

## Thermodynamic considerations on Precambrian seawater and porewater chemistry from equilibrium in the greenalite- siderite system

L.J. ROBBINS<sup>1</sup>, S.V. LALONDE<sup>2</sup>, N.L.  
MACPHERSON<sup>1</sup>, S.L. FLYNN<sup>1</sup>, D.S. ALESSI<sup>1</sup> AND  
K.O. KONHAUSER<sup>1</sup>

<sup>1</sup>1-26 Earth Sciences Building, University of Alberta,  
Edmonton, Alberta, Canada, T6G 2E3  
(\*correspondence: lrobbins@ualberta.ca).

<sup>2</sup>UMR6538 Laboratoire Domaines Océaniques,  
European Institute for Marine Studies  
Technopôle Brest-Iroise, Place Nicolas Copernic,  
29280 Plouzané, France

It has been suggested that either the ferrous carbonate siderite [1], or the ferrous silicate greenalite [2,3], may have provided a control on the upper limits of Fe(II) in the early oceans. However, the potential for these two minerals to exist in equilibrium and the resultant implications for ancient seawater and porewater chemistry have not yet been fully considered. Inspired by the work of Holland [1], we present a thermodynamic investigation of aqueous systems in equilibrium with siderite and greenalite. In order to assess a broad set of potential paleomarine conditions, we vary  $p\text{CO}_2$ ,  $\text{Fe(II)}_{(\text{aq})}$ , and  $\text{SiO}_{2(\text{aq})}$  concentrations across a range of conditions that could account for the mineralogy of Precambrian iron formation and chert. We also explore the application of equilibrium in these systems to fluxes in and out of porewaters as predicted by the iron shuttle hypothesis [4].

Our model results re-define fields of possible  $p\text{CO}_2$ , Fe, and Si concentrations permissible for the deposition of ancient chemical sedimentary units where both greenalite and siderite are present. Our results further indicate that in terms of mineral phases limiting Fe solubility in ancient oceans and porewaters, a switch between siderite and greenalite may occur as a function of  $p\text{CO}_2$ , with siderite limiting Fe solubility at  $p\text{CO}_2$  above 0.05 atm (seawater pH  $\sim 7$ ). However, the greenalite-siderite system is highly sensitive to assumptions regarding aqueous silica concentration, with important implications for the conditions under which Precambrian iron formation and chert were deposited.

[1] Holland (1984) *The Chemical Evolution of the Atmosphere and Oceans*. Princeton University Press p. 1-582. [2] Tosca et al. (2015) *Geol. Soc. Am. Bull.* B31339.1.

[3] Rasmussen et al. (2015) *Geology* **43**: 303-306.

[4] Fischer & Knoll (2009) *Geol. Soc. Am. Bull.* **121**: 222-235.