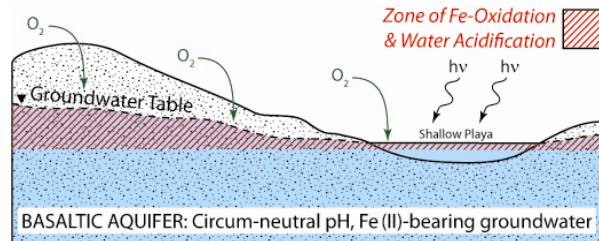


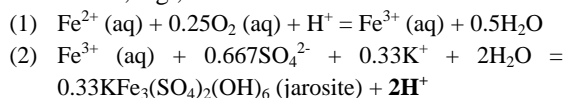
**REDOX CHEMISTRY AND THE ORIGIN OF ACIDITY ON THE ANCIENT SURFACE OF MARS.** J. A. Hurowitz<sup>1\*</sup>, W. W. Fischer<sup>2</sup>, N. J. Tosca<sup>3</sup>, and R. E. Milliken<sup>1</sup>, <sup>1</sup>Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Drive, Pasadena, CA, 91109, <sup>2</sup>Division of Geological and Planetary Sciences, 107 North Mudd Laboratory, California Institute of Technology, Pasadena, CA 91125, <sup>3</sup>Department of Earth Sciences, University of Cambridge, Cambridge CB2 3EQ, United Kingdom, \*joel.a.hurowitz@jpl.nasa.gov.

**Introduction:** *In-situ* and orbital exploration have demonstrated that surface waters at Meridiani Planum, Mars were acidic [1-4]. However, the origin of this acidity is unknown. Constrained by chemical and mineralogical analyses from the Mars Exploration Rover *Opportunity* [5-8], we show that Fe-oxidation and Fe<sup>3+</sup>-mineral precipitation yields an excess of acid relative to the amount of titrant available in outcrop [9]. Our results indicate that Fe<sup>2+</sup>-bearing subsurface waters, buffered to circum-neutral pH and anoxia, were subject to rapid oxidation and acidification upon exposure to O<sub>2</sub> and/or UV light (**Fig. 1**).



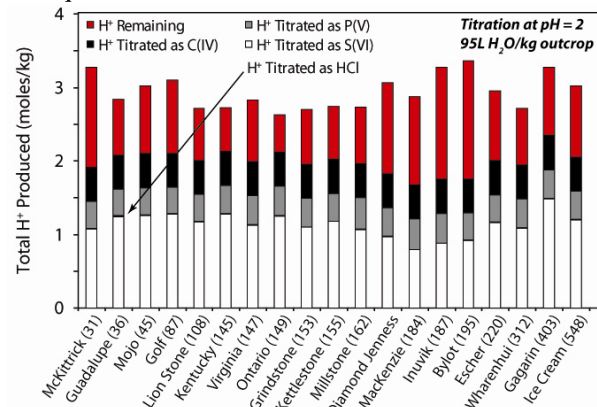
**Fig. 1:** Schematic cross-section showing the oxidation and acidification of groundwater at Meridiani Planum.

**Approach:** *In-situ* measurements of Meridiani outcrop chemistry and mineralogy make it possible to quantify the amount of acid consumed or produced during Fe-oxidation and Fe<sup>3+</sup> mineral precipitation. The acid produced can then be “titrated” against the available base anion content measured in outcrop (i.e., SO<sub>4</sub><sup>2-</sup>, Cl<sup>-</sup>, PO<sub>4</sub><sup>3-</sup>, and CO<sub>3</sub><sup>2-</sup>), yielding a net proton balance reflective of the parent fluid. For our titration method, we sum the number of moles of H<sup>+</sup> generated during precipitation of the measured quantity and distribution of jarosite, hematite, and schwertmannite, using data collected through sol 548 of the *Opportunity* mission on 19 Meridiani Planum outcrop targets. Our approach is based on a straightforward accounting of the number of moles of acid produced when Fe<sup>3+</sup> minerals are formed from dissolved Fe<sup>2+</sup>, e.g.,:



**Results:** For all outcrop analyses there is an excess of H<sup>+</sup> generated in forming the observed secondary Fe<sup>3+</sup> mineral phases relative to the available titrant in

outcrop (**Fig. 2**). Our calculations imply that so long as redox conditions in the aquifer were conducive to the transport of Fe<sup>2+</sup>(aq), oxidation and formation of jarosite, hematite, and schwertmannite would have resulted in the generation of low-pH fluids at the site of Fe<sup>3+</sup>-mineral precipitation (**Fig. 1**). Accordingly, input of additional acid volatiles (e.g., SO<sub>2</sub>, H<sub>2</sub>SO<sub>4</sub>) at the site of sediment formation [10, 11] is not required and SO<sub>4</sub><sup>2-</sup> can be considered a background constituent of the aquifer fluid.



**Fig. 2:** Total acid production and titration against a pH=2 base species distribution for analyses collected between sols 31 and 548 on abraded outcrop targets.

Finally, because gaseous H<sub>2</sub> is a by-product, Fe-oxidation processes have an impact on the redox state of the atmosphere. We will show that the Martian sedimentary record provides quantitative insight into the magnitude and timing of atmospheric H<sub>2</sub> loss processes required for oxidation at Meridiani Planum.

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