Molecular nitrogen in comet 67P/Churyumov-Gerasimenko indicates a low formation temperature

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One sentence summary: The first direct detection of dinitrogen in a cometary coma by Rosetta/ROSINA indicates a low formation temperature of comet 67P/Churyumov-Gerasimenko.

Abstract: Molecular nitrogen (N_2) is thought to have been the most abundant form of nitrogen in the protosolar nebula. N_2 is also the main N-bearing molecule in the atmospheres of Pluto and Triton, and was probably the main nitrogen reservoir from which the giant planets formed. Yet in comets, often considered as the most primitive bodies in the solar system, N_2 has not been detected. Here we report the direct *in situ* measurement of N_2 in the Jupiter family comet 67P/Churyumov-Gerasimenko made by the ROSINA mass spectrometer aboard the Rosetta spacecraft. A N_2/CO ratio of $\left(5.70 \pm 0.66\right) \times 10^{-3}$ was measured, corresponding to depletion by a factor of ~25.4 ± 8.9 compared to the protosolar value. This depletion suggests that cometary grains formed at low temperature conditions below ~30 K, and that the amount of N_2 delivered by comets to the terrestrial planets was a small fraction of that contributed by the other N-bearing species.

Main text: Thermochemical models of the protosolar nebula (PSN) suggest that molecular nitrogen N_2 was the principal nitrogen species during the disk's phase (*1*) and that the nitrogen present in the giant planets was accreted in this form (*2*). Moreover, Pluto and Triton, which are both expected to have formed in the same region of the PSN as Jupiter family comets (JFCs), have N_2-dominated atmospheres and surface deposits of N_2 ice (*3, 4*). However, so far, this molecule has never been firmly detected in comets while CN, HCN, NH, NH_2, and NH_3 among others have been observed spectroscopically (*5, 6*). The abundance of N_2 in comets is therefore a key to understanding the conditions in which they formed. Condensation or trapping of N_2 in ice occurs at similar thermodynamic conditions as those needed for CO in the PSN (*7, 8*). This requires very low PSN temperatures and implies that the detection of N_2 in comets and its abundance ratio with respect to CO would put strong constraints on comet formation conditions (*7, 8*). Ground-based spectroscopic observations of the N_2^+ band in the near UV are very difficult due to the presence of telluric N_2^+ and other cometary emission lines. Searches conducted with high-resolution spectra of comets 122P/de Vico, C/1995 O1 (Hale-Bopp) and 153P/2002 C1 (Ikeya-Zhang) have been unsuccessful and yielded upper limits of 10^{-5} to 10^{-4} for the N_2^+/CO^+ ratio (*9, 10*). Only one N_2^+ detection in C/2002 VQ94 (LINEAR) from ground-based observations is convincing because the comet was at sufficient distance from the Sun to prevent C_3

contamination (*11*). The *in situ* measurements made by Giotto in 1P/Halley did not help: the resolution of the mass spectrometers aboard the spacecraft (*12*) was insufficient to separate the nearly identical masses of N_2 and CO during the 1P/Halley encounter and only an upper limit could be derived for the relative production rates ($Q(N_2)/Q(CO) \leq 0.1$) (*13*).

Here we report the direct *in situ* measurement of the N_2/CO ratio by the Rosetta Orbiter Spectrometer for Ion and Neutral Analysis (ROSINA) in the JFC 67P/Churyumov-Gerasimenko (hereafter 67P). ROSINA is the mass spectrometer suite on the European Space Agency's Rosetta spacecraft (*14*) and measures the gas density and composition at the location of the spacecraft (*15*). The Double Focusing Mass Spectrometer (DFMS) has a high mass resolution of $m/\Delta m$ about 3000 at the 1% level (corresponding to ~9000 half peak width at the 50% level) at atomic mass per unit charge 28 u/e, allowing the separation of N_2 from CO (Δm = 0.011 u) by numerical peak fitting. Neutral gas is ionized by electron-impact and then deflected through an electrostatic, then magnetic, filter onto a position-sensitive micro-channel plate (MCP) detector. The peak shape of a single species on the MCP is well known and therefore numerical fitting can distinguish overlapping contributions from different atoms and molecules. A detailed description of the instrument and the data treatment can be found in the supplementary material.

Starting on August 5, 2014, ROSINA observed the cometary gas flux rise above spacecraft background for the major species including H_2O, CO, and CO_2. For N_2, which has a higher relative spacecraft background, the cometary signal became apparent a few days later. The spacecraft background signal (*16*) for both species, CO and N_2, was derived at different times before detecting the coma and shown to be temporally quite stable (see discussion in supplementary material). Figure 1 depicts two atomic mass per unit charge 28 u/e spectra, the first represents Rosetta spacecraft background on May 11, 2014 (A), while the spacecraft was still at a distance of 1.65 x 10^6 km from the comet. A comparable N_2 background was measured on August 1, 2014, at almost 800 km from the nucleus before the cometary signal became apparent. The second mass spectrum, a representative for the measurements within a distance of 10 km from the nucleus, was obtained on October 18, 2014 (B). The spacecraft background obtained in May is indicated in the October observation and has subsequently been removed from all spectra, leaving therefore only cometary CO and N_2. Furthermore CO from dissociative electron-impact ionization of cometary CO_2 inside DFMS' ion source has been removed and the signal has been corrected for the instrument alignment with respect to the comet (see supplementary material for details).

This procedure has been carried out for 138 spectra over two terminator orbits of the Rosetta spacecraft from October 17 to October 23, 2014. Fig. 2 shows clear diurnal variations in the detector signal of both species associated to the 12.4 h rotation period of the comet (A). The signal is to first order correlated to the comet's cross-section exposed to the Sun and depending on the position of Rosetta (thus also peaks at half rotation can be seen). The resulting mean N_2/CO ratio of $(5.70 \pm 0.66) \times 10^{-3}$ corresponds to the mean ratio of each individual measurement and includes the 2-σ standard deviation of the sampled mean. The position of Rosetta with respect to the comet is indicated in plates (B-D). Higher outgassing is found at positive latitudes corresponding to the summer hemisphere. Other species also show significant diurnal variations: the CO/H_2O ratio changes depending on the location of the spacecraft with respect to the position of the comet and to nucleus surface illumination conditions (*17*). Over the sun-lit hemisphere the CO/H_2O ratio varies between 0.1 to 0.3, which is in agreement to variations observed at other comets (*6*). Since these measurements were achieved when the comet was at a heliocentric distance of 3.1 AU, the water production rate may increase relative to both CO and N_2 as the comet approaches the Sun. We therefore expect the N_2/CO ratio to be more representative of the N_2 content in the coma than N_2/H_2O. Fig. 3 shows the correlation between the N_2 signal and the CO signal. The measurements exhibit a significant variation depending on the position of Rosetta above the surface of the comet nucleus, masking a potential increase in the production rate of either species as the comet approaches the Sun. The black line shows the average N_2/CO ratio and the variation of the individual measurements is indicated by the two bracketing lines.

With a protosolar ratio N/C of 0.29 ± 0.10 (*18*) and assuming to first order that all of N and C were in the form of N_2 and CO in the PSN (*1*), we derive an N_2/CO ratio of 0.145 ± 0.048 in the PSN gas phase. The comparison with the N_2/CO

measurement performed in the near coma of 67P shows that the cometary N_2/CO ratio is depleted by a factor of about 25.4 ± 8.9 compared to the value derived from protosolar N and C abundances. This depletion of N_2 relative to CO in comet 67P may be a consequence of how cometary ice formed. According to one model, comets agglomerated from pristine amorphous water ice grains originating from the interstellar medium (ISM) (*19*). In this case, the low N_2/CO ratio in 67P is the result of inefficient trapping of N_2 in amorphous water ice compared to CO. This possibility is supported by laboratory experiments in which a mixture of water vapor with N_2 and CO was directed onto a cold plate in the 24-30K temperature range (*7*). In these experiments, gases initially trapped in growing amorphous ice were later released when ice warmed up, and the evolved gases were measured by mass spectrometry. Results show that N_2 is trapped in the ice much less efficiently than CO in this temperature range. For instance, at 24 K, the depletion factor for the N_2/CO ratio was found to be ~19, a value within the range of the one observed in 67P of 25.4 ± 8.9. This yields a lower limit for the temperature experienced by the grains agglomerated by 67P because the N_2/CO ratio in amorphous ice would increase for temperatures lower than 24 K due to increasing efficiency of N_2 trapping.

An alternative interpretation of the low N_2 abundance in 67P is that the comet agglomerated from grains consisting of clathrates, which are ice-like crystalline solids formed by cages of water molecules that contain small non-polar molecules (*20*). This hypothesis is based on models showing that the vaporization distance of ISM ices could have been as high as about 30 AU from the Sun when they entered the PSN (*21*). With time, the decrease of the gas temperature and pressure allowed water to condense at ~140-150 K in the form of crystalline ice, leaving negligible water in the gas phase to condense at low temperatures where amorphous ice is expected to form (*22*). During the cooling period of the PSN, isotopic exchange took place between gaseous water, which was initially extremely deuterium-rich as it came from the ISM, and protosolar hydrogen with much lower D/H. This isotopic exchange allowed the deuterium-to-hydrogen ratio in water to decrease to the values observed in comets until it condensed again in the form of crystalline ice (*20, 23, 24*). Depending on the nature of the entrapped species, clathrates formed from preexisting crystalline water ice when the PSN temperature was lower than about 80 K, provided that the slow kinetics of the process is balanced by sufficient formation time (*8*). As in the case of trapping in amorphous ice, experiments and models suggest that N_2 is poorly trapped in clathrate cages, because of its small size (*8, 25-27*). In particular, statistical thermodynamics models (*28*) used to compute the composition of clathrates formed from a protosolar composition gas in the PSN show that an N_2/CO ratio in the comet's nucleus is consistent with the measured value in the coma if the nucleus agglomerated from grains formed in the 26-56 K temperature range (*8*).

Both interpretations are consistent with the idea that 67P agglomerated from grains formed at about 30 K or below. The detection of noble gases in JFCs will be important to further constrain their formation temperature. However, the measured N_2/CO ratio may reflect in whole or in part the comet's post-formation evolution. A possibility is that 67P agglomerated from grains formed at a lower temperature (around 20 K) in the PSN, favoring the trapping of significantly more N_2 in its building blocks, in a way consistent with the known compositions of the atmospheres and surfaces of Pluto and Triton (*3, 4*). This possibility would be consistent with an inferred Kuiper Belt origin for 67P and its high D/H ratio (*24*). In these conditions, 67P could have been initially N_2-rich but subsequent post-accretion heating due to the radiogenic decay of nuclides and/or thermal cycles during its transit from the Kuiper Belt and its subsequent history in a short period orbit could have been sufficient to trigger the outgassing of N_2 (*8*). A scenario like this may explain how initial nitrogen-rich cometesimals similar to Triton and Pluto evolved to nitrogen-depleted comets.

Because N_2 trapped in 67P is presumably protosolar nebula gas, its $^{14}N/^{15}N$ ratio should be about 441, the value found in Jupiter and the solar wind (*29*). This is much higher than values measured in other cometary N-bearing species like NH_3 and HCN (~130) (*5*). Thus depending on the proportions of N_2 relative to other N-bearing species, the terrestrial $^{14}N/^{15}N$ ratio of 272 could possibly be cometary in origin, given an appropriate mix of the different nitrogen species in the comets that contributed to terrestrial volatiles. Our initial ROSINA measurement for N_2/CO of 0.57% may be compared with NH_3/CO of 6% and HCN/CO of ~2% in the Oort cloud comet Hale-Bopp (*6*). The production rates of volatiles relative to water vary from one comet to another one, but their values normalized to CO remain close to those measured in Hale-Bopp (*6*). If 67P is a typical JFC, then the ROSINA value for N_2/CO implies that the amount of N_2 reaching the surface of a solid body in the inner solar system from a JFC impact was almost 15 times less than the amounts of NH_3, HCN, and certain organic compounds (*6*). This comparison suggests that JFC comets were not the main source of the Earth's nitrogen.

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Acknowledgments: The authors would like to thank the following institutions and agencies, which supported this work: Work at UoB was funded by the State of Bern, the Swiss National Science Foundation and by the European Space Agency PRODEX Program. Work at MPS was funded by the Max-Planck Society and BMWI under contract 50QP1302. Work at Southwest Research institute was supported by subcontract #1496541 from the Jet Propulsion Laboratory. Work at BIRA-IASB was supported by the Belgian Science Policy Office via PRODEX/ROSINA PEA 90020. This work has been carried out thanks to the support of the A*MIDEX project (n° ANR-11-IDEX-0001-02) funded by the « Investissements d'Avenir » French Government program, managed by the French National Research Agency (ANR). This work was supported by CNES grants at IRAP, LATMOS, LPC2E, UTINAM, CRPG, and by the European Research Council (grant no. 267255 to B. Marty). A. Bar-Nun thanks the Ministry of Science and the Israel Space agency. Work at the University of Michigan was funded by NASA under contract JPL-1266313. Work by JHW at Southwest Research Institute was funded by the NASA JPL subcontract NAS703001TONMO710889. ROSINA would not give such outstanding results without the work of the many engineers, technicians, and scientists involved in the mission, in the Rosetta spacecraft, and in the ROSINA instrument team over the last 20 years whose contributions are gratefully acknowledged. Rosetta is an ESA mission with contributions from its member states and NASA. We acknowledge herewith the work of the whole ESA Rosetta team. All ROSINA data will be released to the PSA archive of ESA and to the PDS archive of NASA.

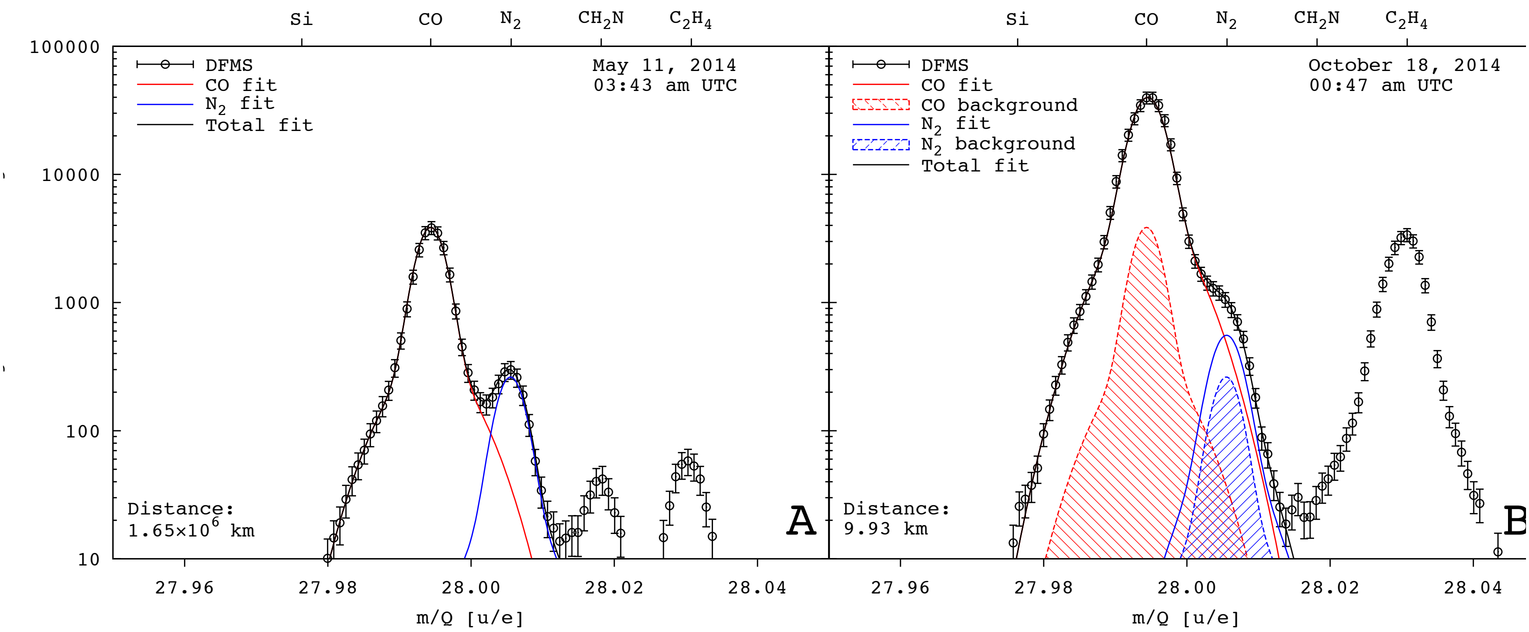

Fig. 1. Background mass per charge 28 u/e spectrum obtained on May 11, 2014, 03:43 UTC at 1.65 x 10^6 km from the comet (**A**) and representative spectrum in the coma of the comet on October 18, 2014, 00:47 UTC at almost 10 km from the center of mass of the nucleus (**B**).

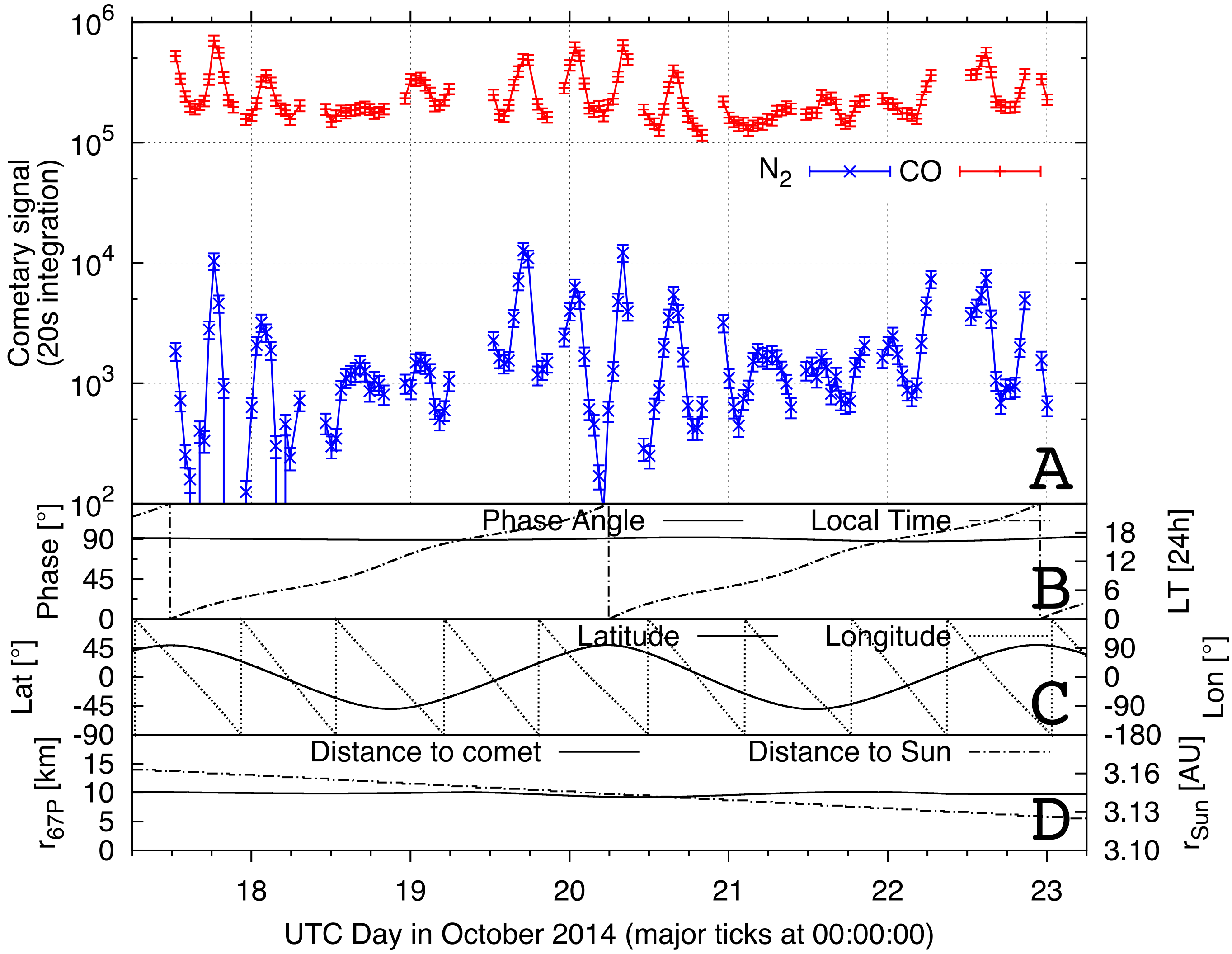

Fig. 2. Detector signal of CO and N_2 during two full terminator orbits of the Rosetta spacecraft (**A**). Spacecraft background is subtracted, the contribution of CO generated by electron-impact dissociation of CO_2 in the ion source is removed, and the geometrical area of the ion source exposed to the comet is corrected for off-pointing. Both signals show significant diurnal variations associated with the comet's 12.4 h rotation period (6.2 h half rotation). The points have been connected except where gaps indicate times when ROSINA is off due to thruster operations. The plates below show phase angle and local time (**B**), latitude and longitude of the sub-spacecraft point (**C**) in the Cheops coordinate system (*30*), and the distances of Rosetta to the comet and the comet to the Sun (**D**). The summer hemisphere is at positive latitudes.

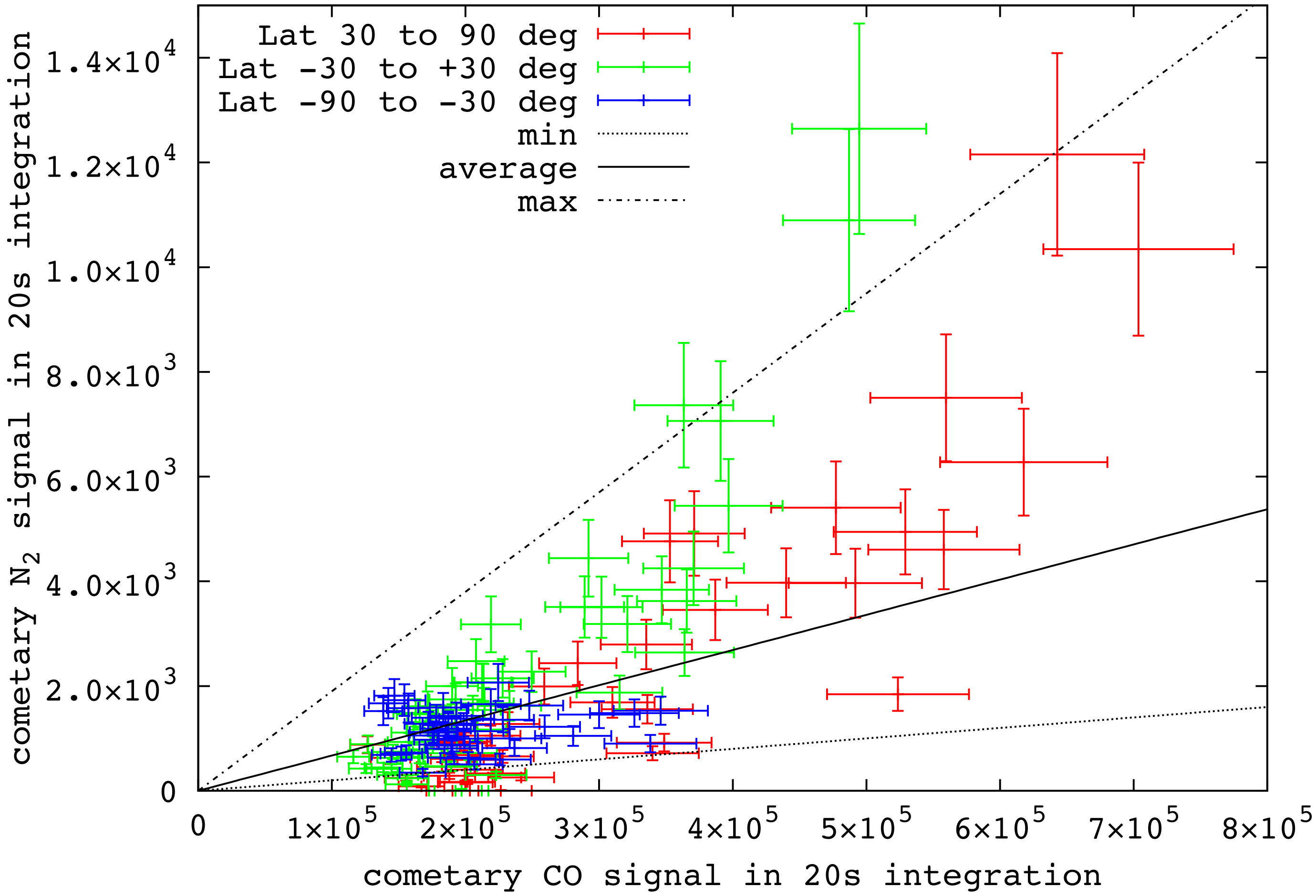

Fig. 3: N_2 versus CO detector signal for the whole time period from Figure 2. The min and max lines bracket most measurements. To derive the N_2/CO ratio, correction for differential sensitivities has to be applied, i.e. the detector signal ratio in the plot has to be divided by 1.175. The average N_2/CO ratio of 5.70×10^{-3} is indicated by the solid black line; the min line and the max line correspond to ratios of 1.7×10^{-3} and 1.6×10^{-2}, respectively, and indicate the variation in the observed ratios.