Rapid Photocatalytic Oxidation of Dissolved Manganese with TiO_2

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Abstract:

Manganese(III/IV) (hydr)oxides (hereafter Mn oxides) occur ubiquitously in terrestrial and marine systems, and play crucial roles in natural electron and element cycles. However, the understanding of their occurrence is limited due to the slow oxidation of Mn^{2+}(aq) to Mn(IV) which precedes the formation of Mn oxides. Through the photocatalytic process with TiO_2 (the 9th most abundant compound in the Earth's crust), we found very fast oxidation of Mn^{2+}(aq) to Mn(IV). The reaction rate is even much faster than microbial processes, which has been believed to be the primary mechanism for the oxidation. We studied the oxidation process under a variety of conditions, such as different TiO_2 structures (anatase vs rutile), different solution chemistry (saltwater vs freshwater), and different oxygen content (open air vs nitrogen). These analyses show that the fast photocatalytic oxidation occurs primarily due to direct electron transfer between Mn^{2+}(aq) and photo-excited TiO_2. This understanding will enable us to explain the abundance of natural Mn oxides on rock surfaces. In addition, because the redox processes of Cr and Tl isotope systems, which are newly emerged paleoredox proxies, are significantly influenced by Mn oxides, understanding of Mn oxide formation will help calibrate these redox proxy systems for tracing the oxygen evolution on early Earth.

Experimental Method:

The oxidation reaction was run for 8 hours with a xenon lamp as the light source. Every hour, 2 samples were collected and analyzed using UV-vis spectroscopy to determine the concentration of manganese in each sample. Leucoberbelin Blue (LBB) was used as an indicator for oxidized Mn(III/IV) on the TiO_2 surface and porphyrin was used as an indicator for unoxidized aqueous Mn^{2+}. After the reaction finished, the solid products were removed from the reactor via centrifugation for further analyses with XRD and XPS. The reaction was first tested in saltwater and freshwater conditions and compared to the dark controls. The solution used for saltwater tests was artificial seawater (ASW). Deionized (DI) water at pH 7.3–7.7 was used for freshwater tests. Both anatase and rutile TiO_2 were tested in fresh and saltwater conditions.

To elucidate the mechanisms of fast oxidation, several variables were altered in the anatase ASW system. First, the reaction was run with light filters on xenon lamp to select wavelengths at or below 400 and 550 nm. This allowed us to determine the effective wavelength for the reaction. Second, the reaction was tested in an anoxic environment to determine if the oxidation was caused by molecular oxygen or through water oxidation. Third, the reaction was run with superoxide scavengers (superoxide dismutase) to test the effect of superoxide on the reaction. The next reaction was run with hydroxyl radical scavengers (t-BuOH) to test the effect of hydroxyl radical. Finally, in order to determine which cations in ASW affected the reaction, the reaction was run with the three major cations in seawater (Na^+, Mg^{2+}, and Ca^{2+}) individually.

Results:

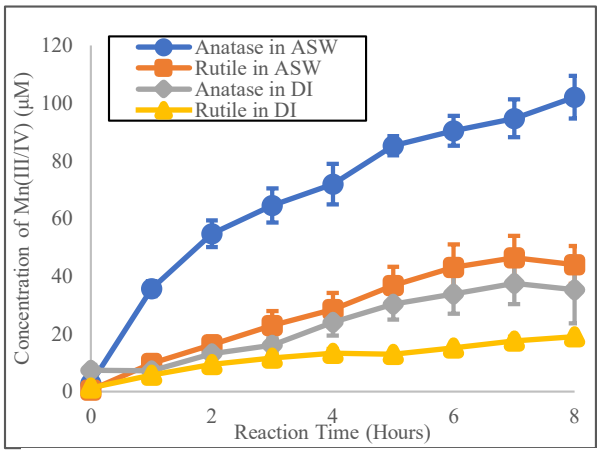

Figure 1. Rate of Mn(II) oxidation under standard conditions on the surface of anatase and rutile.

Figure 1 shows that the oxidation rate is faster with anatase, which is likely due to the higher surface area exhibited by the anatase particles. In addition, Figure 1 shows that the reaction occurs faster in seawater. After testing the reaction with the three major cations in seawater individually (Na^+, Mg^{2+}, and Ca^{2+}), it was concluded that Na^+ and Mg^{2+} have most significant influences on the increased oxidation rate in ASW. It is worth noting that the dark control reactions showed no obvious signs of significant oxidation.

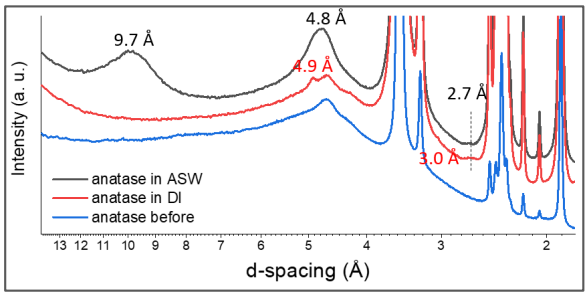

Figure 2. XRD data for anatase samples showing the formation of tunnel structured manganese oxide. Note that the XRD data we collected from rutile samples showed similar diffractions.

One of the most significant findings in this study came from the structural analysis of the Mn oxides after the completion of the reactions. The diffractions shown by the XRD data in Figure 2 are characteristic of tunnel structured Mn oxides. The samples from artificial seawater show diffractions characteristic of todorokite, which is the first time been produced in the laboratory at low temperature circumneutral pH conditions. The DI samples show diffractions

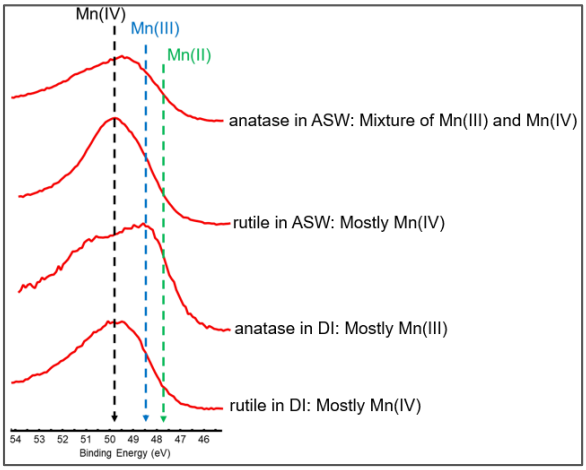

Figure 3. XPS data for anatase and rutile samples show different oxidation states of manganese products on the surface on anatase and rutile.

characteristic of romanechite, which is a Mn oxide phase with different tunnel structure from todorokite.

The data shown in Figure 3 shows that different Mn oxidations states are produced depending on the solution chemistry and TiO_2 structure. In general, anatase promotes the formation of Mn(III), while rutile promotes the oxidation of Mn(II) to Mn(IV).

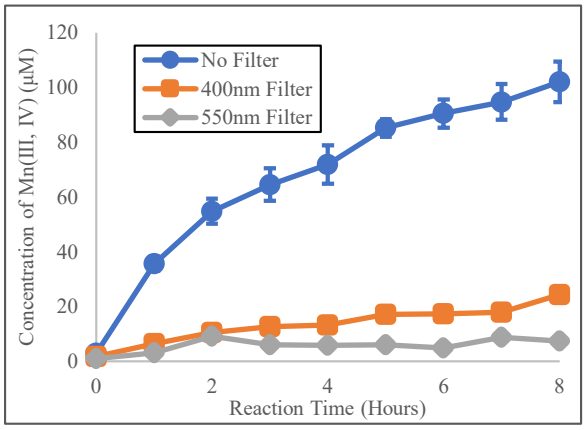

Figure 4. Rate of Mn(II) oxidation with light filters.

Figure 4 shows that the oxidation rate is reduced significantly with the introduction

of a 400 nm light filter on the xenon lamp. Because of this, we can conclude that the photocatalytic reaction is primarily caused by light of wavelengths less than 400 nm.

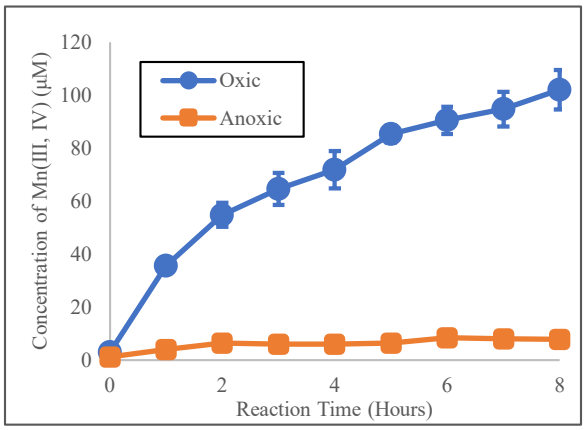

Figure 5 rate of Mn(II) oxidation under anoxic conditions

Figure 5 shows that the oxidation is negligible under anoxic conditions. This finding is of particular significance because it shows that Mn oxides can be useful in geological studies for oxygen evolution in Earth's atmosphere.

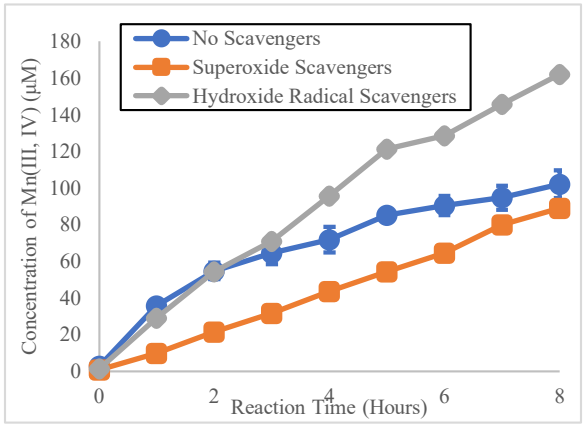

Figure 6 rate of Mn(II) oxidation with scavengers present in solution

Figure 6 shows that superoxide has a significant impact on the reaction rate. Because of this, we can conclude that electron transfer directly from TiO_2 and indirectly from O_2^- are both responsible for the oxidation. The presence of hydroxyl radical scavenger caused an increase in the reaction rate, and the cause warrants further investigation.

Conclusions:

The photocatalytic oxidation of Mn^{2+} to Mn(III/IV) on the surface of TiO_2 was found to be heavily influenced by a variety of factors. The structure of TiO_2 catalyst affected not only the reaction rate, but also the degree of oxidation. Anatase yielded a higher reaction rate but favored the production of Mn(III) oxides in both ASW and DI conditions, whereas rutile yielded more Mn(IV) oxides. The reaction was significantly impacted by superoxide and hydroxyl radicals that are produced in solution. Furthermore, the reaction was found to be primarily catalyzed by light of wavelengths of less than 400 nm.

The first finding of major significance in this study was the formation of tunnel structured manganese oxide todorokite and romanechite. Todorokite is one of the most common forms manganese oxides in natural systems. There have been no previous studies showing the production of todorokite under low temperature circumneutral pH conditions.

The second finding of major significance in this study was the effect molecular oxygen on the oxidation. The photocatalytic oxidation was found to be negligible without oxygen presence. This strengthens the utilization of manganese oxides in geological studies for evaluating oxygen evolution on early Earth.

Acknowledgements:

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