UNIVERSITY OF GOTHENBURG

The role of complexation in metal partitioning between solution and particles

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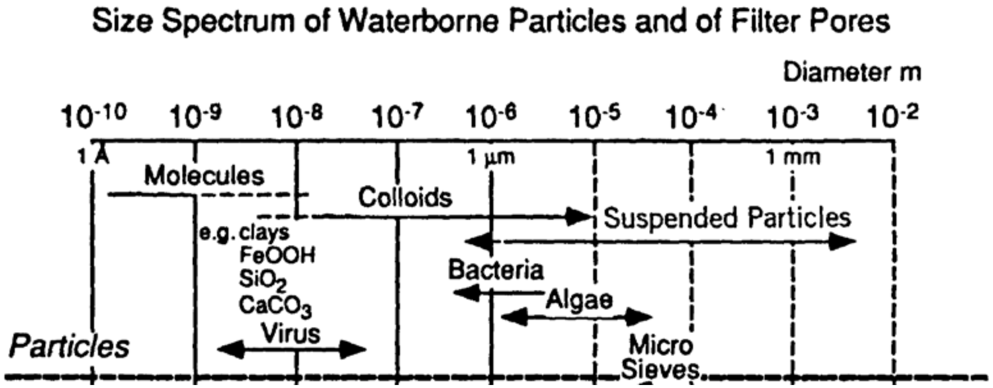
Faculty of Science

Overview

- Partitioning, particles and colloids
- Quantitative (thermodynamic) description of complexation
- Master variables
- Cu at a GEOSECS station as an illustrative example
- Organic complexation?
- Speciation modelling in GEOTRACES?

What do we mean by ”particulate” and ”dissolved”?

The traditional division is based on filtration at 0.45 µm, so that particles retained by the filter are those that can sediment by gravity. However, this leaves a wide size range down to about 1 nm where particles are large enough to develop a surface charge, but too small to settle.



”how do you define particles?”

This has led to the concept of ”truly dissolved” for entities smaller than 1 nm. Inorganic complexes of trace metals lie within this region, while much of the organically complexed metal may lie in the colloidal region. Separating the truly dissolved metal is a very challenging task. GEOTRACES has opted for the traditional approach.

Particulate/dissolved partitioning of trace metals

An approach much loved by modellers is the partition coefficient K_D:

$$K_D = \frac{[\text{particulate concentration}]}{[\text{dissolved concentration}]}$$

This is a reasonable approach where we know nothing about the chemical processes involved. In order to move beyond this approach we need to describe the trace metal chemistry in both the particulate and dissolved phases.

Uptake by particles includes active (biological) uptake and chemical adsorption to particulate material. Both types of process are governed by the trace metal's chemical speciation.

Particulate and colloidal material includes both mineral phases such as oxides, and organic matter. Metal binding to pure oxide phases is described by the surface complexation model, while binding to natural organic matter (humic substances) can be described by models developed for fresh waters that are now also being applied to seawater (WHAM, NICA-Donnan).

Description of inorganic complexation reactions

A general complexation reaction between a metal cation M and a ligand L:

$M^{z+} + H_nL^{y-} = ML^{(z-y-n)+} + nH^+$

e.g. $Zn^{2+} + H_2O = ZnOH^+ + H^+$

With charges omitted, the equilibrium state is described by the concentration product *K* and the thermodynamic stability constant K^0

$$K = \frac{[\mathrm{ML}][\mathrm{H}]^n}{[\mathrm{M}][\mathrm{H}_n\mathrm{L}]} \qquad K^0 = \frac{a_{\mathrm{ML}}a_{\mathrm{H}}^n}{a_{\mathrm{M}}a_{\mathrm{H_nL}}} \qquad K = K^0\frac{\gamma_{\mathrm{M}}\gamma_{\mathrm{H_nL}}}{\gamma_{\mathrm{ML}}\gamma_{\mathrm{H}}^n}$$

Two approaches: can be adopted:

- Describe K' as a function of S, T and P based on measurements at many S and T values (this is for example the basis of programmes such as CO2SYS)
- Use values of K^0 together with γ values (e.g. from Pitzer models).

What do measurements and models at 25°C and 1 atmosphere tell us about the ocean as a whole?

The great majority of thermodynamic data are at a pressure of 1 atmosphere, and much trace metal data at a temperature of 25°C. However, the interior of the ocean is significantly colder and at much higher pressure. If we are to develop useful models of trace metal chemistry for the ocean as a whole, then we need to address this range of conditions.

For inorganic trace metal complexation, there is an increasing amount of data available for temperature dependence, while information on pressure dependence is still relatively sparse.

Modelling dissolved phase complexation: master variables

Complexation of trace metals in seawater is largely controlled by four master variables:

- Salinity
- Temperature
- pH
- Pressure (depth).

For redox-sensitive metals, dissolved oxygen can constitute a fifth master variable.

The master variables’ importance in speciation calculations

Master variable	Major effect	Data needed
Salinity	Activity coefficients, ligand concentrations	Pitzer parameters, stability constants for reactions with sea salt components
Temperature	Stability constants, activity coefficients	Enthalpies, specific heats, T coefficients for Pitzer parameters
pH	$[H^+]$, ligands that are formed by ionisation of weak acids, e.g. carbonate	Ionisation constants
Pressure	Stability constants, activity coefficients	Partial molar volumes and compressibilities

The GEOTRACES metals

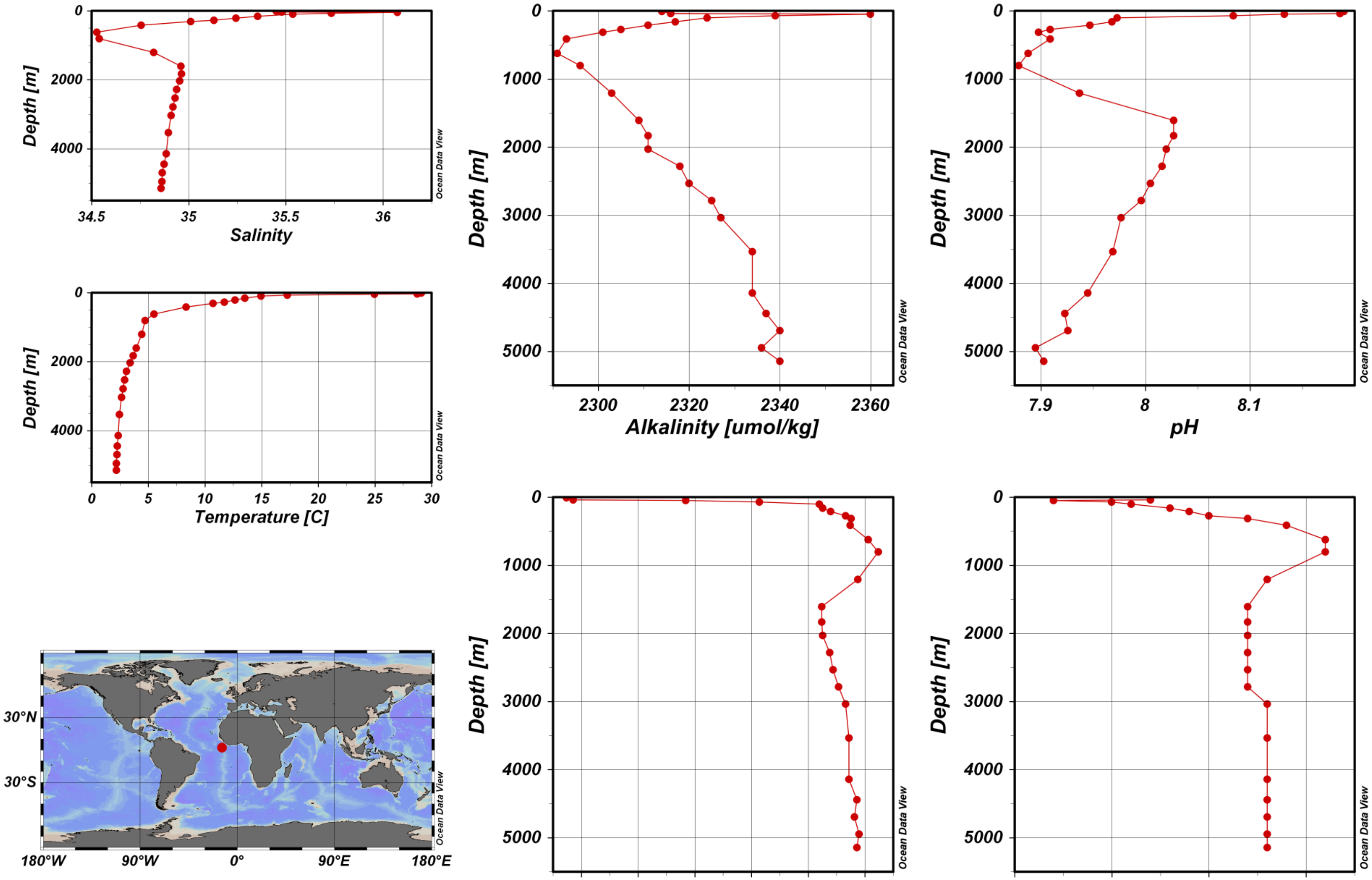
GEOTRACES metal	**Fully oxidised, high $[O_2]$**		**At low $[O_2]$[1]**	
	Oxidation state	Major ligand	Oxidation state	Major ligand
Al	Al(III)	OH^- [2]		
Cd	Cd(II)	Cl^-		
Cu	Cu(II)	CO_3^{2-}	Cu(I)	Cl^-
Fe	Fe(III)	OH^- [2]	Fe(II)	CO_3^{2-}
Mn	Mn(IV)	insoluble[3]	Mn(II)	CO_3^{2-}
Zn	Zn(II)	CO_3^{2-}		

1. This summary does not cover strongly anoxic environments where additional ligands such as HS^- become important
2. It has been recently suggested that the role of carbonate in complexing these metals has been grossly underestimated (Byrne, 2010)
3. Mn(II) can be present at nM concentrations even at high $[O_2]$.

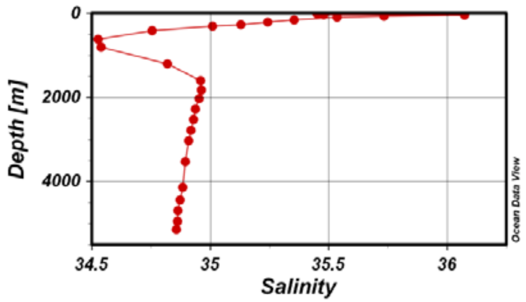
How do the master variables affect the inorganic complexation of trace metals – an example?

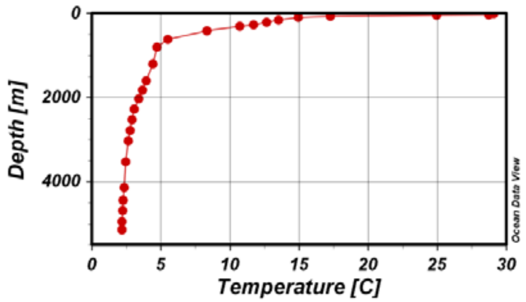
As an example I have taken a GEOSECS station ISTA 111 from the Lamont database. This station is close to the equator, so that the temperature gradient is at a maximum. Copper(II), one of the GEOTRACES metals is used as an example.

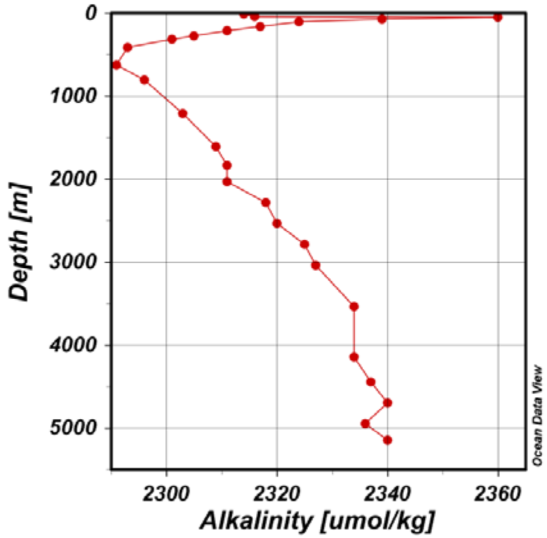
Calculations have been carried out using a Pitzer model for the seawater medium and for copper complexation. The results should be interpreted as indicative since the Cu parameters have not been subject to a full quality review.

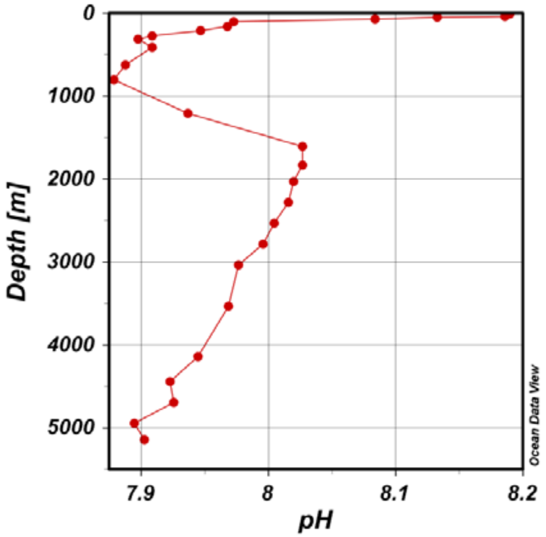


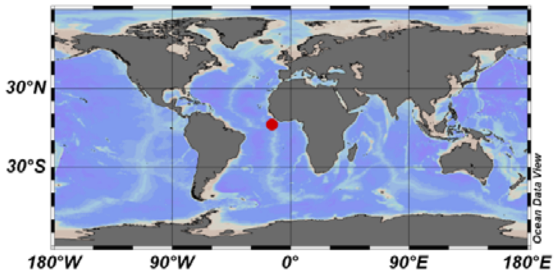
GEOSECS station ISTA 111











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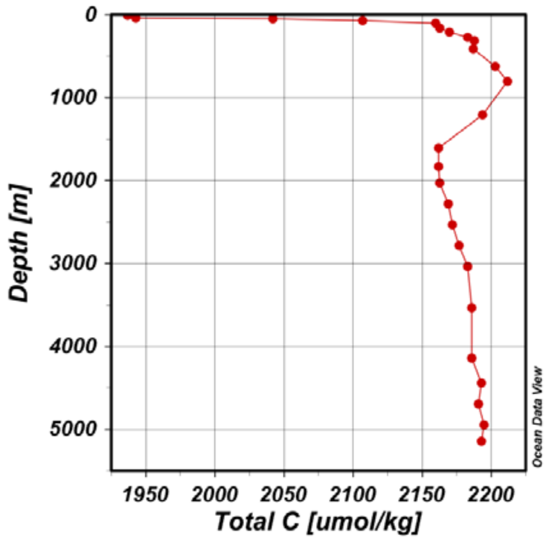

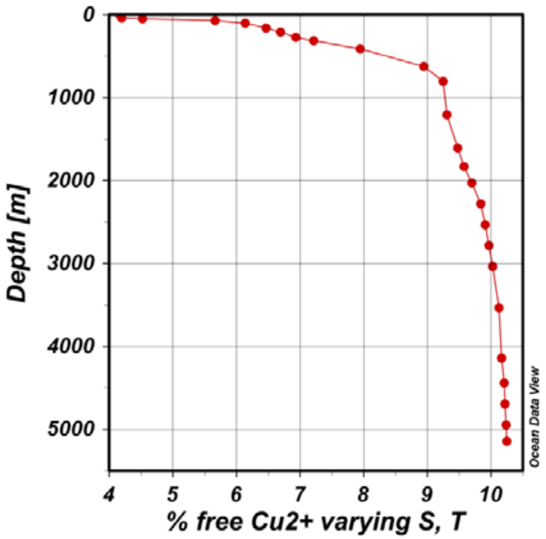

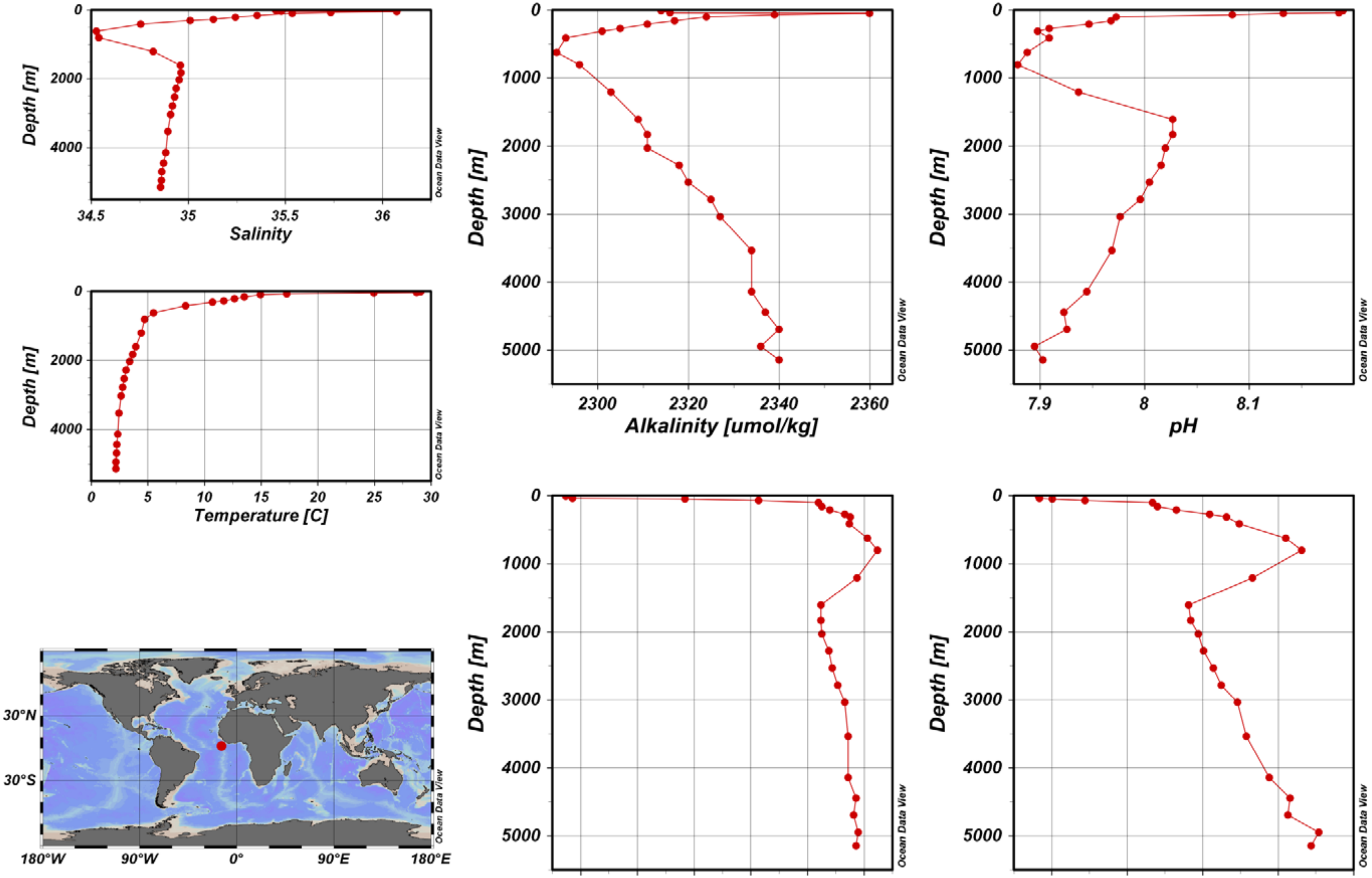

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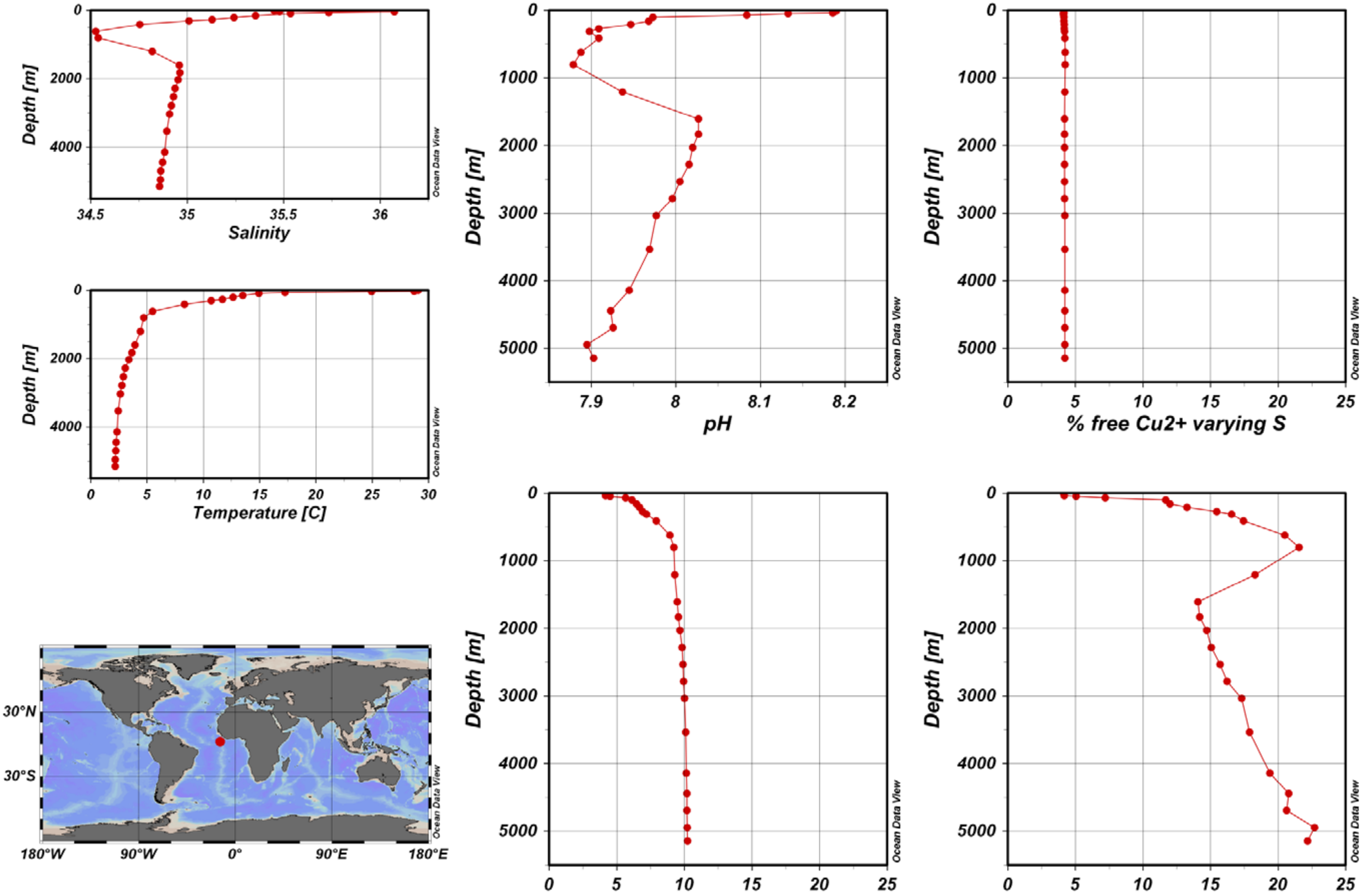

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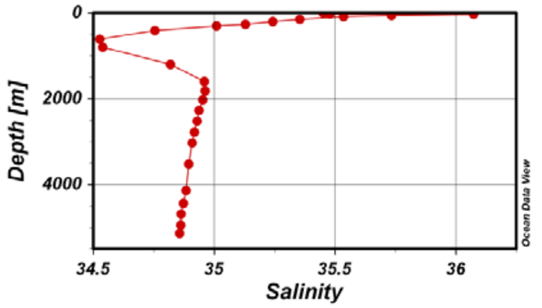

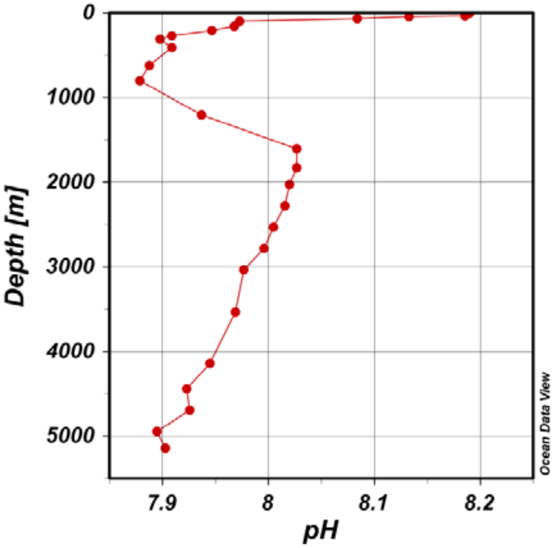

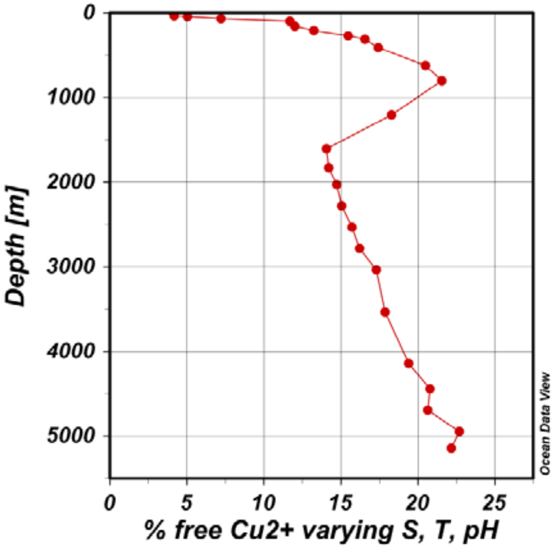

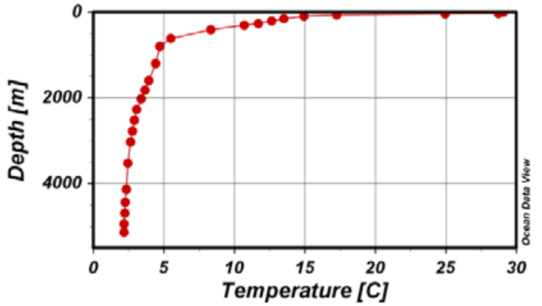

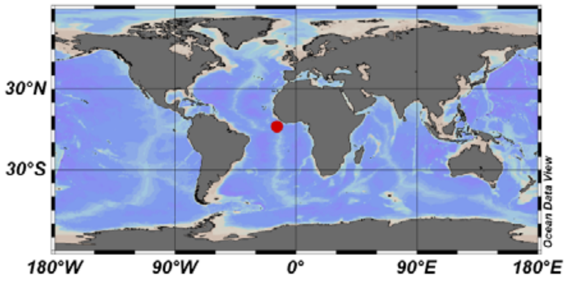

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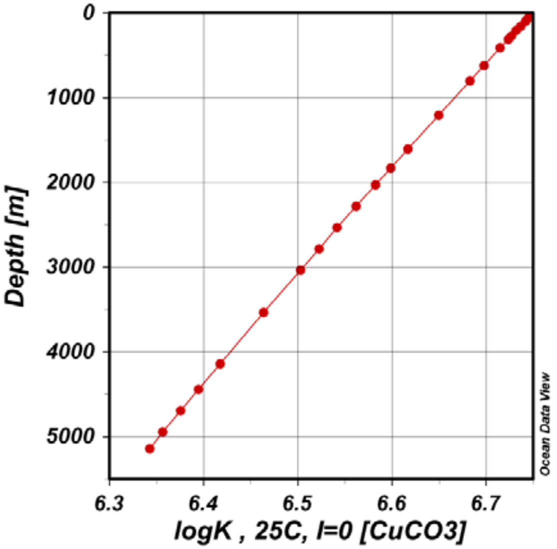

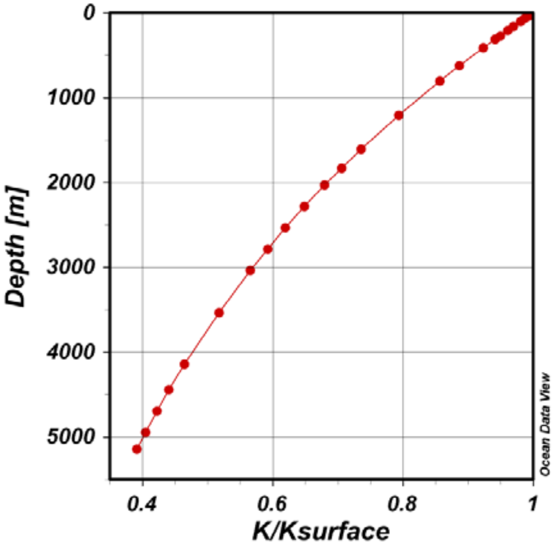

Based on estimates by Millero, 2011

Complexation with natural organic matter

For natural organic complexation, where much of the data has been acquired using CLE-AdCSV, this is restricted to fixed temperature and 1 atmosphere pressure, and reflects only binding within a limited detection window defined by the concentration and stability constant of the competing ligand.

A recent paper by Stockdale et al. has compared this type of data with predictions of complexation by humic substances in the ocean, using the WHAM model developed for freshwater. Agreement ranges between very poor and relatively good.

Speciation modelling in GEOTRACES?

GEOTRACES is assembling a truly impressive database of trace metal concentrations, both dissolved and particulate, in the world ocean. In order to make full use of these data, it would be very valuable to develop state of the art models of trace metal speciation including both inorganic and organic complexation and relevant to *in situ* conditions, not just at the surface but also in the interior of the ocean.