

## High-O<sub>2</sub> atmosphere on early Mars? Interpretation of Mn-oxide on Gale crater by laboratory experiments

N. NODA<sup>1\*</sup>, S. IMAMURA<sup>1</sup>, Y. SEKINE<sup>1</sup>, S. UESUGI<sup>1</sup>, M.  
KURISU<sup>1</sup>, T. MURAKAMI<sup>1</sup>, AND Y. TAKAHASHI<sup>1</sup>

<sup>1</sup>Department of Earth and Planetary Science, The University  
of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033  
Japan (\*correspondence: summerberry81@g.ecc.u-  
tokyo.ac.jp)

### Introduction

The Curiosity rover has found deposition of manganese (Mn) oxide in an ancient aquifer at Gale Crater [1]. This implies a possible oxidizing water environment on Mars at the time of formation, i.e., ~3.5 Ga. However, required O<sub>2</sub> level strongly depends on the redox state of Mn-oxide [2]. In the present study, we aim to reveal the redox state of Mn oxide found on Gale crater by performing laboratory experiments of Mn oxide precipitation by investigating constration pattern of trace metals co-precipitated with Mn. Based on the results, we constrain the atmospheric composition of early Mars at the time of the deposition.

### Methods

Different types of Mn oxides (MnO<sub>2</sub> and Mn<sub>3</sub>O<sub>4</sub>) were precipitated from aqueous solutions including dissolved Mn<sup>2+</sup>, Ni<sup>2+</sup>, Zn<sup>2+</sup>, and CrO<sub>4</sub><sup>2-</sup> by reactions with KMnO<sub>4</sub> and H<sub>2</sub>O<sub>2</sub>, respectively. After the reactions, both filtrate and precipitates separated by filtration were analyzed with ICP-AES and Mn K-edge XANES, respectively, to investigate co-precipitation patterns and minerals.

### Results and Discussion

Our results showed that Ni and Zn co-precipitated with MnO<sub>2</sub>, but Cr did not tend to be incorporated into MnO<sub>2</sub>. This pattern is consistent with the chemical composition of Mn oxides found on Gale crater. On the other hand, Cr co-precipitated with Mn<sub>3</sub>O<sub>4</sub>. These results suggest that Mn oxide found on Mars is highly likely MnO<sub>2</sub>. On Earth, deposition and preservation of MnO<sub>2</sub> in sediments require highly oxidizing water environment, i.e., dissolved O<sub>2</sub> levels > 10 μM (corresponding to pO<sub>2</sub> > ~10<sup>-2</sup> bar) [3]. Accordingly, our results strongly suggest the presence of an O<sub>2</sub>-rich atmosphere at the time when groundwater was active within Gale crater. These results, in turn, imply effective formation of O<sub>2</sub> via H<sub>2</sub>O photolysis and/or ineffective loss of O<sub>2</sub> due to limited amounts of reductants on early Mars.

### References

- [1] Lanza et al. (2016) *Geophys. Res. Lett.*, 43, 7398-7407.
- [2] Usui et al. (2015) *Geoscience of Marine Manganese Deposits*, 1st ed., University of Tokyo Press.
- [3] Shaw et al. (1990) *Geochim. Cosmochim. Acta*, 54, 1233–1246.