

that the distance between the 5- and 5'-carbons of the two thiophene rings of 1,2-bis(2,5-dimethyl-3-thienyl)perfluorocyclopentene is shortened as much as ~10%, and unit cell lengths and volume tend to decrease during the cyclization reaction in the crystal. X-ray crystallographic analysis of **1b** similarly confirmed that the distance between the edges of two phenyl rings was shortened from 1.41 to 1.39 nm when **1a** was converted to **1b** (Fig. 4). The cofacial orientation of the coplanar planes of **1b** (Fig. 5B) allows the molecules to pack each other closely, which decreases the unit cell along the *c* axis. This effect would explain the valley formation on the sectional B surface after UV irradiation. The direction of the valley is the same as the direction of the red arrow in Fig. 5B (76.5° tilted from the *b-c* plane) to within ±2°. Upon visible-light irradiation, the thiophene rings again rotated to the twisted conformation and expanded the *c* axis to fill up the valley.

The shortening in the distance between the phenyl ring edges by the cyclization reaction results in the decrease in the thickness of the molecular layers shown in Fig. 5B. The shrinking of the molecular layers produces vacancies in the crystal bulk. Accumulation of vacancies deep within the crystal allows the surface molecular layer to sink as much as one layer (~1 nm). According to the geometrical structural change shown in Fig. 4, the one-layer vacancy requires the photocyclization reactions of at least 60 molecular layers. Irradiation for 10 s with 366-nm light (intensity 12 mW/cm²) induces the photocyclization reactions of 1.0 × 10¹⁷ molecules/cm² in the single crystal by taking into account 50% transmittance of the thin crystal at 366-nm light and the quantum yield of 0.96 (21). This corresponds to the photocyclization reactions of 600 molecular layers. The reactions take place as deep as 500 μm (Fig. 1). Therefore, the reacted molecules are not localized in the 600 layers but are distributed in about 5 × 10⁵ layers (= 500 μm). The number of reacted molecules in 600 (versus 60) molecular layers is necessary to produce the one-molecular layer vacancy. When the number of reacted molecules is less than 1.0 × 10¹⁷ molecules/cm², the steps have been barely formed. The induction period is the accumulation time of the reacted molecules until 1.0 × 10¹⁷ molecules/cm². This process would explain step formation on the A crystal surface. Upon prolonged irradiation, the vacancies increase and two or more molecular layers sink. The direction of the step formation was along the *c* axis (Fig. 5A, red arrow). The rather weak interaction between perfluorocyclopentene groups possibly induces the step formation along the *c* axis. The cycloreversion reaction filled up the vacancies, and the surface with steps again returned to the initial flat surface.

The crystal reversibly shrank and expanded by alternate irradiation with UV and visible light. The shrinkage of the surface was digital, and each step corresponded to the thickness of one molecular layer as short as 1 nm. The reversible surface morphological changes could be applied to photodriven, nanoscale actuators that reversibly change thickness stepwise by alternate irradiation with UV and visible light.

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29. X-ray crystallographic analysis was carried out using a Bruker SMART1000 charge-coupled device-based diffractometer (50 kV, 40 mA) with Mo Kα radiation. Crystal data for **1a**: C₂₉H₂₂F₆S₂, MW = 548.59, monoclinic, space group C2/c, Z = 4, T = 298(2) K, a = 24.023(4) Å, b = 8.466(2) Å, c = 13.350(2) Å, β = 109.235(3)°, V = 2563.6(8) Å³, goodness of fit = 0.944, R1[I] > 2σ(I)] = 0.0485, wR2 (all data) = 0.1421. Crystal data for **1b**: C₂₉H₂₂F₆S₂, MW = 548.59, monoclinic, space group P2₁/c, Z = 4, T = 296(2) K, a = 18.472(6) Å, b = 10.884(2) Å, c = 10.659(3) Å, β = 100.87(3)°, V = 2491.3(11) Å³, goodness of fit = 1.051, R1[I] > 2σ(I)] = 0.0794, wR2 (all data) = 0.2259. Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications CCDC 155979 and 155980. Copies of the data can be obtained, free of charge, from CCDC (e-mail: deposit@ccdc.cam.ac.uk). Details of x-ray crystallographic analysis are also available at Science online (www.sciencemag.org/cgi/content/full/291/5509/1769/DC1).
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Ablation, Flux, and Atmospheric Implications of Meteors Inferred from Stratospheric Aerosol

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Single-particle analyses of stratospheric aerosol show that about half of the particles contain 0.5 to 1.0 weight percent meteoritic iron by mass, requiring a total extraterrestrial influx of 8 to 38 gigagrams per year. The sodium/iron ratio in these stratospheric particles is higher and the magnesium/iron and calcium/iron ratios are lower than in chondritic meteorites, implying that the fraction of material that is ablated must lie at the low end of previous estimates and that the extraterrestrial component that resides in the mesosphere and stratosphere is not of chondritic composition.

Accurate measurement of the flux of interplanetary material to Earth has proven difficult because the majority of extraterrestrial matter incident on the atmosphere is in the

form of micrometeors that ablate at ~100-km altitude when atmospheric pressure causes sufficient frictional heating (1–6). Only a minor fraction reach the surface without va-

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porizing as the interiors of large bodies, small (<100- μm diameter) particles that survive deceleration without alteration, and the melted remnants of meteors known as spherules (1–8). Some estimation of the flux can be based on observations above the atmosphere, before substantial alteration of the objects has occurred. Measurements have been constrained to the examination of impact craters such as those on the Long Duration Exposure Facility satellite (40 ± 20 Gg/year) (9) because the large relative velocities involved have precluded systematic material collection. Attempts to estimate the flux have also come from models of meteoritic iron in the mesosphere (8 Gg/year) (2), a region where the ablation process leads to persistent layers of metal atoms and ions (1, 2, 5, 6, 10), but this material represents only a small fraction of the vaporization products. Composites of these estimation types have used satellite-borne impact detectors and meteor trail radio echoes and visual counts (8 to 30 Gg/year, best estimate = 16.2 Gg/year) (11). Measurement of extraterrestrial iridium after ablated material has settled from the atmosphere and been deposited to the sea floor has also been used for budget calculations (78 Gg/year) (12).

An ideal location for a collection of ablated meteoritic material is the layer of sulfuric acid and water particles found in the stratosphere. Model studies show that condensation and coagulation of the ablation products result in the formation of nanometer-sized smoke particles in the mesosphere (3) that sediment and are transported into the stratosphere, predominantly over the winter pole because of atmospheric circulation (13). Meteoritic material is incorporated into the background sulfate aerosol (14, 15) in the stratosphere and remains for an average of 12 to 16 months (16) because of the extreme stability of this region. The material that ablates in the upper atmosphere—the majority of the incident material—will consequently remain in the sulfate layer for an extended period of time before deposition to the surface. The extended residence time also prevents sporadic events, such as meteor showers, from creating transient extraterrestrial material loads within the sulfate layer. Sampling the large repository of meteoritic material in this region can therefore overcome the aforementioned difficulties in attempting to estimate flux from a minor subset of material and can also be used to provide detailed

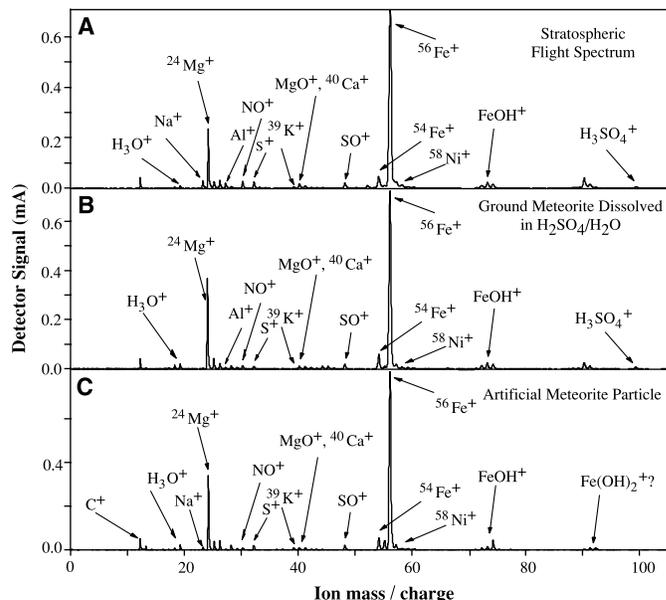
information on the ablation process.

The Particle Analysis by Laser Mass Spectrometry (PALMS) instrument has been used to obtain high signal-to-noise measurements of meteoritic material in stratospheric aerosol particles (17). Measurements were made aboard a NASA aircraft during April and May 1998 as part of the WB-57F Aerosol Mission (WAM) and September 1999 in the Atmospheric Chemistry of Combustion Emissions Near the Tropopause (ACCENT) study. PALMS uses an yttrium-aluminum-garnet laser to detect particles from 0.2- to 3- μm diameter by light scattering and to trigger an excimer laser that vaporizes and ionizes the components (18). During the missions, more than 2500 spectra of stratospheric aerosol particles that contained meteoritic material were obtained (Fig. 1). The sensitivity of the PALMS instrument to meteoritic metals allowed us to quantify the amount of extraterrestrial material present in stratospheric aerosol and to characterize the ablation process by identifying the relative abundances of individual components in laboratory experiments.

Initial laboratory experiments were conducted by dissolving ordinary chondrites from the L- and H-groups (relative low and high iron, respectively) in 65 weight % (wt %) H_2SO_4 . Aerosol was produced by bubbling dry nitrogen through the solution, and particles were selected at 0.3- μm diameter with a differential mobility analyzer. Although experiments were normally performed on particles of this diameter, no size dependence was noted from 0.2 to 0.5 μm for any of the results presented here. The solution acid concentration and particle size were chosen to closely represent stratospheric particles

(16). Particles produced from dissolved ground meteorite were sampled with the PALMS instrument, and the spectra exhibited good correlation with those obtained during flight (Fig. 1). This result demonstrated that it was possible to represent stratospheric particles by preparing aerosol in the laboratory from the individual components associated with those particles. The second step of laboratory experiments was to prepare “artificial meteorite” solutions by dissolving commercially available chemicals in sulfuric acid to mimic the principal components of chondritic meteorites (19). Fe, Mg, Ca, Na, Ni, Mn, and K, which are moderately soluble in sulfuric acid (20), were added to solution as neutral metals or sulfate salts. Silicon and aluminum were not included because they form insoluble oxides that would not mix homogeneously during particle generation. Sulfur and oxygen are substantial meteorite components but were not added because they could not be distinguished from the sulfuric acid matrix. Experiments were conducted on artificial meteorite particles and not just those produced from dissolved ground meteorite for two reasons. First, ground meteorite contains insoluble components that precluded the quantification of dissolved material and identification of which components were in solution. Second, the preparation of solutions from laboratory chemicals allowed us to vary the quantity of components with respect to one another, a flexibility not available with addition of a ground sample of fixed composition. Particles produced from artificial meteorite solution were sampled with the PALMS instrument under the same conditions used for dissolved ground meteorite, and these spectra also exhibited good correlation with

Fig. 1. Typical positive ion mass spectra. (A) Stratospheric aerosol particle that contained meteoritic material (17). (B) Ground meteorite particle composed of H-group chondritic matter (Field Museum of Natural History sample Me 2076) dissolved in 65 wt % sulfuric acid such that there was ≤ 1.0 wt % Fe in solution (some fraction, possibly SiO_2 , remained visibly undissolved). (C) Artificial meteorite particle prepared in the laboratory that was 65 wt % sulfuric acid, 0.75 wt % Fe, 0.23 wt % Mg, and minor species in the abundance found in chondritic meteorites (19) with respect to the given iron concentration. Particle mass is balanced by H_2O in all cases.



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those obtained during flight (Fig. 1).

Laboratory studies were critical to quantify the amount of meteoritic matter present in stratospheric sulfate aerosol and thus the extraterrestrial flux. The quantity of dissolved artificial meteorite components was gradually increased from a level of 0.1 to 5.0 wt % Fe. With

the exception of magnesium, which was depleted by a factor of 2 (explanation in following paragraphs), all species were added in the relative abundances to iron found in ordinary chondrites. The S⁺ and SO⁺ ion peaks, the dominant positive ion fragments produced when sulfuric acid and water particles are laser ablated,

were compared with Fe⁺ as the concentration of the solution from which the particles were produced was increased. Artificial meteorite particles with 0.5 to 1.0 wt % Fe exhibited good correlation for these two ratios with stratospheric particles containing meteoritic material.

Mossop (21) and Bigg *et al.* (22) have noted the presence of meteoritic inclusions, frequently several per droplet, within sulfate particles in previous studies. This is consistent with the presence of insoluble silicon and aluminum oxide fragments in stratospheric sulfuric acid and water particles. Sheridan *et al.* (23) observed infrequent inclusions of >30-nm diameter in stratospheric particles. Meteoritic iron present at the lower limit found here of 0.5 wt % in a 0.3- μ m diameter, 65 wt % H₂SO₄ particle would correspond to a sphere containing all extraterrestrial material of diameter ~70 nm at a density (3) of 3 g/cm³, which should have been detected. It is unlikely, however, that smoke particles form spheres. Instead, a loose aggregate, much like soot, may be formed during coagulation. Once present in solution, soluble components would be eliminated from the aggregate, leaving behind several smaller insoluble fragments below the detection limit of the Sheridan *et al.* observations.

Once laboratory experiments had been used to show that stratospheric particles contain ~0.75 wt % extraterrestrial iron, the ratios of the other meteoritic metals were characterized by variation of magnesium and the minor components at this fixed concentration of iron in sulfuric acid and water solutions (Figs. 2 and 3). Although the composition of extraterrestrial material incident on the atmosphere is believed to be predominantly chondritic in nature (6, 10), the ablation process may cause preferential vaporization of the more volatile species from the precursor bodies. For example, McNeil *et al.* (5) proposed "differential ablation" of meteorite components at various altitudes to explain observations that show higher mesospheric concentration of more volatile species than chondritic composition would suggest (6, 10). This concept is consistent with the findings of Hashimoto (24), which show that melts of FeO-MgO-SiO₂-CaO-Al₂O₃ exhibit a volatility sequence such that the iron fraction vaporizes more readily than magnesium. Taylor *et al.* (25, 26) noted that a well-preserved collection of spherules from the South Pole exhibit a range of compositions that can be explained by various stages of evaporation from an idealized chondritic melt.

Experiments performed on artificial meteorite particles formed from solutions with the chondritic Mg/Fe ratio had comparable mass spectral Mg/Fe ratios to those formed from ground meteorite solution (Fig. 2). Although these experiments strengthened the assertion that artificial meteorite solution was a suitable surrogate for dissolved ground chondrites, they also showed that the flight data

Fig. 2. Normalized histograms of the spectral ratio of Mg to Fe. Shown in shaded green are fractions of spectra versus Mg to Fe ratio for artificial meteorite solutions. Numbers indicate the relative quantity of magnesium added with respect to chondritic abundance ("0.5" represents depletion by half from the chondritic abundance, whereas "2.0" represents enrichment by two times). Studies were performed on artificial meteorite particles at 65 wt % sulfuric acid containing 0.75 wt % Fe. Histograms from two recent WB-57F aircraft missions for stratospheric aerosol that contained meteoritic matter best match artificial meteorite particles when magnesium was depleted by a factor of two ("0.5"). Histograms for ground meteorite particles produced from dissolved L- and H-group chondrites (Field Museum of Natural History samples Me 1990 and 2076, respectively) exhibit best correlation with artificial meteorite particles with chondritic Mg composition ("1.0") but do not agree with the flight data. All histograms are of the same scale with offsets for clarity.

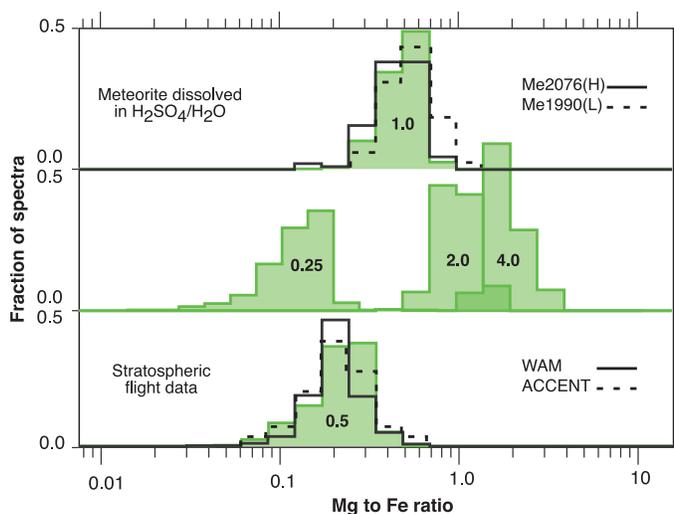
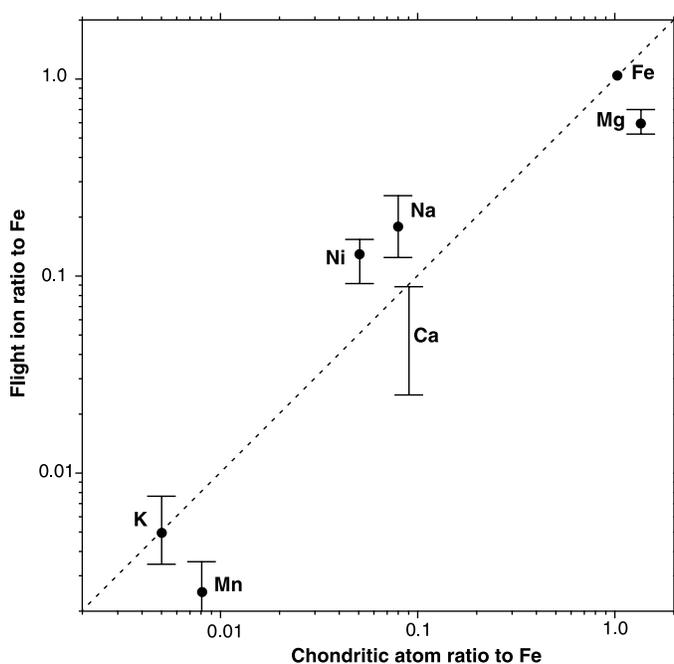


Fig. 3. Ion ratios of magnesium and the minor meteoritic elements to Fe observed in flight versus the chondritic atom ratio normalized to iron. The values are based on the mass spectral ratio from flight and the relative sensitivity factor (RSF) of the PALMS instrument to each species as determined from laboratory experiments. For example, the RSF for magnesium was determined with the histograms shown in Fig. 2, which yield a value of 0.33. Similar laboratory experiments yielded RSF values for Na, Ni, Mn, and K of 0.20, 0.21, 6.3, and 1.6, respectively. The error bars in the ion ratios are given by the combination of the linearity of the RSF as a function of solute concentration from laboratory studies on artificial meteorite particles and the uncertainty in the modes of the histograms observed in the laboratory and in flight. No specific value is given for calcium, but the possible range observed in flight is shown (27). Values that fall below the 1:1 line (dashed) are therefore depleted in stratospheric aerosol relative to chondritic, whereas values that lie above the line are enriched. Ni, Mn, and K each represented less than 10⁻¹⁷ g in a 0.3- μ m diameter artificial meteorite or stratospheric particle containing meteoritic material and are consequently less certain than the other species because of proximity to the level of noise in the mass spectra investigated.



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were comparable only to artificial meteorite particles formed from solutions with half the chondritic Mg/Fe ratio and not the nominal value (Fig. 2). Likewise, calcium is depleted in stratospheric aerosol by up to a factor of 3.5 (27). Sodium, the most volatile species investigated, is enriched by about a factor of 2 with respect to Fe (Fig. 3).

The relative ratios of meteoritic metals in the ablation products that reside in stratospheric sulfate aerosol determined in this work can be used to estimate the fraction of extraterrestrial matter that is vaporized if a chondritic precursor is assumed. Ordinary chondrites are about 20% Fe, 10% Si, and 10% Mg by mass. Calcium and aluminum represent ~1% each. If all of the Na ablates, consistent with the suggestion by Brownlee (28) that a criterion for judging the extraterrestrial origin of spherules be the almost complete depletion of volatile species, and the Na/Fe and Mg/Fe ratios are as determined by our calibrations, then the implication is that about 50% of the Fe and 75% of the Mg does not ablate. Under reasonable assumptions (Si and Al ablate like Fe, Ca like Mg, and the portion that remains in a melt is as FeO, MgO, SiO₂, Al₂O₃, and CaO), then a best estimate for the fraction of incident mass that ablates is 58%. A reasonable upper limit for vaporization can be calculated by assuming that the Na/Fe and Mg/Fe enrichments are 1.3 and 0.75, respectively (about the 1 σ deviations of the histograms as shown in Fig. 2 for Mg), and maintaining the remainder of the above method. This corresponds to a vaporization of 75% of the Fe and 56% of the Mg and 78% overall ablation of the incident mass. These levels of vaporization are consistent with previous studies, falling toward the low end of estimates based on isotopic fractionation in spherules (52 to 99%) (29) and ablation (~70%) (3) and thermal modeling (70 to 90%) (4).

Ablation of extraterrestrial material forces the majority of the mass incident on the atmosphere to become incorporated in stratospheric aerosol. Our measurements of these particles, in conjunction with laboratory studies, can be used to estimate the influx without constraint by a minor fraction of the precursor bodies or incoming velocity and material property assumptions. As shown, 0.5 to 1.0% by mass of ~50% of stratospheric particles is extraterrestrial Fe. The influx of S to the stratosphere is 100 to 160 Gg/year (16), representing 472 to 755 Gg/year condensable matter at 65 wt % H₂SO₄. For a 12- to 16-month average aerosol lifetime (16), an influx of 4 to 19 Gg/year of meteoritic material is required to maintain the observed Fe signal in the stratospheric sulfate layer. This calculation assumes that all of the ablated material is incorporated into stratospheric sulfate aerosol (30). For 58% ablation, this corresponds to an extraterrestrial mass influx between 8 and 33 Gg/year. Maurette *et al.* (31) found that the abundance of unmelted mi-

cro-meteorites was 25 to 40% of the spherule mass in a collection from Antarctic blue ice. Adopting this value, the total micrometeorite flux to Earth is 8 to 38 Gg/year.

The presence of several wt % of metal ions and insoluble oxides in a large fraction of stratospheric particles has interesting implications for our understanding of the sulfate layer. For example, the artificial meteorite solutions of ≥ 0.75 wt % Fe used in these studies exhibit a visible tint. The existence of chromophores in stratospheric aerosol could have chemical and radiative importance. Several other atmospherically relevant consequences must also be considered. Particle formation in the stratosphere is often assumed to predominantly proceed homogeneously from the gas phase, but heterogeneous aerosol formation may occur as sulfuric acid vapor condenses on smoke nuclei as they sediment from the mesosphere. Meteoritic particles are one of several possible explanations for the enhancement of aerosol in the stratosphere during polar spring as smoke-rich mesospheric air downwells (32). This result is not restricted to the terrestrial atmosphere. Particles originating from meteor ablation and capable of acting as condensation nuclei are probably present for all solar system bodies with an atmosphere (for example, Mars and Titan). As discussed by Prather and Rodriguez (13), ions derived from meteoritic metals could act as a source of alkalinity for acidic sulfate aerosol. If meteoritic particles do gradually acquire a sulfuric acid coat as they descend through the stratosphere, they would also traverse a range from basic to acidic as vapor uptake occurs. This condition may have unconsidered heterogeneous chemical implications. One of the more puzzling atmospheric issues is the uncertainty of what process induces the freezing of the aerosol that forms polar stratospheric clouds, the site of ozone depletion (33). Meteoritic material, incorporated in stratospheric aerosol as a combination of solution ions and insoluble material altered to some extent during the ablation process, could be a candidate for this phase change. Past studies have suggested that meteoritic material does not cause heterogeneous freezing (34) but that work used undissolved chondritic meteorite fragments and micrometeorites that are shown here not to be representative of the morphology or chemical composition in sulfate aerosol. Finally, the extraterrestrial flux stated here corresponds to an ablation of 0.5 to 1.7 Gg/year of sulfur. This represents 0.3 to 1.7% (16) of the total current stratospheric sulfur budget estimate. Although this flux is insignificant in the lower stratosphere, it may dominate in the upper stratosphere, above the sulfate layer wherein most of the sulfur of terrestrial origin resides.

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