

MINERALOGY, ABUNDANCE, AND HYDRATION STATE OF SULFATES AND CHLORIDES AT THE MARS PATHFINDER LANDING SITE. M. Yu. Zolotov¹, R. O. Kuzmin², and E. L. Shock^{1,3}, ¹Department of Geological Sciences, Arizona State University, Tempe, AZ 85287, ²Vernadsky Institute of Geochemistry and Analytical Chemistry, Russian Academy of Sciences, 19 Kosygin str., Moscow 119991, Russia. ³Department of Chemistry and Biochemistry, Arizona State University, Tempe, AZ 85287. E-mail: zolotov@asu.edu.

Introduction: Detection of elevated concentrations of S and Cl at the landing sites of Viking 1 and 2 [1], and Mars Pathfinder (MP) [2-5] reveals the presence of sulfates and chlorides in soil and rock samples [1-10]. These data are consistent with the findings of Ca sulfates and NaCl in Martian meteorites [11,12], and with Earth-based spectroscopic observations [13,14] tentatively indicating the presence of sulfates on Mars. Although the correlation of S and Mg in Viking and MP samples could reveal the occurrence of Mg sulfate [1-10], the mineralogy of sulfates and chlorides remains unclear.

The hydration state of surface sulfates and chlorides is also unknown, which makes a long list of salts possible, as shown in Table 1. Taking into account likely aqueous origins of sulfates and chlorides [e.g., 7,15,16], periodic (seasonal and daily) presence of water ice condensates at a significant part of the surface, and recycling of mineral dust through polar regions could account for hydration of salts, at least at high latitudes and at depth [17]. Hydration of surface salts, which could account for up to 15-25 vol. % in Viking soils [7], could partially account for bound water in the regolith. In fact, from 0.5 wt. % to 4 wt. % of bound water is present in the soil based on ground [e.g., 13,18,19], Hubble Space Telescope [20], Mariner 6 [21-23] and Phobos 2 [24] spacecraft spectroscopic data in the near-infrared (3 μ m), Mars Odyssey neutron spectroscopy [25], a Viking biological experiment [26], APXS analyses of soils and rocks at the MP landing site (based on "excess" oxygen) [4], and the clear absorption of bound water (6.1 μ m) at the landing site of Spirit rover (Mini-TES data) [27]. Both hydrated silicates (e.g., zeolites, clays) and salts (sulfates, carbonates, chlorides) could be host minerals for Martian bound water.

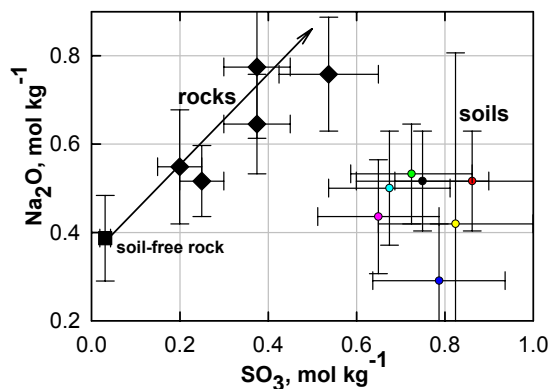
Table 1. Sulfates and chlorides that could be abundant on the Martian surface

<i>Magnesium sulfates:</i> MgSO_4 , $\text{MgSO}_4 \cdot \text{H}_2\text{O}$ (kieserite), $\text{MgSO}_4 \cdot 5\text{H}_2\text{O}$, $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ (epsomite)
<i>Sodium sulfates:</i> Na_2SO_4 (thenardite), $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ (mirabilite), $\text{Na}_2\text{Mg}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ (bloedite)
<i>Magnesium chlorides:</i> $\text{MgCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{MgCl}_2 \cdot 4\text{H}_2\text{O}$, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (bischofite)
<i>Sodium chlorides:</i> NaCl , $\text{NaCl} \cdot \text{H}_2\text{O}$ (hydrohalite)

Here we evaluate the mineralogy of sulfates and chlorides in rock and soil samples based on APXS analyses at the MP landing site [2-5]. This work is aimed to complement earlier investigations [2,3,4,5,8,9,10] that reveal the abundant occurrence of Mg sulfate mixed with mainly silicate components of soil and rocks. We also analyze the hydration state of salts equilibrated with atmospheric $\text{H}_2\text{O}(\text{g})$ at the temperatures of the MP landing site.

Salt mineralogy: We examined correlations and performed balance calculations in the $\text{SO}_3\text{-Cl-MgO-Na}_2\text{O-SiO}_2$ system based on recalibrated MP APXS chemical data for

Figure 1. Molar concentrations of Na_2O and SO_3 in MP samples [4]. The arrow represents the concentration trend caused by addition of Na_2SO_4 to the soil-free rock.



soils and rocks, and evaluated composition for the soil-free rock [4]. In contrast to Viking data for soils [1], MP data reveal significant excess of Mg relative to S for both rock and soil samples [10]. The average MgO/SO_3 mole ratio in rocks and soils of 2 to 2.5 indicate that more than half of the Mg atoms are not associated with sulfates. Only a minor amount of the "excess" Mg can be in MgCl_2 [10] and the rest of the Mg could be in carbonates such as magnesite [10, 28], hydromagnesite and artinite [22], as well as in secondary (e.g., saponite, serpentine) and fine-grained magmatic silicates (e.g., olivine). Therefore, the strong correlation of Mg and S could be caused by addition of Mg-bearing minerals together with non-Mg sulfates rather than exclusively by addition of MgSO_4 to fresh, soil-free rocks. The absence of positive Ca – S and K – S correlations in MP samples [3-5] indicates that sulfates of Ca and K are not abundant. A positive Fe – S correlation is not indicative for Fe sulfates [10]. However, Na_2O correlates with SO_3 in rock samples [4]. The linear fit of Na_2O and SO_3 molar ratios for rock samples gives a slope close to unity (Fig. 1). Similar molar amounts of Na_2O and SO_3 could reflect a predominance of Na_2SO_4 over MgSO_4 in rock samples. The possibility of an association between Na sulfates and weathering crusts of the rocks, as well as with soil and dust coatings on rocks is also illustrated in Fig. 2.

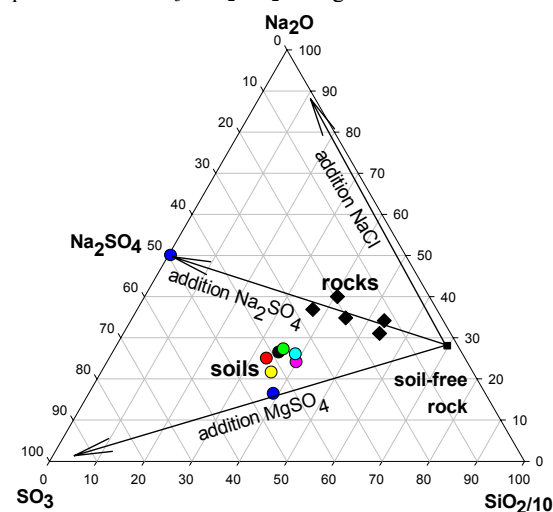
The possible presence of Na_2SO_4 in the secondary mineralogy also implies the association of S and Na in soil samples. However in soils, the $\text{Na}_2\text{O}/\text{SO}_3$ molar ratio is much lower than unity. This likely represents a predominance of Mg_2SO_4 over Na_2SO_4 in soils.

The lack of clear positive correlations of Ca and K with Cl in MP soils [4,8] suggest low abundances of corresponding chlorides and the association of Cl mostly with Na and Mg. Since molar amounts of Cl (M_{Cl}) are significantly less

than those for MgO (370-1100 % of M_{Cl}) and Na_2O (120-460 % of M_{Cl}), Cl could be present both in Na and Mg chlorides. We were unable to infer any meaningful correlations to reveal the association of Cl in MP samples. For example, the Na-Cl correlation in rock samples could be caused either by addition of NaCl or by additions of Na_2SO_4 and MgCl_2 .

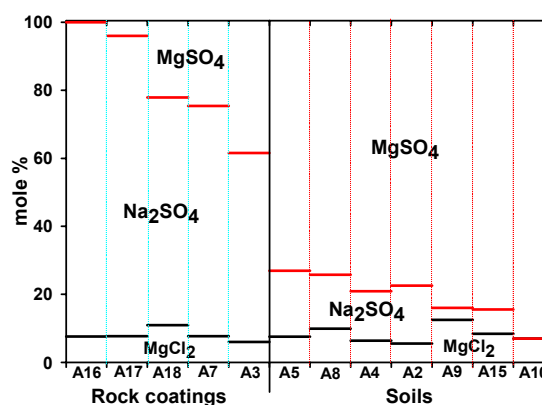
Amounts of sulfates and chlorides in MP samples were evaluated by subtracting the composition of soil-free rocks (for Na_2O we took 2.4 wt. %, see [3-5]) from H_2O -free APXS data [4] followed by calculations of normative mineralogy and the “excess” amount of Mg that cannot be bound with S and Cl. In our models, Cl was associated with either MgCl_2 or NaCl, Na was in Na_2SO_4 and NaCl, and Mg was in MgSO_4 and MgCl_2 . These mole balance calculations show that the association of Cl does not strongly affect calculated abundances of Na_2SO_4 and MgSO_4 . In our nominal model shown in Fig. 3, Cl is present as MgCl_2 . The normative model demonstrates high abundances of Na_2SO_4 in the weathering products and coatings and the predominance of MgSO_4 in soils. Since the presence of Na in the non-sulfate part of the secondary assemblage was not considered (except sample A16), calculated amounts of Na_2SO_4 give maximum concentrations.

Figure 2. MP soil and rock compositions (in molar ratios) plotted at the SO_3 - SiO_2 - Na_2O diagram.



Hydration state: We evaluated thermodynamic stabilities of potential salt hydrates from Table 1 at surface temperatures [29] and partial pressures (p) of atmospheric $\text{H}_2\text{O(g)}$ [30] at the latitude of the MP landing site (19.3°N) throughout the Martian year. At the average values for annual temperature and $p\text{H}_2\text{O}$, $\text{MgSO}_4\cdot\text{H}_2\text{O}$, Na_2SO_4 and $\text{MgCl}_2\cdot 6\text{H}_2\text{O}$ are stable at the surface. In the summer seasons, $\text{MgSO}_4\cdot\text{H}_2\text{O}$, Na_2SO_4 and $\text{MgCl}_2\cdot\text{H}_2\text{O}$ are stable; and in the winter seasons, $\text{MgSO}_4\cdot 7\text{H}_2\text{O}$, Na_2SO_4 , $\text{MgCl}_2\cdot 2\text{H}_2\text{O}$ and $\text{MgCl}_2\cdot 6\text{H}_2\text{O}$ are stable. Because of inhibition of corresponding hydration-dehydration reactions at low-temperatures (except Na sulfates) [31], many of these salts could be present as metastable phases. At mean daily temperatures, $\text{Na}_2\text{SO}_4\cdot 10\text{H}_2\text{O}$ is stable in the winter season pole-ward of latitudes $\sim 30^\circ$. However during winter nights, $\text{Na}_2\text{SO}_4\cdot 10\text{H}_2\text{O}$ is stable at the MP landing site. If formed together

Figure 3. Relative mole amounts of sulfates and chlorides at the MP landing site. Hydration state of salts is not taken into account.



with the night ice condensate, mirabilite may dehydrate over the daytime. Throughout the year, kieserite, metastable epsomite in air-blown dust, and bischofite may contain much of the bound water associated with sulfates and chlorides. The stabilities of bloedite and hydrohalite remain to be explored. Note that the assemblage of stable hydrates is different at other latitudes [17] and elevations.

Summary: Secondary S is likely to be presented by Mg sulfate and Na sulfate, which is abundant in weathering crusts and rock coatings. Chlorine could be in Mg and/or Na chlorides. Magnesium sulfates and chlorides are likely to be hydrated, but Na sulfate and NaCl are probably anhydrous.

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