ORBITAL EVIDENCE OF FERRIHYDRITE IN THE MARTIAN DUST: IMPLICATIONS FOR THE ANCIENT CLIMATE ON MARS.

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Introduction: Ferrihydrite is an amorphous and hydrated iron oxyhydroxide ($5Fe^{3+}{}_2O_3 \cdot 9H_2O$) [1]. On Earth, it forms in cool-temperate soils, low temperature hydrothermal springs, environments marked by changing redox conditions and commonly results from the alteration of igneous mafic minerals [2-5]. Several iron oxide phases that may explain the characteristic Mars' red hue have been proposed over the past decades [e.g. 6-8]. However, only recently important clues were provided by the Mars Science Laboratory (MSL) rover, which discovered that the Martian dust contains amorphous nanophase iron oxides and structurally bound water, but the oxidation state of the Martian dust could not be determined [9-11]. Here, by employing reflectance spectral slope and band depth measurements of novel orbital and laboratory data we find evidence for ferrihydrite being the dominant iron oxide phase in the Martian dust. The presence of ferrihydrite suggests a unique cold and wet weathering environment on early Mars, but limited interaction with liquid water later in its geologic history. In addition, our observations suggest that ferrihydrite-rich dust may be sourced from eroding bedrock in several places on Mars. This supports the interpretation that the Martian dust is not Amazonian but instead a product of ancient weathering in the Noachian period.

Methods: Orbital observations of Martian dusty areas were acquired by the Colour and Stereo Surface Imaging System (CaSSIS) onboard the ESA's Trace Gas Orbiter (TGO) [12]. We targeted thick deposits of dust in Arabia, Tharsis, Elysium and Isidis. Spectra of the Martian dust were extracted from over 500 individual CaSSIS cubes in four filters (BLU = 497 nm, PAN = 677 nm, RED = 835 nm and NIR = 940 nm). Using the PHysikalisches Institut Radiometric Experiment-2 (PHIRE-2) [13], which was equipped with four flight spare CaSSIS filters, we measured the bidirectional reflectance of eight laboratory iron oxides (e.g., ferrihydrite, hematite, schwertmannite, akageneite, feroxyhyte, maghemite, lepidocrocite and goethite). Lab samples were acquired from the University of Arkansas. PHIRE-2 measurements were conducted in the phase angle range of 4–70º, i.e. at illumination geometries similar to the CaSSIS observations. Both orbital and lab spectra were quantitatively characterized using standard spectral slope and band depth measurements used widely in the field [e.g. 14]. The CaSSIS observations include the latest absolute and radiometric calibration, which provides photometric precision up to ~3% [15,16]. The atmospheric conditions (i.e., optical depth τ) in each CaSSIS observation were estimated using the climatological assimilation of dust opacities derived from the Mars Climate Sounder (MCS) instrument [17].

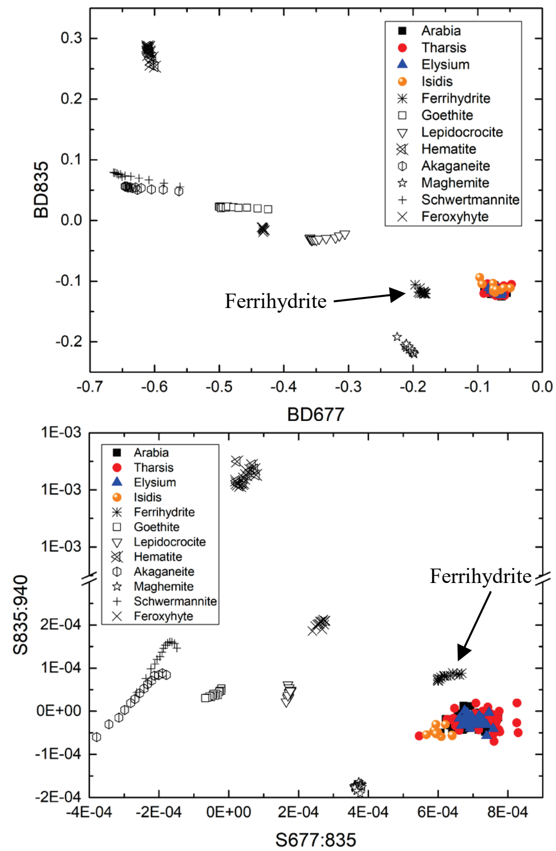

Figure 1. Spectral slope and band depth parameters for eight lab ferric oxides (gray) and CaSSIS observations of Martian dust (colored data points). Both results suggest that the Martian dust spectrum in the visible/NIR wavelengths is dominated by ferrihydrite. Additionally, the data points of Martian dust are tightly clustered supporting the interpretation that dust is well mixed across the planet.

Results: Reflectance spectral slope (S835:940 vs S677:835) and band depth measurements (BD835 vs

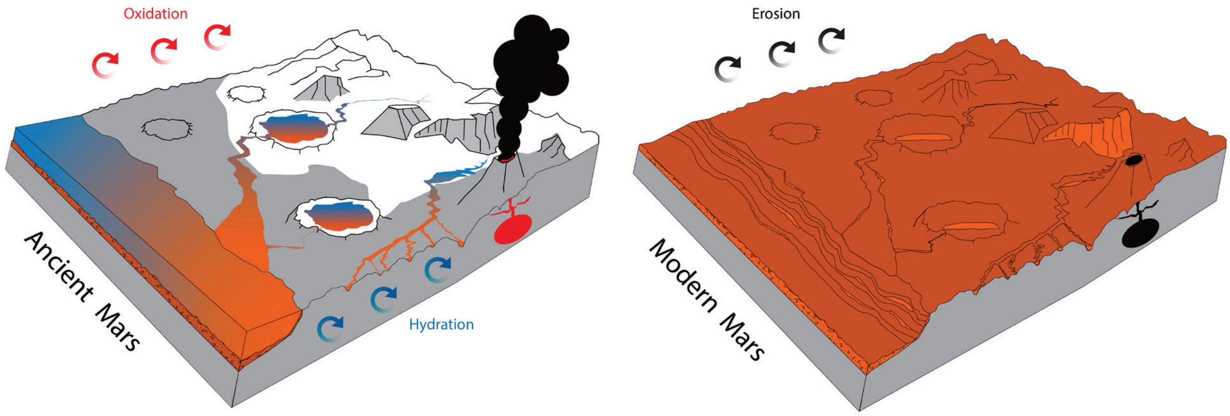

Figure 2. The dominant processes on early and modern Mars. Initially Mars starts as a 'gray' planet and then acquires its characteristic red hue by erosion of altered ferrihydrite-rich rocks and dispersal of dust by aeolian processes.

BD677) for the orbital observations of Martian dust and eight lab ferric iron oxides are given in Fig.1. Each lab oxide occupies a distinct region in both plots. Some oxides (e.g. akaganeite) exhibit a large spread, which suggests a dependence of spectral slope and/or band depth on phase angle of the observation. In addition, hematite is not a good spectral match to the observations. While ferrihydrite is significantly close to the values of Martian dust. This suggests that ferrihydrite is the dominant phase in the Martian dust (some impurities are also possible). The tightly clustered CaSSIS observations imply that dust is compositionally identical across the four bright regions of Mars.

Cool and wet Mars: The environment on early Mars must have been relatively cool and wet to support the formation of metastable ferrihydrite. Conditions supporting liquid water may have been highly intermittent although laboratory studies have shown that silica, phosphates and/or organic anions may inhibit the crystallization of ferrihydrite into other more stable ferric iron phases [e.g. 18,19]. Abundant X-ray amorphous materials including ferrihydrite have been found in cold and periodically wet settings on Earth, which may explain the origin of amorphous products in Gale Crater [20].

Ancient dust: The hydration and oxidation of the igneous early Mars crust would have resulted in sediments and rocks rich in ferrihydrite (e.g. Fig. 2). Over time, such geologic units would be susceptible to erosion and would shed off dust, which would later be redistributed over the entire planet. Rocks spectrally resembling dust (also known as 'duststones') have been identified in the mounds of Becquerel and Gale craters, in the Medusae Fossae Formation and in a few other locations on Mars [21-24]. In addition, the CaSSIS color images revealed dozens of sites where dust may be actively eroding out in Arabia Terra. The dichotomy between Mars dark and bright regions suggests that oxidizing/aqueous conditions that formed ferrihydrite-rich rocks existed early in its geologic history, and the dark unaltered regions may have formed much later under an arid, oxygen-free atmosphere.

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