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TITLE: Primary Volatile Abundances in Comets from Infrared Spectroscopy: Implications for Reactions on Grain Surfaces in the Interstellar/Nebular Environment

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Abstract Body: Comets retain relatively primitive icy material remaining from the epoch of Solar System formation, however the extent to which they are modified from their initial state remains a key question in cometary science. High-resolution IR spectroscopy has emerged as a powerful tool for measuring vibrational emissions from primary volatiles (i.e., those contained in the nuclei of comets). With modern instrumentation, most notably NIRSPEC at the Keck II 10-m telescope, we can quantify species of astrobiological importance (e.g., H2O, C2H2, CH4, C2H6, CO, H2CO, CH3OH, HCN, NH3). In space environments, compounds of keen interest to astrobiology could originate from HCN and NH3 (leading to amino acids), H2CO (leading to sugars), or C2H6 and CH4 (suggested precursors of ethyl- and methylamine). Measuring the abundances of these precursor molecules (and their variability among comets) is a feasible task that contributes to understanding their delivery to Earth's early biosphere and to the synthesis of more complex prebiotic compounds.

Over 20 comets have now been measured with IR spectroscopy, and this sample reveals significant diversity in primary volatile compositions. From this, a taxonomic classification scheme is emerging, presumably reflecting the diverse conditions experienced by pre-cometary grains in interstellar and subsequent nebular environs.

The importance of H-atom addition to C2H2 on the surfaces of interstellar grains to produce C2H6 was validated by the discovery of abundant ethane in comet C/1996 B2 (Hyakutake) with C2H6/CH4 well above that achievable by gas-phase chemistry [1], and then in irradiation experiments on laboratory ices at 10 – 50 K [2]. The large abundance ratios C2H6/CH4 observed universally in comets establish H-atom addition as an important and likely ubiquitous process, and comparing C2H6/C2H2 among comets can provide information on its efficiency. The IR is uniquely capable since symmetric hydrocarbons (e.g., C2H2, CH4, C2H6) have no electric dipole moment and thus no allowed pure rotational transitions.

CO should also be hydrogenated on grain surfaces. Irradiation experiments on interstellar ice analogs show this to require very low temperatures, the resulting yields of H2CO and CH3OH being highly dependent on temperature in the range ~10 – 25 K [3]. The relative abundances of these chemically-related molecules in comets provide one measure of the efficiency of H-atom addition to CO.

Oxidation of CO is also important on grain mantles, as evidenced by the widespread presence of CO2 ice towards interstellar sources observed with ISO [4] and in a survey of 17 comets observed with AKARI [5]. H-atom addition to C2H2 produces the vinyl radical, and through subsequent oxidation/reduction reactions can lead to vinyl alcohol, acetaldehyde, and ethanol [6, 7]. This may have implications for interpreting observed abundance ratios CO/C2H2.

We will discuss possible implications regarding formation conditions in the context of measured primary volatile compositions, emphasizing recently observed comets and published results. These are continually providing new insights regarding our taxonomic scheme and also delivery of pre-biological material to the young Earth.

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[1] Mumma etal 1996 Science 272:1310 [2] Hiraoka etal 2000 ApJ 532:1029 [3] Watanabe etal 2004 ApJ 616:638 [4] Ehrenfreund etal 1997 Icarus 130:1 [5] Ootsubo etal 2012. [6] Charnley 2004 Adv Sp Res 33:23. [7] Hiraoka etal 2000 ApJ 532:1029

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