DISSOLVED MANGANESE OXIDATION BY BROMATE AND CHLORATE: AN ALTERNATE HYPOTHESIS OF MANGANESE OXIDE FORMATION ON MARS.

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Introduction: High concentrations of manganese have been detected at two separate locations on Mars by *in situ* rover measurements. The Mars Science Lab (MSL) Curiosity rover detected Mn-rich veins (MnO > 25 wt.%) in the fracture filling material in the Dillinger member crosscutting the Kimberly formation sandstones in Gale crater [1]. The Mars Exploration Rover (MER) Opportunity discovered Mn-rich coatings (> 2.3 wt.%) on two rocks at the Cook Haven outcrop in Endeavour crater [2]. Opportunity also observed enrichment of Mn (>1 wt.%) in various other altered rock samples during its exploration (e.g., Monjon gray, Tick Bush) [3]. These elevated Mn concentrations have been attributed to the presence of Mn(III/IV) oxides formed following Mn(II) oxidation [1, 2]. Mn oxides on Mars are therefore important environmental indicators of ancient redox conditions and understanding the geochemistry of these deposits provides critical insight into past habitability.

Mn(II) primarily occurs substituting for Fe(II) and Mg in ferromagnesian minerals, such as olivine. Martian basalts contain slightly elevated levels of Mn(II) compared to Earth (0.4 wt.%) [4] which may serve as a source of dissolved Mn(II) in aqueous systems on Mars. Mn(II) is highly mobile under a wide range of conditions but it is immobile when oxidized to Mn(III) or Mn(IV) [5]. Oxidized Mn has been cited as evidence for the presence of O_2 on early Mars [1], but there are two difficulties with this argument. First, this fails to recognize that there are no plausible oxidants on Mars with redox potentials between those of Fe(II) and Mn(II). The presence of oxidized Fe already indicates a "high-redox potential" oxidant. Second, despite being thermo-dynamically favorable, the oxidation of Mn(II) by O_2 is kinetically slow except under alkaline conditions [5, 6]. Mn oxidation on Mars may thus indicate the activity of some other oxidant(s) rather than O_2.

Our recent study has demonstrated that chlorate (ClO_3^-) oxidizes Fe(II) in Mars-relevant fluids at rates faster than by O_2 or UV photooxidation [7]. This and other oxychlorine species on Mars are produced by various atmospheric and surficial processes. The same formation processes also likely produce other oxyhalogen species (e.g., BrO_3^-) [8] because of the similar chemical behavior among the halogens. Mars has higher Br concentration than Earth, with Br often occurring at 1-10% of the Cl concentration on Mars. The Alpha Particle X-ray Spectrometer (APXS) onboard MER (both Spirit and Opportunity) [3] and MSL [10] detected bromine (Br) in nearly all samples analyzed. Recent work suggests that this may predominantly occur as bromate (BrO_3^-) in soils and sediments [8], in part

because of the high volatility of other Br species. BrO_3^- is a strong oxidant and has been shown to oxidize Fe(II) [11]. Mn(II) can also be oxidized by BrO_3^- in highly acidic solutions [12] and by chlorate at high temperatures (~160°C) [13]. In this study, we investigate the ability of BrO_3^- and ClO_3^- to oxidize Mn(II) in Mars-relevant fluids at 24°C and the mineral products that may result.

Methods: Laboratory experiments were conducted to explore the ability of BrO_3^- and ClO_3^- to oxidize Mn(II) in Mars-relevant fluids at ambient conditions (24°C, 1 atm). In order to isolate the effects of BrO_3^- or ClO_3^- on dissolved Mn(II), all reactions were conducted inside an anaerobic chamber [$N_2 = 97\%$, $H_2 = 3\%$, $O_2 < 1$ ppmv] or in sealed bottles to preclude oxidation of Mn(II) by O_2. All samples were wrapped with Al foil to inhibit photooxidation. 150 ml solutions containing ~10 or 100 mM Mn(II) were prepared in background salt mixtures of either 0.1 M Mg chloride, or Mg sulfate. The background salts serve as ionic strength buffers and provide anions with different ability to complex dissolved Mn. Aliquots of stock solution of 2 M $NaBrO_3$ or $NaClO_3$ was added to the experimental solutions to reach final BrO_3^- or ClO_3^- concentration of ~10 and ~100 mM, providing equimolar Mn/BrO_3^- or Mn/ClO_3 ratios. The pH values of the solutions were set to ~3, 5, or 7 by adding small amounts of HCl or NaOH. The pH was allowed to drift with the reaction to determine the effect of Mn(II) oxidation on the acidity of the solution.

Bromate-free control experiments were set up at pH 8 to evaluate the extent of inadvertent oxidation, if any. All experimental and control samples were sealed in air-tight serum bottles and placed on a shaker table outside of the anaerobic chamber. The starting ClO_3^- and BrO_3^- concentration were measured prior to the addition of Mn(II) using ion chromatography (IC) and then corrected for dilution. The minerals that precipitated were collected at the end of the experiment by vacuum filtration. The filtered solids were dried in a vacuum desiccator and characterized using X-ray diffraction (XRD), visible to near infrared (VNIR) spectroscopy, and X-ray photoelectron spectroscopy (XPS).

Results: Control and chlorate containing solutions did not show detectable Mn(II) oxidation in ~30 days, the duration of our experiments. However, all solutions containing BrO_3^- displayed Mn(II) oxidation within the same time period, accompanied with a decrease in solution pH. The oxidized Mn minerals precipitating during the reaction formed thin, dark layers on the inside of the serum bottles despite being constantly agitated on

a shaker table. Fuming brownish-red Br-containing gases volatilized from the solutions when the bottles were decapped, likely indicating the production of Br_2.

XRD indicates that nsutite (γ-MnO_2), a disordered intergrowth between pyrolusite (β-MnO_2) and ramsdellite (MnO_2) [14], forms in all experiments (Fig. 1). All mineral products were black in color and had weak VNIR reflectance (Fig. 2) characteristic of Mn oxides [2]. SO_4-rich solutions produced texturally softer minerals [14] than Cl-rich solutions and had relatively higher reflectance values (Fig. 2). The minerals precipitated in SO_4-rich fluids have a weak 1.9 μm absorption feature indicative of water within their structure. All minerals display a featureless flat slope between 0.4 to 0.9 μm and a red slope in the NIR [15]. These Mn oxide precipitates have similar spectral characteristics to those observed on Mars [1, 2]. Results from XPS indicate that solids formed from Cl fluids contain predominantly Mn(IV) while those formed in SO_4 fluids produced a mixed Mn(III/IV) phase (data not shown). As no discrete Mn(III) phase occurs in the SO_4
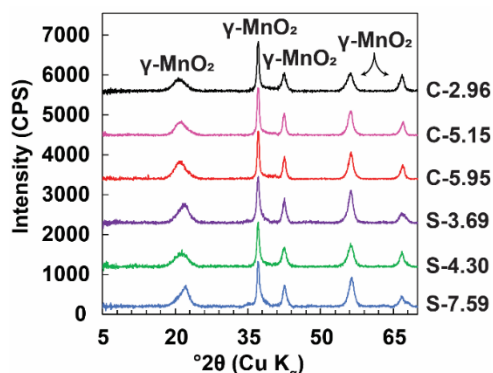

Figure 1: *XRD patterns of solids produced during Mn^{2+} oxidation by BrO_3^-. The abbreviated names of each experiment represent the fluid composition (C = chloride, or S = sulfate), and the initial pH.*
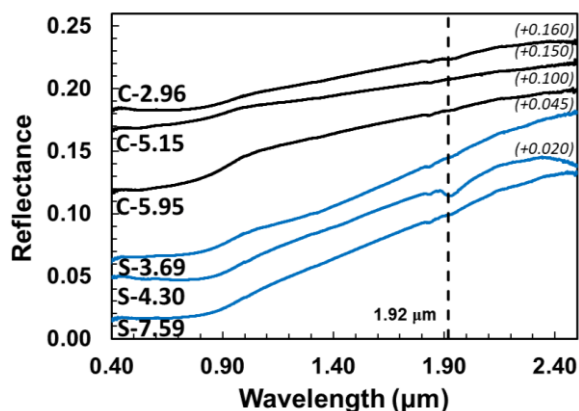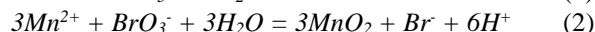

Figure 2: *VNIR spectra of solids produced during Mn^{2+} oxidation by BrO_3^-. The abbreviated names of each experiment represent the fluid composition (C = chloride, or S = sulfate), and the initial pH. The 1.92 μm band marked in dashed line. The spectra are offset.*
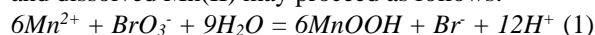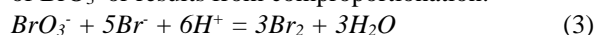
experiments it likely replaces Mn(IV) in nsutite, accompanied by protonation of an oxygen site for charge balance. Mn(III) sites are Jahn-Teller distorted, imperfections that the defective nsutite structure, as indicated by broad XRD peaks (Fig. 1), can likely accommodate. This ability to accept Mn(III) is consistent with nsutite being used in battery cathodes [16].

Discussion and Conclusion: BrO_3^- is an effective Mn(II) oxidant in Mars-relevant solutions in near-neutral to acidic solutions. The rate of Mn(II) oxidation by BrO_3^- is likely proportional to the concentration of BrO_3^-, Mn(II) and the solution pH [17]. The reaction of BrO_3^- and dissolved Mn(II) may proceed as follows:

$6Mn^{2+} + BrO_3^- + 9H_2O = 6MnOOH + Br^- + 12H^+$ (1)
$3Mn^{2+} + BrO_3^- + 3H_2O = 3MnO_2 + Br^- + 6H^+$ (2)

These reactions should be considered approximate owing to the complex redox chemistry of oxyhalides. The Br_2 that may have formed by incomplete reduction of BrO_3^- or results from comproportionation:

$BrO_3^- + 5Br^- + 6H^+ = 3Br_2 + 3H_2O$ (3)

Future study is required to quantify the rate of Mn(II) oxidation by BrO_3^- and identify the Br reaction products.

In contrast to BrO_3^-, the behavior of ClO_3^- mirrors that of previously reported studies on O_2 [5, 6] and did not produce any measurable oxidation under the conditions studied. The Br/Cl ratios on the Martian surface vary by three orders of magnitude and the Martian subsurface displays preferential Br enrichment compared to Cl. Therefore, the relative amount of BrO_3^- as compared to ClO_3^- increases with depth in the Martian subsurface [8, 18]. The presence of BrO_3^- as a major Br species on Mars and its ability to oxidize Mn(II) in diverse fluids suggest that this species may be a key oxidant responsible for Mn oxides observed by the MSL and MER missions. Mn oxides detected on Mars thus do not provide unequivocal evidence of past O_2 as viable formation pathways exist using other plausible oxidants.

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