UV photolysis of formaldehyde: Fractionation between the coma and surface composition of comets.

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Introduction:

Cometary organic matter: The organic component of comets is of great astrobiological importance. Cometary bodies escaped incorporation into larger planetesimals during the condensation of the interstellar disk which formed our solar system, and they are believed to have formed and spent much of their history further out than meteorites, beyond the ice line. Because of this, comets are believed to host the least altered and processed material in the solar system, preserving a primordial volatile organic fraction, that is elsewhere lost, and therefore may hold the key to understanding solar system formation. Comets have also been suggested to have 'seeded' the early Earth (and perhaps other planetary bodies) with the necessary ingredients to kick start the complex prebiotic chemistry which eventually led to the development of life (*1*).

Spectroscopic observations of organic matter: Much has been made about the relative abundances and isotope ratios of species detected in the coma of comets (and active asteroids) via spectroscopic (both remote, telescope, and in situ, orbiter) measurements as if they can be directly assigned to the composition and physical state of the nucleus itself (*2–4*). These assumed compositions have been used to infer constraints to models of formation of these primitive bodies, and by extension the solar system. However, little is known about the kinetics of the sublimation/degassing processes during the state change from the icy solid to the (detectable) volatile phase. Some correction must be necessary to back-calculate the original composition of the body due to fractionation processes – some species will partition preferentially into the vapor or stay in an undetectable (with current spectroscopic techniques) refractory solid phase. Simulation experiments on synthetic analogues with known compositions must therefore be carried out, as actual samples of comet return are rare (*5, 6*), so that the volatile phases degassing, under various interplanetary conditions, can be transcribed to the actual primary composition of the nucleus.

Formaldehyde as a model compound: Formaldehyde (CH_2O) is one of the simplest organic molecules. It is an excellent standard model compound for these experiments as both the monomer and its polymerized form $HO\text{-}(CH_2O)_n\text{-}H$, polyoxymethylene (POM), form readily in analogue experiments of interstellar and cometary ices (*7–9*). Formaldehyde and POM also appear to be ubiquitous in extraterrestrial samples, having been detected in interstellar space, through remote spectroscopic observations of the coma of comets and in directly sampled cometary and meteoritic material (*10*) with POM suggested to be a major constituent of comets (*11, 12*). Thermal polymerization reactions of formaldehyde have been explored as a potentially important formation mechanism for complex organic molecules in interstellar and cometary ice analogues at very low temperatures (*8, 9*) making this a molecule of great astrobiological importance in understanding prebiotic chemical evolution, and ultimately the emergence of life.

Effect of water: The productivity of the coma of comets (and of active meteorites) is greatest at or near their perihelion and this is also when most compositional observations are made. Modelling and flyby data have shown that surface temperatures of comets can reach the melting point of water at ≈ 1 Au (*13–15*) and so it is interesting to carry out experiments at increased temperatures and in the presence of liquid water. Increased temperatures will enhance the rate of reaction and, in liquid water, as opposed to solid water ice, organic molecules will be free to react rather than being isolated in frozen clathrates in hydrogen bonded lattices.

Experimental: We use the new Imperial College Impacts and Astromaterials Research Group's planetary environmental chamber (Fig 1) to simulate the exposure of the astrobiologically important organic molecule formaldehyde, CH_2O, to ultraviolet irradiation and liquid water in an inert atmosphere for periods ranging from 1 to 72 hours.

Volatile phases generated are drawn off using a TENAX® trap and analysed via thermal desorption - gas chromatography - mass spectrometry (TD-GC-MS) and isotope ratio - mass spectrometry (IR-MS) to analyse gas phase mixtures, volatile organic compound production and carbon and oxygen isotopes. The composition of water-soluble or insoluble organic residues left behind after the experiment are analysed by GC-MS and pyrolysis-GC-MS respectively.

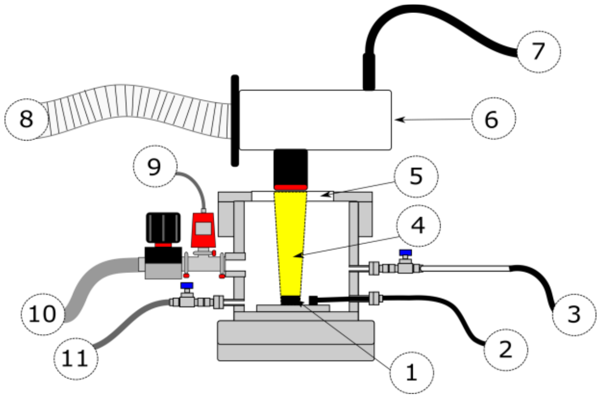

Figure 1: Schematic of the Imperial planetary Environmental Chamber (1) Irradiated sample; (2) UV monitoring fibre optic cable to spectrometer; (3) TENAX® thermal desorption tube and sampling pump for volatile organic compound sampling; (4) Focussed UV beam; (5) Fused silica window; (6) Xenon UV light source; (7) To Xenon UV light control module; (8) To ozone scrubber; (9) Vacuum/headspace gas monitoring pressure gauge; (10) To vacuum pump; (11) Headspace gas supply.

Importance: The results from these analogue experiments are directly comparable to observations of comets and active asteroids. This will allow for more informed speculation as to the surface composition, formation and alteration history of these primitive bodies, and, by extension, improve models of solar system formation.

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