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**COSMOCHEMISTRY**

Xenon isotopes in 67P/Churyumov-Gerasimenko show that comets contributed to Earth's atmosphere

B. Marty, K. Altweeg, H. Balsiger, A. Bar-Nunn, D. V. Bekaert, J.-J. Berthelier, A. Bieler, C. Briols, U. Calmonte, M. Combi, J. De Keyser, B. Fiethe, S. A. Fuselier, S. Gasc, T. I. Gombosi, K. C. Hansen, M. Hässig, A. Jäckel, E. Kopp, A. Korth, L. Le Roy, U. Mall, O. Mousis, T. Owen, H. Rème, M. Rubin, T. Sémond, C.-Y. Tzou, J. H. Waite, P. Wurz

The origin of cometary matter and the potential contribution of comets to inner-planet atmospheres is a long-standing problem. During a series of dedicated low-altitude orbits, the Rosetta Orbiter Spectrometer for Ion and Neutral Analysis (ROSINA) on the Rosetta spacecraft analyzed the isotopes of xenon in the coma of comet 67P/Churyumov-Gerasimenko. The xenon isotopic composition shows deficits in heavy xenon isotopes and matches that of a primordial atmospheric component. The present-day Earth atmosphere contains 22 ± 5% cometary xenon, in addition to chondritic (or solar) xenon.

Comets are among the most pristine solar system systems (7). Their abundant volatile species, mainly in the form of ices, are intimately mixed with refractory silicate-rich phases and organics, the origins of which—either in the protosolar disk or interstellar medium—are still under debate (7). The discovery that Comet 81P/Wild contains high-temperature minerals akin to those found in primitive meteorites with key isotopic signatures (e.g., that of oxygen) typical of solar system reservoirs (2) suggests that some of the cometary constituents were cycled close to the proto-Sun and were radially transported outward. However, the case of ice is less clear. Enrichments in deuterium and nitrogen-15 in comets (3, 4) have been regarded as either originating from processing in the disk outskirts under irradiation or resulting from low-temperature ion-molecular reactions in molecular clouds. Another unresolved problem is the possible contribution of comets to inner-planet atmospheres. Although the D/H and 15N/14N signatures of the terrestrial atmosphere and oceans suggest an inner solar system origin for volatile elements on Earth (5), variations in the D/H ratio in primitive meteorites point to the contribution of interstellar water to asteroids (6).

Xenon, the heaviest stable noble gas, with nine isotopes of different nucleosynthetic origins (7, 8), is a key element for identifying nuclear components present in presolar material. The composition of solar system Xe, represented by measurements of the solar wind (7), is the result of the homogenization of such components. Several radioactive decays also produce Xe isotopes, among which that of 129I (half-life of 15.6 million years) decaying into 129Xe provides time constraints on the early evolution of the solar system. Earth's atmosphere has a xenon composition that is unique among solar system objects and reservoirs (9). It is depleted relative to expectations based on the extrapolated behavior of the lighter noble gases Ne, Ar, and Kr, by a factor of ~20 relative to Kr (normalized to the abundance in chondritic meteorites). Atmospheric Xe is also isotopically (mass-dependently) fractionated, being enriched in heavy isotopes by 30 to 40 per mil per atomic mass unit (u) compared with chondritic xenon (hereafter, Q-Xe) or solar wind xenon (hereafter, SW-Xe); this is known as the xenon paradox (10). When corrected for mass-dependent isotopic fractionation (MDF), atmospheric Xe does not directly correspond to any known solar system component. These observations have led to the definition of a theoretical primordial component termed U-Xe (9) (where U stands for Ur, the German word for primordial, and not for uranium-derived fission Xe). U-Xe is close to SW-Xe for the 124Xe–136Xe isotopes but is depleted in the heavy Xe isotopes, particularly 131Xe and 132Xe. U-Xe has not been clearly identified in meteorites or planetary samples.

We report the determination of the isotopic composition of xenon in a comet. Xenon isotopes were measured with the Double Focusing Mass Spectrometer (DFMS) of the Rosetta Orbiter Spectrometer for Ion and Neutral Analysis (ROSINA) instrument suite (11) on the Rosetta spacecraft. DFMS is a high-mass-resolution instrument (mass divided by change in mass = 3000 at 1% peak height at a mass/charge ratio of 28 u/e) that measured gases emitted by comet 67P/Churyumov-Gerasimenko (67P/C-G), presumably from sublimation of ice (3). The Xe measurements were carried out during a series of dedicated low-altitude orbits, between 10 and 7 km from the comet's center of mass, from 14 to 31 May 2016 (12). Because of the high resolution of DFMS, mass/charge ratios of 129, 131, 132, 134, and 136 u/e were essentially free of interfering species of similar mass, as confirmed by the shapes of the peaks, whereas interference presumably due to S, was detected at mass/charge = 128 u/e and corrected using peak deconvolution (12). A slight contribution of a few percent at mass/charge = 130 u/e, due to S-containing 34S, was also corrected. The average Xe isotope ratios were derived from this database, with uncertainties corresponding to 1 standard deviation (σ) of the mean. The ROSINA instrument was equipped with a gas calibration unit that permitted in-flight analysis of reference gases, including xenon (12).

Figure 1 shows the xenon composition of 67P/C-G, normalized to that of the solar wind (horizontal orange line) and to 130Xe (the most abundant Xe isotope in most cases), together with other solar system compositions (terrestrial atmosphere and chondritic). The data obtained from the in-flight calibration runs are consistent with a terrestrial Xe composition, as expected, but the 67P/C-G Xe isotopic ratios deviate markedly from solar, or chondritic, values. Whereas 128Xe/130Xe, 130Xe/132Xe, and 132Xe/134Xe are solar-like within uncertainties, 67P/C-G Xe is strongly depleted in 132Xe and 134Xe, by ~40 and ~60%, respectively.

We first tested the possibility that the observed variations are due to MDF, in which case the data should align along the dotted curve of Fig. 1. The 129/130Xe and 130/132Xe ratios could be reasonably accounted for by MDF affecting a solar-like Xe component. The required fractionation factor, however, should be extremely high, around 14% per atomic mass unit, higher than ever observed for Xe (or other noble gases) in any solar system object or reservoir. Notesco et al. (13) found no evidence for Xe isotopic fractionation upon trapping of 67P/C-G Xe in a MDF of no more than 1% (14). Alternatively, MDF could also be due to distillation enhancing isotopic fractionation during loss of Xe isotopes from a reservoir (e.g., cometary ice). To produce...
Mixing of Q-Xe or SW-Xe with 67P/C-G Xe is able to reproduce the composition of U-Xe (Fig. 4). Likewise, none of the MDF curves from 67P/C-G Xe can reproduce U-Xe, SW-Xe, or Q-Xe compositions. Mixing of Q-Xe or SW-Xe with 67P/C-G Xe is able to reproduce the composition of U-Xe (Fig. 4).

Solar system xenon is the result of mixing of three different nucleosynthetic sources: the p-process, producing the rare $^{134}$Xe and $^{136}$Xe isotopes (which could not be measured here); the s-process, producing $^{128-135}$Xe isotopes; and the r-process, producing $^{134,136}$Xe isotopes (8). Thus, the isotopic composition of cometary xenon is possibly the result of a nucleosynthetic mix that is different from that which produced solar xenon. From theoretical considerations and correlations of Xe isotopes observed in presolar grains [SiC and nanodiamonds (9)], the s-process Xe composition is reasonably well defined, but Xe isotope variations in presolar material require at least two different r-process compositions (8). Figure 3 shows mixing of 35% s-process Xe with 65% r-process Xe (12), the latter being defined by the two r-process compositions identified by (8).

This scenario accounts reasonably well for the deficits of $^{134}$Xe and $^{136}$Xe observed in 67P/C-G and is more consistent with the cometary $^{128}$Xe/$^{132}$Xe ratio than the MDF model is. It implies that $^{129}$Xe is enriched relative to $^{127}$Xe and the solar composition by $34 \pm 11%$ (1e). This large monoisotopic excess could be due to a specific nucleosynthetic process preferentially producing $^{129}$Xe, a possibility supported by some nanodiamond fractions with $^{129}$Xe/$^{132}$Xe ratios up to 2.2 (16). Alternatively, in situ (within ice) decay of $^{129}$I (half-life of 15.6 million years) after the start of solar system formation (SSSF) is unlikely: The $^{129}$I/$^{127}$I ratio at the SSSF was $~1 \times 10^{-4}$ (17), and an in situ origin after the SSSF would require an enrichment of iodine relative to xenon by three to four orders of magnitude, which is not observed in the coma of 67P/C-G (12). This $^{129}$Xe excess could then result from in situ (within ice) or ex situ (in the ambient gas) decay of $^{129}$I before the SSSF. In this case, xenon trapped in ice would be much older, by several tens of millions of years, than the SSSF. Assuming that $^{127}$I and $^{129}$I were produced in comparable proportions during r-process nucleosynthesis, icy grains should have trapped both I and Xe relatively shortly after their last nucleosynthetic event. This exotic Xe component would have to be older than 100 million years before the SSSF, given the initial solar system abundances of $^{129}$I, $^{244}$Pu, and $^{237}$Cm (18).

Cometary noble gases are concentrated in ice (13, 19, 20), and a presolar origin for Xe would imply that cometary ice is also presolar. Such an origin is in agreement with the detection of abundant O$_2$ (1 to 10% relative to H$_2$O) released by 67P/C-G (21). Indeed, molecular oxygen might be released...
have been produced from the radiolysis of H$_2$O icy grains by cosmic rays and/or hard photons before the comet was assembled (22), and this process would require long periods of time (10$^5$ to 10$^6$ years) in the protosolar nebula and/or low-density environments such as molecular clouds (22). A presolar origin is independently supported by the presence of S$_2$ in 67P/C-G (23) and HD/O and D$_2$O/HDO ratios closely resembling those of interstellar material (3).

The peculiar Xe isotopic composition of 67P/C-G provides a fingerprint of the contribution of comets to the terrestrial atmosphere. 67P/C-G Xe, which is largely depleted in $^{132}$Xe and $^{136}$Xe, indicates that comets may be the source of U-Xe. Mixing 22 ± 5% (1σ) cometary (67P/C-G) Xe with Q-Xe reproduces the composition of U-Xe (Fig. 4). The choice of Q-Xe for the second component—instead of, for example, solar—is consistent with observations that (i) the H, N, and Ar isotopic compositions of the atmosphere and oceans are within the range of variations observed in chondrites and different from solar values (5, 7) and (ii) xenon in Earth’s interior contains a chondritic component (24). A cometary contribution to atmospheric noble gases, suggested independently by modeling to be 19 to 27% (25), might have taken place during the proto-Earth growing stages (25) or later during the Hadean era (4.5 to 3.8 billion years ago) (20). Such a contribution would, however, have been minimal for the terrestrial oceans (≤1% (22)) and, by consequence, would not have affected the terrestrial D/H ratio.

A 22 ± 5% contribution of comets to atmospheric Xe also reproduces the 6.8 ± 0.3% (1σ) $^{129}$Xe excess observed in the atmosphere (Fig. 4). This excess, classically attributed to the decay of radioactive $^{129}$I trapped in the growing Earth, has previously allowed researchers to set time constraints on the accretion of Earth and the development of its atmosphere (17). Degassing of mantle Xe containing radiogenic $^{129}$Xe through geological periods of time also contributed $^{129}$Xe to the atmosphere, but probably no more than ~1% (22). Thus, a large fraction of the monoisotopic $^{129}$Xe excess in the terrestrial atmosphere may be inherited, implying that the $^{129}$I/$^{129}$Xe system as a geochronological tool should be reconsidered and that the Wetherill’s retention time of ~100 million years after the SSSF (17) should be seen as a lower limit. It remains unclear whether inherited cometary $^{129}$Xe is consistent with the presence in the present-day Earth atmosphere of a component derived from the fission of $^{244}$Pu.

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SUPPLEMENTARY MATERIALS
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Comets contributed to Earth's atmosphere

Models of xenon's origin in Earth's atmosphere require an additional, unknown source that has been a mystery for several decades. Marty et al. measured isotopic ratios of xenon released from comet 67P/Churyumov-Gerasimenko and found that they match the heretofore unknown source. The xenon appears to have been trapped in ice within the comet since before the solar system formed. Comets contributed about a quarter of the xenon on Earth, which constrains the amount of other materials (such as water) delivered to our planet by comets.

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