

THE FATE OF ELECTRONS IN OCEANIC ALTERATION OF MID-OCEAN RIDGE BASALT. T. D. Ely¹ and E. L. Shock^{1,2}, ¹School of Earth and Space Exploration, Arizona State University, 550 E. Tyler Mall, Tempe, AZ 85287, USA. Tely1@asu.edu ²Everett.Shock@asu.edu

Introduction: The connection between water-rock reactions and habitability is the flow of electrons (e^-). Nowhere is this process more significant on Earth in its nearness to both extant life and life's origins than among the aqueous alteration environments throughout mid-ocean ridge systems and cooling oceanic crust. The e^- flow is derived almost exclusively from host rock Fe(II), given its propensity to oxidize to Fe(III) when in contact with seawater. The complex behavior of how and why Fe(II) is successfully oxidized to Fe(III) in such systems is a primary environmental consideration when attempting to understand and search for habitable environments.

We have modeled the progressive alteration of all Mid-Ocean Ridge Basalts (MORB) from the Gale et al. (2013) database with bottom seawater; 2000 examples chosen at random were selected here. Designed to mimic known alteration paths in mid-ocean ridge hydrothermal systems, the calculated titrations are accompanied by an increase in temperature to 350°C at an ultimate water-to-rock ratio (w:r) of 1:1 (kg:kg). All 2000 of these reaction paths, calculated separately, are shown in Fig 1 where their abilities to transfer e^- from the Fe(II) in the MORB to the alteration assemblages and vent fluids are depicted. The half reaction for this process can be imagined simply as:



In order for half-reaction (1) to proceed (initiating electron flow), both the Fe(III) and the e^- must have destinations in the various coupled oxidation half-reactions throughout the alteration paths.

Beginning at low temperatures, all MORB Fe(II) not required to stabilize sulfide in pyrite is successfully converted to Fe(III), being chiefly housed in hematite, goethite, and andradite. This trend continues until the oxidants in seawater are either exhausted or precipitated (as is the case for seawater CO_2 and HCO_3^- precipitating early on as calcite). In this initial low T/w:r regime ($\leq 110^\circ\text{C}/\sim 4$), the FeO content of the initial host rock is exactly predictive of e^- transferred into the alteration system (shown in color in Fig 1). This is because Fe(II) is limiting in half-reaction (1) given the presence of ample oxidation power to pull the reaction to the right. This relation breaks down at higher T/w:r as the right side of equation (1) becomes limiting. With no oxidants to consume e^- all MORB compositions converge near a single e^- transfer quantity (0.2 mols)

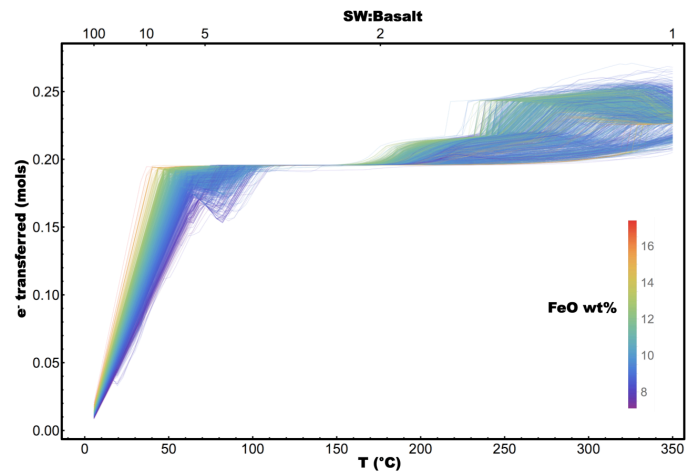


Fig 1: Alteration path calculations for the titration of 2000 MORB compositions chosen at random from the Gale et al (2013) database into bottom seawater. Depicted is the quantity of electrons transferred from the pristine host rock to mineral and aqueous alteration products. The color displays the initial FeO content of the host rock being reacted.

until higher temperature and greater extent of reaction can provide access to new oxidative power. All Fe(II) is now stabilized unoxidized in Fe-chlorite. This trend demonstrates that the prediction of a given MORB's ability to facilitate the transfer of e^- in T/w:r regimes where the oxidants are limiting requires no knowledge of host rock components other than the FeO.

As the system is heated further and accompanied by ever more reaction, two distinct e^- increases occur. The first, at about 200°C is the result of the dissolution of calcite back into solution, providing a temporary source of oxidative power (HCO_3^-), and allowing half-reaction (1) to precede to the right again. The second increase beginning at about 240°C, results from the stabilization of pyrrhotite (FeS) over pyrite (FeS_2). The ability to predict e^- transfer from host-rock FeO is replaced in this T/w:r regime by the combination of system components that stabilize the limiting species in half-reaction (1). At temperatures $>200^\circ\text{C}$ the prediction of e^- transfer depends on the combination of FeO, Al_2O_3 , and CaO, given their mutual effects in stabilizing epidote, the primary Fe(III) hosting phase in the entire oxidant-limiting regime.

References:

[1] Gale A., Dalton C. A. and Langmuir C. H. (2013) *Geochem. Geophys. Geosyst.*, 14, 489–518.