

Understanding the sulfates on mars from surface exploration, orbital remote sensing and laboratory experiments

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Sulfur enrichment has been found in martian surface materials therein all landed missions to date, including Viking 1 and 2, Mars Pathfinder, and the Mars Exploration Rovers. During surface exploration by both Spirit and Opportunity at Gusev Crater and Meridiani Planum, respectively, the correlations between sulfur and other elements in rocks and soils have been found that indicate the existence of Mg-, Ca-, and Fe-sulfates. A ferric sulfate, jarosite, was identified in the Mössbauer spectra (MB) obtained by Opportunity from the outcrop exposed in craters and at the surface of Meridiani Planum; the MiniTES spectral signature of sulfate has also been observed there.

Mixing-model analyses based on APXS data of S-rich targets at both landing sites, coupled with mineralogical and $\text{Fe}^{3+}/\text{Fe}_{total}$ constraints from MB analyses indicate the presence of Mg-, Ca-, and Fe-sulfate. The dominant sulfate types, however, differ at different locations. In the subsurface regolith exposed by two trenches dug by Spirit in the basaltic Gusev Plains, Mg-sulfate dominates by ~ 85 mole% in the total sulfate deposits that make up to ~ 22 wt% in *The Boroughs* trench regolith. Mg-sulfate is also the major sulfate mineral found in the rock *Peace* (up to ~ 21 wt%) on the *Columbia Hills*. Ca-sulfate makes up ~ 75 mole% of the sulfate minerals found in the rocks of the *West Spur* area at the foot of the *Columbia Hills*, where the highest sulfate content was ~ 11 wt%. Fe^{3+} -sulfate is the major constituent of sulfate deposits found in two patches of regolith at Gusev: the one on the *Columbia Hills (Paso Robles)* has a sulfate content up to ~ 47 wt%, the percentage in *Arad* at the *South Inner Basin* is even higher. At Meridiani Planum, the maximum S concentration measured thus far is ~ 27 wt% as SO_3 in the abraded rock *Gagarin*. Typically, the sulfates make up ~ 40 wt% of the Meridiani outcrop materials, including >60 mole% as Mg-sulfate, ~ 20 -30 mole% as Ca-sulfate, and ~ 10 mole% as Jarosite.

Mg-, Fe, and Ca-sulfates are important components of the martian surface and subsurface materials. Their compositional features and regional distribution are closely bound to local geological and geochemical processes. Furthermore, their structural character (e.g. crystallinity) and especially their hydration states could be crucial

indicators for short-term and long-term hydrologic evolution on Mars. The specific mineralogy and hydration states are also significant in martian H₂O and S cycles, and play key roles in the potential for habitability. Among the nine hydrous Mg-sulfates, the two hydrous Ca-sulfates, and many hydrous Fe-sulfates, orbital remote sensing (OMEGA on Mars Express) has identified kieserite (MgSO₄·H₂O), gypsum (CaSO₄·2H₂O), and bassanite (CaSO₄·0.5H₂O), along with NIR spectral features that match with epsomite (MgSO₄·7H₂O), copiapite (Fe²⁺Fe₄³⁺(SO₄)₆(OH)₂·20H₂O), or halotrichite (FeAl₂(SO₄)₄·22H₂O). The gamma-ray spectrometer on Mars Odyssey has also identified high concentrations of water-equivalent-hydrogen (WEH) in two large equatorial regions, and has provided strong evidence for the residence of water-bearing minerals in near-surface regolith.

Laboratory experiments under well-controlled conditions provide a fundamental understanding for linking the surface and orbital observations, as well as to address possible reasons for observational discrepancies (e.g., water contents). We are investigating the stability fields and reaction pathways for the hydrous Mg-sulfates under controlled humidity and temperature conditions, and we are using Raman and infrared spectroscopy, and X-ray diffraction to identify the various hydrated species generated in the experiments. Results to date indicate that Mg-sulfates with hydration states higher than kieserite (MgSO₄·H₂O), especially starkeyite (MgSO₄·4H₂O), could be stable under current martian surface conditions at mid-low latitudes.