POSSIBLE MICROBIAL ENERGY PATHWAYS FROM IRON AND SULFUR REDOX GRADIENTS AT MAWRTH VALLIS AND GALE CRATER, MARS.
B. Horgan[1], M. S. Rice[2], W. Farrand[3], N. D. Sheldon[4], and J. L. Bishop[5]. [1]Purdue University (briony@purdue.edu), [2]Western Washington University, [3]Space Science Institute, [4]University of Michigan, [5]SETI Institute.

Introduction: Redox gradients and other chemical disequilibria are a key source of energy for chemoautotrophic microbes, and thus an indicator of habitability. Here we review recent studies using near-infrared spectra from the CRISM imaging spectrometer of possible reduced and oxidized phases at two sites on Mars.

In the vicinity of Mawrth Vallis, Arabia Terra is capped by ~200 m of layered deposits with some of the strongest clay spectral signatures on Mars [1]. The clays are divided between lower Fe/Mg-smectite and upper Al/Si-clay units. The context and mineralogy of Mawrth is consistent with a paleosol sequence, most likely formed under a semi-arid climate [2].

Mars Science Laboratory (MSL) is investigating Gale Crater, and will ultimately climb the 5 km layered Gale central mound [3]. Previous spectral investigations of Gale have shown that the NW portion of the mound that MSL will investigate *in situ* exhibits diverse mineralogy, including smectites, sulfates, and iron oxides, which may indicate changing climates and/or aqueous environments on early Mars [4].

Evidence for reducing conditions: An enigmatic spectral signature found at Mawrth Vallis and the western Gale mound is a strong red slope between 1.1-1.8 μm, consistent with reduced iron-bearing minerals. In Gale, this ferrous signature is found above and overlapping onto the underlying smectite clay unit [5]. At Mawrth, the ferrous signature occurs in the upper unit and at the contact between the units [6]. In the Al-unit, the ferrous signature is often associated with absorption bands consistent with Al-sulfates (alunite) or Al-clays (*e.g.*, kaolinite) in acidic environments. This signature has been interpreted as olivine [4], but is also consistent with ferrous clays (*e.g.*, chlorite) [6]. However, the ferrous phases at Mawrth and Gale do not exhibit clay OH bands, and are more consistent with poorly-crystalline ferrous alteration phases, like the "green rust" that gives reducing soils their green-grey color [2]. Thus, we hypothesize that the ferrous signature is indicative of reducing alteration conditions.

Evidence for oxidizing conditions: The ferrous unit in the Gale mound is either stratigaphically above or at the same level as a resistant ridge containing the iron oxide hematite, thought to be formed from oxidation of Fe^{2+}-bearing fluids [7]. Both the ridge and ferrous unit are underlain by Fe/Mg-smectites. At Mawrth, patches of the Fe-sulfates jarosite and copiapite as well as acid-treated Fe/Mg-smectites are found just below the contact between the upper and lower units and in the upper unit [2,6,8,9]. These phases are produced during oxidation and acidification of Fe and S-bearing fluids, usually derived from iron sulfides.

Interpretation: We hypothesize that the association between reduced and oxidized phases at Gale and Mawrth indicate redox gradients. In this scenario, the reducing fluids were created by long-term oxygen limited alteration of Fe-bearing minerals in the near-surface, most likely along with sulfides at Mawrth. At both sites, downward movement of these fluids may have been limited by the underlying smectite layers, forcing lateral flow. On emergence at the surface (sub-aerial or sub-aqueous), the fluid was oxidized by photochemical or other redox reactions. On Earth, this process forms hematite ironpans on slopes surrounding poorly-drained hilltops [10], as well as some ancient banded iron formations in shallow coastal waters [11]. At Mawrth, we suggest that reducing conditions occured in fluctuating ground-water tables in a sub-aerial "wetland", with localized acid sulfate alteration. At Gale, either a sub-aerial or sub-aqueous environment is possible, but should be distinguishable *in situ* by MSL.

Implications: Both the hypothesized wetlands environment at Mawrth and the less well-constrained aqueous environment at Gale exhibit clear mineralogical signs of local chemical disequillibria, which could have provided metabolic pathways for Fe or S oxidizing or reducing microbes, all common on Earth. Thus, these would have been highly habitable environments. Furthermore, reducing conditions and high clay content both promote preservation of organic matter. Indeed, organic carbon has been identified in Archean reduced soils on Earth, and is used as evidence of early colonization of land by microbes [12,13]. Thus, the reduced unit at Gale will be an intriguing target for MSL, and Mawrth has the potential to be a high priority target for future landed missions.

References: [1] Loizeau *et al*. (2007) *JGR* 112, E08S08. [2] Horgan *et al*. (2014) *8th Mars* #1276. [3] Grotzinger et al. (2014) *Science 343*, doi:10.1126/science.12 42777. [4] Milliken *et al*. (2010) *GRL* 37, L04201. [5] Horgan *et al*. (2015) *LPSC 46* #2923. [6] Bishop *et al*. (2013) *PSS* 86, 130-149. [7] Fraeman *et al*. (2013) *Geol.* 41, 1103-1106. [8] Farrand *et al*. (2009) *Icarus* 204, 478-488. [9] Farrand *et al*. (2014) *Icarus* 241 346-357. [10] Mann & Ollier (1985) *Catena Supp. 6*, 151-157. [11] Canfield (1998) *Nature 396*, 450-453. [12] Gay & Grandstaff (1980) Precam Res *12* 349-373. [13] Rye & Holland (2000) Geol *28* 483-486.