Comets contain relatively well preserved icy material remaining from the epoch of Solar System formation, however the extent to which these ices are modified from their initial state remains a fundamental question in cometary science. As a comet approaches the Sun, sublimation of the ices contained in its nucleus (termed “native ices”) releases parent volatiles into the coma, where they can be measured spectroscopically.

One means of assessing the degree to which interstellar ices were processed prior to their incorporation into cometary nuclei is to measure the relative abundances of chemically-related parent volatiles. For example, formation of C$_2$H$_6$ by hydrogen atom addition (e.g., to C$_2$H$_3$) on surfaces of ice-mantled grains was proposed to explain the high C$_2$H$_6$/CH$_4$ abundance observed in C/1996 B2 (Hyakutake) [1]. The large C$_2$H$_6$/CH$_4$ abundance ratios measured universally in comets, compared with those predicted by gas phase production of C$_2$H$_6$, establishes H-atom addition as an important and likely ubiquitous process.

CO should also be hydrogenated on grain surfaces. Laboratory irradiation experiments on interstellar ice analogs indicate this to require very low temperatures (T $\sim$ 10-25 K), the resulting yields of H$_2$CO and CH$_3$OH being highly dependent both on hydrogen density (i.e., fluence) and on temperature ([2],[3]). This relatively narrow range in temperature reflects a lack of mobility below 8-10 K on the one hand, and reduced sticking times for H-atoms as grain surfaces are warmed above 20 K on the other. The relative abundances of these three chemically-related molecules in comets provides one measure of the efficiency of H-atom addition to CO on pre-cometary grains (Fig. 1).

Here, we compare the oxidation sequence of carbon in several comets observed with modern near-infrared echelle spectrometers, which favor the detection of native ices. We use our measured native abundances of CO, H$_2$CO, and CH$_3$OH (Fig. 1, top panel) to assess the efficiency of H-atom addition. Our results show their relative abundances to vary considerably among comets (Fig. 1, bottom panel), suggesting a range of conditions experienced by their nascent ices. Comparison with laboratory yields can provide information on conditions in the formative environment.

Fig. 1. A. Abundances (relative to H$_2$O) of oxidized carbon in several comets. Error bars show 1σ uncertainties, and upper limits (†) are 3σ. The small beams afforded by modern IR spectrometers favor detection of native ices. B. Corresponding CO conversion efficiencies. These are expressed in terms of the ratio ([H$_2$CO]+[CH$_3$OH])/([CO]+[H$_2$CO]+[CH$_3$OH]), where [] indicates mixing ratio (abundance relative to H$_2$O). This approach assumes that formaldehyde and methanol are produced solely from CO, and that they are the only products. It does not include potential loss of CO (e.g., in the subsequent proto-solar environment) or its incorporation into more complex entities (e.g., polymers such as polyoxymethylene, POM). Note that, by the above definition, for comets in which H$_2$CO was not measured (e.g., C/2006 M4), or for which only upper limits for H$_2$CO or CH$_3$OH were obtained (8P/Tuttle, C/2007 W1, C/2001 S4), the conversion efficiency could be higher than shown. Conversely, loss of CO by other means (such as incorporation into POM) would lower the efficiency.