Reverse weathering reactions and the marine silica cycle

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The biogeochemical cycles of Si and C are intimately linked in the global ocean by processes such as primary production, the biological portion of the carbon pump, and reverse weathering reactions (e.g.,authigenic clay formation). As the reconstitution or neoformation of aluminosilicate phases occur during early diagenesis, reactions consume alkalinity and produce CO_2. Rapid authigenic clay formation in the proximal zone of continental margins likely represents the single largest sink of biogenic silica (bSi_{opal}) in the ocean. Estimates of this flux have evolved over the past few decades from 0.4 Tmol Si $year^{-1}$ to 4 – 5 Tmol $year^{-1}$ with emerging evidence from non – traditional proxies, in particular the cosmogenic radionuclide ^{32}Si. By directly tracing the fate of initially deposited unaltered bSi_{opal}, ^{32}Si ($t_{1/2}$ ~ 140 yrs) can be used to constrain burial of early diagenetic altertion products of biogenic silica ($bSi_{altered}$), including authigenic aluminosilicates (bSi_{clay}).

^{32}Si activities in operational pools in tropical deltaic sediments indicate the method widely used to determine bSi_{opal} recovers only a minor fraction of the total initially deposited biogenic silica (bSi_{total}). Traditional biogenic silica leaches can underestimate bSi_{total} in subtropical deltas and temperate estuaries by two to four – fold. Results are consistent with rapid alteration of bSi_{opal} and bSi_{clay} formation. ^{32}Si – based estimates of bSi_{total} storage ($bSi_{total} = bSi_{opal} + bSi_{clay}$) ~are 1Tmol/y in temperate estuaries and 3.5 – 3.9 Tmol/y in tropical and subtropical depocenters.

The magnitude of this sink in near – shore high – deposition margins and its impact on global OC burial, consumption of cations (Mg^{2+}, K^{+}, Li^{+}) and alkalinity, sequestering of trace elements (Ge), and production of CO_2 strongly indicates a need to focus on these under – studied systems when attempting to resolve controls on climate and interpretation of paleopoxies ($\delta^{7}Li$, $\delta^{30}Si$, $\delta^{26}Mg$, Ge/Si) in the marine record. Most shelf and slope regions where authigenic clay formation is inferred remain relatively unexplored, implying this sink may be larger, or that the marine silica is not at steady – state, or that inputs of dissolved silica are greater than current estimates.