

Supplementary Materials for

Isotopic evidence of long-lived volcanism on Io

Katherine de Kleer1\*, Ery C. Hughes1,2, Francis Nimmo3, John Eiler1, Amy E. Hofmann4, Statia Luszcz-Cook5, Kathy Mandt6.

\*Corresponding author, email: [dekleer@caltech.edu](mailto:dekleer@caltech.edu)

**The PDF file includes:**

Materials and Methods

Supplementary Text

Figs. S1 to S6

Tables S1 to S5

Materials and Methods

Observations

Observations were made with ALMA of Io’s leading and trailing hemispheres on UT 2022 May 24 and 2022 May 18 (respectively) through program 2021.1.00849.S. QSO B0420-0127 and QSO B2251+155were used for flux calibration. The time on source was 1h40m for the leading hemisphere observation, and 50 minutes for the trailing hemisphere observation, because better weather conditions allowed the desired SNR to be obtained in a shorter time. Parameters of the observations and Io’s geometry at the time are given in Table S1. For the leading hemisphere observation, Io rotated 28 degrees during the observation, which smears the data by 0″.23 in the rotation direction; this is more than half the spatial resolution, but does not affect our interpretation because all presented spectra are averaged over a larger region.

The observations were conducted while ALMA was in its C-4 antenna configuration, which provides a spatial resolution of about a quarter to a third of Io’s diameter (~1000 km) at the frequencies of observation. The maximum baselines were 780 and 740 m for the leading and trailing hemisphere observations respectively.

The observations used ALMA’s Band 8 receivers, operating between 416 and 432 GHz. Within this frequency coverage we selected 13 spectral windows, each with a frequency resolution of 244 kHz (corresponding to a velocity resolution of 170 m s-1) and a bandwidth of either 235 or 118 MHz, for a total recorded bandwidth of 1.5 GHz. Band 8 covers rotational lines of all 4 targeted species (SO2, SO, NaCl, KCl) and their isotopologues in a single spectral set-up (Table S2). ALMA’s frequency tunings were set to track the changing line-of-sight velocity of Io during the observations, so there is no spectral smearing provided the tracking uses an ephemeris sampled at sufficient precision. For these observations the ephemeris (*34*) was sampled at 10 minute intervals; the resulting spectral smearing is < 2 kHz, which is a small fraction of the spectral resolution. The full width at half maxima for the observed lines are in the range of 0.6 to 1.0 MHz for the sulfur-bearing species and 0.95-1.15 MHz for the chlorine-bearing species. A tuning error resulted in some of the spectral windows being tuned incorrectly for the leading hemisphere observation such that two SO2 lines (430.229 and 430.232 GHz) were not covered by that observation. These lines are not used in our analysis.

Data reduction

The data were processed through the standard ALMA pipeline (*35*) to produce a calibrated measurement set (MS) containing the interferometric visibilities, which are the amplitude and phase of the cross-correlated signal between each pair of antennas. The line-free spectral channels across all spectral windows were split out to produce a continuum MS. This continuum MS was self-calibrated (*36*) then imaged using the Casa software (*37,38*) with an iterative procedure. First, a continuum limb-darkened disk the size of Io at the time of observation was produced and converted to visibilities; a limb darkening parameter of 0.2 was used, but the final image is only weakly sensitive to the choice of coefficient. The data were then phase calibrated using the model visibilities and subsequently imaged using the same model as an initial guess. This provided a starting point for the deconvolution algorithm; delta functions are then added to approximate Io’s observed continuum. The data were iteratively self-calibrated with increasingly shorter solution intervals, then processed using the CLEAN algorithm (*39*) as implemented in Casa. We used three iterations of increasingly deeper cleans; further iterations did not improve the SNR.

We apply the phase calibration derived from the continuum data (described above) to the continuum-subtracted spectral line data, then image each channel in the spectral line data channel separately. This produces a spectral data cube for each spectral window with ~0″.28 resolution and a spectral sampling of 244 kHz, and a frequency-averaged continuum image at ~0″.28 resolution. Figures S1 and S2show the continuum-subtracted image integrated over each spectral line listed in Table S2. We find that each spectral line from a single species, including both isotopologues, has the same spatial distribution, which indicates that the spatial distributions of the species are not biased by artifacts.

The 1D spectrum in each spectral window was extracted using an aperture that includes all pixels that are 5% of the peak continuum level or higher. This produces an aperture whose diameter is 1.3× the diameter of Io, i.e., extending one resolution element beyond the edge of Io.

The uncertainties on the datapoints in the spectra were estimated in two ways. First, a 1D spectrum was extracted in a region absent of sources, in exactly the same way as for the source and using the same aperture size; the standard deviation of the spectrum across each spectral window was used as an estimate of the noise in that spectral window. Second, the standard deviation of the spectrum of Io in spectral regions without apparent spectral lines was calculated, again providing a noise estimate per spectral window. We adopt the uncertainties derived from the latter method, because it incorporates the thermal noise from Io’s continuum. The first method gave uncertainties that were a factor of 1 to 3 lower, which we regard as under-estimates. The degree of bandpass calibration noise varies between spectral windows, and is non-negligible in some windows. The bandpass calibrator spectrum was smoothed using a frequency width of 7.8 MHz; this smoothing reduces the noise introduced by the bandpass calibrator, and although it can introduce spectral artifacts, these are similar in width to the smoothing window and hence much broader than Io’s emission lines. The uncertainties on the datapoints incorporate this noise, which is particularly high in the spectral windows containing the lines at 419.640, 428.298, 429.863, 429.952, and 420.887 GHz. The 1σ noise is shown in Figures 2 and 3and incorporated into the maximum-likelihood calculations (see below).

Radiative-transfer modeling and atmospheric retrievals

Model spectra are generated using a radiative transfer model designed for the atmosphere of Io (*8*), which we updated to add additional species. Our model includes opacity from SO2, SO, NaCl, and KCl, including the 32S and 34S isotopes of sulfur and the 35Cl and 37Cl isotopes of chlorine.

Models were fitted to the data using a Nelder-Mead minimization algorithm as implemented in the optimize package in the Scipy software (*40*). We then use the Emcee software (*41*) to perform Markov chain Monte Carlo (MCMC) simulations that determine the uncertainties on the measurements. The parameter values that correspond to the maximum likelihood values output by the MCMC simulations match the best-fitting values found by the minimization, with differences well below 1σ. We report the resulting uncertainties as the 1σ range measured from the posterior probability distributions output by the MCMC simulations. Table 1 reports the best-fitting parameters and MCMC-derived uncertainties for all free parameters in the models.

The line frequencies and strengths were adopted from the Cologne Database for Molecular Spectroscopy [CDMS (*42, 43*)]. We also tested line lists from the JPL Molecular Spectroscopy repository (*44*), but found they did not match the observed line positions in our datasets for any species except 32SO2 and 34SO2. The CDMS frequencies for the lines of the sulfur-bearing molecules agree with our observations after accounting for the line-of-sight velocity of Io. For NaCl, KCl and their isotopologues, we observe an additional velocity shift that we ascribe to bulk motion of the gas and include as a free parameter in our model fitting. The observed ~100 m s-1 velocity shift is the same across all chlorine-bearing species within each dataset; it is smaller than the velocities of Io’s largest class of plumes [500-1000 m s-1 (*45*)]. A velocity shift parameter is not included in the SO2 model because the line positions match the expected frequencies from CDMS. The velocity difference between the chlorine- and sulfur-bearing species could arise because SO2 and SO are more uniformly distributed, such that gas velocity components produce line broadening rather than a frequency shift. The broadening of the SO2 and SO lines due to Io’s rotational motion is included in the model (see below). The velocity shifts for the chlorine-bearing gasses are unlikely to be due to line list errors, because the shift is the same across NaCl and KCl lines (per dataset), whereas line list errors introduce offsets that differ between lines but are the same between datasets (per line). The frequency errors that would be introduced by using the JPL line lists are much larger than the observed frequency shifts due to gas velocity.

The strengths of the emission lines are sensitive to temperature, and the temperature profile in Io’s atmosphere is poorly known. The isotope ratio also varies with altitude due to gravitational stratification. Our observations therefore targeted lines that are sensitive to the same atmospheric altitudes. Figure 1 shows that the brightest emission in the sulfur lines is at the low-to-mid-latitude limbs of Io. The bright limb emission arises from the greater emitting column, due to the longer path length through the atmosphere towards the limbs. The emission lines therefore need to be produced at the same atmospheric altitudes in the center of the disk as well as at the limbs, where the gas column is longest. For the strong SO2 lines used in previous studies

(*14, 46*), the line opacities are high, such that emission arises predominantly from altitudes of roughly tens of kilometers. Figure S3 shows the contribution functions calculated from the model opacities at line center for the 32SO2 and 34SO2 lines targeted in our observations, compared to those used for the previous isotope ratio measurement (*14*). Particularly near the limb, all the 32SO2 lines used in the past work, and most of the 32SO2 lines covered by our data, are sensitive to different altitudes than the 34SO2 lines. To determine the isotope ratio, we therefore use only the two lines of 32SO2 that are sensitive to the lower atmosphere (418.815 and 429.863 GHz). Because the SNR of the 34SO line is low (and only detected in the leading hemisphere), the 34S/32S ratio is derived from SO2 alone, but we use the SO data as a consistency check.

The SO2 gas temperature is tightly constrained by our observations because the SO2 model fitting includes six emission lines from high to low excitation (Table S2). Temperature affects both the line widths and the relative strengths of the lines. If each line were fitted independently, the temperature would be degenerate with column density and with the velocity distribution of the gas, leading to much larger uncertainties. However, because we fit multiple lines simultaneously, the best-fitting temperature is constrained by the relative line strengths. The resulting best-fitting temperature, in combination with Io’s rotation, then determines the model line widths. The imperfect match between the model line widths and some of the observed spectra (Fig. 2) could arise from velocity components (e.g. from winds or plumes) that are not included in our model.

To determine a disk-integrated model spectrum for comparison with the data, we model the emission from Io’s atmosphere as a function of latitude and longitude, accounting for the changing gas column with emission angle and the Doppler shift corresponding to Io’s solid-body rotation at that latitude and longitude. The model was output with a range of spatial resolutions, from which we selected the coarsest model resolution that did not result in a disk-integrated spectrum that differed substantially from that produced by higher resolution models. Based on this criterion, we selected models generated with a spatial resolution of 0″.06 (about 6% of Io’s diameter), which were then spatially integrated to produce a disk-integrated model spectrum. Changing the spatial resolution of the model causes minor changes in the derived column densities, but does not affect the derived isotopic ratios.

For the 34S/32S model fitting, we assume that the molecular species are uniformly distributed across Io’s entire surface. Figure 1 indicates that the fractional coverage (fraction of the surface area of Io above which there is SO2 gas) is closer to ~50%. If the lines are optically thin, there is a linear trade-off between column density and fractional coverage: if column density is increased and fractional coverage decreased proportionally, the model line strength remains the same. Provided the fractional coverage is above ~15%, which is the case in our observations, there is a linear relation between column density and fractional coverage for the lines used in the 34S/32S analysis. Our assumption of uniform coverage therefore does not impact the derived isotope ratio, but it does affect the derived column densities.

For NaCl and KCl, the fractional coverage is unclear from the images; Figure S3 shows that if the fractional coverage is below ~10% there is enough opacity in the Na35Cl line that it no longer traces emission from the same altitudes as the Na37Cl line. This necessitates our inclusion of fractional coverage as a free parameter in the chlorine model fitting; if a broad range of fractional coverages is allowed by the data, the effect is to increase the derived uncertainties on all parameters that are correlated with fractional coverage. In our analysis, including this free parameter primarily increases the uncertainties on the gas column densities, because the best-fitting models are in a region of the parameter space where opacity is low and the derived isotope ratio is not strongly impacted. Figure S3shows the contribution functions have the same disk-integrated column for both 20% and 5% fractional coverage; in the former case opacity is unimportant and in the latter case opacity strongly affects the altitudes the emission lines arise from.

As an additional check of whether opacity effects bias the derived isotope ratio, we extracted spectra from localized regions on Io’s disk with both low and high path lengths (disk center and low-latitude limbs, respectively) then applied the sulfur model fitting. For the chlorine model fitting, we performed the same check using spectra from both fainter and brighter emission regions. These tests used circular apertures with 0″.3 diameters, shown in Fig. S4, to extract the spectra.The best-fitting parameters for each region are given in Table S3. This test assumes a coverage fraction of 1.0 within the 0″.3 aperture. Some of the NaCl and KCl emission occurs very close to the limb. We find that the derived column densities are sensitive to the exact emission angle used in the models, so should be interpreted with caution, but the derived isotope ratios are not sensitive to this parameter. The results of this test show that the 34S/32S and 37Cl/35Cl ratios derived from all spectra extracted within a given hemisphere differ by <1.5σ from the values derived from the disk-integrated spectra. The lack of systematic differences in the isotope ratios derived for low and high emission regions indicates that local opacities do not bias our derived isotope ratios. For the best-fitting atmospheric parameters and model resolution adopted above, the optical depths of all lines are <0.1 over most of the surface, always <0.5 for the sulfur-bearing species and <0.7 for the chlorine-bearing species (with in the highest values being for the strongest lines at the limbs).

The lines of Na35Cl and Na37Cl are detected at a much higher SNR than K35Cl and K37Cl, due to the higher abundance of NaCl relative to KCl. Therefore the chlorine model fitting is dominated by NaCl; using the Na35Cl and Na37Cl lines alone gives the same 37Cl/35Cl ratio, within the 1σ uncertainties, as using both NaCl and KCl. The Na/K ratios for both hemispheres, including the disk-integrated and local analyses, are all in the range 3 to 10, which is consistent with previous studies (*13*).

Figure S5 shows a random selection of model spectra drawn from the posterior probability distribution, compared to the observed sulfur data for the trailing hemisphere, to illustrate the variations in the spectra produced by varying the parameters within their uncertainties. Figure S6 shows models in which the SO2 column density was fixed at its best-fitting value but the 34S/32S ratio is varied from 0.040 (below the Solar System average) to 0.080 (above our best-fitting value).

**Supplementary Text**

Patera co-located with chlorine-bearing gasses

Our models indicate that NaCl and KCl have high gas temperatures, and Fig. 1 shows they are localized to discrete locations. As discussed in the main text, we interpret them as only present in volcanic plumes. For each of the two dates of observation, we determined the position of each source in the NaCl image and converted it to a latitude and longitude on Io using the geometry at the time of observation (Table S1). The latitudes and longitudes of the sources marked in Fig. 1 are given in Table S4. The uncertainties on the latitudes and longitudes were determined by calculating the latitude and longitude of every pixel within a 10×10 pixel box (roughly one resolution element on each side) surrounding the determined source center, then taking the standard deviation within the box. We investigated whether these correspond to known surface features (*47*). Table S4 lists the most likely patera as well as all paterae that fall within the 1σ uncertainties.

Volcanic activity at Kurdalagon Patera (consistent with location 1 in Figure 1), is thought to have been at least partially responsible for the massive brightening of Jupiter’s sodium nebula in early 2015 (*48*); our identification of NaCl gas at the location of the patera is consistent with this connection because it suggests that the style of volcanism taking place at Kurdalagon Patera produces Na-bearing gas. However, infrared images taken simultaneously with our ALMA observations on 2022 May 24 (*49*) do not show thermal emission at the latitudes and longitudes where we observe NaCl and KCl gasses. If the regions of high NaCl and KCl gas density are indeed volcanic plumes, they originate from volcanic centers that are not actively extruding large volumes of lava.

Rayleigh distillation model

We use a Rayleigh distillation model to relate the present-day ratio of two isotopes to the fraction of material that has been lost from the system over time. This relationship is quantified through the Rayleigh equation, which is 34*R*=34*R*0 *f* α-1 for the 34S and 32S sulfur isotopes. We use this to determine the value of *f*, the fraction of Io’s original sulfur inventory remaining at present day, based on our measured 34*R*.

Rayleigh fractionation entails the progressive and irreversible removal of material from a system (referred to as a reservoir). We assume an initial 34S/32S (34*R*0) for our system and a value for the fractionation factor (34αloss), which describes the instantaneous isotopic partitioning between the modelled system and each packet of material removed at each time step. The Rayleigh distillation framework assumes that i) the material is being removed continuously, and ii) the residue is well mixed.

For the case of sulfur on Io, we propose that the well-mixed system consists of all of Io’s sulfur that is not in the moon’s core. It is also possible that a smaller shallow system, consisting just of Io’s atmosphere and crust (and perhaps some portion of the upper mantle), is mixed more rapidly, due to shallow re-melting of surface frosts recycled into the crust. In such a scenario, this smaller well-mixed sulfur reservoir would become isotopically fractionated more rapidly than the full mantle plus crust system. However, to maintain the crust-atmosphere reservoir, mantle material would need to be continuously injected to balance Io’s mass loss rate. This injection of essentially unfractionated mantle material would buffer the near-surface system such that the atmospheric 34S/32S could not become highly fractionated: the atmospheric 34S/32S would take values between those of steady-state and Rayleigh fractionation scenarios (*19*). Fractionation in the shallower, smaller system could only produce a highly fractionated atmospheric 34S/32S if there is no addition of unfractionated mantle. We consider that scenario highly unlikely, given the observed mantle-derived volcanism and the amount of sulfur input into the crust that is required to balance Io’s mass loss.

By assuming the well-mixed reservoir consists of all Io’s sulfur that is not in the core, our model calculation also requires that there is no sulfur exchange between the core and mantle. The sulfur isotopic fractionation factor between metal and silicates is close to 1 (*50*), so we expect that the formation of Io’s core left it with the moon’s initial sulfur isotope composition. If Io’s core supplies sulfur to the mantle, this provides a source at Io’s initial 34S/32S ratio and therefore lowers the average 34S/32S ratio of the sulfur that is available for loss. This would therefore require even greater sulfur loss to explain our measurement.

The derived fraction of sulfur lost from Io depends on our adopted initial isotope ratio 34*R*0 and 34αloss. As discussed in the main text, potential deviations in the 34S/32S ratio of Io-forming material from the Solar System average are expected to be four orders of magnitude smaller (in δ34S) than our observed fractionation. Adopting the Solar System average for 34*R*0 is therefore not a large source of uncertainty. The value we adopt for 34αloss assumes that all loss takes place at or above an exobase located at 600 km altitude. The altitude of the exobase is uncertain and could be as low as 100 to 200 km (*51, 52*). During Io’s night time, the exobase might be at the surface itself. If we adopted an exobase at a lower altitude than 600 km, it would result in an 34αloss value closer to 1. This would put our loss fraction derived from the Rayleigh equation at the upper end of our reported range but does not qualitatively change our conclusions.

In our implementation of the Rayleigh model, we assume a constant fractionation factor, 34αloss. On Io, however, 34αloss probably changes on diurnal, seasonal, and stochastic timescales, as Io’s exobase altitude changes in response to changing atmospheric densities. We made the simplifying assumption of a fixed altitude because we expect the exobase is typically at or below our adopted value, such that any deviation from our assumption would result in the same conclusion, or even greater sulfur loss.

A group of images of a number of objects

Description automatically generated with medium confidence

Fig. S1. **Distributions of all observed molecular emissions from Io’s leading hemisphere.** Same as Figure 1, but for all the lines we observed (listed in Table S2) on the leading hemisphere for (**A-G**) 32SO2, (**H-K**) 34SO2, (**L**) 32SO, (**M**) 34SO, (**N**) Na35Cl, (**O**) Na37Cl, **(P**) K35Cl, and (**Q-R**) K37Cl. A tuning error led to no recorded data for the SO2 lines at (**F**) 430.229 and (**G**) 430.232 GHz. Colorbars are in the intensity units given in Panel R.

A collage of images of a cell

Description automatically generated with medium confidence

Fig. S2. **Distributions of all observed molecular emissions from Io’s trailing hemisphere.**  Same as Fig. S1, but for the trailing hemisphere.

A graph of a graph of the same size

Description automatically generated with low confidenceA diagram of different types of data

Description automatically generated with medium confidence

Fig. S3. **Contribution functions for emission lines from this and previous work.** Contribution functions for all observed lines of the species used to derive the sulfur and chlorine isotope ratios. The lines used in previous work (*14*) are shown for comparison. (**A,C,E**) Calculated values for the center of the disk and (**B,D,F**) the limb, for the species indicates on the panels. The SO2 contribution functions assume an SO2 column density of 1x1016 cm-2 and gas temperature of 240 K, corresponding to the best fitting values in Table 1. For 32SO2, only the lines at 418.816 and 429.864 GHz are used to derive the isotope ratio because they are sensitive to the same atmospheric altitudes as the 34SO2 lines, especially near the limb where much of the emission appears. The NaCl and KCl contribution functions assume a temperature of 800 K and 20% fractional coverage unless otherwise indicated; some contribution functions assume an alternative 5% coverage (for an equivalent disk-integrated column) to show how much the fractional coverage can impact the relative altitudes the isotopologues are sensitive to.

A screenshot of a diagram

Description automatically generated

A diagram of a graph

Description automatically generated with medium confidence

Fig S4. **Locations used for local model fitting.** Images of (**A-B**) the leading and (**C-D**) trailing hemisphere in example emission lines of (**A,C**) 32SO2 and (**B,D**) Na35Cl (frequencies labeled above each panel). Red circles indicate the apertures used for our tests (see text). For sulfur, the identified regions are the east limb (EL), west limb (WL), and disk center (DC). For chlorine, the identified regions are the three brightest emission locations in each observation. Other symbols are the same as in Figure 1.

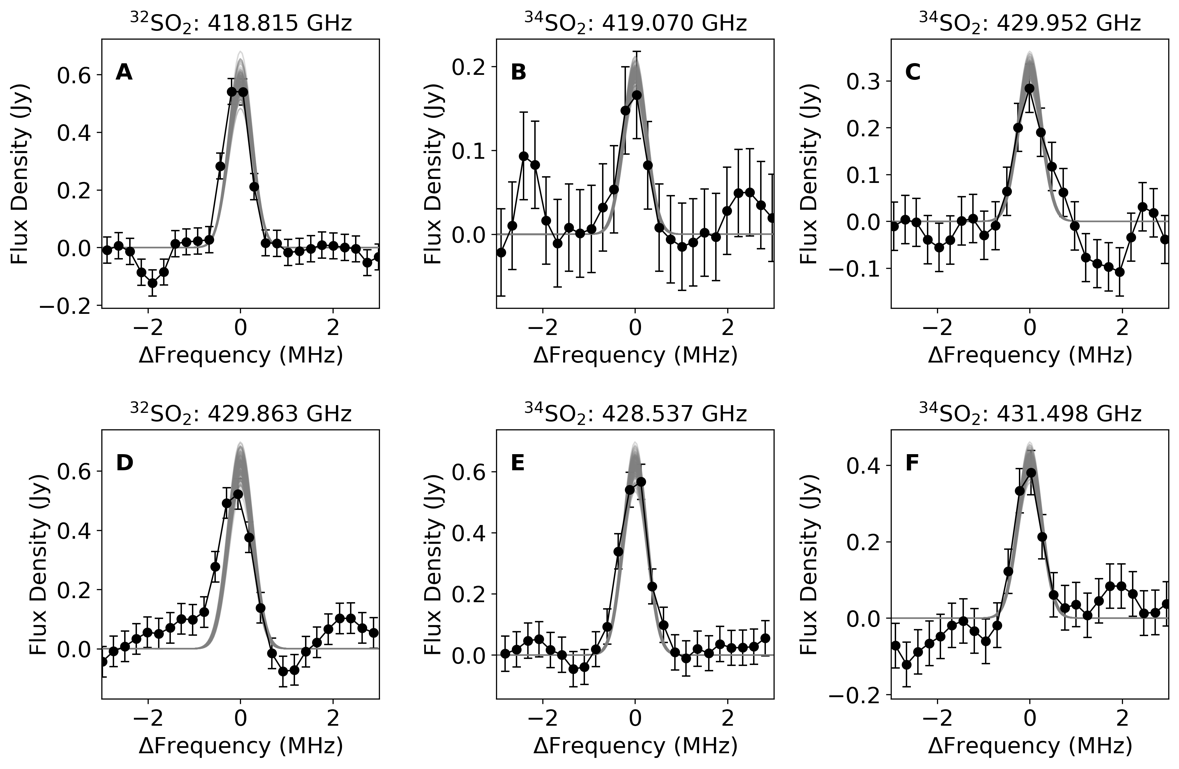


Fig S5. **Visualization of parameter uncertainties.** Same as Fig. 2I-K and M-O but with multiple models (gray curves) corresponding to 150 parameter combinations randomly selected from the joint posterior probability distribution determined by the MCMC simulation.

**A group of graphs showing different types of frequency

Description automatically generated**

Fig S6. **Visualization of different isotope ratios.** Same as Fig. S5, but with models corresponding to different isotope ratios (see legend). The models shown all adopt the best-fitting 32SO2 column density for this observation. The 34*R* values shown for 34SO2 were chosen to be ±5σ from the best fitting value.

Table S1.

**Observing parameters for the two observations presented in this paper.** Pwv is precipitable water vapour.

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Hemisphere | Date/Time  [UT] | Time on Source | Pwv [mm] | Angular Resolution | Angular Diameter | Sub-obs longitude  [°W] | Sub-obs latitude  [°N] | North pole angle |
| Leading | 2022-05-24  12:48 to 16:07 | 1h40m | 0.7 to 0.8 | 0.23″×0.35″ | 0.937″ | 73 to 101 | 2.1 | 335° |
| Trailing | 2022-05-18  10:28 to 12:02 | 50m | 0.5 | 0.27″×0.29″ | 0.924″ | 27 to 287 | 2.1 | 335° |

Table S2.

**Molecular data for all emission lines detected in our observations.** Quantum numbers (QN) are given for the total rotational quantum number (J), the total rotational angular momentum (N), and the projections of N onto the A and C inertial axes (Ka and Kc respectively), for the upper and lower state. Data from CDMS (*42, 43*, *53-61*).

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Species | Frequency [MHz] | EL  [cm-1] | Line Strength at 300 K [cm-1/mol/cm2] | QN | Detected  Leading | Detected  Trailing |
| 32SO2 | 416825.5576±0.0019 | 289.053 | 6.87986×10-22 | J=28  Ka=4←5  Kc=24←23 | Y | Y |
| 32SO2 | 418815.8002±0.0020 | 192.736 | 1.03748×10-22 | J=18←17  Ka=7←8  Kc=11←10 | Y | Y |
| 32SO2 | 419019.0378±0.0019 | 331.436 | 5.58444×10-22 | J=31  Ka=3←4  Kc=29←28 | Y | Y |
| 32SO2 | 429863.8467±0.0019 | 659.183 | 1.91637×10-22 | J=44  Ka=3←4  Kc=41←40 | Y | Y |
| 32SO2 | 430193.7070±0.0015 | 180.632 | 1.05604×10-21 | J=23←24  Ka=2←1  Kc=22←23 | Y | Y |
| 32SO2 | 430228.6487±0.0016 | 168.493 | 1.66180×10-21 | J=23←24  Ka=1←0  Kc=23←24 | N/A | Y |
| 32SO2 | 430232.3126±0.0017 | 138.228 | 1.02560×10-21 | J=20←21  Ka=1←2  Kc=19←20 | N/A | Y |
| 34SO2 | 419070.9415±0.0056 | 222.079 | 5.31348×10-22 | J=25←26  Ka=3←2  Kc=23←24 | Y | Y |
| 34SO2 | 428537.9435±0.0065 | 167.768 | 1.63448×10-21 | J=23←24  Ka=1←0  Kc=23←24 | Y | Y |
| 34SO2 | 429952.4205±0.0075 | 188.460 | 8.54829×10-22 | J=22  Ka=4←5  Kc=18←17 | Y | Y |
| 34SO2 | 431498.3574±0.0061 | 179.871 | 1.07468×10-21 | J=23←24  Ka=2←1  Kc=22←23 | Y | Y |
| 32SO | 431808.196±0.020 | 67.731 | 8.78778×10-21 | J=9←10  N=10←11 | Y | Y |
| 34SO | 419640.353±0.014 | 68.080 | 6.61728×10-21 | J=9←10  N=8←9 | Y | N |
| Na35Cl | 428518.5512±0.0040 | 229.071 | 2.99626×10-19 | J=32←33 | Y | Y |
| Na37Cl | 419381.1264±0.0044 | 224.178 | 2.86536×10-19 | J=32←33 | Y | Y |
| K35Cl | 428297.8176±0.0027 | 393.948 | 1.58008×10-19 | J=55←56 | Y | Y |
| K37Cl | 416185.8003±0.0027 | 382.778 | 1.52012×10-19 | J=55←56 | Y | N |
| K37Cl | 430886.5999±0.0028 | 410.788 | 1.47360×10-19 | J=57←58 | Y | N |

**Table S3. Best-fitting model parameters for local analysis.** Same as Table 1, but for the local regions shown in Fig S4, with 1σ uncertainties from MCMC simulations.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
|  | Sulfur-bearing molecules |  |  |  |  |
| Region | SO2 column density [cm-2] | Tgas [K] | 34SO2/32SO2 |  |  |
| Leading: EL | (1.306±0.034)×1016 | 238.8±2.9 | 0.0579±0.0020 |  |  |
| Leading: WL | (7.19±0.34)×1015 | 236.8±5.5 | 0.0574±0.0038 |  |  |
| Leading: DC | (1.971±0.090)×1016 | 198.4±4.0 | 0.0526±0.0028 |  |  |
| Trailing: EL | (3.59±0.19)×1015 | 260.5±7.9 | 0.0659±0.0051 |  |  |
| Trailing: WL | (4.22±0.31)×1015 | 240.3±9.4 | 0.0660±0.0061 |  |  |
| Trailing: DC | (5.61±0.55)×1015 | 210.2±9.7 | 0.0682±0.0081 |  |  |
|  |  | Chlorine-bearing molecules |  |  |  |
| Region | NaCl column density [cm-2] | KCl column density [cm-2] | Tgas [K] | 37Cl/35Cl | Velocity [m s-1] |
| Leading: 1 | (4.18±0.23)×1012 | (7.79±0.77)×1011 | 934±59 | 0.405±0.020 | 19±11 |
| Leading: 2 | (4.99±0.23)×1012 | (5.3±1.4)×1011 | 727±49 | 0.348±0.021 | 52±11 |
| Leading: 3 | (2.82±0.40)×1011 | (4.0±1.1)×1010 | 1320±180 | 0.399±0.044 | 275±22 |
| Trailing: 1 | (4.38±0.13)×1012 | (5.4±1.1)×1011 | 639±28 | 0.419±0.018 | -90.3±6.4 |
| Trailing: 2 | (7.12±0.31)×1011 | (7.5±1.3)×1010 | 796±42 | 0.417±0.016 | -150±11 |
| Trailing: 3 | (6.21±0.62)×1011 | (3.7±2.1)×1010 | 1290±130 | 0.350±0.029 | -24±15 |

Table S4. NaCl and KCl source locations and possible identifications with paterae. Location numbers correspond to Figure 1. The most likely patera is identified if there is a clear, isolated patera at the identified latitude and longitude. All other named paterae within the uncertainties on the latitudes and longitudes are also listed. The latitudes and longitudes of leading hemisphere location 1 and trailing hemisphere location 3 are consistent within 1σ of one another so might be the same gas source.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Location | Latitude | Longitude | Most likely patera | Other paterae within uncertainties |
| Leading hemisphere |  |  |  |  |
| 1 | 27±10ºS | 20±14ºW |  | Kanehekili Fluctus,  Cataquil Patera, Uta Patera, Angpetu Patera |
| 2 | 66±11ºS | 136±17ºW |  |  |
| 3 | 22±10ºN | 159±14ºW |  | Thomagata Patera, Reshef Patera, Surya Patera, Chaac Patera |
| Trailing hemisphere |  |  |  |  |
| 1 | 58±10ºS | 218±17ºW | Kurdalagon Patera | Gabija Patera |
| 2 | 30±11ºN | 211±13ºW | Isum Patera | Susanoo Patera |
| 3 | 24±10ºS | 355±15ºW |  | many |
| 4 | 33±12ºN | 330±15ºW | Fuchi Patera | Manua Patera |
| 5 | 59±11ºS | 341±15ºW | Creidne Patera | Hiruko Patera, Inti Patera |

**Table S5.** Data sources for previous isotope measurements shown in Fig 4.

|  |  |  |
| --- | --- | --- |
|  | **Sample** | **Reference** |
| **Sulfur** | Solar wind | (*62*) |
|  | Bulk Silicate Earth (BSE) | (*63*) |
|  | Earth sediments | (*64*) |
|  | Earth volcanic gasses | (*65*) |
|  | Lunar melt inclusions (MIs) | (*66*) |
|  | Lunar mare basalts | (*67*) |
|  | Gale crater sediments | (*68*) |
|  | Ordinary chondrites (OC) | (*27*) |
|  | Comet Hale-Bopp H2S | (*69*) |
|  | Comet Hale-Bopp CS | (*70*) |
|  | Comet 67P/Churyumov-Gerasimenko | (*28*) |
|  | Comet C/2014 Q2 (Lovejoy) | (*71*) |
|  | Comet C/2012 F6 (Lemmon) | (*71*) |
|  | Interstellar medium (ISM) | (*72*) |
|  | Galactic cosmic rays | (*73*) |
| **Chlorine** | Venus, HCl gas | (*74*) |
|  | Moon, basalts and soils | (*75, 76*) |
|  | Mars, HCl gas | (*77*) |
|  | Vesta, from apatite in eucrites | (*78*) |
|  | Comet 67P/Churyumov-Gerasimenko, from HCl gas | (*79)* |