GOSSANS ON MARS: SPECTRAL FEATURES ATTRIBUTED TO JAROSITE.

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Summary. Jarosites, $(K^+,Na^+,H_3O^+)(Fe^{3+},Al^{3+})_3(SO_4)_2(OH)_6$, which are present in terrestrial gossans capping oxidized sulfides associated with mafic igneous rocks, may also be present in martian regolith. Spectral characteristics of jarosites, attributed to Fe^{3+} in the visible region and to water or hydroxyl groups in the infrared region, are also displayed in remote-sensed reflectance spectra of bright regions of Mars' surface. The occurrence of jarosite in the regolith would imply that acidic permafrost and sulfide ores exist beneath the surface of Mars.

Introduction. The Viking XRF experiment detected high sulfur and iron contents in the martian fines [1]. These elements are believed to exist as oxidized SO_4^{2-} and Fe^{3+} species, respectively [2]. Although the majority of ferric iron on Mars is probably derived from chemical weathering of ferromagnesian silicates, some Fe^{3+} may have originated from oxidation of iron sulfides present as accessory minerals in iron-rich basalts or as massive pyrrhotite ores associated with ultramafic igneous rocks. Several hydroxo ferric sulfate minerals could be stabilized at low temperature and pH conditions in martian permafrost [3]. However, as a constituent of martian regolith, jarosite is the prime candidate because in arid regions on Earth it is associated with mixtures of poorly crystalline ferric oxides ("limonite") and silica (jasper) found in gossans. Spectral features summarized here of assemblages containing jarosites and poorly crystalline FeOOH plus silica or clay silicates match closely profiles measured in remote-sensed reflectance spectra of Mars.

Spectra. Reflectance spectra of ubiquitous bright dust and soil on Mars in the near UV-visible region are highly diagnostic of ferric iron [4]. Distinguishing features include a slope change at 0.5-0.6 µm and a broad band centered at 0.8-0.9 µm. A variety of candidate ferric-bearing phases have been suggested [4,5], and it is generally agreed that Fe^{3+} occurs in amorphous or poorly crystalline hydrated ferric oxide-silica gel and clay silicate phases. However, jarosite has similar spectral features in the UV-visible region [6]. In the near infrared, spectral features between 1.4-1.7 µm, around 2.3-2.4 µm, and at 2.9 µm have been assigned to H_2O and OH^- in phyllosilicates. Again, jarosite spectra possess similar features [7]. In addition, the mid-infrared feature near 9 µm observed in suspended martian dust [2] also occurs in spectra of jarosites.

Formation of Jarosite. Near-surface oxidation of sulfides on Earth proceeds by electrochemical processes involving oxygenated groundwater and dissolved Fe^{3+} ions [8,9]. Primary pyrrhotite in mafic igneous rocks is oxidized by Fe^{3+} to secondary pyrite well below the water table ($Fe_7S_8 + 6Fe^{3+} = 4FeS_2 + 9Fe^{2+}$). Nearer the water table, oxidation of pyrite occurs ($4FeS_2 + 2H_2O + 15O_2 = 4Fe^{3+} + 8SO_4^{2-} + 4H^+$), leading to dissolved Fe^{2+}, Fe^{3+}, and SO_4^{2-} in acidic groundwater, in which complex ferric ions predominate (e.g. $FeSO_4^+$, $FeOH^{2+}$, etc.). Monodispersed sols of hydronium jarosite (carphosiderite) may form by reactions involving these complex ions ($2FeSO_4^+ + FeOH^{2+} + 6H_2O = (H_3O^+)Fe_3(SO_4)_2(OH)_6 + 4H^+$), or by direct oxidation of dissolved Fe^{2+} ($6Fe^{2+} + 4SO_4^{2-} + 11H_2O + 3/2\ O_2 = 2(H_3O^+)Fe_3(SO_4)_2(OH)_6 + 4H^+$). In the presence of alkali metal cations and Al derived from chemically weathered feldspars in basalt, extremely insoluble jarosites are precipitated. Stability relationships [10] indicate that jarosite compositions as sodic and aluminous as $(K_{0.5}Na_{0.5})(Fe_{0.5}Al_{0.5})_3(SO_4)_2(OH)_6$ are stable at pH 5 and $298\,^{\circ}K$. Below the freezing point of water, they might be stable to pH 6 and form near permafrost on Mars.

Applications to Mars. Independent evidence for the occurrence of jarosite on Mars stems from its suggested presence in shergottite and nakhlite meteorites [11,12]. The existence of jarosites on Mars provides important clues about the inventory of volatiles, degassing of the mantle, evolution of the atmosphere, and acidity of groundwater and permafrost there [2,3,9]. The presence of jarosite in the highly colored gossan-like regolith might also indicate that massive sulphide ore deposits occur beneath the permafrost of Mars [13].

References.

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