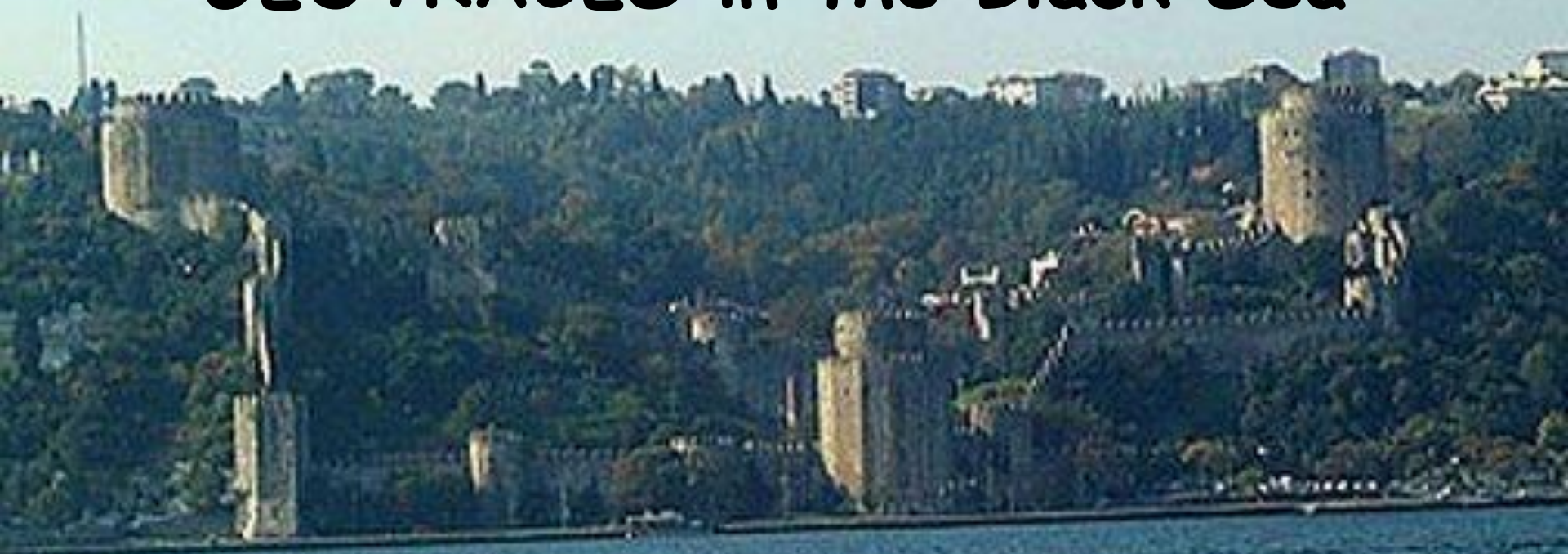


Tracers for Redox Environments: *GEOTRACES* in the Black Sea



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3 Oct 2010

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

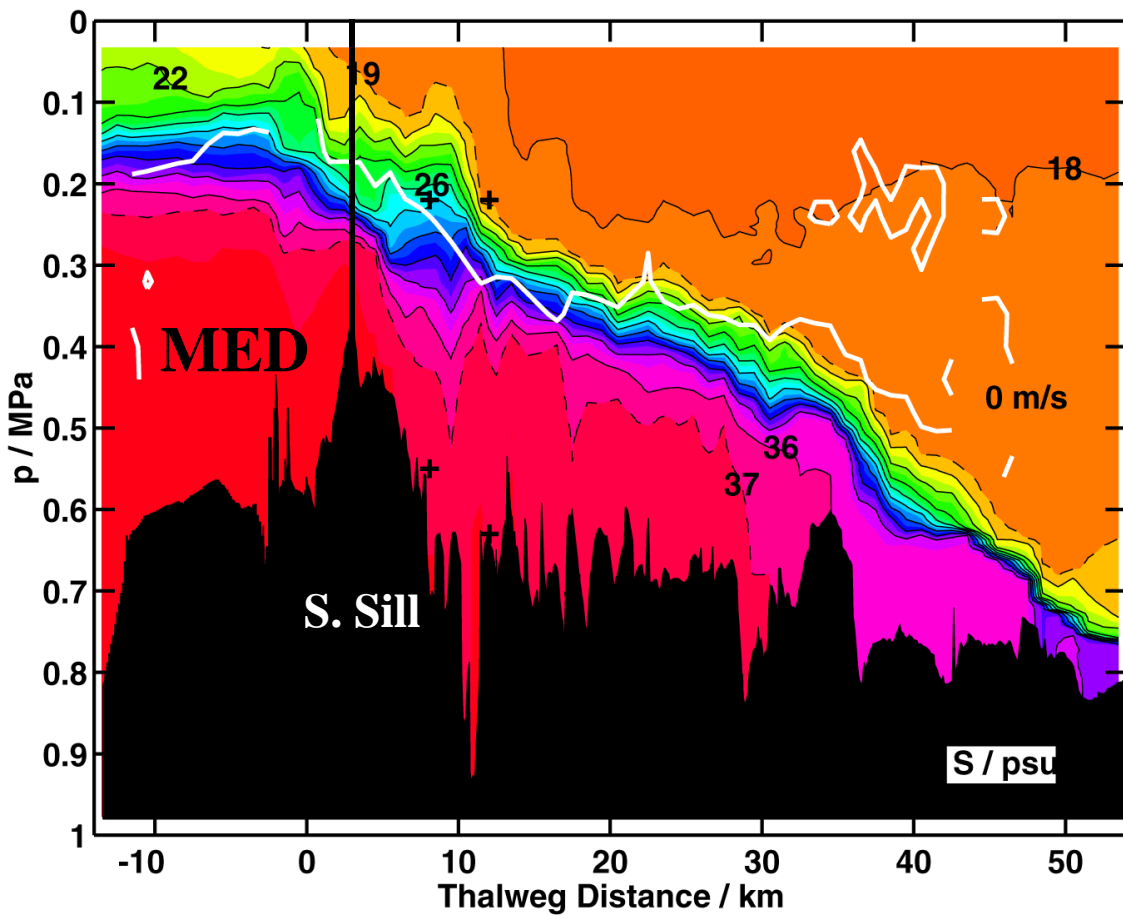
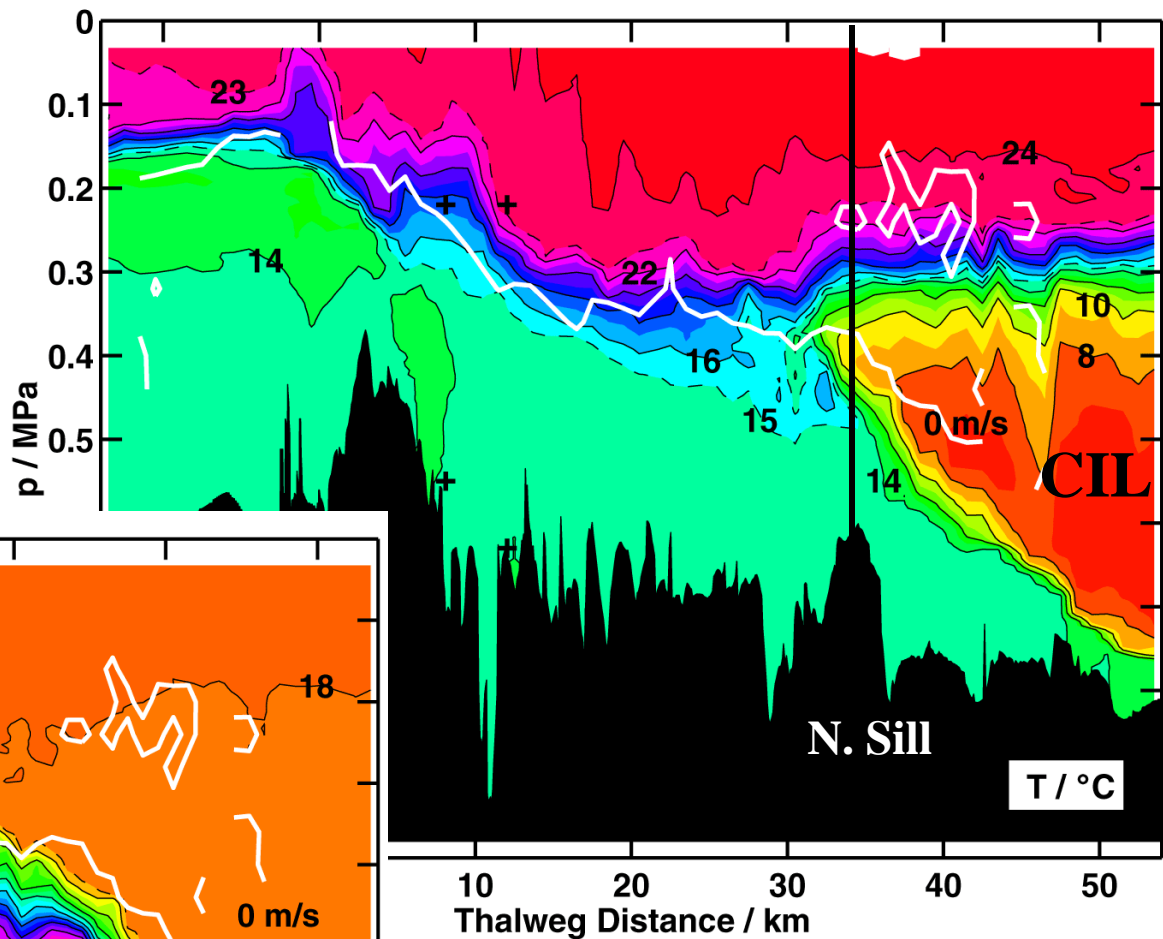
Why is the Black Sea Interesting to Oceanographers?

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 Bosphorus



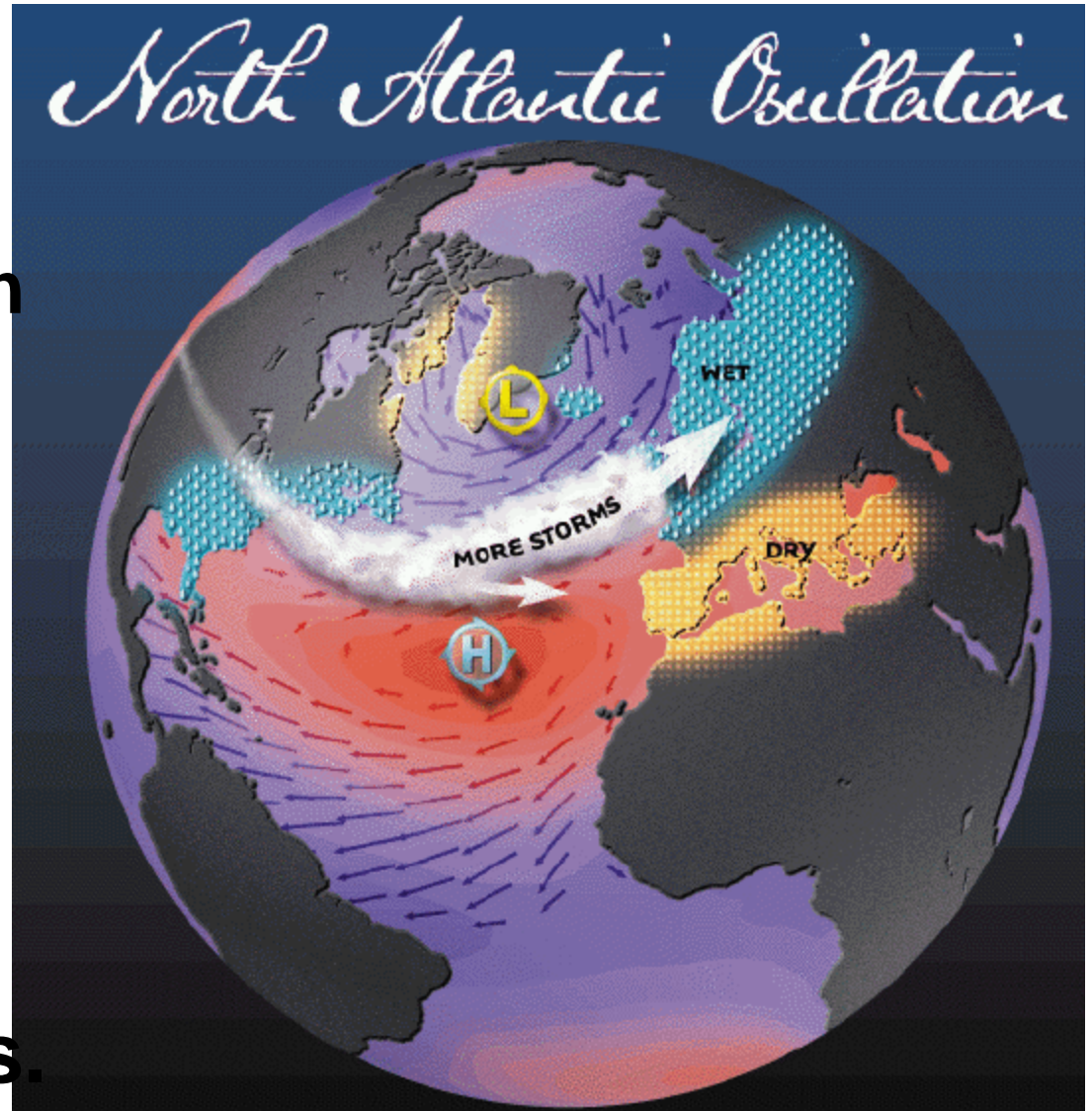
Black Sea has estuarine style circulation. High salinity Flows in at the bottom. Low salinity flows out at the surface.

Gregg et al (1999)

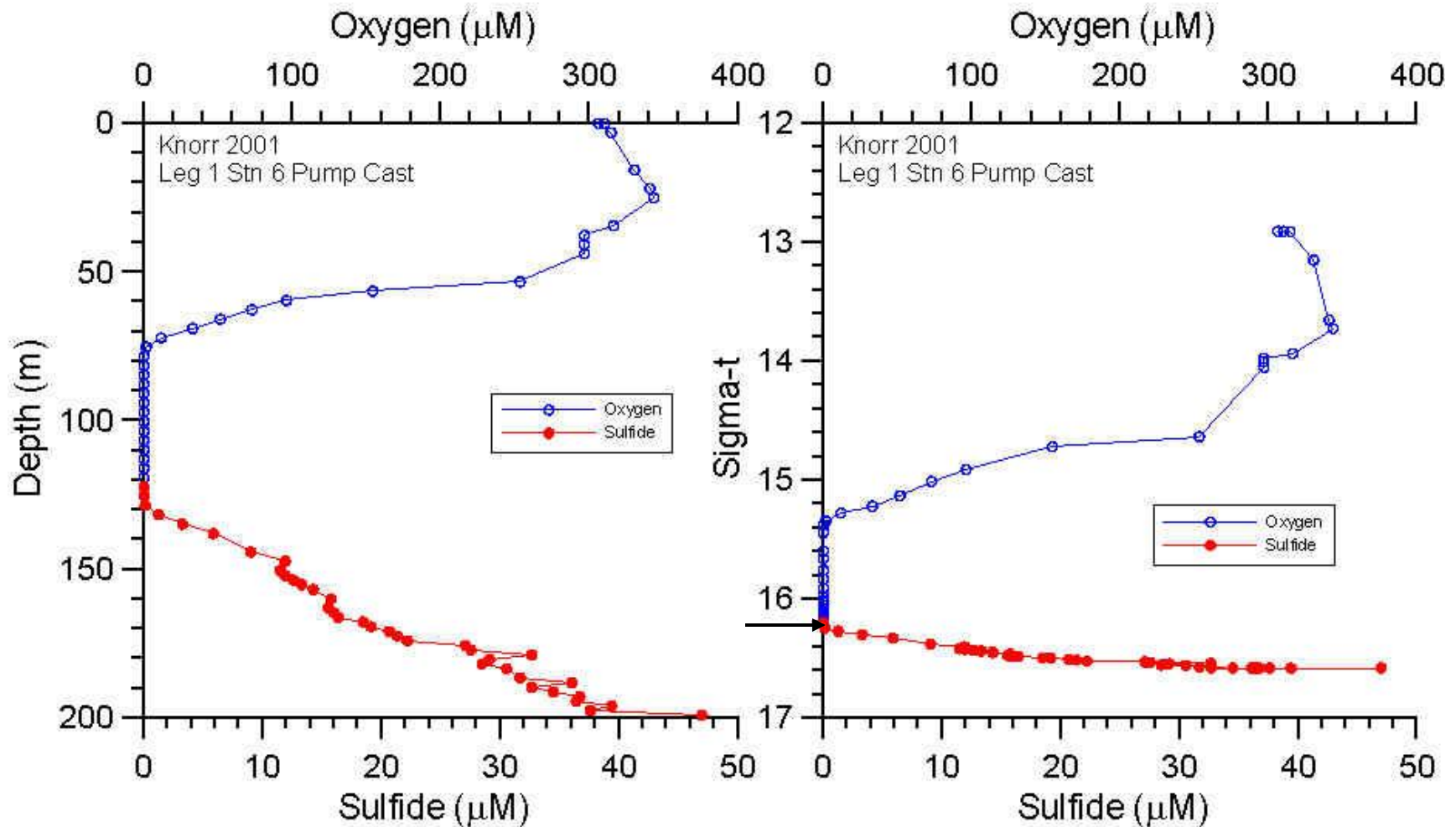
Positive NAO

Strong Pressure Gradient Between Azores High and Iceland Low.

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

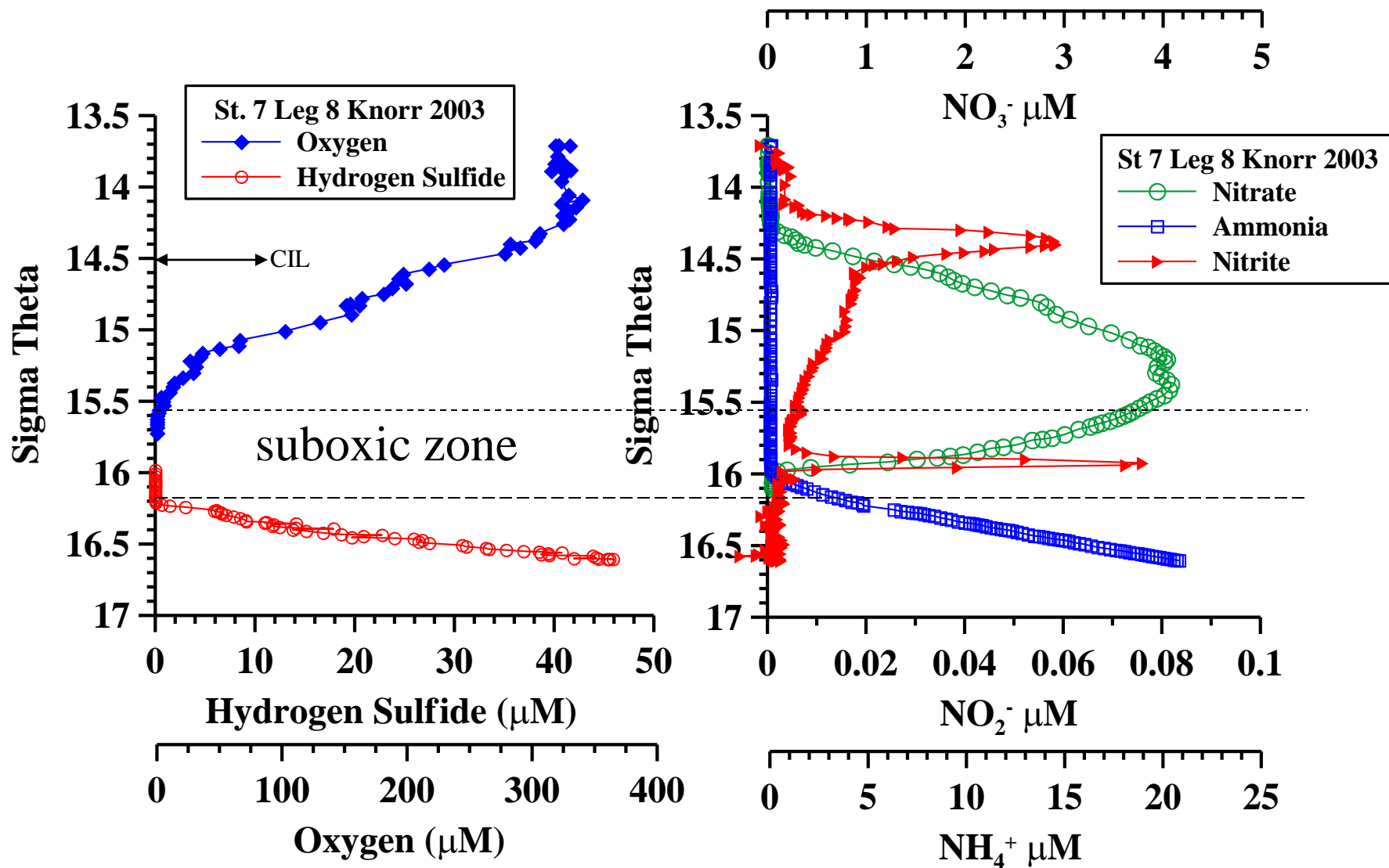


The Suboxic Zone: Oxygen – Sulfide Depth versus Density



Total depth = 2200m

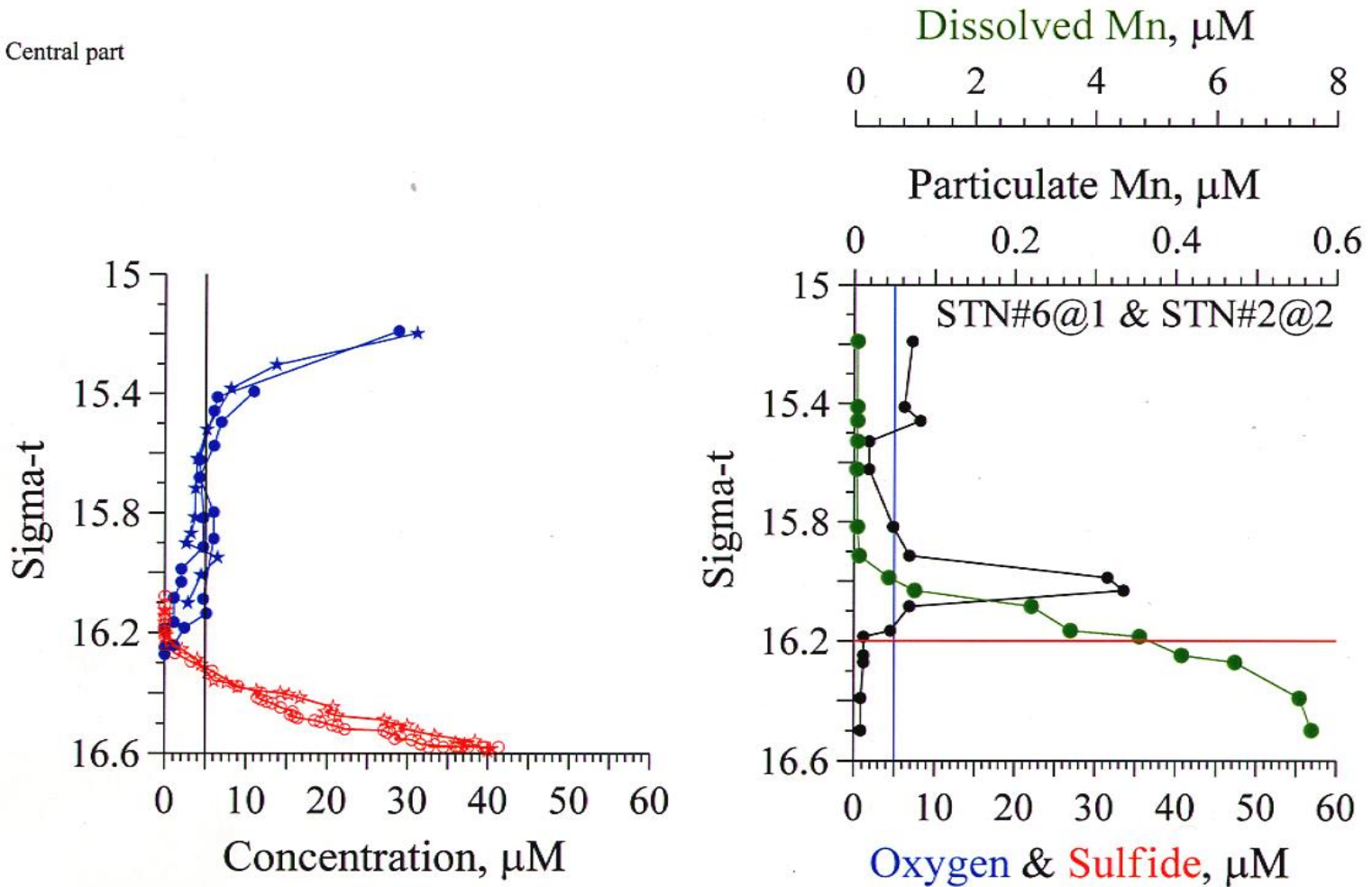
Example of NO_3^- , NO_2^- and NH_4^+ for R/V *Knorr* 2003



First seen during 1988 Expedition

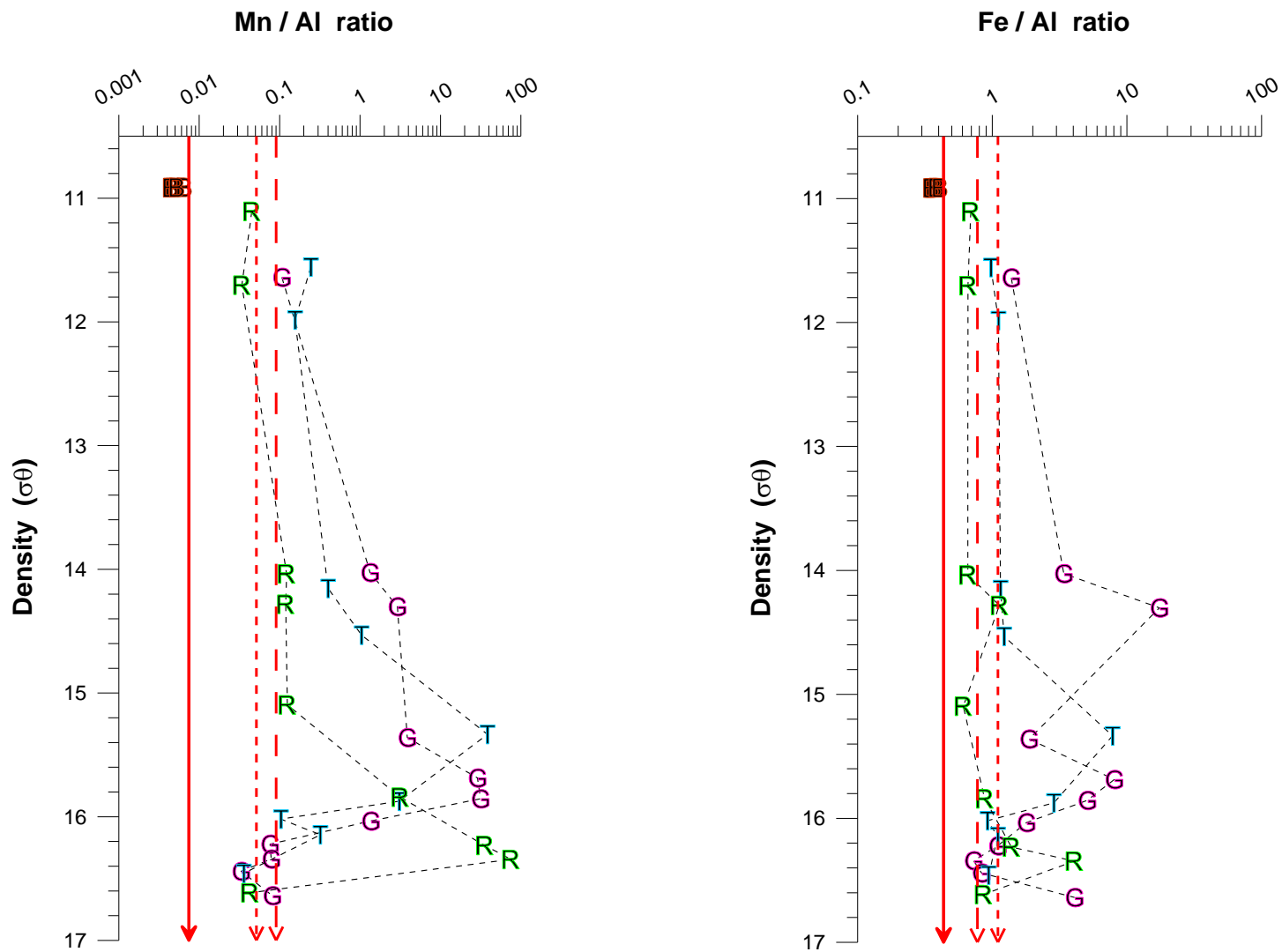
Data suggests anammox

Central part



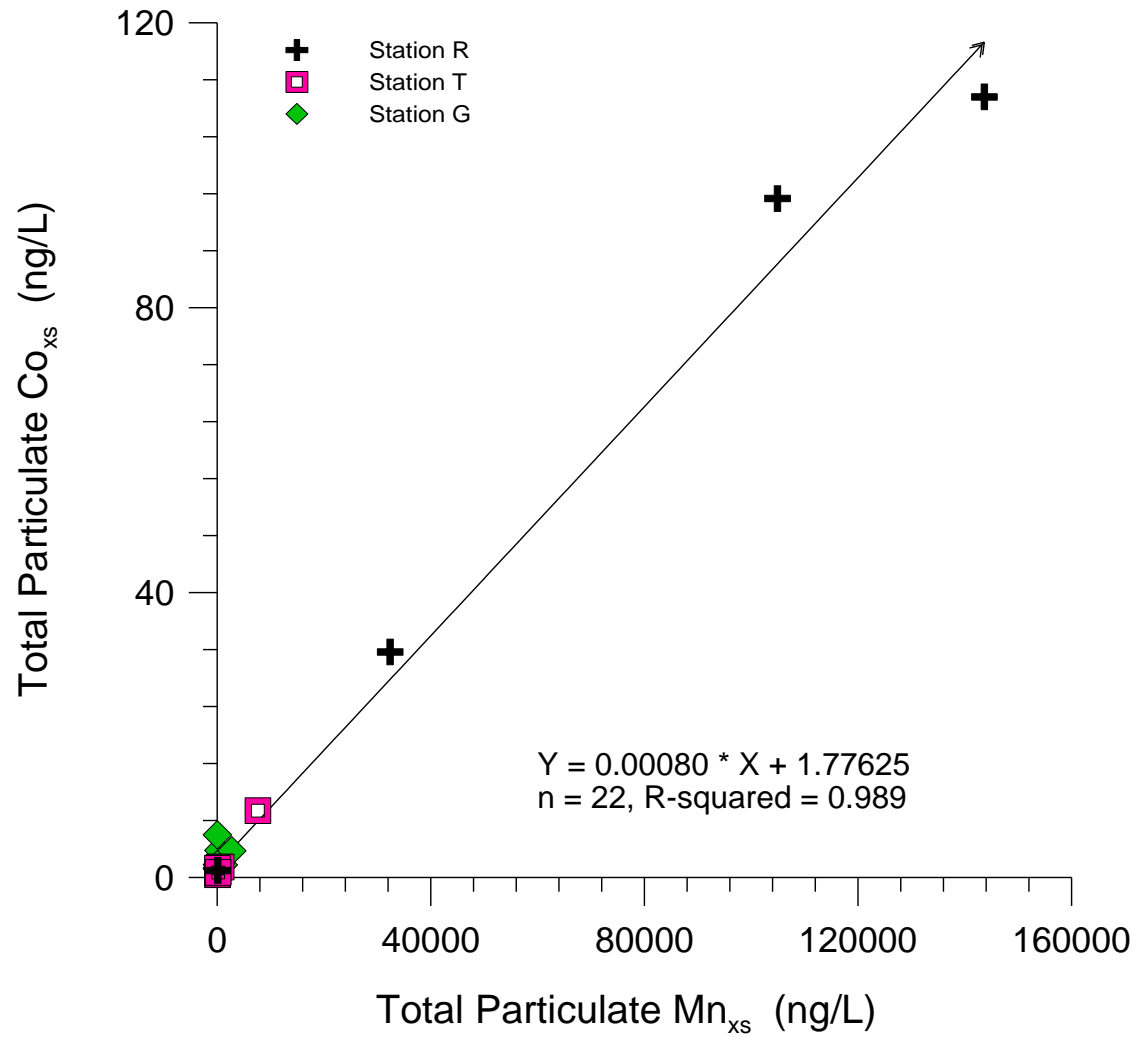
**Classic Example of Mn(II) – Mn (IV) Redox Cycling
e.g., Spencer and Brewer, Lewis and Landing, Tebo**

Metals to Al in suspended particulate matter



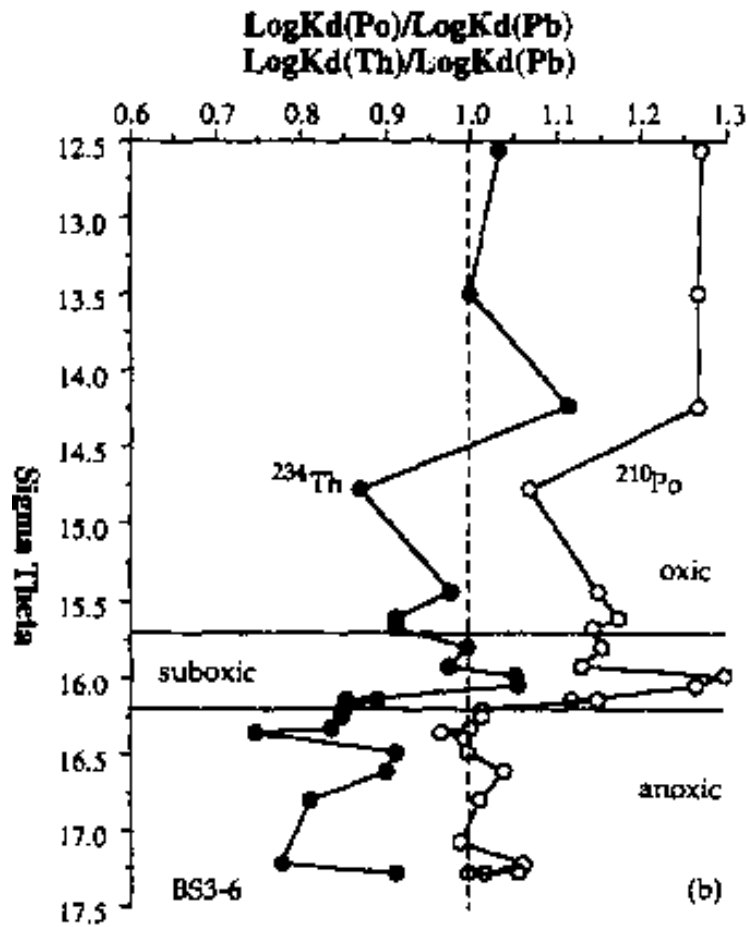
Metal oxide cycling (Mn and Fe Redox Cycling)

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)	$\text{CdCl}^+(\text{aq})$	Nutrient cycling	Cd(II)	$\text{CdS}(\text{s})$	Released during diagenesis of organic matter. Complexes strongly with bisulfide. Likely precipitates in the presence of micro quantities of free sulfide.
Cu	Cu(II)	$\text{CuCl}^+(\text{aq})$	Nutrient cycling, scavenging	Cu(II), Cu(I)	$\text{CuS}(\text{s}), \text{Cu}_2\text{S}$	Released during diagenesis of organic matter. Precipitates as disseminated sulfides.
Mo	Mo(VI)	$\text{MoO}_4^{2-}(\text{aq})$	Conservative behavior	Mo(V), Mo(IV)	$\text{MoO}_2^{2+}(\text{aq}), \text{MoS}_2(\text{s})$	Diffuses across sediment-water interface to precipitation depth. Free sulfide required to accumulate. Removal as a mixed Mo-Fe-S begins at $\sim 0.1 \mu\text{M}$ sulfide. Direct Mo-sulfide precipitation occurs at above $100 \mu\text{M}$.
Re	Re(VII)	$\text{ReO}_4^-(\text{aq})$	Conservative behavior	Re(IV)	$\text{ReO}_2(\text{s})?, \text{ReS}_2(\text{s})?, \text{Re}_2\text{S}_7(\text{s})?$	Diffuses across sediment-water interface to precipitation depth. Removal mechanism is poorly understood.
U	U(VI)	$\text{UO}_2(\text{CO}_3)_3^{4-}(\text{aq})$	Conservative behavior	U(IV)	$\text{UO}_2(\text{s})$	Diffuses across sediment-water interface to precipitation depth. Removal appears controlled by kinetic factors.
V	V(V)	$\text{HVO}_4^{2-}(\text{aq}); \text{H}_2\text{VO}_4^-(\text{aq})$	Nearly conservative, perhaps some nutrient cycling.	V(IV), V(III)?	$\text{VO}^{2+}(\text{aq}), \text{VO}(\text{OH})_3^-(\text{aq}), \text{V}(\text{OH})_3(\text{s})$	V is released from sediments when Mn reduction occurs near the sediment-water interface (where oxygen penetrates $< 1 \text{ cm}$). 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 Husted (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

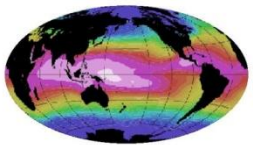
Kubilay et al (1995) atm aerosols

Yigiterhan et al (2009, in press) particulate matter

Thank You



Rush hour on the Bosphorus



Program on Climate Change
UNIVERSITY OF WASHINGTON