

LOW-CO₂ ATMOSPHERE ON EARLY MARS? AN INTERPRETATION OF MANGANESE OXIDE ON GALE CRATER BY LABORATORY EXPERIMENTS. N. Noda¹, S. Imamura¹, Y. Sekine¹, H. Tabata¹, S. Uesugi¹, T. Murakami¹, and Y. Takahashi¹, ¹Department of Earth and Planetary Science, University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033 Japan (summerberry81@g.ecc.u-tokyo.ac.jp)

Introduction: Both CO₂ and O₂ are key atmospheric components for climatic and chemical evolution of early Mars. However, their ancient partial pressures have been poorly constrained. Multiple lines of geological and geochemical evidence support the existence of liquid water on Mars, at least episodically, during the late Noachian and early Hesperian [1]. This implies the presence of greater amounts of greenhouse gas, representatively CO₂, than that of today [2]. On the other hand, *in-situ* analyses for sandstones in the Kimberley region on Gale crater by the Curiosity rover have found Mn enrichments in fracture-filling materials, i.e., veins, crosscutting the surrounding rocks [3]. The Mn enrichments were highly likely caused by deposition of Mn oxides from reducing, soluble Mn (Mn²⁺) within ancient groundwater, rather than depositions of evaporites such as Mn carbonate [3]. Since oxidation of Mn requires high levels of redox potential (Eh) (Fig. 1), these findings indicate a possible coexistence of a highly oxidizing atmosphere and wet conditions on early Mars [3].

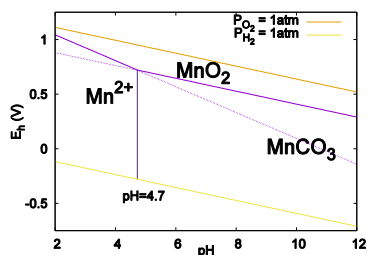


Fig. 1: Eh-pH diagrams of Mn-O-C system at pCO₂=0.5 bar Equilibrium calculations were performed based on Henry's law and Nernst equation [4].

The present study aims to further constrain the composition of early Mars' atmosphere, especially the O₂/CO₂ ratio, that allows the formation of Mn oxides found in Gale crater. Even under high CO₂ conditions, Mn oxide is thermochemically stable for high pO₂ (Fig. 1). However, the oxidation of Mn²⁺ is known to be slow [5]. Thus, Mn-oxide formation could be kinetically inhibited under high CO₂ conditions due to efficient formation of Mn carbonate and subsequent depletion of Mn²⁺ in the solution. We performed laboratory experiments, in which gas mixtures of artificial air (N₂/O₂ = 4) and pure CO₂ were introduced into Mn²⁺ solutions. We conducted five experiments (run #1–5: Table 1) by varying the mixing ratio of air and CO₂ and analyzed solid precipitations.

Materials & Methods: The experiments were performed in a flow system using a Pyrex-glass reaction vessel (Fig. 2). Starting solutions of dissolved Mn were

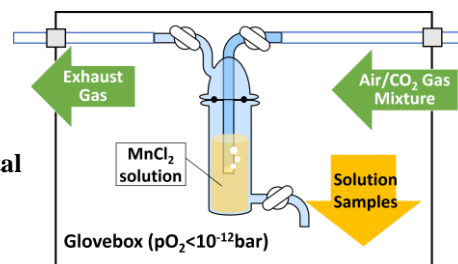
Table 1. Experimental conditions of the present study. The flow rate of gas mixtures was adjusted using a rotameter and mass flow controller. The mixing ratio of O₂/CO₂ in the gas mixture was determined by calibration using a quadrupole mass spectrometer (QMS)

Run #	Air flux [L/min]	CO ₂ flux [L/min]	Mixing ratio O ₂ /CO ₂	Duration [min]
1	0.5	0		30
2	0	0.5		180
3	0.5	0.5	0.6	330
4	1	0.05	5	35
5	1	0.005	40	240

prepared in three steps. First, solutions of ~0.1 M *N*-Tris-methyl-3-aminopropanesulfonic acid (TAPS) and 0.1 M NaOH were made in order to buffer solution pH around 8–9 during the experiments. Then, the solutions were deaerated by bubbling pure Ar gas in an Ar-purged glovebox for more than 6 hours. Finally, 99.0+% MnCl₂·4H₂O was introduced as a source of Mn²⁺ in the glovebox. The initial concentrations of dissolved Mn were 20 mM.

The gas mixture of artificial air and CO₂ was then bubbled into the starting solution within the reaction vessel for 0.5–5.5 hours of reaction time (Table 1). The total pressure of the gas mixture in the reaction vessel was ~1 bar. Solution samples were collected several times through the valve during the reaction. These solution samples were collected by a syringe with 0.22-μm filter and added into ~5 ml of 0.1 M HNO₃ to prevent oxidation by air during the analysis. After the reaction, solid precipitates were recovered by filtering the rest of the solutions through 0.22-μm membranes. All these procedures were conducted in the Ar-purged glovebox, in which low-O₂ conditions (pO₂ < 10⁻¹² bar) were maintained out of the reaction vessel by a circulation pump and O₂ removal system. Mn²⁺ concentrations of collected solution samples were measured using inductively coupled plasma atomic emission spectroscopy (ICP-AES) to examine loss of Mn²⁺ due to precipitation. Recovered solid precipitates were analyzed with X-ray

Fig. 2. Schematic diagram of experimental system.

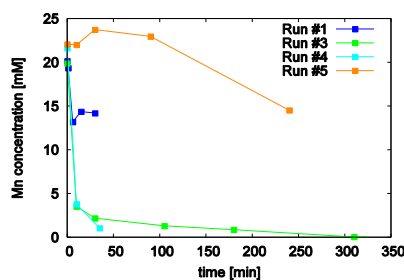


absorption fine structure (XAFS) and X-ray diffraction (XRD) to determine the mineral compositions and oxidation state of Mn.

Dissolved Mn in solution: Time evolution of Mn^{2+} concentrations for each run is shown in Fig. 3. In all runs, the Mn concentrations decreased from the initial concentrations of ~ 20 mM. Under high CO_2 conditions (i.e., the runs #3 and 4), the Mn concentrations declined rapidly within 50 mins of reaction time. After 310 mins of reaction time for the run #3, the Mn concentration in the solution was nearly zero within the error, which indicates that most of initial Mn^{2+} was precipitated as solid particles.

Fig. 3: Time evolution of concentrations of Mn in solution.

The procedure error would be a few mM. Thus, apparent increase in Mn for the run #5 would be due to the procedure error.



Solid precipitates: The XANES spectra for the collected solid precipitates are shown in Fig. 4. Comparing with the results of the standard materials, all of the solid precipitates collected from the experimental runs #2–5 are predominated by MnCO_3 . The results of XRD analysis support this conclusion. The major peaks of the XRD spectra are attributed from MnCO_3 . The XANES spectrum for run #1 cannot be simply explained by the standard materials of MnO_2 , Mn_2O_3 , Mn_3O_4 , and MnCO_3 suggesting that the solid precipitates would be a mixture of Mn (hydr)oxidants with different valences.

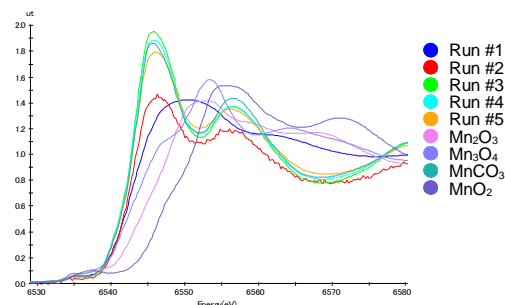


Fig. 4: XANES spectra of solid precipitates and standard materials.

Discussion: The Eh-pH diagrams for the experimental conditions indicate that Mn oxide (i.e., MnO_2) is thermochemically stable for all of our experimental conditions (Fig. 1). However, our results show that

even for low- CO_2 , high- O_2 gas mixtures (e.g., $\text{O}_2/\text{CO}_2 = 4$ (the run # 4) and 40 (the run #5), efficient precipitation of MnCO_3 occurs before the formation of MnO_2 (Fig. 4). In the solution, dissolved Mn is highly depleted due to the precipitation of MnCO_3 (Fig. 3). These results suggest that kinetics of these two competition reactions are the critical factor that determines the formation of Mn oxides.

As mentioned above, the Curiosity rover has found Mn-oxide enrichments in veins of sandstones in the Kimberley region [3]. Precipitation of Mn carbonate cannot explain the Mn enrichments [3]. Mn carbonate does not form in a solution for $\text{pH} < \sim 4-5$ (Fig. 1); however, oxidation of Mn in an acidic solution does not proceed effectively due to a strong pH dependence of the reaction rate [5]. In addition, the long-term presence of acidic groundwater may be inconsistent with less-chemically-altered surrounding rocks [3]. Thus, our results suggest that the findings of Mn oxides by Curiosity indicate not only oxidizing conditions but low- CO_2 ones in the ancient groundwater of Gale crater.

One possible explanation of the low CO_2 conditions is that the groundwater was not equilibrated with the atmosphere. This could have happened if efficient precipitation of carbonate minerals occurred in an open water (e.g., Gale's crater lake [6]) and consequent CO_2 -depleted water transported into the subsurface, including fractures of the Kimberley region. However, a lack of sedimentary carbonates on Mt. Sharp of Gale crater by remote sensing might not be consistent with this idea. Further *in-situ* investigations of Mt. Sharp sediments would be important to evaluate this possibility.

Alternatively, if the groundwater was equilibrated with the atmosphere, our results imply low pCO_2 at the time of deposition of the Mn oxides. For instance, assuming pO_2 of 0.2 bar, pCO_2 should have been < 5 mbar in order to avoid efficient precipitation of MnCO_3 (the run #5). Given $\sim 0.1-1$ bar of pO_2 for formation of MnO_2 , required pCO_2 would be $< \sim 10$ mbar. These values are comparable to or less than pCO_2 in today's atmosphere (i.e., 6 mbar). This could imply that early Mars' atmosphere may have contained additional greenhouse gases to keep the surface warm, or that Mars had been basically cold and arid, similar to that of today, at the time when groundwater was active within Gale crater.

References: [1] Ehlmann, B.L. et al. (2011). *Nature* 479, doi:10.1038/nature10582. [2] Wordsworth, R.D. (2016). *Annu. Rev. Earth Planet. Sci.* 44, 381-408 [3] Lanza, N.L. et al. (2016). *Geophys. Res. Lett.*, 43, 7398-7407. [4] Usui, A. et al. (2015). *Geoscience of Marine Manganese Deposits*, 1st ed., University of Tokyo Press. [5] Stumm, W. and Morgan, J.J. (1996). *Aquatic Chemistry: Chemical Equilibria and Rates in Natural Waters*, 3rd Edition, Wiley-ii. [6] Grotzinger, J.P. et al. (2015). *Science* 350, doi:10.1126/science.aac7575.