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67P/Churyumov-Gerasimenko, a Jupiter family comet with a high D/H ratio

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The provenance of water and organic compounds on the Earth and other terrestrial planets has been discussed for a long time without reaching a consensus. One of the best means to distinguish between different scenarios is by determining the D/H ratios in the reservoirs for comets and the Earth's oceans. Here we report the direct in situ measurement of the D/H ratio in the Jupiter family comet 67P/Churyumov-Gerasimenko by the ROSINA mass spectrometer aboard ESA's Rosetta spacecraft, which is found to be (5.3 ± 0.7) × 10⁻⁴, that is, ~3 times the terrestrial value. Previous cometary measurements and our new finding suggest a wide range of D/H ratios in the water within Jupiter family objects and preclude the idea that this reservoir is solely composed of Earth ocean-like water.

The delivery of water and organic compounds to the Earth and other terrestrial planets is still under debate (*1*–*4*). Existing scenarios range from negligible (*1*, *2*) to significant (*3*, *4*) cometary contributions to terrestrial water. Hence, the comparison of the deuterium-to-hydrogen ratio (D/H) in water between the different populations of comets and the Earth's oceans is crucial if one wants to distinguish among these scenarios. Previous D/H measurements have been made for a dozen comets from the Oort cloud and the Jupiter family (e.g., (*5*) and refs therein). So far, only one measurement has been made in situ, in the coma of the Oort-cloud comet 1P/Halley, via the mass spectrometers present aboard the ESA Giotto spacecraft, and based on an assumption made on the oxygen isotopic composition (*6*, *7*). Here we report the direct in situ measurement of the D/H ratio in the Jupiter family comet 67P/Churyumov-Gerasimenko.

The mass spectrometer ROSINA-DFMS (Rosetta Orbiter Sensor for Ion and Neutral Analysis, Double Focusing Mass Spectrometer) on the European cometary space mission Rosetta is designed to measure isotopic ratios (*8*). Its mass resolution and high dynamic range enable it to detect very rare species such as $HD^{18}O$ relative to the most abundant isotope $H_2{}^{16}O$ (*9*). ROSINA has the capability to measure all isotopic ratios in water independently (D/H, $^{17}O/^{16}O$, $^{18}O/^{16}O$) and the D/H ratio can be deduced from two different species, namely $HD^{16}O/H_2{}^{16}O$ and $HD^{18}O/H_2{}^{18}O$.

Rosetta has a neutral gaseous background due to spacecraft outgassing. The permanent particle density in the close vicinity of the spacecraft far away from the comet is around 10^6 / cm^3 consisting mostly of water, but also of organic material, fragments of hydrazine and vacuum grease (fluorine). Even after 10 years in space and after hibernation the background from Rosetta can be measured and characterized by ROSINA (*10*). The D/H ratio in water outgassed from the Rosetta spacecraft is compatible with the terrestrial value of 1.5×10^{-4}, as expected (*9*), and did not vary with time of degassing, indicating negligible isotope fractionation. These observations demonstrate the capability of DFMS and of the analysis method. On August 1, 2014, Rosetta was within 1000 km from comet 67P/Churuymov/Gerasimenko at 3.6 AU from the Sun, and the coma was still hidden beneath the spacecraft background for in situ measurements. However, a few days later, it approached the comet to within 100 km. The factor of 100 larger densities at this distance surpassed the spacecraft background by more than a factor of 2; the difference between background (May 26) and coma (Aug. 22) at mass 19 Da is evident (Fig. 1). There are four peaks on mass 19 Da: fluorine, which is due to background (vacuum grease) from the spacecraft (*10*), $H^{18}O$, a fragment from $H_2{}^{18}O$ due to electron impact ionization in the instrument and a minor contribution from photodissociation of water in the coma, $H_2{}^{17}O$ and $HD^{16}O$. All mass peaks have the same shape. $H_2{}^{17}O$ is hidden in the shoulder of the much larger peak of HDO. As the positions of the masses are known the only fit parameters remaining are the amplitudes. In this way $H_2{}^{17}O$ can clearly be separated from $HD^{16}O$.

Before August 5 all four species had a very similar intensity. However, on Aug. 8 the intensity of $HD^{16}O$ was more than double the height of the ^{18}OH peak, while fluorine stayed constant. This can only be attributed to a much higher D/H ratio in water. By August 22, the background was almost negligible as the spacecraft was now within 50 km from the nucleus. However, the signal on mass 21 ($HD^{18}O$) was still very low. Water peaks on mass 18 and 19 Da were therefore analyzed using more than 50 spectra taken between Aug. 08 and Sep. 05, leading to a derivation of D/H from $HD^{16}O/H_2{}^{16}O$ [analysis is described in (*9*)].Uncertainties of the measurements are carefully estimated by error propagation, taking into account statistical uncertainties in the measured signal and uncertainties originating from calibration, background subtraction and fitting methods. The biggest contribution is probably the uncertainty for the background as Rosetta is now permanently in the cometary coma and background corrections have to be done with data from before August 2014. Analysis of the spacecraft background over the 10 years of the cruise phase, however, has shown that for a stable spacecraft attitude the background remains stable over very long times outside of reaction wheel offloadings (*10*). The value derived from our analysis for D/H is $(5.3 \pm 0.7) \times 10^{-4}$ (2 sigma error, where sigma is the standard deviation as described above).

By deriving HDO relative to $H_2{}^{16}O$, we also find the $^{17}O/^{16}O$ ratio. Additionally, the ratio of $^{18}O/^{16}O$ follows from the analysis of m/z = 20 Da, which contains 2 well separated peaks: $H_2{}^{18}O$ (20.0148 Da) and HF (20.0062 Da) (Fig. 2). HF is almost entirely due to spacecraft background. The results for the oxygen isotopic ratios in cometary water are compatible with solar system values with $^{17}O/^{16}O = (3.7 \pm 0.9) \times 10^{-4}$ and $^{18}O/^{16}O = (1.8 \pm 0.2) \times 10^{-3}$. Although from the figure one might see a small modulation for the ratios as a function of rotation of the comet, statistics are too poor to come to a conclusion. Once the comet activity increases it should be feasible to narrow down the values for the heavy isotopes of water.

The D/H ratio shows dramatic variations among solar system reservoirs of water (Fig. 3). The protosolar nebula (PSN) D/H value is estimated to be $(2.1 \pm 0.5) \times 10^{-5}$ based on measurements of H_2 in the atmosphere of Jupiter (*11*) and (^{3}He+D)/H in the solar photosphere (*12*). This value is close to interstellar D/H ratios of H_2 around $(2.0\text{-}2.3) \times 10^{-5}$ (*13*). In contrast, most solar system objects are enriched in deuterium (Fig. 3), with an enrichment factor f (defined as the ratio $[D/H]_{object}/[D/H]_{PSN}$) averaging 6 for the inner solar system (including the Earth, the Moon and volatile-rich primitive meteorites, e.g., carbonaceous chondrites). Comets analyzed so far, mostly long period ones, display higher f values, typically in the 10-20 range. The cause of the deuterium enrichment in solar system bodies is usually attributed to water-ice rich in deuterium infalling from the presolar cloud onto the nebula disk (*5*). Thereafter, because comets may have accreted ice with various chemical histories (*14*), several mechanisms have been proposed that would induce a deuterium fractionation in the early PSN. Because a part of the ice accreted by comets could have vaporized and recondensed within the PSN, an isotopic exchange could have occurred between the initially deuterium-rich water and molecular hydrogen in the warm regions of the disk (*15*). At low temperatures, this reaction favors the concentration of deuterium in HDO, but the extremely slow kinetics tend to inhibit the reaction. In these models, isotopic exchange occurs as long as H_2O does not crystallize, implying that the observed D/H ratios should be representative of the local values where and when the building blocks of the host objects condensed (*16*). Alternatively, a part of the ice accreted by comets could have remained pristine (*14*). Under these circumstances, gas-grain reactions could have induced deuterium fractionation in the cold outer part of the PSN (*17*, *18*). Regardless of the fractionation mechanism, all these models are consistent with a deuterium enrichment profile following a radial increase throughout the PSN from low values close to the Sun to high values in the outer part of the disk (*16*–*18*).

Most D/H ratio measurements in water in comets come from long period comets, presumably originating from the Oort cloud (Oort Cloud Comets; OCCs). Population of this cometary reservoir is attributed to the scattering of icy bodies originally located in the Uranus-Neptune formation region between ~10 and 15 AU in the PSN (*19*), although a non-solar, external origin for a large fraction of OCCs has been recently proposed (*20*). In contrast, JFCs are expected to have formed in the Kuiper belt region beyond Neptune (*21*). Deuterium-to-hydrogen ratios of OCCs, analyzed either in situ by mass spectrometry in the case of Comet Halley (*6*, *7*) or by spectroscopy (*5*) show a range varying from ~1.3 to 2.9 times the terrestrial value (f ~9.8-21.9) (Fig. 3). In addition, the D/H ratio was found to be similar to the Comet Halley in in situ measurements in the water plume of Saturn's satellite Enceladus (*22*). These values support the predicted D/H radial increase with distance from the Sun and the origin of OCCs from a common, localized region of the disk (*16*–*18*).

Recent D/H measurements in water in the two JFCs analyzed so far, namely $(1.61 \pm 0.24) \times 10^{-4}$ (f ~ 7.8) for 103P/Hartley 2 (*23*) and an upper limit of 2.0×10^{-4} (f < 9.5) for 45P/Honda–Mrkos–Pajdušáková (*5*) contradict this view. The hydrogen isotope composition of 103P/Hartley 2 is closer to the terrestrial value than the OCCs average, reviving the possibility of a cometary, rather than asteroidal, origin for the oceans. These data lead to two possible conclusions: either JFCs originate from the Kuiper Belt and the chemical models developed so far (*16*–*18*) are not representative, or these comets formed over a wide range of heliocentric distances in the outer part of the PSN. With regard to the first possibility, a recent chemical model leading to a non-monotonic *f* profile throughout the PSN (*24*) matches these observations if the JFCs were formed in the Kuiper Belt (*21*). In contrast with previous PSN models evolving as closed systems, this model assumes that the disk continues to be fed by material infalling from the presolar cloud. Alternatively, it has been proposed that JFCs and OCCs could originate from the same extended outer region of the PSN (*25*), such that 103P/Hartley 2 and 45P/Honda–Mrkos–Pajdušáková (45P/HMP) may simply have formed in the inner part of this common reservoir. In this case, the range of D/H ratios measured in JFCs should be similar to the one found in OCCs, as suggested by observations.

The new D/H value of $(5.3 \pm 0.7) \times 10^{-4}$ ($f \sim 25.2$) from comet 67P/Churyumov-Gerasimenko is not consistent with previous JFC data, and is even higher than values characteristic of OCCs (~30-120% higher than that of Comet Halley). In contrast to previous JFCs measurements, this estimate matches models predicting a monotonic radial increase of the enrichment profile (*16*–*18*). From the ROSINA measurements on comet 67P/Churyumov-Gerasimenko, we conclude that the D/H values of JFCs may be highly heterogeneous, possibly reflecting the diverse origins of JFCs. If this is the case, then the new measurement supports models advocating an asteroidal (i.e., carbonaceous chondrite-like), rather than cometary origin for the oceans, and by extension for the terrestrial atmosphere (*1*, *2*).

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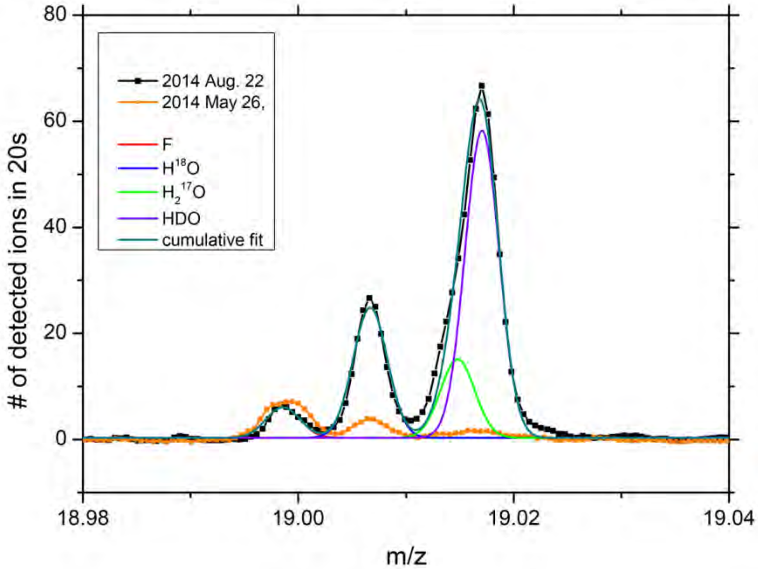

Fig. 1. Typical mass/charge 19 Da/e spectra from DFMS data are shown for 2014 May 26, when the spacecraft was at 800000 km and for August 22, with the spacecraft at 60 km from the nucleus. The integration time was 20 s. The number of ions detected are plotted as a function of mass/charge. The peak fits for Aug. 26 are also shown for fluorine (F), $H^{18}O$, $H_2{}^{17}O$ and HDO using the same peak width for all species.

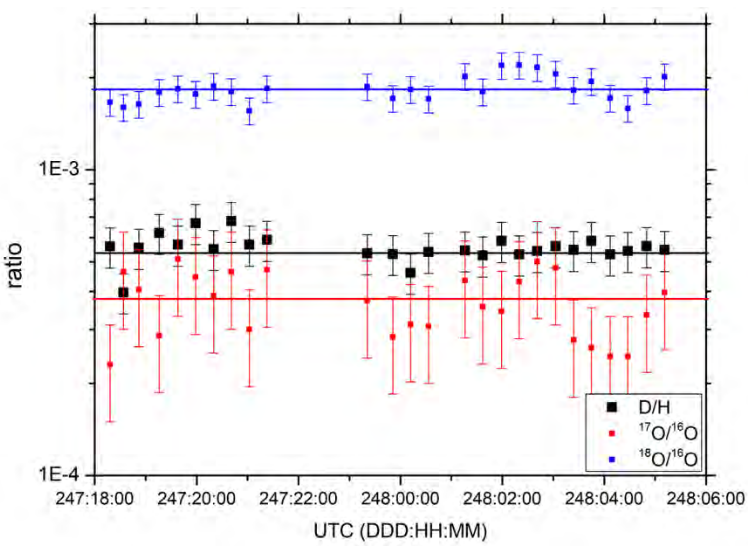

Fig. 2. Ratios of D/H, $^{17}O/^{16}O$ and $^{18}O/^{16}O$ for Sep 4/5. The period of 12 hours corresponds almost to a comet rotation (12.4 hour period). The times given are those for the measurement of m/z 18 ($H_2{}^{16}O$). m/z 19 (HDO and $H_2{}^{17}O$ and 20 ($H_2{}^{18}O$) are measured 30 s and 1 min later respectively. The error bars represent statistical errors from the low count rates and errors from the fit. Errors due to background and due to uncertainties in the detector gain, which are of a systematic nature, are only considered for the mean ratios given in the text.

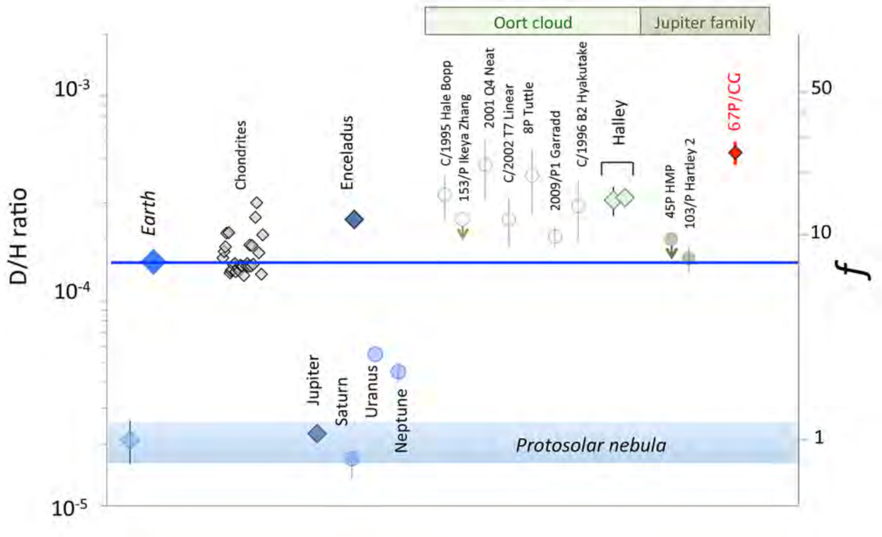

Fig. 3. D/H ratios in different objects of the solar system. Data are from (*1*, *2*, *5*–*7*, *26*–*28*) and references therein. Diamonds represent data obtained by in-situ mass spectrometry measurements, and circles refer to data obtained by astronomical methods.