ASTRONOMY

Detection of argon in the coma of comet 67P/Churyumov-Gerasimenko

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Comets have been considered to be representative of icy planetesimals that may have contributed a significant fraction of the volatile inventory of the terrestrial planets. For example, comets must have brought some water to Earth. However, the magnitude of their contribution is still debated. We report the detection of argon and its relation to the water abundance in the Jupiter family comet 67P/Churyumov-Gerasimenko by in situ measurement of the Rosetta Orbiter Spectrometer for Ion and Neutral Analysis (ROSINA) mass spectrometer aboard the Rosetta spacecraft. Despite the very low intensity of the signal, argon is clearly identified by the exact determination of the mass of the isotope ^{36}Ar and by the ^{36}Ar/^{38}Ar ratio. Because of time variability and spatial heterogeneity of the coma, only a range of the relative abundance of argon to water can be given. Nevertheless, this range confirms that comets of the type 67P/Churyumov-Gerasimenko cannot be the major source of Earth's major volatiles.

The role of comets in the formation of the solar system has been the subject of numerous models and speculations. In particular, contributions to the volatiles of the inner planets, to Earth's water reservoir, and even to life have been advocated [for example, (*1*) and references therein]. In any case, comets are thought to be among the most primitive objects in the solar system, having kept at least partially the volatile constituents of the solar nebula. Of the two identified families, the Oort Cloud Comets (OCCs) and the Kuiper Belt (also known as Jupiter family) Comets, the latter is considered to have formed beyond the orbit of Neptune at even lower temperatures than the OCCs.

One of the prime goals of the Rosetta mission (*2*) to comet 67P/Churyumov-Gerasimenko (hereafter 67P/CG), a Jupiter family comet, is the in situ measurement of the volatile inventory of 67P/CG with high sensitivity and high mass resolution. This allows comparisons to remote sensing measurements and to the only previous in situ measurement of a comet, Halley, an OCC. The Rosetta Orbiter Spectrometer for Ion and Neutral Analysis [ROSINA (*3*)] includes two mass spectrometers for this purpose, RTOF (reflectron type time of flight) and DFMS (double focusing mass spectrometer).

The determination of noble gases plays a key role in that volatile inventory. The abundance patterns and the isotope composition of the heavy noble gases, especially Xe, in the atmospheres of Earth and Mars do not fit the solar wind or the chondritic meteorites [for example, (*1*) and references therein]. To begin its study of noble gases, ROSINA detected argon in the coma of 67P/CG.

DFMS is a mass spectrometer that measures the neutral composition of the coma at the position of the spacecraft with unprecedented mass resolution. The DFMS capability to measure argon at 67P/CG has been demonstrated using the DFMS laboratory model and adapted to the expected signal at the comet (*4*). However, the measured spectrum (Fig. 1) shows other mass peaks near m/z (mass/charge ratio) = 36 (m/z = 35.9670, electron subtracted) that must be considered. $H^{35}Cl$ (m/z = 35.9761) is present in the background because of spacecraft outgassing (*5*). The spacecraft background shown in Fig. 1 was measured on 2 August 2014, when Rosetta was at a heliocentric distance of 3.6 AU, almost 800 km from the nucleus and clearly before the cometary signal became apparent. In the mass spectrum near m/z 38, the only signal close enough to interfere with ^{38}Ar (m/z = 37.9622) was assumed to be $H^{37}Cl$ (m/z = 37.9732). Its amount, evaluated from $H^{35}Cl$ assuming a solar isotopic ratio for chlorine, was found to be small due to higher mass separation at m/z = 38 (see overlap in Fig. 1). Not foreseen by Hässig *et al.* (*4*) was the interference by $C^{32}S_2^{++}$ (m/z = 37.9715) on m/z 38. Together with $H^{35}Cl$, it led to corrections in the procedure. The identification of $C^{32}S_2^{++}$ was confirmed by identifying $C^{32}S_2^{+}$ at m/z 76. The cross section for electron-impact ionization for $C^{32}S_2^{++}$ is 3 to 6% of $C^{32}S_2^{+}$ (*6*), which agrees with our finding.

The argon data presented here were taken on 19, 20, 22, and 23 October 2014. Comet 67P/CG was at ~3.1 AU from the Sun, and the spacecraft was roughly 10 km away from the comet during this time period. To resolve the peaks at m/z 36 and the peaks at m/z 38 (Fig. 1), we used a fitting method corresponding to Hässig *et al.* (*4*). A possible interference from ^{36}S (m/z = 35.9665) is <2% based on the signal for ^{32}S. Because the signal for ^{38}Ar was close to the instrument background,

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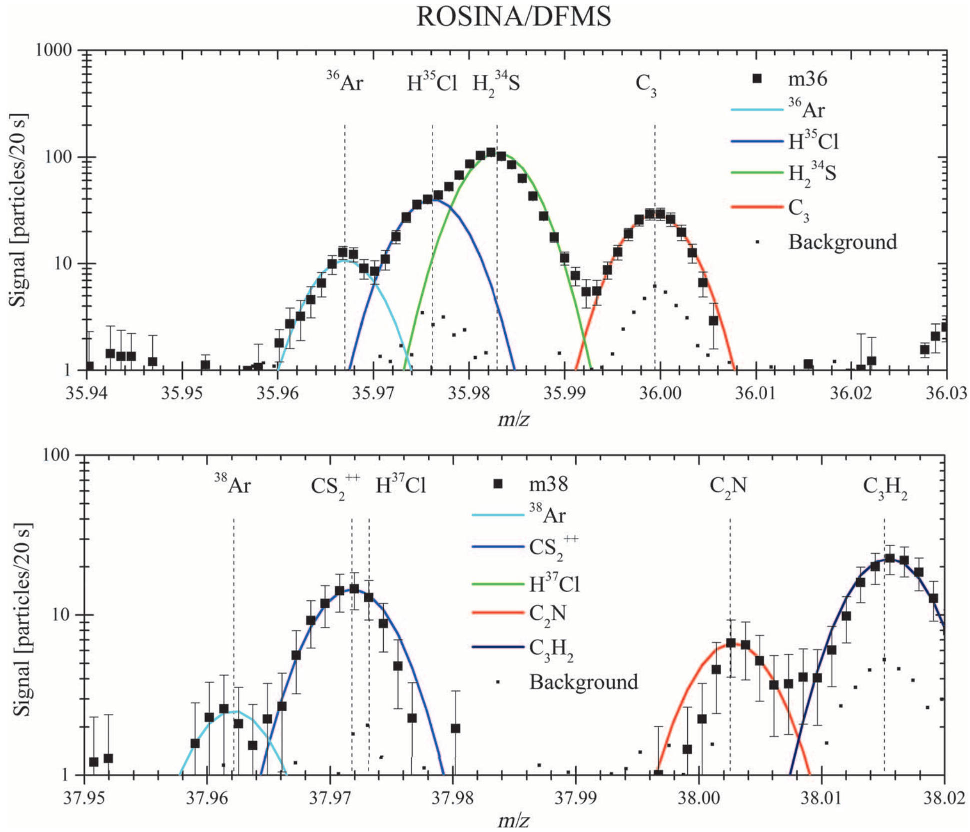

Fig. 1. DFMS mass spectra in the *m/z* ranges of 36 and 38. The spectra demonstrate the clear identification of the two isotopes ^{36}Ar and ^{38}Ar and of the interfering molecules. The exact *m/z* locations are given in the text. The spacecraft background spectra were obtained before the cometary signal became apparent (2 August 2014, heliocentric distance of 3.6 AU, almost 800 km from the nucleus).

it was summed up over the full time period to reduce statistical uncertainties. The same method was applied to ^{36}Ar. Uncertainties of the measurements were estimated by error propagation and were due to the ion counting statistics, offset variation, and nonsynchronous measurements of the two isotopes (25%). The resulting average ratio $^{36}Ar/^{38}Ar$ was 5.4 ± 1.4 (Earth, 5.3; solar wind, 5.5). Hence, despite the very low intensity of the signal, argon is clearly identified by the exact determination of the mass of the isotope ^{36}Ar and by means of the $^{36}Ar/^{38}Ar$ isotopic ratio, which is compatible with solar system values.

To constrain a possible contribution of cometary argon to Earth's atmosphere, the abundance of argon relative to water is important. ^{36}Ar and H_2O were measured during the abovementioned four periods in October 2014, with individual measurements covering 20 s (Fig. 2A). The spread of data, as given in Fig. 2A and Table 1, is due to temporal variability and spatial heterogeneity of the coma (*7*). Our values for $^{36}Ar/H_2O$, (0.1 to 2.3) × 10^{-5} (molecular ratio), are compatible with (*8*), one to two orders of magnitude below their upper limits determined by remote sensing of three long-period comets.

Correlations with other molecules were also investigated. The good correlation between ^{36}Ar and N_2 (Fig. 2B) due to their very similar volatility is noteworthy. The relative abundance is (9.1 ± 0.3) × 10^{-3} (molecular ratio). However, one has to be careful; carbon monoxide of similar volatility does not show such a strong correlation to molecular nitrogen and hence argon (*9*) as well. This indicates that other processes are involved, causing the observed temporal variability and spatial heterogeneity.

The argon we detected comes from inside the icy nucleus of the comet. The nature of that ice and how, when, and where it formed determined how it captured and released the gases we are measuring. The two simplest forms of ice are crystalline and amorphous. They form at different temperatures and pressures, capturing and releasing gases in different ways. Ar, N_2, CO, Kr, and Xe are particularly useful for distinguishing among these various possibilities; they lead us back to the manner of the comet's origin. They also constrain possible cometary contributions to the inner planets. Thus, the detection of Ar is a major step forward in our investigation of the comet. Several models predict the inclusion of highly volatile gases into the icy grains that grew at low temperature in the protosolar nebula. The high abundance of argon as well as the good correlation with N_2 are both consistent with these ideas. For a discussion, we refer to Ruben *et al.* (*9*).

The high content of argon in comet 67P/CG, if typical of outer solar system bodies, has strong implications for the origin of volatile elements on Earth and the other terrestrial planets. The elevated deuterium/hydrogen (D/H) ratio of 67P/CG [three times the ocean value (*10*)] is not consistent with a comet like this supplying Earth's oceans. However, the recent report of an ocean-like D/H value in the Jupiter family comet 103P/Hartley 2 (*11*) has revived the idea of a possible cometary contribution to Earth's volatiles and suggested that, even within an established "family," comets are isotopically heterogeneous. The present measurement offers an independent test for a possible link between a cometary reservoir and the terrestrial atmosphere and oceans, albeit in the same comet. The $^{36}Ar/H_2O$ ratio of Earth's

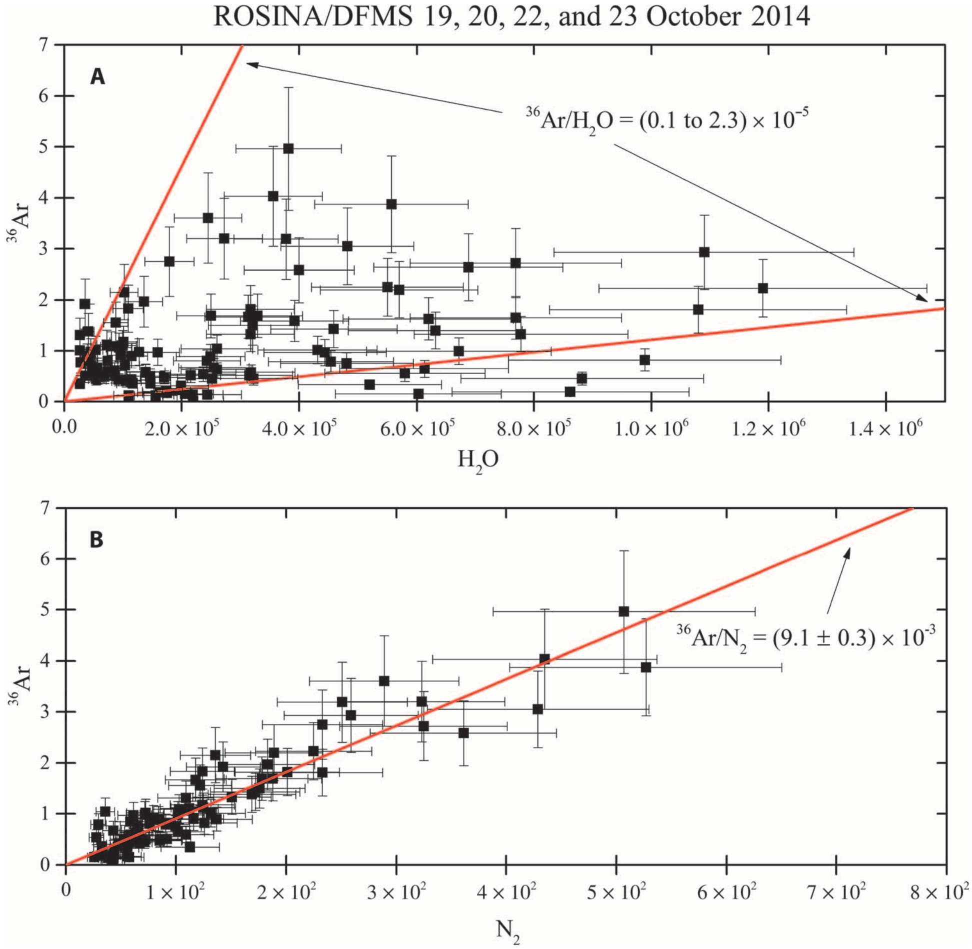

Fig. 2. (A and B) Comparison of argon abundances to water (A) and to molecular nitrogen (B). (A and B) Relative abundances of ^{36}Ar versus H_2O (A) and N_2 (B). ^{36}Ar abundances were measured relative to water and molecular nitrogen during four periods in October 2014, when Rosetta was close to 67P/CG (10 km). Individual measurements cover 20 s. Measured particles per 20 s are plotted. Ratios are molecular ratios. (A) Large spread of the relative abundances due to the high temporal variability and spatial heterogeneity of the coma (*7*). (B) Good correlation between ^{36}Ar and N_2 due to their similar volatility.

Table 1. Argon isotopic ratio and relative abundances to H_2O and N_2. The isotopic ratio of the comet's argon is in agreement with the solar system values.

$^{36}Ar/^{38}Ar$	**5.4 ± 1.4**
$^{36}Ar/H_2O$	(0.1 to 2.3) × 10^{-5}
$^{36}Ar/N_2$	(9.1 ± 0.3) × 10^{-3}

The ratio of argon to water is given as a range because of heterogeneity in the coma (Fig. 2A). ^{36}Ar and N_2 are closely correlated owing to their similar volatility; an average ratio of (9.1 ± 0.3) × 10^{-3} has been determined for the investigated periods (Fig. 2B).

surface (hydrosphere plus atmosphere) is 6.5 × 10^{-8} (*12*, *13*), that is, more than one to two orders of magnitude lower than the range of values [(0.1 to 2.3) × 10^{-5}] measured in 67P/CG gases. Thus, adding 67P/CG-like water to a dry Earth would result in several orders of magnitude more argon in the atmosphere than is observed. Unfortunately, there is no measurement of argon from comet 103P/Hartley 2. It is possible that atmospheric gases could have been lost preferentially relative to the ocean water during giant impacts characterizing the end of the terrestrial accretion (*14*, *15*) and/or irradiation of the early atmosphere from the young active sun (*16*, *17*). However, the efficiency of such a process is unlikely to have resulted in the loss of >99% Ar while essentially preserving liquid water on Earth's surface.

Combining the D/H and $^{36}Ar/H_2O$ ratios measured in the coma of 67P/CG provides a means of quantification of a possible cometary contribution to Earth from a body with volatile content, such as 67P/CG (Fig. 3). Earth is represented by the surface inventory (hydrosphere plus atmosphere) and by bulk Earth (surface plus deep Earth) estimates from (*17*) and (*18*), respectively. Clearly, an asteroidal component, represented by carbonaceous chondrites CI and CM in Fig. 3, makes a better potential contributor to terrestrial water [and other major volatiles such as C and N (*17*)] than comets. Mixing curves between the two components allows the definition of potential cometary contributions, assuming no fractionation of the $^{36}Ar/H_2O$ ratio during delivery. Depending on the $^{36}Ar/H_2O$ values adopted for bulk Earth, a contribution of cometary argon to the atmosphere is possible, but a contribution of 67P/CG-like material to terrestrial water is negligible in all cases. If one considers bulk Earth composition as defined by Marty (*17*) (lower limit of the $^{36}Ar/H_2O$ in Fig. 3), a bulk terrestrial $^{36}Ar/H_2O$ ratio close to chondritic leaves no room for significant contribution of 67P/CG-like material to the major volatiles on Earth.

Have comets left any traces of their undeniable impacts on the inner planets? Later in the mission, when the density in the coma has

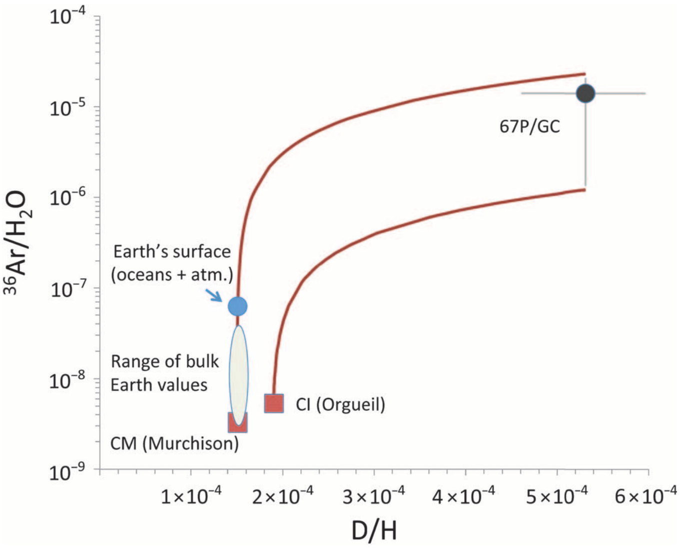

Fig. 3. D/H versus $^{36}Ar/H_2O$ mixing of 67P/CG-like and asteroidal materials. The asteroidal composition is represented by the Orgueil (CI) and Murchison (CM) carbonaceous chondrites. CI/CM chondrites are considered as the best representatives of volatile-rich primitive meteorites (*19*). Cometary data: this work, Altwegg *et al*. (*10*). Meteorite data: Mazor *et al*., Bogard *et al*., and Kerridge (*20–22*). Earth data, surface inventory: Lécuyer *et al*. and Ozima *et al*. (*12*, *13*). Range of estimates for bulk Earth: Marty and Halliday (*17*, *18*).

increased, ROSINA will seek to add the abundances of krypton and xenon in 67P/CG to the argon we now know is present, as one more test of this possibility. In conclusion, the high argon content of Comet 67P/CG argues against a cometary origin for terrestrial water, as does independently the elevated D/H ratio of this comet (*10*).

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