nature geoscience

LETTERS

PUBLISHED ONLINE: 2 DECEMBER 2012 | DOI: 10.1038/NGEO1650

Variations of sulphur dioxide at the cloud top of Venus's dynamic atmosphere

Emmanuel Marcq[1]*, Jean-Loup Bertaux[1]*, Franck Montmessin[1] and Denis Belyaev[2]

Sulphur dioxide is a million times more abundant in the atmosphere of Venus than that of Earth, possibly as a result of volcanism on Venus within the past billion years[1,2]. A tenfold decrease in sulphur dioxide column density above Venus's clouds measured by the Pioneer Venus spacecraft during the 1970s and 1980s has been interpreted as decline following an episode of volcanogenic upwelling from the lower atmosphere[3,4]. Here we report that the sulphur dioxide column density above Venus's clouds decreased by an order of magnitude between 2007 and 2012 using ultraviolet spectrometer data from the SPICAV instrument onboard the Venus Express spacecraft. This decline is similar to observations during the 1980s. We also report strong latitudinal and temporal variability in sulphur dioxide column density that is consistent with supply fluctuations from the lower atmosphere. We suggest that episodic sulphur dioxide injections to the cloud tops may be caused either by periods of increased buoyancy of volcanic plumes, or, in the absence of active volcanism, by long-period oscillations of the general atmospheric circulation. The 30-year observational record from Pioneer Venus and Venus Express confirms that episodic injections of sulphur dioxide above the clouds recur on decadal timescales, suggesting a more variable atmosphere than expected.

SO_2 is a key minor species in both Earth's and Venus's atmospheres. On Earth, its main sources are volcanic outgassing and anthropogenic emissions. Stratospheric sulphuric aerosols, whose intentional engineering has been advocated to mitigate global warming[5], occur on Earth after large volcanic eruptions. On Venus, SO_2 is also thought to originate from volcanic outgassing, albeit no volcanic activity has ever been directly witnessed[1,3]—it could also be in geochemical equilibrium on the surface[6] if pyrite and magnetite dominate the surface composition. Nonetheless, the venusian SO_2 atmospheric inventory is at least 6 orders of magnitude higher than on Earth, and actually SO_2 is the main progenitor of the thick H_2O–H_2SO_4 clouds enshrouding all of its lower atmosphere. These clouds exhibit a yellowish hue due to a yet unknown 'ultraviolet absorber'[7] that extends to the blue end of the visible spectrum. Previous works[8] evidenced a correlation (0.74) between the sulphur chemistry and this ultraviolet absorber, providing a better understanding of Venus's (and possibly Earth's) stratospheric aerosols.

Above the cloud layers, SO_2 is readily destroyed by the intense solar ultraviolet radiation, initiating chemical reactions leading to the formation of the cloud layers through oxidization[9,10] of SO_2 into SO_3, which reacts rapidly with H_2O to form H_2SO_4. This very destruction by absorption of solar ultraviolet photons makes SO_2 spectroscopic measurements such as ours possible in the near ultraviolet range, and indeed SO_2 was first detected above Venus's clouds in the ultraviolet range[11]. The first observation campaign took place in the 1970s and 1980s (refs 4,12) using data from UVS/Pioneer Venus and Venera 15, and reached the following conclusions: the SO_2 observable column density (defined as the column density integrated from the top of the atmosphere down to $\tau_{haze+clouds} = 1$ at 250 nm) is highly variable; the mean haze opacity experienced a secular decrease on a decennial timescale, as revealed by the increasingly darker (in the near ultraviolet) appearance of Venus; spatial and temporal mean SO_2 values point to a secular decrease on a decennial timescale, leading to barely detectable column densities in the early 1990s; and its spatial variations exhibit an equator-to-pole increase in the northern hemisphere, consistent with a slower photolysis rate at higher solar zenithal angles. Some of these trends were not observed by the beginning of the Venus Express ESA mission, which has been operating since 2006. SO_2 abundances, measured using the Spectroscopy for Investigation of Characteristics of the Atmosphere of Venus (SPICAV) and Solar Occultation in the Infrared (SOIR) spectrometer at cloud-top level[13,14] (70 km, $P = 40$ mbar) were more than one order of magnitude too high to be consistent with the decreasing trend observed before. Furthermore, the latitudinal gradient was reversed, with more SO_2 at lower latitudes—this was interpreted in terms of a stronger advection from the SO_2-rich lower layers in the ascending branch of the general circulation at low latitudes and cloud-top level. In the present paper, we now examine the spatial and temporal variability of SO_2 as measured by SPICAV-UV day-side nadir observations over the full mission up to February 2012.

According to our measurements (see Methods), SO_2 variability spans at least two orders of magnitude, in agreement with previous studies[4,13,14]. Both SO_2 absorption bands centred at 215 and 280 nm are readily seen in the SO_2-rich spectrum, leading to an unambiguous detection. SO_2 column density retrievals in excess of 10 μm-atm were found not to be sensitive to a variation in ultraviolet brightness factor (see Supplementary Fig. S2). Therefore, the actual uncertainty in retrieved SO_2 abundance is markedly greater below 10 μm-atm of SO_2. Cloud and haze variability can also affect our retrieved column densities, with a lower cloud top and haze opacity yielding larger observable SO_2 column densities even with the actual SO_2 mixing ratio kept constant. Previously reported cloud-top altitudes measured from Venus Express at 1.6 μm show a standard deviation of only ±1 km at low and mid-latitudes[15]. This would only change the apparent SO_2 column density by ±25%, far less than the observed order-of-magnitude changes—however, it must be noted that the cloud-top altitude observed at 1.6 μm is ~4 km lower than that at which the SPICAV-UV measurements are probing. We attempted to measure cloud-top altitude using CO_2

[1]LATMOS/CNRS/UVSQ, 11 Boulevard d'Alembert, F-78280 Guyancourt, France, [2]Space Research Institute (IKI), 117997, 84/32 Profsoyouznaya Street, Moscow, Russia. *e-mail: emmanuel.marcq@latmos.ipsl.fr; jean-loup.bertaux@latmos.ipsl.fr.

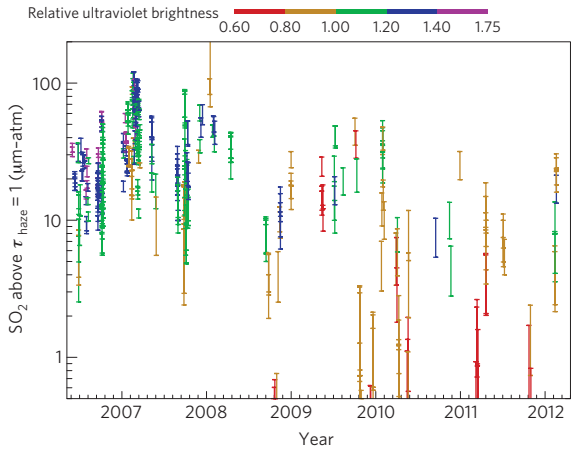

Figure 1 | Secular evolution of SO_2 column density between 2006 and 2012. Restricted to latitudes between ±25° so that latitudinal variability does not enter into account. Colours indicate the scaling factor representative of the mean ultraviolet brightness (corrected for SO_2 spectral absorption). Error bars represent 1σ random uncertainties in our fits.

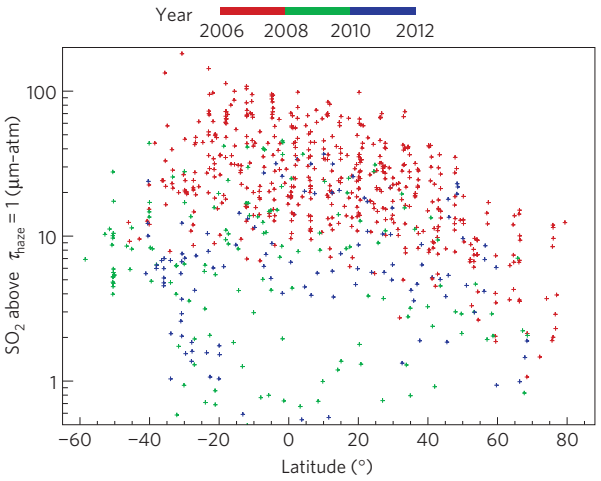

Figure 2 | Latitudinal profiles of SO_2 column density. Data points are coloured according to date of observation. The data show increasing SO_2 column densities with decreasing latitude particularly before 2008.

bands near 200 nm using SPICAV-UV, but the accuracy was far lower (±6 km) and no consistent variation in cloud-top altitude can be seen in this signal. Recent observations of SO_2 in the infrared range[16] were used to estimate a typical conversion factor around 10 ppbv at 72 km per 1 μm-atm.

Our main result is that, on average, SO_2 column densities increase before 2007, and then decrease by a factor of 5× for at least five years, as shown on Fig. 1, probably interspersed with shorter increases in early 2009 and mid 2010, although our relatively sparser sampling past 2008 prevents us from confirming these temporary increases. There is extensive observation-to-observation variability over almost two orders of magnitude—consistent with that reported by previous observers[3,14,16]. As for previous measurements[8], SO_2 variations are not correlated with solar local time nor with cloud height as measured by SPICAV-IR[15]. This decrease is highly reminiscent of the situation observed by Pioneer Venus[4], in terms of evolution as well as typical abundances at the cloud top, with maximal values at 72 km on the order of 1 ppmv in 2007 (0.1–0.2 ppmv in 2011) compared with 0.5 ppmv in 1980 and 0.1 ppmv in 1986. Figure 1 also shows that the mean ultraviolet brightness in the 200–310 nm range also started a steady decrease after 2007. This provides more evidence for a causal link between the ultraviolet absorber and SO_2 availability at cloud-top level and is consistent with SO_2 dissociation by-products being progenitors of a sulphur-based ultraviolet absorber such as amorphous elemental sulphur, as previously suggested[17]. Latitudinal variations of ultraviolet brightness have also been evidenced using VMC observations on-board Venus Express[18].

The aforementioned latitudinal (as well as temporal variability) is best seen on Fig. 2. SO_2 column density is decreasing with increasing latitude (especially past 25°) when SO_2 is very abundant, confirming previous findings from 2006 Venus Express observations[13,14]. But this latitudinal gradient is reversed at very low SO_2 abundances, even though our typical errors on SO_2 measurements (a few μm-atm) are too large to dismiss a latitudinally homogeneous distribution. This is still in full agreement with the latitudinal gradients derived from Venera 15 and rocket observations during the late 1980s and early 1990s (ref. 12), when SO_2 column densities were also measured barely above the detection threshold.

We suggest the following mechanism to account for this variability. SO_2 is steadily supplied from the lower atmosphere, where it is ubiquitous— SO_2 abundance below the clouds is around 150 ppmv (refs 19–21)—by the general equator-to-pole circulation at cloud-top level. Then, SO_2 in the horizontal upper branch of the circulation is gradually depleted in SO_2 by photo-dissociation and subsequent chemistry involving its photolysis products (SO and O) while being advected towards the pole, leaving virtually no SO_2 at the highest latitudes. This latitudinal distribution is reproduced well by a very simple one-dimensional-model (see Supplementary Movie S1), the best fit is for a minimal photochemical lifetime for SO_2 around 5×10^4 s at the equator. The opposite latitudinal gradient that occurs during the SO_2-poor periods can also be qualitatively explained (see Supplementary Movie S2): considering the very short lifetime of SO_2 in the equatorial regions, a temporary decrease in the vertical extent and/or intensity of the convective cells can lead to a lesser supply of SO_2, resulting in a fast depletion of SO_2 at lower latitudes, that is on a timescale of 24 hours. On the other hand, SO_2 in the polar regions is partially sheltered by the very high solar zenithal angles and thicker polar haze, resulting in a slower photochemistry. In conjunction with less convection, this causes much smaller variations of SO_2 mixing ratios at higher latitudes, which is the observed behaviour: SO_2 column densities beyond 60 °N are identical in early 2007 and late 2011 within the observational uncertainty (Fig. 2). A more sophisticated chemical modelling[22] reaches similar conclusions: a vertical displacement of a few kilometres of the tropopause level (parametrized by the eddy diffusion vertical profile) leads to variations of SO_2 column density above the cloud top (70 km) of about two orders of magnitude, which is the observed situation in this paper as well as during previous observation campaigns[4,13,14].

The secular variations of SO_2 observed by Pioneer Venus and shown on Fig. 3 have been interpreted[3,4] as evidence of episodic variation of a currently active volcanogenic upwelling of SO_2 through increased buoyancy. We observe at least one secular increase in SO_2 between mid-2006 and 2007, but its typical timescale (at least a year) suggests the aggregate of multiple volcanic eruptions rather than a sudden single volcanic outburst. We also note that no noticeable contemporaneous increase of thermal emission from the surface could be seen by other instruments on-board Venus Express sensitive to the near-infrared windows, although the spatial and temporal coverage may be too sparse to be conclusive. We conclude that, in all cases, the observed SO_2 variability is caused by fluctuations on various timescales in upwards transport from the troposphere to the mesosphere. By Occam's razor, we are inclined to think that this variability

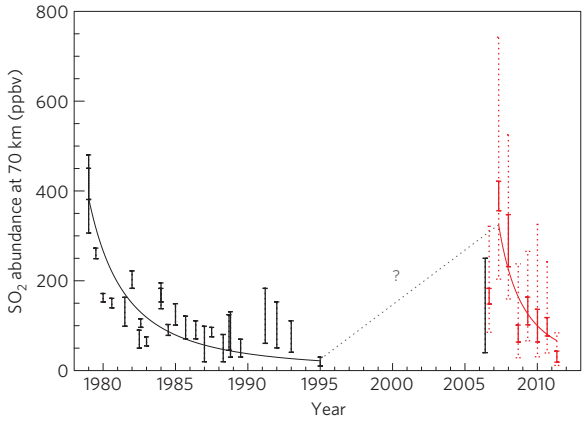

Figure 3 | More than thirty years of SO_2 measurements at Venus's cloud top. Black stands for previously published measurements[26]. Red stands for the 8-month moving average of the retrievals also shown in Fig. 1. Solid red error bars represent 1σ random uncertainty, and dotted red error bars represent measurement dispersion in each temporal bin.

originates from intrinsic dynamical variability in the ascending sub-solar branch of the global circulation at cloud-top level on a decennial timescale rather than from an external forcing such as extra buoyancy caused by volcanic eruptions, but we cannot dismiss a volcanic forcing through our study alone. Observations of other trace species such as carbon monoxide (CO) above the clouds during extensive monitoring campaigns could help in discriminating between a volcanic and a dynamical cause. Intrinsic dynamical variability on this decennial timescale might seem surprising considering the absence of a seasonal regime on Venus with its very low obliquity, but some general circulation models[23] have shown changes of the general circulation patterns with similar time constants. Let us also keep in mind that Earth's atmosphere also experiences cyclic patterns, for example El Niño-La Niña and QBO (stratospheric quasi-biennial oscillation), whose periods cannot be related to orbital forcing. Venus's atmosphere is without any doubt surprisingly much more variable than one could have imagined in the first place, and an extension of the Venus Express continuous monitoring beyond 2014 would definitely allow a better characterization of this variability.

Methods

Observations and forward model. Observations consist of ultraviolet spectra recorded by SPICAV on-board Venus Express, analysed using a forward radiative transfer model improved from our previous studies[13]. The SPICAV instrument has been extensively described[24]. We used only the ultraviolet channel (λ : 110–320 nm, $\Delta\lambda \simeq 1.3$ nm) in nadir geometry, which is best suited to probe SO_2 in the upper cloud deck region as its broad absorption bands near 215 and 280 nm can be detected in the reflected ultraviolet sunlight (our study is thus restricted to the day hemisphere only). We processed spectra from most orbits with relevant data acquired between 2006/04/14 (orbit #23) and 2012/02/18 (orbit #2130). The first stages of data processing, yielding calibrated spectral radiance factors—defined as the ratio between the spectral radiance received by SPICAV and incident solar spectral radiance at the top of the atmosphere and at normal solar zenithal angle (SZA)—have not changed since our first study[13]. A first estimate of SO_2 column density, mean ultraviolet brightness and optical depth of the haze layer is performed using look-up tables of precomputed spectra, then the last iterations of the model are called directly by the Levenberg–Marquardt fitting routine with the correct emission angles and phase angles because they were not considered in the previous look-up tables. Our data set is thus expanded with higher emission angle observations. Examples of fittings are shown in Supplementary Fig. S1.

Sensitivity study. A possible concern in our methodology would lie in a spurious correlation between the brightness factor and SO_2 abundance: because SO_2 variations alter the whole spectrum (even if its absorption is spectrally non-uniform), an increase in SO_2 could be compensated by the fitting routine with an increase in brightness factor. Therefore a sensitivity study was performed, shown in Supplementary Fig. S2. SO_2 column densities in excess of 10 µm-atm are found to be quite robust with respect to any miscalculation of the mean ultraviolet brightness factor, as expected from the distinctive spectral shape of SO_2 absorption provided there is enough SO_2. Below 10 µm-atm, this remains valid only from a statistical point of view.

Simple model of SO_2 abundance above the clouds. To strengthen our qualitative interpretation of SO_2 latitudinal profiles, we developed a crude model to estimate the typical timescales for the destruction process with respect to supply from the lower atmosphere. A single hemisphere from the equator to the pole was divided into 32 zonal cells extending along parallels—only meridional and vertical circulation are considered.

A single underlying cell represents the atmosphere below the clouds, acting as a source and/or sink for SO_2. SO_2 abundance is considered uniform within a given cell, and kept constant below the clouds at 2 ppmv (representative of its mean mixing just below the upper clouds). An ideal, day-side average circulation is then prescribed to account for SO_2advection. Meridional wind speed v is assumed to vary with latitude λ following $v = 12\,\mathrm{m\,s^{-1}} \cdot \sin(2\lambda)$, picturing the mean Hadley cell circulation at cloud-top level[25]. Vertical wind speed w is then computed assuming a null divergence of the wind vector field (conservation of mass within cells). This yields upwards winds below 45° in latitude and downwards winds above 45°. Last, SO_2 in each of the cells is assumed to be depleted by the ultraviolet solar flux and subsequent chemical reactions, following a exponential decrease with a lifetime $\tau = 5 \times 10^4\,\mathrm{s}/\cos(\lambda)$, where λ should be understood as a proxy for the mean solar zenithal angle—for optically thin layers, we expect the dissociation rate to be proportional to the ultraviolet flux.

Results are shown in Supplementary Movies S3 and S4. Assuming no SO_2 above the clouds at the start of the first simulation, a steady state with qualitatively correct abundances and latitudinal gradient is established in less than 12 Earth days (see Supplementary Movie S1). The fair agreement with observations (compare with Fig. 2) indicates that the main processes governing the SO_2 distribution during the SO_2-rich episodes are identified. Furthermore, the short timescale involved allows for relatively fast changes (at least at lower latitudes) at the cloud top, as observed: starting from the steady state reached previously, we suddenly shut down the advection (see Supplementary Movie S2). A weakening latitudinal gradient resulting from the faster depletion of SO_2 at lower latitudes is reached within a few Earth days, with latitudinal profile and mixing ratios typical of SO_2-poor periods.

Data repository. SPICAV-UV data are publicly available at the ESA archive website http://www.rssd.esa.int/psa for data older than 6 months.

Received 13 June 2012; accepted 1 November 2012; published online 2 December 2012

References

1. Fegley, B. & Prinn, R. G. Estimation of the rate of volcanism on Venus from reaction rate measurements. *Nature* **337,** 55–58 (1989).
2. Smrekar, S. E. *et al.* Recent hotspot volcanism on Venus from VIRTIS emissivity data. *Science* **328,** 605–608 (2010).
3. Esposito, L. W. Sulfur dioxide—Episodic injection shows evidence for active Venus volcanism. *Science* **223,** 1072–1074 (1984).
4. Esposito, L. W. *et al.* Sulfur dioxide at the Venus cloud tops, 1978–1986. *J. Geophys. Res.* **93,** 5267–5276 (1988).
5. Crutzen, P. J. Albedo enhancement by stratospheric sulfur injections: A contribution to resolve a policy dilemma?. *Climatic Change* **77,** 211–220 (2006).
6. Hashimoto, G. L. & Abe, Y. Climate control on Venus: Comparison of the carbonate and pyrite models. *Planet. Space Sci.* **53,** 839–848 (2005).
7. Pollack, J. B. *et al.* Distribution and source of the UV absorption in Venus' atmosphere. *J. Geophys. Res.* **85,** 8141–8150 (1980).
8. Esposito, L. W. & Travis, L. D. Polarization studies of the Venus UV contrasts—Cloud height and haze variability. *Icarus* **51,** 374–390 (1982).
9. Mills, F. P. & Allen, M. A review of selected issues concerning the chemistry in Venus' middle atmosphere. *Planet. Space Sci.* **55,** 1729–1740 (2007).
10. Mills, F., Esposito, L. & Yung, Y. (eds) *Atmospheric Composition, Chemistry and Clouds* 73–100 (Exploring Venus as a Terrestrial Planet, American Geophysical Union, 2007).
11. Barker, E. S. Detection of SO_2 in the UV spectrum of Venus. *Geophys. Res. Lett.* **6,** 117–120 (1979).
12. Zasova, L. V., Moroz, V. I., Esposito, L. W. & Na, C. Y. SO_2 in the middle atmosphere of Venus: IR measurements from Venera-15 and comparison to UV data. *Icarus* **105,** 92–109 (1993).
13. Marcq, E. *et al.* An investigation of the SO_2 content of the venusian mesosphere using SPICAV-UV in nadir mode. *Icarus* **211,** 58–69 (2011).
14. Belyaev, D. *et al.* First observations of SO_2 above Venus' clouds by means of solar occultation in the infrared. *J. Geophys. Res.* **113,** E00B25 (2008).
15. Ignatiev, N. I. *et al.* Altimetry of the Venus cloud tops from the Venus Express observations. *J. Geophys. Res.* **114,** E00B43 (2009).

16. Encrenaz, T. *et al.* HDO and SO_2 thermal mapping on Venus: Evidence for strong SO_2 variability. *Astron. Astrophys.* **543,** A153 (2012).
17. Toon, O. B., Pollack, J. B. & Turco, R. P. The ultraviolet absorber on Venus—Amorphous sulfur. *Icarus* **51,** 358–373 (1982).
18. Molaverdikhani, K., McGouldrick, K. & Esposito, L. W. The abundance and vertical distribution of the unknown ultraviolet absorber in the venusian atmosphere from analysis of Venus monitoring camera images. *Icarus* **217,** 648–660 (2012).
19. Bertaux, J-L., Widemann, T., Hauchecorne, A., Moroz, V. I. & Ekonomov, A. P. VEGA 1 and VEGA 2 entry probes: An investigation of local UV absorption (220–400 nm) in the atmosphere of Venus (SO_2 aerosols, cloud structure). *J. Geophys. Res.* **101,** 12709–12745 (1996).
20. de Bergh, C. *et al.* The composition of the atmosphere of Venus below 100 km altitude: An overview. *Planet. Space Sci.* **54,** 1389–1397 (2006).
21. Marcq, E., Encrenaz, T., Bézard, B. & Birlan, M. Remote sensing of Venus' lower atmosphere from ground-based IR spectroscopy: Latitudinal and vertical distribution of minor species. *Planet. Space Sci.* **54,** 1360–1370 (2006).
22. Krasnopolsky, V. A. A photochemical model for the Venus atmosphere at 47–112 km. *Icarus* **218,** 230–246 (2012).
23. Parish, H. F. *et al.* Decadal variations in a Venus general circulation model. *Icarus* **212,** 42–65 (2011).
24. Bertaux, J-L. *et al.* SPICAV on Venus Express: Three spectrometers to study the global structure and composition of the Venus atmosphere. *Plan. Space Sci.* **55,** 1673–1700 (2007).
25. Newman, M. & Leovy, C. Maintenance of strong rotational winds in Venus' middle atmosphere by thermal tides. *Science* **257,** 647–650 (1992).
26. Esposito, L. W., Bertaux, J-L., Krasnopolsky, V., Moroz, V. I. & Zasova, L. V. Chemistry of lower atmosphere and clouds. in *Venus II: Geology, Geophysics, Atmosphere, and Solar Wind Environment* (eds Bougher, S. W., Hunten, D. M. & Phillips, R. J.) 415–458 (1997).

Acknowledgements

The authors wish thank F. W. Taylor and C. Wilson for their valuable comments and insights. Venus Express is a space mission from the European Space Agency (ESA). Denis Belyaev acknowledges support from CNES for a post-doc position at LATMOS. SPICAV-UV data are publicly available at the ESA archive website for data older than 6 months. We wish to acknowledge support from CNES and CNRS.

Author contributions

E.M. developed the forward model of the venusian upper atmosphere used in this analysis, applied it to the processed observations and wrote the paper. J-L.B. is the Principal Investigator of the SPICAV instrument on-board Venus Express. F.M. maintained the entire workflow and contributed to the scientific discussions. D.B. created and maintained the data pipeline from raw observations to usable radiance factors.

Additional information

Supplementary information is available in the online version of the paper. Reprints and permissions information is available online at www.nature.com/reprints. Correspondence and requests for materials should be addressed to E.M. or J-L.B.

Competing financial interests

The authors declare no competing financial interests.