The stability of the stratospheric ozone layer during the end-Permian eruption of the Siberian Traps

BY DAVID J. BEERLING 1,*, MICHAEL HARFOOT 2, BARRY LOMAX 1 AND JOHN A. PYLE 2,3

1 Department of Animal and Plant Sciences, University of Sheffield, Sheffield S10 2TN, UK
2 Centre for Atmospheric Science, Department of Chemistry, and 3 National Centre of Atmospheric Science (NCAS), Atmospheric Chemistry Modelling Support Unit, University of Cambridge, Cambridge CB2 1EW, UK

The discovery of mutated palynomorphs in end-Permian rocks led to the hypothesis that the eruption of the Siberian Traps through older organic-rich sediments synthesized and released massive quantities of organohalogens, which caused widespread O3 depletion and allowed increased terrestrial incidence of harmful ultraviolet-B radiation (UV-B, 280–315 nm; Visscher et al. 2004 Proc. Natl Acad. Sci. USA 101, 12 952–12 956). Here, we use an extended version of the Cambridge two-dimensional chemistry–transport model to evaluate quantitatively this possibility along with two other potential causes of O3 loss at this time: (i) direct effects of HCl release by the Siberian Traps and (ii) the indirect release of organohalogens from dispersed organic matter. According to our simulations, CH3Cl released from the heating of coals alone caused comparatively minor O3 depletion (5–20% maximum) because this mechanism fails to deliver sufficiently large amounts of Cl into the stratosphere. The unusual explosive nature of the Siberian Traps, combined with the direct release of large quantities of HCl, depleted the model O3 layer in the high northern latitudes by 33–55%, given a main eruptive phase of less than or equal to 200 kyr. Nevertheless, O3 depletion was most extensive when HCl release from the Siberian Traps was combined with massive CH3Cl release synthesized from a large reservoir of dispersed organic matter in Siberian rocks. This suite of model experiments produced column O3 depletion of 70–85% and 55–80% in the high northern and southern latitudes, respectively, given eruption durations of 100–200 kyr. On longer eruption time scales of 400–600 kyr, corresponding O3 depletion was 30–40% and 20–30%, respectively. Calculated year-round increases in total near-surface biologically effective (BE) UV-B radiation following these reductions in O3 layer range from 30–60 (kJ m⁻² d⁻¹)BE up to 50–100 (kJ m⁻² d⁻¹)BE. These ranges of daily UV-B doses appear sufficient to exert mutagenic effects on plants, especially if sustained over tens of thousands of years, unlike either rising temperatures or SO2 concentrations.

Keywords: atmospheric O2; atmospheric CO2; flood basalt eruptions; genome stability; mutations, ozone photochemistry; polar stratospheric clouds

* Author for correspondence (d.j.beerling@sheffield.ac.uk).

One contribution of 18 to a Discussion Meeting Issue ‘Trace gas biogeochemistry and global change’.
1. Introduction

The Permo-Triassic (P-Tr) mass extinction, 251 Myr BP, is recognized as the largest extinction event in the Phanerozoic, with the global loss of up to 95% of all marine species (for reviews, see Erwin (1994) and Benton & Twitchett (2003)). The dramatic nature of the extinction itself, associated environmental disturbance, and the recovery of ecological and climatic systems have been extensively documented and continue to remain the focus of considerable research effort (Erwin 1994; Benton & Twitchett 2003). One of the most remarkable claims to emerge in recent years is that extensive volcanic activity over a vast area of Siberia coincident with the extinctions (Renne et al. 1995) led to a worldwide depletion of stratospheric O$_3$ (Visscher et al. 2004). The basis for this palaeobotanical hypothesis was the identification of unusual ‘mutated’ forms of fossil spores and pollen (palynomorphs) in end-Permian rocks (Visscher et al. 2004; Foster & Afonin 2005; Looy et al. 2005). Mutated spores of herbaceous lycopsids are represented by a permanent tetrad configuration indicative of a failure of individual spores to separate and complete the normal process of development. These mutations have been identified in end-Permian sediments from a global suite of localities ranging from Greenland to Australia (Visscher et al. 2004; Looy et al. 2005). Subsequently, fossil gymnosperm pollen mutations with disrupted sacci that are indicative of a failure to form normal bisaccate grains have been reported from localities in Russia and northwest China (Foster & Afonin 2005).

The widespread occurrence of mutated fossil palynomorphs has been suggested to represent a chronic mutagenesis event brought about by worldwide increases in near-surface fluxes of ultraviolet-B radiation (UV-B, 280–315 nm; Visscher et al. 2004; Looy et al. 2005). Visscher et al. (2004) postulated that increased surface UV-B radiation resulted not from the direct chemical effects of the massive Siberian flood basalt eruption, but instead from the production of large quantities of organohalogens produced by the heating of organic-rich rocks and hydrothermal fluids as the Siberian Traps erupted over several million square kilometres. Halogen emissions are extremely important to atmospheric chemistry because they have the potential to destroy stratospheric O$_3$. Limited experimental evidence from Glycine max (soybean) supports the contention that moderately enhanced fluxes of UV-B radiation can induce damage to pollen and impair germination (Koti et al. 2005). However, exposure of gymnosperm trees to high SO$_2$ in polluted areas in the former Soviet Union has also produced aberrant pollen and spore mutations (Mičieta & Murín 1996; Tretyakova & Noskova 2004), and substantial SO$_2$ production from the Siberian Traps may represent another causal agent involved in the mutated fossil spores.

We are unaware of any investigations examining the direct or indirect effects of the Siberian Traps eruptions on the chemistry of the atmosphere, although other modelling studies have considered the aspects of environmental change associated with a major end-Permian carbon cycle perturbation (Berner 2002; Schmidt & Shindell 2003; Grard et al. 2005; Lamarque et al. 2006) and anoxic oceans (Kump et al. 2005; Berner & Ward 2006). Therefore, the central aim of the present paper is to provide a quantitative framework for evaluating the possible effects of the Siberian eruptions on the photochemistry of the atmosphere, with particular emphasis on stratospheric O$_3$ chemistry and transport.
We first briefly review the nature of the eruptions of Siberian Traps and regional geology, and detail our assessment of the masses of gases released directly, and indirectly, by the heating of organic- and halogen-rich Neoproterozoic and Palaeozoic sediments. Section 2 outlines the Cambridge two-dimensional atmospheric chemistry–transport model and the modifications incorporated to simulate the photochemical effects of large volcanic eruptions, including representation of the catalytic properties of polar stratospheric clouds (PSCs) on O₃ destruction (Hanson & Mauersberger 1988), the absorption and scattering of UV-B radiation by sulphate aerosols (Kreidenweis et al. 1999; Chin et al. 2002) and a sulphate aerosol scheme to calculate the aerosol surface area and heterogeneous reaction rates (Bekki & Pyle 1992). We then present a series of model sensitivity studies for the end-Permian, investigating how O₃ chemistry is influenced by (i) the HCl release from main eruptive phase of the Siberian Traps, (ii) organohalogen (CH₃Cl) emissions from the heating of coals, (iii) rocks containing dispersed organic matter, and (iv) the influences of simultaneous releases from sources (i) to (iii). Our analyses include a preliminary assessment of the effect of uncertainties in the time span of the main eruptive phase of the Siberian Traps (Kamo et al. 2003). The results are discussed in the context of increased near-surface UV-B radiation fluxes and tropospheric SO₂ loading and their possible impacts on plant genome stability.

2. The Siberian Traps and estimated gas emissions

The Siberian Traps flood basalt province is the largest known subaerial event of its kind and presently covers a modest 3.4×10⁵ km² of northwest Siberia. Inclusion of pyroclastic and intrusive sediments increases the total area of the province to 1.5×10⁶ km² although the original area was undoubtedly much larger (Wignall 2001). The eruptions are estimated to have produced an immense volume of basalt lava, with estimates ranging from 2 to 4×10⁶ km³, although only 4×10⁵ km³ remain (Courtillot et al. 1999). Radiometric dating (⁴⁰Ar/³⁹Ar) indicates that the main eruptive phase was broadly contemporaneous with the P-Tr boundary extinction event (Renne et al. 1995; Reichow et al. 2002), and U–Pb dating of lava flows indicates that the Siberian flood volcanism was initiated at 251.7 ± 0.4 Ma and waned by 251.1 ± 0.3 Ma (Kamo et al. 2003). These dates establish the duration of the main eruptive duration as 600 kyr and are in line with earlier estimates derived from magnetostratigraphy (Haag & Heller 1991); more detailed consideration of the ages of the different intrusive complexes suggests a substantial proportion of the main Siberian flood basalt eruption lasted only 100 kyr (Kamo et al. 2003).

Geological evidence indicates that the Siberian eruptions may have been unusually explosive (Campbell et al. 1992), with pyroclastic deposits reaching a thickness of up to 800 m (Khain 1985). The highly explosive nature of the Siberian eruptions expelled Permian coal-bearing deposits and Devonian sediments from a depth of 0.3–1.5 km, and occasionally from depths of 10 km (Campbell et al. 1992). Current estimates suggest that the igneous province contains approximately 20% pyroclastic material (by volume), with the remainder comprising intrusive dykes and sills (50%) and basalt lava flows (30%; Reichow et al. 2002). The unusually explosive nature of the eruptions
is noteworthy because this could represent the primary transport mechanism for injecting O$_3$-depleting halogen gases through the troposphere and into the stratosphere.

The potential for the Siberian eruptions to disrupt the balance between photochemical production/destruction and transport of stratospheric O$_3$ depends on the mass of inorganic and organic gases released. For the present simulations, we estimated the mass of hydrochloric acid (HCl) and sulphur dioxide (SO$_2$) emissions by scaling the detailed inventory of emissions drawn up for the Columbia River Basalt (CRB) Group that erupted approximately 14.7 Ma (Thordarson & Self 1996). According to Thordarson & Self (1996), the CRB produced $1.3 \times 10^3$ km$^3$ of basalt and liberated 12 425 Mt SO$_2$ and 704 Mt HCl (table 1). The approximate mass of trace organic gases released is estimated by scaling the global average fumerolic and diffuse halocarbon source strengths for the current annual gaseous volcanic CO$_2$ release (78 Tg yr$^{-1}$; Schwandner et al. 2004) by the mass of CO$_2$ released during the Siberian eruptions, given a known volume of basalt produced and a CO$_2$ degassing rate of $1.6 \times 10^4$ Tg of CO$_2$ per 1 km$^3$ of basalt erupted (Gerlach & Graeber 1985; table 1).

A further unusual aspect of the Siberian eruptions was the nature of regional geology of the Siberian platform. The main lithologies of the region are coals (Czamanske et al. 1998), hydrocarbon source rocks (Kontorovich et al. 1997) and evaporites (Melnikov et al. 1997). The juxtaposition of a volcanic province with coal-bearing deposits, Neoproterozoic oil accumulations and salt layers (evaporites) may have produced massive quantities of organohalogenes (Visscher et al. 2004). In particular, contact metamorphism of coals and the development of hydrothermal systems rich in chlorine, produced from the pressure dissolution of the surrounding evaporites, potentially synthesized large amounts of the organohalogens methyl chloride (CH$_3$Cl) and methyl bromide (CH$_3$Br).

As the relative proportions of the organohalogens emitted is unknown, and because Br availability is severely limited when compared with Cl, for the purposes of the present simulations, we estimated the mass of CH$_3$Cl released as follows. The concentration of Cl in coal varies from 300 to 1100 ppmv (Vassilev et al. 2000), but because of the high Cl concentration of Russian ‘salt coals’ (Goodarzi 1987; Bragg et al. 1991; Greive & Goodarzi 1993; Vassilev et al. 2000), we assume the upper concentration for the Siberian coals. The thermal maturity of the Siberian coals at the time of the eruption is unknown. Therefore, we have assumed that the Palaeozoic Siberian coals at the time of emplacement are better approximated by semi-anthracite than thermally immature peats. Semi-anthracite has a typical aliphatic content of approximately 20% (Suggate & Dickinson 2004) and an ash content, which can dilute the aliphatic content of coal, of approximately 30% (Medina et al. 2006) and so contains 0.0098 moles of CH$_2$ and up to $3.1 \times 10^{-5}$ mol of Cl.

In the case of CH$_3$Cl, the supply of both Cl and H may not have been limited due to the nature of the regional geology, allowing 1 g of semi-anthracite to release 0.49 g of CH$_3$Cl, calculated as the product of the molar concentration of CH$_2$ (0.0098) and the molecular weight of CH$_3$Cl (50.5). The generation of a higher mass of organohalogens than the original mass of semi-anthracite occurs owing to the high atomic weight of chlorine when compared with the methyl group.
### Table 1. Estimated volcanic release of gases during the Siberian Traps eruptions included in model simulations: runs 1 and 4.

<table>
<thead>
<tr>
<th>gas emitted</th>
<th>release rate (Mg per Mg CO₂)</th>
<th>basalts&lt;sup&gt;a&lt;/sup&gt; total degassed (Tg)</th>
<th>pyroclastics&lt;sup&gt;a&lt;/sup&gt; total degassed (Tg)</th>
<th>intrusives&lt;sup&gt;a&lt;/sup&gt; total degassed (Tg)</th>
<th>total degassed (Tg)</th>
<th>flux 100 kyr time scale (Tg yr&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>flux 600 kyr time scale (Tg yr&lt;sup&gt;-1&lt;/sup&gt;)</th>
</tr>
</thead>
<tbody>
<tr>
<td>hydrochloric acid&lt;sup&gt;b&lt;/sup&gt;</td>
<td>3.4×10&lt;sup&gt;-2&lt;/sup&gt;</td>
<td>6.5×10&lt;sup&gt;5&lt;/sup&gt;</td>
<td>4.3×10&lt;sup&gt;5&lt;/sup&gt;</td>
<td>1.1×10&lt;sup&gt;6&lt;/sup&gt;</td>
<td>2.2×10&lt;sup&gt;6&lt;/sup&gt;</td>
<td>22.0</td>
<td>3.7</td>
</tr>
<tr>
<td>sulphur dioxide&lt;sup&gt;b&lt;/sup&gt;</td>
<td>6.0×10&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>1.2×10&lt;sup&gt;7&lt;/sup&gt;</td>
<td>7.7×10&lt;sup&gt;6&lt;/sup&gt;</td>
<td>1.9×10&lt;sup&gt;7&lt;/sup&gt;</td>
<td>3.8×10&lt;sup&gt;7&lt;/sup&gt;</td>
<td>380.0</td>
<td>63.3</td>
</tr>
<tr>
<td>methyl bromide&lt;sup&gt;c&lt;/sup&gt;</td>
<td>1.3×10&lt;sup&gt;-8&lt;/sup&gt;</td>
<td>0.24</td>
<td>0.16</td>
<td>0.4</td>
<td>0.8</td>
<td>8.0×10&lt;sup&gt;-6&lt;/sup&gt;</td>
<td>1.3×10&lt;sup&gt;-6&lt;/sup&gt;</td>
</tr>
<tr>
<td>methyl chloride&lt;sup&gt;c&lt;/sup&gt;</td>
<td>9.9×10&lt;sup&gt;-7&lt;/sup&gt;</td>
<td>19.1</td>
<td>12.7</td>
<td>31.8</td>
<td>63.6</td>
<td>6.4×10&lt;sup&gt;-4&lt;/sup&gt;</td>
<td>1.0×10&lt;sup&gt;-4&lt;/sup&gt;</td>
</tr>
<tr>
<td>methylene chloride&lt;sup&gt;c&lt;/sup&gt;</td>
<td>2.7×10&lt;sup&gt;-7&lt;/sup&gt;</td>
<td>5.2</td>
<td>3.5</td>
<td>8.6</td>
<td>17.3</td>
<td>1.7×10&lt;sup&gt;-4&lt;/sup&gt;</td>
<td>2.9×10&lt;sup&gt;-5&lt;/sup&gt;</td>
</tr>
<tr>
<td>trichloromethane&lt;sup&gt;c&lt;/sup&gt;</td>
<td>1.2×10&lt;sup&gt;-6&lt;/sup&gt;</td>
<td>23.4</td>
<td>15.6</td>
<td>38.9</td>
<td>77.9</td>
<td>7.7×10&lt;sup&gt;-4&lt;/sup&gt;</td>
<td>1.3×10&lt;sup&gt;-4&lt;/sup&gt;</td>
</tr>
<tr>
<td>tetrachloromethane&lt;sup&gt;c&lt;/sup&gt;</td>
<td>4.4×10&lt;sup&gt;-8&lt;/sup&gt;</td>
<td>0.84</td>
<td>0.6</td>
<td>1.4</td>
<td>2.8</td>
<td>2.8×10&lt;sup&gt;-5&lt;/sup&gt;</td>
<td>4.7×10&lt;sup&gt;-6&lt;/sup&gt;</td>
</tr>
<tr>
<td>trichlorofluoromethane&lt;sup&gt;c&lt;/sup&gt;</td>
<td>1.1×10&lt;sup&gt;-7&lt;/sup&gt;</td>
<td>2.1</td>
<td>1.4</td>
<td>3.5</td>
<td>7.0</td>
<td>7.0×10&lt;sup&gt;-5&lt;/sup&gt;</td>
<td>1.2×10&lt;sup&gt;-5&lt;/sup&gt;</td>
</tr>
<tr>
<td>chlorobenzene&lt;sup&gt;c&lt;/sup&gt;</td>
<td>1.8×10&lt;sup&gt;-7&lt;/sup&gt;</td>
<td>3.1</td>
<td>2.1</td>
<td>5.2</td>
<td>10.4</td>
<td>1.0×10&lt;sup&gt;-4&lt;/sup&gt;</td>
<td>1.7×10&lt;sup&gt;-5&lt;/sup&gt;</td>
</tr>
<tr>
<td>p-dichlorobenzene&lt;sup&gt;c&lt;/sup&gt;</td>
<td>9.4×10&lt;sup&gt;-8&lt;/sup&gt;</td>
<td>1.8</td>
<td>1.2</td>
<td>3.0</td>
<td>6.0</td>
<td>6.0×10&lt;sup&gt;-5&lt;/sup&gt;</td>
<td>1.0×10&lt;sup&gt;-5&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

<sup>a</sup>Total CO₂ emission for each rock type calculated as volume×degassing rate (1.6×10<sup>13</sup> g CO₂ km<sup>-3</sup>; Gerlach & Graeber 1985). We take total volume of basalt produced by the Siberian Traps to be equal to 4.0×10<sup>6</sup> km<sup>3</sup>, with 30% basalts (1.2×10<sup>6</sup> km<sup>3</sup>), 20% pyroclastics (8.0×10<sup>5</sup> km<sup>3</sup>) and 50% intrusives (2.0×10<sup>6</sup> km<sup>3</sup>; Kamo <i>et al.</i> 2003).<sup>b</sup>Release rates calculated from total volume and estimated total masses of HCl and SO₂ produced by the Columbia River Basalt Group (<i>Thordarson & Self 1996</i>).<sup>c</sup>Release rates calculated from global estimates of volcanic fumarolic and diffuse degassing summed and scaled by global CO₂ degassing (78.0 Tg yr<sup>-1</sup>; Schwandner <i>et al.</i> 2004).
Finally, the calculated release of CH$_3$Cl per unit mass of semi-anthracite heated was scaled against two estimates of total organic carbon. The first was based on the mass of organic carbon buried as Palaeozoic coals in the Tunguska basin, taken to be approximately 2000 Gt (Czamanske et al. 1998; Akulov 2006; table 2). However, a further source of organic matter is that dispersed in clastic sediments of the region, which although not explicitly recognized by Visscher et al. (2004), may represent a large additional source of organic precursor for organohalogen synthesis. An estimate of the mass of organic carbon present can be made, given the Tunguska basin is approximately $1 \times 10^6$ km$^2$, and assuming an average thickness of 0.5 km, a bulk density of shale rock of 2100 kg m$^{-3}$ and a total organic carbon content of 2% by mass. These figures yield 21 000 Gt C that may additionally be available for the synthesis of organohalogens. Therefore, a second estimate of the total mass of organohalogens has been obtained by scaling the emission of CH$_3$Cl per unit mass of semi-anthracite with this figure.

3. Two-dimensional atmospheric chemistry–transport modelling

(a) Model outline

All the modelling experiments were undertaken using the Cambridge two-dimensional atmospheric chemistry–transport model (Harwood & Pyle 1975; Law & Pyle 1993). The two-dimensional model includes the two key transport processes governing the global distribution of atmospheric O$_3$ as a function of altitude and latitude: advection due to the zonal mean circulation and eddy transport arising from departures from the zonal mean. The zonal mean circulation is calculated from forcing by radiative, latent and sensible heating. Departures from the zonal mean are parametrized by eddy diffusion coefficients; see Harwood & Pyle (1975, 1980) for further details. The inclusion of these transport processes overcomes a major limitation in the use of one-dimensional models in investigations of stratospheric O$_3$ photochemistry (e.g. Kump et al. 2005).
The model has been used extensively to consider the chemistry and dynamics of the middle atmosphere (Harwood & Pyle 1980; Haigh 1984; Bekki & Pyle 1992; Bekki et al. 1994), the region of interest for this investigation.

The two-dimensional model chemistry scheme includes 178 reactions, involving the main species governing the chemistry of the atmosphere. The basic model used here includes the gas phase chemistry of the O$_x$, HO$_x$, NO$_y$, ClO$_y$, BrO$_y$, SO$_x$ families, as well as an oxidation scheme for methane and other representative non-methane hydrocarbons. We have implemented a sulphate aerosol scheme as detailed by Bekki & Pyle (1992), which provides the aerosol surface area used to calculate heterogeneous reaction rates. Details of calculation procedures, including the treatment of stratospheric photolysis, cloud, aerosol and tropospheric water vapour schemes implemented are given in Harfoot et al. (2007).

The model atmosphere is heated from below by prescribed mean monthly sea-surface temperatures (SSTs). SSTs influence surface-to-air heat fluxes in the lowest level and, following the adiabatic lapse rate, the temperature up to the tropopause. Radiative heating is calculated interactively for the stratosphere: in the long wave from the mixing ratios of CO$_2$, H$_2$O, O$_3$, SO$_2$ and N$_2$O (Haigh 1984); and, in the shortwave, from O$_2$ and O$_3$ mixing ratios. Radiative cooling is fixed at 1.5 K d$^{-1}$ in the lower troposphere and 0.75 K d$^{-1}$ in the upper troposphere. Because the heating rate of the troposphere is prescribed, increasing CO$_2$ exerts no changes in the heating rate there; however, imposing elevated SSTs representative of warmer climate does influence tropospheric conditions as described in §3c.

(b) Model development

We made two modifications to the model for the purposes of the present investigations. First, we developed and incorporated a simple parameterization for empirically representing the chemical effects due to the formation of HNO$_3$–H$_2$O clouds, otherwise known as type I PSCs. For those grid boxes containing water vapour and HNO$_3$ at temperatures below 195 K, a threshold temperature for type I PSC formation under typical stratospheric conditions (Hanson & Mauersberger 1988), heterogeneous activation of reservoir forms of chlorine (described by reactions (4.1) and (4.2) in §4) was assumed with a time constant of 7 days. This time constant is consistent with the time scale observed for formation of the springtime ‘active chlorine’ layer within the present day Antarctic lower stratosphere (Solomon et al. 2002). Second, we included a scheme to account for the absorption and scattering of solar UV-radiation by sulphate aerosol from Kreidenweis et al. (1999). Because calculation of the particle size and wavelength-dependent aerosol extinction coefficient, $Q_{ext}$, is computationally expensive, we use here a constant mean value of 1.4, the value for sulphate aerosol reported by Chin et al. (2002) at $\lambda = 500$ nm.

In all the simulations of the Siberian Traps volcanism, gases are emitted directly into the atmosphere in a single pulse (table 1) and distributed over different heights, according to the eruption phase from which they originate and the water solubility of each species (Textor et al. 2003). More highly soluble gases are likely to be incorporated into hydrometeors formed in the rapidly ascending eruption column and are consequently more likely to be precipitated out of the atmosphere. HCl is the most chemically important halogenated compound, released directly by the Siberian Traps volcanism, comprising some 5% by mass of the volcanic.

Phil. Trans. R. Soc. A (2007)
emissions (table 1). Owing to its high solubility in water, Textor et al. (2003) estimated the proportion of HCl reaching the stratosphere within an explosive volcanic eruption plume would be around 25%. However, this value is relevant for a tropical (i.e. low-latitude) eruption and the Siberian Traps erupted at a much higher latitude where the tropopause is lower. Based on measurements of the volcanic plume from the 2002 eruption of Hekla volcano on Iceland made in the lower stratosphere (Millard et al. 2006; Rose et al. 2006), we allow 75% of the emitted HCl to reach the model stratosphere. This stratospheric injection is distributed uniformly over all stratospheric levels below approximately 18 km.

(c) Boundary conditions for model simulations

All simulations include the effects of the warm end-Permian climate and a low O2/high CO2 atmospheric composition (Berner 2005) on O3 chemistry and transport. We used zonally averaged SSTs reported for a coupled ocean–atmosphere model simulation for the warm end-Permian climate (Kiehl & Shields 2005). This altered the chemical composition of the troposphere, particularly by elevating tropospheric water vapour concentrations and exerted a strong influence on stratospheric H2O. The major source of stratospheric H2O is transport from the troposphere through the tropical tropopause ‘cold trap’, although the oxidation of CH4 in the stratosphere also makes a contribution. Assuming a constant adiabatic lapse rate through the troposphere, warmer SSTs would give rise to a corresponding change in the temperature of the cold trap, where tropospheric water vapour is dehydrated to its local saturation pressure. The warm end-Permian SSTs could therefore have strongly influenced stratospheric water vapour content, and hence stratospheric O3 through the chemical cycles of hydrogen radical species. This effect has been included in our simulations by imposing a warmer tropical tropopause cold trap temperature value equivalent to the difference in pre-industrial and end-Permian tropical SSTs (Kiehl & Shields 2005); at the bottom boundary of the model stratosphere, the H2O concentration is fixed at the saturation vapour pressure over ice for the temperature of the tropopause.

The end-Permian atmospheric composition influences O3 chemistry and transport in different ways that are important to represent in the modelling. Reducing the atmospheric O2 content from the present-day value of 21% to a late Permian low of 15% (Berner 2005) can exacerbate stratospheric O3 loss over mid- and high latitudes (Harfoot et al. 2007). Stratospheric O3 is produced by photolysis of O2 (Chapman 1930) with a rate determined by the product of the photolysis frequency, J2, and the concentration of O2, [O2]. In the subtropical stratosphere a ‘self-healing’ effect occurs. Decreased [O2] leads to a reduction in O3 production in the upper atmosphere and lower [O3]. Given that the photolysis frequency at any altitude is itself dependent on the concentrations of O2 and O3 at higher levels in the atmosphere, decreased [O2] and [O3] above enhance the rate of J2 at lower levels and therefore [O3]. The net result is effectively no major changes in the total low latitude O3 column amount. At high latitudes in the middle and upper stratosphere, [O3] decreases with [O2] decline in a similar manner. However, in the lower stratosphere, where the chemistry is slower and transport dominates, the effect of self-healing is masked. Consequently, at high latitudes the O3 column thins as atmospheric O2 falls. A CO2-rich atmosphere traps outgoing long-wave
radiation in the lower atmosphere. In our model, a 2000 ppm CO₂ atmosphere reduces the annual mean temperature of the mid-stratosphere by as much as 10 K, when compared to the pre-industrial atmosphere, resulting in temperatures below 195 K, especially at high latitudes in both hemispheres and persisting for much of the year. Therefore, high CO₂ effectively creates more widespread and long-lived conditions for the formation of PSC.

Using the modified two-dimensional model and the above boundary conditions, we performed the following suite of experiments to investigate the sensitivity of stratospheric O₃ to Siberian Traps volcanism and organohalogen release from coals and rocks (table 3). Run 1: calculated the effects of HCl release from the Siberian Traps, with different durations of the main eruptive phase (100, 200, 400 and 600 kyr) to encompass uncertainties in the dating. These experiments were performed by decreasing the annual flux of HCl injected into the stratosphere, as given by total mass of HCl/duration. Runs 2 and 3 investigated the effects of CH₃Cl emissions by heating coals and dispersed organic matter, respectively, given a main eruptive phase of either 100 or 600 kyr. Run 4 investigated the combined influences of runs 1, 2 and 3 occurring simultaneously with main eruption phases of 100, 200, 400 and 600 kyr.

### 4. Results and discussion

#### (a) Siberian Traps versus CH₃Cl release from rocks

The simulated degree of total O₃ column depletion due to HCl release from the Siberian Traps, with a representative Late-Permian climate and atmospheric composition (run 1), depends upon the duration of the main eruptive phase
Zonally averaged, O$_3$ depletion is the greatest in the Northern Hemisphere and least in the Southern Hemisphere (figure 1a–d). In high northern latitude regions above the local injection of HCl into the stratosphere, O$_3$ depletion reaches 55 to 33% for the 100 and 200 kyr simulations, respectively, and compares with 26 to 14% depletion in the high southern latitudes for the same simulations (figure 1c,d). For the two longer eruption time scales considered, the total O$_3$ layer column thinned by approximately 20 and 10% in the high northern and southern latitudes, respectively. As a sensitivity test, we also undertook a further simulation to evaluate the possible influence of a short discrete pulse in which one-quarter of the total mass of HCl is released within a few tens of thousands of year, in this case 20 kyr. The results indicate the potential for greater O$_3$ depletion shown for the 100 kyr simulation and highlight the possibility that discrete abrupt pulses of volcanic activity could increase the severity of atmospheric disturbance.

In all of these simulations, high latitude O$_3$ depletion occurs because extensive PSC formation provides suitable conditions for conversion of chlorine held as reservoir species to active ‘Cl’ via reactions (4.1) and (4.2)

\[
\text{ClONO}_2 + \text{H}_2\text{O} \rightarrow \text{HNO}_3 + \text{HOCl}, \tag{4.1}
\]

\[
\text{ClONO}_2 + \text{HCl} \rightarrow \text{HNO}_3 + 2\text{Cl}. \tag{4.2}
\]

The HOCl produced via reaction (4.1) is rapidly photolysed in sunlight to form Cl. Active chlorine (ClO$_2$) in the form of Cl or ClO can participate in catalytic O$_3$ recombination in the stratosphere. In all of these simulations, high latitude O$_3$ depletion occurs because extensive PSC formation provides suitable conditions for conversion of chlorine held as reservoir species to active ‘Cl’ via reactions (4.1) and (4.2).
destruction cycles, the most general example being
\[ \text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2, \] \[ \text{ClO} + \text{O} \rightarrow \text{Cl} + \text{O}_2, \]
Net: \[ \text{O}_3 + \text{O} \rightarrow \text{O}_2 + \text{O}_2. \]

Under conditions of elevated active Cl and particularly in the cold, high-latitude lower stratosphere where atomic oxygen is less common, catalytic \( \text{O}_3 \) destruction proceeds via the ClO dimer cycle \((\text{Molina & Molina 1987})\):
\[ 2(\text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2), \]
\[ \text{ClO} + \text{ClO} \rightarrow \text{ClOOCl}, \]
\[ \text{ClOOCl} + h\nu \rightarrow \text{Cl} + \text{ClOO}, \]
\[ \text{ClOO} + \text{M} \rightarrow \text{Cl} + \text{O}_2, \]
Net: \[ 2\text{O}_3 + h\nu \rightarrow 3\text{O}_2. \]

In the model, the creation of PSCs leading to \( \text{O}_3 \) loss sets up a positive feedback because \( \text{O}_3 \) absorbs incoming short-wave radiation as well as outgoing long-wave radiation. Significant \( \text{O}_3 \) depletion leads to a local cooling of the depleted region of the atmosphere, so increasing the prevalence of PSC formation and hence reinforcing \( \text{O}_3 \) depletion.

The second set of model calculations (runs 2 and 3) directly evaluated the suggestion \((\text{Visscher et al. 2004; Looy et al. 2005})\) that organohalogenes released by the heating of organic-rich sediments as the Siberian eruptions proceeded was
a primary mechanism of stratospheric O$_3$ depletion. In these experiments, volcanic emissions were switched ‘off’ and the largest estimated mass of CH$_3$Cl released through this route ($9.8 \times 10^5$ Tg; table 2) was introduced into the lowermost troposphere on a time scale of 100 or 600 kyr to represent the same time scale as the eruption of the Siberian Traps. Results indicate that neither experiment had substantial deleterious effects on stratospheric O$_3$, with the 100 kyr simulation (run 2A) thinning the O$_3$ column by 20% (figure 2a, b). These reductions in O$_3$ are comparable to those resulting from the volcanic runs 1C and 1D and contrast with the greater losses that occurred on shorter time scales (figure 1). The difference arises primarily because the mass of CH$_3$Cl released from the heating of organic-rich sediments into the bottom of the atmosphere is around half that of HCl released by the volcanism ($2.2 \times 10^6$ Tg; table 1) and only three times larger than the mass of HCl emitted directly into the stratosphere through pyroclastic volcanism ($3.25 \times 10^5$ Tg). CH$_3$Cl in the model end-Permian atmosphere has a relatively short lifetime of around six months, so that most CH$_3$Cl is oxidized to form inorganic chlorine, ClO$_y$ (Cl, ClO, HOCI, Cl$_2$O$_2$, ClOO, ClONO$_2$, HCl), and only a small fraction is transported up into the stratosphere. ClO$_y$ is removed from the troposphere by rainout of HCl, the only loss process for chlorine in the model, calculated using latitudinally and

Figure 3. Changes in annual mean O$_3$ column depth (DU and percentage loss) due to HCl release from the Siberian Traps and CH$_3$Cl release from the heating of coals and rocks combined (run 4) as a function of (a,b) the duration of the main eruptive phase (background, 100, 200, 400 and 600 kyr) and (c,d) expressed as a function of latitude. Du, Dobson units.
seasonally varying first-order loss rates following Giannakopoulos (1998), which are the same for all integrations. As a result, increasing the ClO$_y$ burden of the atmosphere, by adding large amounts of volcanic chlorine, for example, extends its lifetime correspondingly and so increases the amount of ClO$_y$ that reaches the stratosphere. Comparing the steady-state stratospheric burden of chlorine, in the form of ClO$_y$, for the different simulations highlights the impact that each scenario has upon levels of chlorine in the stratosphere. The stratospheric burden calculated for CH$_3$Cl release from coal heating over 100 kyr (run 2A) is 0.87 Tg, around twice the burden for the end-Permian background atmosphere (run 0; 0.48 Tg) and only half that calculated for 100 kyr of Siberian Traps volcanism (run 1A) at 2.13 Tg. The comparatively small impact of CH$_3$Cl released from the heating of organic-rich sediments results in correspondingly reduced O$_3$ destruction through photochemical cycles involving Cl, giving rise to the lower O$_3$ depletion calculated for this scenario.

In an additional scenario, we consider the possibility that the thermal degradation of dispersed organic matter in rocks provided the organic precursors for generating organohalogenes (run 3). Here, the estimated total mass of CH$_3$Cl emitted is approximately ten times larger than that generated by heating coals alone (table 2), giving rise to high tropospheric CH$_3$Cl concentrations with
mixing ratios of 5–10 ppb in the Northern Hemisphere. The tropospheric lifetime of CH$_3$Cl is governed primarily by its reaction with OH, the main source of which is from reaction of H$_2$O with O(1D) from the photolysis of O$_3$ by UV-B radiation. Significant thinning of the stratospheric O$_3$ layer enhances the penetration of UV-B into the troposphere, which increases the O$_3$ photolysis frequency and results in OH concentrations comparable to those calculated for the end-Permian background atmosphere, despite the addition of large quantities of CH$_3$Cl. Consequently, the rate of CH$_3$Cl oxidation in the troposphere remains fast, with a steady-state lifetime of around six months, equivalent to that for the heating of coals only, and a similarly limited fraction of the tropospheric CH$_3$Cl burden is transported to the stratosphere. However, given the elevated tropospheric mass that results for the heating of dispersed organic matter, this equivalent fraction equates to a more significant mass of CH$_3$Cl. Levels of ClO$_y$ are enhanced considerably in the troposphere due to its oxidation, greatly extending the lifetime of the ClO$_y$ family, with more ClO$_y$ reaching the stratosphere as a result. The stratospheric burden of Cl in the form of ClO$_y$ is 4.5 Tg for a 100 kyr release of CH$_3$Cl from heating of dispersed organic matter (run 3A)—over five times that for the heating of coals alone (run 2A)—and produces significant O$_3$ depletion, with 50% losses in both the high northern and southern latitudes (figure 2c, d). The O$_3$ depletion at high latitudes occurs as a result of the low stratospheric temperatures over these latitudes, which are below the formation threshold of the PSCs in the model over much of the year. The heterogeneous activation of such a large mass of chlorine by PSCs provides abundant ClO$_x$ to catalyse photochemical O$_3$ destruction.

In the final set of model simulations (run 4), we investigated the effects of both mechanisms of O$_3$ depletion, HCl injection from the Siberian Traps and organohalogen release from the heating of organic-rich sediments, occurring simultaneously. As would be expected, this scenario produced significant O$_3$ depletion, with average losses in the Northern and Southern Hemispheres of 20–30% for the 600 kyr duration experiment, increasing to 60–80% depletion for the 100 kyr simulation (figure 3a, b). In these experiments, the natural latitudinal gradient in O$_3$ column thickness was severely disrupted, with losses of 70–90 and 55–80% in the high northern and southern latitudes, respectively, for emission durations of 100 and 200 kyr. Even in the 400 and 600 kyr simulations, the high northern and southern latitudes lost 30–40% and 20–30%, respectively, of total O$_3$ column (figure 3c, d).

(b) Pattern and mechanism of O$_3$ depletion

Figure 4 shows annually averaged, latitude–altitude cross-sections of O$_3$ loss for the 100 kyr simulations of (i) the eruption of the Siberian Traps (run 1A), (ii) CH$_3$Cl release from heating coals (run 2A), (iii) CH$_3$Cl release from country rocks (run 3A), and (iv) all three mechanisms together (run 4A), when compared with the background end-Permian atmosphere (run 0). All simulations show O$_3$ depletion in a band that stretches across all latitudes in the upper stratosphere between 30 and 40 km (figure 4). The patterns of O$_3$ loss are well explained by the corresponding distribution of annually averaged active chlorine (ClO$_x$) in the atmosphere that lies in the upper stratosphere around 35 km and is enhanced for all simulations (figure 5). The higher ClO$_x$ concentrations drive faster O$_3$ destruction through photochemical cycles, such as described by reactions.
(4.3)–(4.5). Peak O$_3$ depletion in the upper stratosphere occurs over subtropical latitudes, where solar irradiance is most intense and thus drives faster photochemistry, including the Cl-catalysed O$_3$ destruction pathways. Owing to this, in the simulated CH$_3$Cl release from heating of dispersed organic matter, and of all mechanisms together, O$_3$ is depleted by maximum values of 7–9 ppm over the equator at approximately 30 km (figure 4c,d). Beneath this region, at an altitude of 15–25 km, areas of less severe O$_3$ loss are apparent due to increased penetration of UV-B through the depleted region above, which increases the photolysis frequency of O$_2$, $J_2$, and accelerates the rate of O$_3$ production, thus offsetting much of the O$_3$ depletion in these regions.

For the Siberian Traps simulations, maximum O$_3$ depletion is not as significant, reaching 4–5 ppm in the tropical mid-stratosphere, with comparable O$_3$ losses of approximately 3 ppm in the lower stratosphere above the latitude of eruption (figure 4a). This more localized depletion is driven by the direct injection of pyroclastic volcanic emissions, giving rise to local sulphate aerosol surface area densities that are higher than anywhere else in the atmosphere and elevated ClO$_x$ mixing ratios up to 9 ppb that together activate high local concentrations of ClO$_x$.

In the simulations of CH$_3$Cl release from dispersed organic matter, and all mechanisms together, very substantial upper stratospheric O$_3$ depletion appears where ClO$_x$ mixing ratios are between 4 and 6 ppb (figure 5c,d). Even higher ClO$_x$ concentrations occur in the polar stratosphere, in excess of 9 ppb, however, less intense solar radiation and polar night reduce the impact of such high values in the model. For comparison, peak ClO$_x$ values of approximately 2 ppb at approximately 20 km are observed and predicted by chemical–transport models in the present day springtime Antarctic polar vortex, where complete O$_3$ column destruction occurs (World Meteorological Organisation 2003). Simulating the formation of the stratospheric O$_3$ hole is problematic in a two-dimensional model, requiring a formulation that simulates an isolated air mass and accurately calculates the distribution of PSCs in regions that are often very close to the critical conditions for PSC formation (Chipperfield & Pyle 1990). However, given the extremely high chlorine loading and cold stratospheric temperatures suggested by our end-Permian stratosphere, it is reasonable to expect that analogous polar O$_3$ hole events might have occurred.

Substantial depletion of stratospheric O$_3$ occurs rapidly; within 15 years for the 100 kyr simulation of Siberian Traps volcanism and all associated rock heating (run 4, figure 6a). Given that there is no direct removal process for chlorine in the stratosphere, O$_3$ recovery following cessation of emissions is governed by the timescale for transport of chlorine from the stratosphere into the troposphere where it can then be rained out. In the two-dimensional model, hemispheric mean O$_3$ columns rise quasi-exponentially following the termination of volcanic activity and, after a 20 year period have recovered to around 90% of the pre-eruption value (figure 6b). Such rapid recovery, on a geological time scale, even from an atmosphere with severe O$_3$ depletion, is significant because it suggests that the influence via O$_3$ loss of the Siberian Traps volcanism on levels of UV–B radiation reaching the earth’s surface, is only exerted for the duration of volcanic activity. This suggests that the ‘spikes’ in the abundance of mutated lycopsid spores observed in Greenland (Visscher et al. 2004; Looy et al. 2005) may relate to discrete pulses of volcanic activity. There is no evidence in our two-dimensional model sensitivity studies for persistent or long-term damage to the ozone layer.

Phil. Trans. R. Soc. A (2007)
Near-surface increases in UV-B radiation

We calculated the resulting increases in UV-B fluxes arising from O₃ depletion for experiments in run 4 (Siberian Traps and CH₃Cl release from coals and dispersed organic matter combined) to determine if they might be sufficient to destabilize plant genomes based on experimental evidence. To allow direct comparison between model output and experimental investigations of plant responses to UV-B radiation, all UV-B fluxes are expressed using a generalized plant action spectrum normalized at 300 nm, termed BE (Caldwell 1971; figure 7). Genomic stability is assessed by measuring changes in the frequency of homologous recombination (HR) of DNA in somatic tissue, a central mechanism of DNA repair that confers protection against the deleterious effects of UV-B radiation (Schuermann et al. 2005). HR frequency is assessed by resolving HR events within individual cells using transgenic plants carrying a visible ‘reporter’ gene that switches from an inactive to an active state whenever a DNA rearrangement occurs and causes them to stain blue.

According to our results, the 600 kyr experiment leads to the year-round UV-B fluxes of 30–40 (kJ m⁻² d⁻¹)BE throughout a broad region in the tropics and into the mid-latitudes of the Northern Hemisphere (figure 7). This pattern reflects a

(c) Near-surface increases in UV-B radiation

Figure 5. Changes in the annually averaged ClOₓ mixing ratio by altitude and latitude for four scenarios given releases over 100 kyr for (a) the eruption of the Siberian Traps (run 1A), (b) CH₃Cl release from the heating of coals (run 2A), (c) dispersed organic matter (run 3A) and (d) releases from all sources combined (run 4A). Note the different scale used for (a,b) and (c,d).
combination of O\textsubscript{3} loss and intensity of incoming solar energy and compares with 10–20 (kJ m\textsuperscript{-2} d\textsuperscript{-1})\textsubscript{BE} for the control Permian atmosphere (figure 7). In the 400 kyr experiment, the tropical region of high year-round UV-B broadens further to reach 30\textdegree S and the values rise to 40–60 (kJ m\textsuperscript{-2} d\textsuperscript{-1})\textsubscript{BE}. The two shorter simulations have a more dramatic impact resulting from the greater severity of O\textsubscript{3} depletion (figure 3). With the 200 kyr simulation, the region of year-round high UV-B expands considerably exposing large areas of the low- and mid-latitudes of the Northern and Southern Hemispheres to 50–70 (kJ m\textsuperscript{-2} d\textsuperscript{-1})\textsubscript{BE}, while the 100 kyr simulation raises the intensity of UV-B fluxes further to in excess of 100 (kJ m\textsuperscript{-2} d\textsuperscript{-1})\textsubscript{BE}.

In summary, UV-B fluxes ranged from 30 to 60 (kJ m\textsuperscript{-2} d\textsuperscript{-1})\textsubscript{BE} throughout the growing season for the 600–400 kyr simulations and 50–100 (kJ m\textsuperscript{-2} d\textsuperscript{-1})\textsubscript{BE} for the 100–200 kyr simulations. Current experimental evidence suggests that these ranges are sufficient to trigger instabilities in plant genomes, especially if sustained over tens of thousands of years. Experimental studies, for example, indicate that HR frequency increased substantially in Arabidopsis thaliana and Nicotiana tabacum when the daily UV-B dose rose from a control ‘background’
value from 2.3 (kJ m$^{-2}$ d$^{-1}$)$_{BE}$ to 6.6 (kJ m$^{-2}$ d$^{-1}$)$_{BE}$ (Ries et al. 2000). Further experiments increasing the daily flux up to 27.1 (kJ m$^{-2}$ d$^{-1}$)$_{BE}$ produced much higher HR frequencies—14 times in Arabidopsis and 7 times in tobacco. Furthermore, the genomic instability of Arabidopsis increased with each generation; second generation progeny plants had HR rates two to five times higher than those of their parents when exposed to the same UV-B dosage. This suggests that UV-B fluxes induce mutations in reproductive (germ) cells (i.e. was heritable), and highlights the possibility of long-term cumulative effects of exposure to moderately high UV radiation.

It is also possible that rising global temperatures of approximately 3 K due to CO$_2$ degassing from the Siberian Traps (Grard et al. 2005) exerted an effect on plant mutation rates. If correct, this would implicate temperature as another possible mutagenic factor alongside UV-B. However, experiments with one of the same transgenic lines of Arabidopsis used by Ries et al. (2000) fails to support this possibility, with only a 1.4-fold increase in HR events in response to a 11°C temperature increase from 22 to 33°C (Boyko et al. 2005). Collectively, these data indicate that simulated increases in UV-B radiation (figure 7) might destabilize plant genomes to a significantly greater extent than any increases in temperature.

(d) Sulphur dioxide and mutagenesis

In addition to UV-B and temperature, there is also a possible mutagenic influence of SO$_2$. The evidence for this possibility is circumstantial, deriving from the occurrence of mutated gymnosperm pollen grains in highly industrialized locations in the former Soviet Union (Micieta & Muñín 1996; Tretyakova & Noskova 2004). The mutated grains show morphological similarities to those from the P-T boundary. So, we have modelled tropospheric SO$_2$ concentrations resulting from large releases of SO$_2$ (table 1) to determine how these levels compare with those in industrial regions. Our calculations indicate SO$_2$ concentrations were generally less than 3 ppb throughout the Northern Hemisphere and considerably lower (by a factor 10–10 000) in the Southern Hemisphere. The only exception to this pattern was the high northern latitudes where SO$_2$ concentrations reached 13 ppb (figure 8). The marked latitudinal gradient reflects the short residence time of SO$_2$ in the atmosphere owing to its rapid oxidation to H$_2$SO$_4$ and its subsequent washing out in precipitation. These concentrations are relatively low and comparable to the range typical for rural areas (1–30 ppb). In moderately polluted areas, SO$_2$ concentrations reach 30–200 ppb and highly polluted regions experience reach values even higher 200–300 ppb (Finalyson-Pitts & Pitts 1986). Moreover, even if the SO$_2$ concentration was sufficiently high in the Northern Hemisphere, the strong latitudinal gradient it exhibits (figure 8) means it is unable to account for the global distribution of mutated palynomorphs (Visscher et al. 2004; Foster & Afonin 2005).

(e) Modelling caveats

We have not included the effects of massive H$_2$S and CH$_4$ release in our modelling simulations, events interpreted from various lines of palaeo-evidence to have taken place during the end-Permian (Berner 2002; Kump et al. 2005). Modelling studies suggest that large-scale emission of H$_2$S (Kump et al. 2005) or CH$_4$ (Lamarque et al. 2006) at the end-Permian had the potential to cause
significant O₃ depletion. Therefore, incorporating elevated CH₄ and H₂S into an investigation of the effects of the Siberian Traps is important to build an overall picture of atmospheric response to the eruptions. Enhanced CH₄ concentrations cause depressed OH concentrations in the troposphere, but generate H₂O and consequently elevate HOₓ radical concentrations in the stratosphere. Since HOₓ is photochemically important for both catalytic O₃ destruction cycles and oxidation of SO₂ through to H₂SO₄, gas-phase chemistry would be influenced, as well as heterogeneous chemistry occurring on expanded sulphate aerosol surface area. Significantly enhanced levels of CH₄ would increase the tropospheric lifetimes of organohalogen species such as CH₃Cl, the main sink for which is reaction with OH, consequently increasing the halogen loading of stratosphere resulting from the Siberian Traps volcanism. Elevated H₂S concentrations give rise to substantially elevated SO₂ and sulphate aerosol concentrations. Since both SO₂ and sulphate aerosol have the potential to absorb UV, high levels of these species would attenuate the amount of UV penetrating through the atmosphere to the surface, so limiting the radiative impact of an end-Permian O₃ layer collapse.

5. Conclusions

From our analyses, we conclude that (i) a 100–200 kyr main eruptive phase had the potential to produce high latitude stratospheric O₃ depletion due to large releases of HCl (figure 1), (ii) organohalogen release from heating of organic-rich rocks was insufficient to extensively damage the ozone layer. However, including the possibility that dispersed organic matter provided a precursor for organohalogen synthesis results in massive CH₃Cl production that could lead to substantial O₃ depletion when released over 100 kyr (figure 2), (iii) the potential for severe O₃ depletion is greatest when the simultaneous release of HCl from the Siberian Traps and CH₃Cl release from coals and rocks are considered together, and (iv) calculated increases in UV-B radiation resulting from this latter scenario (figure 7) appear sufficient in destabilize plant genomes.

Finally, we point out that increases in UV-B radiation we report for the same combined scenario (figure 7) here might have left a distinct geochemical signature in the sedimentary record by influencing the isotopic fractionation taking place during the biogeochemical cycling of sulphur. This may offer an independent means for evaluating our simulations and the interpretation of a mutagenesis event in the fossil record. Mass-independent isotope fractionation (MIF) of sulphur has been observed in laboratory experiments subjecting SO₂ to UV radiation of less than 220 nm (Farquhar et al. 2001). This important observation has been exploited by analysing crustal and sedimentary rocks for a MIF signal, where its presence represents UV-transparency of the Earth’s early (Archean) atmosphere with reduced O₂ and O₃ levels (Farquhar et al. 2000). Furthermore, studies of ice from snow pits and ice cores indicate that a similar MIF signal is recorded following major volcanic eruptions that inject SO₂ into the stratosphere, where it is exposed to high energy UV radiation and photo-oxidized, mainly as a result of UV photochemistry in the 248 nm wavelength region rather than 220 nm (Savarino et al. 2003; Baroni et al. 2007). The MIF anomaly may occur because the absorption of 248 nm produces SO₂⁺ (excited triplet and singlet states) and eventually SO₃ and H₂SO₄. This suggests that if

Phil. Trans. R. Soc. A (2007)
Figure 7. Calculated latitudinal and seasonal daily near-surface UV-B radiation fluxes using a generalized plant action spectrum normalized at 300 nm (kJ m$^{-2}$ d$^{-1}$)$_{BE}$ (Caldwell 1971) for the (a) end-Permian ‘control’ atmosphere and for (b) 600 kyr, (c) 400 kyr, (d) 200 kyr and (e) 100 kyr simulations of releases from all sources combined (run 4).
the Earth experienced a major UV crisis at the end-Permian during the eruption of the Siberian Traps, it may be recorded as a MIF preserved in the rock record. However, the magnitude of the signal, its preservation and our capacity to actually detect it, remain open questions given the high solubility and relatively small quantities of sulphate involved.

We thank Mark Sephton (Imperial College), University of London for advice on calculating organohalogen emissions from coals, Henk Visscher for helpful comments on an earlier draft, and Karl Turekian (Yale University) for pointing out the possible consequences of increased UV-B radiation for mass-independent sulphur isotope fractionation. M.H. was supported by an NERC studentship (NER/S/J/2003/11963) and B.H.L. by Natural Environment Research Council award to D.J.B. and J.A.P. (NER/A/S/2002/00865) and a Leverhulme Trust Early Career Fellowship (ECF/2006/0492).

Figure 8. Calculated latitudinal and seasonal tropospheric SO$_2$ concentrations for (a) the shortest (100 kyr, run 4A) and (b) the longest (600 kyr, run 40) duration of the main eruptive phase.

References


Phil. Trans. R. Soc. A (2007)


**Phil. Trans. R. Soc. A** (2007)


