Complex organic macromolecular compounds in ice grains from Enceladus. F. Postberg[1], N. Khawaja[1], S. Kempf[2], J.H. Waite[3], C. Glein[3], H.W. Hsu[2], R. Srama[4]. [1]Institute of Earth Sciences, University of Heidelberg, Germany, [2]Laboratory for Athmospheric and Space Physics, University of Colorado, USA [3]Southwest Research Institute, San Antonio, Texay, USA, [4]Institute of Space Systems, University of Stuttgart, Germany

Introduction: The mass spectrometers on board the Cassini spacecraft frequently carried out compositional in situ measurements in both the plume and the E ring. The Cosmic Dust Analyser (CDA) proved that a large fraction of the ice grains are direct samples of a subsurface alkaline ocean with mild salinity [1,2]. The CDA also found strong indications of hydrothermal activity at the interface of the moon's probably porous, rocky core and the ocean [3]. The detection of molecular hydrogen in the plume by the Ion and Neutral Mass Spectrometer (INMS) confirmed water mineral interaction and in addition indicated exothermic serpentinization reactions between rock and water [4] similar to the hydrothermal systems of Earth.

Previous CDA and INMS measurements showed that the plume emits organic material both in the gas phase [5] and in the ice grains [6]. In about 25% of the ice grains detected in the E ring, called Type 2 grains, organic compounds can be identified [1,6]. Here we present evidence that a small subgroup of these Type 2 grains contains highly complex organic material with molecular masses in excess of 200u.

Results: The CDA produces time-of-flight mass spectra of cations generated by high-velocity impacts of individual grains onto a metal target. Over 7000 individual E ring ice grain spectra were investigated. Within the group of organic bearing spectra (Type 2) we found a subgroup of 75 spectra with high mass organic cations (HMOC) characterized by a repetitive pattern of peaks above 80u (Fig. 1). Each of the spectra also exhibits water signatures, indicating a water ice / organic mixture as the bulk composition.

HMOC are always found with a number of aliphatic and aromatic mass lines, in particular a broad peak with a maximum at 77u – 79u indicative of the deprotonated (C_6H_5, 77u) and protonated (C_6H_7, 79u) forms of a benzene ring. Individual spectra show frequent evidence of O and/or N bearing cations at 30u - 31u and 43u – 45u respectively. Na^+ ions appear in most of the spectra but at a much lower level than in Type 3 spectra, that are defined by ≈ 1% of sodium and potassium salts that likely originate from frozen spray of Enceladus' salty ocean [1,2]. The Na/H_2O ratio inferred from HMOC spectra is generally below 10^{-5}, similar to the low abundance found in Type 1 particles [1]. Compared to other organic bearing particles spectra with HMOC exhibit a particularly high abundance of organic material in each ice grain and are indicative of an organic fraction on the percent level.

HMOC mass peaks are generally broad and often irregularly shaped, indicating that each of these signatures comprise multiple mass lines that cannot be resolved at the CDA mass resolution of (m/Δm) 30 - 40. In most cases HMOC occur up to the maximum mass covered by CDA at about 200u. The HMOC pattern in individual spectra exhibits a spacing of 11u to 14u indicatative of unsaturated cationic fragments with 7 to 15 carbon atoms (Fig. 1). It is highly likely that these are fragments of larger organic molecules outside the CDA's mass range. This conclusion is supported by the fact that the detection probability of ice grains with HMOC cation characteristics in the E ring is dependent on impact speed and increases from about 0.5% at 5 km/s to 3% at 10 - 12 km/s. Above 12 km/s no further increase is observed. Obviously the likelihood to produce characteristic cations inside the CDA mass range (approx. 1 – 200u), that allow indentification of an HMOC type spectrum, increases with the available kinetic energy. Fragmentation of organic parent species outside the CDA mass range are the most plausible explanation for this observation.
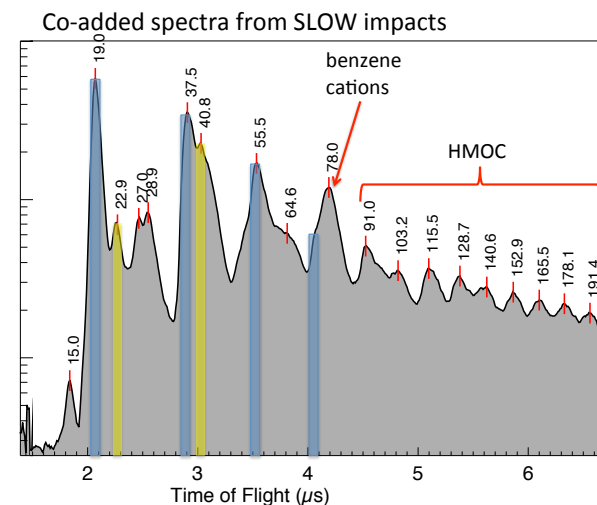

Fig. 1 *Co-added CDA cation spectra from 48 HMOC events with impact speeds below ≈ 10 km/s. Blue markers indicate water ice species, yellow markers indicate sodium and sodium-water cluster. The rest of the spectrum is mostly from a wide variety of organic fragment cations. The indicated cation masses have an uncertainty of about ±1u.*

A similar effect has been seen by Cassini's INMS. In integrated plume spectra a striking overabundance is observed of mostly organic species in spectra obtained

at high flyby speeds compared to those obtained at slower velocities [7]. High-speed impacts lead to fragmentation of large organic parent molecules beyond the INMS mass range of 99u. Only these high-speed INMS spectra show mass lines at 77u - 79u in full agreement with the CDA finding of aromatic species. Species with molecular masses above 99u in the plume do not exist in the gas phase at the given temperatures but likely stem from HMOC-type ice grains entering the INMS's aperture.

We conclude that the actual proportion of ice grains carrying abundant high mass organic species is about 3% in the E ring, indicated by the CDA spectra recorded at high impact speed. Only these events provide sufficient kinetic energy to efficiently fragment the bulk organic species with molecular masses well above 200u into cations identifiable by CDA and INMS. Mass spectrometers with an extended mass range would be able to characterize the HMOC parent molecules, preferably at speeds below 10 km/s.

During the only occasion where CDA recorded a large number of spectra with high cadence directly in the plume during Cassini's E5 flyby, the spectral range was truncated below about 100u. This unfortunately did not allow the identification of the defining HMOC signatures. During the E17 flyby, where CDA recorded about 40 plume spectra with its full mass range, one spectrum was of the HMOC type (see Poster by Khawaja et al., this conference), in agreement with a proportion of a few percent.

Discussion: We consider the observed complex, partially aromatic, substructures to be of Enceladus origin. An efficient photometric processing of initially simple organics trapped in the ice grains is highly unlikely: CDA observes many HMOC very close to Enceladus where most grains have been ejected from the plume only days or weeks ago and during the E17 flyby one HMOC was observed inside the plume. Moreover, INMS observes the coincident organic fragments in the plume. This raises the question as to whether these grains deliver chemical footprints from Enceladus subsurface ocean. The HMOC parent species with molecular masses larger than 200u cannot be in the gas phase at plausible physical conditions above the evaporating water table inside ice vents (T $\leq$ 0°C). The refractory organic material is observed mostly in salt poor ice grains and thus did not form from the salty ocean spray that preserves the liquid composition upon flash freezing [1]. From the low sodium concentrations in the HMOC grains we conclude that the bulk of the observed organic compounds are poorly dissolved in water and are likely hydrophobic.

The most plausible way to form HMOC grains is if the organic material exists as a separate phase, such as

a thin film of mostly refractory, poorly soluble organic species floating on top of the water table inside near-surface vents. When bubbles burst in such a scenario [1,8], they tear apart the organic film and, besides salty water droplets, throw up droplets or flakes of hydrophobic organic material. They would serve as efficient nucleation cores for ice condensation: droplets ascending in the icy vents will become coated by water ice condensing from the vapor carrying the grains.

The formation of aerosols from bubble bursting is a well-studied process in Earth's oceans, which are covered by an organic micro layer of mostly biogenic origin. There, an organic-free sea spray forms in parallel with an organic enriched sea spray and pure organic aerosols [e.g. 9]. Bubbles are not only responsible for producing an aerosol, they are also very efficient in 'harvesting' organic molecules from the oceanic environment during their ascent and accumulating them at the surface. The increase of relative organic concentrations observed in near surface ocean water [10] suggests a selective transport of organic matter from the bulk seawater to the water table and then from the microlayer to atmospheric aerosols [9,11].

On Enceladus the organic material originates from sites, possibly hydrothermal, at depth in the Enceladean ocean. It is likely that CDA and INMS only saw the hydrophobic insoluble portion of the putative organic film because it is easy to identify with the instrument's limited capabilities. Other valuable chemical footprints of Enceladus' organic chemistry buried in ice grains are already indicated in the CDA data in the large number of 'non-HMOC' Type 2 grains as well as in organic-bearing salty grains (not discussed here). HMOC mass spectra demonstrate that a space mission flying through the plume or the E ring can probe an amazingly complex organic chemistry emerging from Enceladus' subsurface. Cassini's instruments do not have the range or resolving power to determine if this material is of primordial, of hydrothermal, or even of biogenic origin. Future space missions with improved mass spectrometers [12] will have the unique opportunity to explore a rich organic chemistry occurring in the depths of Enceladus with surprisingly little effort.

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