Introduction: Iron oxides are sensitive tracers of past Martian climate, as their formation depends on environmental conditions including pH, temperature, redox state, and water availability [1]. Despite decades of Martian exploration, the identity of the iron oxide phase that dominates the surface remains elusive and enigmatic [2–6]. Common mineralogical models [7] suggest anhydrous hematite, which forms in trace amounts on rocks and soils by photo-oxidation and minimal water involvement. However, this does not explain the presence of thick layers of “duststones” near the equator [8] and elsewhere on Mars [9]. Moreover, hematite formation is favored in tropical soils on Earth [10], whereas Martian surface conditions are likely to have remained cold over extensive geological timescales [11]. Additionally, NASA’s Curiosity rover detected volatiles such as H2O and abundant X-ray amorphous materials in the Martian soil [12,13]. Ferrihydrite is an amorphous iron oxyhydroxide that occurs in glacial environments on Earth [14] and has been proposed to exist on Mars [15]. However, attempts to identify ferrihydrite from orbit are challenging due to admixtures of multiple components in the Mars dust spectrum at 1–2.5 µm. In this study, we explore several potential explanations for the missing hydration features, such as the spectral effects of intimate mixtures of ferrihydrite and silicates, and the dehydration of the 1.4-, 1.9- and 3 µm bands. Furthermore, we find that the ferric iron absorptions of a hyperfine mixture of ferrihydrite and basalt, with a particle size of less than 1 µm, closely match the Martian orbital spectrum of dust and bedrock. This is in line with field observations, which indicate that ferrihydrite is commonly found in mixtures with other minerals [16]. This finding has implications for the ancient Martian climate and water budget history.

Methods: This study encompasses the analysis of spectral properties of nine different iron oxides (ferrihydrite, hematite, schwertmannite, akageneite, fereroxylhite, maghemite, lepidocrocite, goethite and magnetite). Spectroscopic analyses were conducted at the University of Bern, Brown University’s RELAB facility and Université Grenoble Alpes, IPAG. Ferrihydrite was synthetically produced at the University of Arkansas, and X-ray diffraction analysis conducted at Brown University confirmed the 2L amorphous variety. Ferrihydrite and basalt samples were ground at IPAG using a planetary ball mill. Nanophase hematite was acquired from Sigma Aldrich. Particle sizes were confirmed to be around 500 nm with Scanning Electron Microscopy (SEM). Finally, dehydration experiments (heating) were performed at IPAG and Brown University.

Results: From all our investigated iron oxides in the lab, ferrihydrite offers the best spectral match to CRISM observations of dust (see Fig. 1), which agrees with our previous quantitative multispectral analysis in the 0.4–1.0 µm range [18]. The visible slope in the range from 500-700 nm, reflectance maximum in the VNIR at ~750 nm and ferric absorption at around 950 nm are consistent with ferrihydrite. Comparison to other iron oxide minerals including hematite do not provide a good match (not shown). The featureless part of the Mars spectrum from 1–2.5 µm may result from a combination of factors such as mixing with spectrally neutral materials like the basalt used in Figure 1, or the particle size range is so small [19] that features are weak or the amount of water is very low. Together these factors could hinder the hydration features (at 1.4 and 1.9 µm) of ferrihydrite. Note that even in a mixture mass ratio
(Fig. 1) of one part ferrihydrite to two parts basalt (1:2) and under ambient lab conditions the 1.4- and 1.9 µm bands were not observed. Furthermore, our results also show that the 3 µm band contains more strongly bound water and is still apparent after heating at 80°C under vacuum for 24 h. We also note that ferrihydrite did not change phase. This suggests that ferrihydrite would still retain some chemically bound water even in the extremely dry conditions at the surface of Mars.

**Bedrock.** We find that CRISM observations of thick ‘duststone’ deposits at the equator provide a good spectral match to our lab mixture of ferrihydrite and basalt (Fig. 2). The bedrock is unlikely to be covered by airfall dust because it is undergoing active erosion and THEMIS night IR support the presence of exposed bedrock. The positive NIR slope of the continuum may be the result of compact materials [20].

**Sulfates.** Our observations also reveal that the addition of hydrated sulfates into our lab mixture (1 to 1 with ferrihydrite by mass) under ambient conditions results only in a small 1.9 µm band and a decrease of reflectance at ~4 µm (plus multiple absorptions due to SO$_4^{2-}$ at ~4.5 µm). Under dehydration the 1.9 µm band was completely removed and therefore the presence of sulfates in the Martian dust and bedrock cannot be ruled out from spectroscopy alone.

**Silica.** Some studies suggested that ferrihydrite may be found with amorphous silica in rocks/dust on Mars [21]. We tested the latter by preparing mixtures of ferrihydrite and silica in different ratios (1:99, 1:9 and 1:1). Our results show that silica is a weak absorber in the near infrared and ferrihydrite dominates the infrared spectrum. We did not observe the flat and featureless part of the spectrum shown in Fig. 1. Thus, we exclude the possibility of significant amounts of silica in the Martian dust.

**Discussion:** Our work provides spectral evidence of ferrihydrite in dust and bedrock on Mars. This detection along with many other lines of evidence from previous workers suggests that Mars may have been a slushball, which transitioned into a cold and dry desert world that it is today. Observations of ferrihydrite-rich ‘duststones’ shown here and in other places on the planet suggest that ferrihydrite formation may have been a global phenomenon. These geologic units may be sources of elevated hydrogen signatures detected by neutron spectrometers [22,23].

**Future work:** To investigate the stability of ferrihydrite on Mars, we are performing a 30-day experiment under simulated Martian conditions (appropriate temperature, UV, and pressure).