ALUMINA+SILICA±GERMANIUM ALTERATION IN SMECTITE-BEARING MARATHON VALLEY, ENDEAVOUR CRATER RIM, MARS. D. W. Mittlefehldt[1], R. Gellert[2], S. Van Bommel[2], R. E. Arvidson[3], B. C. Clark[4], D. W. Ming[1], C. Schröder[5], A. S. Yen[6], V. K. Fox[3], W. H. Farrand[4], B. L. Jolliff[3] and the Athena Science Team, [1]NASA Johnson Space Center, Houston, TX, USA (david.w.mittlefehldt@nasa.gov), [2]University of Guelph, Guelph, Ontario, Canada, [3]Washington University in Saint Louis, St. Louis, MO, USA, [4]Space Science Institute, Boulder, CO, USA, [5]Stirling University, Stirling, UK, [6]Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA, USA.

Introduction and Geological Setting: Mars Exploration Rover Opportunity has been exploring Mars for 12+ years, and is presently investigating the geology of a western rim segment of 22 km diameter, Noachian-aged Endeavour crater. The Alpha Particle X-ray Spectrometer has determined the compositions of a pre-impact lithology, the Matijevic fm., and polymict impact breccias ejected from the crater, the Shoemaker fm. [1-3]. Opportunity is now investigating a region named Marathon Valley that cuts southwest-northeast through the central portion of the rim segment (Fig. 1) and provides a window into the lower stratigraphic record. (Geographic names used here are informal.) At the head of Marathon Valley, referred to here as Upper Marathon Valley, is a shallow, ovoid depression ~25×35 m in size, named Spirit of Saint Louis. Layering inside Spirit of Saint Louis appears continuous with the Upper Marathon Valley rocks outside, indicating they are coeval. Spirit of Saint Louis is partly bounded by a ~10-20 cm wide zone containing reddish altered rocks (red zone). Red zones also form prominent curvilinear features in Marathon Valley. Compact Reconnaissance Imaging Spectrometer for Mars (CRISM) spectra provide evidence for areally extensive Fe-Mg smectite in the Marathon Valley region, indicating distinct styles of aqueous alteration [4]. The CRISM detections of smectites are based on metal-OH absorptions at ~2.3 and 2.4 µm that are at least two times the background noise level [4].

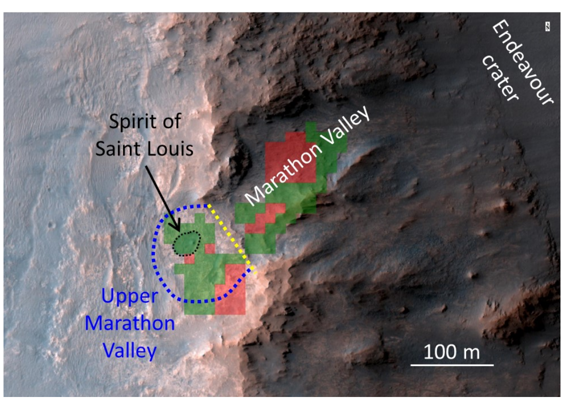

Figure 1. HiRISE image overlain with CRISM detections of smectite (red - strongest; green - less strong).

Textures: The rocks are breccias (Fig. 2a) composed of darker-toned clasts up to a few cm in size in a lighter-toned, fine-grained matrix. They are generally finer grained and clast-poor compared to typical Shoemaker fm. breccias from Murray Ridge and Cape York. Many of the rocks have an indurated appearance, with clasts and matrix only poorly distinguished. Red zones consist of discontinuous cm-sized knobs of rock with a hackly, cemented appearance (Fig. 2b).

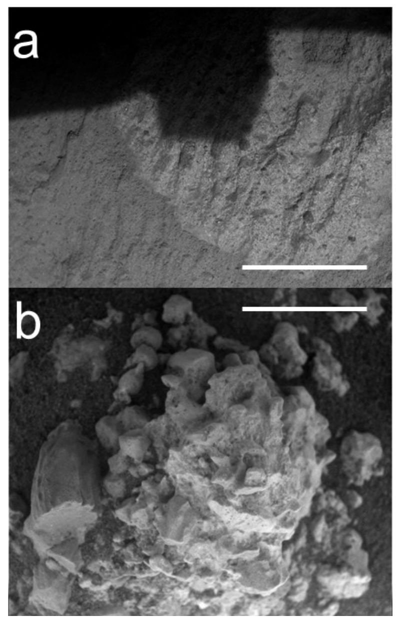

Figure 2. Microscopic Imager views of Upper Marathon Valley breccia Athens (brushed) (a) and red zone rock Pvt. William Bratton (b). Scale bars are 1 cm.

Compositions: Excluding SO_3 and Cl, rocks of the Marathon Valley region are of similar, essentially basaltic composition. They are similar in non-volatile-element composition to Shoemaker fm. breccias (for example, Al_2O_3-SiO_2-FeO; Figs. 3a, b). Marathon Valley region rocks are compositionally distinct from the pre-impact Matijevic fm. (Fig. 3b).

Red zone rocks have higher Al_2O_3, SiO_2 and TiO_2 contents and lower FeO contents compared to nearby, less-altered rocks (Figs. 3a, b; TiO_2 not shown). In this they mimic the boxwork vein targets Lihir and Espérance from the Matijevic fm. on Cape York (Figs. 3a, b) [5]. However, the most silica-rich red zone targets have higher Si/Al than do the boxwork vein targets. Red zone targets also have lower SO_3, MnO, Ni and Zn contents compared to adjacent, non-red-zone rocks. Some non-red-zone rocks in Upper Marathon Valley have higher Al_2O_3 and SiO_2 contents indicating red-zone-style alteration extended beyond the narrow, visually defined red zones. Rocks on either side of the red zone and patches within it have the multispectral signature (determined by the Panoramic Camera) of red hematite, indicating oxidation [6].

Some rocks from the Upper Marathon Valley and Spirit of Saint Louis have Ge contents up to 850 µg/g that are correlated with Al_2O_3 and SiO_2 (Figs. 3c, d). Rocks from within Marathon Valley proper do not have detectable Ge, including the only Al_2O_3-SiO_2-rich red zone target analyzed (Figs. 3c, d).

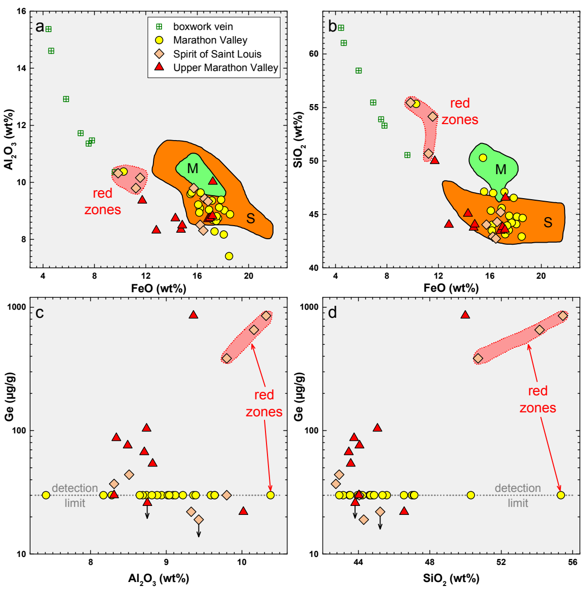

Figure 3. Compositions of Marathon Valley region rocks compared to boxwork veins from Cape York [5] and fields for Shoemaker fm. (S) and Matijevic fm. (M). Arrows indicate 2σ upper limits on Ge. Rock spectra lacking a Ge peak are plotted at a conservative detection limit of 30 µg/g.

Discussion: Rocks from the Marathon Valley region are breccias broadly similar in texture to the Shoemaker fm. that makes up the western rim of Endeavour crater. Excluding SO_3 and Cl, they are basaltic in composition and similar to the Shoemaker fm. Marathon Valley region rocks are texturally and compositionally distinct from the pre-impact Matijevic fm. The simplest interpretation is that Marathon Valley region rocks are stratigraphically lower exposures of breccias formed by the Endeavour impact. However, red-zone-type alteration is unique to the Marathon Valley region. Elsewhere on the rim, alteration resulted in enrichments in Mn-oxides and/or sulfates [1, 2, 5, 7]. Because Marathon Valley is a fracture zone [8], fluid transport could have been concentrated there, facilitating a distinct type of alteration. An alternative interpretation is that the Marathon Valley region rocks are an earlier generation of breccias that form part of the pre-Endeavour-impact surface. According to this alternative, this terrane would have been variably altered along fractures to produce the distinctive red zones prior to the Endeavour impact.

Germanium is mobilized in hydrothermal fluids, and hydrothermally-altered seafloor basalts on Earth show modest enrichments (few µg/g) in Ge [9]. The high Ge contents of some red zone rocks, but not all, suggests that there may have been differences in fluid compositions and/or properties (temperature, pH, etc.). However, rocks with identical enrichments in Al_2O_3 and SiO_2 and depletions in FeO have Ge contents that differ by more than a factor 30 (Fig. 3); any differences in fluid compositions and properties would have to be such that the major elements were not affected. Fluid composition could have been affected by earlier mineral precipitation, and in terrestrial systems, the Ge/Si of fluids can be increased by this process [9, 10]. This is unlikely to explain high- and low-Ge red zones with similar major element contents as early precipitation of silica is commonly invoked to explain fluids with high Ge/Si [9, 10]. In terrestrial hydrothermal deposits, Ge substitutes in Fe-oxyhydroxides, sulfides or sulfosalts [11]. A working hypothesis is that in the Upper Marathon Valley/Spirit of Saint Louis region, Ge-bearing minor phases were precipitated while in Marathon Valley they were not. Because bulk-rock Ge contents are ≥850 µg/g, Ge must be a major constituent of any minor phases. Lack of Ge in Marathon Valley proper indicates that these minor phases were not precipitated there, for reasons that remain elusive.

Key Finding: *In situ* observations identify rocks locally enriched in Al_2O_3+SiO_2±Ge by alteration that are widely scattered throughout a region containing orbital signatures of Fe-Mg smectite.

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