As part of an ongoing study of terrestrial samples that exhibit spectroscopic and/or weathering/alteration similarities to those known or inferred for Mars, we have analyzed a suite of thermally altered palagonitic tephra samples from a Mauna Kea, Hawaii cinder cone. Laboratory analysis techniques included visible to near-IR and Mössbauer spectroscopy, XRD, and magnetics. The thermal alteration of these samples was caused by the emplacement of a meter-thick lava slab over a pre-existing tephra cone. Tephra that was not heated by the slab is composed of black, coarse-grained glassy basaltic particles, some of which have been moderately palagonitized since formation of the cone in the late Pleistocene. The most thermally altered sample from the zone adjacent to the slab has undergone a two-step process (palagonitization and intense heating) that has led to the formation of crystalline hematite and anion-deficient magnetite. These interpretations are based on (1) reflectance spectra that show evidence of crystalline iron oxide absorptions (due to hematite) in the samples closest to the heat source and a weak ferrous absorption in the less thermally altered samples; (2) Mössbauer spectra that clearly show (likely Ti-bearing) hematite and cation-deficient magnetite sextets in the most thermally altered samples, a nanophase ferric oxide and/or paramagnetic Fe$^{3+}$ doublet that increases in strength at the finer fractions of all samples, and ferrous doublets resulting from olivine, pyroxene, and/or glass that appear strongest and most prominent in the coarsest fractions of the less thermally altered samples; (3) water analysis and particle size distribution data that indicate that the samples closest to the heat source were substantially "baked" and rendered most susceptible to comminution; and (4) magnetic measurements that indicate that the samples closest to the heat source contain a highly magnetic component in their coarse size fractions.

Palagonitic materials similar to those that make up the finest fractions of our least thermally altered samples have been shown by many workers to be good Mars visible to near-IR spectral analogs [1-4]. We have found that the thermally altered palagonitic samples studied here are even better spectral analogs to Mars, in that they exhibit absorption features indicative of both poorly crystalline phases as well as crystalline ferric oxides (similar to several new Mars telescopic spectra [5,6]). Figures A and B show direct comparisons between previously published VIS-NIR Mars spectra and reflectance spectra of our thermally altered palagonitic tephra samples. Evidence for crystalline iron oxides (most likely hematite) in these spectra include the 0.6-0.7 μm absorption "shoulder" caused by the $^6A_1 \rightarrow ^4T_2$($^4G$) Fe$^{3+}$ electronic transition and the weak 0.80-0.95 μm absorption band caused by the $^6A_1 \rightarrow ^4T_1$($^4G$) Fe$^{3+}$ electronic transition [7-9,13]. Evidence for poorly-crystalline or even amorphous ferric-bearing phases is primarily from the relatively smooth near-UV O$^{2-} \rightarrow$Fe$^{3+}$ charge-transfer absorption edge, which is much less intense than in pure ferric oxides, especially in the 0.4-0.5 μm region [4,7-9].

Crystalline iron oxides are such strong pigmentation agents that only minor amounts are needed to completely dominate the VIS-NIR spectral behavior of rocks and soils. Morris et al. [10] were able to match a Mars bright region spectrum [11] using a mixture containing only 4.7 wt.% hematite powder. These authors also showed that mixtures of bulk and nanophase hematite that contained more than about 6-9 wt% bulk hematite show crystalline absorption features (including a much more intense near-UV O$^{2-} \rightarrow$Fe$^{3+}$ charge-transfer absorption edge) that are stronger than those seen in the Mars spectrum [10; figure 13]. These results are consistent with earlier mixing results using iron oxides and unoxidized basalts [12]. Clearly, while crystalline iron oxides are present on Mars, they appear to be a volumetrically minor constituent relative to the more poorly crystalline component.

How are the poorly crystalline components of the martian soil and dust formed? Four principal environments for the production of poorly crystalline palagonite-like materials on Mars by the weathering or alteration of primary igneous rocks have been proposed: hydrothermal alteration induced by impact, volcanism, or geothermal gradients; sub-permafrost magmatic intrusion; sub-aerial intrusion above the permafrost layer; and static gas-solid weathering [see review and references in 14]. The relative importance of each of these mechanisms in altering the composition and mineralogy of martian surface materials is determined by a number of factors, including the contemporaneous state of the martian climate and hydrosphere, and the amount of time that the process operates.
The short-timescale, spatially restricted heat pulse that thermally altered the tephra samples discussed above may be a terrestrial analog to similar processes that occur on Mars involving lava flows, dikes, or small impact craters and their interactions with unaltered volcanic tephra. In either wet or relatively dry environments such an influx of heat and energy will result in the alteration of more poorly ordered phases to more crystalline ones. This process provides a way to generate the crystalline hematite recently discovered spectroscopically on Mars [9,10] and possibly other ferric oxides, however it is not unique.

Such small-scale heating events may provide the dominant mechanism for the production of crystalline ferric oxides and/or less crystalline palagonite-like phases globally. Calculations of the amount of impact melt created globally on Mars are relevant, since small and medium-sized impacts are short-timescale heating events in many ways similar to the thermal alteration event discussed above [14]. Various models and scaling laws have been used to predict an impact-derived global melt thickness ranging from 6 to 60 m [15-16]. Although there are large uncertainties, it is clear that even small impact events produce melt and, thus, by inference, could thermally alter substantial amounts of local, unmelted material. A more quantitative estimate of the global amount of thermally altered material requires assumptions about the surface and subsurface water content, the temperature of intrusive plutons and impact melt sheets, and the composition of the martian crust. Other recent calculations have predicted a total volume of martian plutonic magma of more than 4 times the extrusive volume [17]. This implies that subterranean magmatic intrusion could be more volumetrically important for the alteration of crustal materials on Mars than subaerial processes. This further emphasizes the importance of model parameters which have not been directly measured in estimating the abundances of poorly- vs. well-crystalline materials in the martian crust.

Figures A and B: Comparisons between previously published VIS-NIR Mars spectra and reflectance spectra of our thermally altered palagonitic tephra samples. See [9,14] for telescopic data references.