Using basalt oxide compositions to predict redox buffering capacity

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Earth's surface environments (upper crust and hydrosphere) and the life they support, exist in a state of redox stress; the result of oxidants and reductants in a continuously replenished state of disequilibrium. Subaerial and submarine volcanism provides globally distributed conduits for relatively reduced mantle material to communicate via mass and energy transfer with relatively oxidized surface environments. Aqueous alteration of mid-ocean ridge (MOR) basalts by seawater represent the dominant submarine expressions of this processes. Electrons are drown out of basalt, and thus the mantle, by oxidation of its Fe(II) to Fe(III). In this study we calculate the progressive alteration of MOR basalts form the Gale et al. (2013) database ($\sim$13,000 compositions) with seawater [1]. Designed to mimic known alteration paths in MOR systems, the calculated titrations are accompanied by an increase in temperature (T) to an eventual water-to-rock ratio (w:r) of 1:1 (kg:kg), and 350°C. The half reaction for this process can be written as $Fe(II)_{MORB} \rightarrow Fe(III) + e^-$. If this half-reaction proceeds (initiating e- flow from what is ultimately the mantle to surface environments), both the Fe(III) and the e- must have destinations in the various coupled half-reactions throughout the alteration paths – destinations dependent upon the various host rock components – complicating the prediction of e$^-$ flow beyond assuming a dependence on the Fe content of the host rock. In fact, each of the major oxide components of MOR basalt has a characteristic influence on e$^-$ flow initiated by alteration. These influences are now quantified. The information content inherent to each oxide component of basalt is measured as a function of T and w:r via Shannon entropy. This allows the influence of each oxide component to be assessed individually, insofar as knowing any one of them reduces uncertainty in the possible e$^-$ flow range from variation in all others. These data allow calculations of the buffering of surface O_2 with mantle-derived reducing power even from partial or limited knowledge of basalt and other rock compositions.

[1] Gale et al., (2013) Geochem. Geophys. Geosyst., 14, 489–518.