Experimental constraints on Precambrian seawater chemistry: Solubility in the Fe^{2+}-SiO_2(aq) system

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Despite evidence that Precambrian seawater was commonly elevated in both SiO_2(aq) and Fe^{2+} (e.g., 1, 2), we know little about the interaction of these two components, or solubility-limiting phases in this system. Here, we investigate the precipitation of Fe^{2+} and SiO_2(aq) in anoxic synthetic seawater at 25ºC as a function of pH, (Fe^{2+}) and (SiO_2(aq)) in an attempt to connect aqueous phenomena to the somewhat poorly understood distribution of Precambrian Fe-silicates.

Our experiments indicate the rapid nucleation of a colloidal Fe^{2+}-silicate phase across a broad range of [SiO_2(aq)] and (Fe^{2+}). The structure of the precipitate is closely related to greenalite, but instead lacks FT-IR and electron diffraction evidence for linkages between 1:1 trioctahedral islands, or domains. Because these islands are linked in a completely disordered fashion in natural greenalite [3], we hypothesize that greenalite genesis at 25ºC involves the rapid nucleation of 1:1 domains or nano-particles that are limited in lateral size by the misfit between silica tetrahedra and Fe^{2+} octahedra [3]. Subsequent linkage between these domains, either by oriented nano-particle agregation or burial diagenesis may be responsible for poorly-resolved domain boundaries, and the considerable defect nature in domain size, shape and lateral positions in natural greenalite [3].

Because this formation pathway implies that solubility equilibrium is closely approached during initial nucleation, we may constrain the (Fe^{2+}), (SiO_2(aq)) and pH which Fe^{2+}-silicate nucleation will occur. Solubility estimates show that Fe^{2+}-silicate formation is highly pH dependent, placing strong constraints on the pH associated with primary basin-scale greenalite deposition in Superior-type BIF (e.g., 4). Our calculations also show that Fe^{2+}-silicate nucleation would have acted as a limiting factor on (SiO_2(aq)), (Fe^{2+}) or both, depending on P_{CO2} and siderite precipitation kinetics. Continued investigation of precipition kinetics and phase solubility in ferruginous seawater systems will allow quantitative estimation of seawater marine (Fe^{2+}), (SiO_2(aq)), and DIC, and lend special insight into how Precambrian Fe, Si, C and alkalinity cycles were linked by key precipitates.

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