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FIG. 3 Isovalue surfaces of electron density corresponding to an electronic state localized at the interface between the diamond and graphite phases. The figure shows a section of the system of Fig. 2, corresponding to the insertion into diamond of the first few graphite sheets. (Two isovalue surfaces are shown, in yellow and blue, corresponding to high and low values of the electronic density, respectively). The electronic state illustrated is the lowest unoccupied one, its energy eigenvalue being only ~ 0.02 eV above the Fermi energy in our finite-size calculation. Although the orbital is partially spread into the sub-surface region of both graphite and diamond in the vicinity of the interface, its prominent feature consists of the large density lobes located at the insertion into diamond of the first graphitic layer. The density lobes have a clear p character, and point into the vacuum region. Where this state is found, the surface C atoms are expected to act as chemically active sites (for hydrogen chemisorption, for example). The presence of this state (and other localized electronic states of similar energy) at the diamond/graphite surface phase boundary could play an important role in atomic-H etching of any graphitic nuclei which may form in diamond-like films.

hydrogen in inhibiting graphite growth. We also note that the electronic properties of diamond-graphite hybrids, as derived from empirical models^{20,21}, are consistent with our results. Indeed, Balaban and co-workers²¹ suggested the existence of localized electronic states at a diamond/graphite interface resulting from the coupling between the π -like graphitic states and the σ -like diamond states. They also suggested²¹ that semimetallic or metallic conduction might be observed along the diamond/graphite interface, which is consistent with our findings. $\square$

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Satellite confirmation of the dominance of chlorofluorocarbons in the global stratospheric chlorine budget

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OBSERVED increases in concentrations of chlorine in the stratosphere^{1–7} have been widely implicated in the depletion of lower-stratospheric ozone over the past two decades^{8–14}. The present concentration of stratospheric chlorine is more than five times that expected from known natural ‘background’ emissions from the oceans and biomass burning^{15–18}, and the balance has been estimated to be dominantly anthropogenic in origin, primarily due to the breakdown products of chlorofluorocarbons (CFCs)^{19,20}. But despite the wealth of scientific data linking chlorofluorocarbon emissions to the observed chlorine increases,

the political sensitivity of the ozone-depletion issue has generated a re-examination of the evidence^{21,22}. Here we report a four-year global time series of satellite observations of hydrogen chloride (HCl) and hydrogen fluoride (HF) in the stratosphere, which shows conclusively that chlorofluorocarbon releases—rather than other anthropogenic or natural emissions—are responsible for the recent global increases in stratospheric chlorine concentrations. Moreover, all but a few per cent of observed stratospheric chlorine amounts can be accounted for by known natural and anthropogenic tropospheric emissions. Altogether, these results implicate the chlorofluorocarbons beyond reasonable doubt as dominating ozone depletion in the lower stratosphere.

The Halogen Occultation Experiment (HALOE), described in detail elsewhere²³, has been operating from the Upper Atmosphere Research Satellite platform almost continuously since it was first turned on in orbit on 11 October 1991. It uses the technique of solar occultation to provide vertical profiles through the global stratosphere of HCl, HF, O₃, CH₄, H₂O, NO, NO₂, aerosol extinction and temperature. All HALOE data have undergone an extensive validation process that included a number of internal data consistency studies, comparisons with model simulations and detailed comparisons with remote observations made from the ground, balloon, aircraft and satellite platforms. Results for HF (ref. 24) show the on-orbit data precision to be ~ 0.04 – 0.06 parts per 10⁹ by volume (p.p.b.v.) throughout the stratosphere and

lower mesosphere. The estimated accuracy is 14–27% depending on altitude. These estimates appear to be quite conservative because comparisons with a set of nine HF profiles measured in balloon underflights show mean differences of only <7% from 5 to 50 mbar which is well within the error bar overlap of the two measurement sets. In general the HF results are very robust. HCl studies²⁵ show an on-orbit precision of 0.1–0.2 p.p.b.v. and the estimated accuracy ranges from 12% to 24% depending on altitude. The mean difference between HALOE HCl and results from a set of 14 balloon underflights varies from 8% to 16% over the 5–70 mbar range; HALOE values are lower than the balloon

FIG. 1 HALOE HCl (top) and HF (bottom) time series over the range from 100 mbar (roughly the tropopause) to 0.1 mbar (~65 km) using data collected at all β angles. The data have been globally and zonally averaged. On any given day, all sunrise and sunset data are zonally averaged separately and then a combined average is obtained without regard to latitude location of the sunrise or sunset measurements. Temporal increases in HCl and HF are clear at the highest altitudes near the top of each panel but with careful inspection they can be seen in the mid-stratosphere as well. At 0.3 mbar, for example, HCl starts out at ~2.7 p.p.b.v. and at the end of the record it reaches ~3.1 p.p.b.v. HF varies similarly from 1.1 p.p.b.v. to ~1.4 p.p.b.v. over the period. We note that the half-yearly variations in both HCl and HF that are most apparent near the 10 mbar level are due to a sampling artefact of the occultation geometry, causing certain latitudes to be preferentially sampled at a given time of year. The high HCl and HF in the lower stratosphere at the start of the data record as due to oversampling of high latitudes during this period. The 15 mbar level HCl varies with latitude from ~1.6 p.p.b.v. in the tropics to 2.1 p.p.b.v. at high latitudes. HF varies from 0.3 p.p.b.v. to 1 p.p.b.v. over this same range. Note that around the stratopause, latitudinal changes in both HCl and HF are small.

data. A HCl data artefact appears as a dependence of HCl on β , the angle between the orbit plane and the Earth–Sun line. HALOE HCl varies in a systematic way in the upper stratosphere by $\pm 9\%$ over a β angle cycle. The instrumental cause of this artefact has now been identified and it will be removed in future data processing. As we shall show later, the β angle variation has negligible effect on HCl annual increase rates determined from HALOE data. The important parameter for time trend comparisons is data precision, which is high for both HF and HCl.

FIG. 2 A steady-state model simulation at the equator for 1990 halocarbon tropospheric boundary conditions showing altitude-dependent model ratios of HCl, HF, inorganic Cl and F, and organic Cl and F to model ΣCl and ΣF obtained by using the NCAR two-dimensional chemistry-transport model³². The HALOE HCl and HF over model ΣCl and ΣF ratios are also shown. Note that near the Earth surface, ΣCl and ΣF equal Cl_T and F_T respectively. As altitude increases, the organic compounds decompose owing to photolysis and chemistry forming inorganic compounds until in the upper stratosphere and higher they dominate ΣCl and ΣF . At these altitudes $\Sigma\text{Cl} = \text{HCl} + \text{Cl} + \text{ClO} + \text{ClONO}_2 + \text{HOCl} + \dots$ and $\Sigma\text{F} = \text{HF} + 2\text{CF}_2\text{O} + \text{CClFO} + 2\text{CHF}_2\text{Cl} + \dots$. The HALOE data were collected in 1994 and averaged over the range 10°S to 10°N . The 1994 HALOE measurements are compared with 1990 model steady-state data to roughly take into account the lag time for chlorine and fluorine in the troposphere to reach the upper stratosphere and lower mesosphere. We note that the vertical profile shapes of HALOE data and model simulations are in good agreement. These results show that above the $\sim p = 1$ mbar level, nearly all the Cl and F that can be converted to the inorganic forms HCl and HF has been converted, as seen by the nearly constant HCl/ ΣCl and HF/ ΣF ratios, which have values approaching 1.0. The cause of residual Cl and F (that is, ratios <1.0) above the $p = 1$ mbar level is mainly HCFC-22, which has a stratospheric lifetime of over 200 yr (ref. 33). In this altitude range, HCFC-22 comprises only 1–2% of ΣCl but 2–5% of ΣF . Because the HCl and HF mixing ratios are nearly constant with altitude for $p < 1$ mbar, seasonal and dynamical effects are less important and to first order can be ignored in trend determinations. For these reasons we selected 55 km as the basis for the time series comparisons (for example, $\text{Cl}_T(t)$ against $\text{HCl}_T(t)$). At this altitude, HCl and HF levels are ~93% and ~81% of ΣCl and ΣF levels respectively at the equator. These ratios increase to ~95% and ~88% at high latitudes. Other model results³⁴ give a HF to Σ (inorganic F) ratio (that is, HCHC-22 is neglected) of ~90%. Spacelab 3 ATMOS data for 28°N (ref. 5) show ratios at 55 km of $95 \pm 5\%$ and $79 \pm 14\%$ for HCl/ ΣCl and HF/ ΣF respectively, in good agreement with model results.

Because stratospheric HF has no significant known natural sources^{17,26} its observation in the stratosphere is especially important as positive proof of transport of CFCs from the troposphere to the stratosphere, their photolysis, and liberation of chlorine and fluorine. For comparison with our observations of HF and HCl in the stratosphere, we have calculated tropospheric mixing ratios of total organic chlorine (Cl_T) and total organic fluorine (F_T) on the basis of concentrations of key gases measured at over 20 stations worldwide^{27,28}. We calculated Cl_T and F_T using the Cl or F atom-weighted sum for the years 1985–87, 1989, 1990 and 1992. We omitted CF_4 and C_2F_6 in the calculation because, owing to their extremely long lifetimes ($>1,000$ yr; ref. 28), they do not contribute significantly to the stratospheric inorganic fluorine amount. We have not included the recently introduced CFC substitutes HCFC-142b (CH_3CClF_2), HCFC-141b ($\text{CH}_3\text{CCl}_2\text{F}$), and HFC-134a ($\text{CF}_3\text{CH}_2\text{F}$) because their pre-1990 concentrations are very small compared with the 1992 CFC levels and in addition the available data on these compounds cover only the period 1991–94 (ref. 29). Also we ignore tropospheric HCl and HF from sources other than organic compounds, an assumption that will be seen to be valid in our results. All other important organic-chlorine and fluorine compounds with a lifetime >1 year were included (see Fig. 3). After making appropriate calibration adjustments³⁰, the yearly total organic Cl_T and F_T data between 1985 and 1992 were fitted with linear regression lines to show the kinds of increasing trend that have been monitored near the Earth surface. On average, the fits show tropospheric total organic chlorine and

fluorine growing at the rates of 116 ± 12 parts per 10^{12} by volume (p.p.t.v.) and 88 ± 8 p.p.t.v. per year respectively for the period 1985–92. Recent analyses show that the growth rates of CFC-11 and CFC-12 have significantly decreased because of the phasing out of production of these compounds as a result of international protocol agreements². The growth rates of other halocarbons, including H-1301, H-1211 and CH_3CCl_3 , are also decreasing^{30,31}. Stratospheric chlorine arising from CFC-11 and CFC-12 should reach a maximum before the turn of the century and then begin to decline, assuming that the tropospheric growth rates of these two species continue to decrease as projected industrial emissions decline²⁷.

Our first objective is to compare HALOE observations of HCl and HF rates of increase (Fig. 1) with tropospheric rates irrespective of absolute values or lag times for tropospheric Cl_T and F_T to be transported to the stratosphere. Such a comparison directly addresses the question of whether CFCs drive the stratospheric chlorine input, dominating over any natural input. The best region for comparison with Cl_T and F_T trends is in the upper altitudes, where almost all of the organic chlorine and fluorine have been converted to the inorganic forms, HCl and HF. We determined the altitude range where this has occurred (about 55 km, ~ 0.5 mbar), using the NCAR two-dimensional chemistry transport model³² to examine the changes in the ratio of HCl to ΣCl and HF to ΣF with altitude (Fig. 2). The terms ΣCl and ΣF are the atom-weighted sum totals of organic plus inorganic chlorine and fluorine respectively, again ignoring tropospheric HCl and HF from sources other than organic compounds. The trend comparisons (Fig. 3) show HALOE HCl and HF 55 km increase rates of 102 ± 6 p.p.t.v. yr^{-1} and 72 ± 2 p.p.t.v. yr^{-1} respectively, compared with 116 ± 12 p.p.t.v. yr^{-1} and 88 ± 8 p.p.t.v. yr^{-1} for $\text{Cl}_T(t)$ and $\text{F}_T(t)$, where t indicates time. When the model ratios for HCl to ΣCl and HF to ΣF are used to obtain HALOE-derived $\Sigma\text{Cl}(t)$ and $\Sigma\text{F}(t)$, the rates are 108 ± 7 p.p.t.v. yr^{-1} and 85 ± 2 p.p.t.v. yr^{-1} respectively. This close agreement (3–7%) clearly shows that CFCs strongly, if not completely, dominate chlorine inputs to the stratosphere.

We can strengthen our argument by examining the HALOE derived chlorine amount at 55 km versus tropospheric organic chlorine, Cl_T . To do this we must take into account the time lag required for tropospheric gases to be transported to 55 km. We determined this by calculating the time separation between given

FIG. 3 HALOE global average HCl and HF time series at 55 km (solid lines) compared with tropospheric Cl_T and F_T time series (dashed lines) shifted in time using tropospheric starting values normalized to HALOE values taken at the beginning of the HALOE data record. $\text{Cl}_T = 3\text{CFC}_1 + 2\text{CFC}_2 + 3\text{C}_2\text{Cl}_3 + 2\text{C}_2\text{F}_4\text{Cl}_2 + \text{C}_2\text{F}_5\text{Cl} + \text{CH}_3\text{Cl} + 4\text{CCl}_4 + 3\text{CH}_3\text{CCl}_3 + \text{CF}_2\text{BrCl} + \text{CHF}_2\text{Cl}$, and $\text{F}_T = \text{CFC}_1 + 2\text{CFC}_2 + 3\text{C}_2\text{F}_3\text{Cl}_3 + 4\text{C}_2\text{F}_4\text{Cl}_2 + 5\text{C}_2\text{F}_5\text{Cl} + 2\text{CHF}_2\text{Cl} + 2\text{CF}_2\text{BrCl} + 3\text{CF}_3\text{Br}$. Data collected at all β angles were used. HALOE-derived $\Sigma\text{Cl}(t)$ and $\Sigma\text{F}(t)$ were obtained by linearly interpolating the model HCl to ΣCl and HF to ΣF ratios with latitude and then applying these ratios to each HCl and HF data point. The effect of β angle dependence in the HCl data was evaluated by fitted only high- β ($> 45^\circ$) and low- β ($< 45^\circ$) data. These fits gave negligible differences for increase rates.

FIG. 4 Time series of HALOE HF at 55 km, HALOE-derived total organic plus inorganic fluorine (ΣF), and tropospheric organic fluorine (F_T). The hatched area represents the range of HALOE-derived ΣF when uncertainties associated with the straight-line fit, HALOE measurements and the model factor for HF/ ΣF are considered. The vertical bar on the HF plot is the HALOE systematic error. The vertical bars on the tropospheric data are uncertainties due to measurement error. The fluorine lag time of 5.9 ± 2 yr is in good agreement with results inferred from ATMOS HF and CO_2 (ref. 35) and the 5.6 ± 1.1 yr deduced from balloon CO_2 cryogenic samples^{36,37} for transport to the middle stratosphere.

values in the HALOE-derived $\Sigma F(t)$ time series and the same values in tropospheric $F_T(t)$, taking into account accuracies for both data sets (Fig. 4). We obtained a value of 5.9 ± 2 yr. We chose the HF-derived lag time to do the chlorine budget calculation because it is an independently derived parameter and it is the proxy for the main chlorine carrier to the stratosphere, that is, the CFCs. Also, the HF measurement by HALOE is robust, it agrees very well with correlative underflight data, and it has no known artefacts to hinder the interpretation. We determined a 1 June 1995 expected total chlorine value at 55 km due to tropospheric emissions of 3.44 ± 0.23 p.p.b.v.. This compares with HALOE-derived total chlorine, ΣCl , of 3.3 ± 0.33 p.p.b.v. using data for all β angles, 3.44 ± 0.34 p.p.b.v. for $\beta > 45^\circ$, and 3.22 ± 0.33 p.p.b.v. for $\beta < 45^\circ$. The HALOE mean ΣCl value of 3.3 p.p.b.v. is less than the tropospheric value by only 6%. Also, the HALOE-derived ΣCl trend and amount will increase slightly in the next round of data reprocessing for two reasons. First, the annual CO_2 increase of $\sim 0.5\%$ yr $^{-1}$ was not taken into account in the pressure registration algorithm used for inversion of the transmittance

data. Second, the CO_2 band intensities used in the pressure registration algorithm will increase slightly owing to a spectroscopic reanalysis, which is nearing completion. The net result is that HALOE-derived ΣCl at 55 km will agree with amounts predicted from tropospheric total organic chlorine to within a few per cent. This close agreement between the two data sets means that there are no important missing links in our understanding of the chlorine budget. Note that we ignored tropospheric HCl and HF from sources other than organic compounds in this analysis. If direct emissions of these compounds, surface or volcanic, were influencing the stratosphere, this excellent mass balance would not have been obtained. We further point out that the HALOE-derived mean total chlorine is ~ 2.7 p.p.b.v. higher than the 0.6 p.p.b.v. level that it would reach if only the main natural source, CH_3Cl , were present. When these facts are considered together with observations showing that both Antarctic and Arctic chemical ozone depletion is caused by elevated chlorine in the atmosphere⁸⁻¹⁴, the inescapable conclusion is that the depletion is caused by continued use of the CFCs. □

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Magma mixing by convective entrainment

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RECENT studies of volcanic eruptions have brought to light a puzzling sequence: the ejection of dense and mixed liquids followed by a larger volume of unmixed, less dense liquid¹⁻⁴. Although these studies have shown that the mixing is associated with the injection of basaltic liquid into a more silicic magma chamber, a paradox remains. Basaltic magma is denser than silicic magma, and should flow along the floor of the magma chamber. This configuration impedes mixing of the two liquids, and appears incompatible with the early eruption of basaltic liquid from the top of the chamber. Previously proposed mixing processes explain neither the eruption sequence nor the eruption of dense liquid during the time of lowest eruption rate¹⁻⁸. We report here fluid-mechanical experiments that suggest a solution: a thermal plume forms over the replenishment inlet, dragging basaltic liquid upward by viscous coupling, and producing mixing only in a localized area without affecting the bulk of the chamber.

Although such a mixing sequence is common, we concentrate on the well documented 1991 eruption of Pinatubo^{1,2} as the

compositions of its ejecta are known in the context of a detailed eruption chronology. In this eruption, the compositions of ejecta increased in silica content from andesitic (in the initial dome and tephra emissions) to dacitic (in the paroxysmal and subsequent eruptions). The andesites appear to be roughly a 64:36 heterogeneous mixture of the dacite and blobs and streaks of basaltic magma². The characteristic sizes of these blobs and streaks vary from millimetres to centimetres¹, as in other eruptions^{3,9,10}. The dacite appears not to be a mixture. We address three questions. First, how does dense, basaltic liquid get transported to the top of the chamber? Second, why were the first ejecta a mixture, whereas afterwards, during the highest eruption rate, the ejecta were unmixed dacite (a composition less dense than the preceding andesite)? Third, why are mixing scales of the order of millimetres to centimetres?

This combination of observations is compatible with none of the previously proposed mechanisms (although they may take place in other circumstances). Turbulent fountaining during injection¹¹ would produce extensive mixing near the base of the chamber and not favour the later eruption of a large volume of unmixed fluid. Draw-up of the basaltic liquid due to the draining of the chamber through a narrow conduit⁵ would first tap the overlying silicic layer and would entrain the most basaltic liquid during the period of the highest eruption rate. At Pinatubo, mixed magmas were erupted first, whereas only unmixed liquid was erupted during the highest eruption rate^{1,2}. Gravitational overturn of the basaltic liquid by vesiculation^{1,2,6} predicts mixing throughout the chamber and hence does not explain the later, unmixed dacites.