Magnetite authigenesis and the ancient martian atmosphere

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MSL data from Yellowknife Bay have revealed a sedimentary environment unlike any examined by previous rover missions to Mars. *In-situ* physical, chemical and mineralogical analyses reveal that lacustrine diagenesis of basaltic mud produced authigenic magnetite and trioctahedral smectitic clay in significant abundance [1, 2, 3]. However, bulk rock geochemistry indicates that the protolith was essentially unaltered by chemical weathering and received little input from volatile (e.g., SO_4^{2-}, Cl^-, CO_3^{2-}) components, pointing to a process that occurred in relatively dilute water at circum-neutral pH [3]. Constraining the geochemistry that led to these products will unlock the climate history archived by Gale Crater sediments. Here, we present experimental evidence that deposition of basalt mud into dilute anoxic water was responsible for magnetite at Yellowknife Bay, and that this took place under low P_{CO2} conditions.

We observe that the immersion of <63μm basalt in O_2- and CO_2-free de-ionized water leads to the immediate release of cations (mainly Ca, Mg and Fe and some SiO_2(aq)) driving the pH of initially pure water rapidly to ≥8.7, which then results in supersaturation with respect to Fe^{2+}-bearing hydroxides. Within hours, Fe concentrations in solution decrease to the level of $Fe(OH)_2$ solubility. $Fe(OH)_2$, a key reactive intermediate, then disproportionates to magnetite within days. We also find that green rust (GR) can form in our experiments, due to reaction with trace quantitites of O_2(aq), and through photochemical oxidation; GR also rapidly converts to magnetite in our experiments. Our calculations indicate that in order for either of these authigenic pathways to take place, P_{CO2} must be < ~10^{-4} bar to prevent siderite precipitation. We are better calibrating this boundary by examining siderite precipitation kinetics as a function of dissolved CO_2 in these systems.

Our results uncover an authigenic pathway triggered by the simple deposition of basalt in anoxic, dilute water bodies on Mars devoid of CO_2; this is consistent with *in-situ* observations collected to date. Our results also allow for the possibility that dissolved CO_2 at Gale Crater at this time may have been negligible, raising broader questions about its role in maintaining climate conditions that favored liquid water on the ancient martian surface.

[1] Grotzinger, J. *et al* (2014) *Science*, **343** [2] Vaniman, D. *et al* (2014) *Science*, **343** [3] McLennan, S. *et al* (2014) *Science*, **343**