

measured with high-resolution infrared spectroscopy is presented. Some trends are beginning to emerge when mixing ratios in individual comets are compared to average mixing ratios obtained for all species within the population. The variation in mixing ratios for all measured species is at least an order of magnitude. Overall, Jupiter-family comets are depleted in volatile species with respect to H₂O compared to long-period Oort cloud comets, with the most volatile species showing the greatest relative depletion. There is a high positive correlation between the mixing ratios of HCN, C₂H₆, and CH₄, whereas NH₃, H₂CO, and C₂H₂ are moderately correlated with each other but generally uncorrelated or show only weak correlation with other species. CO is generally uncorrelated with the other measured species possibly because it has the highest volatility and is therefore more susceptible to thermal evolutionary effects. Molecular mixing ratios for CH₃OH, HCN, C₂H₆, and CH₄ show an expected behavior with heliocentric distance suggesting a dominant ice source, whereas there is emerging evidence that the mixing ratios of NH₃, H₂CO, and C₂H₂ may increase at small heliocentric distances, suggesting the possibility of additional sources related to the thermal decomposition of organic dust. Although this provides information on the composition of the most volatile grains in comets, it presents an additional difficulty in classifying comet chemistry because most comets within this dataset were only observed over a limited range of heliocentric distance. Optical and infrared comparisons indicate that mixing ratios of daughter species and potential parents from cometary ices are sometimes but not always consistent with one another. This suggests that in many comets there are significant sources of C₂ and/or CN from grains, and that the importance of these sources is variable within the comet population.

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330.03 – Survey for Ortho-to-Para Abundance Ratios (OPRs) of NH₂ in Comets: Revisit to the Meaning of OPRs of Cometary Volatiles

Since molecules having identical protons can be classified into nuclear-spin isomers (e.g., ortho-H₂O and para-H₂O for water) and their inter-conversions by radiative and non-destructive collisional processes are believed to be very slow, the ortho-to-para abundance ratios (OPRs) of cometary volatiles such as H₂O, NH₃ and CH₄ in coma have been considered as primordial characters of cometary molecules [1]. Those ratios are usually interpreted as nuclear-spin temperatures although the real meaning of OPRs is in strong debate. Recent progress in laboratory studies about nuclear-spin conversion in gas- and solid-phases [2,3] revealed short-time nuclear-spin conversions for water, and we have to reconsider the interpretation for observed OPRs of cometary volatiles. We have already performed the survey for OPRs of NH₂ in more than 20 comets by large aperture telescopes with high-resolution spectrographs (UVES/VLT, HDS/Subaru, etc.) in the optical wavelength region [4]. The observed OPRs of ammonia estimated from OPRs of NH₂, cluster around ~1.1 (cf. 1.0 as a high-temperature limit), indicative of ~30 K as nuclear-spin temperatures. We present our latest results for OPRs of cometary NH₂ and discuss about the real meaning of OPRs of cometary ammonia, in relation to OPRs of water in cometary coma. Chemical processes in the inner coma may play an important role to achieve un-equilibrated OPRs of cometary volatiles in coma.

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330.04 – Beyond 3 AU from the Sun: “Hypervolatiles” in Distant Comets

Our understanding of inner coma composition in comets has long been biased towards heliocentric distances (R_h) smaller than 2-3 AU. However, observations far from the Sun are also of high value for better understanding the nucleus structure and outgassing of volatiles. Substantial and very important evidence for the activity of distant comets has been accumulated from photometry and analyses of light curves, but direct detections of primary (parent) volatiles are still rare. For example, comet C/2006 W3 (Christensen) remained outside 3.1 AU throughout its apparition, yet it presented the best opportunity since Hale-Bopp (1997) for detailed spectroscopic studies in a distant comet. C/2006 W3 was observed from several space- and ground-based facilities using both infrared and radio techniques. CO, CH₄, and C₂H₆ were measured via infrared spectroscopy at ESO-VLT at R_h = 3.25 AU. Production rates were found to exceed those measured for each of these species in most other comets, despite those comets being observed much closer to the Sun. With its relatively high CO/CO₂ ratio, C/2006 W3 also appears as an outlier in the AKARI comet survey of 18 comets. The detections of H₂O (Herschel Space Observatory) and CO (ESO-VLT) allow for constraining the coma abundance ratio H₂O/CO at R_h = 5 AU.

We will compare the C₂H₆/CH₄/CO ratios in C/2006 W3 with those in other comets spanning a large range in R_h: from D/2012 S1 ISON (~0.7 AU) to 29P/Schwassmann-Wachmann 1 (~ 6.3 AU). Notably in situ measurements by the Rosetta mission were performed in the coma of 67P/Churyumov-Gerasimenko, at a very similar heliocentric distance to C/2006 W3 (3.15 AU). While comparisons of column-integrated remote sensing measurements and abundances from in-situ mass spectrometry (as performed by the ROSINA instrument) are not straightforward, both types of measurement are of high value for constraining models of nucleus outgassing beyond 3 AU from the Sun, where the inferred nucleus structure and differences in volatility among nucleus ices are very important.

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330.05 – The OD/OH Isotope Ratio in Comets 8P/Tuttle and C/2012 F6 (Lemmon)

The determination of isotopic ratios in solar system objects is an important source of information about their origin, especially for