REFLECTIVITY SPECTRA OF SULFATE ALTERATION PRODUCTS OF VOLCANIC TEPHRA FROM THE SUMMIT OF MAUNA KEA VOLCANO: IMPLICATION FOR MARTIAN SULFATE MINERALOGY, R. V. Morris[1], D. C. Golden[2], D. W. Ming[1], and D. R. Thompson[1]; [1]NASA Johnson Space Center, Houston, TX 77058, [2]Dual Inc., Houston TX 77058.

Summary. We report XRD and reflectivity data for samples of tephra from the summit cones of Mauna Kea Volcano that have been oxidatively altered to the hydoxysulfate minerals alunite and jarosite, presumably by hot, sulfur-bearing magmatic gas and/or fluids percolating up through the cinder cone. This process could also occur on Mars, where the heat source could be impact processes in addition to volcanic processes. It is possible that the ~900 nm band observed in certain Martian spectral data results from jarosites and is evidence for these processes.

Introduction. An important basis for mineralogical assignment of visible and near-IR spectral features observed in Martian spectral data is analysis of terrestrial analogue samples where the mineralogy of iron-bearing phases could be determined. Samples that contain palagonite (alteration product of basaltic glass) have received much attention, in part because many palagonitic samples are reasonable Martian spectral analogues and in part because processes favorable to palagonite formation are considered to be active on Mars, both now and in times past. Samples of palagonitic tephra collected from the same site on the Puu Nee cinder cone, Hawaii, are among the best spectral analogues and have been studied in detail (e.g., sample PN-9 of [1]). Collectively, these studies show that the visible absorption edge in Martian spectral data results predominantly from Fe^{3+} present as nanophase ferric oxide particles embedded in a spectrally-neutral matrix material. In addition, subordinate amounts of well-crystalline hematite are also indicated for Martian bright regions where hematite spectral features at ~860, 750, 620 and 520 nm are present [1,2,3].

Because Martian surface fines contain ~7% SO_3 [4], sulfur-bearing phases may be optically-important components of Martian surface materials at visible and near-IR wavelengths if they also contain iron. Spectral analogues like PN-9 do not contain sulfur-bearing mineralogies [Morris et al., 1993]. We report here reflectivity and X ray diffraction XRD data for tephra samples from the summit cones of Mauna Kea Volcano, Hawaii, that have been oxidatively altered to sulfate-bearing phases.

Samples and Methods. Tephra samples HWMK504, HWMK507, HWMK508, and HWMK515 were collected as <1 mm sieve fractions from a ~8 m vertical section formed during excavation for the foundation of the Gemini telescope on the second-highest summit cone of Mauna Kea Volcano in September, 1995. To concentrate alteration products, the samples were fractionated in the laboratory to obtain the <5 μm size fraction by ultrasonic dispersion and water sedimentation; all data reported here are for this separate. In the sample order listed above, the separates are red, yellow, white, and green in color.

Diffuse reflectivity spectra (350 - 2100 nm) were obtained on a Cary-14 spectrophotometer configured with an integrating sphere. Powder X ray diffraction patterns of oriented samples were obtained on a Scintag XDS200 diffractometer using CuKα radiation.

Results and Discussion. Based on XRD peak heights, HWMK504, HWMK507, and HWMK515 are >90% jarosite, a ferric hydoxysulfate mineral having the general composition $(H_3O,Na,K)Fe_3(SO_4)_2(OH)_6$. In addition, the red sample HWMK504 contains a minor amount (<5%) of hematite (α-Fe_2O_3). Sample HWMK508 is >90% alunite, an aluminous hydroxysulfate mineral having the general composition $(H_3O,Na,K)Al_3(SO_4)_2(OH)_6$. No evidence for the presence of phyllosilicates was indicated by the XRD data. As discussed by [5,6], HWMK515 appears to be titanium-substituted jarosite (Na > K).

Reflectivity spectra for the four jarositic samples are shown in Figure 1. Also shown for comparison is the spectrum of the <5 μm size fraction of HWMK24 (yellow colored), which was collected at another summit cone on Mauna Kea and is also >90% jarosite (K > Na) [7]. At most, four band minima are present. The two at 430 and 870-920 nm result from the ${}^6A_1$ to $({}^4E,{}^4A)$ and ${}^6A_1$ to ${}^4T_{1g}$ electronic transitions of ferric iron, and the two at 1480 and 1840 nm result from vibrations involving the FeOH and OH groups. The spectrum of HWMK508 does not have these bands (and is thus white) because the alunite apparently has very little Fe^{3+} substituted for Al^{3+}. The spectra of HWMK508 (alunite) and HWMK24 and HWMK507 (jarosites) are consistent with previously published spectra of those mineralogies [e.g., 8,9] except that the vibrational bands are weaker or not apparent in our spectra.

The spectra of HWMK515 (green) and especially HWMK504 (red) are distinctly different from those of "normal" jarosite. The band minimum which occurs at 910 nm in normal jarosite is near 920 nm in HWMK515. Reflectivity is also higher in the region around 500 nm, and this is responsible for its characteristic green color. Because HWMK515 is a Ti-bearing jarosite [5], it is possible that these differences result from Ti substitution in the jarosite structure. For HWMK504, the band minimum is near 870 nm and a significant change in slope occurs near 550 nm. Both of these features are consistent with the presence of hematite [e.g., 10], which is observed in the XRD data.

Implications for Martian Spectral Data. As discussed by [11] for an alunite occurrence on Mauna Kea, a possible formation process for alunite and jarosites in our samples is alteration of pre-existing tephra by hot, sulfur-bearing magmatic gas and/or fluids percolating up through the cinder cone. This process could also occur on Mars, as previously advocated by [12,13], where the heat source could be impact processes in addition to volcanic processes. It is possible that the ~900 nm band observed in certain Martian spectral data [14] results from jarosites and is evidence for these processes. Sample HWMK504 demonstrates that regions of the Martian surface that show spectral evidence for hematite (a ~870 band minimum) can in fact have jarosite as the major iron-bearing mineralogy.

References: [1] Morris R. V. et al. (1993) *GCA, 57,* 4597-4609; [2] Bell III J. F. et al. (1993) *JGR, 98,* 3373-3385; [3] Morris R. V. and Lauer Jr. H. V. (1990) *JGR, 95,* 5101-5109; [4] Clark B. C. et al. (1982) *JGR, 87,* 10059-10067; [5] Golden et al., this volume; [6] Ming et al., this volume; [7] Morris et al., submitted, 1996; [8] Hunt G. R. and Ashley R. P. (1979) *Econ. Geol, 74,* 1613-1629; [9] Clark R. N. et al. (1990) *JGR, 95,* 12653-12680; [10] Morris et al (1985) *JGR, 90,* 3126-3144; [11] Wolfe E. W. (1996) USGS Professional Paper on Mauna Kea, in press; [12] Burns R. G. (1988) *PLPSC18,* 713-721; [13] Burns R. G. (1993) *GCA, 57,* 4555-4574; [14] Murchie S. et al. (1993) *Icarus, 105,* 454-468.