LOW-CO_2 ATMOSPHERE ON EARLY MARS INFERRED FROM MANGANESE OXIDATION EXPERIMENTS.

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Introduction

Both CO_2 and O_2 are important atmospheric components for climate and chemical evolution on early Mars. Several lines of geological and geomorphological evidence show that early Mars has been once warm sufficient to hold liquid water on the surface at least episodically in the late Noachian and early Hesperian [1]. Although early Mars would not be warmed sufficiently by CO_2 alone, climate models presume the presence of a thick CO_2 atmosphere to decrease outgoing longwave radiation and to cause effective collision-induced absorption. However, pCO_2 on early Mars is poorly constrained by geochemical evidence thus far. On the other hand, the Curiosity rover has discovered Mn oxides in fracture-filling materials in sandstones of the Kimberley region of the Gale crater [2]. Given pO_2 capable for deposition of Mn oxides (pO_2 > ~0.01 bar) [3], the findings of Mn oxides indicate that early Mars had a substantial O_2 in the atmosphere.
The present study aims to further constrain the composition of early Mars' atmosphere, especially the CO_2/O_2 mixing ratio, at the time when the Mn oxides were formed. We performed laboratory experiments to generate Mn precipitates from Mn^{2+} in solutions by introducing CO_2/O_2 gas mixtures. We investigated the compositions of Mn precipitates under various compositions of CO_2/O_2.

Materials & Methods

The Mn^{2+} starting solution with 20 mM and pH 8–9 was prepared in an Ar-purged glovebox, where pO_2 remained < 10^{-12} bar. The starting solution was deaerated by pure Ar gas for more than 6 hours prior to the use. Then, we introduced gas mixtures of pure CO_2 and artificial air (N_2/O_2 = 4; pCO_2 < 1ppm) into the starting solution at four different mixing ratios (CO_2/O_2 = 2, 0.2, 0.02, and artificial air) in the glovebox. Note that MnO_2 is thermochemically stable under all of these conditions. Solution samples were collected in several times during the experiments. The samples were filtered through a membrane with pore size of 220 nm. After the reactions, Mn precipitates were collected by filtering the rest of the solutions using a membrane with 220 nm. Mn^{2+} concentrations of the filtered solution samples were measured using inductively-coupled plasma atomic emission spectroscopy (ICP-AES). The collected Mn precipitates were analyzed with X-ray absorption fine structure (XAFS) and X-ray diffraction (XRD).

Results

Our results of the ICP-AES analysis show that Mn^{2+} concentrations in the filtered solutions decrease over reaction time, which indicate that a part of dissolved Mn^{2+} was converted into solid precipitates. Despite both the wide range in CO_2/O_2 ratios and thermochemical stability of MnO_2 under the experimental conditions, the results of XAFS analyses show that all of the Mn solid precipitates formed under these conditions are mainly composed of Mn carbonate, namely $MnCO_3$. These results are consistent with our XRD results. Our results show that $MnCO_3$ precipitated before the formation of MnO_2 even very low CO_2/O_2 of 0.02. This suggests that kinetics of formation of $MnCO_3$ and Mn oxides are the critical factor. On the other hand, the major peaks of the XANES spectra for the collected solid precipitates at CO_2/O_2 = 0 (namely, pure artificial air) would be a mixture of Mn oxides and $Mn(OH)_2$.

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Discussion

Our results show that, in order to form MnO_2 in Mn^{2+} solutions by reactions with CO_2/O_2 gas mixtures, the CO_2/O_2 ratio should be lower than 0.02. Assuming pO_2 of ~0.01–0.2 bar, which is capable to form and preserve MnO_2 in sediments [3], the observations of both a lack of $MnCO_3$ and presence of MnO_2 in Gale infer that pCO_2 on early Mars would have been less than 0.004 bar, or 4 mbar. This implies that early Mars may have possessed a low-CO_2 and high-O_2 atmosphere.

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