

Probing Archean climate using rare earth element signatures of putative microbialites

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Ancient chemical sediments that contain putative microbialites (i.e., organosedimentary structures known as stromatolites) are thought to preserve Earth's earliest biosphere [1]. Shale-normalized rare earth element (REE) patterns of ancient chemical sedimentary rocks have been investigated as indicators of secular changes in ocean chemistry through geologic time [2]. Furthermore, shale-normalized REE patterns of Archean putative microbialites strongly suggest these structures formed as biochemical precipitates within shallow marine environments [3]. Here, we apply a Bayesian inverse model to compute the most probable carbonate alkalinity, within a likely pH range, for Archean seawaters using the shale-normalized REE patterns of putative microbialites as the constraint. The model assumes that the shale-normalized REE patterns of putative microbialites were incorporated from Archean seawater without fractionation, and further, that the shape of the REE patterns reflects competition between solution and surface complexation reactions, as is the case in modern seawater. Henry's Law is subsequently applied to estimate the partial pressure of CO₂ in the Archean atmosphere, which we assume was in equilibrium with shallow waters of the Archean ocean. The model was tested using REE contents of putative microbialites, including those from the 3.45 Ga Strelley Pool Formation of the Warrawoona Group, Pilbara Craton in Western Australia [3]. Model results are discussed in context with previous models and computed estimates. Our results compare well with recent estimates of atmospheric CO₂ levels for the Archean [4], but are lower than previous models [5].

[1] Rosing (1999) *Science* **283**, 674 [2] Bau and Möller (1993) *Geochim. Cosmochim. Acta* **57**, 2239 [3] Van Kranendonk *et al* (2003) *Geobiol.* **1**, 91 [4] Hessler *et al* (2004) *Nature* **428**, 736 [5] Kasting (1987) *Precambrian Res.* **34**, 205