EXPERIMENTAL STUDY ON MANGANESE OXIDE FORMATION: INTERPRETAION OF MANGANESE OXIDE ON GALE CRATER AND OXIDIZING ENVIRONMENT ON EARLY MARS.

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The Curiosity rover has found Mn enrichments within sandstones in the Kimberley region of the Gale crater on Mars [1]. These enrichments were detected within fracture-filling materials, *i.e.*, veins, crosscutting the surrounding sandstones, implying that Mn was once concentrated in subsurface fluids and then precipitated within ancient aquifers [1]. The chemical composition analysis for the Mn-rich materials also show that the abundance of Mn is coupled with those of transition trace metals, particularly Ni and Zn; meanwhile, Si, Ca, Cl and/or S are inversely correlated or not correlated with Mn [1]. This indicates that Mn exists as oxides in the fracture-filling materials, rather than silicate, carbonate, or chloride [1]. Since oxidation of Mn requires high levels of redox potential [2], the findings of Mn oxides indicate a possible coexistence of a highly oxidizing atmosphere and wet conditions on early Mars [1]. However, the pO_2 level at the time of deposition of Mn oxides remains poorly constrained.
In the present study, we conducted laboratory experiments in order to constrain the pO_2 level at the time of deposition of the Mn oxides based on the elemental pattern of coprecipitation of Mn oxides. In the experiments, we synthesized MnO_2, Mn_3O_4, and $Mn(OH)_2$ from solutions of dissolved Mn, Ni, Zn, and Cr using different oxidants, such as $KMnO_4$ [8] or H_2O_2 [9]. After the reactions, filtered solutions and solid precipitates were collected. The recovered solid precipitates were analyzed with X-ray absorption fine structure (XAFS) and X-ray diffraction (XRD). In addition, concentrations of dissolved Mn, Cr, Ni, and Zn in the remnant solution samples were measured using inductively coupled plasma atomic emission spectroscopy (ICP-AES). We found that only formation of MnO_2 can explain the enrichments of Mn together with Ni and Zn, which is consistent with the pattern of trace metal enrichments of the Mn oxides in the Gale crater. On the other hand, formations of Mn_3O_4 or $Mn(OH)_2$ cannot account for the observations. Given that precipitation of MnO_2 requires a high level of O_2 (>0.01 bar), our results strongly suggest the presence of an O_2-rich atmosphere on early Mars at the time when groundwater was active within the Gale crater. These results, in turn, imply effective formation of O_2 via H_2O photolysis and/or ineffective loss of O_2 due to limited amounts of reductants on early Mars.

References: [1] Lanza, N.L. et al. (2016). *Geophys. Res. Lett.*, 43, 7398-7407. [2] Usui, A. et al. (2015). Geoscience of Marine Manganese Deposits, 1st ed., University of Tokyo Press. [3] Holland, H.D. (1984). *Princeton Univ. Press, Princeton, NJ.* 582 pp. [4] Forget, F. & Pierrehumbert, R.T. (1997). *Science* 278:1273-76 [5] Wordsworth, R.D. (2016). *Annu. Rev. Earth Planet. Sci.* 44, 381-408 [6] Noda, N.et al. (2017). *LPSC abstract,* 48th, 1786 [7] Imamura, S. et al. (2017). *JpGU,* this meeting [8] Uesugi, S. (2017) master’s thesis [9] Mu, J. et al. (2006). *Journal of Dispersion Sci. and Tech.* 27:1223-1225

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