Paleosols with Strong Fe Loss: Direct Geological Evidence for A Reducing Greenhouse Warming on Early Mars.

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Introduction: Redox state of the early Martian atmosphere is an important consideration for understanding the paleoclimate of early Mars, which might have been strongly affected by reducing gases, e.g. H_2 and CH_4 [1, 2]. Paleosols record chemical processes at the Martian surface, therefore shedding light on the Martian paleoclimatic conditions and redox state of early Mars atmosphere. In this study, we relate spectral and mineralogical indexes to basic chemical processes during weathering, e.g. hydration, hydrolysis and (reducing) leaching, to discriminate palo-weathering sequences on early Mars surface and identify whether there was a reducing atmosphere on Early Mars [3].

Identification of weathering sequences: Silicate rocks chemically weathered through hydrolysis reactions are initially hydrated, and the presence of bound water with alkali (earth) elements can be identified spectroscopically by the occurrence and intensity of HOH absorptions at ~1900 nm (wavelength). The subsequent leaching of alkali elements leads to gradual decomposition of their water complexes. Further hydrolysis reactions result in the decomposition of silicates and formation of metal-OH bonds, the evidence of which can be observed in metal-OH infrared spectral absorption intensity around 1400 nm and 2100-2400 nm. One measure of weathering intensity is the band depth ratio of spectral absorption related to hydroxyls in the rock (1400 nm) to hydration in the rock (1900 nm). This spectral index has been demonstrated to map hydrolysis and leaching intensity in a long drill core through deeply weathered basalt on Earth [4]. The index is correlated with other indicators of weathering intensity, such as enrichment in immobile elements (e.g. Al^{3+}). Figure 1 shows the application of this spectral weathering intensity index to the an exposure of the uppermost crust in the Mawrth Vallis area. From an apparent depth of approximately 150 meters to the surface, there is a consistently positive increase in the spectral weathering index from ~0.05 to 0.35. In addition, the observed mineralogical transition, from nontronite to a mixture of nontronite and kaolinite, and finally to a mixture of kaolinite with possible alunite, reflects the gradual upward silicate decomposition and leaching of alkaline elements. This weathered section of rocks shows increasing degree of hydrolysis and enrichment in Al moving upward in section, as indicated by the mineral assemblages and as deduced from the increasing spectral weathering index values. These observed trends on Mars mirror the spectral, mineralogical and chemical trends observed in weathered basalt in Hainan Island in southern China (Fig. 1).

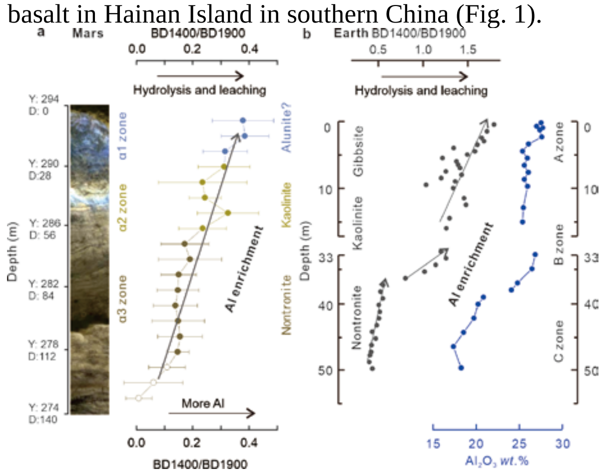

Fig.1 Spectroscopic indices applied to weathering trends on the Earth and Mars. Spectral index BD1400 measuring hydroxyl divided by BD1900 measuring water complexes increases with intensity of weathering from ~130 meters depth toward the surface at Muara Crater on Mars (a). The same spectral index ratio applied to a drill core through weathered basalt from Hainan Island [4] shows how the index relates to weathering intensity, Al-enrichment and mineralogy with depth (b).

An early reduced atmosphere on Mars: We have applied the same spectral filters used by HiRISE to spectra we measured in the laboratory and to those from a spectral library in order to quantify relevant aspects of the observations such as “blueness” and “brightness,” relating these measurements to concrete values of Fe-content and Fe-abundance proxies measured by CRISM. Fe-poor minerals have high blueness, high brightness and low values of the CRISM Fe-index. Fe^{2+}-rich materials (including basaltic sand and Fe^{2+}-rich hydrated minerals) have lower brightness than Fe-poor materials.

The lowest concentrations of Fe^{3+} occur in the blue unit (upper weathering sequence) and the highest concentrations occur in the yellow unit just below it. Al-rich rocks are also located near the top of the stratigraphic profile, but it is clear that the pattern of Al-enrichment is somewhat decoupled from the pattern of Fe-depletion (Fig. 2). All of the patterns of Fe-enrichment or depletion, and Al-enrichment appear to cut across stratigraphic boundaries, suggesting that these mineralogical trends were imposed upon pre-existing bedrock during top down chemical weathering. The spectral and chemical trends observed for ancient

Martian rocks bear a striking resemblance to trends observed in rocks formed on Earth in the Archean (Fig. 2).

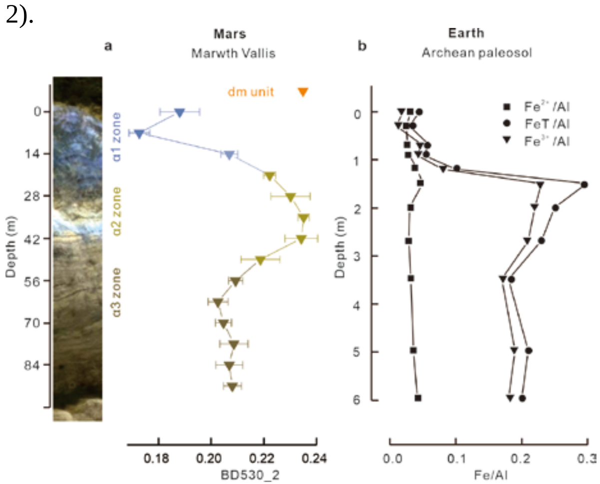

Fig. 2. Similar Fe3+ distribution patterns in early Martian and terrestrial Archean weathering sequences. CRISM Fe-oxide index (BD530_2) measures Fe3+ variation in weathering profiles on Mars (e. g. Mawrth Vallis shown in "a"). The Fe3+ variation pattern of the Pronto/NAN paleosol formed before GOE on Earth (b).

The evidence presented here points not only to thick accumulations of clay rich material but more importantly to the occurrence of an Fe-poor zone 10s of meters thick, which could imply a single, sustained reduced climate rather than multiple cycles between oxic and anoxic conditions. In addition, the widespread nature of the compositional stratigraphy and occurrence of blue-toned rocks overlying yellow-toned rocks around the planet [5] indicate that the extensive units represent a global scale process [3].

The separation of Fe from Al in Martian paleosols, which is comparable to trends observed in paleosols before the Great Oxidation Event on Earth, suggests that the ancient Martian surface was chemically weathered under a reducing greenhouse atmosphere.

References:

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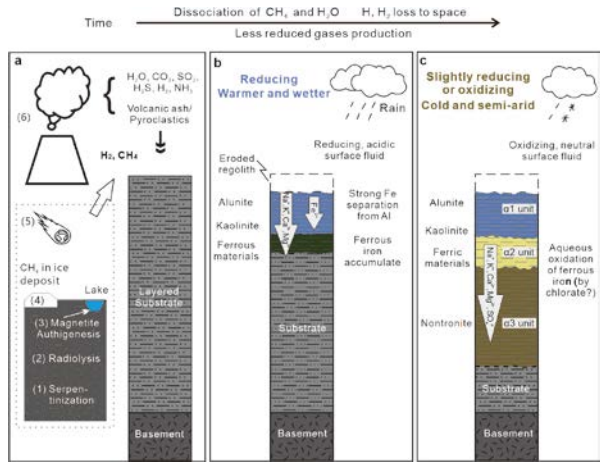

Fig. 3. Ancient weathering processes and atmospheric evolution on Mars. Formation of layered fine-grained tephra and several production mechanisms of reduced gases (a). Anoxic and acidic weathering caused downward transportation of ferrous iron, and formation of alunite and Al-clays (b). Ferrous iron accumulated around the anoxic weathering front. With dissociation of methane and water (c), and loss of hydrogen (gas) to space, Mars atmosphere and surface transitioned to oxidizing gradually. The oxic fluid penetrated into depth to form thick nontronite zone. The accumulated ferrous minerals in α2 zone were also oxidized to form ferric minerals (c).