SATBILITY FIELDS OF HYDROUS FERROUS SULFATES AND THEIR PATHWAYS IN DEHYDRATION-REHYDRATION PROCESSES
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Introduction: Hydrous sulfates are one of the two major types of secondary minerals (the other type is phyllosilicates) that have been found on the surface of Mars, in large quantities and with wide spreading. Among them, Ca-, Mg-, Fe-, Al-sulfates have all been identified. A commonly accepted concept is that the Mg, Fe, Ca, Al cations in those sulfates are released from basaltic minerals by chemical weathering. Among the Gibbs Free energy for weathering reactions of major basaltic silicates: those of olivine are the lowest (~ - 6.58 to - 4.0 Kcal/atom), those of feldspar are the highest (ΔG_f^0 ~ - 1.32 to - 0.32 Kcal/atom), and those of pyroxene are in the middle (- 2.72 to -2.98 Kcal/atom). These values imply that following the increasing degree of chemical weathering, the releasing of Mg and Fe^{2+} from olivine and pyroxene would happen much easier than Al, K, and Na, whose release would happen only from high degree, extensive, weathering process. Because of these reason, the finding of large quantity and wide spreading of Mg-sulfates, Fe-oxides, ferric sulfates, localized Ca-sulfates, and Mg, Fe-smectite on Mars all demonstrates a moderate degree of chemical weathering (except at specific locations by hydrothermal process) of Mars surface materials [1].

Hydrous Fe^{2+}-sulfates would precipitate together with hydrous Mg-sulfates, during the evaporation of primary salty brines generated from chemical weathering of olivine (or pyroxene). The stability and reaction pathways of hydrous ferrous sulfates are important to understand the processes that have happened on the surface of Mars. This abstract reports a systematic laser Raman spectroscopic study on Temperature-Relative Humidity (T-RH) driven dehydration/rehydration processes of Fe^{2+}-sulfates. The emphasis of this study is the stability field and phase transition pathway in *solid-vapor reaction process,* not the ion reactions in liquid [2, 3]. Solid-vapor reaction processes for dehydration-rehydration of hydrous Mg- and Fe^{3+}-sulfates have been reported previously [4-9].

Samples and Experiments: Melanterite $FeSO_4.7H_2O$ (Fe7w), rozenite $FeSO_4.4H_2O$ (Fe4w), and szomolnokite $FeSO_4.H_2O$ (Fe1w) are three common Fe^{2+}-sulfates found in nature. For each of them, we conducted 30 T-RH driven dehydration/rehydration experiments at three temperure (50, 21, and 5 ℃) and 10 relative humidity levels (RH=6-100%). The monitoring of the molecular phase transitions was made by non-intrusive laser Raman Spectroscopic (LRS) measurements for phase ID and gravimetric measurements to derive the changes in H_2O number per molecule.

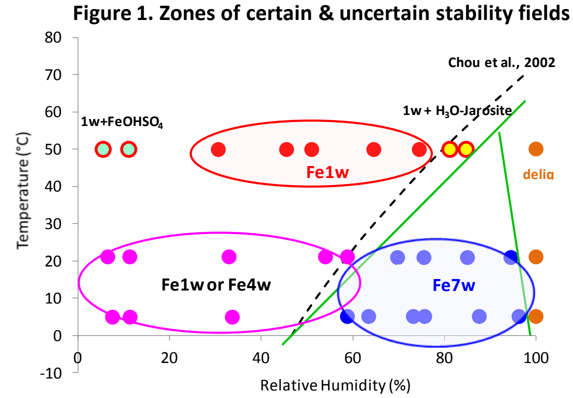
Pure crystalline melanterite $FeSO_4 \cdot 7H_2O$ was purchased from ACROS (code 201390010, CAS 7782-63-0, lot A0242021), whose identity, status of crystallinity, and hydration degrees were confirmed by XRD. The melanterite grains were hand-grounded and sieved, and fine powder samples of 90 -150 μm grain sizes were used to ensure sufficient surface area for reaction. To generate the starting samples for Fe7w, Fe4w, and Fe1w, three Petri dishes filled with grounded $FeSO_4 \cdot 7H_2O$ powder were placed into three glass jars filled with RH buffer solutions, KCl-H_2O, $MgCl_2$-H_2O, and LiCl-H_2O (RH=85%, 33%, and 11% respectively at room T), in which the powder samples were kept for a few days to reach the desired hydration degrees. During the sample preparation, the color of sample powder was carefully monitored, to prevent potential oxidation of Fe^{2+}-sulfate to Fe^{3+}-sulfates. 100 LRS measurements were made on each of the final sample powders. No Raman peaks of ferric-sulfates were observed [7], the homogeneity in hydration degree of each powder sample was confirmed as well.

90 T-RH driven experiments at Earth atmospheric pressure were started in August, 2013. LRS and gravimetric measurements of reaction products were made at pre-determined time intervals (3, 8, 16, 32, 56, 120, 192 ... 4872 hours) until present day.

Zones of stability fields: Based on the LRS phase identifications of the reaction products of 90 experiments, we can approximately define five zones of stability field of this Fe^{2+}-SO_4-H_2O system (Figure 1, [10]).

<u>*Zone of deliquescence*</u> -- the boundary between deliquescence and Fe7w was defined based on the ob-

Figure 1. Zones of certain & uncertain stability fields



served deliquescence of 9 experiments (started from Fe7w, Fe4w, and Fe1w) at three Ts and 100% RH and the observed unchange powder samples of another 9 experiments at same Ts but 85-96%RH (in KNO_3-H_2O buffer).

Zone of melanterite Fe7w stability field – the boundary between Fe7w and other ferrous sulfates were defined by the observed phase transition from Fe4w and Fe1w to Fe7w in 20 experiments at two Ts and 4-6 RH levels.

Zone of szomolnokite Fe1w stability field – it was defined by observed phase transition from Fe7w and Fe4w to Fe1w in 10 experiments at 50 ℃ and five RH levels.

Zone of non-separated stability field for rozenite Fe4w and szomolnokite Fe1w – at 21 ℃ and 5 ℃, RH=6-59%, stable Fe1w and Fe4w were observed in 16 experiments and phase transition from Fe7w to Fe4w happened in 8 experiments. The potentially slow kinetics between Fe4w ←→ Fe1w prevented us to separate the stability fields of Fe4w and Fe1w in this T-RH space.

Zones of Fe^{2+} to Fe^{3+} transformation: Among the 90 experiments run under Earth atmospheric pressure for 8 months, oxidation from Fe^{2+}-sulfates to Fe^{3+}-sulfates were only observed at 50 ℃, in 9 experiments at four RH levels (Figure 1, 2). Among them, the phase transition from $FeSO_4.H_2O$ to $FeOHSO_4$ were observed in 3 experiments at RH=5% and 11%. Phase transition from $FeSO_4.7H_2O$ and $FeSO_4.4H_2O$ to hydronium jarosite $H_3OFe_3(SO_4)_2(OH)_6$ was observed in 6 experiments at RH=81% and 85%. We currently interpret the first reaction at low RH represents a solid-state transition, and the second reaction at high RH may represent a dissolution-recrystalization reaction (potential liquid film at grain surface at high RH cannot be excluded). Compared with fast $Fe^{2+} \rightarrow Fe^{3+}$ transformation in Fe-Mg-SO_4-bearing liquid [2, 3], the slow $Fe^{2+} \rightarrow Fe^{3+}$ reaction rate in these solid-vapor experiments posts questions on the actual formation pathways of Fe-oxides and Fe-hydroxides on Mars,

Comparison of Fe^{2+}- and Mg-sulfates: When compared the current data with a similar set of 90 experiments started from $MgSO_4.xH_2O$ (x=1, 4, 7, [4, 5, 6]), three types of very different properties were found.

Difference #1 – $FeSO_4.6H_2O$ was never observed as a stable phase during all dehydration-rehydration experiments, but $MgSO_4.6H_2O$ is a stable phase, having a well defined stability field in T-RH space.

Difference #2 – the stability of rozenite $FeSO_4.4H_2O$ against dehydration is much weaker than starkeyite $MgSO_4.4H_2O$. The dehydration of epsomite $MgSO_4.7H_2O$ at T≤ 50 ℃ would normally stop at the stage of $MgSO_4.4H_2O$, only by the help of specific catalysis effect, the dehydration would develop toward forming kieserite $MgSO_4.H_2O$. However the dehydration of $FeSO_4.7H_2O$ in the same T range has easily passed the stage of $FeSO_4.4H_2O$ and reached $FeSO_4.H_2O$ (Figure 3). The less stable rozenite structure is caused by the larger size of four-member-ring sub-structural units that exist in both rozenite and starkeyite [4, 5].

Difference #3 -- the stability of szomolnokite $FeSO_4.H_2O$ against rehydration is much higher than kieserite $MgSO_4.H_2O$. Figure 4 shows at 50 ℃ and mid-RH, $MgSO_4.H_2O$ started to rehydrate forming $MgSO_4.4H_2O$ or $MgSO_4.6H_2O$ while $FeSO_4.H_2O$ remained unchanged. A similar higher stability against rehydration was also observed for rozenite at mid-T (21 ℃) experiments. The reason that caused the high stability of szomolnokite and rozenite against rehydration is under investigation.

Implication to Mars sulfates is under development.

Figure 2. from Fe^{2+} to Fe^{3+} sulfates

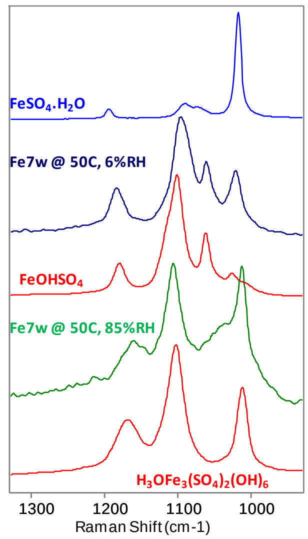


Figure 3. Unstable Fe7w & Fe4w against dehydration

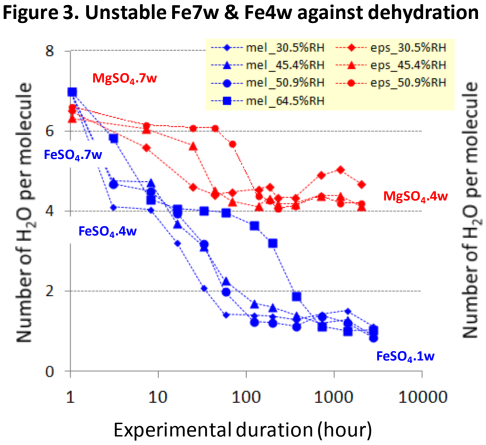
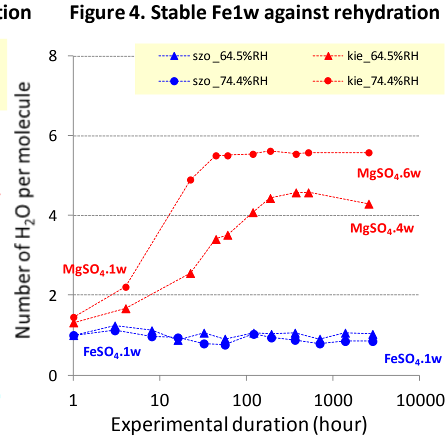


Figure 4. Stable Fe1w against rehydration



Acknowledgement: Thanks for NASA funds NNX10AM89G, NNX09AE80A, #1295053, NNX13AM22G, and discussion with McLennan, Tosca, Zhao; **References:** [1] McLennan et al., 7th Mars conference, 2007; [2] Tosca et al., JGP, 2008; [3] Zhao et al., GCA, 2013; [4] Wang et al., GCA, 2006; [5, 6] Wang et al., JGR, 2009, 2011; [7, 8, 9] Wang et al., Icarus, 2012, 2013, 2014; [10] Chou et al., Am. Minerals. 2002;