# Tracers for Redox Environments: GEOTRACES in the Black Sea

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GEOTRACES Themes

1. Fluxes and processes at ocean interfaces

   **oxic/suboxic/anoxic (sulfidic) interface**

2. Internal Cycling

   **redox sensitive cycling +**
   **euphotic zone versus chemosynthetic biology**

3. Development of proxies for past change

   **tracers for redox environments**

# Why is the Black Sea Interesting to Oceanographers?

1. The classic anoxic basin. Oxic layer over sulfidic layer.

2.Model for modern and ancient anoxic environments.

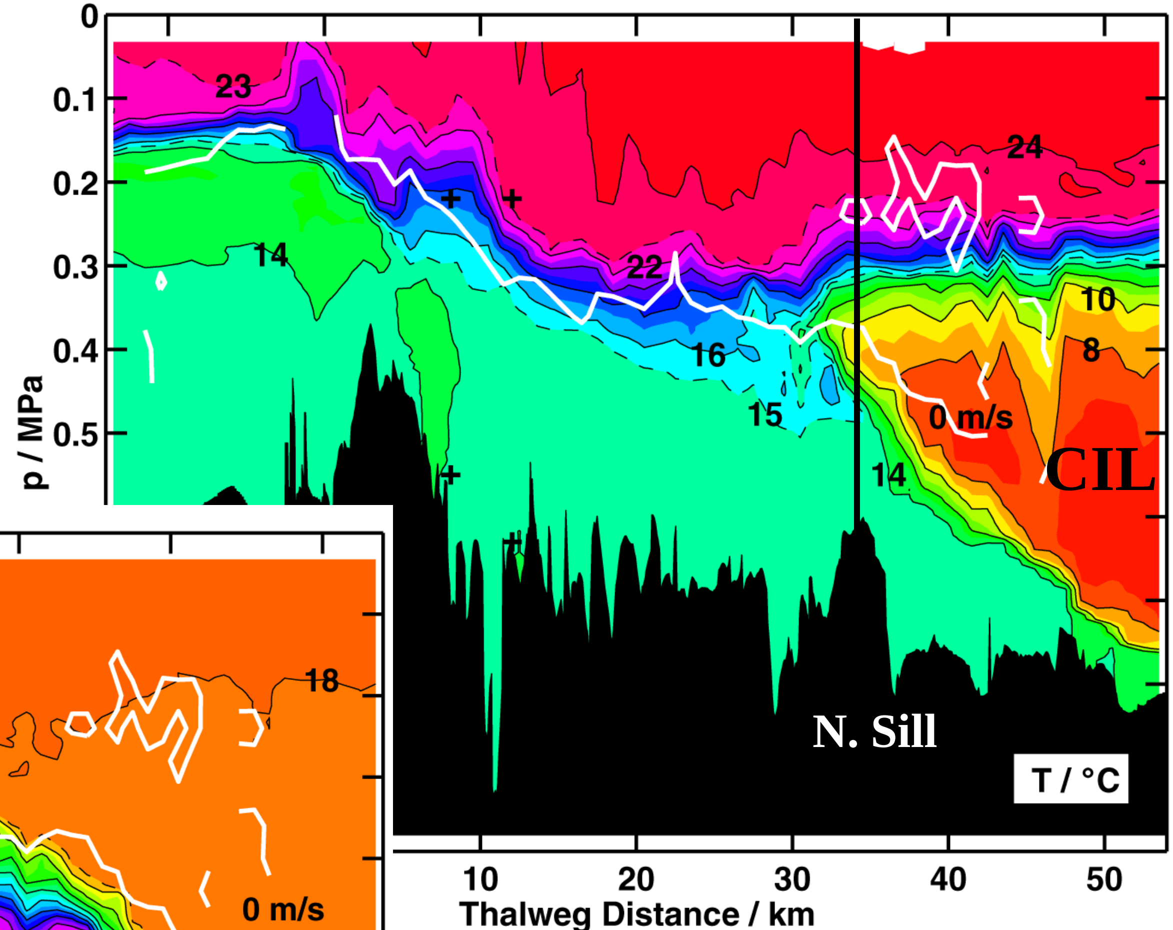
3. Well developed transition or suboxic zone. Model for world's organic rich sediments.

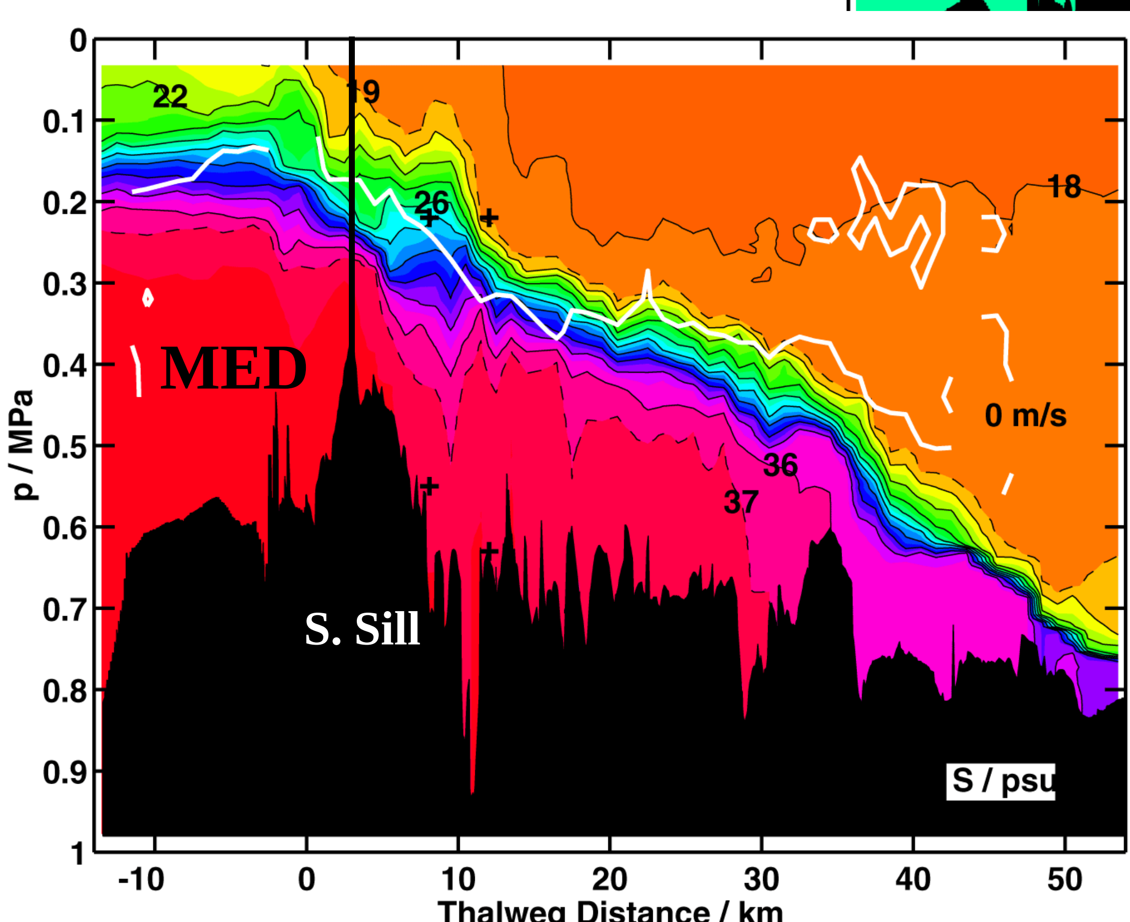
4. Suboxic reactions easy to study here because of predictable depth locations.

5. An ideal location to study effect of climate forcing on ocean distributions.

Climate ⇒ Physical ⇒ Chemical ⇒ Biological

# Temperature and Salinity along the Bosporus



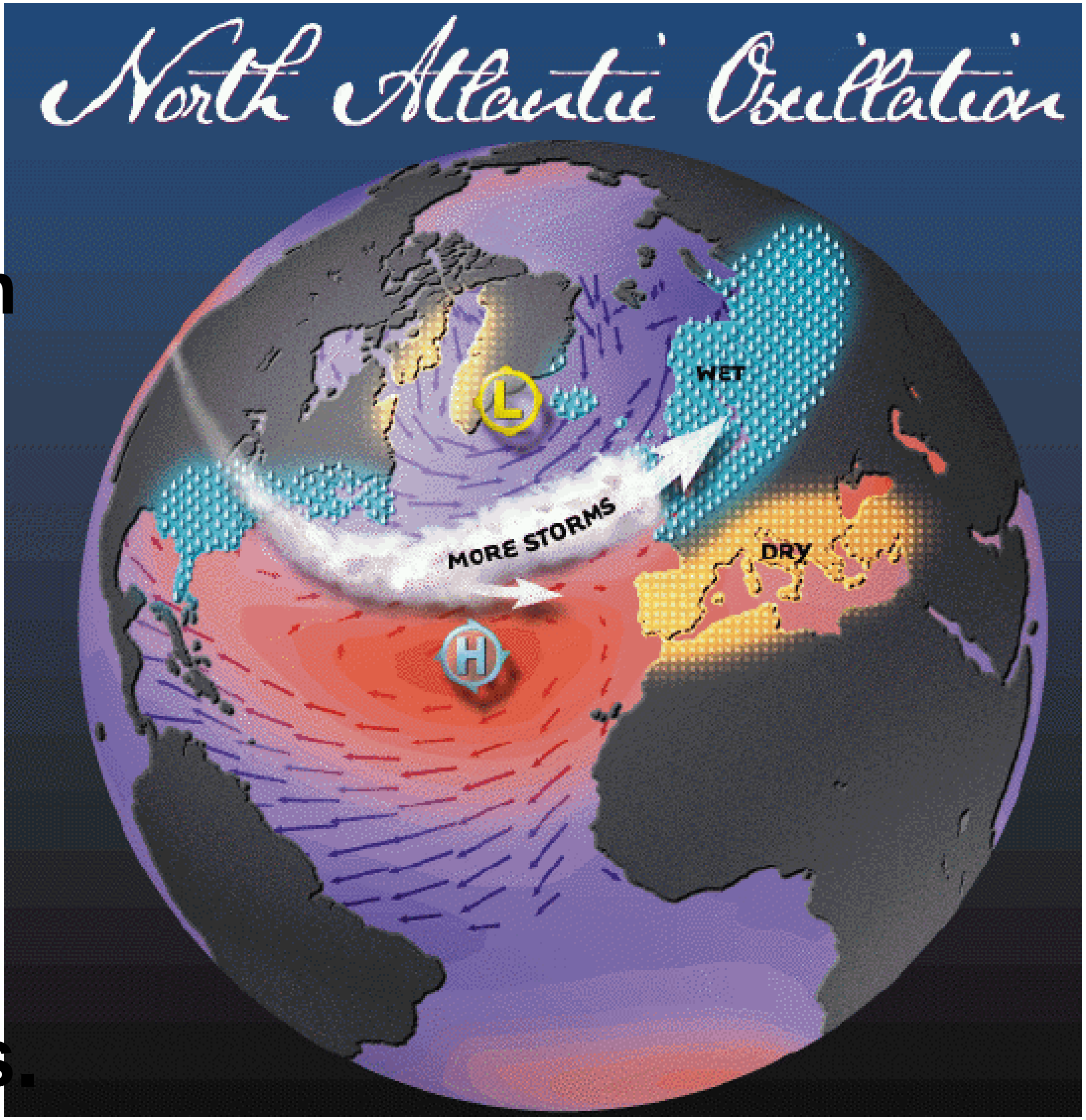

Black Sea has estuarine style circulation. High salinity Flows in at the bottom. Low salinity flows out at the surface.

Gregg et al (1999)

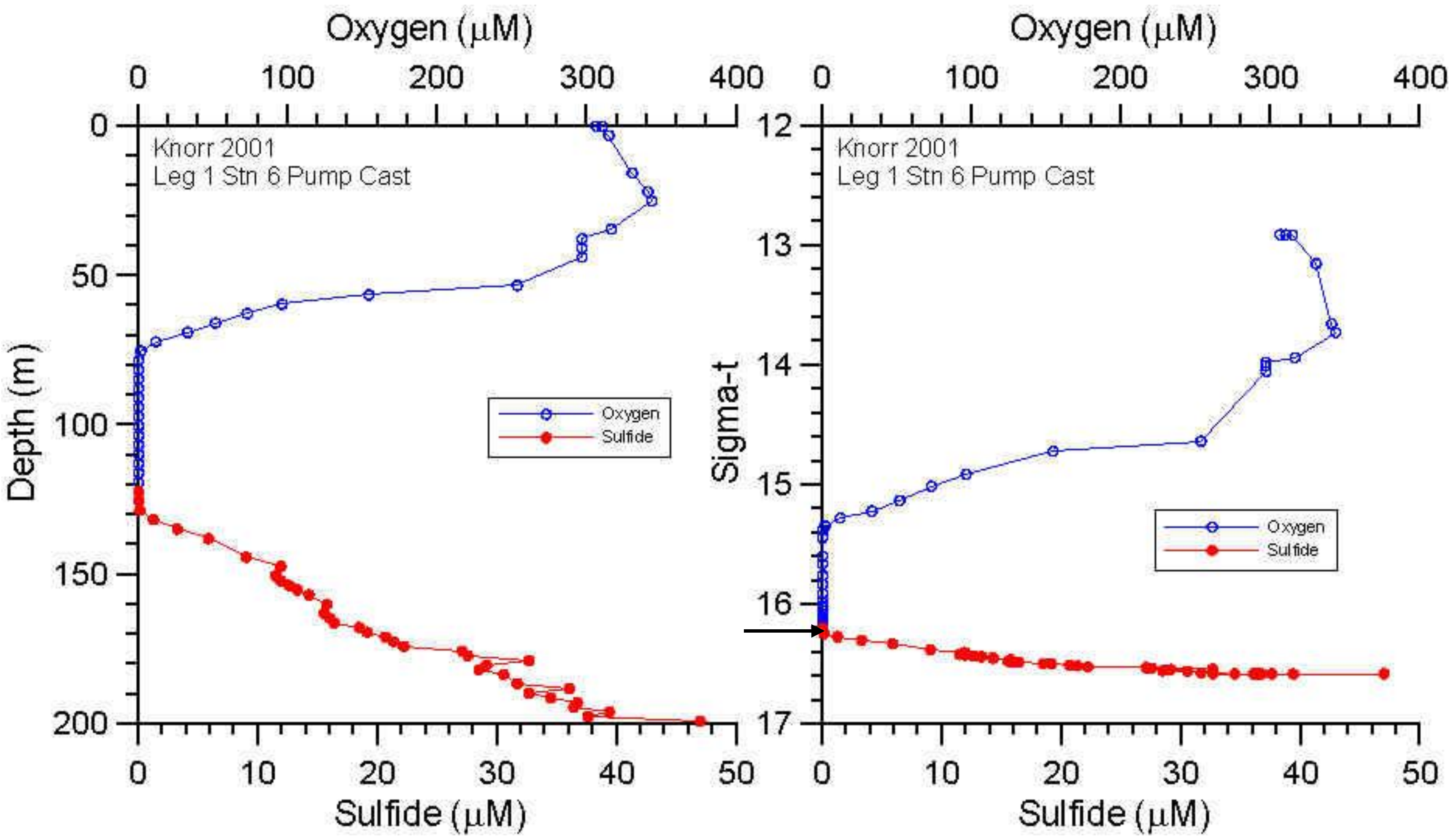
# Positive NAO

Strong Pressure Gradient Between Azores High and Iceland Low.

Cold and Dry Conditions in the Black Sea Region. Strong Westerly Winds.

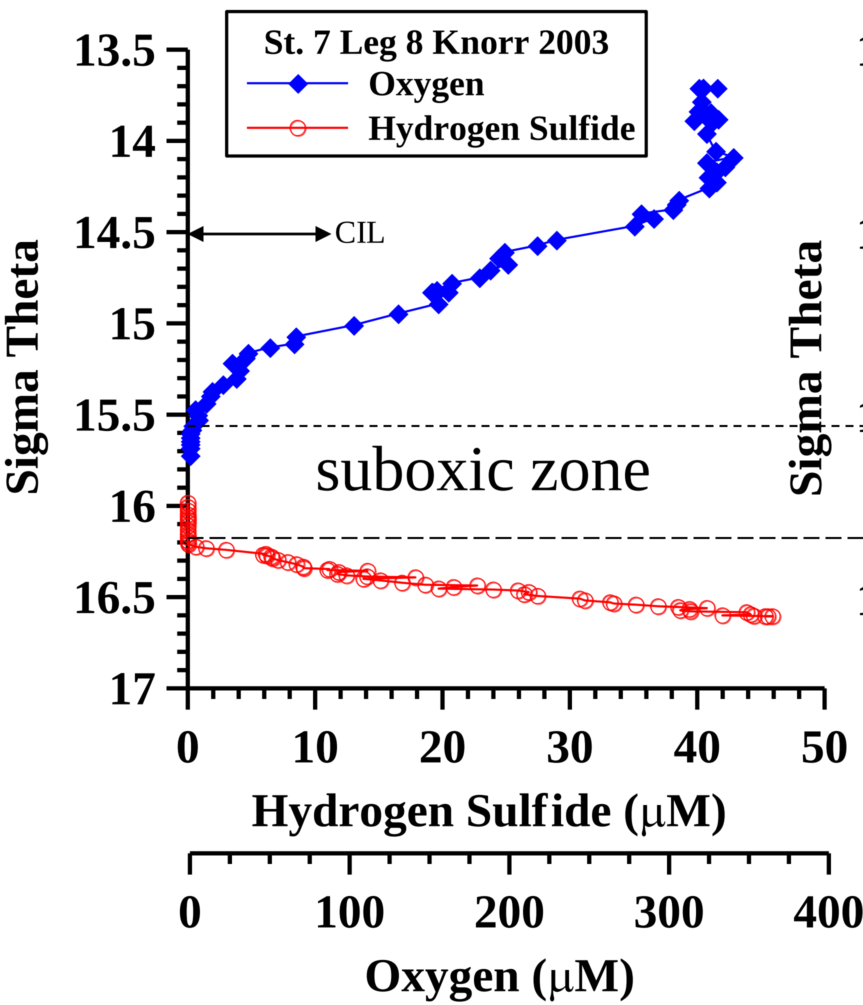


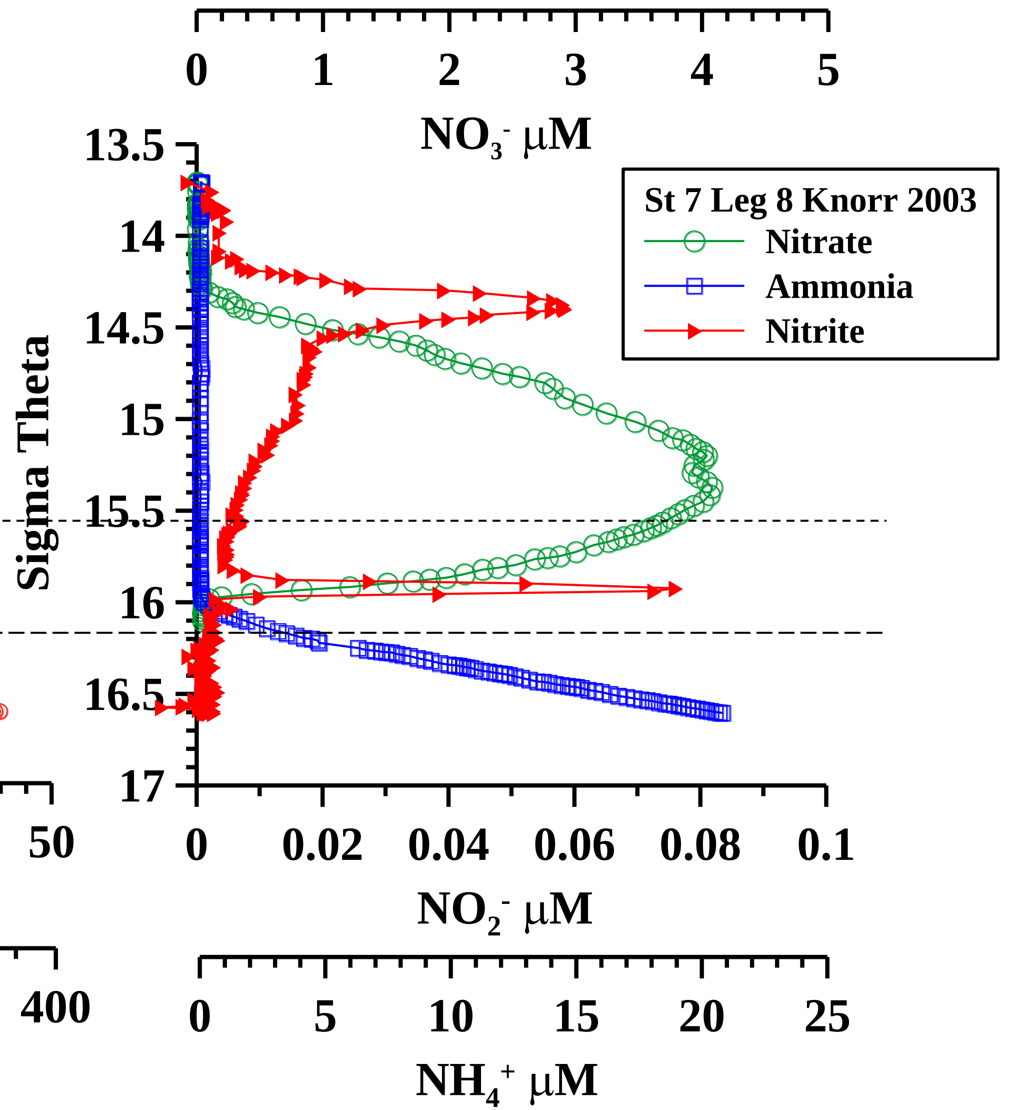
# The Suboxic Zone: Oxygen – Sulfide Depth versus Density




**Total depth = 2200m**

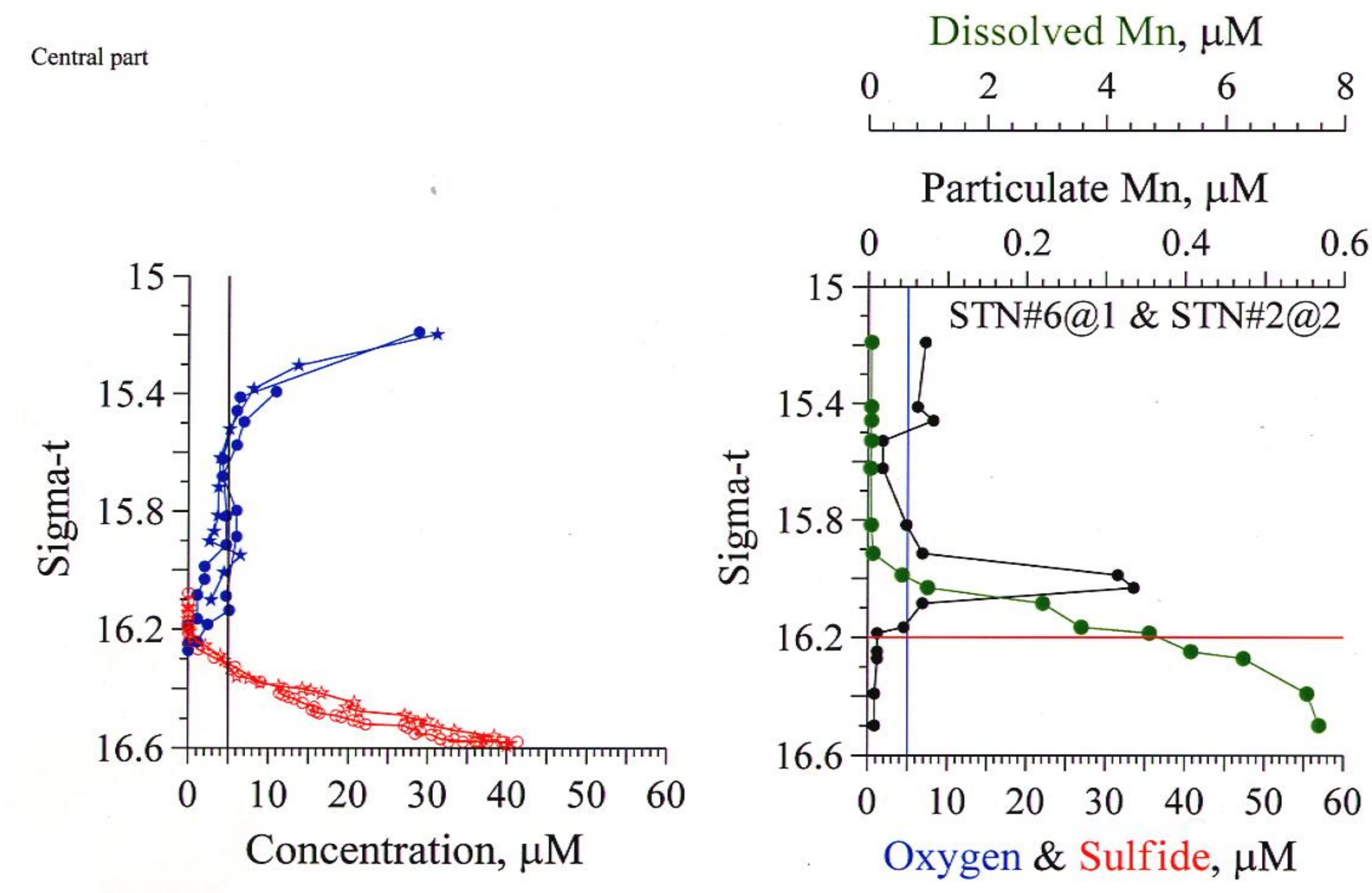
# Example of $NO_3^-$, $NO_2^-$ and $NH_4^+$ for R/V *Knorr* 2003



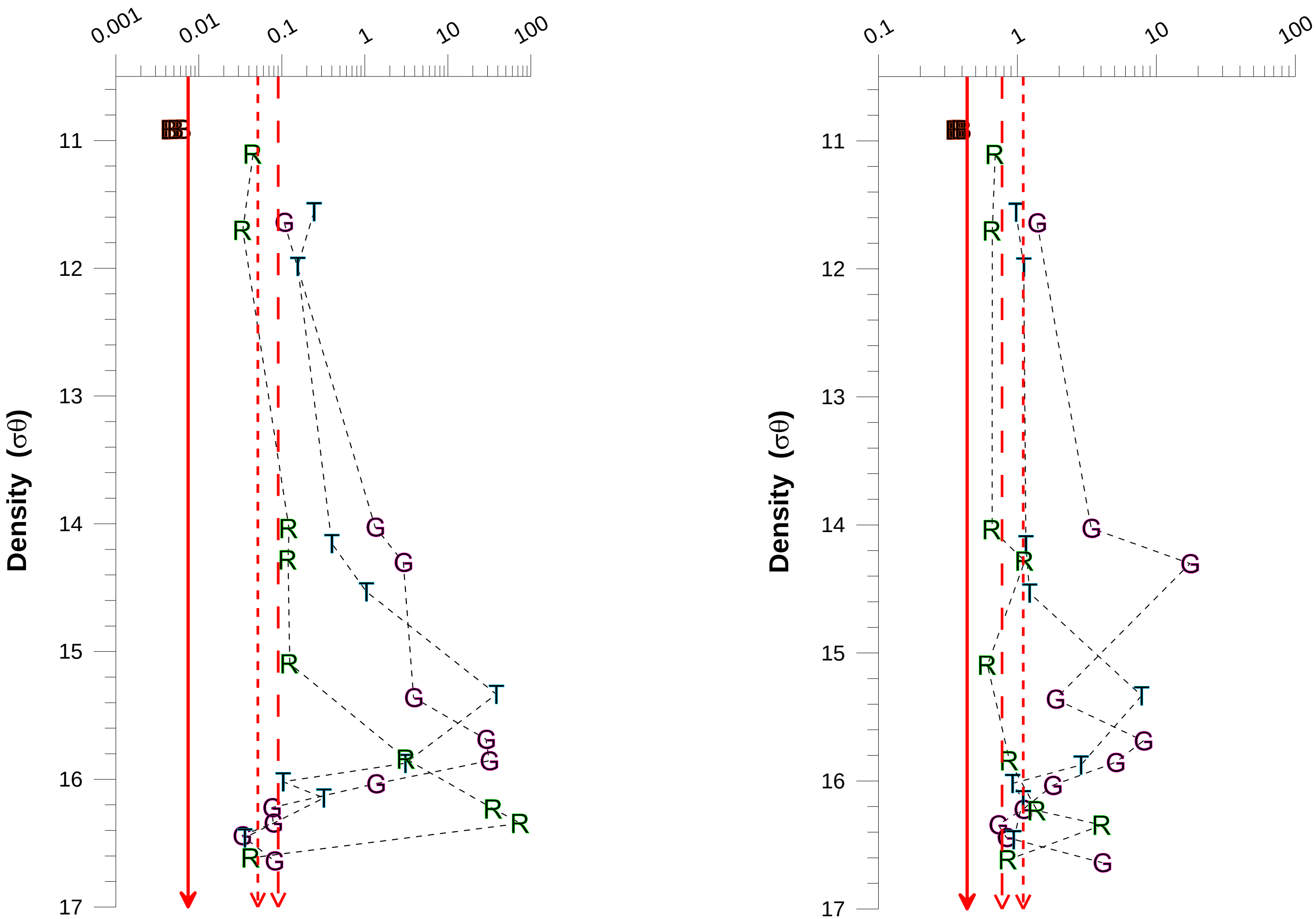

First seen during 1988 Expedition

Data suggests anammox



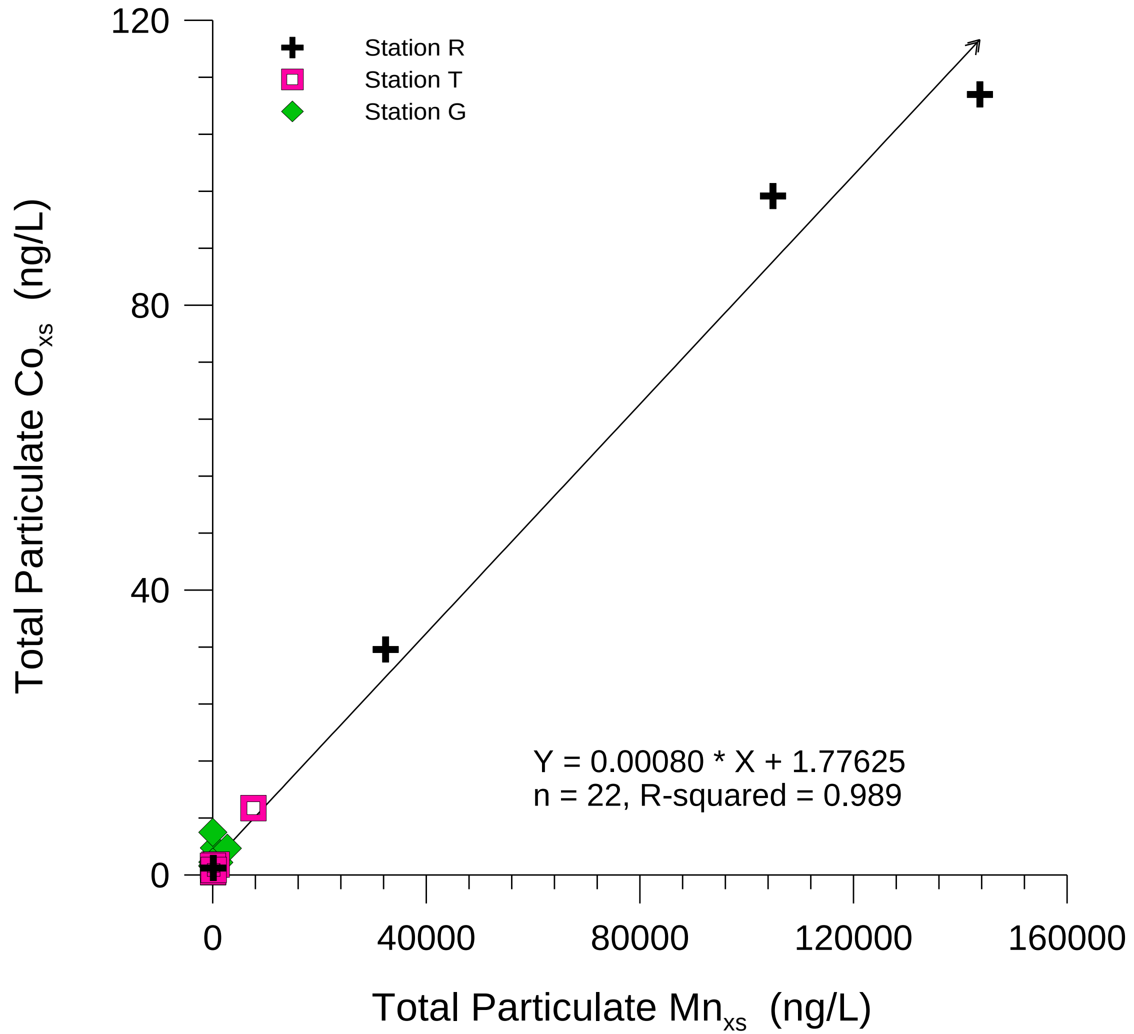

**Classic Example of Mn(II) – Mn (IV) Redox Cycling**
**e.g., Spencer and Brewer, Lewis and Landing, Tebo**

# Metals to Al in suspended particulate matter



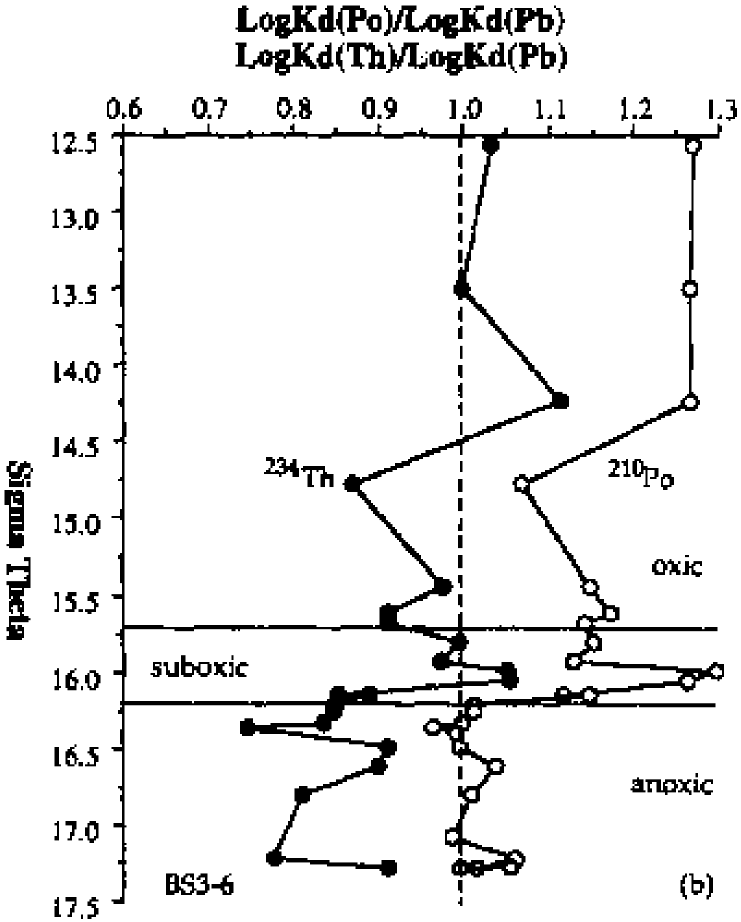

# Metal oxide cycling (Mn and Fe Redox Cycling)

**From Yigiterhan, submitted**




**Scavenging by metal oxides – Co by MnO2**

**Th – a class A metal**
**Po and Pb – class B metals**




| Zones | BS3-2 | BS3-6 |
|---|---|---|
| Oxic | Po~Th>Pb | Po>Th~Pb |
| Upper Suboxic | Po>Th~Pb | Po>Th~Pb |
| Lower Suboxic | Po~Pb>Th | Po~Pb>Th |
| Anoxic | Po~Pb>Th | Po~Pb>Th |

# Redox Tracers in Geochemistry

| | Oxidation state in oxic sea water | Speciation in oxic sea water | Major processes that control distribution in oxic sea water | Oxidation state when reduced | Speciation in reducing environment | Major processes that control accumulation in sediments |
|---|---|---|---|---|---|---|
| **Cd** | Cd(II) | $CdCl^+$ (aq) | Nutrient cycling | Cd(II) | CdS (s) | Released during diagenesis of organic matter. Complexes strongly with bisulfide. Likely precipitates in the presence of micro quantities of free sulfide. |
| **Cu** | Cu(II) | $CuCl^+$ (aq) | Nutrient cycling, scavenging | Cu(II), Cu(I) | *CuS (s),* $Cu_2S$ | Released during diagenesis of organic matter. Precipitates as disseminated sulfides. |
| **Mo** | Mo(VI) | $MoO_4^{2-}$ (aq) | Conservative behavior | Mo(V),<br>Mo (IV) | $MoO^{2+}$ (aq),<br>$MoS_2$ (s) | Diffuses across sediment-water interface to precipitation depth. Free sulfide required to accumulate. Removal as a mixed Mo-Fe-S begins at ~0.1 µM sulfide. Direct Mo-sulfide precipitation occurs at above 100 µM. |
| **Re** | Re(VII) | $ReO_4^-$ (aq) | Conservative behavior | Re(IV) | $ReO_2$ (s)?,<br>$ReS_2$ (s)?,<br>$Re_2S_7$ (s)? | Diffuses across sediment-water interface to precipitation depth. Removal mechanism is poorly understood. |
| **U** | U(VI) | $UO_2(CO_3)_3^{4-}$ (aq) | Conservative behavior | U(IV) | $UO_2$ (s) | Diffuses across sediment-water interface to precipitation depth. Removal appears controlled by kinetic factors. |
| **V** | V(V) | $HVO_4^{2-}$ (aq);<br>$H_2VO_4^-$ (aq) | Nearly conservative, perhaps some nutrient cycling. | V(IV),<br>V(III)? | $VO^{2+}$ (aq),<br>$VO(OH)_3^-$ (aq),<br>$V(OH)_3$ (s) | V is released from sediments when Mn reduction occurs near the sediment-water interface (where oxygen penetrates <1 cm). Accumulates in anoxic sediments via diffusion across sediment-water interface to removal depth. Reduced V(III) species are strongly scavenged. |

## Trace Metals in the Black Sea (a partial list)

Spencer and Brewer (1971 Classic paper on Mn and Fe)
Spencer et al (1972) Sc, La, Fe, Mn, Co, Sb, Hg
Brewer et al (1972)
Wei and Murray (1991, 1994) $^{234}Th$, $^{210}Po$, $^{210}Pb$
Haraldsson and Westerland (1988, 1991) Co, Fe, Mn, Cu, Ni, Pb, Zn
Lewis and Landing (1991, 1992) Mn, Fe, Cu, Ni, Pb, Zn
Jacobs and Emerson (1982) sulfide stripping hypothesis
Anderson et al (1989)] U
Emerson and Huested (1991) Re, Mo, U
Colodner et al (1993, 1995) Re
Wong and Brewer (1977) I
Luther and Campbell (1991) I
Cutter (1991) As, Sb
Schijf et al (1991) REE
Falkner et al (1993) Bs
Kubilay et al (1995) atm aerosols
Yigiterhan et al (2009, in press) particulate matter

# Thank You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