Elemental cycling and storage within source to sink sedimentary systems:

the critical importance of energetic topset and coastal facies.

Robert C. Aller School of Marine and Atmospheric Sciences Stony Brook University Stony Brook, NY

Contributions from many colleagues





Forcing Functions for Southern New Guinea Sedimentation Processes

Idealized clinoform diagenetic regimes and redox reaction signatures



Plan View: Energetic coastal processing and storage system (relative geometries variable)



Example elemental cycle vignettes :

 $\mathbf{C}_{\mathrm{org}}$ Fe S (^{18,16}O) Si Li+, K+ F-Some other time: Mg²⁺,Ca²⁺ N, P, As **|**-U, Ra



Schlünz and Schneider, 2000



•Accumulation rate (advection into anoxic storage regime)

•C_{org} – mineral associations (stabilization)

•Oxygen exposure time (oxidant reactivity - energy yield)

C_{org} preservation: role of sediment accumulation rates (emphasis early 1990's)



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Sedimentary incinerators: energetic facies, enhanced by transitions of sea level



Aller and Blair, 2006, CSR

Diagenetic Fractionation: Gulf of Papua



Aller, et al., 2008, JGR-ES

Net loss of ancient, refractory C_{org}



Aller, et al, 2008, JGR-ES





Middle Topset

GH14 Nov 03

10 cm

120



Aller, 2004, JMR

Suboxic, seasonally reworked layers characterize the topset

GH14 topset



Quantity of reactive Fe determines relative reaction balances and timing of redox stages in response to physical dynamics.



The initial quantity and reactivity of Fe phases are largely determined by the weathering regime in the drainage basin and coastal wetlands.



Examples of reaction processes in the unsteady, suboxic diagenetic reactor

Aller, et al., 2010, GCA

O isotope modification of seawater SO_4^{2-} in mobile suboxic muds



• Oxygen isotope (SO₄⁼) evolution indicates redox cycling without net reduction in the suboxic zone.

$$SO_4^= \longrightarrow S^= \xrightarrow{H_2O} SO_4^=$$

Most diagenetically reduced Fe(II) is not associated with S.

Deposits are relatively S poor compared to C_{org} content.



Unsteady topset diagenetic regimes favor preservation of isotopically heavy S



Amazon - Guianas mud belt

Implications for paleoenvironment reconstruction

Aller, et al, 2010, GCA

Properties:

- •Abundant supply of reactive Fe, Al –oxides (source region)
- •Supply of reactive C_{org} , high remineralization rates (productive, source region)
- •Suboxic diagenetic conditions (reducing, nonsulfidic)
- •High flux of reactive biogenic SiO₂ (productive)
- •Alkali and alkaline earth rich solutions (seawater)



Reverse weathering

Amazon – Guianas





High flux of Li⁺, K⁺, and F⁻ into mobile suboxic zone



- Li^+ diffusive flux: 0.4 3 mmol m⁻² yr⁻¹ (up to 60% local river supply)
- No water column expression ("conservative" Li⁺, F⁻ versus salinity relation)





Moore, et al, 1996, CSR

Oxic water column



Seabed compositional trends imposed by boundary conditions

Not unidirectional transport

Characteristic properties of tropical mobile deltaic muds :

- Unsteady, episodically mixed suboxic reactor (minor bioturbation)
- High reactive Fe $(300 400 \mu mol g^{-1}; 2 3X \text{ temperate})$
- High fraction reactive Fe reduced (>0.8)
- Low fraction Fe(II) as sulfide (<0.1)
- $C/S \sim 4-6$
- δ^{34} S > 0 (10 to 30)
- $C_{org} / SA < 0.4 \text{ mg C m}^{-2}$
- Authigenic Fe rich clays, carbonates

Environmental reconstruction?

Anoxic ocean (reactive Fe relations; sedimentary structures)

Low productivity (low C_{org})

Low SO₄²⁻ ocean (low S, high C/S, high δ^{34} S ‰)

no S disproportionation (high δ^{34} S ‰)

•Require criteria independent of commonly used geochemical properties to constrain nature of depositional environment

•Energetic topset mud deposits behave as unsteady, suboxic batch reactors

•Terrestrial and marine sedimentary debris, river and sea water solutes are imported, modified in the topset reactor, and exported both seaward and shoreward (material exchange, storage)

•Diagenetic reaction types, magnitudes, balances, products and net fluxes depend on:

reactant inputs (e.g., reactivity - kinetics, mass) frequency, magnitudes, duration of physical disturbance (sedimentary dynamics) residence times of particles within mobile suboxic zone geomorphology – oceanographic coupling (facies geometry)

•A wide spectrum of C_{org} pools of varied reactivity are efficiently remineralized

•Biogenic Si, alkalis, alkaline earths, and halides are consumed by reverse weathering processes

•Isotopic signatures are modified, including SO₄ and Fe

•Permeable sand facies properties / fluxes remain largely unknown

Despite their central importance in governing the net output of source to sink systems, modifying solute and particle compositions, and controlling material storage properties at the continent – ocean -atmospheric boundary, relatively few geochemical / biogeochemical studies of energetic topset muds, and even fewer of deltaic sand deposits, have been made.

Why?

•The complexity associated with the unsteady nature and physical setting of these systems is not amenable to quick results using standard sampling methods (e.g., characterization by 1 time sampling) and requires integrated interdisciplinary effort and new methodologies to make headway (difficult to organize, fund, and sustain).

•Enertia of traditional models.

•Lack of interest by biogeochemists in seabed relative to water column processes (out of sight out of mind).

Perpetuates an under appreciation or misunderstanding of the central role of the seabed and sedimentary dynamics in elemental cycling in shallow water systems.

Future biogeochemical study designs in energetic shallow systems should include:

Sedimentary reflux dynamics:

Frequency Duration (event, rest state) Intensity (mass / depth scales) Net accumulation rate

Water column: Composition and productivity Transport regime

Coupling to seafloor biogeochemical cycling:

Reoxidation / exchange efficiency Reaction progression - extent Benthic fluxes (eddy correlation based) Storage Properties Formulate coupled, probabilistic sediment dynamics – biogeochemical response models of :

Topset reworking / re-exposure frequencies / duration / magnitudes (reflux) (

Diagenetic reaction kinetics

Residence times within depositional regime

Export to foreset

Wetland – Topset exchange

Bioturbation – recolonization patterns (transient)

Primary production response to sediment remobilization