MINERALOGICAL AND THERMAL PROPERTIES OF JAROSITIC TEPHRA ON MAUNA KEA, HAWAII: IMPLICATIONS FOR THE SULFUR MINERALOGY ON MARS, D. W. Ming1, D. C. Golden2, J. L. Gooding1, R. V. Morris1, D. R. Thompson1, and J. F. Bell, III3; 1SN4, NASA Johnson Space Center, Houston, TX 77058, 2Dual Inc., Houston, TX 77058, and 3Cornell University, Ithaca, NY 14853.

Summary. Jarosite, a ferric hydroxysulfate, occurs in some tephra samples on Mauna Kea volcano in Hawaii. The mineralogy and thermal properties of two jarositic tephra samples were characterized by X-ray diffraction (XRD) analysis and differential scanning calorimetry (DSC). XRD analysis of the <5 μm fraction of the tephra indicated nearly monomineralic jarosite in both samples. DSC signatures indicated two strong endoenthalpic transitions for jarosite at near 670 and 950 K, which represent dehydroxylation and ferric sulfate decomposition of jarosite, respectively. If jarosite exists on the surface of Mars, it should be easy to identify with DSC interfaced to an evolved-gas analyzer during a robotic mission (e.g., Mars Surveyor Program).

Introduction. Samples of volcanic tephra from Mauna Kea, Hawaii provide important chemical and mineralogical information on the surface of Mars because some are good spectral analogues for the Martian bright regions. The surface materials on Mars contain ≈7 wt. % SO3 [1], therefore, sulfur-bearing phases (e.g., sulfides, sulfates) must be chemically important components at the surface. Burns [2] and Burns and Fisher [3] have argued that jarosite may precipitate under Martian surface conditions. Recently, Morris et al. [4] have shown that sulfur-rich tephra sample HWMK24 on Mauna Kea is nearly monomineralic jarosite and that the occurrence of band minima near 910 nm in spectral data for certain Martian regions might indicate the presence of hydronium jarosite.

The objectives of this paper were to i) characterize the mineralogy of several jarosite-rich tephra at the summit of Mauna Kea and ii) to characterize the thermal properties of jarosite in these samples. Throughout this paper, the term jarosite will refer to the general composition (H2O,Na,K)Fe3(SO4)2(OH)6; however, the K-, H2O-, and Na-endmembers are jarosite, hydronium jarosite, and natrojarosite, respectively.

Samples. Two tephra samples that contained jarosite were sampled from the summit of Mauna Kea, Hawaii. Sample HWMK24 is the <1 mm sieve fraction of yellow-colored tephra collected from a road cut on the northwest flank of the unnamed summit cone where the Japan National Subaru Telescope is located. Sample HWMK515 is the <1 mm sieve fraction of light green-colored tephra collected from an exposed surface during the construction of the Gemini Telescope.

Figure 1. XRD patterns for jarosite-containing samples. All d-spacings are in nm. All peaks in HWMK515 are for natrojarosite. All peaks in HWMK24 are for jarosite, except for those labeled F where F = plagioclase feldspar.
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Methods. X-ray diffraction (XRD) mineralogy was determined on powdered samples (<5 μm size fraction) by using a Scintag XDS 2000 X-ray diffractometer with monochromatic CuKα radiation. Differential scanning calorimetry (DSC) was used to characterize thermal properties of tephra. Accurately-weighed samples (< 5 μm size fraction) were heated at 10 K/min in a Perkin-Elmer DSC-2C using 20 cm³/min purge of nitrogen.

Mineralogy. Jarosite (or natrojarosite) was identified in both tephra samples (Figure 1). Jarosite (K-rich as indicated by SEM EDS) and plagioclase feldspar (Ca-rich) have been identified in a bulk sample (< 1 mm) of HWMK24 [4]. The <5 μm fraction of HWMK24 was nearly monomineralic jarosite (see Fig. 1). The primary XRD d-spacings used to identify jarosite were 0.591 nm (101), 0.504 nm (003), 0.311 nm (021), 0.197 nm (033), and 0.183 nm (220) peaks. The diffraction pattern of jarosite in sample HWMK24 consists of sharp, narrow diffraction peaks, suggesting a high degree of crystallinity, which has been supported by SEM morphological analysis [4]. Jarosite in HWMK24 has XRD d-spacing very similar to a K-rich jarosite from near Grant County, NM [4].

Sample HWMK515 was nearly monomineralic natrojarosite. Chemical analysis of the sample indicated a Na-rich phase with minor amounts of K present [5]. Primary peaks used to identify natrojarosite were 0.500 nm (012), 0.310 nm (021), and 0.304 nm (113) peaks. The natrojarosite occurrence in sample HWMK515 is very similar to another occurrence near Luning, NV [4].

Thermal Properties. The DSC signatures for the two jarosite-containing samples are compared in Figure 2. The strong endothermic transition near 690 K marks the dehydroxylation of the ferric-OH bonds in jarosite and the evolution of water (e.g., 2KFe₃(SO₄)₂(OH)₄ → K₂SO₄ + Fe₂(SO₄)₃ + 2FeO + 3H₂O). Dehydroxylation reactions occurred at 684 and 695 K for samples HWMK24 and HWMK515, respectively. A second major endothermic transition near 950 K represents the breakdown of sulfate in jarosite. During this transformation, K₂SO₄ and Na₂SO₄ and Fe₂O₃ form as SO₃ is evolved (e.g., K₂SO₄ + Fe₂(SO₄)₃ → K₂SO₄ + Fe₂O₃ + 3SO₃ + 3/2O₂). The breakdown of sulfate occurred at 953 K for HWMK24, whereas, sample HWMK515 had a strong endothermic transition at 967 K. The higher endothermic transition temperature in HWMK515 may be due in part to a higher Ti content in the structure [6].

Relevance for Mars. The XRD data show that jarosite occurs as the sulfur-bearing, oxidative alteration product in some Mauna Kea tephra. Jarosite forms primarily in acid-sulfate weathering environments on Earth [7] and several researchers have suggested that an acid-weathering environment may exist on the surface of Mars (e.g., [8]). If jarosite exists on the surface of Mars, it should be easy to identify with DSC linked to an evolved-gas analyzer during a robotic mission (e.g., Mars Surveyor Program).