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Isotopic Ratios in Water and the Origin of Earth's Oceans

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Abstract

Comets contain some of the most pristine ice-rich material left over from the formation of the Solar System. Measurements of the D/H ratio in cometary water provide key constraints on the origin and thermal history of water, and the contribution of comets to Earth's oceans. Over the past 35 years, a dozen D/H measurements have been painstakingly gathered, using ground-based, suborbital, and space facilities. A significant isotopic diversity has been shown to exist, in both Oort-Cloud and Jupiter-Family comets. The recent discovery that hyperactive comets have a terrestrial D/H ratio in water has further renewed interest in cometary isotopic measurements. Measurement of the D/H ratio in a *statistically significant sample* of comets has been identified by the community as a high-priority goal for the next decade, important for understanding Earth's habitability and the distribution of volatile material during the Solar System's formation. In addition, measurements of the oxygen isotopic ratios in cometary water are of paramount importance for explaining the puzzling isotopic anomalies observed in meteorites and the solar wind.[†]

Comets and the Origin of Earth's Water

One of the key questions of modern planetary science concerns the development of the conditions of habitability in planetary systems, such as the early protosolar nebula. Water, an essential ingredient for carbon-based life as we know it (Westall 2018), is formed primarily via surface reactions in icy mantles of interstellar dust grains (the gas-phase chemistry only becomes efficient at temperatures above ~ 300 K). These grains subsequently find their way to dense protostellar cores and then into protoplanetary disks. They are partially reprocessed thermally in the inner disk, before being locked up in small bodies, such as comets or asteroids (van Dishoeck et al. 2014), although this aspect remains to be unequivocally confirmed by observations.

In the standard model of the protosolar nebula, the temperature in the terrestrial planet forming zone was too high for water ices to survive (O'Brien et al. 2018). The snow line separating the inner dry and outer wet part of the disk was outside of the terrestrial planet zone (see Figure 1). In this simple scenario, any water ice that might have been initially present in the inner disk

[†] The present white paper focuses on submillimeter/far-infrared spectroscopic remote-sensing measurements of isotopic ratios. A broader context is provided in the white paper by Miller et al.

Figure 1. Water content in the Solar System bodies at the time of Earth's growth as a function of heliocentric distance (from van Dishoeck et al. 2015, adapted from Morbidelli et al. 2012).

would have evaporated and escaped. Consequently, the Earth accreted dry and the present-day water would have been delivered in a later phase, together with organics, from external sources such as impacts of comets or asteroids (O'Brien et al. 2018).

Comets are small, icy bodies with radii less than 20 km that have formed and remained for most of their lifetimes at large heliocentric distances. They thus contain some of the least-processed, pristine ices from the solar nebula disk. Comets have often been described as “dirty snowballs”, following the model of Whipple (1950), in which the nucleus is visualized as a conglomerate of ices, such as water, ammonia, methane, carbon dioxide, and carbon monoxide, combined with meteoritic materials. Numerous complex molecules have been identified in comet 67P/Churyumov-Gerasimenko by *Rosetta*. The composition of cometary ices is in fact very similar to that of low-mass star-forming regions, suggesting synthesis in the pre-solar cloud or in the cold outskirts of the solar nebula (Drozdovskaya et al. 2018).

Dynamically, comets can be separated into two families: short-period, Jupiter-family comets and long-period comets. Short-period comets are thought to originate from the Kuiper belt, or the associated scattered disk, beyond the orbit of Neptune, while long-period comets formed in the Jupiter-Neptune region and were subsequently ejected into the Oort cloud by gravitational interactions with the giant planets. In reality, the picture is significantly more complex due to migration of the giant planets in the early solar system (Raymond et al. 2018). In fact, recent evidence suggests that the formation zones of the two families largely overlapped and extended over a broad range of heliocentric distances (Brasser et al. 2013). In addition, the Sun may have captured comets from other stars in its birth cluster (Levison et al. 2010). Consequently, there is increasing emphasis on classifying comets based on their chemical and isotopic composition rather than orbital dynamics (Mumma & Charnley 2011).

Deuterium-to-Hydrogen Ratio

Measurements of the D/H ratio in cometary water provide key constraints on the origin and thermal history of water molecules, and the contribution of comets to Earth's oceans. Deuterium was produced in the Big Bang, with an abundance of about 2.5×10^{-5} with respect to hydrogen (Cooke et al. 2014). The reference protosolar D/H ratio in hydrogen is 2.1×10^{-5} , close to the Big Bang value (Geiss et al. 1998). However, in the cold, dense, CO-depleted interstellar medium, deuterium atoms are sequestered in heavy molecules due to differences in zero-point vibrational energies (Ceccarelli et al. 2014).

Figure 2. D/H ratio in water in the solar system bodies and planetary materials (from the Origins Report). Cometary D/H ratios vary in both dynamical groups, Oort Cloud and Jupiter Family.

Consequently, the D/H ratio in heavy molecules may be enhanced by orders of magnitude, and doubly or even triply deuterated species have been detected in interstellar clouds (Lis et al. 2002; Parise et al. 2004). Deuteration in water is less extreme than in other molecules, with water D/H ratios of order $0.001\text{--}0.01$ typically measured in low-mass protostars similar to our Sun (Ceccarelli et al. 2014). This can be taken as the initial value for the protosolar nebula water. Subsequent isotopic exchanges between water molecules and molecular hydrogen in the warm inner disk will drive the ratio back toward the protosolar value (Drouart et al. 1999). The highest solar system D/H ratios in water, about 7.3×10^{-4} measured in LL3 matrix clays or R chondrites (Deloule et al. 1998; Alexander et al. 2012; McCanta et al. 2008), are in fact close to the interstellar medium values. The D/H ratio in Earth's ocean water, the Vienna Standard Mean Ocean Water (VSMOW), is significantly lower, $(1.5576 \pm 0.0001) \times 10^{-4}$, although still enhanced with respect to the protosolar ratio in hydrogen. How representative this value is for the bulk of Earth's water is a subject of discussion in the light of recent measurements of a low D/H ratio in deep mantle materials (Hallis et al. 2015). Currently, carbonaceous chondrites, in particular CI and CM types, appear to best match the terrestrial D/H ratio (Alexander et al. 2012).

The D/H ratio has been measured in a handful of Oort-Cloud comets, with typical values of about twice VSMOW (Bockelée-Morvan et al. 2015; Figure 2). *Herschel* provided first measurements of the D/H ratio in two Jupiter-Family comets, 103P/Hartley (Hartogh et al. 2011) and 45P/Honda-Mrkos-Pajdusáková (Lis et al. 2013), both consistent with VSMOW. A relatively high D/H ratio, three times VSMOW, was subsequently measured by *Rosetta* in another Jupiter-Family comet 67P/Churyumov-Gerasimenko (Altwegg et al. 2015). The VSMOW D/H value measured in the Oort-Cloud comet C/2014 Q2 (Lovejoy) suggests that the same isotopic diversity is present in the two comet families (Biver et al. 2016).

Although the statistics are limited, interesting trends are becoming apparent in the existing data. A striking anti-correlation is seen between the D/H ratio in water and the active fraction, defined as the ratio of the active surface area to the total nucleus surface (Figure 3; Lis et al. 2019). Hyperactive comets with high active fractions typically have D/H ratios in water **consistent with the terrestrial value**. These comets require an additional source of water vapor in their coma, explained by the presence of subliming icy grains expelled from the nucleus. The observed anti-correlation may suggest that hyperactive comets belong to a population of ice-rich objects that formed just outside the snow line or in the outermost regions of the solar nebula, from water thermally reprocessed in the inner disk that was transported outward during early disk evolution. However,

Figure 3. D/H ratio in water as a function of the active fraction of the nucleus. Hyperactive comets have terrestrial D/H ratios (from Lis et al. 2019).

based on a large comet sample, hyperactivity is only observed for small comet nuclei. This seems to argue against the first interpretation, as planetesimals near the snow line are expected to undergo rapid growth. Alternatively, isotopic properties of water outgassed from the nucleus and icy grains may be different due to fractionation effects at sublimation. In this case, many comets may share the same Earth-like D/H ratio in water, with profound implications for the early Solar System and the origin of the Earth's oceans. Increasing the number of D/H measurements in comets is thus a key goal for the future.

Oxygen Isotopic Ratios

Oxygen isotopic ratios with heavy element enrichments have long been detected in meteorites, where they exhibit mass-independent fractionation (slope 1 line in the oxygen three-isotope plot; Figure 4), while interstellar chemistry predicts a mass-dependent fractionation (slope 1/2 line). The origin of these puzzling anomalies is highly debated, but the only measurements are in the inner Solar System (e.g., the Earth, Mars, meteorites, and the Sun). Excluded are the objects with the highest water ice content by mass today and during the early formative stages of the Solar System: comets. Selective photodissociation of CO within the collapsing protosolar cloud in a stellar cluster with an enhanced radiation field is a proposed explanation for the enhanced abundances of ^{17}O and ^{18}O , which then freeze onto grains and form isotopically enriched water that is preserved in cometary ices (Lee et al. 2008). Rosetta measured $\text{H}_2^{16}\text{O}/\text{H}_2^{18}\text{O} = 445 \pm 35$ (1σ ; $\delta^{18}\text{O}=121$) in comet 67P. The $\text{H}_2^{16}\text{O}/\text{H}_2^{17}\text{O}$ ratio was difficult to measure directly, as the H_2^{17}O signal was too low in addition to being buried in the shoulder of the much brighter HDO peak; the estimated $^{16}\text{O}/^{17}\text{O}$ ratio was 2182 ± 170 (1σ ; $\delta^{17}\text{O}=206$; Schroeder et al. 2019).

A much higher measurement accuracy is required, which can be achieved using FIR rotational spectroscopy. This is possible, because multiple isotopic water lines can be observed simultaneously, mitigating systematic errors (pointing, calibration, time variability). Such observations could prove that cometary water follows the same mass-independent oxygen fractionation pattern seen in meteoritic materials, confirming that water was the main carrier of the Solar System oxygen.

Figure 4. Oxygen three-isotope plot showing representative compositions of major primary components of Solar System matter, the solar wind (SW), and preferred value for the Sun. It is customary to present the relationships among oxygen isotopes using per mil differences from standard mean ocean water (SMOW): $\delta O = 1000 \times ((^{i}\text{O}/^{16}\text{O}) / (^{i}\text{O}/^{16}\text{O})_{\text{SMOW}} - 1)$, where i refers to either 17 or 18. Data fall on a single mixing line characterized by excess (lower left) or depletions (upper right) of ^{16}O relative to the Earth and Moon samples. High-precision measurements in comets are lacking (from McKeegan et al. 2011).

Existing and Future Observational Capabilities

The current sample of D/H measurements in cometary water is small. While rotational transitions of HDO can be observed from the ground at submillimeter or infrared wavelengths, observations of water are extremely challenging, as the low-energy rotational transitions of water are not accessible even from sub-orbital platforms. Cometary water production rates are thus traditionally inferred indirectly from radio observations of its photodissociation product, OH, at 18 cm (Crovisier et al. 2002). While often the only measurement available, OH observations are not necessarily directly comparable to many other molecular line detections due to the extended distribution and other model dependent analysis. The first direct detection of gaseous water in comet 1P/Halley, through its v_3 vibrational band at 2.65 μm , was obtained using the KAO (Mumma et al. 1986). The 557 GHz transition of ortho-water was observed by SWAS (Neufeld et al. 2000) and *Odin* (Lecacheux et al. 2003), whereas *Herschel* provided first access to multiple rotational transitions of both ortho- and para-water (Hartogh et al. 2011).

The atmosphere at stratospheric altitudes is sufficiently transparent at the frequencies of low-energy transitions of H_2^{18}O . In particular, the 547 and 509 GHz $1_{10} - 1_{01}$ transitions of H_2^{18}O and HDO, previously observed in several comets by *Herschel*, are now accessible using the 4GREAT instrument on SOFIA, and can be used to accurately measure the D/H isotopic ratio (Lis et al. 2019). Given the sensitivity and operational constraints, SOFIA may significantly increase the number of D/H measurements during its lifetime. Such a sample, while significant, is still insufficient to answer unequivocally the questions posed here. Moreover, such measurements require assumptions about the $^{16}\text{O}/^{18}\text{O}$ isotopic ratio, which, however, has been shown to be relatively uniform in comets, 500 ± 50 , and close to the terrestrial ratio (Bockelée-Morvan et al. 2015).

ALMA now gives access to several (sub)millimeter HDO lines. For cometary observations, the most sensitive use of ALMA would be in the autocorrelation mode, as 50 independent single-dish antennas (Cordiner et al. 2019). Such an observing mode is not currently offered, but should become available in the future. In addition, simultaneous determinations of the water production rate using other techniques will be required to accurately measure the D/H ratio based on such observations, as the excited (sub)millimeter water lines that are accessible from the ground have been often shown to be masing in astrophysical environments.

The lowest rotational lines of water and its isotopologues, H_2^{18}O , H_2^{17}O , and HDO occur in the 600 μm wavelength range, and the emission lines from comets are extremely narrow, $\sim 1 \text{ km s}^{-1}$ FWHM. This makes a heterodyne system, capable of resolving the lines, ideal – comparable to previous measurements conducted with *Herschel*. These systems have the advantage that they do not require a cold telescope, and hence a relatively modest Discovery class mission can devote available budget to maximizing telescope collecting area, necessary to observe a statistically significant sample of comets as discussed here. Within anticipated budget cap, we envision a mission with a dedicated 4m class FIR telescope, diffraction limited up to about 200 μm , and a spectroscopic system covering the above lines and also the lowest transition of para- H_2O at 270 μm . This will allow measurement of the D/H ratio in about 50 comets over a 5-year mission lifetime, based on characteristics of known comets and an

assumed water production/visual magnitude correlation. In addition to answering the key question posed above, this mission will enable study of the D/H ratio during the entire water trail from the interstellar medium to habitable planets.

A large survey of comets in the far-infrared, with a high spectral resolution and broadband spectrometer covering H₂O, HDO, H₂¹⁸O, as well as *ortho* and *para* lines simultaneously would be ideal. Sensitivity will be the limiting factor in a survey towards 100s of targets due to the generally shorter observation windows typically accessible with such telescopes (due to constraints such as moving target rate of motion, field-of-regard, and peak flux from short-lived apparitions). In order to achieve this, an estimate sensitivity of $\sim 1 \times 10^{-20}$ Wm⁻² at 179 μ m with a spectral resolution $R > 10^4$ and a cooled aperture would enable D/H measurements in hundreds of comets. The *Origins* mission concept has prioritized such studies in its “Water Trail” science goal and estimates D/H measurements in comets down to ~ 0.1 times VSMOW (for typical apparitions) with those requirements. Detections towards the brighter objects should be followed-up with heterodyne observations, in which detailed line profile analysis can be conducted to better constrain the physical parameters of the volatiles.

Recommendations

To accurately measure the D/H ratio in comets, we need near-simultaneous observations of both water and HDO, ideally with the same instrument, in the same field of view. SOFIA, with its 4GREAT spectrometer, or possible future heterodyne instrumentation, now allows such measurements in moderately bright comets, such as comet 46P/Wirtanen in December 2018. This will result in measurements of D/H ratio in up to a dozen comets over SOFIA’s 15–20 years lifetime. However, a much larger sample, of order 100 comets, is needed to search for correlations with physical or orbital properties, to fully understand the underlying physics. Such measurements can only be carried out from space, with future far-infrared missions such as *Origins*, SPICA, or a dedicated Discovery-class spectroscopic mission, targeting low-energy lines of water isotopologues. This high-priority goal for the next decade must be achieved to fully understand Earth’s habitability. Moreover, in order to derive precise D/H ratios from the observations, accurate excitation models are needed. This requires, in particular, computation of collisional excitation rates of water by water and HDO by water, which will have to be combined with spatially-resolved studies of the coma temperature distribution at far-infrared/millimeter wavelengths. Accurate measurements of the oxygen isotopic ratios are also possible using FIR rotational spectroscopy and are an important objective for future missions.

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