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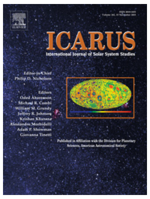

Amorphous salts formed from rapid dehydration of multicomponent chloride and ferric sulfate brines: Implications for Mars

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ABSTRACT

Salts with high hydration states have the potential to maintain high levels of relative humidity (RH) in the near subsurface of Mars, even at moderate temperatures. These conditions could promote deliquescence of lower hydrates of ferric sulfate, chlorides, and other salts. Previous work on deliquesced ferric sulfates has shown that when these materials undergo rapid dehydration, such as that which would occur upon exposure to present day Martian surface conditions, an amorphous phase forms. However, the fate of deliquesced halides or mixed ferric sulfate-bearing brines are presently unknown. Here we present results of rapid dehydration experiments on Ca–, Na–, Mg– and Fe–chloride brines and multicomponent ($Fe_2(SO_4)_3 \pm$ Ca, Na, Mg, Fe, Cl, HCO_3) brines at ~21 °C, and characterize the dehydration products using visible/near-infrared (VNIR) reflectance spectroscopy, mid-infrared attenuated total reflectance spectroscopy, and X-ray diffraction (XRD) analysis. We find that rapid dehydration of many multicomponent brines can form amorphous solids or solids with an amorphous component, and that the presence of other elements affects the persistence of the amorphous phase under RH fluctuations. Of the pure chloride brines, only Fe–chloride formed an amorphous solid. XRD patterns of the multicomponent amorphous salts show changes in position, shape, and magnitude of the characteristic diffuse scattering observed in all amorphous materials that could be used to help constrain the composition of the amorphous salt. Amorphous salts deliquesce at lower RH values compared to their crystalline counterparts, opening up the possibility of their role in potential deliquescence-related geologic phenomena such as recurring slope lineae (RSLs) or soil induration. This work suggests that a wide range of aqueous mixed salt solutions can lead to the formation of amorphous salts and are possible for Mars; detailed studies of the formation mechanisms, stability and transformation behaviors of amorphous salts are necessary to further constrain their contribution to Martian surface materials.

1. Introduction

Orbital and landed instruments at Mars have provided significant advances in our understanding of Martian surface materials, as well as a number of new questions and enigmatic observations. For example, the Mars Science Laboratory CheMin instrument (Bish et al., 2013), which contains an X-ray diffractometer, has detected X-ray amorphous (hereafter, "amorphous") materials in every soil and rock measurement thus far, with abundance estimates ranging from ~15–75 wt% (e.g., Blake et al., 2012; Blake et al., 2013; Treiman et al., 2016; Yen et al., 2017). Supporting measurements from the APXS and SAM instruments have constrained the bulk chemistry (including S and Cl) and hydrated nature of the amorphous fraction (Leshin et al., 2013; McAdam et al., 2014; Dehouck et al., 2015; Morris et al., 2015a); however, in general, the phase(s) that comprise this fraction are poorly constrained. A variety or combination of phases are plausible, including volcanic glasses, allophane (Morris et al., 2013), hisingerite (Milliken and Bish, 2014), amorphous sulfate (Sklute et al., 2015; Dehouck et al., 2014), chemisorbed sulfate on nanophase materials (McAdam et al., 2014; Rampe et al., 2016), or other nanophases (e.g., Dehouck et al., 2016). Important steps toward constraining the composition(s) of the constituents of the amorphous fraction include determining the possible formation mechanisms of amorphous materials, their stability under Martian conditions (e.g., Dehouck et al., 2016), and their spectral and X-ray diffraction characteristics.

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Amorphous salts represent a potential component of Martian soils, but thus far have received little attention. In this work, we first review previous laboratory studies in which amorphous salt was reported, and describe known pathways under which amorphous salts form (Section 2). Next, we present methods for brine dehydration using chloride and multicomponent solutions (Section 3). X-ray diffraction (XRD), visible/near-infrared (VNIR) reflectance, and mid-infrared (MIR) attenuated total reflectance (ATR) data for the brine dehydration products are shown in Section 4. Last, we discuss potential implications related to the formation and persistence of amorphous salts on the Martian surface and subsurface (Sections 5 and 6).

2. Background

The body of literature describing the formation and stability of amorphous salts is relatively small, usually with amorphous phases reported as an intermediate or final run product of experiments designed to explore phase transitions as a function of temperature (T), relative humidity (RH), or precipitation rate. Generally, there are two broad pathways through which amorphous salts have been shown to form: (1) rapid dehydration of crystalline hydrates or (2) direct precipitation from brines, under non-equilibrium conditions. Higher crystalline hydrates (>$6H_2O$ per sulfate) of Mg- or Fe(II)-sulfate exposed to vacuum will form an amorphous phase through rapid dehydration (Vaniman et al., 2004; Wang et al., 2006; Chipera and Vaniman, 2007; Wang et al., 2009, 2011, 2012, 2013; Sklute et al., 2015). However, the rate of dehydration and amorphization from a crystalline starting material is temperature dependent (Wang et al., 2009, 2013). For example, vacuum desiccation of epsomite leads to an amorphous phase within two hours at 21 °C, but at −8 °C, an amorphous phase was not observed, even after ~200 h at that temperature (Wang et al., 2009). It is not clear whether amorphization would occur over longer timescales at cold temperatures.

Direct precipitation of amorphous salts from brines usually requires rapid (non-equilibrium) precipitation, driven by liquid instability and/or supersaturation (e.g., Franks, 1993). For example, amorphous ferric sulfate solids were produced from rapid dehydration of ferric sulfate brines, either by decreasing RH or decreasing atmospheric pressure (Xu et al., 2009; Xu and Parise, 2012; Sklute et al., 2015). Rapid precipitation has also been accomplished through cryoprecipitation, wherein liquids become quickly supersaturated through a rapid decrease in temperature (Toner et al., 2014; Morris et al., 2015b). In kinetic precipitation experiments of CO_2-supersaturated Ca–Mg–Fe–H_2O solutions at low-temperatures (~25 °C) and neutral pH, amorphous Fe-rich carbonate phases were early precipitates (Golden et al., 2000). For Na- and Mg-perchlorates, brine supersaturation achieved by cooling the liquid below the eutectic temperature (supercooling) has also been shown to yield amorphous phases (Toner et al., 2014). Toner et al. (2014) suggested that brine viscosity is a major factor in whether a salt glass forms via supercooling, and speculated that viscous ferric sulfate brines would show similar behavior to perchlorates.

These findings raise several questions, such as: Do other, pure component brines (such as chloride brines) or multi-component brines form amorphous solids upon rapid dehydration? How do additional elements in ferric sulfate brines affect the stability of the dehydration product to RH fluctuations? What are the IR spectral properties and XRD characteristics of these amorphous products? To that end, we conducted a series of experiments to investigate the rapid dehydration products of chloride and multi-component (ferric sulfate; iron-, magnesium-, and calcium-, and sodium-chloride; and sodium bicarbonate) brines. These brine compositions were chosen because calculations of the Martian amorphous composition (e.g., Morris et al., 2016, 2015a; Rampe et al., 2017; Treiman et al., 2016; Yen et al., 2017) demonstrate that Fe^{2+}, Fe^{3+}, Mg^{2+}, Ca^{2+}, and Na^+ cations may be associated with the S and Cl volatiles. Furthermore, geochemical models of evaporation of sulfur-rich brines, derived from weathering of Martian basalt, indicate that the final liquid phase is concentrated in Fe^{3+}, Mg^{2+}, Na^+, Cl^-, and $SO_4{}^{2-}$ (Chevrier and Altheide, 2008). Thus the solution compositions explored in this study are plausible for Martian surface and subsurface materials. The addition of bicarbonate to these initial mixtures served to investigate the potential interaction these highly acidic brines may have with native Martian carbonates, and the effect those carbonates would have on the resultant spectra.

For these initial experiments, samples were rapidly dehydrated at 21 °C in both vacuum and in 11% RH to force non-equilibrium precipitation conditions (Ling and Wang, 2010; Sklute et al., 2015; Wang et al., 2012; Xu et al., 2009; Xu and Parise, 2012). Though these low RH values are consistent with daytime RH values observed on the Martian surface (Harri et al., 2014; Savijarvi, 1995), and Martian surface temperatures can exceed 20 °C at the equator (Spanovich et al., 2006), this combination of RH-T values represents a narrow range of current Martian conditions. However, the goal of this study is to explore whether amorphous products can form from mixed component brines under rapid precipitation conditions, which could occur through multiple pathways (described above). The XRD characteristics, spectral properties, and preliminary observations of relative persistence under RH fluctuations of these newly considered mixed phases are presented."

3. Materials and methods

3.1. Brine dehydration experiments

The salt mixtures analyzed in this study are listed in Table 1. Each solution was made using ultrapure $Fe_2(SO_4)_3$ that had first been heated at 350 °C for 2 h to transform it from the bottled phase, which does not occur in nature, to the mineral mikasaite (Xu et al., 2009). Because Sklute et al. (2015) showed that amorphous phases formed through the deliquescence and dehydration of different starting materials show subtle spectral variations, the phase found in nature was considered the more appropriate starting material. Each salt was mixed with doubly de-ionized (DDI) water to create concentrated solutions: 0.10 M $Fe_2(SO4)_3$ (Alfa Aesar Puratronics, 99.998%), 1.00 M $CaCl_2 \cdot 2H_2O$ (VWR Amresco Life Science), 2.25 M $MgCl_2 \cdot 6H_2O$ (Acros Organics, 99+%), 0.348 M $FeCl_3 \cdot 6H_2O$ (VWR Amresco Life Science, 99+%), 0.596 M $NaHCO_3$ (BDH, 99.7+%), and 3.96 M NaCl (Fischer Scientific, 99+%). These solutions were then combined to create the molar ratio mixtures listed in Table 1. Initial 1:1 molar ratios were chosen for experimental simplicity with the exception of the $MgCl_2$-containing brines, where 2:1 ratios were also explored. Preliminary work (Rogers et al., 2016), which allowed each salt to deliquesce and then mixed them in volume ratios, produced similar results; variations between this and the preliminary work in Rogers et al., (2016) can be attributed to differing molar ratios.

Each mixed solution was split into two aliquots that were simultaneously dried at 21 °C in 1) 11% RH (LiCl buffered individual RH chambers, continually monitored by Lascar EL-USB-2-LCD Humidity Data Logger) to simulate evaporation on the Martian surface, and 2) under vacuum (Edwards E2M2 vacuum pump attached to an Applied Vacuum Engineering VF range bell jar) to simulate boiling on the Martian surface. The solutions were dried for 5 days under these conditions. Preliminary assessments of the relative stability of the amorphous solids were determined by monitoring the sample state during transfer from vacuum/low RH buffer to the VNIR/ATR spectrometers and XRD (Section 3.2) and later by