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Ocean-like water in the Jupiter-family comet 103P/Hartley 2

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For decades, the source of Earth's volatiles, especially water with a deuterium-to-hydrogen ratio (D/H) of $(1.558 \pm 0.001) \times 10^{-4}$, has been a subject of debate. The similarity of Earth's bulk composition to that of meteorites known as enstatite chondrites[1] suggests a dry proto-Earth[2] with subsequent delivery of volatiles[3] by local accretion[4] or impacts of asteroids or comets[5,6]. Previous measurements in six comets from the Oort cloud yielded a mean D/H ratio of $(2.96 \pm 0.25) \times 10^{-4}$. The D/H value in carbonaceous chondrites, $(1.4 \pm 0.1) \times 10^{-4}$, together with dynamical simulations, led to models in which asteroids were the main source of Earth's water[7], with $\leq$10 per cent being delivered by comets. Here we report that the D/H ratio in the Jupiter-family comet 103P/Hartley 2, which originated in the Kuiper belt, is $(1.61 \pm 0.24) \times 10^{-4}$. This result substantially expands the reservoir of Earth ocean-like water to include some comets, and is consistent with the emerging picture of a complex dynamical evolution of the early Solar System[8,9].

On 17 November 2010, using the Herschel Space Observatory, we determined the D/H ratio in a comet from a reservoir other than the Oort cloud—103P/Hartley 2. Such Jupiter-family comets are believed to originate from the Kuiper belt, which exists beyond the orbits of the giant planets at radii between 30 and 50 astronomical units[10] (1 AU is the average Earth–Sun distance). In contrast, Oort-cloud comets are theorized to have originated from radii near the gas giants and to have been subsequently ejected to the Oort cloud (>5,000 AU)[11]. The Herschel measurement therefore traces the water D/H ratio in a new population of water-ice-rich bodies in the Solar System that are a potential source of water on the Earth.

To obtain an accurate determination of the D/H ratio in water, we carried out simultaneous observations of optically thin isotopic variants of water, specifically HDO and $H_2{}^{18}O$ (Fig. 1), as part of our Solar System observing programme[12]. This was critical for comet 103P/Hartley 2, whose activity and water outgassing rates exhibited significant short-term variations[13]. We used state-of-the-art excitation models to determine the HDO and $H_2{}^{18}O$ beam integrated column densities and production rates from the measured line intensities. Observation and modelling details are given in Supplementary Information. A critical point is that all observations sampled the same region of the coma, about 6,500 km in diameter.

The retrieved gas column densities and production rates are sensitive to collisional cross-sections, along with the density and temperature profiles of H_2O and electrons, and we thus considered a range of model parameters (Table 1). Although the production rates determined for the various model parameters differ slightly, the value of the D/H ratio is estimated to be $(1.61 \pm 0.24) \times 10^{-4}$. In our analysis, we assumed an $H_2{}^{16}O/H_2{}^{18}O$ ratio of 500 ± 50, a range that encompasses the Earth value and is consistent with previous measurements in cometary water[14] (see also Supplementary Information). The quoted 1σ uncertainty in the D/H ratio includes a 5% uncertainty related to modelling.

Our measured D/H value is substantially larger than that which characterized the young Sun (4.5 Gyr ago; the protosolar ratio), believed to be about 2.1×10^{-5}, which in turn is slightly higher than the value found in the local interstellar medium today (1.6×10^{-5}) and

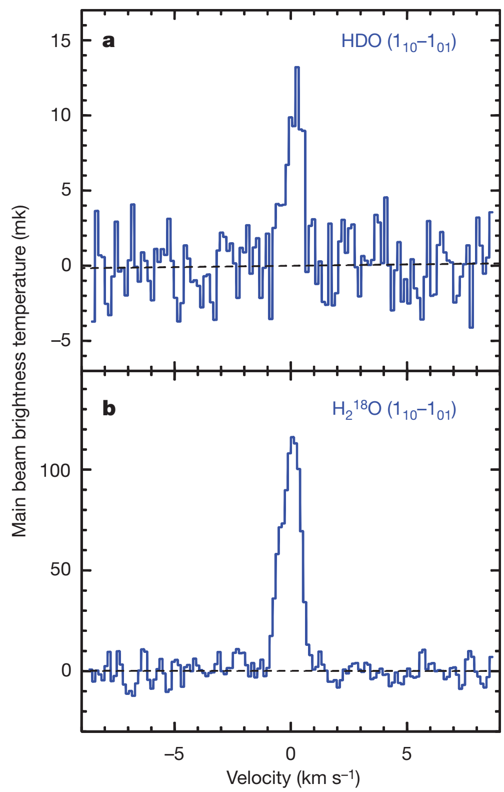

Figure 1 | Submillimetre water emission lines from comet 103P/Hartley 2. The time of the observations was 20 days after perihelion, when the comet was 1.095 AU from the Sun and 0.212 AU from Herschel. Because the H_2O ground state rotational lines in comets are optically thick[29,30], observations of the rare oxygen isotopic counterpart, $H_2{}^{18}O$, provide a more reliable reference for the D/H determination. The spectra of the 1_{10}–1_{01} lines of HDO (**a**) and $H_2{}^{18}O$ (**b**) at 509.292 and 547.676 GHz, respectively, were obtained with the Heterodyne Instrument for the Far Infrared (HIFI) High Resolution Spectrometer (HRS) between 17.28 and 17.64 November 2010 UT. The line intensities, expressed in the main-beam brightness temperature scale, are 0.011 ± 0.001 and 0.117 ± 0.002 K km s^{-1}, for HDO and $H_2{}^{18}O$ respectively, averaging the two instrument polarizations. The velocity scale is given relative to the velocity of the comet's nucleus. The spectral resolution is 141 and 132 m s^{-1} for the HDO and $H_2{}^{18}O$ spectra, respectively. For details of the observational sequence and basic parameters of the data analysis, see Supplementary information.

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Table 1 | Calculating the D/H ratio in water in comet 103P/Hartley 2

Model	T_{gas} (K)	x_{ne}	$<N(HDO)>$ (10^{10} cm^{-2})	$Q(HDO)$ (10^{24} s^{-1})	$<N(H_2{}^{18}O)>$ (10^{11} cm^{-2})	$Q(H_2{}^{18}O)$ (10^{25} s^{-1})	D/H
(1)	50	0.	4.9	3.1	3.5	2.1	1.49×10^{-4}
	50	0.2	3.6	2.3	2.5	1.5	1.55×10^{-4}
	70	0.2	3.7	2.4	2.5	1.5	1.60×10^{-4}
	Law	0.1	5.7	3.6	3.7	2.2	1.63×10^{-4}
(2)	50	0.2	4.3	2.7	2.9	1.8	1.54×10^{-4}
	Law	0.1	4.8	3.1	3.2	1.9	1.58×10^{-4}

The parameter x_{ne}, scaling the electron density profile in the models, is constrained by mapping observations. $<N>$ and Q are respectively beam integrated column density and production rate, determined using different parameters in the excitation models[14,29]. Production rates were computed assuming isotropic outflow of water from the nucleus, with a velocity of 0.6 km s^{-1}, consistent with the width of the $H_2{}^{18}O$ line. We accounted for the 10″ offset between the centre of the beam and the position of the peak of the H_2O distribution. Values of 50 and 70 K for the gas kinetic temperature, T_{gas}, are consistent with multi-transition measurements of gaseous species in the millimetre and near-infrared range, respectively. The gas kinetic temperature is expected to decrease with increasing distance owing to quasi-adiabatic expansion of the escaping gases: the temperature law assumes that $T_{gas} = 80$ K for $r < 270$ km, $T_{gas} = 12$ K for $r > 630$ km, with a linear decrease between 270 and 630 km, where r is the distance from the nucleus. Collision cross-sections involving water molecules and electrons are modelled differently in models (1) and (2). Both models use an electron density profile based on *in situ* measurements in comet 1P/Halley scaled to the activity of 103P/Hartley 2 (ref. 29). The D/H ratio is equal to $0.5 \times Q(HDO)/Q(H_2O)$, with $Q(H_2O) = 500 \times Q(H_2{}^{18}O)$. See Supplementary information for details of the models and model parameters.

comparable to the primordial D/H ratio in the Universe after the Big Bang (Fig. 2)[15]. Protosolar water, on the other hand, is believed to be highly enriched (D/H $\approx 1 \times 10^{-3}$)[16] due to the low-temperature (~10–30 K) non-equilibrium chemistry that characterizes the dense interstellar medium[17], either via gas-phase isotopic exchange reactions involving ions and radicals, or grain-surface processes. Consequently, the resulting D/H ratio in water ice is very sensitive to the physical conditions, in particular the kinetic temperature of the medium. After the protosolar cloud collapsed to form the solar nebula, isotopic exchange reactions between molecular hydrogen and HDO molecules would have led to a gradual reduction of D/H in water[18], as compared to the initial interstellar medium value. Because the efficiency of these reactions and the turbulent mixing within the solar nebula is correlated with the gas density and temperature, the deuterium enhancement in water has been predicted to increase with the heliocentric distance[19–21]. Ices, captured by planetesimals and cometesimals, would have then preserved the deuterium enrichment in water from this early epoch. As a result, small Solar System bodies are expected to exhibit different D/H ratios in their water ice depending on the distance from the Sun at which they were formed.

In the context of this simple nebular model, the D/H ratio of $(1.61 \pm 0.24) \times 10^{-4}$ in comet 103P/Hartley 2—a factor of two lower than that measured in Oort-cloud comets (Fig. 2) and, within uncertainties, consistent with that of the Earth's oceans (for which the Vienna Standard Mean Ocean Water (VSMOW) value is $(1.558 \pm 0.001) \times 10^{-4}$)—is therefore surprising, and compatible with two different schemes: (1) either this comet did not form in a region that was further from the Sun than the assembly zone of the Oort-cloud comets, or (2) the dependence of the water D/H ratio with distance from the Sun is not as expected on the basis of current models. Concerning the first possibility, dynamical models indeed suggest that a fraction of the Jupiter-family comets originate in the Oort cloud[22]. Still, even if comet 103P/Hartley 2 stems from the Oort cloud, this would not explain why its D/H ratio is different from that seen in other Oort-cloud comets. Models also suggest that a fraction of the Jupiter-family comets may have originated from the Trojan asteroid swarms sharing the orbit of Jupiter[23]. The Trojans are generally thought to have resided at their current location since the formation of the Solar System. Therefore, Jupiter family comets originating in the Trojan region could, in theory, display deuterium enrichment values lower than those for bodies originating in the Kuiper belt, if they indeed formed in the vicinity of Jupiter. However, the most probable scenario is that 103P/Hartley 2 originated in the Kuiper belt.

It is difficult to explain the low D/H ratio in 103P/Hartley 2 (compared to that of previous measurements in comets) with the formation regions of comets, thus models of the gradient of D/H in the Solar System—predictions not yet directly confirmed by observations, owing to scarcity of accurate isotopic measurements—may need to be revisited. In fact, one recent model has suggested that the D/H ratio of water vapour can be locally enhanced[24]. However, the vapour must then be implanted into cometary ices. Moreover, until the measurement of 103P/Hartley 2 there was no observational confirmation of variations in the D/H ratio. One possible solution is that there was large-scale movement of material between the inner and outer Solar

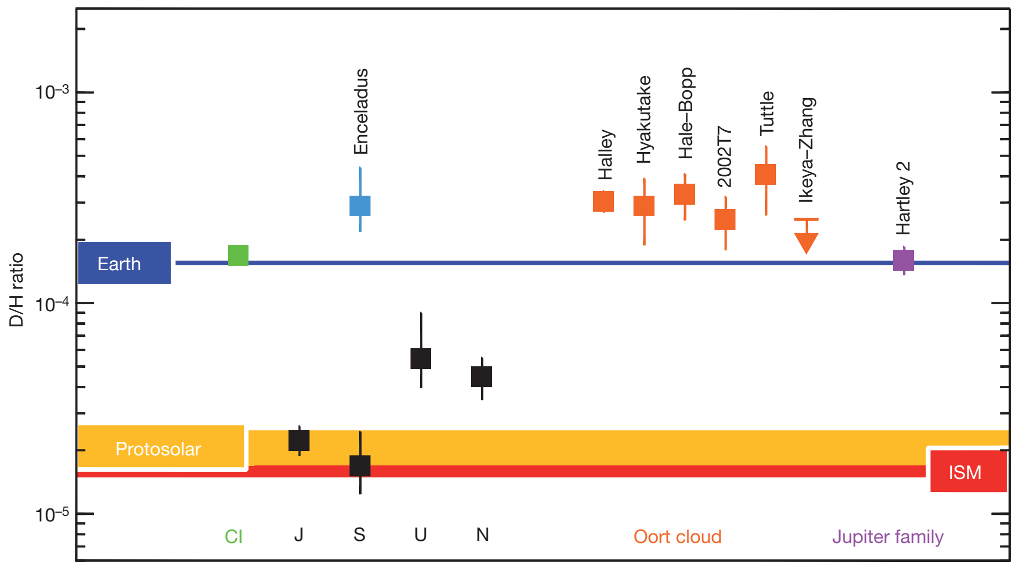

Figure 2 | D/H ratios in the Solar System. Orange squares, values measured for water in the Oort-cloud comets 1P/Halley, C/1996 B2 (Hyakutake), C/1995 O1 (Hale–Bopp), C/2002 T7 (LINEAR) and 8P/Tuttle. Arrow (for 153P/Ikeya–Zhang), upper limit. Purple square, present measurement in the water of 103P/Hartley 2. Black symbols, D/H ratio in H_2 in the atmosphere of the giant planets—Jupiter (J), Saturn (S), Uranus (U) and Neptune (N). Light blue and green symbols, D/H values for water in the plume of Saturn's moon Enceladus and in CI carbonaceous chondrites, respectively. Error bars, 1σ. The D/H determinations in comets originating from the Oort cloud are twice the value for the Earth's ocean (blue line) and about a factor of ten larger than the protosolar value in H_2 (broad yellow line), the latter being comparable to the value in atomic hydrogen found in the local interstellar medium (ISM, red horizontal line). The D/H ratio in the Jupiter-family comet 103P/Hartley 2 is the same as the Earth's ocean value and the chondritic CI value. Uranus and Neptune have been enriched in deuterium by the mixing of their atmospheres with D-rich protoplanetary ices. For further details, see Supplementary Table 1.

System. According to a recent theory proposed for the early Solar System (the Grand Tack scenario), when the giant planets were still embedded in the nebular gas disk, there was a general radial mixing of the distribution of comets and asteroids born in different regions[25]. The similarity of the D/H ratio in comet 103P/Hartley 2, which probes the Kuiper belt, with that found in CI chondrites tracing the asteroid belt, would be in agreement with a general shake-up of the Solar System at early times.

In more 'orderly' models, the high D/H values derived from the earlier observations of Oort-cloud comets suggested that at most 10% of the Earth's water could have been supplied from the outermost Solar System, but even under these circumstances a number of scenarios have been developed suggesting that terrestrial water could have in fact been delivered by comets. Such models are based on assumptions about the heliocentric D/H gradient[26], and the analysis of lunar samples[27] and telluric sedimentary rocks formed at the end of the Late Heavy Bombardment phase[28]. Our Herschel observations of a VSMOW-like D/H ratio in 103P/Hartley 2 enlarge the region of the solar nebula known to have a D/H ratio similar to that of Earth's oceans; this region now includes both the asteroid belt and the much larger Kuiper belt, thereby providing support for the theory of a common water source for the inner Solar System bodies (including the Earth) in which comets play an important part.

Further constraints on the delivery of volatiles to the early Earth and an improved understanding of the origin of the different dynamical classes of comets will require significantly larger sample sizes than those at present available. A handful of additional measurements can be expected from Herschel before its cryogen supply is exhausted, but the comparison of D/H ratios in the inner and outer Solar System must necessarily utilize very different objects and materials. For the inner Solar System, *in situ* space missions or sample return missions to the outer asteroid belt would provide critical new data. Astronomically, the minuscule strength of HDO spectroscopic signatures makes D/H measurements extremely challenging, and dedicated programmes using new facilities will be required to substantially increase the inventory of high-precision D/H ratios in comets and other icy Solar System bodies, including the Jovian satellites.

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Supplementary Information is linked to the online version of the paper at www.nature.com/nature.

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1. Herschel Observations

The observations of comet 103P/Hartley 2 were carried out using the HIFI[31] instrument aboard the *Herschel Space Observatory*[32]. The observational sequence consisted of ten 32-min long observations of the HDO 1_{10}–1_{01} rotational line at 509.292 GHz, interleaved with simultaneous 6-min measurements of the H_2O and $H_2^{18}O$ 1_{10}–1_{01} lines at 556.936 and 547.676 GHz, respectively. The H_2O and $H_2^{18}O$ lines were observed in the upper and lower sideband of the HIFI band 1a receiver, respectively, tuned to a local oscillator (LO) frequency of 551.88 GHz. The HDO line was observed in the lower sideband of the band 1a receiver, with the LO frequency tuned to 514.092 GHz. In addition to these single point measurements, five on-the-fly maps of the H_2O 1_{10}–1_{01} transition, of 16-min duration, were acquired. All lines were observed in the two orthogonal HIFI polarizations. To achieve cancellation of the instrumental background, the HDO and $H_2O/H_2^{18}O$ single point observations were carried out in the frequency-switching observing mode, with a frequency throw of 94.5 MHz. Spectra were acquired with both the Wideband Spectrometer (WBS) and High Resolution Spectrometer (HRS), which provide spectral resolutions of 1.1 MHz and 140 kHz, respectively. The telescope beam sizes at the frequencies of the three lines are very similar (half power beam widths of 38.1″, 38.7″ and 41.6″ for the H_2O, $H_2^{18}O$, and HDO lines, respectively), so that the three molecules were observed in the same, ~6500 km diameter, region of the coma.

H_2O maps were used to place these single point measurements into context, by allowing a check of the telescope pointing accuracy and enabling an investigation of the morphology of the coma. In all maps, the H_2O 1_{10}–1_{01} line peaks approximately 10″ westward of the tracked nucleus position, toward the tail direction. The comet was tracked using an up-to-date ephemeris provided by the JPL Horizons system and the Herschel r.m.s. pointing accuracy is approximately 1″. Therefore, the excess emission westward of the nucleus, also observed in early November 2010 with the PACS and SPIRE instruments aboard Herschel, is likely explained by an asymmetric distribution of water molecules that may be related to a production from large icy grains accelerated in the anti-solar direction by non-gravitational forces[13].

2. HDO and $H_2^{18}O$ excitation models

The excitation models used in the interpretation of the data include collisions with H_2O and electrons, which dominate the excitation in the inner coma, as well as solar infrared pumping of vibrational bands followed by spontaneous decay, which establishes fluorescence equilibrium in the outer coma. Self-absorption effects are insignificant for HDO and $H_2^{18}O$ lines, except in the very inner coma, unresolved by the HIFI beam. The observed 1_{10}–1_{01} HDO and $H_2^{18}O$ transitions are optically thin. For $H_2^{18}O$, we used the same solar pumping rates as determined for the $H_2^{16}O$ isotopologue[29]. Solar excitation of HDO was modelled including excitation by collisions and absorption of the solar IR radiation[35]. With a beam diameter of ~6500 km projected on the comet, the HIFI measurements mostly sample molecules with an excitation state intermediate between Local Thermal Equilibrium (LTE) and fluorescence equilibrium. Hence their level populations depend on collisional rates involving water and electrons, as well as on the gas kinetic temperature. We used two approaches to model the collisional excitation. In model (1), water-water collisional cross-sections are modelled following commonly accepted methods[45] and water-electron cross-sections are derived from Itikawa's formulae[46]. The same model was used to interpret submillimetre HDO observations in comets C/1996 B2 (Hyakutake)[35] and C/1995 O1 (Hale-Bopp)[36]. Model (2) uses water-water and water-electron cross-sections according to[47,48,49]. Both models use electron density and temperature profiles based on in situ measurements in comet 1P/Halley, scaled to the activity of 103P/Hartley 2 at the time of the observations[49]. A scaling factor x_{ne} is further applied to the electron density. A value $x_{ne} = 0.2$ best fits the brightness radial profiles of the 557 GHz line observed in comets[50,51]. The distribution of water density is represented by the standard Haser distribution, which assumes isotropic outgassing at constant velocity. The water production rate in the calculations is taken equal to 1×10^{28} s^{-1}. We assumed an ortho-to-para ratio of 2.8 in the $H_2^{18}O$ model, consistent with infrared measurements[52,53] of comet 103P/Hartley 2.

3. Gas kinetic temperature

Constraints on the gas kinetic temperature in comet 103P/Hartley 2 at or near the time of the HIFI measurements are available. The rotational temperature of H_2O and other molecules was determined from ro-vibrational emission lines observed in the near-infrared at scales of 0.5–2″ (100–300 km at the distance of the comet)[53,54]. Values range from 70 to 85 K. In contrast, a gas kinetic temperature of 50 K is inferred from millimetre observations of methanol lines that probe outer regions of the coma (N. Biver, personal communication). A decrease of the gas kinetic temperature with increasing distance from the nucleus is consistent with a quasi-adiabatic expansion of cometary gases.

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Supplementary Table S1: D/H ratios in the solar system

Object	Species	D/H $\times 10^{-4}$	Reference
Earth (VSMOW)	H_2O	1.558 ± 0.001	33
103P/Hartley 2	H_2O	1.61 ± 0.24	this work
1P/Halley	H_2O	3.06 ± 0.34	34
C/1996 B2 (Hyakutake)	H_2O	2.90 ± 1.00	35
C/1995 O1 (Hale-Bopp)	H_2O	3.3 ± 0.8	36
153P/Ikeya-Zhang	H_2O	< 2.50	37
C/2002 T7 (LINEAR)	H_2O	2.5 ± 0.7	38
8P/Tuttle	H_2O	4.09 ± 1.45	39
Enceladus	H_2O	$2.5^{+1.5}_{-0.7}$	40
CI chondrites	H_2O	1.70 ± 0.10	41
Protosolar	H_2	0.21 ± 0.04	15
Interstellar medium	H	0.16 ± 0.01	15
Jupiter	H_2	0.225 ± 0.035	42
Saturn	H_2	$0.17^{+0.075}_{-0.045}$	42
Uranus	H_2	$0.55^{+0.35}_{-0.15}$	43
Neptune	H_2	0.45 ± 0.1	44

Compilation of the D/H ratios in the solar system following Figure 1: name of the object, species from which the D/H ratio was determined, D/H ratio with the corresponding uncertainty, reference to the measurement.