D/H Ratio of Water on Earth Measured with DFMS
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Introduction: Key to understand the origin of water in the solar system is the D/H ratio. This ratio gives clues about the different water reservoirs in the solar system, about the formation temperature of water as well as the mixing in the solar system itself. Deuterium in comets is of special interest because comets are believed to contain the most primitive matter in the solar system. On one hand it is an indicator of the deuterium content at the location of comet formation and of the mixing in the solar system and on the other hand, by studying cometary deuterium, the question about the origin of the water and other volatiles on Earth can be answered [1].

Measurements of D/H in comets: Several measurements to derive the D/H ratio in comets have been performed by in situ massspectrometry in the coma of a comet or by remote sensing. For 1P/Halley with the IMS-HIS [2] and the NMS [3] instruments on Giotto the D/H ratio in water ratio was derived from DH_2O^+ / H_3O^+ in the coma and was found to be twice the value in the SMOW (standard mean ocean water on Earth). The same values within error bars were later found for comet Hyakutake and Hale-Bopp, both belonging also to the Oort cloud family [4,5]. For C/1995 O1 Hale-Bopp the D/H in DCN was found to be further enriched (0.23%) [6], which is consistent with an interstellar origin of at least part of the cometary water and HCN. Recently ocean-like water was detected in the Jupiter family comet 103P/Hartley 2 by the Herschel Space Observatory [7]. The D/H ratio was determined from the intensities of the lines of HDO and $H_2{}^{18}O$. The ratio of $^{18}O/^{16}O$ was assumed to be solar, an assumption which is probably justified by in situ measurements at 1P/Halley [2], although the error bars are quite large. This result is quite surprising because Jupiter family comets are believed to originate from further out than Oort cloud comets. If Oort cloud comets are enriched by a factor of 2 compared to SMOW, then Jupiter family comets might have ratios which are even higher. It is not clear of course if all or most Jupiter family comets have the same D/H ratio in water or if 103P/Hartley 2 is exceptionally low in Deuterium. The Herschel Space Observatory might be able to measure more Jupiter family comets in the near future.

So far the D/H ratio could not be measured directly for water without at least the assumption of the ratio for $^{18}O/^{16}O$. The Rosetta mission will be the first mission to perform in situ mass spectrometry at the Jupiter family comet 67P/Churyumov-Gerasimenko. ROSETTA is a European space mission to orbit comet 67P/Churyumov-Gerasimenko and characterize it.

ROSINA on Rosetta consists of three instruments [8]: a cometary pressure sensor (COPS), a reflectron time-of-flight massspectrometer (RTOF) and DFMS. **ROSINA-DFMS:** The double focusing massspectrometer (DFMS) has a mass resolution of $m/\Delta m \sim 3000$ at the 1% level and is therefore able to measure the D/H ratio directly for the water molecule. The double focusing mass spectrometer is designed to measure isotopic ratios. It consists of an ion source where neutrals are ionized by electron impact, an electrostatic analyzer (ESA), a magnet and a detector package consisting of a faraday cup, a channeltron and a multichannel plate with a linear detector array. The ion beam is doubly focused (energy and angle) during its travel trough the instrument. This results in a mass resolution which is high enough to resolve ^{16}O, CH_4 and H_2N for mass 16 amu or CO and N_2 for mass 28 amu.

D/H measurements with DFMS: To measure the D/H ratio for water there exists several possibilities: one is to derive the ratio from $HD^{16}O$ and $H_2{}^{16}O$. On mass 19 amu ($HD^{16}O$) there are other molecules or fragments like $H_2{}^{17}O$ or $H^{18}O$. Whereas the latter two can be easily resolved, $HD^{16}O$ and $H_2{}^{17}O$ still partly overlap at the resolution of the instrument. However, the peak shape is well defined and a mathematical fit helps to resolve these two peaks. DFMS is therefore the first instrument able to measure directly water with all its isotopes without making assumption on the oxygen isotopic ratios.

We will present measurements of the D/H and $^{18}O/^{16}O$ ratio directly deduced from water from the flight spare instrument on Earth in order to demonstrate DFMS capabilities at comet 67P/C-G.

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