

## IMPACT OF UVC EXPOSURE ON THE WATER RETENTION OF THE LICHEN *BUELLIA FRIGIDA*.

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**Introduction:** New results on extremophiles and observations of Mars missions regarding the detailed mineralogy, the occurrence of water in the equatorial region of Mars [1-3], new announcements of MSL findings and their implications for the surface conditions at Gale crater [4, 5] as well as measurements of the Mars surface radiation environment [6] fuel the debate about possible developments of life on Mars.

Based on previous studies [7-8] we examined water vapor interaction and water-bearing properties of *B. frigida* before and after UVC irradiation. The measurements have been partially conducted after simulation of environmental conditions which are supposed to be Mars-like. Lichens are symbiotic organisms that are able to colonize a broad range of extreme habitats and, therefore, represent useful model systems in astrobiological research.

Our aim is to contribute to an improved understanding of extremophiles under exobiological aspects within the frame of BIOMEX (*Biology and Mars Experiment*) at the ISS, in respect to irradiation effects on water retention properties. The results may also support data evaluation of *in-situ* missions such as MSL and ExoMars.

**Experimental: Samples.** *Buellia frigida* Darb. (1910) represents a symbiotic and eukaryotic association formed by a heterotrophic fungus (cf. Fig. 1) and a photoautotrophic green alga. *B. frigida* is an endemic Antarctic extremophile that is well adapted to drought and high levels of solar UV-R experienced at their natural habitats but also to extremes of cold [9]. *B. frigida* was able to survive simulated space exposure, what is due, among other factors, to the formation of UVR-shielding secondary lichen compounds [10].

The set of samples investigated consists of differently treated axenic mycobionts of *B. frigida*. Samples of the mycobiont were exposed to UVC at  $\lambda=254$  nm (lamp performance  $480 \mu\text{W}/\text{cm}^2$ ) under dry (D) and wet (W) conditions. The exposure times were 0 h, 10 h (accumulated dose= $17,280 \text{ J}/\text{cm}^2$ ) and 50 h (=86,400  $\text{J}/\text{cm}^2$ ). The corresponding sample codes were D0, D10, D50 for dry treatment and W0, W10, W50 for exposure of the wet samples, respectively.



Fig. 1 Habitats of *Buellia frigida* (left side) and the cultivated mycobiont of *B. frigida*.

**Methods.** The dehydration properties and the decomposition (thermogravimetry, TG, and differential thermogravimetry, DTG) were measured with a Netzsch STA 409 device applying a heating rate of 10 K/min up to 1273 K. An extra measurement has been carried out on a Netzsch STA 409C coupled to a mass spectrometer (MS). Prior to the TG runs, the lichens were preconditioned in a controlled atmosphere (six days over saturated ammonium chloride solution in an evacuated desiccator,  $p/p_s=0.79$  or  $\text{RH}=79\%$ ). The sorption (hydration) isotherms were measured gravimetrically from 257-293 K with a McBain-Bakr quartz spring balance equipped with MKS Baratron pressure sensors covering a range of  $p=10^{-5}$ - $10^3$  mbar. Prior to each hydration experiment, about 100 mg of the sample was degassed over night at 293 K and  $p<10^{-5}$  mbar.

**Results and discussion:** Our previous studies focused on the hydration and dehydration behavior of *B. frigida* as an entire organism and of its isolated symbionts without irradiation [8]. Fig. 2 and Fig. 3 summarize the comparison of the TG/DTG profiles of *B. frigida*'s mycobiont irradiated with different doses under dry and wet conditions. The TG/DTG curves of D0, D10 and D50 (Fig. 2) are characterized by three TG steps or DTG minima, respectively. The first minimum at 360 K indicates the release of physisorbed water. The second stage around 560 K is due to stronger bonded water or hydroxyls and the beginning decay followed by the last step (660 K) dominated by the thermal decomposition of the mycobiont, predominantly of its main component chitin ( $\text{C}_8\text{H}_{12}\text{NO}_5$ ). The latter could be deduced from separate TG measurements with pure chitin showing its decomposition step around 650 K.

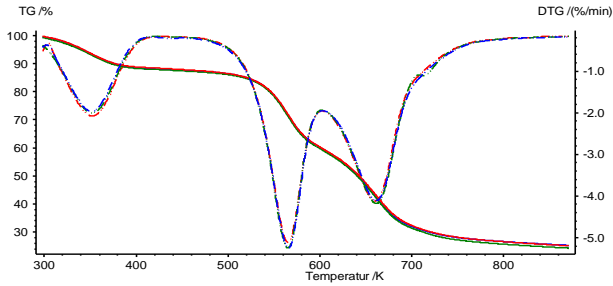


Fig. 2 TG (solid lines) and DTG profiles of the mycobiont of *B. frigida*: after dry treatment: D0 blue, black; D10 red; D50 green (after hydration at RH=79% in a dessicator).

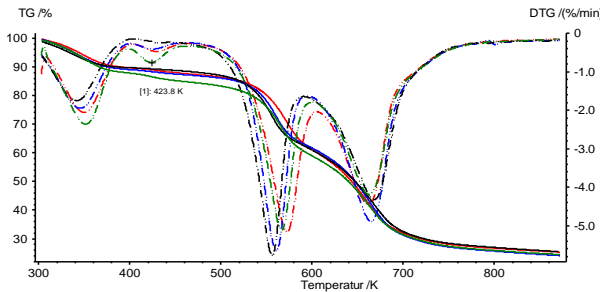


Fig. 3 TG (solid lines) and DTG profiles of the mycobiont of *B. frigida*: after wet treatment: W0 blue, black; W10 red; W50 green; (after hydration at RH=79% in a dessicator).

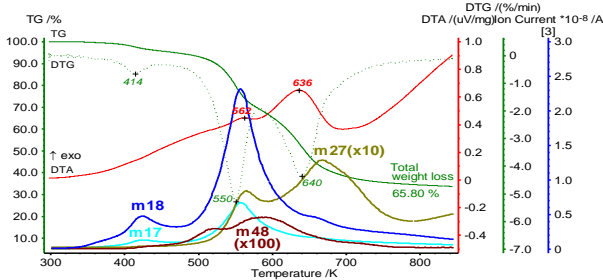


Fig. 4 TA-MS curves for the mycobiont D50 (lab-dry) with the ion current (IC) curves for the mass numbers  $m/z$  17( $\text{OH}^+$ ,  $\text{NH}_3^+$ ), 18( $\text{H}_2\text{O}^+$ ), 27( $\text{C}_2\text{H}_3^+$ ), and 48( $\text{SO}^+$ ). Note the different IC amplifications.

The wet irradiated samples (Fig. 3) show a very similar behavior except a new step/minimum at 420 K. This step increases with the doses of UVC indicating an impact of UVC treatment on the release of physisorbed water.

On line-coupled MS analysis of the evolved gases (Fig. 4) for D50 supports our assumptions. The extra step at about 420 K is due to further release of physisorbed water indicated by the mass numbers 18 and 17. Because the sample was “lab-dry” (no hydration at RH=79%), the first step/minimum of the physisorbed water at 360 K is lacking in Fig. 4. Furthermore, the MS data show the release of water at about 560 K,

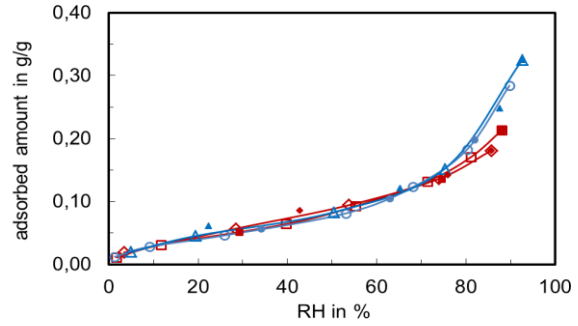


Fig. 5 Hydration/dehydration isotherms of the mycobiont of *B. frigida* at 273 K and 293 K before (red curves) and after irradiation (blue).

accompanied by fragments of hydrocarbons (m27) and tiny amounts of sulfur species (m48) again followed by a release of hydrocarbon fragments around 650 K.

Finally, Fig. 5 shows the sorption isotherms of the physisorbed water on an untreated mycobiont and an irradiated W50 sample. The isotherms for each sample are plotted as a function of the relative humidity (RH) and thus form one bundle of curves for different temperatures. A difference at RH>70% is obvious. The wet irradiated sample sorbs more water compared with the untreated mycobiont which is in line with the TG results showing some extra physisorbed water (step at 420 K). The UVC-treatment improves the ability of physisorption of water by creating extra sorption sites in the mycobiont. The study has to be continued for getting more knowledge into this interesting outcome.

**Conclusion:** The UVC exposure of lichens can influence their water retention ability, thus the examination of the water sorption properties of extremophiles may contribute to an improved understanding as intended within the frame of BIOMEX.

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