

**THE HYDRATION AND DEHYDRATION PROPERTIES OF HYGROSCOPIC CHLORIDES AND BIOFILMS UNDER MARTIAN ENVIRONMENTAL CONDITIONS.** J. Jänchen<sup>1</sup>, N. Feyh<sup>2</sup>, D.T.F. Möhlmann<sup>3</sup>, <sup>1</sup>TH Wildau, c/o ZeoSolar e.V., Volmerstr. 13, D-12489 Berlin-Adlershof, Germany, e-mail address: [j.e.jaenchen@t-online.de](mailto:j.e.jaenchen@t-online.de), <sup>2</sup>TU Berlin, Environmental Microbiology, Franklinstr. 29, 10587 Berlin, Germany, e-mail address: [nina.feyh@tu-berlin.de](mailto:nina.feyh@tu-berlin.de) <sup>3</sup>DLR Institute of Planetary Research, Rutherfordstr. 2, D-12489 Berlin, Germany, e-mail address: [dirk.moehlmann@dlr.de](mailto:dirk.moehlmann@dlr.de)

**Introduction:** Here we present the H<sub>2</sub>O sorption properties of three hygroscopic chlorides recently identified in deposits on the Martian surface [1]. Because Wierzchos [2] and Davila [3] showed that deliquescence of halite in the hyper-arid Atacama Desert provides a habitable environment, the Martian chloride deposits also might have an astrobiological potential [4]. We have included in our study the hydration and dehydration of a biofilm because many of the microorganisms on Earth are hosted by hydrophilic biopolymers. As an example serves the highly desiccation resistant filamentous cyanobacterium *Nostoc commune* collected (dry) in the national park “Unteres Odertal.” In terrestrial environments, *N. commune* forms large biofilms by excreting viscous extracellular polysaccharides (EPS) which play a role for desiccation and freezing tolerance [5]. Finally, bentonite with montmorillonite as main component is included for comparison, as it is identified in the Martian soil as well[6].

Our results are important for understanding of the exobiological aspects on Mars and for future missions such as MSL and ExoMars/MicrOmega beside the speciation of adsorbed H<sub>2</sub>O, hydrated and hydroxylated phase on the Martian surface [7].

**Experimental:** The hydration/dehydration properties of Atacama halite (NaCl), MgCl<sub>2</sub>, CaCl<sub>2</sub>, bentonite (montmorillonite), and *N. commune* were investigated by means of isotherm measurements and thermogravimetry/differential thermogravimetry (TG/DTG). Sorption isotherms were measured gravimetrically from 257-293 K with a McBain quartz spring balance equipped with three MKS Baratron pressure sensors covering a range of 10<sup>-5</sup>-10<sup>3</sup> mbar. TG/DTG measurements were performed on a Netzsch STA 409 apparatus with a heating rate of 3 K/min to 673 K. Prior to the experiments all samples were stored in a controlled atmosphere (evacuated exsiccator, p/p<sub>s</sub> H<sub>2</sub>O = 0.79).

Scanning electron microscopy (SEM, JOEL JSM640 and ZEISS Gemini Ultra Plus) was applied to characterize the morphology of the samples.

Before each sorption experiment, about 100 mg of sample was degassed at 293 K (*N. commune*), 383 K (montmorillonite) and 532 K (salts) and p < 10<sup>-5</sup> mbar for several hours.

**Results and Discussion:** Figure 1 shows the SEM images of halite and bentonite. Bentonite consists of

scaly shaped particles with a N<sub>2</sub> BET surface area of 77 m<sup>2</sup>/g. Halite is almost pure NaCl with some impurities of gypsum (marked particle on the image has composition of gypsum: Ca, S, O).

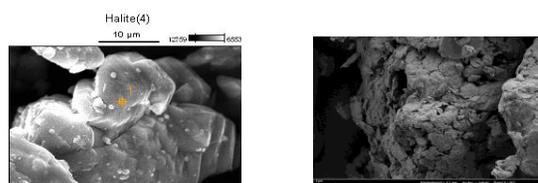


Figure 1. SEM images of Atacama halite (left; marked grain is gypsum) and bentonite (right).

Figure 2 summarizes the TG and DTG data for bentonite, *N. commune* and CaCl<sub>2</sub>. The mass loss (desorption of H<sub>2</sub>O) ranges from 18 wt% for bentonite to ~40 wt% for the other samples. Halite (not shown in the figure) does not form hydrates above 273 K and therefore does not show decomposition of hydrates in the TG experiment (as do CaCl<sub>2</sub> and MgCl<sub>2</sub>). Bentonite loses almost all of its water around 350 K (cf. peak in Figure 2). *N. commune* dehydrates in three steps starting with weakly bonded water (peaks at 300 and 340 K). Different to bentonite *N. commune* shows a considerable mass loss at about 550 K due to dehydratization and dehydroxylation. As could be expected CaCl<sub>2</sub>·6H<sub>2</sub>O decomposes stepwise at relatively low temperatures (cf. peaks at 370 K and 430 K).

Figure 3 gives the H<sub>2</sub>O sorption isotherms for halite at different temperatures. As can be seen halite does not adsorb any water below the deliquescence relative humidity (DRH=75-80%) or the corresponding

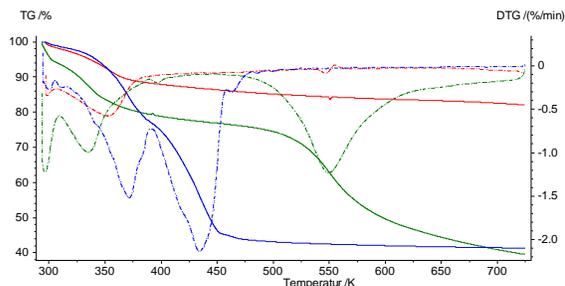


Figure 2. TG (solid lines) and DTG (dotted lines) of (from top to bottom): bentonite, *N. commune* and CaCl<sub>2</sub>.

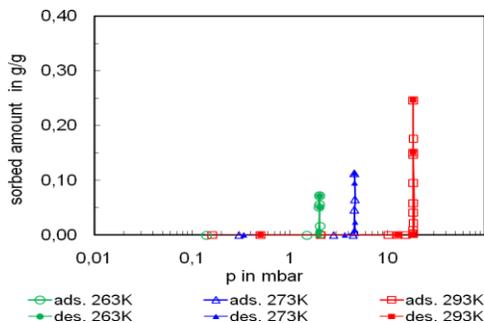


Figure 3. H<sub>2</sub>O sorption isotherms of halite at 263, 273 and 293 K, filled symbols denote desorption.

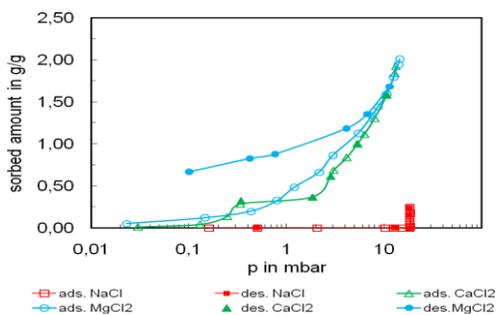


Figure 4. Comparison of the H<sub>2</sub>O isotherms of MgCl<sub>2</sub>, CaCl<sub>2</sub> and halite (NaCl), at 293 K.

water vapor pressure, respectively. However, at the DRH halite gains weight due to forming a saturated solution on the crystals surface at  $T < 273$  K [4].

Figure 4 compares the water isotherms of halite with the other chlorides at 293 K. Ca- and Mg-chlorides form hydrates resulting here in a step-wise course of the isotherms. Importantly, the hydration/dehydration of CaCl<sub>2</sub> is nicely reversible in contrast to isotherms of MgCl<sub>2</sub> showing a strong hysteresis most probably because of kinetic effects. The DRH of these chlorides is much lower and amount to about 28-33% [4] providing a liquid phase on its surface well below 273 K.

The hydration and dehydration isotherms of *N. commune* are displayed in Figure 5 for temperatures of 293 K and below. The sorbed amount of about 0.25 g water/g vacuum dry sample corresponds to the first TG-steps (weakly bonded H<sub>2</sub>O below 370 K) of *N. commune* in Figure 2.

Figure 6 gives a comparison of the hydration and dehydration characteristics of *N. commune* with montmorillonite and halite as function of the relative humidity. This comparison holds well for  $T \ll 293$  K and shows *N. commune* as much more hydrophilic than halite and similarly hydrophilic as the smectite. So halite can provide *N. commune* with liquid water

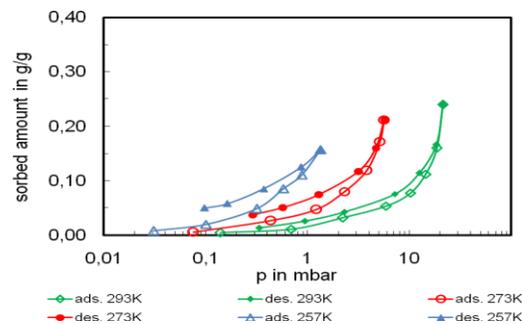


Figure 5. H<sub>2</sub>O sorption isotherms of *N. commune* at 257, 273 and 293 K, filled symbols denote desorption.

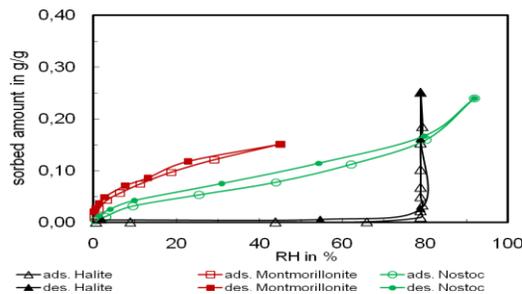


Figure 6. Comparison of the hydration and dehydration behavior (water amount vs. relative humidity) for montmorillonite, *N. commune*, and halite.

because of deliquescence at the DRH=75-80% even below 273 K.

Application of the Dubinin equation on the isotherm data of *N. commune* (Figure 5), as shown in [8] for the smectite, provides the data in a water amount/temperature plot at a certain water vapor pressure.

**Conclusion:** By knowing the water vapor pressure or local humidity of the planet's atmosphere the water content of the biofilm or any other hydrophilic mineral can be determined supporting the evaluation of spectroscopic results from orbit or future rover missions on Mars.

**References:** [1] Osterloo M.M. et al. (2008) *Science* 21 1651-1654. [2] Wierzchos J. et al. (2006) *Astrobiology* 6 415-422. [3] Davila A.F. et al. (2008) *JGR* 113, doi:10.1029/2007JG000561. [4] Davila A.F. et al. (2009) *Astrobiology*, submitted. [5] Tamaru Y. et al. (2005) *Appl. Environ. Microbiol.* 71 7327-7333, doi:10.1128/AEM.71.11.7327-7333.2005. [6] Poulet F. et al. (2005) *Nature* 438, 623-627. [7] Joulet et al. (2007) *JGR* 112, E08S06, doi: 10.1029/2006JE002846 [8] Jänchen et al. (2006) *Icarus*, 180, 353-358.

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