# LOW-$CO_2$ WATER ENVIRONMENT FOR ANCIENT AQUIFER WITHIN GALE CRATER INFERRED FROM MANGANESE OXIDATION EXPERIMENTS.

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**Introduction**: The Curiosity rover recently discovered Mn oxides in fracture-filling materials within sandstones of the Kimberley region of the Gale crater [1]. The Mn oxides are likely to have been deposited in an ancient aquifer immediately after the solidification of the sediments at the period around the Noachian/Hesperian boundary, suggesting the presence of an oxidizing condition at that time [1].

In the present study, we try to further constrain the water environment and atmospheric composition of early Mars that allows the formation of Mn oxides. Under low-$O_2$ and high-$CO_2$ conditions, dissolved $Mn^{2+}$ in water might be converted into Mn-bearing carbonates. Mn oxides can be formed only under high-$O_2$ and low-$CO_2$ conditions, as seen on the Earth after the Great Oxidation Event [2]. The present study aims to constrain $CO_2/O_2$ ratios of the water environment and atmosphere on early Mars at the time of formation of the Mn oxides by performing laboratory experiments to form Mn deposits by reactions of $Mn^{2+}$ with gas mixtures of $CO_2/O_2/N_2$.

**Methods:** In the experiments, we introduced gas mixtures of pure $CO_2$ and artificial air ($N_2/O_2 = 4$; $pCO_2 < 1$ ppm) at different ratios ($CO_2/O_2 = 2$, 0.2, 0.02, and artificial air) into solutions of ~20 mM of $MnCl_2$ at pH 8–9. After reaction time of ~30–310 minutes, solid precipitates were collected by filtering for XANES and XRD analyses to identify their redox state and composition.

**Results & Discussion:** Despite that $MnO_2$ is thermochemically stable, we find that all of the Mn solid precipitates are mainly composed of Mn carbonate, namely $MnCO_3$, except for the case of artificial air only. In especially, $MnCO_3$ is readily precipitated even at low $CO_2/O_2$ of 0.02, suggesting that kinetics of formation reactions of $MnCO_3$ and $MnO_2$ are the critical factor in the competition reactions.

Our results suggest that, in order to form $MnO_2$ found by Curiosity, low-$CO_2$ and high-$O_2$ conditions would be required in the aquifer within the Gale crater for weakly alkaline pH. Acidic aquifer is unlikely given the weakly-chemically-altered surrounding sandstones and extremely low reaction rates for $MnO_2$ formation [3]. Thus, we suggest that the low-$CO_2$ and high-$O_2$ water environment reflect the atmospheric condition at that time.

[1] Lanza, N.L. et al. (2016). *Geophys. Res. Lett.*, 43, 7398-7407. [2] Kirschvink, J.L. et al. (2000). *PNAS, 97,* 1400-1405. [3] Stumm, W., & Morgan, J. J. (1996). *Aquatic Chemistry: Chemical Equilibria and Rates in Natural Waters.* Wiley.