Stability of Mg-sulphate minerals in the presence of smectites: Possible mineralogical controls on H_2O and nutrient cycling on Mars

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Hydrated sulphate minerals, including kieserite ($MgSO_4{\cdot}H_2O$), gypsum ($CaSO_4{\cdot}2H_2O$), and bassanite ($CaSO_4{\cdot}{\sim}0.5H_2O$), have been detected on Mars (Gendrin et al., 2005; Wray et al., 2010), and polyhydrated Mg-sulphate minerals such as epsomite ($MgSO_4{\cdot}7H_2O$) and meridianite ($MgSO_4{\cdot}11H_2O$) may be common near the surface of the planet. Kieserite, gypsum, and bassanite have all been identified in close association with phyllosilicate minerals (most likely Fe-rich smectites such as nontronite) at the surface of Mars (Wiseman et al., 2008; Milliken et al., 2010; Roach et al., 2010; Wray et al., 2010). Layered sedimentary deposits at Gale Crater, the landing site for the Mars Science Laboratory mission, appear to contain polyhydrated Mg-sulphate minerals, kieserite, and Fe-rich smectite in close association (Milliken et al., 2010).

Because water ice is unstable on the surface at the low water-vapour pressures that dominate in near-equatorial regions of Mars (Paige, 1992; Feldman et al., 2004a), some or even much of the H_2O detected near the planet's surface is suspected to reside within the crystal structures of hydrated minerals like Ca- and Mg-sulphates, smectites, and zeolites (Clark, 1978; Bish et al., 2003; Feldman et al., 2004b; Vaniman et al., 2004). The hydration states of these minerals are strongly dependent on the temperature and relative humidity (RH) conditions to which they are exposed. Thus, considering the large diurnal variations in temperature and RH that have been detected at the martian surface (Savijärvi, 1995), hydrated minerals may have an effect on cycling and bioavailability of water on Mars (e.g., Bish et al., 2003; Vaniman et al., 2004; Wang et al., 2006, 2009, 2011; Vaniman and Chipera, 2006; Chipera and Vaniman, 2007; Chou and Seal, 2007; Steiger et al., 2011). Hydrated sulphate minerals and smectites have also been identified as potential targets for astrobiological exploration of Mars because of their potential to preserve organic biosignatures (Summons et al., 2011). Although (1) the behaviour of smectites and (2) the phase relationships amongst hydrated Mg-sulphate minerals have each been examined under various conditions of RH and temperature, the capacity for interaction and reaction between these RH-sensitive minerals has not been assessed in detail.

Using *in situ* experiments that employ powder X-ray diffraction (XRD), we demonstrate that cation-exchange reactions can occur rapidly in mixtures of hydrated Mg-sulphate minerals and smectite clays (Clay Minerals Society Source Clays SAz-1, Ca-montmorillonite, and SWy-1, Na-montmorillonite) under conditions of varying relative humidity (RH) similar to those that operate at or just beneath the martian surface (Wilson and Bish, 2011). These cation-exchange reactions can take place in the absence of free, liquid H_2O and appear to be mediated by the formation of thin films of water at relative humidities below the deliquescence humidity of $MgSO_4 \cdot xH_2O$. Cation exchange produces hydrated Ca-sulphates, gypsum and bassanite, via transfer of cations and H_2O between the smectite interlayer and grains of Mg-sulphate minerals. This process is accompanied by a readily detectable volume increase and can induce mass wasting.

A series of long-term *ex situ* experiments builds upon the results of our *in situ* studies to demonstrate that cation-exchange reactions occur within smectite-sulphate mixtures over a range of temperatures (-25˚C to +23˚C) and RH (7% to 100%) relevant to near-equatorial sites on Mars such as Gale Crater. Thus, hydrated Ca-sulphate minerals may be useful indicators of cycling of H_2O and nutrients within martian regolith and layered sedimentary deposits. Our results suggest that cycling of H_2O between the atmosphere and minerals within the martian regolith could have provided an unexpectedly accessible – and detectable – source of water and nutrients for putative martian micro-organisms.

Deliquescence of hydrated Mg-sulphate phases at high RH is suppressed in the presence of smectites. Rather than producing a slurry of $MgSO_4$ brine and H_2O-saturated smectite, H_2O is consumed during cation-exchange reactions by uptake into the smectite interlayer. Thus, smectite-rich mixtures of RH-sensitive minerals may restrict formation of brines on Mars. Co-existence of smectites and hydrated Mg-sulphate minerals appears to buffer RH within mineral mixtures, which can result in production and preservation of Mg-sulphate phases other than those expected from measured values of atmospheric RH. Dehydration of highly hydrated Mg-sulphate phases slows dramatically in the presence of smectite. For instance, starkeyite ($MgSO_4 \cdot 4H_2O$) is expected to be the most common dehydration product of epsomite ($MgSO_4 \cdot 7H_2O$) at low but non-freezing temperatures and RH values less than ~30%; however, epsomite and hexahydrite ($MgSO_4 \cdot 6H_2O$) persist for months within smectite–sulphate mixtures at T>0˚C and starkeyite is not observed. Epsomite and hexahydrite may be preserved on significantly longer timescales at T<0˚C as the rate of dehydration slows with decreasing temperature (e.g., Vaniman and Chipera, 2005; Wang et al., 2009, 2011). Preservation and detection of viable microbial cells and molecular biomarkers within epsomite crystals has been demonstrated previously (Foster et al., 2010). The ability of smectites to suppress deliquescence of Mg-sulphate minerals at high RH and to slow or limit Mg-sulphate phase transitions could support long-term preservation of biomarkers within pristine crystals of highly hydrated Mg-sulphate minerals.

The results of our *in situ* and *ex situ* XRD experiments suggest that the results of previous studies of mineral stability in the $MgSO_4$–H_2O system may be inadequate predictors of phase stability (and thus H_2O/nutrient cycling and biomarker preservation) within smectite-rich regolith and layered deposits.

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