

Enhanced Iron Silicate Precipitation Kinetics Under Variable pH: Implications for Precambrian Ocean Chemistry

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The intricate interplay between dissolved ferrous iron and silica in anoxic aqueous environments constitutes a fundamental yet underexplored facet of Precambrian (bio)geochemistry. While extensive paleomarine records document the individual behaviors of these elements, their co-precipitation dynamics (e.g. greenalite)—particularly the influence of pH—remain inadequately constrained. This investigation elucidates the kinetic parameters governing Fe(II)-SiO₂(aq) interactions across a range of pH conditions (7.5-8.5) through rigorously controlled experimental protocols. Our time-series analyses reveal pronounced pH-dependent element fractionation patterns: solutions maintained at pH 8.5 exhibit accelerated depletion of both dissolved species, with Fe(II) concentrations diminishing from ~1.0 to 0.1 mmol·kg⁻¹ over 150 hours, while contemporaneous SiO₂(aq) levels decrease from ~1.8 to 0.5 mmol·kg⁻¹. At intermediate pH 8.0, a moderate reaction trajectory is observed, with Fe(II) concentrations gradually declining from ~1.0 to 0.7 mmol·kg⁻¹ while SiO₂(aq) levels decrease from ~1.8 to 1.2 mmol·kg⁻¹, reflecting an intermediate precipitation rate that follows the pH-dependent trend. Conversely, circumneutral conditions (pH 7.5) demonstrate remarkable stability of silica concentrations throughout the experimental duration, whereas Fe(II) undergoes only modest depletion. Similar to the previous studies [1, 2], these differential precipitation trajectories support a critical pH threshold that dictates the coupling efficiency between iron and silica during authigenic mineral formation (greenalite or its precursor phases). The experimentally derived kinetic constraints provide compelling evidence that alkalinity fluctuations could have served as primary modulators of iron-silica partitioning in Precambrian water columns. Furthermore, our findings necessitate the recalibration of theoretical constraints on maximum dissolved Fe(II) concentrations in anoxic ferruginous paleomarine environments. The pH-sensitive precipitation kinetics documented herein illuminate complex feedbacks between seawater chemistry and mineral paragenesis that ultimately shaped the lithological record of Earth's formative eons.

[1] Jiang & Tosca (2019), *Earth and Planetary Science Letters* 506, 231–242.

[2] Tosca, Guggenheim & Pufahl (2016), *Geological Society of America Bulletin* 128, 511–530.