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Continental Emergence and Ocean Chemistry: A Pathway to the Great Oxygenation Event

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Global models of ocean-lithosphere interaction provide critical insights into the evolution of ocean chemistry through time (Chemical Archeoceanography) and serve as a foundation for understanding the planetary surface's changing boundary conditions. These models must integrate fundamental principles of oceanic element fluxes with geological constraints on the lithosphere-ocean-atmosphere system. Here, we outline key considerations:

1. Before *c.*2.7 Ga, most volcanic activity occurred subaqueously in proto-continental settings, indicating an early Earth surface dominantly covered by water.
2. The limited exposed landmass, where intense weathering produced clays, was the sole source of carbonate alkalinity.
3. The pH of the alkalinity-poor ocean was not buffered.
4. Carbonates, often preserved alongside rare mudstones, were minor components of the sedimentary record until *c.*2.6 Ga. Pre-2.6 Ga sediments were instead dominated by greywackes, cherts, and thin Algoma-type banded iron formations (BIFs).
5. More widespread late Archaean emergence of land coincided with subaerial volcanic gas emissions, deposition of platform carbonates and thick Superior-type BIFs.

These constraints suggest that the early terrestrial carbonate alkalinity flux was restricted by limited land exposure and a high CH_4/CO_2 atmosphere, resulting in persistently low oceanic pH. Rare earth element (REE) signatures in pre-*c.*2.6 Ga carbonates indicate deposition in lacustrine, epi-continental, and restricted marine basin settings—isolated oases of elevated alkalinity near low-lying landmasses. The Sr and Nd isotope ratios of these carbonates reflect continental runoff and comparatively short residence times. The relative contributions of high-temperature (MOR-type) hydrothermal systems versus low-temperature alteration of subaqueous mafic lavas are uncertain, given that positive Eu anomalies in deep-water BIFs are lower than expected from dominant high-T sources.

Key questions remain regarding the transition to the *c.*2.35 Ga Great Oxygenation Event (GOE). First, the $\delta^{13}C$ values in marine Archaean microbial carbonates suggest the existence of a large, long-lived organic carbon reservoir with little geological trace, potentially reflecting methane production. Second, how did the increasing continental carbonate alkalinity flux initially fuel the prominent deposition of carbonate on platforms ahead of BIFs? Third, did Fe^{2+} oxidation to magnetite in Superior-type BIF curtail further rise in carbonate alkalinity via reduction to methane, and suppress atmospheric pO_2 until the GOE?