HYDRATION AND DEHYDRATION PROPERTIES OF MgSO$_4$, FeSO$_4$ and Fe$_2$(SO$_4$)$_3$ CLOSE TO MARTIAN SURFACE CONDITIONS.

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Introduction: Hydrated forms of Mg- and Fe-sulfates have been recently identified in deposits of the Martian soil [1, 2]. Phenomena such as deliquescence and the formation of cryo-brines of different salts including Mg(ClO$_4$)$_2$ and Fe$_2$(SO$_4$)$_3$ have been discussed for the stability of liquid water and its consequences on present Mars [3, 4]. The hydration and dehydration properties of MgSO$_4$ and Fe$_2$(SO$_4$)$_3$ with respect to Mars have been previously investigated by XRD [5, 6].

Here we present the H$_2$O sorption properties of Mg- and Fe-sulfates by sorption methods. Our results are important for understanding the speciation of hydrated and hydroxylated phases in the Martian soil and in supporting the interpretation of results of future missions such as MSL and ExoMars/MicrOmega.

Experimental: The hydration/dehydration properties of MgSO$_4$, FeSO$_4$ and Fe$_2$(SO$_4$)$_3$ were investigated by means of isotherm measurements and thermogravimetry/differential thermoanalysis (TG/DTA).

Sorption isotherms were measured gravimetrically from 259-293 K with a McBain quartz spring balance equipped with three MKS Baratron pressure sensors which cover a range of 10^{-5}-10^3 mbar. TG/DTA measurements were performed on a Netzsch STA 409 apparatus with a heating rate of 3 K/min to 673 K.

Over several weeks prior to the TG experiments the delivered samples were stored in a controlled atmosphere meaning an evacuated exsiccator with relative humidity (RH) of 33% and 62%, respectively. Before each sorption experiment, the samples received were dehydrated at 523 K (MgSO$_4$ impregnated into a mesoporous support) or at 543 K (pure Fe-sulfates). The dehydration took place in high vacuum at p<10^{-4} mbar for 1-2 hours.

Results and Discussion: Figure 1and 2 summarize the TG and DTA data of the iron sulfates. The total mass loss of FeSO$_4$ (Figure 1 from top to bottom) is formal due to the decomposition of the FeSO$_4$ with 4, 5 and 7 H$_2$O. The first 3 H$_2$O out of 7 split around 330-350 K followed by the next 3 H$_2$O at 380 K. The (stronger) monohydrate decompose at 525 K. For Fe$_2$(SO$_4$)$_3$ (Figure 2) we get a much more complex picture. With increasing RH different hydrates or mixtures of hydrates have been formed (with formally 5, 8 and 13 H$_2$O, from top to bottom) and decompose upon heating. Storage at RH=79% (different to the other salts) leads to liquefaction. According to the results of Wenqian et al. [6] this complexity is not surprising.
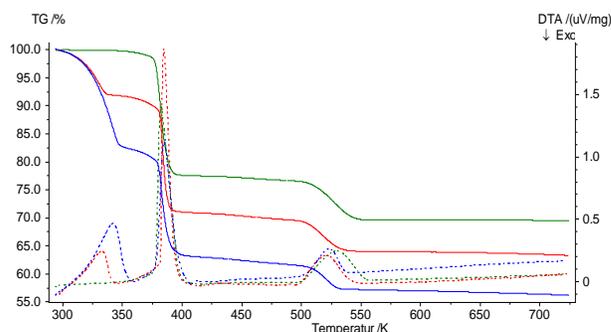

Figure 1. TG (solid lines) and DTA (dotted lines) of FeSO$_4$·nH$_2$O, from top to bottom: green after storage at RH=33% FeSO$_4$·4H$_2$O, red as delivered (storage at ambient, 5H$_2$O) and blue after storage at RH=62% (FeSO$_4$·7H$_2$O).
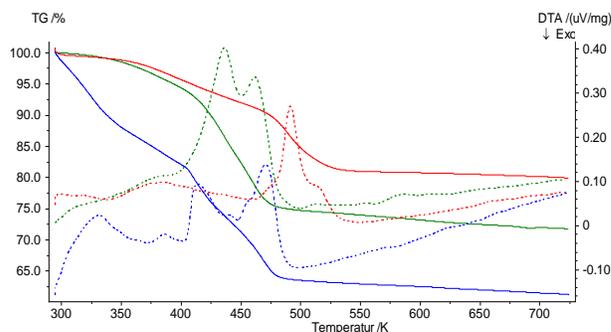
Figure 2. TG (solid lines) and DTA (dotted lines) of Fe$_2$(SO$_4$)$_3$ from top to bottom: red Fe$_2$(SO$_4$)$_3$ "dry" as delivered (5 H$_2$O), green after storage at RH=33% (8 H$_2$O) and blue after storage at RH=62% (13 H$_2$O).
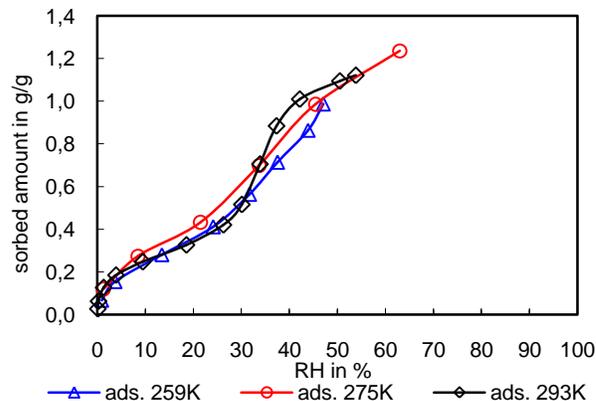

Figure 3. Hydration branch of the isotherms of MgSO$_4$ (impregnated into a mesoporous host) at 259-293 K and between 0.01-10 mbar water vapor pressure.
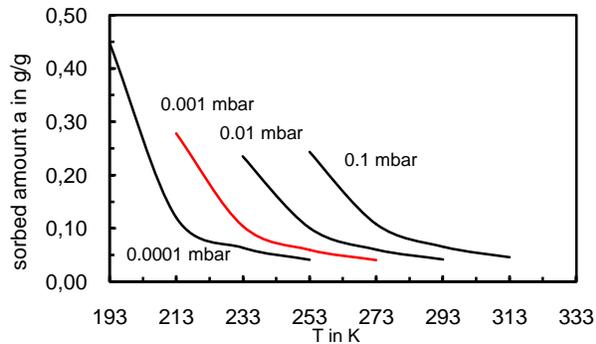
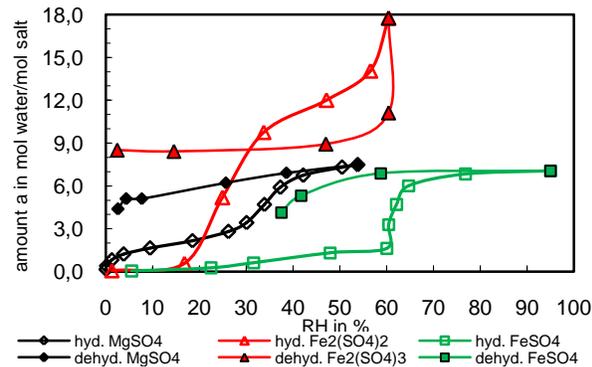Figure 4 Hydration isobars of $MgSO_4$ calculated from the isotherms of Figure 3.

Figure 5. Hydration and dehydration isotherms of Fe_2SO_4, $MgSO_4$ and $FeSO_4$ at 293 K, dehydration filled symbols, still not in equilibrium.

The step by step hydration of $MgSO_4$ under close to Martian surface conditions is shown in Figure 3. The isotherms measured are plotted as function of relative humidity, thus all curves fall into one bundle of curves as expected. Application of the Dubinin equation on the hydratation isotherm data of the $MgSO_4$ (as shown in [7] for the smectites or zeolites) provides the data in a water amount/temperature plot at a certain water vapor pressure. Figure 4 gives the results of the calculated hydration isobars from the measured isotherms. The hydration/dehydration of $MgSO_4$ seems to be reversible from the point of view of the sorption experiments, however, an extended XRD study in [5] shows the high complexity of the desiccation/ rehydration behaviour of $MgSO_4$. In the sorption experiment it takes many days or even weeks to get the dehydration equilibrium probably because of kinetic effects.

The hydration/dehydration isotherms of Fe_2SO_4, $MgSO_4$ and $FeSO_4$ at 293 K are displayed in Figure 5 (plotted as H_2O per mol salt against RH). As can be seen all salts show a hysteresis. Except the ferric sulfate the $MgSO_4$ and $FeSO_4$ dehydration branches move with time closer towards the hydration branches (not shown) pointing to kinetic effects (cf. Figure 6).
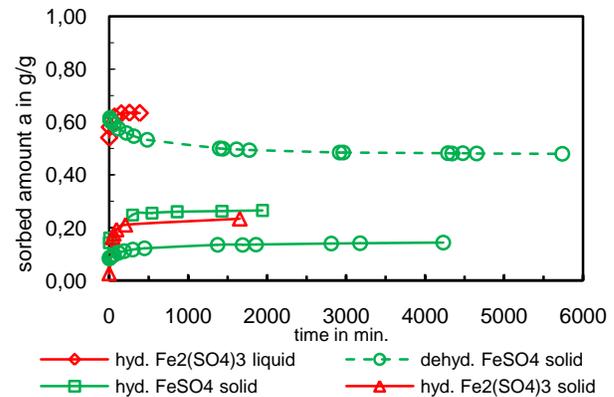

Figure 6. Comparison of the hydration and dehydration kinetics for $Fe_2(SO_4)_3$ (solid and liquid) and $FeSO_4$ (dashed line dehydration).

Figure 6 gives a comparison of the hydration and dehydration kinetics of $Fe_2(SO_4)_3$ (solid and liquid state) and $FeSO_4$ (solid state) as function of time. Ferric sulfate turns into a liquid phase at RH 60% (DRH) because deliquescence starts at that humidity (cf. begin of strong increase of the hydration branch at RH 60% and >14 H_2O in Figure 5). The hydration kinetics in this state is much faster (top most curve in Figure 6) compared to the solid state. So does ferric sulfate behaves in dehydration mode as well. However, fast desiccation of liquid ferric sulfate stops at 9 H_2O/mol salt (formation of coquimbite?) and seems to be stable for a long time at RH<1%.

The $FeSO_4$ isotherm shows a plateau between RH 40-60% characterized by the formation of the monohydrate in good agreement with TG/DTA (Figure 1) representing the stronger hydrate (step/peak at 525 K) of $FeSO_4$.

Conclusion: By knowing the water vapor pressure or local humidity of the planet's atmosphere the water content or the liquefaction properties of the hydrophilic salts can be determined supporting the evaluation of spectroscopic results from orbit or future rover missions such as MSL on Mars.

References: [1] Gendrin A. et al. (2005) *Science* 307 1587-1591. [2] Morris R.V. et al. (2008) *JGR Planets* 113 E12S42, DOI: 10.1029/2008JE003201. [3] Hecht et al. (2009) *Science* 325 64-67. [4] Möhlmann et al. (2010) *Icarus* DOI: 10.1016/j.icarus 2010.11.025. [5] Vaniman D.T. et al. (2004) *Nature* 431 663-665. [6] Wenqian X. et al. (2009) *Am. Mineral.* 94 1629-1637. [7] Jänchen et al. (2006) *Icarus*, 180, 353-358.