotopes (eg. thorium)



Scavenging of trace elements and isotopes (TEIs): a 2-step process



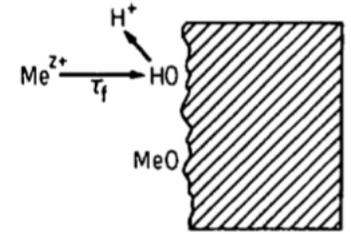
There are 2 distinct steps for the removal of a TEI by scavenging

- 1) Adsorption of the dissolved phase onto suspended particles
- 2) The aggregation of small, suspended particles into large, sinking particles, which can be removed from the water column by sinking

How does scavenging vary in the ocean?

- Step 1: Adsorption should be controlled by the small, suspended particles, which dominate total particulate mass (>80%) and have high surface area
- Step 2: Removal should be controlled by processes that lead to aggregation and sinking of large, sinking particles
 - Particle concentration and composition have been implicated in particle flux (e.g. ballast)

Step 1: Adsorption



Honeyman and
Santschi 1989 JMR

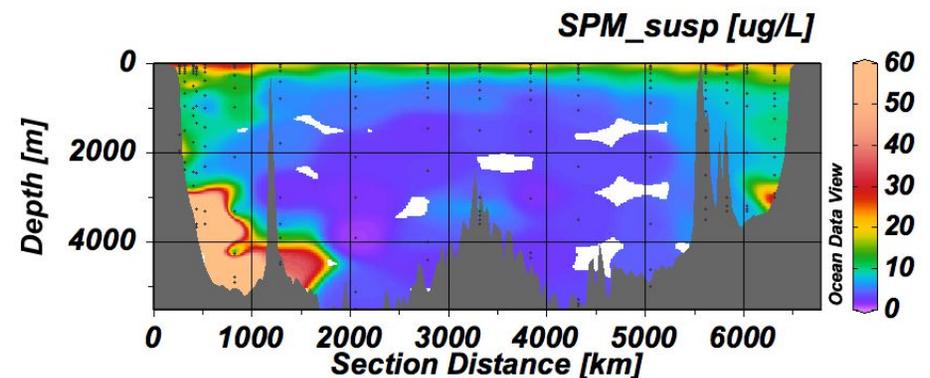
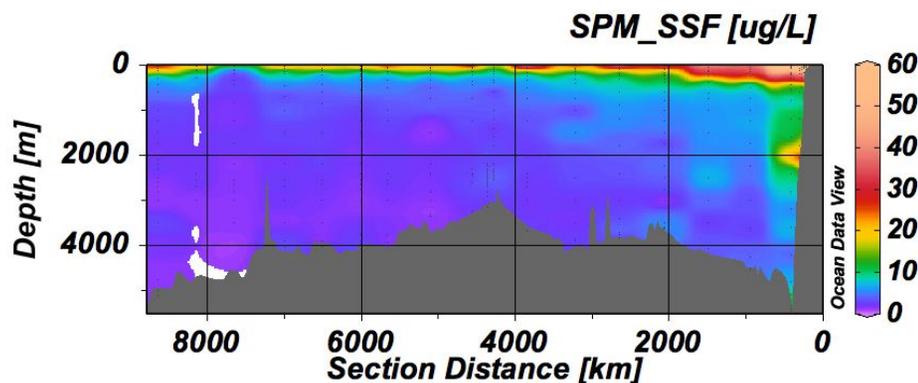
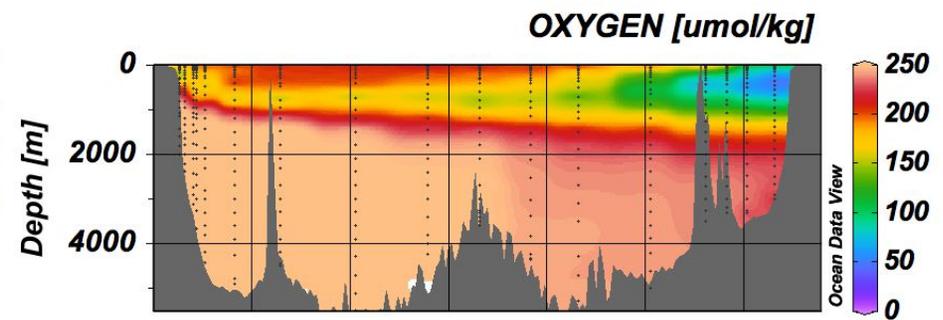
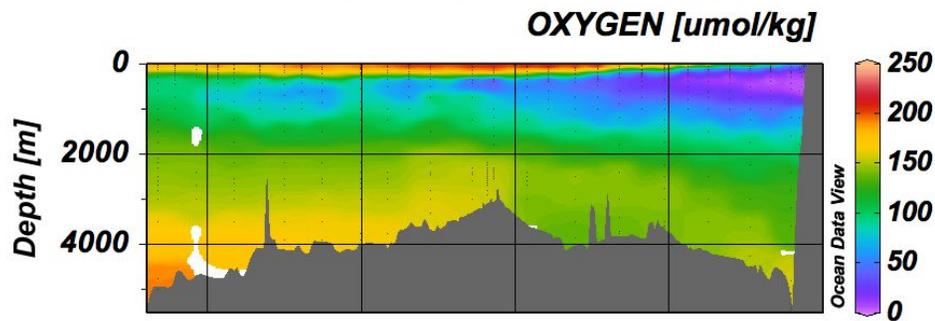
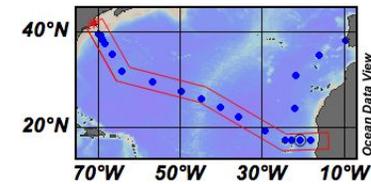
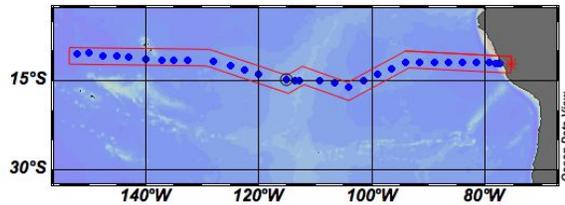
- Adsorption is a function of number and type of particle surface sites
 - Number of sites:
 - particle concentration: more particles \rightarrow more surface sites
 - Particle composition: e.g., oxyhydroxides have more surface area and thus sites than lithogenic particles
 - Type of sites:
 - particle surfaces contain functional groups that behave as ligands, so some particle types form stronger complexes than others

Measuring major particle composition and suspended particulate mass (SPM)

$$\text{SPM} = \sum (\text{POM}, \text{CaCO}_3, \text{bSi}, \text{litho}, \text{oxy})$$

- Major particle phases are:
 - Particulate organic matter (POM)
 - Calcium carbonate (CaCO_3)
 - Biogenic silica (bSi or opal)
 - Lithogenic mass (litho)
 - derived from Aluminum using upper continental crust (UCC) average Al
 - Fe, Mn oxyhydroxides (oxy)
 - Lithogenic Fe, Mn removed from total pFe, pMn using UCC Fe:Ti and Mn:Ti or Fe:Al and Mn:Al
- This is measured for large size fraction=LSF ($>51\mu\text{m}$) and small size fraction=SSF particles ($0.8\text{-}51\mu\text{m}$)

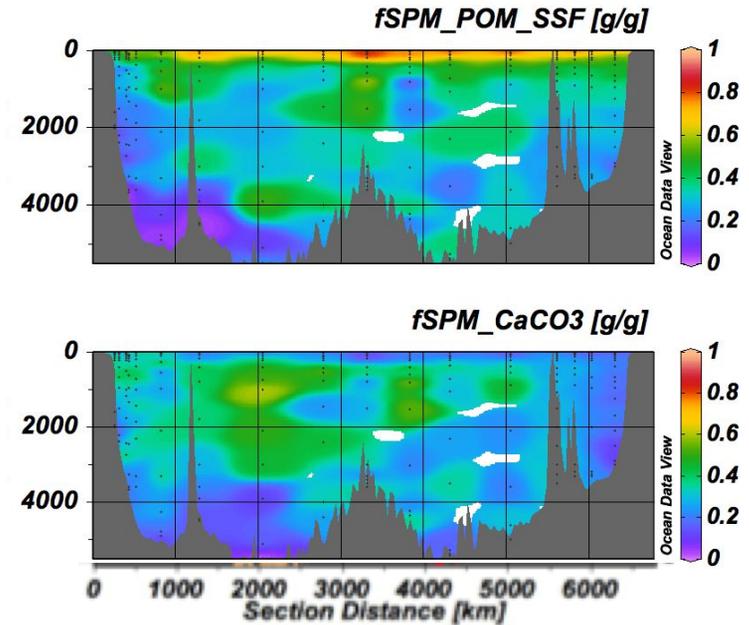
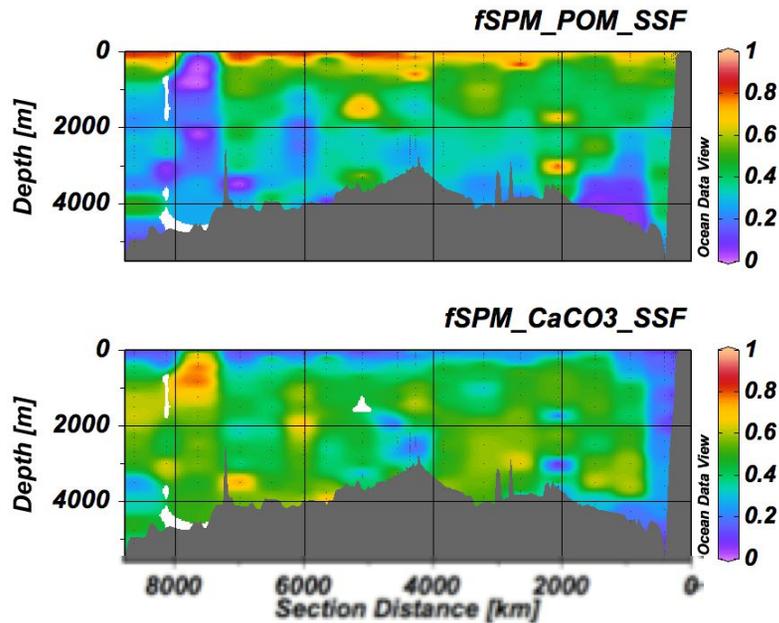
Suspended particulate mass (SPM) of small particles GP16-EPZT vs GA03-NAZT



- Slightly higher surface SPM in EPZT than NAZT
- Intense nepheloid layers in NAZT western boundary are absent in EPZT

Particle composition (1a): POM, CaCO₃

GP16-EPZT vs GA03-NAZT

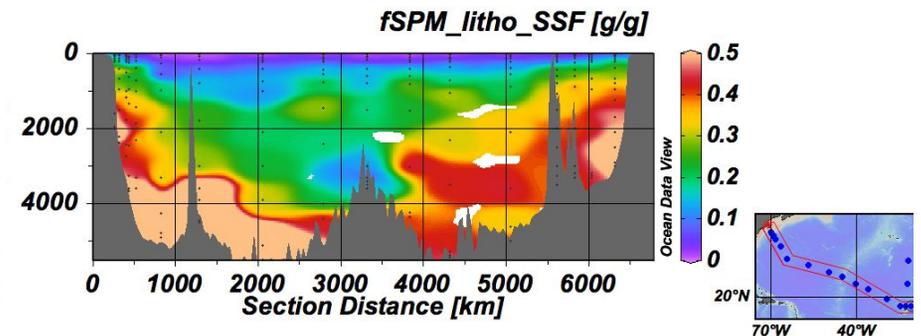
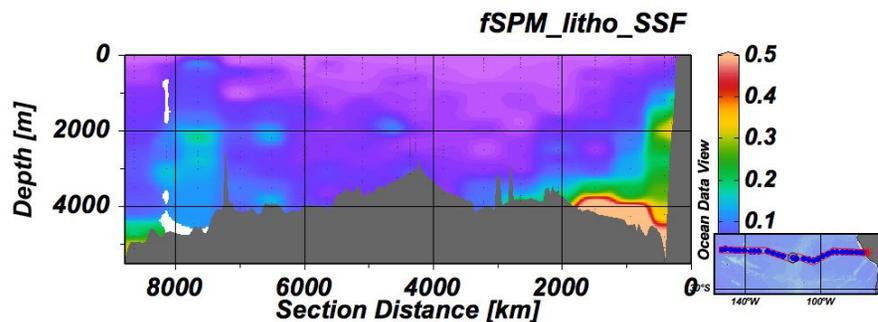
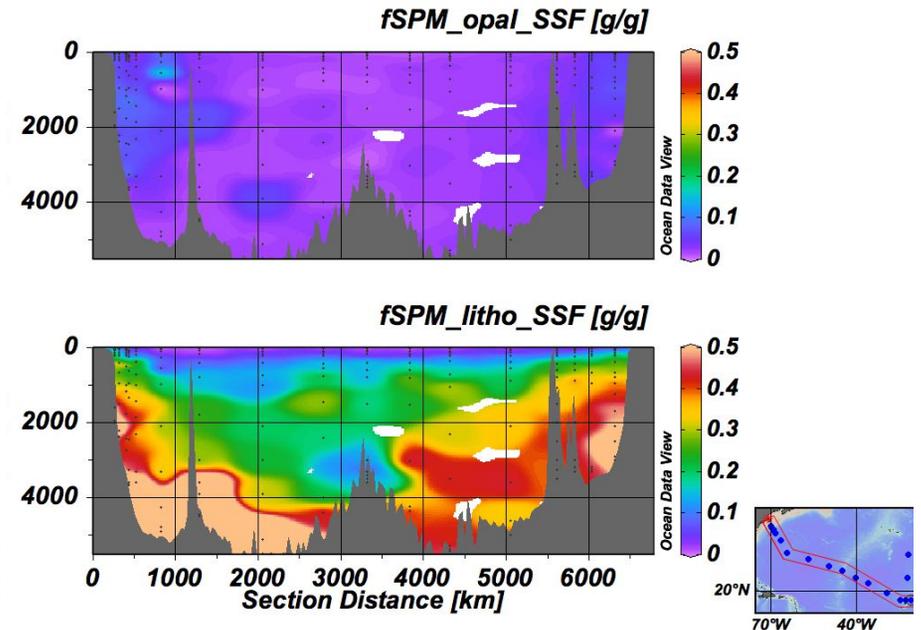
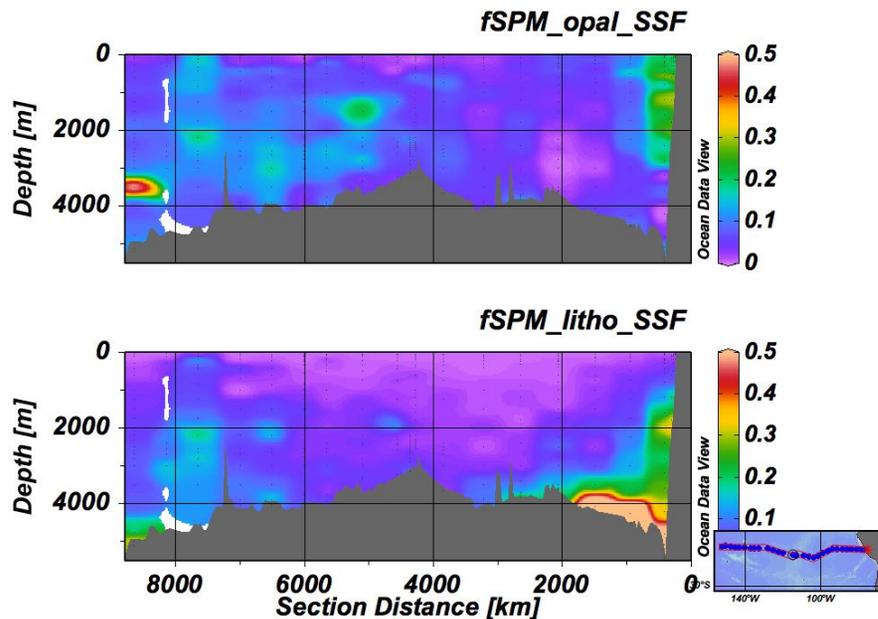


- Colorbars from 0-1 (0-100%) for POM and CaCO₃
- EPZT slightly more enriched in POM and CaCO₃ compared to NAZT

Particle composition (1b): opal, lithogenics

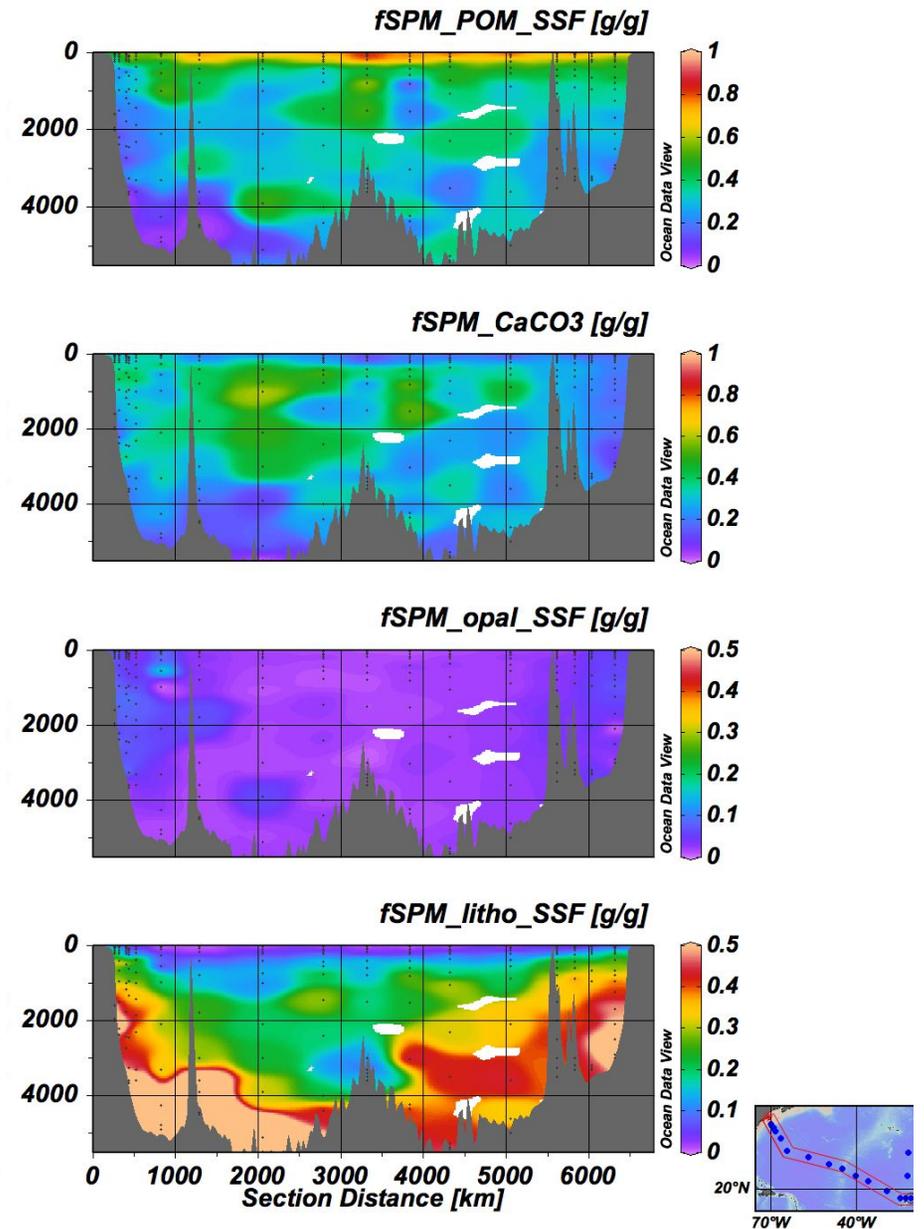
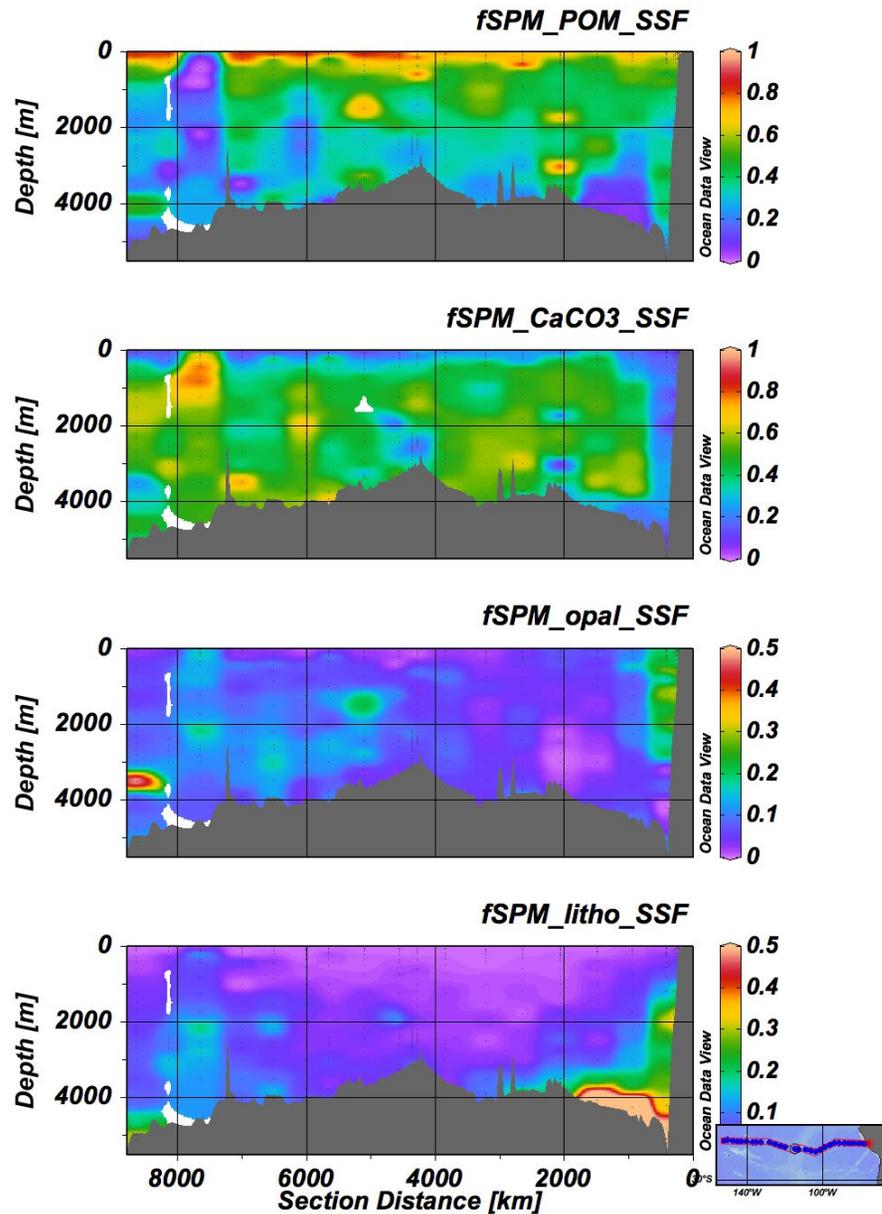
GP16-EPZT vs GA03-NAZT

- Colorbars from 0-0.5 (0-50%) for Opal and Lithogenics
- More opal in EPZT (up to 30% in upwelling region) than NAZT
- Far more lithogenic particles in NAZT (Saharan dust in east; margin transport in west) than EPZT (subsurface transport)



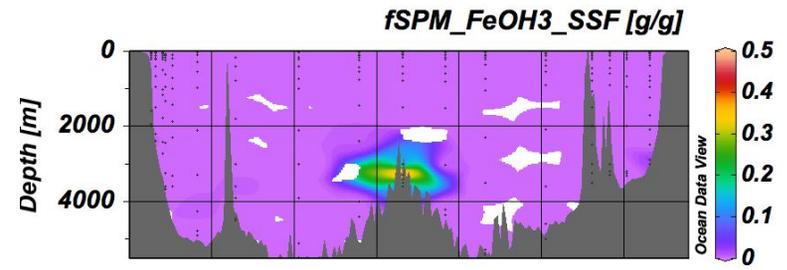
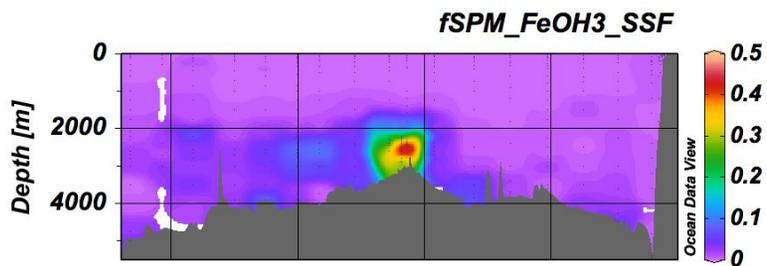
Particle composition (1): POM, CaCO₃, opal, litho

GP16-EPZT vs GA03-NAZT

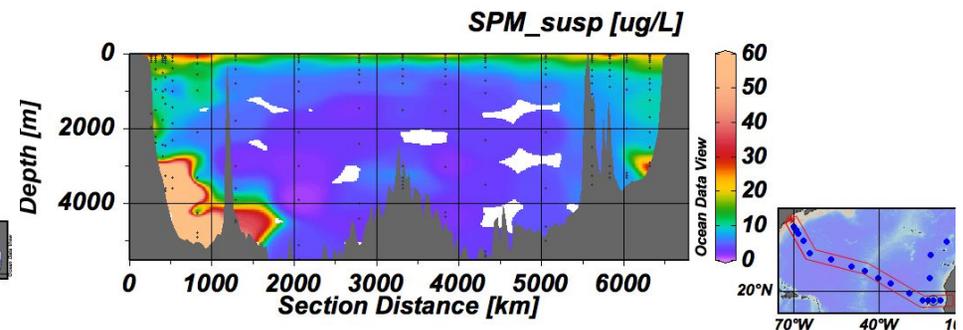
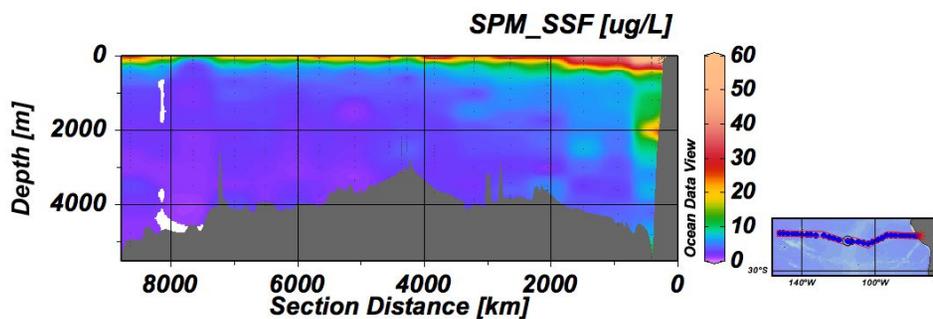
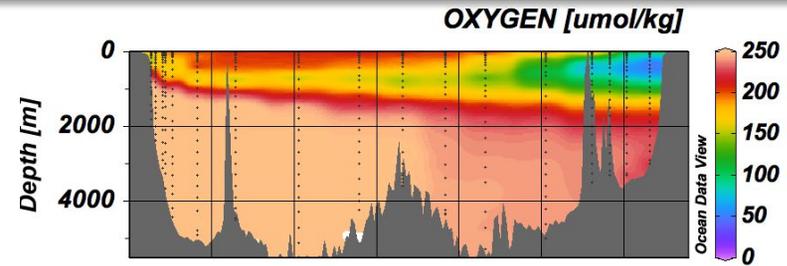
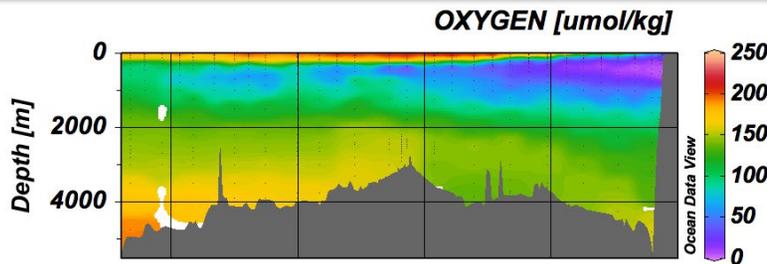


Particle composition (2a): Fe oxyhydroxides

GP16-EPZT vs GA03-NAZT



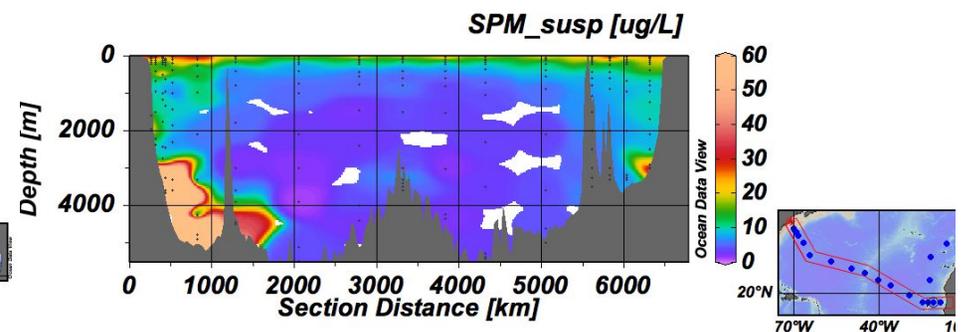
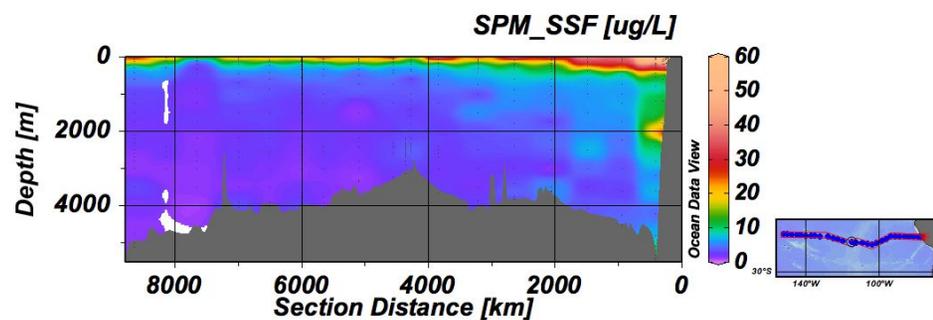
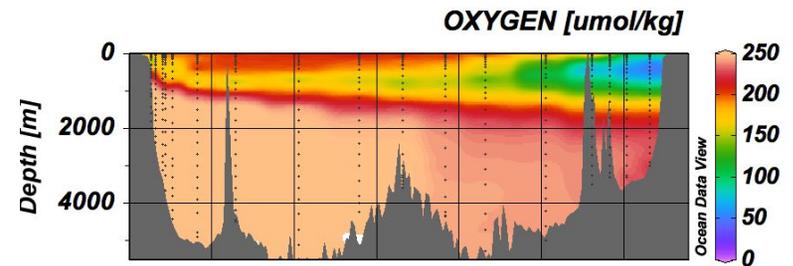
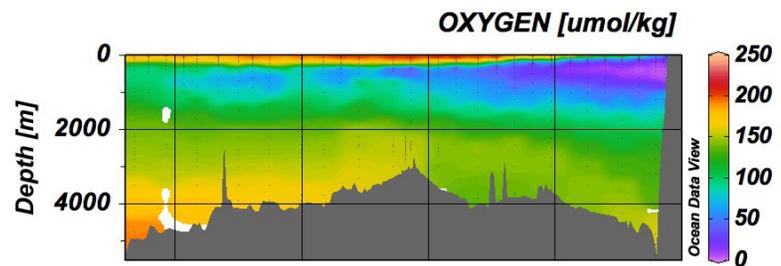
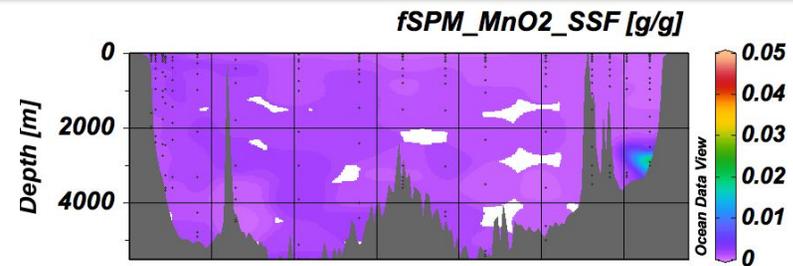
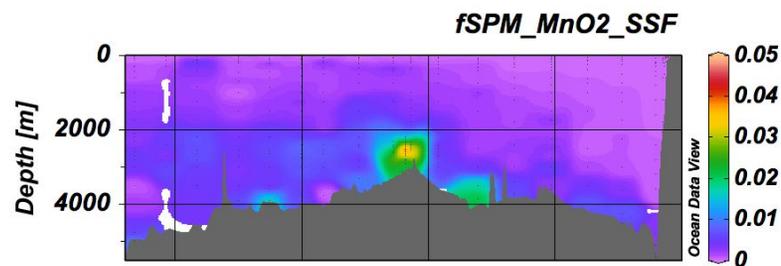
- $\text{Fe}(\text{OH})_3$ scalebar from 0-0.5 (0-50%)
- $\text{Fe}(\text{OH})_3$ prominent (~50% of particle mass) at hydrothermal vent in both basins
- $\text{Fe}(\text{OH})_3$ significant for many more samples in EPZT cruise: far-field hydrothermal plume in western half, but also slightly elevation in eastern half



Particle composition (2b): Mn oxyhydroxides

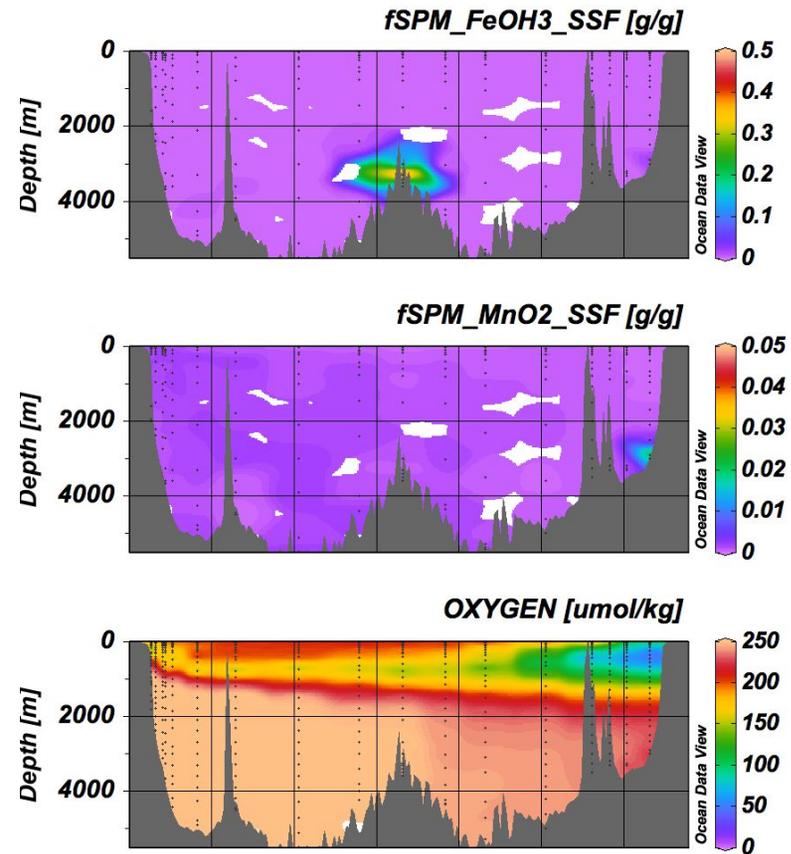
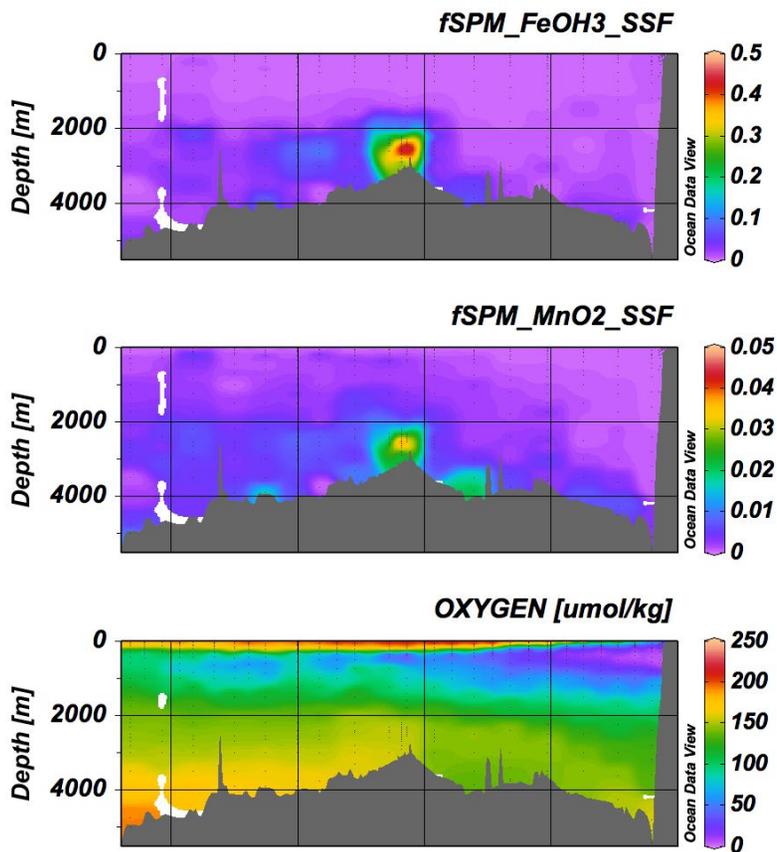
GP16-EPZT vs GA03-NAZT

- MnO_2 scalebar from 0-0.05 (0-5%)
- NAZT had no MnO_2 at hydrothermal vent, whereas EPZT does
- MnO_2 significantly more prominent in EPZT than NAZT cruise, especially in western half, but also near bottom on eastern half



Particle composition (2): oxyhydroxides

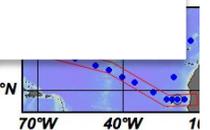
GP16-EPZT vs GA03-NAZT



- Fe and Mn oxyhydroxides are more prominent in the Pacific (EPZT) than Atlantic (NAZT) despite overall lower oxygen

8000 6000 4000 2000 0
Section Distance [km]

0 1000 2000 3000 4000 5000 6000
Section Distance [km]

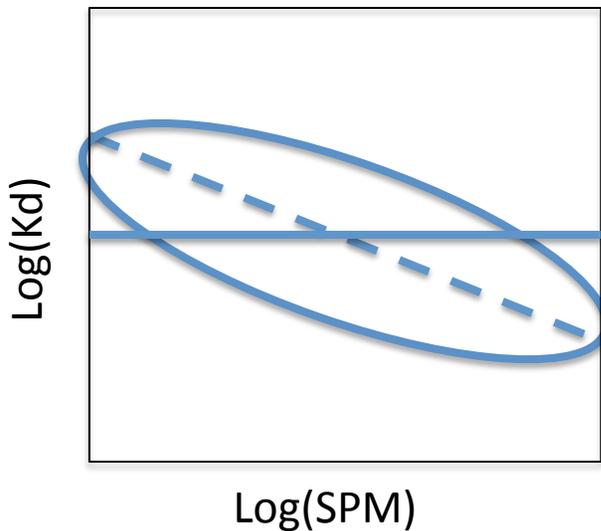


Assessing the extent of scavenging (1)

- A common way to assess the extent of scavenging is using an empirically calculated partition coefficient, K_d :

K_d :

$$K_d = \frac{pTEI_{adsorb}}{dTEI} * \frac{1}{SPM} \quad \left[\frac{TEI / gSPM}{TEI / gSW} \right]$$



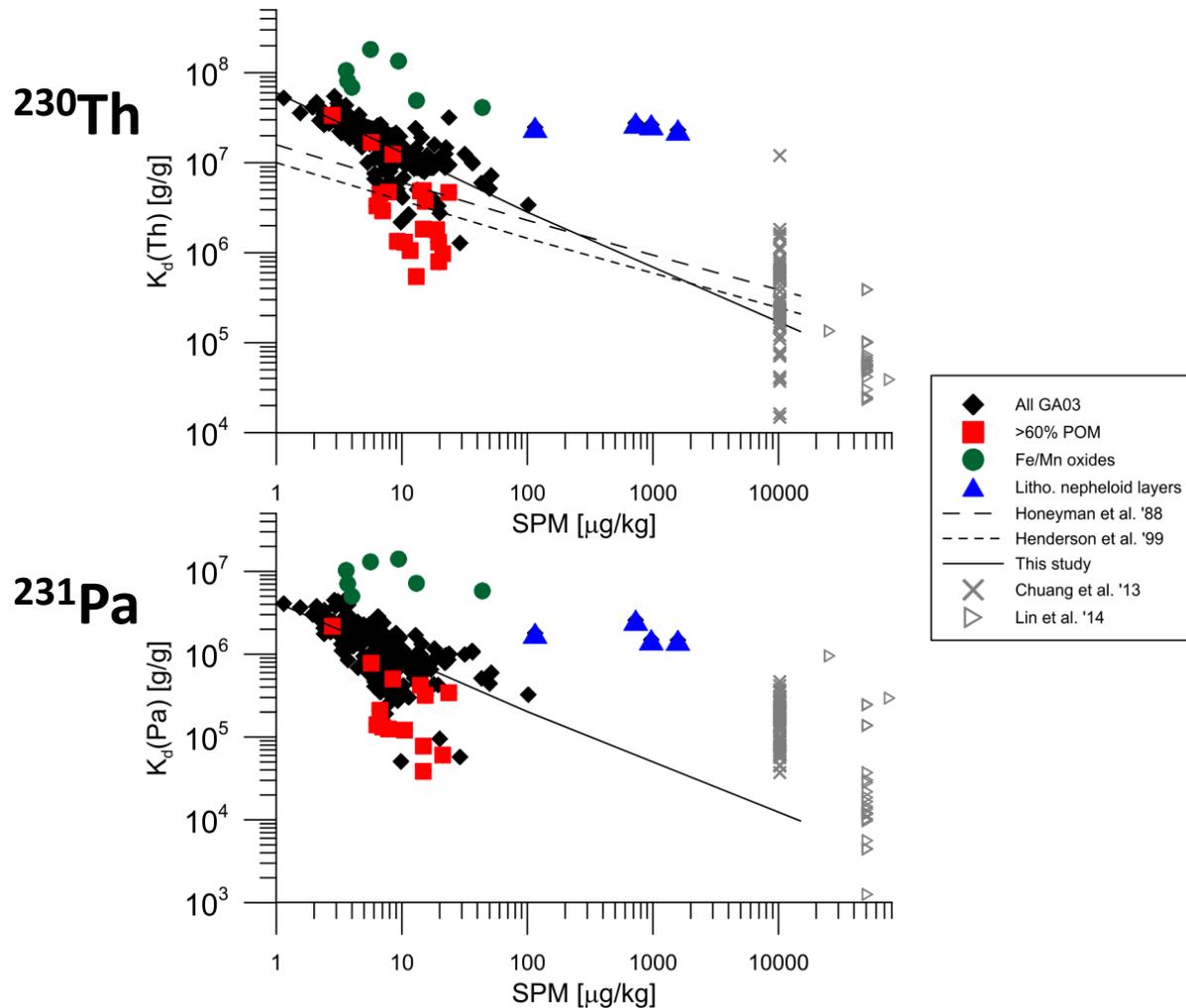
- Ideal
- - - Particle concentration effect
- Particle composition

- Since K_d is normalized by the particle concentration (SPM), if the number of particle surface sites is perfectly described by [SPM], then $\log(K_d)$ vs $\log(SPM)$ should be a horizontal line
- Actual data often show two types of deviations from this line:

- A particle concentration effect 
- Significant scatter about the line 

K_d for ^{230}Th and ^{231}Pa vs SPM in GA03 NAZT

C.T. Hayes et al. / Marine Chemistry 170 (2015) 49–60



- Hayes et al. 2015 observed a particle concentration effect for ^{230}Th and ^{231}Pa in GA03 NAZT cruise
- Also observed scatter about the line, that seemed to group by particle composition

End-member partition coefficients to different particle phases

$$K_d = f(\text{lith}) * K_d^{\text{lith}} + f(\text{CaCO}_3) * K_d^{\text{CaCO}_3} + f(\text{opal}) * K_d^{\text{opal}} + f(\text{POM}) * K_d^{\text{POM}} \\ + f(\text{Fe(OH)}_3) * K_d^{\text{Fe(OH)}_3} + f(\text{MnO}_2) * K_d^{\text{MnO}_2}$$

Hayes et al. 2015 Marine Chemistry

Hayes et al. 2015 Marine Chemistry:

- Assume that the overall partition coefficient (K_d) is a linear combination of contributions from each major particle phase
- Use a multiple linear regression to derive end-member partition coefficients for each particle phase
- Hayes et al. 2015 Marine Chem did this for ^{230}Th and ^{231}Pa on GA03
- Lamborg et al. in press, Phil.Trans.Roy.Soc.London A did this for Hg on GA03
- Boyle et al. in prep, doing this for Pb on GA03

End-member partition coefficients of Th, Pa, Hg to different particle phases from GA03 NAZT

<i>Particle phase</i>	$K_d(\text{Th})_{\text{particlephase}} \text{ g/g}$	$K_d(\text{Pa})_{\text{particlephase}} \text{ g/g}$	$K_d(\text{Hg})_{\text{particlephase}} \text{ L/kg}$
POM	3.0E+06	6.0E+05	5.2E+06
Litho	2.3E+07	2.3E+06	6.9E+05
CaCO ₃	3.0E+07	9.0E+05	5.1E+06
Fe(OH) ₃	3.3E+08	2.9E+07	4.4E+07
MnO ₂	1.2E+09	2.1E+08	1.9E+08
Opal	--	--	--



Hayes et al. 2015

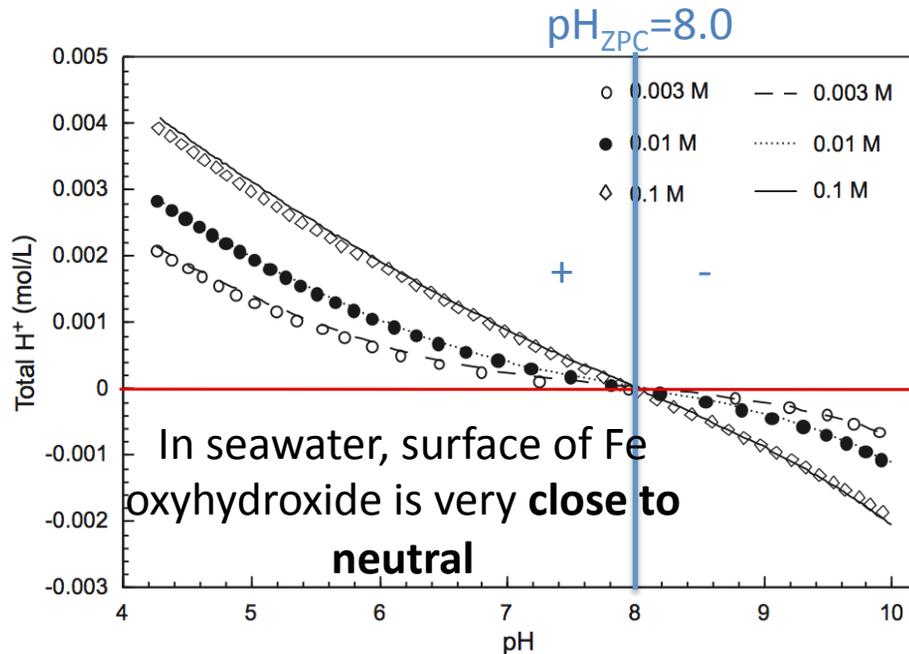
Lamborg et al.
in press

- Note that Fe and Mn (oxyhydr)oxides have 1-2 orders of magnitude high affinity than other particle phases
- Oxyhydroxides have very high surface area (therefore lots of surface sites)
- Why might Mn have higher affinity than Fe?

Surface coordination chemistry: point of zero charge (PZC)

Ferrihydrite: Fe(III) oxyhydroxide

E.M. Moon, C.L. Peacock / *Geochimica et Cosmochimica Acta* 104 (2013) 148–164



Birnessite: Mn(III,IV) oxide

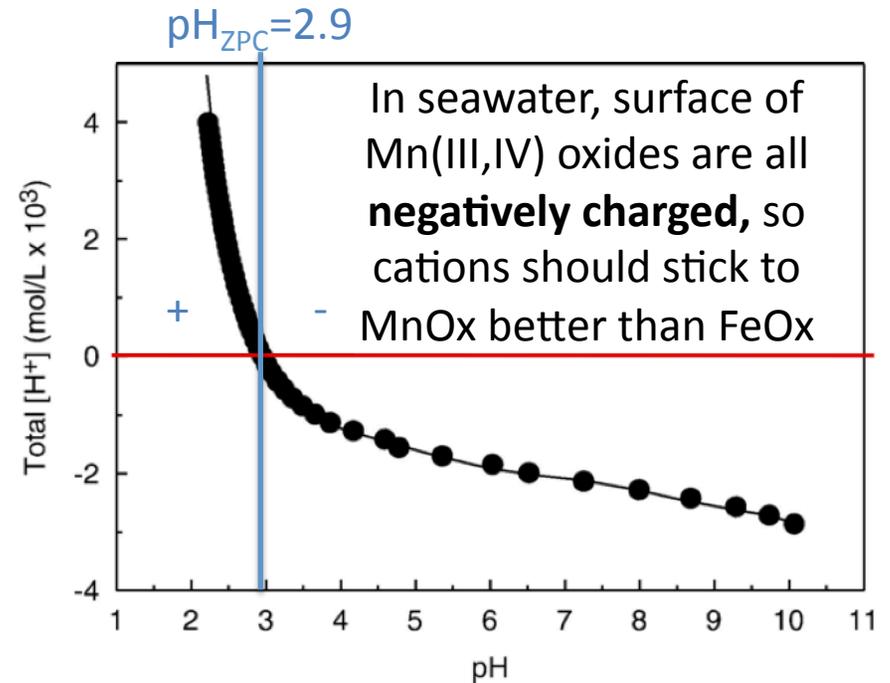


Fig. 9. Hx-birnessite potentiometric titration data at $I=0.1$ NaNO₃ and 25 °C, shown as total $[H^+]$ in mol/L. 2 g/L oxide. Symbols are data points, line is DLM fit.

Contribution of each individual particle phase to the bulk partition coefficient

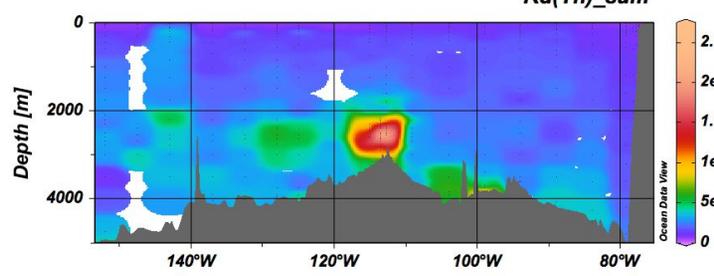
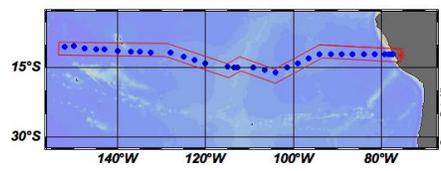
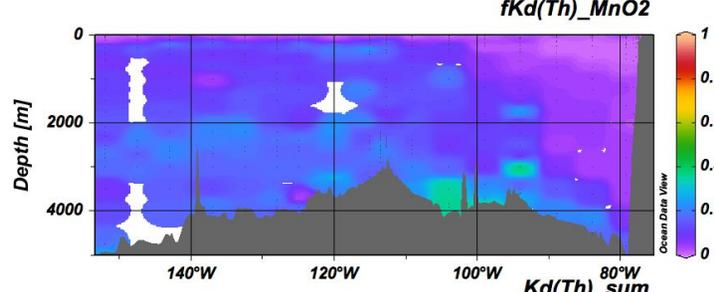
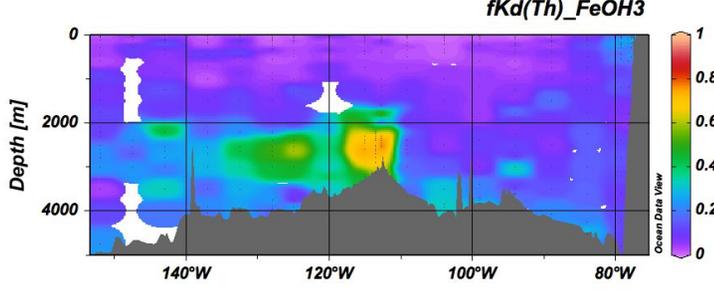
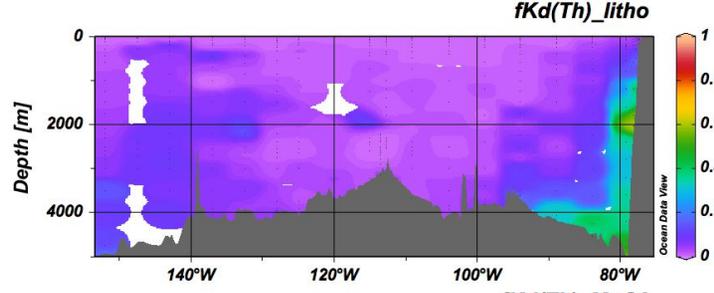
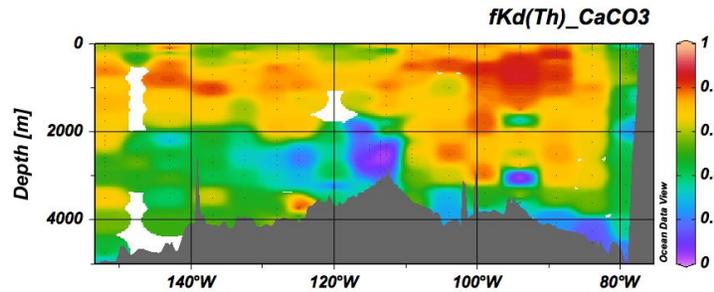
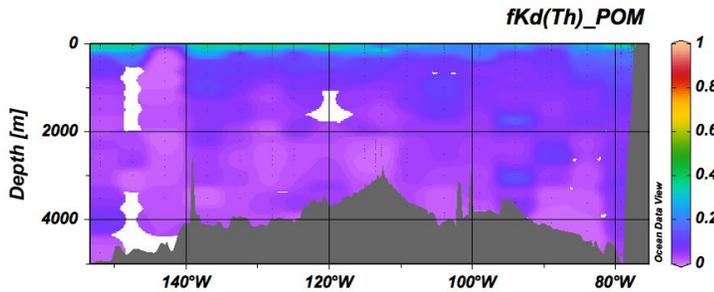
- The importance of a particle phase to the overall partition coefficient is the product of its end-member partition coefficient times the relative concentration of that particle phase

$$fK_d(TEI)_{particlephase} = \frac{\overbrace{K_d(TEI)_{particlephase}}^{\text{End-member } K_d \text{ of particle phase}} * \overbrace{[particlephase] / [SPM]}^{\text{relative concentration of that particle phase}}}{\underbrace{K_d(TEI)_{overall}}_{\text{Overall } K_d}}$$

Predicting scavenging in GP16 EPZT using GA03-derived end-member K_d s

- Since we have particle composition in the GP16 EPZT, we can calculate what TEI-particle associations we might expect in GP16 given the GA03-derived intrinsic K_d s:
- Caveats:
 - K_d s determined on GA03 are empirical, and may not be portable

Predicting ^{230}Th scavenging in GP16 EPZT

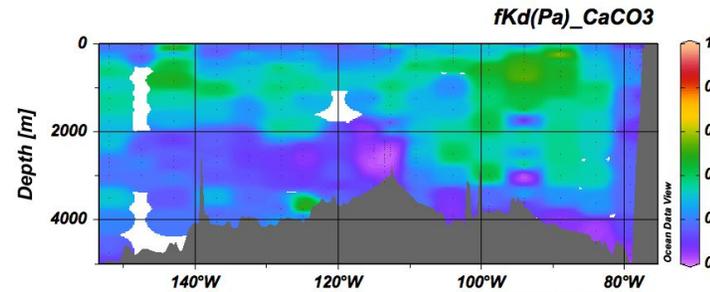
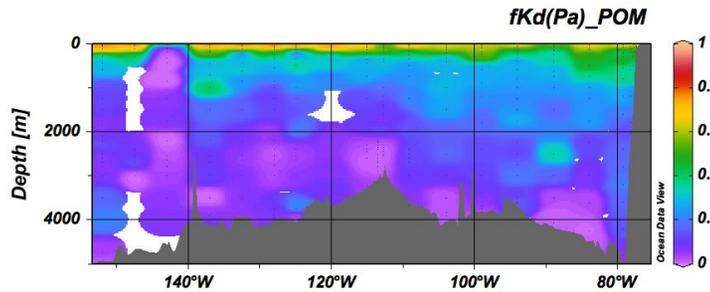


Opal Kd not significant in Atlantic

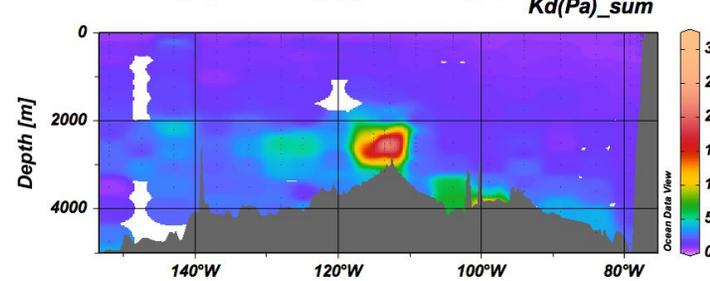
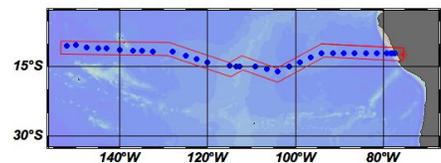
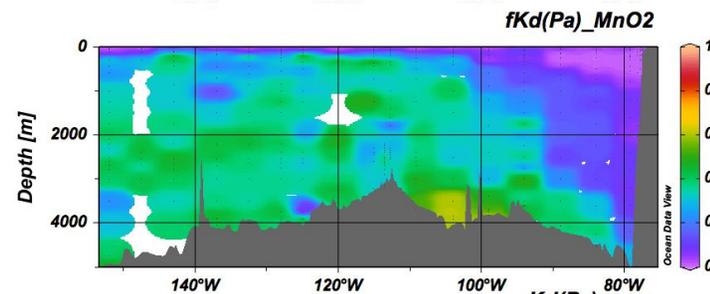
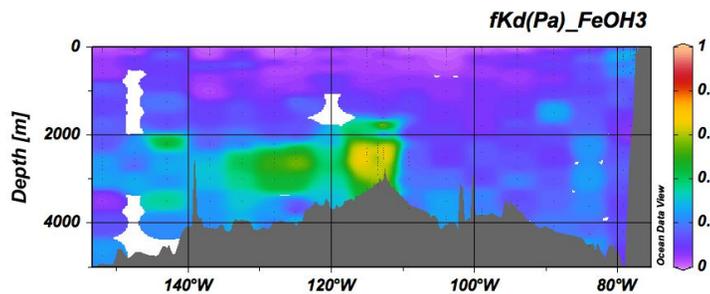
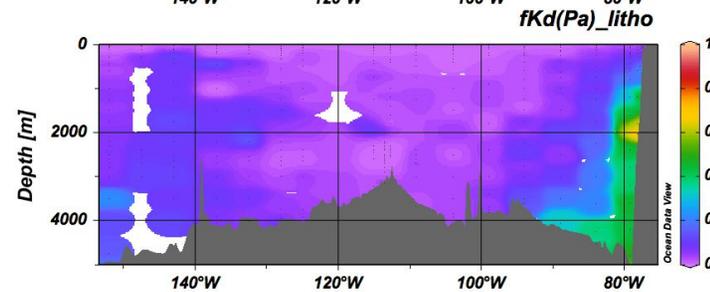
Particle phase	$K_d(\text{Th})_{\text{particle phase}}$ g/g
POM	3.0E+06
Litho	2.3E+07
CaCO ₃	3.0E+07
Fe(OH) ₃	3.3E+08
MnO ₂	1.2E+09
Opal	--

If $K_d(\text{Th})_{\text{particle phase}}$ from GA03 can be applied to EPZT, then CaCO₃ and Fe(OH)₃ are the most important phases for ^{230}Th scavenging

Predicting ^{231}Pa scavenging in GP16 EPZT



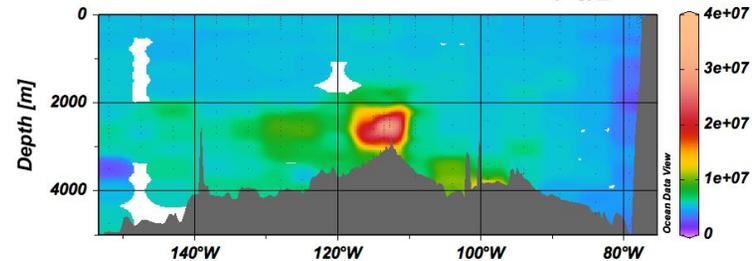
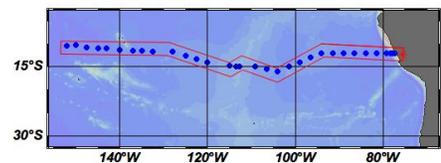
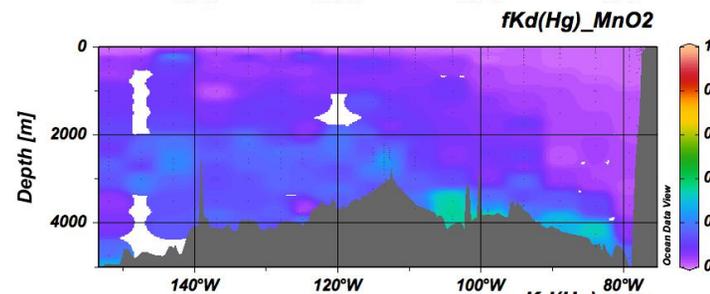
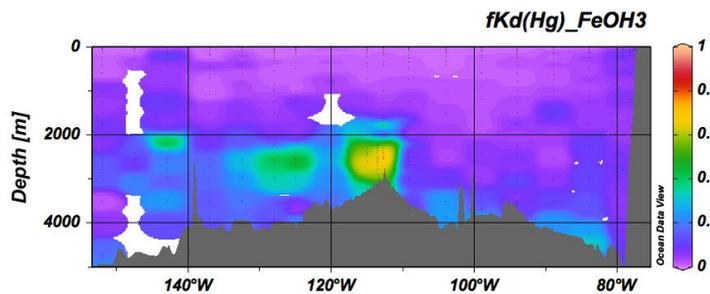
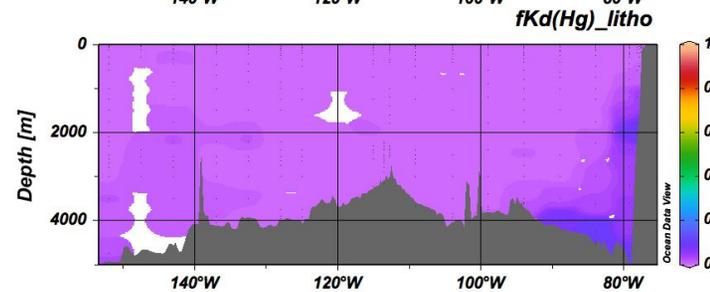
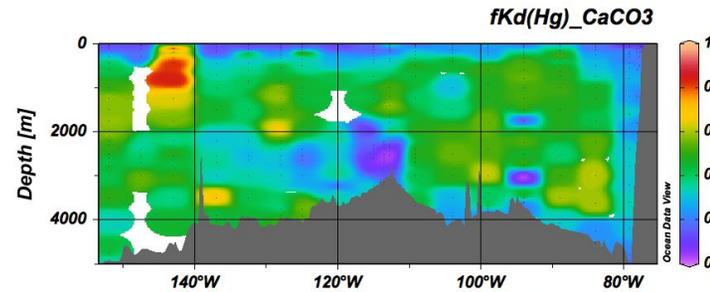
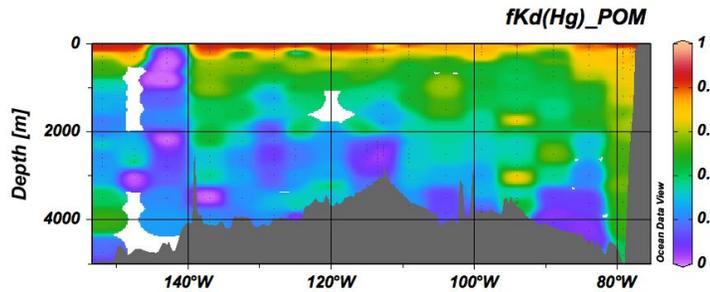
Opal Kd not significant in Atlantic



Particle phase	$Kd(\text{Pa})_{\text{particle phase}}$ g/g
POM	$6.0\text{E}+05$
Litho	$2.3\text{E}+06$
CaCO_3	$9.0\text{E}+05$
$\text{Fe}(\text{OH})_3$	$2.9\text{E}+07$
MnO_2	$2.1\text{E}+08$
Opal	--

If $Kd(\text{Pa})_{\text{particle phase}}$ from GA03 can be applied to EPZT, then MnO_2 very important for ^{231}Pa scavenging

Predicting Hg scavenging in GP16 EPZT



Opal Kd not significant in Atlantic

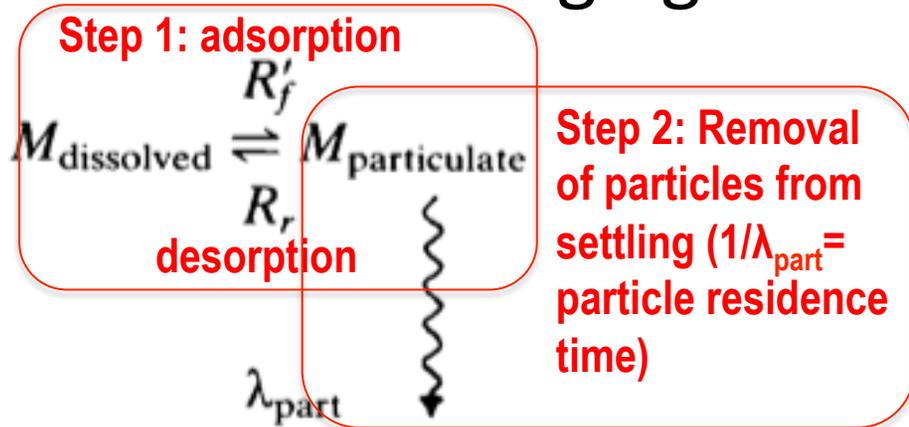
Particle phase	$K_d(\text{Hg})_{\text{particle phase}} \text{ L/kg}$
POM	5.2E+06
Litho	6.9E+05
CaCO ₃	5.1E+06
Fe(OH) ₃	4.4E+07
MnO ₂	1.9E+08
Opal	--

If $K_d(\text{Hg})_{\text{particle phase}}$ from GA03 can be applied to EPZT, then POM and CaCO₃ most important phases for Hg scavenging

- “One of the central problems confronting oceanographers studying marine scavenging is the relationship between what is actually measured and the specific processes producing those observations.”

Honeyman et al. 1988 DSR

Assessing the extent of scavenging (2): Relating a kinetic scavenging model to a partition coefficient



With thorium as an example, write an equation for the change in the activities of dissolved thorium ($A_{\text{Th}_{\text{diss}}}$) and particulate thorium ($A_{\text{Th}_{\text{part}}}$):

$$\frac{\partial A_{\text{Th}_{\text{diss}}}}{\partial t} = \overset{\text{production}}{\lambda_{\text{Th}} A_P} - \overset{\text{decay}}{\lambda_{\text{Th}} A_{\text{Th}_{\text{diss}}}} - \overset{\text{adsorption}}{R'_f A_{\text{Th}_{\text{diss}}}} + \overset{\text{desorption}}{R_r A_{\text{Th}_{\text{part}}}}$$

$$\frac{\partial A_{\text{Th}_{\text{part}}}}{\partial t} = \overset{\text{adsorption}}{R'_f A_{\text{Th}_{\text{diss}}}} - \overset{\text{decay}}{\lambda_{\text{Th}} A_{\text{Th}_{\text{part}}}} - \overset{\text{desorption}}{R_r A_{\text{Th}_{\text{part}}}} - \overset{\text{from settling}}{\lambda_{\text{part}} A_{\text{Th}_{\text{part}}}}$$

Now assume steady state, and relate an observed partition coefficient (K_D) to rate parameters:

$$K_D^{\text{obs}} = \left\{ \frac{A_{\text{Th}_{\text{part}}}}{A_{\text{Th}_{\text{diss}}}} \right\} \left\{ \frac{1}{C_p} \right\} = \left\{ \frac{\overset{\text{adsorb}}{R'_f}}{\underset{\text{desorb}}{R_r} + \underset{\text{decay}}{\lambda_{\text{Th}}} + \underset{\text{sink}}{\lambda_{\text{part}}}} \right\} \left\{ \frac{1}{\underset{\text{SPM}}{C_p}} \right\}$$

Honeyman
 et al. 1988
 DSR

Should K_d be portable between basins?

$$K_D^{\text{obs}} = \left\{ \frac{A_{\text{Th}_{\text{part}}}}{A_{\text{Th}_{\text{diss}}}} \right\} \left\{ \frac{1}{C_p} \right\} = \left\{ \frac{\overset{\text{adsorb}}{R'_f}}{\underset{\text{desorb}}{R_r} + \underset{\text{decay}}{\lambda_{\text{Th}}} + \underset{\text{sink}}{\lambda_{\text{part}}}} \right\} \left\{ \frac{1}{\underset{\text{SPM}}{C_p}} \right\}$$

Honeyman et al. 1988
DSR

- If at steady state, and if decay (λ_{Th}) and sinking (λ_{part}) are negligible compared to desorption (R_r), then $K_d * C_p$ is like an equilibrium constant and might be portable
- But if not at steady state, if sinking is large, or if other processes important (e.g. remineralization, advection), then empirical K_d derived from one basin may not be easily portable to another
- A more kinetic description of scavenging may be helpful
- See Paul Lerner's pop-up talk on using inverse models to estimate scavenging **rate constants**, and their relationship to particle composition

Open questions

- Need to reconcile empirical descriptions of scavenging to mechanistic (kinetic) processes
 - Ongoing work by Paul Lerner and Olivier Marchal suggest some differences → differences can help us understand mechanisms of scavenging
- Given importance of Fe and Mn oxyhydroxides, need to better understand their formation mechanisms
 - EPZT: Fe oxyhydroxide formation in the OMZ was a surprise. Others?
 - Mechanisms of Mn oxidation