

REDETERMINING THE KINETICS OF FERROUS IRON PHOTO-OXIDATION UNDER UV FLUXES RELEVANT TO EARLY MARS AND EARTH. A. W. Heard¹, and N. Dauphas¹. ¹Origins Laboratory, Department of the Geophysical Sciences and Enrico Fermi Institute, The University of Chicago, 5734 South Ellis Avenue, Chicago, IL 60637, United States (andyheard@uchicago.edu).

Introduction: Iron (Fe) plays an important role in regulating the oxidation state of planetary surfaces because of its multiple redox states. On Mars, and Earth, igneous rocks contain mostly reduced, ferrous Fe (Fe^{2+}). During weathering of the Fe-rich igneous crust, Fe^{2+} is soluble, and if the surface environment is sufficiently reducing, this Fe^{2+} can accumulate in standing water bodies and aquifers. Evidence for these Fe-rich and reducing – ‘ferruginous’ – conditions is common through early Earth history, and they have also been inferred for deeper facies of a redox-stratified Gale Crater Lake on Mars [1]. Dissolved Fe^{2+} can be oxidized to ferric iron (Fe^{3+}), which tends to form insoluble minerals that deposit as chemical sediments. When Fe^{2+} oxidation is not coupled to any form of biological carbon fixation, net oxidation of surface Fe is most often balanced, directly or indirectly, by the formation of H_2 from water, and this H_2 can subsequently be lost to space [2]. Nonbiological Fe^{2+} on Mars has been linked to the release of H_2 to the atmosphere, with potential greenhouse warming consequences, and its subsequent loss to space that has caused net oxidation and desiccation of the planet’s surface [3]. Therefore, understanding the kinetics of abiotic Fe^{2+} oxidation on Mars is critical to place time constraints on local and global Martian geochemical evolution.

Iron Oxidation Kinetics On Mars: Assuming an absence of life on ancient Mars, Fe^{3+} minerals in Martian sediments must indicate oxidation occurred either by interaction with free oxygen (O_2), produced by atmospheric photochemistry, or by UV photo-oxidation, the process by which Fe^{2+} in solution absorbs solar UV radiation and a proportion of the resulting excited ions lose an electron, to give Fe^{3+} [1,4-5]. The kinetics of O_2 oxidation of Fe^{2+} are well constrained, but past O_2 levels on Mars are poorly constrained, though they were likely low for most of Mars’ history. By contrast, Mars lacks an ozone layer so that UV radiation, which was enhanced when the Sun was younger, could reach the surface and promote UV photo-oxidation of Fe^{2+} dissolved in subaerial water bodies. The kinetic rates of Fe^{2+} photo-oxidation are calibrated based on experiments which had light sources that did not match well the solar spectrum, making it difficult to model this process [5-7]. Though these kinetics are poorly constrained, photo-oxidation is particularly appealing as a means of oxidizing Fe^{2+} in sites such the Burns Formation on Meridiani Planum, where the mineral jaro-

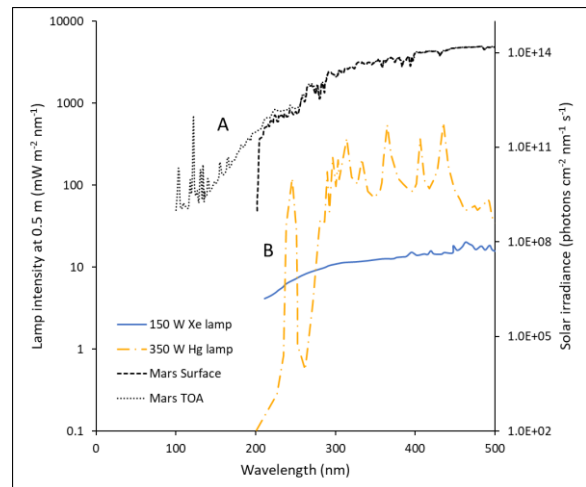


Figure 1: A.) The solar UV radiation spectrum incident at the top of atmosphere, and surface, of Mars 3.5 billion years ago [10]. B) The UV output spectra of Hg vapor and Xe arc lamps. The Xe light source used in this study has fewer sharp lines so the total UV photon flux to experiments is better constrained, and is also a better solar simulator.

site indicates very acidic paleo-pH; conditions which do not favor efficient oxidation of Fe^{2+} by O_2 even when it is abundant [4-5,8-9]. We are conducting experiments to re-determine the kinetic rates of Fe^{2+} photo-oxidation by a UV radiation source with a radiation spectrum similar to the Sun. The specific, poorly-known parameter of interest is the quantum yield, ϕ , which is the efficiency with which absorbed UV photons cause ferrous Fe ions to lose an electron and become ferric Fe. Better determination of the kinetics of UV photo-oxidation will enable future geochemical models to place more accurate time constraints on the deposition of Fe-rich chemical sediments on Mars and thus the minimum lifetime of standing water bodies such as Gale Crater Lake and the playas of Meridiani Planum [5,11].

Experimental Improvements: In earlier Fe^{2+} photo-oxidation studies, experiments made use of medium-pressure mercury (Hg) vapor lamps, which have high intensity in the UV but very sharp spectral lines [5-7]. This makes them an efficient photo-oxidation light source but a poor solar simulator for geoscience-relevant kinetic experiments. The new experiments reported here make use of a xenon (Xe) arc lamp,

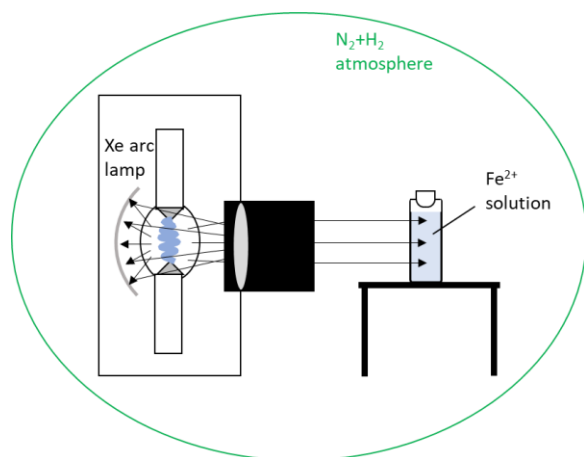


Figure 2: New experiment geometry for Fe^{2+} photo-oxidation kinetics. The linear geometry provides a simpler light model for calculating the photon flux, which is necessary to accurately determine the quantum yield.

which has smoother spectrum in the UV range (Figure 1B), so that contributions from strong lines are lessened and the quantum yield can be more accurately determined. Additionally, this Xe light source is more similar to the solar spectrum incident on early Mars (Figure 1A). The new experiment also makes use of a simpler radiation geometry, with a collimated light beam that irradiates a narrow rectangular reaction cell (Figure 2). This linear geometry makes the photon flux to the solution easier to model and therefore to determine the quantum yield. This represents an improvement over previous experiments which used cylindrical beakers to hold solutions with a partially immersed lamp that resulted in an irradiation pattern partway between an annulus and a top-down geometry, which prove to be difficult to accurately model. To ensure complete elimination of oxidation by O_2 , experiments were run in a nitrogen-hydrogen ($\text{N}_2\text{-H}_2$) atmosphere in an anaerobic chamber that actively removed O_2 , rather than just passively flushing the system by bubbling N_2 or argon (Ar).

Preliminary Results: Several experiments have already been conducted. Buffer solutions with pH 7.5 were used to compare to a recent previous study [5]. Two different initial Fe^{2+} concentrations, ~240 ppm, and 24 ppm, were tested to determine whether dissolved Fe at these levels affected the transmission of UV though the width of the cell. In all experiment solutions irradiated by the Xe lamp for time periods <1 hour to >3 hours, Fe^{2+} photo-oxidation occurred, resulting in a fine grained orange precipitate that sank to the bottom of the reaction cell, and Fe^{2+} concentrations measurably decreased (Figure 3). The maximum degree of photo-oxidation was ~10% of the initial dissolved Fe^{2+} , and there is no evidence for a difference in

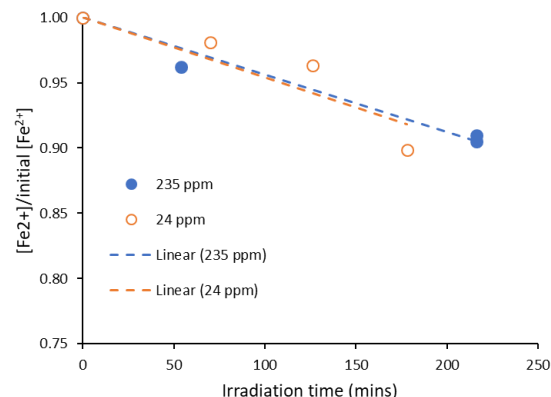


Figure 3: Preliminary results for photo-oxidation kinetic experiments with Fe^{2+} solutions with an order of magnitude concentration difference. There is no definitive evidence for a difference in proportional photo-oxidation rate, which suggests most UV photons were transmitted through the entire reaction cell.

proportional photo-oxidation rate for solutions with an order of magnitude different initial $[\text{Fe}^{2+}]$. All solutions tested allowed effective transmission of UV photons across the reaction cell. Experiments are underway to investigate the role of changing pH (and thus Fe^{2+} ionic speciation) in photo-oxidation rates, and first estimates of improved quantum yields will be reported at the meeting.

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