

# Astrobiologically relevant precursor organic compounds from the subsurface ocean of Enceladus

**Nozair Khawaja** (1,2), Frank Postberg (1,2), Jon Hillier (1), Fabian Klenner (1,2), Lenz Nölle (1,2), Rene Reviol (2)  
(1) Institute of Geological Sciences, Free University Berlin, Germany (2) Institute of Earth Sciences, Heidelberg University, Germany (nozair.khawaja@fu-berlin.de)

## Abstract

Saturn's moon Enceladus emits a plume of ice grains and vapour from vents within fractures in its south pole [1]. Both refractory and volatile organic species are present within the ejected material. The refractory organic material is believed to exist as a separate insoluble phase on the top of Enceladus' subsurface water surface within the ice vents and is also detected in the ice grains [2], both in the plume and the E ring. The volatile species, however, have only previously been detected in the gas phase of the plume [3]. In this work, we find certain volatile organic compounds (VOCs) are also present in the ice grains. Our results show that these VOCs are adsorbed onto the pre-existing ice grains in the ice vents. We suggest that these are low mass, hydrophilic, polar, organic compounds (e.g. carbonyls), which can exist dissolved in the depths of Enceladus' ocean, potentially acting as precursor compounds [4,5] for the hydrothermal synthesis of astrobiologically-relevant organic compounds.

## 1. Introduction

During the Cassini mission, two mass spectrometers onboard the spacecraft — the Cosmic Dust Analyzer (CDA) [6] and the Ion and Neutral Mass Spectrometer (INMS) [7] - frequently sampled Enceladus' subsurface ocean material. The INMS measured the composition of the gas component of the plume, whereas the CDA measured that of ice grains in both the E ring and the plume. These in situ compositional analyses revealed a multitude of organic species between the mass range 15 u —  $\geq 200$  u [2,3]. In the case of CDA, compositions of ice grains impacting its metal target plate at velocities between  $\sim 3.5$  and 20 km/s were measured, using impact ionization time of flight mass spectrometry. Upon impact the ice grains vaporized and partially ionized, forming an impact cloud of

electrons, anions, cations and neutral species. The instrument extracted and accelerated cations towards an ion detector, producing the mass spectra. During the Cassini mission, CDA produced tens of thousands of mass spectra from Enceladean ice grains. These spectra have been characterized into three major compositional types: Type 1, due to grains composed of almost pure water ice (65 % of the sampled population), Type 2 due to organic enriched grains (25 %) and Type 3 from salt-rich grains (10 %) [8].

Within the group of organic-enriched Type 2 ice grains Postberg et al. 2018a found complex organic material, characterized in CDA mass spectra by repetitive peak patterns of high mass organic cations (HMOC) beyond 80 u extending to masses  $> 200$  u. The study suggested that HMOC-type organics is a hydrophobic macromolecular material released from an insoluble organic layer at the top of the water surface within the Enceladean ice fractures. This material is dispersed above the water surface by the bursting of bubbles created by the upwelling and exsolution of volatile gases, and transported into space by entrainment in the emitted plume gases.

In contrast to the HMOC-type grains, which amount to about 5-10 % of all organic bearing grains, a larger fraction of Type 2 grains contains organic compounds with masses below 100 u [9]. The characterisation of these low mass organic compounds in the ice grains is the main focus of the work presented here.

## 2. Results and Discussion

We have further classified Type 2 spectra into subgroups. By performing laboratory experiments utilizing a laser desorption ion generation mechanism, known to accurately reproduce CDA ice grain spectra [10], features were identified as corresponding to

volatile organic compounds (VOCs) at the mmol concentration in the ice grains [9]. Our results show that these VOCs are N-bearing, O-bearing and aromatic-type compounds, characterized by  $\text{NH}_4^+$ ,  $\text{C}_2\text{H}_{3,5}\text{O}^+$ ,  $\text{C}_6\text{H}_{5,7}^+$  respectively. These compounds evaporate at 272 K and then adsorb at cooler temperatures onto pre-existing water ice grains within the cracks, as they approach the surface of Enceladus. VOCs that have binding energies  $\geq 0.7$  eV with water ice [11] are adsorbed onto the icy vent walls and ice grains detected by CDA, thereby reducing their abundance in the gas phase [3,11]. The VOCs in the ice grains are hydrophilic and polar, thus likely to be previously dissolved in the ocean, in contrast to the aromatic compounds with O- and N-bearing functional groups observed in HMOC type spectra. Some of these VOCs (such as carbonyls) are suitable precursor reactants [4,5] in Friedel-Crafts-type reactions that are known to be able to hydrothermally synthesize potentially biogenic organic compounds (e.g. tryptophan) [5]. In another reaction pathway under Enceladus' hydrothermal conditions, the low mass O-bearing compounds can undergo in the reduction and amination to synthesise amino acids (e.g. alanine) and carboxylic acids (e.g. lactic acid) [4].

We propose three parallel mechanisms of ice grain formation and growth to occur within Enceladus: (i) condensation of water vapour, (ii) spray from bubble bursting, and (iii) adsorption of VOCs onto pre-existing ice grains in the ice cracks of Enceladus' crust. The first two mechanisms have been described in previous work [8]: Type 1 grains are formed by the condensation of water vapour, whereas HMOC-containing salt-poor Type 2 and salt-rich Type 3 grains are formed from the spray created by the bursting of bubbles of upwelling gases. Here we find that Type 2 grains containing VOCs are formed when low mass polar VOCs are adsorbed onto pre-existing Type 1 grains. In principle, these VOCs may also be adsorbed on all types of pre-existing icy grains in the vents.

### 3. Summary and Conclusions

We have classified Type 2 spectra with low mass organic compounds into three sub-classes: N-bearing, O-bearing and Aromatic. The spectral features of these subtypes indicate that the identified compounds

are low mass, polar, hydrophilic and volatile in nature. The detection of O- and N-bearing species from Enceladus may be significant for prebiotic chemistry, with similar functional groups and chemical structures observed in biologically-relevant compounds from hydrothermal systems on Earth.

### Acknowledgements

The work was supported by the German Research Foundation (DFG) under projects PO 1015/2-1, /3-1, /4-1, a European Research Council (ERC) Consolidator Grant 724908-Habitat OASIS and the German Space Agency under DLR grant 50OH1501.

### References

- [1] Porco et al.: Cassini observes the active South Pole of Enceladus, *Science*, 5766, p. 1393-1401, 2006.
- [2] Postberg et al.: Macromolecular organic compounds from the depths of Enceladus, *Nature*, 558, p. 564-568, 2018a.
- [3] Waite et al.: Cassini finds molecular hydrogen in the Enceladus plume: Evidence for hydrothermal processes, *Science*, 356, p. 155-159, 2017.
- [4] Barge et al.: Redox and pH gradients drive amino acid synthesis in iron oxyhydroxide mineral systems, *PNAS*, 116 (11), p. 4828-4833, 2019.
- [5] Menez et al.: Abiotic synthesis of amino acids in the recesses of the oceanic lithosphere, *Nature*, 564, p. 59-63, 2018.
- [6] Srama et al.: The Cassini Cosmic Dust Analyzer, *Space Science Reviews*, 114(1-4), p. 465-518, 2004.
- [7] Waite et al.: The Cassini Ion and Neutral Mass Spectrometer (INMS) investigations, *Space Science Reviews*, 114, p. 113-231, 2005.
- [8] Postberg et al.: Plume and surface composition of Enceladus: Enceladus and the Icy Moons of Saturn, *Univ. of Arizona*, p. 129-162, 2018b.
- [9] Khawaja et al.: Low mass organic compounds in Enceladean ice grains, *MNRAS*, in review.
- [10] Klenner et al.: Analogue spectra for impact ionization mass spectra of water ice grains obtained at different impact speeds in space, *Rapid Communications in Mass Spectrometry*, in review.
- [11] Bouquet A., Glein C. R. and Waite J. H.: How adsorption affects the gas-ice partitioning of organics erupted from Enceladus, *The Astrophysical Journal*, 873 (1), 13, 2019.