

Effect of Paleoseawater Composition on Hydrothermal Exchange at Mid-Ocean Ridges

MICHAEL A. ANTONELLI¹ & DONALD J. DEPAOLO¹

¹Dept. of Earth & Planetary Science, University of California, & Earth Science Division, Lawrence Berkeley National Lab, Berkeley, CA, 94720. (Mantonelli@berkeley.edu)

Mid-ocean ridge hydrothermal circulation is a key component in the long-term regulation of global climate and chemical fluxes to the oceans [1]. Models reconstructing past weathering rates and CO₂ concentrations often assume that seawater-basalt hydrothermal exchange worked the same in the past as it does today, yet geochemical proxies [2] suggest that seawater has undergone large changes in chemical composition, which could have influenced the reaction pathways and kinetics during hydrothermal circulation.

The modern ocean has Mg:Ca:SO₄ concentrations of 53:10:28 (mM), implying that Ca (and Sr) can be quantitatively removed by anhydrite precipitation (at ~130 C), and that seawater SO₄ is then left-over to precipitate with Mg (as MSH phases, ~250C) before reaching greenschist-alteration depths and reemerging with approx. 0:30:0 (mM) [and basaltic δ⁴⁴Ca and ⁸⁷Sr/⁸⁶Sr signatures]. The Cretaceous and Ordovician oceans likely had concentrations of approx. 30:30:10 (mM) [2], which could have: i) increased the persistence of seawater Ca (and Sr) after anhydrite precipitation, into the greenschist zone and back into the ocean, ii) quantitatively removed seawater SO₄ as anhydrite, inhibiting subsequent MSH formation (and TSR), and iii) slowed-down hydrothermal reaction kinetics.

We present a conceptual framework for evaluating the potential changes in hydrothermal outputs, and then explore several simplified model systems (dual-porosity [3] and charge-balance), which suggest that these paleo-hydrothermal fluids had significantly more seawater-derived Ca and Sr (agreeing with ⁸⁷Sr/⁸⁶Sr from epidotes in Cretaceous and Ordovician ophiolites [4]). These effects could require a reanalysis of the Sr isotopic evolution of the oceans. Future research into Sr partitioning (anhydrite, MSH, and chlorite) and kinetic effects caused by higher seawater Ca and lower Mg and SO₄, along with reactive transport simulations, will serve to further constrain this hypothesis.

[1] Berner (2003) *Nature* **426**, 323-326. [2] Lowenstein *et al.* (2014), *TOG* 2nd ed., 569-616. [3] DePaolo (2006), *GCA* **70**, 1077-1096. [4] Turchyn *et al.* (2013), *GCA* **123**, 440-458.