Transformations of Mg- and Ca-sulfate hydrates in Mars regolith

DAVID T. VANIMAN* AND STEVE J. CHIPERA

Earth and Environmental Sciences Division, Los Alamos National Laboratory, MS D462, Los Alamos, New Mexico 87545, U.S.A.

ABSTRACT

Salt hydrates have an active role in regolith development on Mars. The Mg-sulfate system, with highly variable values of \( n \) in the formula \( \text{MgSO}_4 \cdot n\text{H}_2\text{O} \), is particularly subject to transformations among several crystalline and amorphous forms. The Ca-sulfate system, \( \text{CaSO}_4 \cdot n\text{H}_2\text{O} \), is likely to be associated with the Mg-sulfates in most occurrences, but is less susceptible to transformations in \( n \). Desiccation of \( \text{MgSO}_4 \cdot n\text{H}_2\text{O} \) occurs in exposed soils at the martian equator in summer where higher daytime temperatures at low relative humidity prevail against sluggish nighttime rehydration at high relative humidity. Desiccation and rehydration are both accelerated in the finest size fractions, particularly in silt-size aeolian particles subject to global redistribution by dust storms. This redistribution and periodic excursions into long-term episodes of high obliquity work to rehydrate desiccated \( \text{MgSO}_4 \cdot n\text{H}_2\text{O} \) to form epsomite, \( \text{MgSO}_4 \cdot 7\text{H}_2\text{O} \), at higher latitudes in the first case and more globally in the latter. Kieserite, a monohydrate form of \( \text{MgSO}_4 \cdot n\text{H}_2\text{O} \) resistant to desiccation, can survive equatorial summer conditions, but not protracted high relative humidity; preservation of kieserite at the surface may place limits on the equatorial distribution of ice during past episodes of high obliquity. Deeper horizons in equatorial regolith may preserve hydrated phases through repeated obliquity episodes, raising the possibility of an ancient regolith archive of past hydration. At shallower depths in the regolith, in situ determination of the hydration states of the Mg-sulfates, and possibly the Ca-sulfates, may be used to constrain regolith dynamics if rates and modes of transitions in \( n \) can be fully characterized.

Keywords: Lunar and planetary studies, crystal growth, phase transition, kinetics

INTRODUCTION

With the Viking landings in 1976, the first chemical analyses of martian soil from near-equatorial and higher latitudes showed that sulfate species are common in the martian near surface (e.g., Toulmin et al. 1977; Clark 1993). The three subsequent landers—Pathfinder in 1997 and the two 2004 Mars Exploration Rovers (MER), Spirit and Opportunity—all found similar occurrences of soil sulfates at widespread locations (Larsen et al. 2000; Rieder et al. 2004). The case for widespread sulfates has been strengthened from orbit with recent visible-near infrared (VIS-NIR) spectral data from the Mars Express OMEGA spectrometer (e.g., Bonello et al. 2005; Langevin et al. 2005). The evidence for Mg-sulfate and Ca-sulfate salt hydrates is now particularly strong, supported by a robust and diverse data set of alpha-proton X-ray Spectroscopy (APXS) data plus thermal emission spectroscopy (THEMIS and TES) data (e.g., Clark et al. 2005; Lane 2005; Squyres et al. 2004). Evidence is also accumulating for the presence of \( \text{Fe}^{3+} \)-sulfate salt hydrates (Lane et al. 2004), and the hydroxylated \( \text{Fe}^{3+} \)-sulfate mineral jarosite has been identified specifically by Mössbauer data from the MER rover Opportunity (Klingelhöfer et al. 2004), but the available data indicate that Mg- and Ca-sulfates have more widespread distribution among soils on Mars.

Clark and coworkers (Clark 1978; Clark and Van Hart 1981) have considered the implications of salty martian regolith and evaluated salt abundances. In least-squares analyses of Viking and Pathfinder data, they used a postulated salt component based on a mixture of the Mg-sulfate mineral kieserite (\( \text{MgSO}_4 \cdot \text{H}_2\text{O} \)), with a much smaller amount of halite plus sylvite to account for measured chloride (Larsen et al. 2000). This approach yielded chemical soil models for Pathfinder and Viking 1 with weight proportions of 10.0% \( \text{MgSO}_4 \) (anhydrous basis) in average Pathfinder soil and 13.7% at Viking 1. As in previous work (e.g., Baird et al. 1976), they noted that shallow duricrust at Viking 1 is enriched in this sulfate component relative to uncemented soil. In these and similar studies, the correlation between Mg and S in regolith chemical analyses consistently implicates some form of \( \text{MgSO}_4 \cdot \text{nH}_2\text{O} \).

In addition to the Mg-sulfates, there is strong evidence from martian meteorites, rover chemical analyses, and orbital spectroscopy for the presence of Ca-sulfates. Studies of many martian meteorites have found \( \text{CaSO}_4 \cdot n\text{H}_2\text{O} \) as a component in fracture fillings that formed on Mars (Bridges et al. 2001; Gooding et al. 1991). Most compelling are the recent APXS data from the MER rover Opportunity indicating an association of Ca-sulfate with Mg-sulfate in the sedimentary outcrops of Meridiani Plenum (Clark et al. 2005) and the UV-VIS data from the OMEGA spectrometer on Mars Express. The OMEGA data have revealed widespread gypsum in surface soils at high latitude (Langevin et al. 2005) and gypsum plus hydrated Mg-sulfates and possible Fe-bearing sulfates in layered terrain at Valles Marineris,