Stratospheric aerosol particles and solar-radiation management

F. D. Pope[1,2]*, P. Braesicke[2], R. G. Grainger[3]*, M. Kalberer[2], I. M. Watson[4], P. J. Davidson[5] and R. A. Cox[2]

The deliberate injection of particles into the stratosphere has been suggested as a possible geoengineering scheme to mitigate the global warming aspect of climate change. Injected particles scatter solar radiation back to space and thus reduce the radiative balance of Earth. Previous studies investigating this scheme have focused primarily on sulphuric acid particles to mimic volcanic injections of stratospheric aerosol. However, the composition and size of volcanic sulphuric acid particles are far from optimal for scattering solar radiation. We show that aerosols with other compositions, such as minerals, could be used to dramatically increase the amount of light scatter achieved on a per mass basis, thereby reducing the particle mass required for injection. The chemical consequences of injecting such particles into the stratosphere are discussed with regard to the fate of the ozone layer. Research questions are identified with which to assess the feasibility of such geoengineering schemes.

Many strategies and techniques for geoengineering Earth's climate have been suggested[1,2]. The deliberate injection of aerosols into the stratosphere is a solar-radiation management (SRM) scheme, and has been suggested to be affordable and have a high effectiveness compared with other geoengineering schemes that have been suggested for mitigation of global warming[1]. However, it has also been suggested that SRM has a low associated safety compared with other geoengineering schemes, because of its possible effects on regional climate, stratospheric ozone, high-altitude tropospheric clouds and biological productivity[1]. The lower stratosphere already contains a sulphuric acid (H_2SO_4) aerosol layer produced from the oxidation of both biogenic and volcanic sulphur gases (OCS and SO_2)[3,4]. In addition to H_2SO_4 aerosol, there are other particulate matters of diverse origin present in the stratosphere, for example, volcanic mineral dusts, meteoric metals/oxides, carbonaceous material injected from aircraft operations and material transported from the underlying tropospheric regions[5]. The amounts from these sources are generally minor except in the event of major perturbations from explosive volcanic eruptions. The mean exchange time between the lower stratosphere and the troposphere is around 1–2 years, and submicrometre aerosols with a low settling velocity introduced into the stratosphere reside there for several years. Significant global surface cooling through the generation of stratospheric H_2SO_4 aerosol is observed after major volcanic eruptions near the Equator. The most significant eruption in recent times was Mount Pinatubo in the Philippines (1991), which reduced the average global temperature by ~0.5 K for ~2 years[6-9]. As a result, research on the deliberate injection of stratospheric aerosol has consequently focused on the introduction of sulphate aerosol or precursor gases (SO_2, H_2S and OCS) so as to mimic the volcanic effect[10–12]. Aerosol compositions other than sulphate have been suggested, because they can offer more-effective radiation scattering by virtue of having greater refractive indices[13-15], or possibly increase the particle lifetime in the stratosphere by the use of photophoretic levitation[16]. Furthermore, if a material with lower solar-radiation absorption is used, modelling suggests significant reduction in stratospheric heating leading to a lower perturbation of stratospheric circulation[17].

The most efficient use of injected particles is achieved when particles are injected into the tropical stratosphere (~20 km; Fig. 1). This injection strategy would maximize their meridional distribution within the atmosphere and atmospheric lifetime, owing to slow overturning (Brewer–Dobson) circulation in the stratosphere as indicated in Fig. 1 (refs 18,19). Optimized particle properties could also minimize the amount of injected geoengineered material required, and hence reduce the deposition flux of aerosol at Earth's surface. Various methods for the introduction of geoengineered particles into the stratosphere have been proposed[20–22] and the choice of delivery mechanism is beyond the scope of this Perspective.

As well as containing a H_2SO_4 aerosol layer, the lower stratosphere also contains the ozone layer, which has the crucial role of protecting Earth's biosphere by absorbing harmful ultraviolet radiation. The ozone layer profoundly influences both atmospheric dynamics and atmospheric chemistry[23]. International regulations are already in place to protect the ozone layer from depletion by human-made halocarbons[23], therefore the deliberate injection of aerosols into the stratosphere must be assessed with respect to the possible interactions between the geoengineered aerosol and the ozone layer.

An ideal particle for use in SRM would maximize the scattering of incoming solar radiation achieved by the stratospheric injection of the particles, while minimizing the stratospheric chemistry impact and any effect on stratospheric circulation and microphysics. Moreover, the particle choice would ideally have minimal impact on precipitation, ecosystems and human health. The cost, and hence the economic viability, of SRM by stratospheric particle injection will be dependent, among other criteria, on the particle size and composition. This Perspective investigates the consequences of these two principal choices of size and composition

[1]School of Geography, Earth and Environmental Sciences, University of Birmingham, Edgbaston, Birmingham B15 2TT, UK, [2]NCAS/Centre for Atmospheric Science, Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, UK, [3]Atmospheric, Oceanic and Planetary Physics, Clarendon Laboratory, University of Oxford, Parks Road, Oxford OX1 3PU, UK, [4]Department of Earth Sciences, University of Bristol, Wills Memorial Building, Bristol BS8 1RJ, UK, [5]Davidson Technology Limited, 8a Village Walk, Onchan, Isle of Man IM3 4EA, UK.
*e-mail: f.pope@bham.ac.uk; r.grainger@physics.ox.ac.uk

1
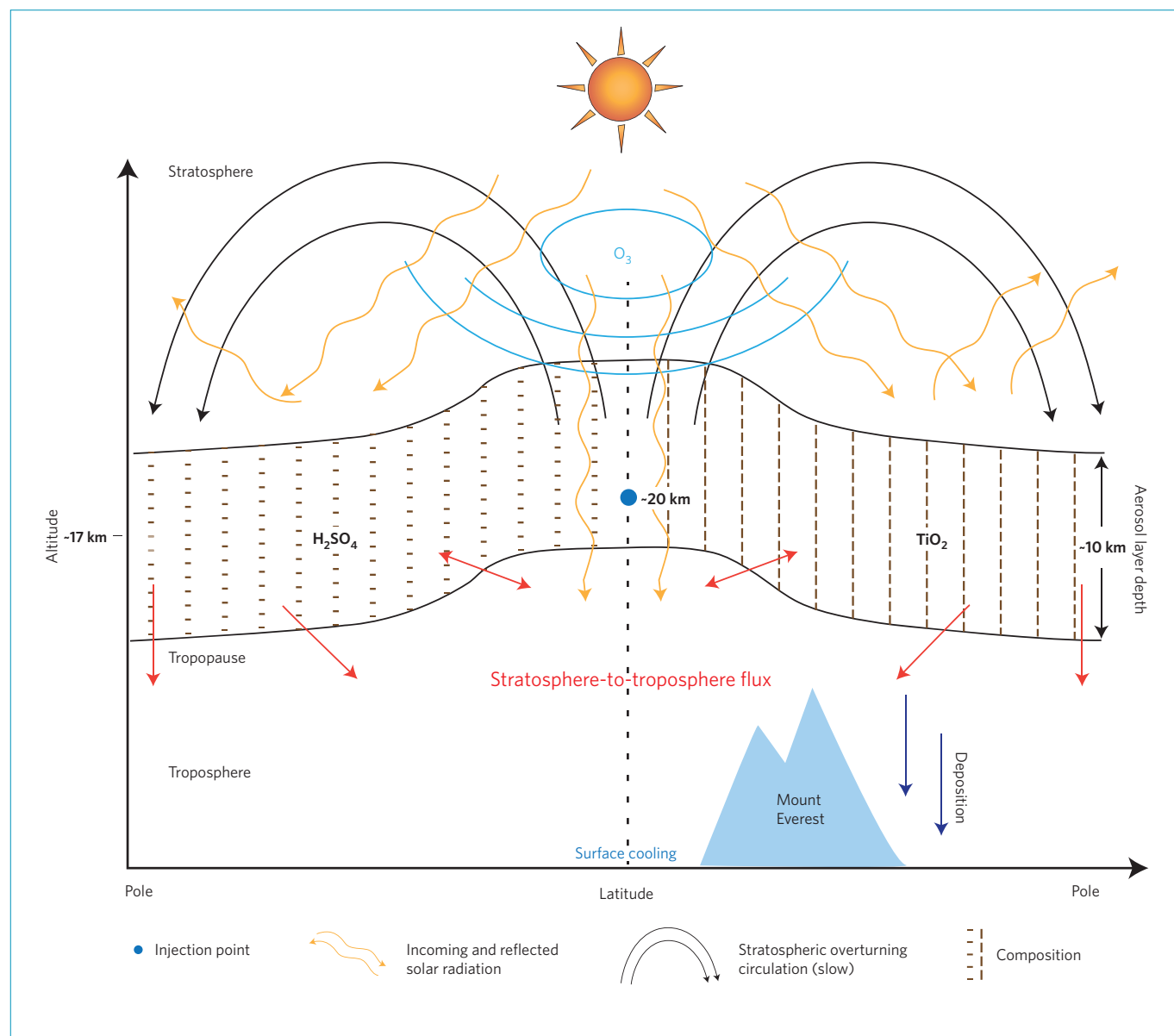
Figure 1 | The stratospheric injection of particles will perturb the atmospheric radiative budget and the chemistry of the atmosphere. The quantitative effect of the injection will depend on the aerosol composition, size, and location and altitude of injection.

with respect to the impact of the particle on the radiative budget and ozone-layer chemistry.

Radiation and Earth's albedo
The goal of SRM is to increase Earth's albedo within the constraints mentioned above. The injection of stratospheric particles achieves this by scattering incoming solar radiation back to space (Fig. 1). The principal factors that determine the ability of a particle to reflect sunlight are the particle's refractive index (and to a lesser extent shape) and size. A useful metric to assess the efficacy of particle scattering is the Bond albedo[24], defined as the ratio of the total radiation reflected from Earth compared with the total incident solar radiation on Earth (a formal definition is given in the Methods). Earth's Bond albedo has a value of 0.30125 and an estimated increase of about 0.018 is required to counteract the effects of doubling atmospheric carbon dioxide[1].

Figure 2 shows the change in Bond albedo for log-normal aerosol distributions with a range of refractive indices, assuming a constant particle concentration equal to one 1-μm-diameter particle per cm³ of air. A maximum change in Bond albedo of about 0.004 is achievable for a median particle size of 0.07 μm and a refractive index of 2.96. An upper limit of approximately ten times greater scattering could theoretically be achieved with monodisperse particles compared with aerosols of volcanic composition and size (Supplementary Fig. S1). However, manufacturing processes, delivery technology and particle coagulation processes taking place in the atmosphere will transform manufactured monodisperse particles to a broader, typically log-normal size distribution. Close to a stratospheric injection point, particle concentrations are large giving the potential for significant coagulation unless rapid dilution or other control mechanisms such as particle charging are introduced.

This assessment does not consider the infrared heating of the stratosphere caused by absorption of long-wave radiation by the particles. This is a potentially important consideration; if the injected particles absorb longwave radiation they can act as warming agents, which can have important consequences for atmospheric dynamics[17]. In particular, a warming of the tropopause region would allow

more water vapour from the troposphere into the stratosphere, which would alter the chemical composition of the stratosphere. Hence, ideal particles would possess negligible absorption features (minimizing stratospheric warming) as well as having high refractive indices (maximizing scattering).

Possible impacts on the ozone layer

The use of particles for SRM would increase the burden of stratospheric aerosol and thus the surface area available for heterogeneous reactions[26]. The production and destruction of gas-phase species from surface-mediated reactions has the potential to perturb the stratospheric photochemistry that controls ozone concentrations. The heterogeneous reactions on H_2SO_4 aerosol are well characterized[27], and this reactivity can be used as a baseline for assessing the ozone-depleting impacts of other aerosol types. This approach demands a reasonable knowledge of the kinetics and mechanisms of the reactions on the new aerosol types, and their dependence on particle size distribution, surface area, temperature and humidity at stratospheric conditions.

Laboratory measurements have shown that the direct conversion of O_3 to O_2 on heterogeneous particle surfaces, which are found in the natural stratosphere, is inefficient. Even after large volcanic injections with the associated increased aerosol surface area, the lifetime of O_3 with respect to heterogeneous decomposition is at least an order of magnitude longer than that of the characteristic transport times of O_3 from the stratosphere to the troposphere. Therefore, direct heterogeneous ozone decomposition is unlikely to be an important O_3 loss process provided the particles are not orders of magnitude more reactive than H_2SO_4.

The important heterogeneous reactions that lead to ozone depletion are those that increase the amount of free-radical catalysts that can participate in the gas-phase catalytic destruction of O_3. The chemical role of the aerosols is to provide sites for heterogeneous reactions between precursor molecules that would otherwise be quite stable in the gas phase. This leads to the creation of new reactive molecules that form ozone-depleting radicals by photochemical dissociation. The catalytic O_3 destruction reaction cycles are as follows (where X = NO, HO, Cl or Br)[27]:

$$X + O_3 \rightarrow XO + O_2 \tag{1}$$

$$XO + O_3 \rightarrow X + 2O_2 \tag{2}$$

$$\text{Net: } 2O_3 \rightarrow 3O_2$$

Precursor species of particular importance for the chlorine cycle are hydrogen chloride (HCl) and chlorine nitrate ($ClONO_2$). These two species can undergo adsorption on particle surfaces and subsequently react there to produce molecular chlorine, which is then released to the gas phase:

$$ClONO_2 + HCl \rightarrow Cl_2 + HNO_3 \tag{3}$$
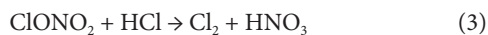
When exposed to ultraviolet/visible sunlight Cl_2 readily dissociates to produce chlorine atoms, which catalytically destroys ozone within reactions (1) and (2). This process is responsible for the large losses of ozone in the polar regions in springtime over Antarctica and in the Arctic[28].

The chemistry of the nitrogen oxide species is also perturbed by heterogeneous chemistry, for example, by the hydrolysis reaction (4) of nitrogen pentoxide (N_2O_5), which is formed by reaction (5), where M is any third body (N_2 or O_2).

$$N_2O_5 + H_2O \text{ (surface)} \rightarrow 2HNO_3 \tag{4}$$

$$NO_3 + NO_2 + M \rightarrow N_2O_5 + M \tag{5}$$
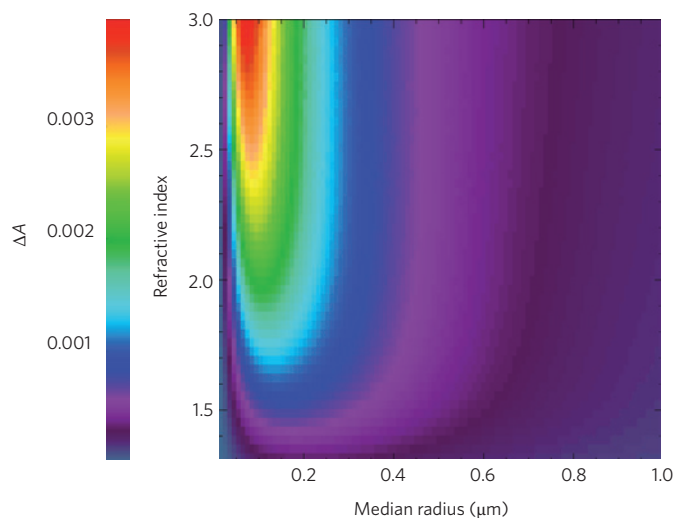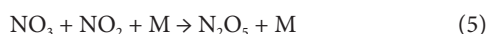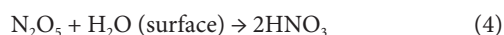
Figure 2 | Change in Bond albedo from a 1-km-thick stratospheric layer of aerosol whose size distribution is log-normal and whose volume fraction is held constant (equivalent to one 1-μm-radius droplet per cm³ of air). This figure identifies the optimal size and composition of a monodisperse population of particles for scattering solar radiation. If the particles are assumed to have the same radii and be spherical then the maximum change in Bond albedo (ΔA) occurs at a particle size of about 0.1 μm and refractive index of about 3.4. For the more realistic log-normal distribution the maximum change occurs at a particle size of about 0.1 μm and refractive index of about 2.96. The albedo calculations for Fig. 2 and Supplementary Fig. S1 have assumed the ability to create and maintain desired aerosol size distributions. The microphysical processes that determine the evolution of the size distribution (for example, coagulation, sedimentation, condensation or evaporation)[53] were not considered. It is likely that the injected size distribution is an initial state that evolves to different steady-state size distributions than are used here. These processes have been shown to occur in the stratospheric aerosol population subsequent to the Pinatubo eruption[53]. The radiation calculations assume the particles are evenly spread over the whole Earth. In reality global circulation will make the particle distribution inhomogeneous[54].

This converts reactive nitrogen oxides (NO and NO_2), which are involved in ozone-depletion cycles, into unreactive nitric acid. N_2O_5 hydrolysis on H_2SO_4 aerosols causes pronounced changes in the partitioning of reactive nitrogen species after volcanic eruptions[29].

Hence heterogeneous reactions involving nitrogen and chlorine oxides can potentially influence ozone concentrations significantly, and reactions (3) and (4) are two of the key reactions to be considered. However, the exact ozone-depletion potential of increased aerosol loading (natural or human-made) depends on a large number of (gas-phase and heterogeneous) reactions also involving OH, HO_2 and brominated compounds. Although the effects of H_2SO_4 particles on these reactions are relatively well known through laboratory studies and atmospheric observations during and after volcanic eruptions, none of these reactions have so far been evaluated for other particle surfaces. However, laboratory procedures that could characterize these reactions under stratospherically relevant temperature and pressure conditions do exist. Previous results from these laboratory procedures have provided data with which to produce realistic, predictive and diagnostic models of other aspects of stratospheric chemistry[30], which ultimately led to the Montreal Protocol being signed by the vast majority of the world's nations to phase-out the manufacture of and reduce emissions of particular ozone-depleting chemicals.

The reactions outlined above need to be evaluated at stratospheric conditions, especially with respect to humidity and
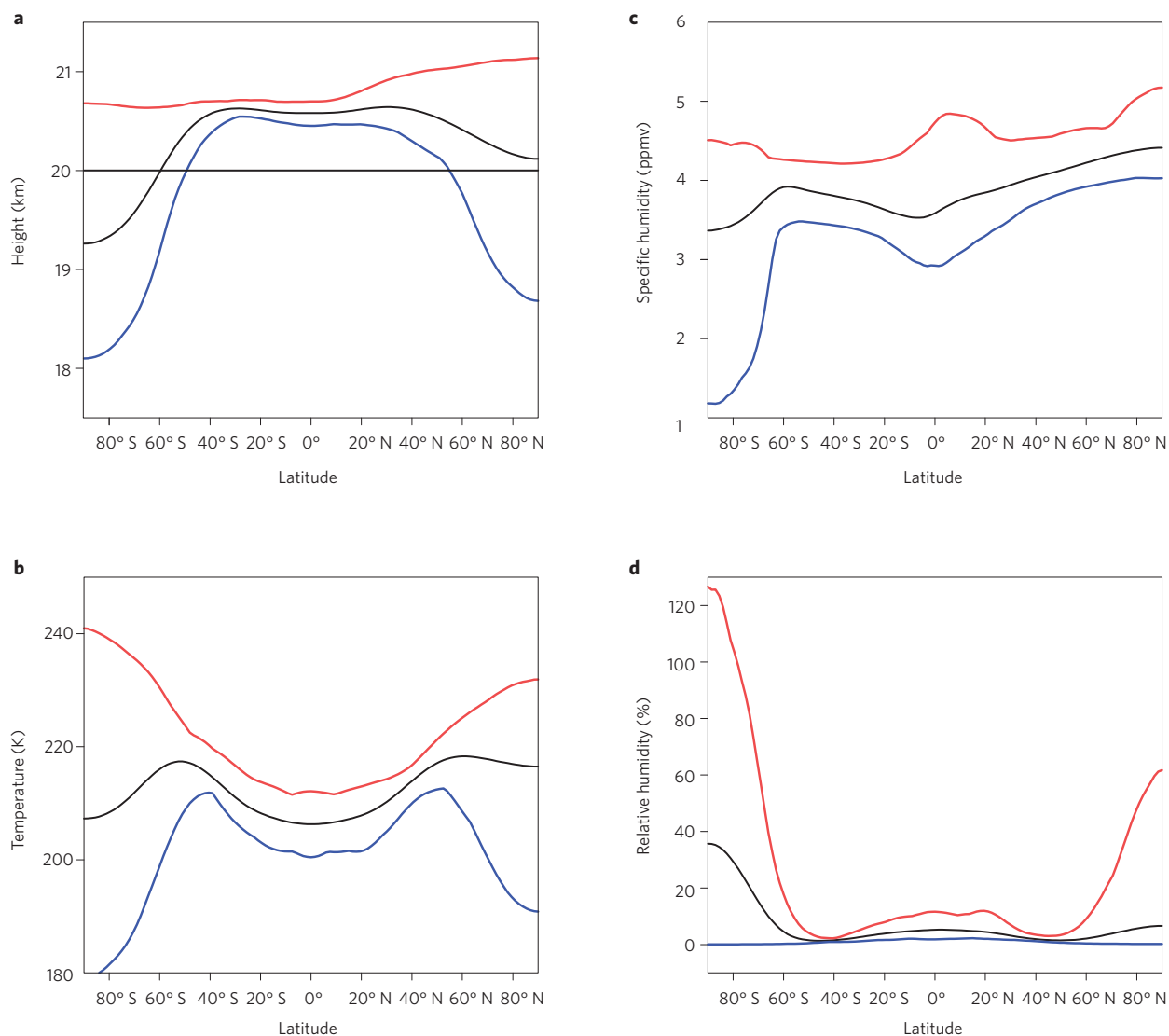
Figure 3 | Temperature and humidity conditions relevant for stratospheric particle chemistry in SRM schemes. a–d, Height (**a**), temperature (**b**) specific humidity (**c**) and relative humidity (**d**) of the 50 hPa (0.05 bar) surface as a function of latitude. In all panels the black line is the long-term annual mean from 1989 to 2009, the red line is the maximum monthly mean and the blue line is the minimum monthly mean over this period. Data from the ERA-Interim data set (www.ecmwf.int)[55].

temperature. Figure 3 indicates the range of temperature and humidity conditions that are pertinent for understanding stratospheric chemistry. Minimum temperatures occur in the winter hemisphere. Relative humidity is highest for cold temperatures at high latitudes, even though the specific humidity decreases during Southern Hemisphere winter, because relatively dry air is descending from above. Although the lower stratosphere is cold ($190 < T < 240$ K) it is also very dry, so water/ice clouds are very seldom seen there, except in polar regions where supersaturations are often achieved. The presence of water on the surface of aerosol particles or within them is important. Water can promote ionic reactions in the liquid phase[31] or, on solid surfaces, block reactive sites involved in surface reactions[32]. Therefore, the physicochemical properties of aerosols can vary widely with particle hygroscopicity. These influences on reactivity need to be deduced from laboratory studies of the relevant reactions on potential SRM particles[33]. It may be that hydrophobic surfaces will show advantages in reducing the impact of the particle on important atmospheric reactions[15].

An additional impact on ozone chemistry could arise from the warming of the tropopause region if the injected aerosols absorb radiation. This could lead to a corresponding increase in lower stratospheric humidity, which could increase ozone loss owing to increased concentrations of catalytic HO_x species (OH and HO_2 radicals), which already contribute to ozone loss in this region by well-established catalytic cycles[34].

A case for non-sulphate aerosol?

Here we present a case study investigating the relative benefits of H_2SO_4 and manufactured mineral particles for use in SRM. We consider particle populations and distributions that would cause similar changes in the Bond albedo as the Mount Pinatubo eruption. The Pinatubo eruption generated an aerosol that was initially concentrated at the Equator, but whose mass spread to both hemispheres over time[35]. This cloud of H_2SO_4 particles has been represented here by a global 10-km-thick aerosol layer with a log-normal size distribution described by number of particles per cm³, $N = 22$, particle radius $r = 0.2\,\mu$m and log-normal size distribution $S = 1.8$. These values are in accord with measurements of the Mount Pinatubo volcanic aerosol[36–38]. Using this size distribution and assuming an aerosol droplet composition of 70% H_2SO_4 by weight gives a total

Table 1 | Refractive indices of candidate particles for solar-radiation management.

Candidate particle composition	Typical refractive index at 0.55 µm	Typical density (kg m^{-3})
Sulphuric acid (H_2SO_4) 70wt% acid	1.5	1,615
Clay	1.55	Range
Titanium dioxide (TiO_2)	2.5	4,230
Alumina (Al_2O_3)	1.77	4,000
Silica (SiO_2)	1.54	2,648
Calcium carbonate ($CaCO_3$)	1.59	2,750
Sea salt (mainly NaCl)	1.55	2,165
Zinc oxide (ZnO)	2.01	5,606
Diamond (C)	2.42	3,500
Silicon carbide (SiC)	2.66	3,210

It should be noted that the cost of aerosol injection for schemes that pump (continuous delivery schemes) the aerosol through a tube will depend more on the volume of material pumped than the particle density. For intermittent delivery (for example, by aircraft or free-flying balloons), the cost will be roughly proportional to the material weight lifted. Hence intermittent delivery schemes are more concerned with particle density than pumping schemes.

aerosol loading of ~30 MT (ref. 39). This is consistent with aerosol measurements after the event[40] and SO_2 concentrations measured immediately after the eruption[41]. The calculated increase in Bond albedo generated by this layer was 0.015. Table 1 provides refractive indices of both H_2SO_4 and common minerals. It can be seen that the refractive index of several minerals (for example, diamond, silicon carbide, titanium dioxide (TiO_2) and alumina) provide refractive indices that are much closer to the optimal values when compared with H_2SO_4. For this case study, TiO_2 is selected as the engineered particle composition because of its near optimal refractive index and its widespread use in submicrometre applications. A log-normal size distribution with a mean particle size of 0.07 µm has been chosen to maximize the Bond albedo change (Fig. 2). Calculations show that to achieve the same increase in Bond albedo as the H_2SO_4 particles from the Pinatubo eruption a mass of ~10 Mt of geoengineered TiO_2 aerosol is required. Therefore the use of the TiO_2 for SRM requires a factor of ~3 less in mass, and a factor of ~7 less in volume than that of H_2SO_4 in the stratosphere. This is a significant reduction of aerosol burden. However, it should be noted that the practical requirements of a particle-injection scheme will necessitate transporting extra mass and volume from that required by a SO_2-precursor scheme because of the need for a carrier gas or fluid. If precursor gases (H_2S, SO_2 or OCS) were used to generate the H_2SO_4, less mass and volume of the precursor would be required compared with the H_2SO_4 end product because of the lower molar masses and volumes of the precursor. Table 2 compares the TiO_2 and H_2SO_4 inputs used and outputs generated in this calculation. Using high-refractive-index mineral particles for SRM clearly would be favourable from a light-scattering perspective. The effect of TiO_2 and other mineral particles with different surface coatings on O_3 chemistry needs much further work, but a preliminary analysis and comparison with H_2SO_4 aerosols follows.

Model calculations carried out by Heckendorn et al. evaluated the likely impact on stratospheric O_3 by different SO_2 stratospheric injection scenarios[34]. The largest injection scenario of 10 MT yr^{-1} of sulphur resulted in a steady state stratospheric burden of 6 Mt of sulphur that caused a 5.3% decrease in the annual mean global mean total O_3 column. This is greater than the mean O_3 loss owing to anthropogenic ozone-depleting substances in the period 2002–2005, compared with the pre-1980 period, as determined both from observations (~3.5%) and model calculations (~3.8%)[42]. Subsequent to the Pinatubo eruption, a 2–3% reduction of the global mean column of O_3 was observed, which can be largely attributed to heterogeneous chlorine activation[43]. Although O_3 loss does not vary linearly with stratospheric aerosol burden, models indicate that as aerosol surface area increases so will the O_3 loss attributable to increased heterogeneous chemistry.

The heterogeneous reaction rates of $ClONO_2$ with HCl on stratospheric H_2SO_4 aerosol is rather inefficient under standard conditions of temperature and humidity at low and mid latitudes[44] owing to the low solubility of HCl in concentrated H_2SO_4 droplets. There are no published data for the reactive uptake of HCl and $ClONO_2$ on most mineral surfaces. The work of Molina et al. showed that heterogeneous reaction of $ClONO_2$ with HCl on alumina (Al_2O_3) surfaces is approximately ten times more efficient than on H_2SO_4 droplets under comparable conditions[45]. Furthermore, the reactive uptake of $ClONO_2$ on borosilicate glass in the presence of HCl was similar to that on alumina, under the same conditions, and it was concluded that the reaction probably occurs on a variety of mineral oxide surfaces at comparable rates provided such surfaces adsorb water as well. Thus the activation of chlorine on mineral aerosols at low and mid latitudes for hydrophilic surfaces is likely to be more efficient than on the equivalent burden of sulphate aerosol. At polar latitudes the activation of chlorine on a SRM aerosol will be small compared with the activation that will occur on polar stratospheric clouds because of their much greater surface area[46].

Hydrolysis of nitrogen pentoxide (N_2O_5) on H_2SO_4 aerosol is an acid-catalysed heterogeneous reaction that occurs rapidly under all stratospheric conditions and is only weakly dependent on relative humidity and temperature. Uptake of N_2O_5 on dry mineral dust aerosols is approximately ten times slower[33]. Therefore particles

Table 2 | Comparison of volcanic H_2SO_4 and TiO_2 particle characteristics.

Assumed quantities	Volcanic H_2SO_4	TiO_2
Layer thickness (km)	10	10
Number density (cm^{-3})	22	278
Median radius (µm)	0.2	0.045
Spread	1.8	1.8
Temperature (K)	240	n/a
Composition (wt% H_2SO_4)	70	n/a
Density (kg m^{-3})	1,615	4,000
Determined quantities		
Effective radius (µm)	0.47	0.11
Surface area density (µm^2 cm^{-3})	22	14
Volume density (µm^3 cm^{-3})	3.5	0.50
Optical thickness at 0.55 µm	0.15	0.09
Aerosol mass (Mt)	29.8	10.3
Aerosol volume (km^3)	0.018	0.003
Bond albedo	0.015	0.015

with pure mineral surfaces are likely to be similar in reactivity to these dust aerosols and hence less reactive than H_2SO_4 particles with respect to N_2O_5 hydrolysis. Thus, from the reactions described above, chlorine activation on mineral particles might be of most concern. However, the uncertainties here are large; for example, the reactivity of mineral dusts at stratospheric temperatures and possible photocatalytic effects are unknown[47]. Consequently the effects on ozone amounts owing to heterogeneous chemistry could be significantly affected by the introduction of mineral aerosol into the stratosphere.

As well as the possibility of lower mass injection, there are other potential benefits for mineral dust injection over H_2SO_4 particles: coating technologies for small particles already exist, on a very large scale, and therefore there might be the possibility of being able to engineer a chemically inert surface for the particle. To investigate the effects of H_2SO_4-precursor injection, very large field experiments are required because of the long time it takes for the particles to reach their final population distribution[48]. The use of manufactured particles of predetermined size offers scope for initially small-scale experiments, in both the laboratory and field, where particle properties (for example, atmospheric chemistry, sedimentation and coagulation rates) could be studied at a modest scale. This would negate the need to perform material experiments on the whole planet with the slowly produced H_2SO_4 mists[2,48]. If these small-scale experiments were encouraging, then progressively larger-scale experiments could be carried out in an appropriate regulatory framework. This framework would have to consider the ethical, legal and political implications of the experiments. There are also some serious potential drawbacks: the injection of mineral dusts does not have the natural analogue in volcanoes that H_2SO_4 has and hence our initial understanding starts from a smaller knowledge base. The dispersion of manufactured particles at altitude would be a significant undertaking, and the cost of the manufactured particles though modest by comparison with the costs of global warming[49] will vary greatly depending on the type of mineral aerosol chosen.

Recommendations for future research

Solid mineral particles offer the possibility of increased light scattering compared with H_2SO_4 particles. However, the chemical response of the stratosphere to the introduction of engineered aerosols cannot be reliably predicted from current knowledge. Research of the natural stratospheric aerosol layer has indicated that increased heterogeneous surface areas can lead to increased ozone depletion. The impact of engineered aerosols is largely unexplored. In particular, various trace-gas reactions that lead to perturbations in the ClO_x, BrO_x, NO_x and HO_x cycles need to be investigated to assess the impact of novel aerosol compositions on the ozone layer. Laboratory data are required for the parameterization of the temperature- and humidity-dependent uptake kinetics of these reactant trace-gas species on the aerosols. Furthermore, the production of reactive products needs to be evaluated. The hygroscopic properties of aerosols are needed for assessment of the likely water/ice content, and hence reactivity, of aerosols under different stratospheric conditions. The surface areas of different particle compositions need to be defined. In particular, the internal porosity of particles can cause large discrepancies between geometric surface area and true surface area.

Investigations into the use of coatings on the solid particles could provide beneficial changes in particle chemistry without changing the superior radiative effects of the particles. Such coatings may arise naturally through uptake of condensable gases (for example, H_2O and H_2SO_4) or coagulation with the natural H_2SO_4 aerosol, or may be part of the candidate particle's construction. It is speculated that hydrophobic and inert coatings could potentially be useful to reduce surface reactivity of the particles with respect to ozone chemistry.

The effectiveness of geoengineering particles is also determined by the lifetime of the particles in the stratosphere, which is influenced by their coagulation rate and sedimentation rate out of the stratosphere, and stratosphere–troposphere exchange rate. Of importance for these calculations is the size and density of the manufactured particle (Table 2). Data on the microphysics and evolution of the particle size distribution of manufactured particles of known initial size needs to be assessed. In the troposphere the particles are quickly removed through wet deposition to Earth's surface. Although the overall particle deposition rate per surface area and time is likely to be minimal compared with deposition rates of naturally occurring aerosols, the potential effects of these particles on ecosystems and human health need to be investigated, especially with respect to long-term exposure. The environmental impact associated with the manufacture of mineral aerosol would have to be compared with the manufacture of the H_2SO_4 aerosol precursors. A comprehensive evaluation of any candidate geoengineering particle will need to consider thoroughly the effects of the particle during its entire life cycle, from production and delivery to the stratosphere, to physical and chemical effects in the stratosphere, to effects after deposition on the ground. Before stratospheric experiments on any significant scale are carried out, an appropriate regulatory process acknowledging political, social and economic factors needs to be put in place.

Methods

Calculating the Bond albedo. The Bond albedo, A, can be expressed in terms of the local albedo $R(\lambda, \theta_0)$ where λ is the wavelength and θ_0 is the solar zenith angle; using the following equation[50]:

$$A = \int_{\lambda_1}^{\lambda_2} \int_0^{2\pi} \int_0^{\frac{\pi}{2}} \cos\theta_0 E_\lambda^{Sun} R(\lambda, \theta_0 : 2\pi) r_0^2 \sin\theta_0 d\theta_0 d\varphi_0 d\lambda \bigg/ \pi r_0^2 \int_{\lambda_1}^{\lambda_2} E_\lambda^{Sun} d\lambda$$

where r_0 is the radius to the top of the troposphere, λ_1 and λ_2 represent the limits of the solar spectral irradiance E_λ^{Sun}. θ_0 and φ_0 are the spherical coordinates for a global coordinate system with its origin at Earth's centre and the z axis orientated to the sub-solar point.

If a homogeneous scattering layer of thickness l is now placed just above the tropopause then the increase in the Bond albedo is modelled under the following assumptions: (1) the Earth is spherical; (2) there is no scattering above the scattering layer; (3) the solar irradiance spectrum at the top of the scattering layer is the same as the superterrestrial solar irradiance spectrum (this is reasonable, as the solar energy absorbed in the stratosphere is very small); (4) the stratospheric aerosol layer is optically very thin so the solar beam undergoes at most one interaction with an aerosol particle; and (5) the reflection from the scattering layer simply adds to Earth's existing directional–hemispherical reflectance.

The optical properties of the layer are the single scatter albedo, $\tilde{\omega}$, the extinction coefficient, β_{ext}, and the phase function, $P(\Theta)$. Note that the input (θ_i, φ_i) and output (θ_o, φ_o) directions in spherical coordinates can be related to the scattering angle by:

$$\cos\Theta = \cos\theta_i \cos\theta_o + \sin\theta_i \sin\theta_o \cos(\varphi_o - \varphi_i)$$

The choice of where $\varphi = 0$ is arbitrary, so by setting it to φ_i the phase function can be shown as $P(\theta_i, \theta_o, \varphi_o)$.

The optical properties calculated using Mie theory[51] are functions of wavelength, particle size and refractive index. However, this dependence is not explicitly shown.

By making use of rotational symmetry and using the substitutions $\mu_0 = \cos\theta_o$ and $\mu = \cos\theta$, the increase in the Bond albedo (ΔA) caused by stratospheric particles is approximated by:

$$\Delta A = 2 \int_{\lambda_1}^{\lambda_2} E_\lambda^{Sun} \tilde{\omega}\tau \int_0^1 \beta(\mu_0) d\mu_0 d\lambda \bigg/ \int_{\lambda_1}^{\lambda_2} E_\lambda^{Sun} d\lambda = 2 \int_{\lambda_1}^{\lambda_2} E_\lambda^{Sun} \omega\tau\bar{\beta} d\lambda \bigg/ \pi \int_{\lambda_1}^{\lambda_2} E_\lambda^{Sun} d\lambda$$

where τ is optical depth, and

$$\bar{\beta} = \int_0^1 \beta(\mu_0) d\mu_0$$

which is called the isotropic upscatter fraction[52].

The changes in Bond albedo were evaluated for the three scenarios discussed in the text: (1) the particles were assumed to all have the same given radius and refractive index; (2) the particles were assumed to have a log-normal radius distribution with a given mode size and refractive index for both the Pinatubo and TiO_2 case studies.

References

1. Shepherd, J. *Geoengineering the Climate: Science, Governance and Uncertainty* (The Royal Society, 2009).
2. Keith, D. W. Geoengineering. *Nature* **409,** 420–420 (2001).
3. Eatough, D. J., Caka, F. M. & Farber, R. J. The conversion of SO_2 to sulfate in the atmosphere. *Isr. J. Chem.* **34,** 301–314 (1994).
4. Solomon, S. *et al.* The persistently variable 'background' stratospheric aerosol layer and global climate change. *Science* **333,** 866–870 (2011).
5. Murphy, D. M., Thomson, D. S. & Mahoney, M. J. *In situ* measurements of organics, meteoritic material, mercury, and other elements in aerosols at 5 to 19 kilometers. *Science* **282,** 1664–1669 (1998).
6. Hansen, J., Lacis, A., Ruedy, R. & Sato, M. Potential climate impact of Mount Pinatubo eruption. *Geophys. Res. Lett.* **19,** 215–218 (1992).
7. Soden, B. J., Wetherald, R. T., Stenchikov, G. L. & Robock, A. Global cooling after the eruption of Mount Pinatubo: A test of climate feedback by water vapor. *Science* **296,** 727–730 (2002).
8. Minnis, P. *et al.* Radiative climate forcing by the Mount Pinatubo eruption. *Science* **259,** 1411–1415 (1993).
9. McCormick, M. P., Thomason, L. W. & Trepte, C. R. Atmospheric effects of the Mt Pinatubo eruption. *Nature* **373,** 399–404 (1995).
10. Crutzen, P. Albedo enhancement by stratospheric sulfur injections: A contribution to resolve a policy dilemma? *Climatic Change* **77,** 211–220 (2006).
11. Rasch, P. J. *et al.* An overview of geoengineering of climate using stratospheric sulphate aerosols. *Phil. Trans. R. Soc. A* **366,** 4007–4037 (2008).
12. Rasch, P. J., Crutzen, P. J. & Coleman, D. B. Exploring the geoengineering of climate using stratospheric sulfate aerosols: The role of particle size. *Geophys. Res. Lett.* **35,** L02809 (2008).
13. Blackstock, J. J. *et al. Climate Engineering Responses to Climate Emergencies* (Novim, 2009); available at http://arxiv.org/pdf/0907.5140.
14. Katz, J. I. Stratospheric albedo modification. *Energ. Environ. Sci.* **3,** 1634–1644 (2010).
15. Davidson, P., Hunt, H. E. M. & Burgoyne, C. J. Atmospheric delivery system. UK patent application GB2476518 (2009).
16. Keith, D. W. Photophoretic levitation of engineered aerosols for geoengineering. *Proc. Natl Acad. Sci. USA* **107,** 16428–16431 (2010).
17. Ferraro, A. J., Highwood, E. J. & Charlton-Perez, A. J. Stratospheric heating by potential geoengineering aerosols. *Geophys. Res. Lett.* **38,** L24706 (2011).
18. Andrews, D. G., Leovy, C. B. & Holton, J. R. *Middle Atmosphere Dynamics* (Academic, 1987).
19. Niemeier, U., Schmidt, H. & Timmreck, C. The dependency of geoengineered sulfate aerosol on the emission strategy. *Atmos. Sci. Lett.* **12,** 189–194 (2011).
20. Davidson, P., Burgoyne, C., Hunt, H., Loew, D. & Causier, M. Lifting options for stratospheric aerosols: Enabling geoengineering by solar radiation management. *Proc. R. Soc. A* http://dx.doi.org/10.1098/rsta.2011.0639 (in the press).
21. McClellan, J., Sisco, J., Suarez, B. & Keogh, G. *Geoengineering Cost Analysis* (Aurora Flight Sciences Corporation, 2010).
22. Robock, A., Marquardt, A., Kravitz, B. & Stenchikov, G. Benefits, risks, and costs of stratospheric geoengineering. *Geophys. Res. Lett.* **36,** L19703 (2009).
23. World Meteorological Organization — Global Ozone Research and Monitoring Project, Report No. 52 *Scientific Assessment of Ozone Depletion: 2010* (2011).
24. Parker, S. P. *McGraw-Hill Concise Encylopaedia of Science and Technology* (McGraw-Hill, 1982).
25. Pallé, E. *et al.* Earthshine and the Earth's albedo: 2. Observations and simulations over 3 years. *J. Geophys. Res.* **108,** 4710 (2003).
26. Molina, M. J., Molina, L. T. & Kolb, C. E. Gas-phase and heterogeneous chemical kinetics of the troposphere and stratosphere. *Annu. Rev. Phys. Chem.* **47,** 327–367 (1996).
27. Solomon, S. Stratospheric ozone depletion: A review of concepts and history. *Rev. Geophys.* **37,** 275–316 (1999).
28. Solomon, S. *et al.* The role of aerosol variations in anthropogenic ozone depletion at northern midlatitudes. *J. Geophys. Res.* **101,** 6713–6727 (1996).
29. Rinsland, C. P. *et al.* Heterogeneous conversion of N_2O_5 to HNO_3 in the post-Mount Pinatubo eruption stratosphere. *J. Geophys. Res.* **99,** 8213–8219 (1994).
30. Sander, S. P. *et al. Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies* (Jet Propulsion Laboratory, 2011).
31. Davidovits, P., Kolb, C. E., Williams, L. R., Jayne, J. T. & Worsnop, D. R. Update 1 of: Mass accommodation and chemical reactions at gas–liquid interfaces. *Chem. Rev.* **111,** PR76–PR109 (2011).
32. Kolb, C. E. *et al.* An overview of current issues in the uptake of atmospheric trace gases by aerosols and clouds. *Atmos. Chem. Phys. Discuss.* **10,** 11139–11250 (2010).
33. Crowley, J. N. *et al.* Evaluated kinetic and photochemical data for atmospheric chemistry: Volume V — heterogeneous reactions on solid substrates. *Atmos. Chem. Phys.* **10,** 9059–9223 (2010).
34. Heckendorn, P. *et al.* The impact of geoengineering aerosols on stratospheric temperature and ozone. *Environ. Res. Lett.* **4,** 045108 (2009).
35. Russell, P. B. *et al.* Global to microscale evolution of the Pinatubo volcanic aerosol derived from diverse measurements and analyses. *J. Geophys. Res.* **101,** 18745–18763 (1996).
36. Grainger, R. G., Lambert, A., Rodgers, C. D., Taylor, F. W. & Deshler, T. Stratospheric aerosol effective radius, surface area and volume estimated from infrared measurements. *J. Geophys. Res.* **100,** 16507–16518 (1995).
37. Russell, P. B. *et al.* Pinatubo and pre-Pinatubo optical-depth spectra: Mauna Loa measurements, comparisons, inferred particle size distributions, radiative effects, and relationship to LiDAR data. *J. Geophys. Res.* **98,** 22969–22985 (1993).
38. Deshler, T., Liley, J. B., Bodeker, G., Matthews, W. A. & Hoffmann, D. J. Stratospheric aerosol following Pinatubo, comparison of the north and south mid latitudes using *in situ* measurements. *Adv. Space Res.* **20,** 2089–2095 (1997).
39. Grainger, R. G. Infrared absorption by volcanic stratospheric aerosols observed by ISAMS. *Geophys. Res. Lett.* **20,** 1283–1286 (1993).
40. Lambert, A., *et al.* Measurements of the evolution of the Mt. Pinatubo aerosol cloud by ISAMS. *Geophys. Res. Lett.* **20,** 1287–1290 (1993).
41. Guo, S., Bluth, G. J. S., Rose, W. I., Watson, I. M. & Prata, A. J. Re-evaluation of SO_2 release of the 15 June 1991 Pinatubo eruption using ultraviolet and infrared satellite sensors. *Geochem. Geophys. Geosyst.* **5,** Q04001 (2004).
42. Fischer, A. M. *et al.* Interannual-to-decadal variability of the stratosphere during the 20th century: Ensemble simulations with a chemistry-climate model. *Atmos. Chem. Phys.* **8,** 7755–7777 (2008).
43. Telford, P., Braesicke, P., Morgenstern, O. & Pyle, J. Reassessment of causes of ozone column variability following the eruption of Mount Pinatubo using a nudged CCM. *Atmos. Chem. Phys.* **9,** 4251–4260 (2009).
44. Hanson, D. R. & Ravishankara, A. R. Reactive uptake of $ClONO_2$ onto sulfuric acid due to reaction with HCl and H_2O. *J. Phys. Chem.* **98,** 5728–5735 (1994).
45. Molina, M. J., Molina, L. T., Zhang, R., Meads, R. F. & Spencer, D. D. The reaction of $ClONO_2$ with HCl on aluminum oxide. *Geophys. Res. Lett.* **24,** 1619–1622 (1997).
46. World Meteorological Organization — Global Ozone Research and Monitoring Project, Report No. 44 *Scientific Assessment of Ozone Depletion: 1998* (1999).
47. Linsebigler, A. L., Lu, G. & Yates, J. T. Photocatalysis on TiO_2 surfaces: Principles, mechanisms, and selected results. *Chem. Rev.* **95,** 735–758 (1995).
48. Robock, A., Bunzl, M., Kravitz, B. & Stenchikov, G. L. A Test for Geoengineering? *Science* **327,** 530–531 (2010).
49. Stern, N. *The Economics of Climate Change: The Stern Review* (Cambridge Univ. Press, 2007).
50. Liou, K-N. *An Introduction to Atmospheric Radiation* (Academic, 1980).
51. Van de Hulst, H. C. *Light Scattering by Small Particles* (Wiley, 1957).
52. Boucher, O. On aerosol direct shortwave forcing and the Henyey–Greenstein phase function. *J. Atmos. Sci.* **55,** 128–134 (1998).
53. Fussen, D., Vanhellemont, F. & Bingen, C. Evolution of stratospheric aerosols in the post-Pinatubo period measured by solar occultation. *Atmos. Environ.* **35,** 5067–5078 (2001).
54. Hitchman, M. H., McKay, M. & Trepte, C. R. A climatology of stratospheric aerosol. *J. Geophys. Res.* **99,** 20689–20700 (1994).
55. Dee, D. P. *et al.* The ERA-Interim reanalysis: Configuration and performance of the data assimilation system. *Q. J. R. Meteorol. Soc.* **137,** 553–597 (2011).

Additional information

Supplementary information accompanies this paper on www.nature.com/natureclimatechange. Reprints and permissions information is available online at www.nature.com/reprints. Correspondence and requests for materials should be addressed to F.D.P and R.G.G.

Competing financial interests

P.J.D. is employed by Davidson Technology Limited, the company holding the patent application mentioned in ref. 15.