

**MINERALOGICAL AND SPECTROSCOPIC PROXIES FOR FE AND AL MOBILITY IN WEATHERED ROCKS SUGGEST ANOXIC WEATHERING ON EARLY MARS.** J. C. Liu<sup>1</sup>, J. R. Michalski<sup>1</sup>, W. Tan<sup>2</sup>, H. P. He<sup>2</sup>, L. Xiao<sup>3</sup> and B. L. Ye<sup>1</sup>. Division of Earth and Planetary Sciences (cugjliu@foxmail.com), The University of Hong Kong, <sup>2</sup>Key Laboratory of Mineralogy and Metallogeny, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, <sup>3</sup>Planetary Science Institute, China University of Geosciences (Wuhan).

**Introduction:** A warmer and wetter Martian paleoclimate cannot be adequately explained only through CO<sub>2</sub>-driven greenhouse warming [1,2] suggesting that reduced greenhouse gases might be part of the climate puzzle [1]. Though several plausible mechanisms to produce adequate reducing gases on early Mars [3-8] have been proposed, geological/mineralogical evidence for reducing atmosphere on early Mars remains difficult to document. The primary reason is that indicative redox-sensitive materials/elements are easily oxidized, destroyed and removed by later chemical or photo oxidation processes at the surface [2, 9-11]. However, some paleosols retain a record of ancient communication between the atmosphere, hydrosphere and lithosphere. Chemical weathering under reducing or anoxic environment can lead to leaching of mobile Fe<sup>2+</sup>, which is an irreversible process and not easily erased. Therefore, the iron distribution pattern of paleo-weathering profiles is a useful proxy for redox state of early Mars surface and atmosphere [12]. The objective of the study is to test whether thick layered clay profiles in the Mawrth Vallis region were formed by a leaching process, whether there is Fe loss in the upper profiles, and to constrain the surface/atmosphere redox state on early Mars.

**Method:** The geologic interpretations developed here utilize enhanced false-color images of the Martian surface provided by the High Resolution Imaging Science Experiment (HiRISE) camera. Reference spectra of hydrated minerals are resampled to 3 bands (BG, RED and NIR), according to reflectance at their central wavelengths. The brightness in HiRISE color image is defined here as (BG+RED+NIR)/3. The blueness is defined as 2\* BG/( RED+NIR). The combination of brightness and blueness are used to discriminate existence of Fe<sup>3+</sup> and Fe<sup>2+</sup> in minerals and rocks.

Spectra of regions of interest from the Compact Reconnaissance Imaging Spectrometer for Mars (CRISM) were firstly collected to identify minerals and observe major spectral trends. After that, 5\*1 pixel spectra along transect, crossing different portions of thick layered clay profiles, were collected and continuum-removed to extract variations and trends of related spectral parameters. Spectral parameters were calculated from the atmospherically corrected CRISM data. The same spectral parameters of organic-poor basaltic weathered products from Hainan Island in China were calculated using the same methods. In addition, NIR

slope degree is defined by ratio of reflectance at 1.6 to 1.2 μm (R1.6/R1.2).

**Results:** Thick layered clay profiles with similar characteristics in HiRISE color image are observed at numerous locations in the Mawrth Vallis region. From top to bottom, four different units with gradual boundaries are observable: (dm) a dark mantling unit, composed of relatively unaltered indurated material; (α1) a light-toned and bluish zone; (α2) a light-toned and reddish zone; (α3) a brown darker zone. The similar structure and color pattern in many localities indicate that they share similar geological occurrence and mineralogical distribution, which is controlled by a widespread process in the region. One of the best continuous exposures with little sand cover occurs in Muara crater located at 340.68°E, 24.35°N (FRT000094F6).

Fe<sup>2+</sup> rich minerals and basalt exhibit low brightness and higher blueness. The Fe-poor hydrated minerals possess both high blueness and high brightness. Fe<sup>3+</sup> rich minerals and rocks have low blueness. The visual physical characteristics in HiRISE color image can highly improve identification speed of existence and valence state of iron in rocks or minerals. For organic-poor weathered basaltic rocks in Hainan Island, their concentration of ferric iron is positively correlated with band depth of absorption around 530 nm (530BD\_2) and negatively correlated with their calculated HiRISE blueness. Both low BD530\_2 of CRISM and high blueness in HiRISE image are good indicators of depletion of Fe<sup>3+</sup> in rocks, whereas high BD530\_2 and high redness indicate the enrichment of Fe<sup>3+</sup> in rocks.

Blue-toned zones in HiRISE color image match well with the low Fe<sup>3+</sup> area. Al-OH rich zone (high BD2210\_2) is distributed in a wider area, but overlaps with low Fe<sup>3+</sup> area, suggesting surface Al-clays are separated from ferric iron. The blue-toned zone below the capping layer exhibits the lowest concentration of Fe<sup>3+</sup> (the smallest BD530\_2), which is even smaller than that of the dark sand dunes in the center of the crater. However, the concentration of Fe<sup>3+</sup> suddenly jumps to the largest value at the reddish zone, which then decreases gradually in the below darker brown zone.

The capping layer shows no absorption in the short wavelength infrared range (1.3-2.5 μm), but exhibits strong absorption around 0.53 μm. In the upper blue-toned zone (α1) below the capping unit, the spectral

absorption around 2.2  $\mu\text{m}$  was previously attributed to silica, Al-clays or amorphous clays. But, the spectra also show an obvious absorption at 2.17  $\mu\text{m}$ , which is as strong as the absorption at 2.21  $\mu\text{m}$ . It is difficult to explain by kaolinite or any other mineral mentioned above. The strong absorption at 2.17  $\mu\text{m}$ , combining with positive SINDEX 2 and weak absorptions around 1.44, 1.48, 1.76, 1.92, 2.32 and 2.45  $\mu\text{m}$ , is indicative of the existence of alunite, which is recently identified in the Mawrth Vallis area [13]. The weak diagnostic absorptions of alunite suggest the alunite formed at low-temperature condition rather than hydrothermal condition [13]. In addition, the doublets around 1.4 and 2.2  $\mu\text{m}$  and absorption around 1.91  $\mu\text{m}$  suggest the existence of poorly crystallized kaolinite in the upper profile. In the light-toned and reddish zone ( $\alpha_2$ ), the co-appearance of absorptions at 2.21 and 2.29  $\mu\text{m}$  implies the co-existence of kaolinite and nontronite. In the darker brown zone ( $\alpha_3$ ), no absorption is observed at 2.21  $\mu\text{m}$ , whereas the absorption at 2.29  $\mu\text{m}$  is strong.

**Discussion:** From the bottom of the profile to top, the weak BD2290 increases upwards firstly and then decreases with increasing BD2210\_2. The trend shows gradual formation of nontronite, which then coexists with kaolinite and sequentially transforms to kaolinite. In the upper sections, kaolinite content decreases consequently and is replaced by alunite in the Mawrth Vallis area. The gradual decomposition of silicates, and gradual upwards enrichment of Al, as exhibited by these special spectral trends, strongly indicates top-down leaching process.

$\text{Fe}^{3+}$  is strongly depleted in the uppermost 20 m of weathering sequences but concentrated in the middle sequences (reddish zone). The low abundance of  $\text{Fe}^{3+}$  but high abundance of Al-rich minerals is suggestive of strong separation of  $\text{Fe}^{3+}$  from Al in the uppermost zone. The separation of  $\text{Fe}^{3+}$  from Al is also consistent with the existence of alunite, which generally form where Al is much more concentrated than  $\text{Fe}^{3+}$ . However, both  $\text{Fe}^{3+}$  and  $\text{Al}^{3+}$  are relatively immobile elements in weathering profiles on the modern Earth owing to the oxidizing character of surface fluids and the near-neutral pH of many surface fluids.  $\text{Fe}^{3+}$  can be mobilized by low pH fluids (or high pH fluids) or organic iron-binding ligand. However, acidic fluids also greatly increase the solubility of  $\text{Al}^{3+}$ , which is, therefore, unlikely to cause Fe separation from Al. In addition, no or little organic matter existed in the Fe depletion zone, suggested by its high albedo. Therefore, to separate Fe from Al, the most straightforward pathway is through redox chemistry. For example, the variation of Fe/Al of ancient terrestrial paleosols formed before

the Great Oxidation Event (GOE) shows strong Fe loss, because iron was mobilized as  $\text{Fe}^{2+}$  under reduced surface conditions [12]. The Fe separation from Al in the Mawrth Vallis area suggests that the dissolved  $\text{Fe}^{2+}$  was oxidized much slower than its dissolution rate from substrates during weathering. Although the oxidation rate of  $\text{Fe}^{2+}$  in the upper profile in the Mawrth Vallis area is partly limited by acidic conditions, the strong Fe-depletion zone (up to 20m) suggests that the Martian surface was not oxic during the formation of the upper profile in the Mawrth Vallis.

Al-clays in proposed weathering sections on Mars are generally blue in HiRISE color images [14]. The blue tone of Al-clays rich weathered products in several regions, including Mawrth Vallis, North Hellas basin, Nili Fossae, Eridania basin and Valles Marineris regions, is indicative of widespread strong iron depletion in paleosols on Mars.

**Conclusion:** The vertical spectral mapping of thick layered clay profile in the Mawrth vallis region shows gradual formation of nontronite, then gradual decrease and transformation from nontronite to kaolinite and finally to alunite. The gradual enrichment trend of Al and decomposition of silicates from bottom to top is very similar to terrestrial weathering profile, indicative of a leaching formation mechanism of the thick layered clay profile in the Mawrth Vallis area. On the other hand, the BD530\_2 in CRISM image and blueness in HiRISE image are demonstrated as useful proxies of the abundance of  $\text{Fe}^{3+}$  in basaltic weathered rocks. The deficiency of Fe oxides but enrichment in Al-rich minerals in upper weathering sections is comparable to these of weathering sequences before the GOE, suggesting that the early-stage leaching fluid is anoxic. The widespread Al clays with strong Fe loss in paleosols all around ancient Martian terrains suggests that early Mars atmosphere and surface was anoxic. Reduced nature of atmosphere might have been responsible for an (episodic?) warmer and wetter climate on early Mars.

**References:** [1] Wordsworth, R. et al. (2017), *GRL*, 44, 665-671. [2] Ramirez, R. M. et al. (2013), *Nature Geo*, 7, 59-63. [3] Sholes, S. F. et al. (2017), *Icarus*, 290, 46-62. [4] Tarnas, J. et al. (2018), *EPSL*, 502, 133-145. [5] Tosca, N. J., et al. (2018), *Nature Geo*, 11, 635. [6] Oze, C. & Sharma (2005), *M. GRL* 32. [7] Kite, E. S. et al. (2017), *Nature Geo*, 10, 737. [8] Haberle, R. M. et al. (2019), *GRL*. [9] Chemtob, S. M. (2017), *JGR Planets*, 122, 2469-2488. [10] Mitra, K. & Catalano, J. G. (2019), *JGR Planets*. [11] Rivera-Banuchi, W. et al. (2018), *LPSC*, 49, 2550. [12] Rye, R. & Holland, H. D. (1998), *AJS*, 621-672. [13] Sessa, A. M. (2018), *LPSC*, 49, 2983. [14] Carter, J. et al. (2015), *Icarus*, 248, 373-382.