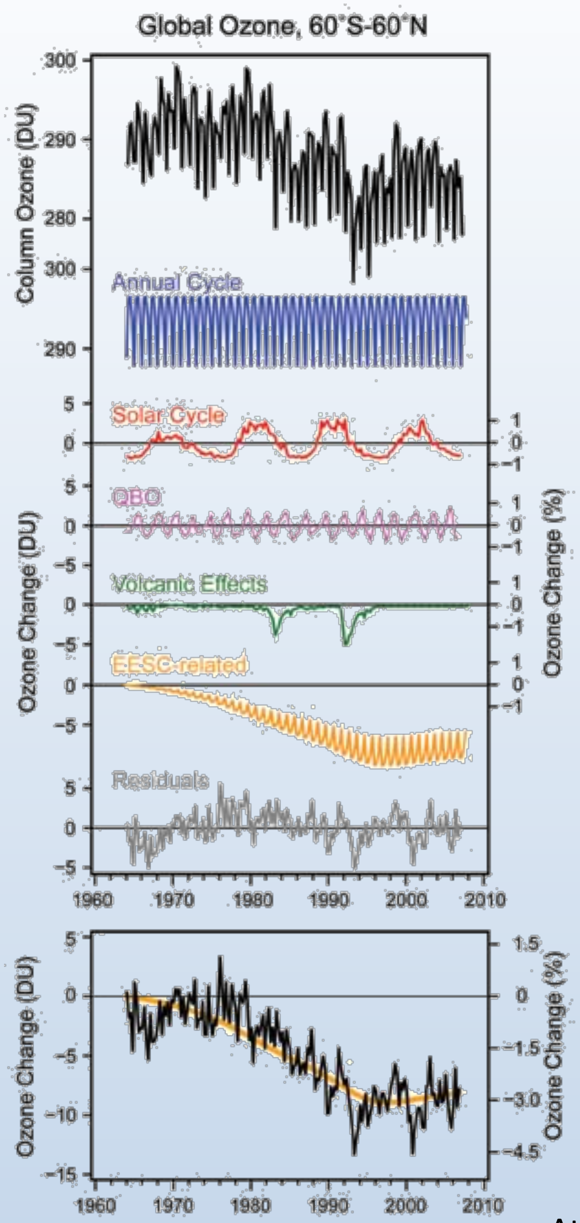
Atmospheric Chemistry

Lecture 14

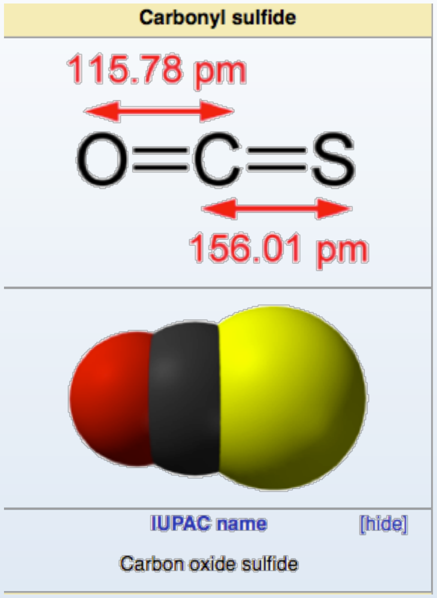
What else affects the ozone record?



- Seasonal cycle
- 11-year sunspot cycle
- Quasi-biennial oscillation (internal variability with 26-27 month period)
- El Nino Southern oscillation (ENSO)
- Volcanoes

Background sulfate aerosol layer

- Why sulfate?
  - Condenses to liquid at higher temperature than H_2O, HNO_3, HCl
- Where does it come from?
  - Carbonyl Sulfide (OCS) is a natural source
  - OCS + hν (λ < 296 nm) → CO + S
- How is S converted to H_2SO_4


Carbonyl sulfide

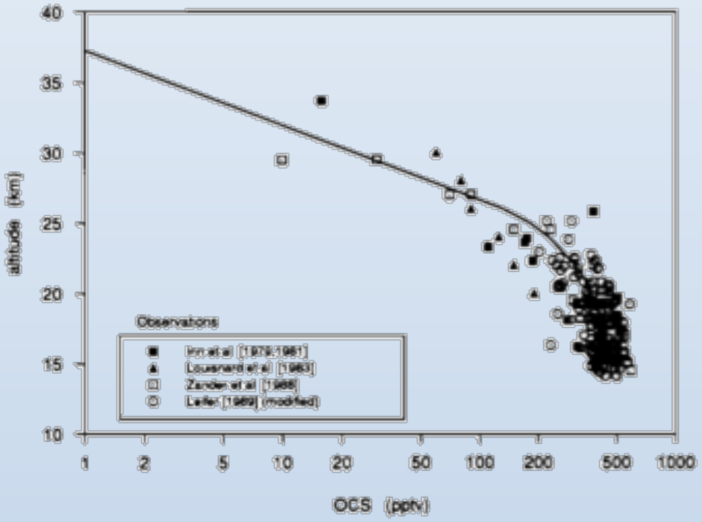
IUPAC name [hide]

Carbon oxide sulfide

$$SO_2 + OH + M \rightarrow HSO_3 + M$$

$$HSO_3 + O_2 \rightarrow SO_3 + HO_2$$

$$SO_3 + H_2O \rightarrow H_2SO_4$$



Boiling point/Condensation temperature

Boiling point: Sulfuric acid 310 ^{o}C at STP
Nitric acid 120 ^{o}C at STP
Water vapor 100 ^{o}C at STP

Water vapor 45^{o}C at 50 hPa

Sulfuric acid condenses before nitric acid or water vapor

Mixtures condense at somewhat different temperatures

Sulfate aerosols tend to have small-sized particles (< 1 micron)

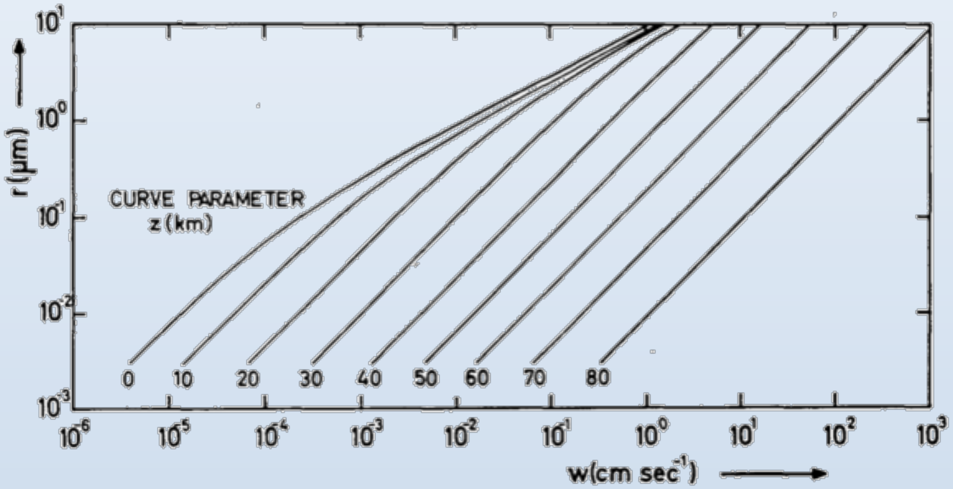
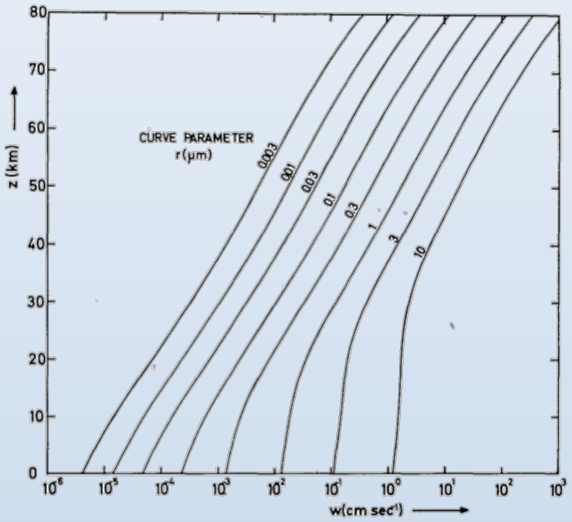


Fig. 2. Falling speed w of spherical particles of mass density 1.0 gm cm^{-3} in the 1962 U. S. Standard Atmosphere as a function of particle radius r, for several heights z above mean sea level.



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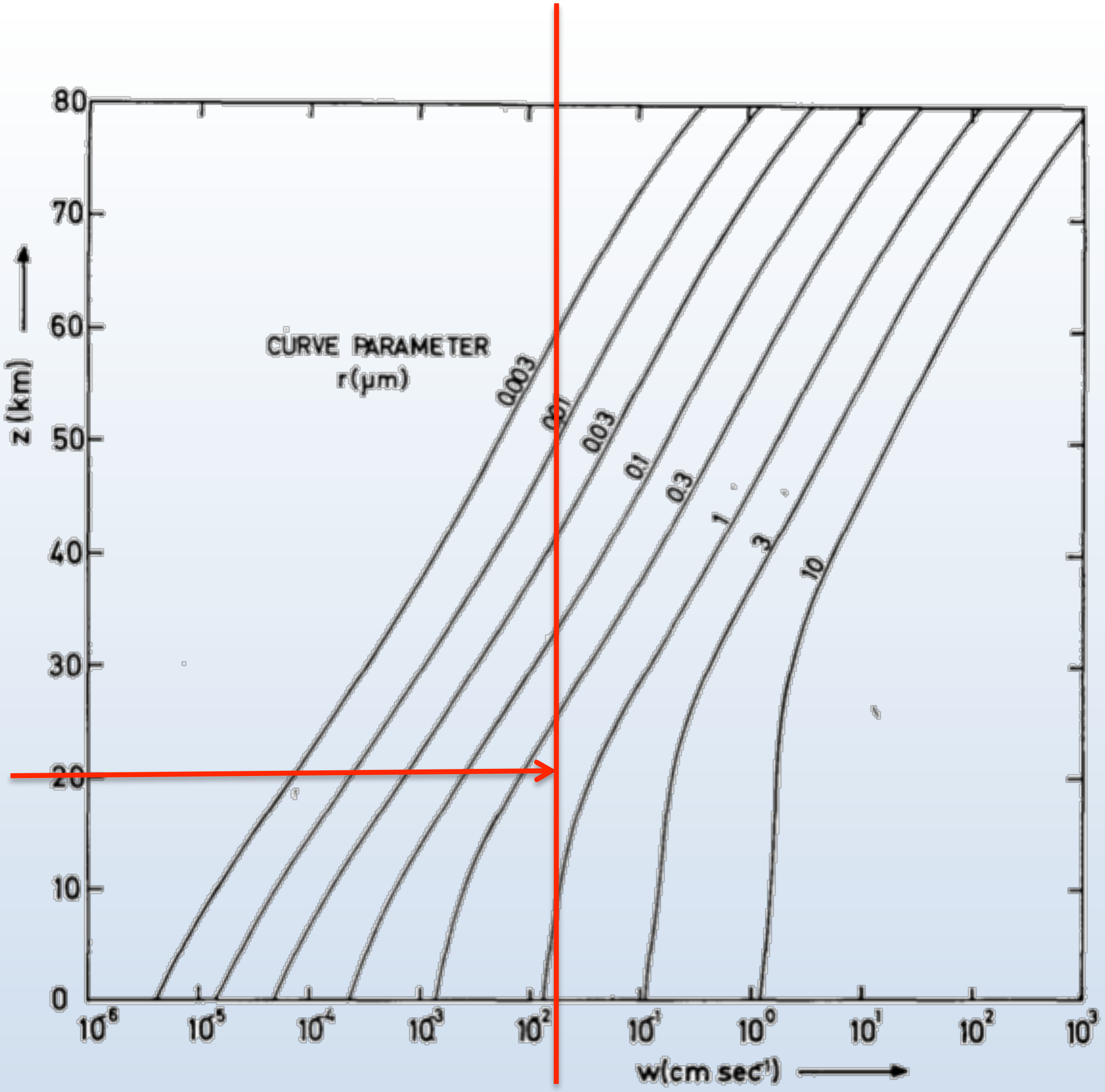


FIG. 1. Falling speed w of spherical particles of mass density 1.0 gm cm^{-3} in the 1962 U. S. Standard Atmosphere as a function of height z above mean sea level, for several particle radii r.

w ≅ .01 cm/sec

≅ .01 km/day

for 0.5 μ particles
at 20 km

Volcanoes can add sulfur to the stratosphere

Halemaumau

Redoubt

St. Helens

Katmai

Pinatubo

Many possible effects of explosive volcanoes that inject material directly into the stratosphere

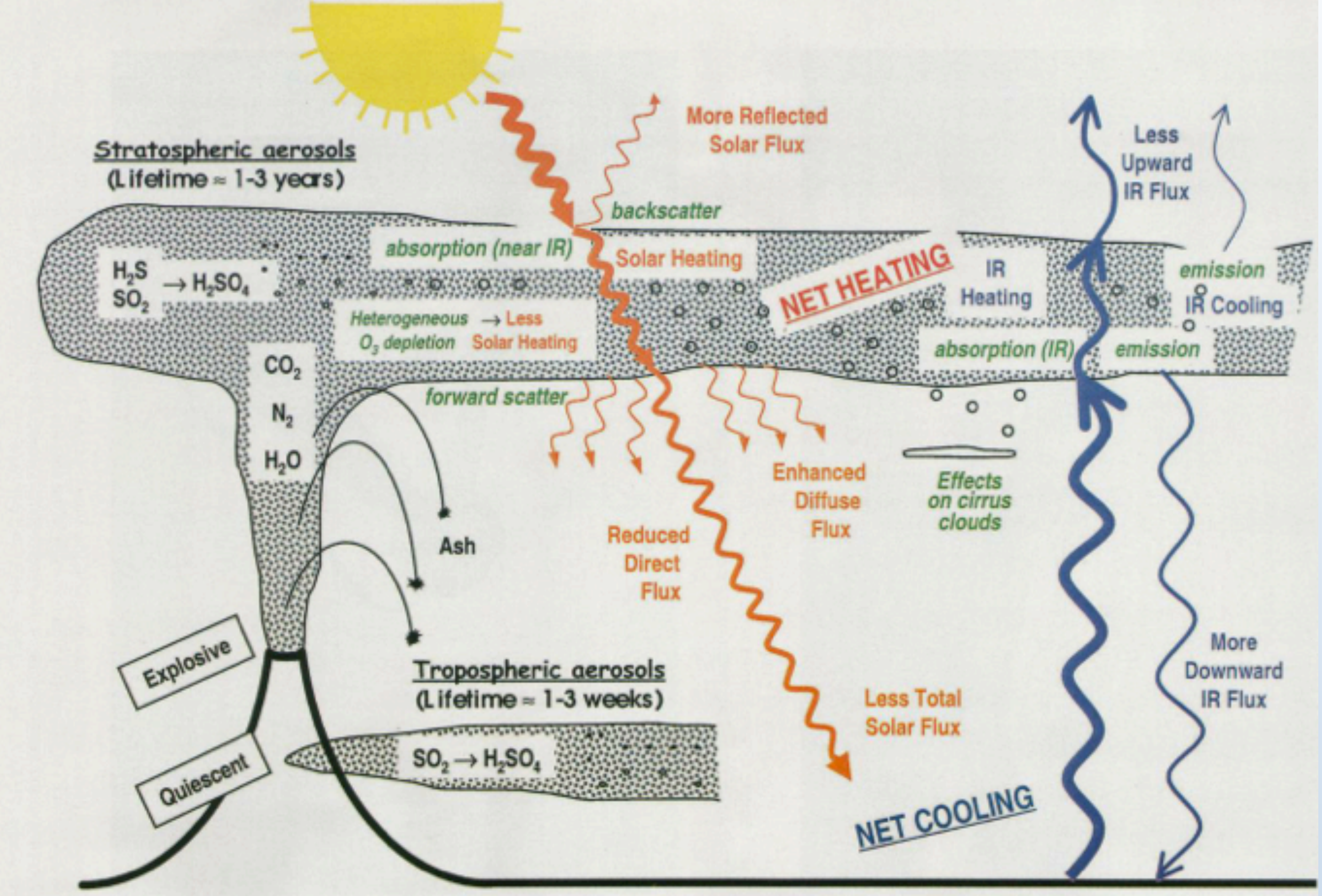


Plate 1. Schematic diagram of volcanic inputs to the atmosphere and their effects. This is an extended version of Figures 1 and 2 of *Simarski* [1992], drawn by L. Walter and R. Turco.

Mechanism by which volcanic sulfur impacts stratospheric ozone

- N_2O_5 is formed at night by

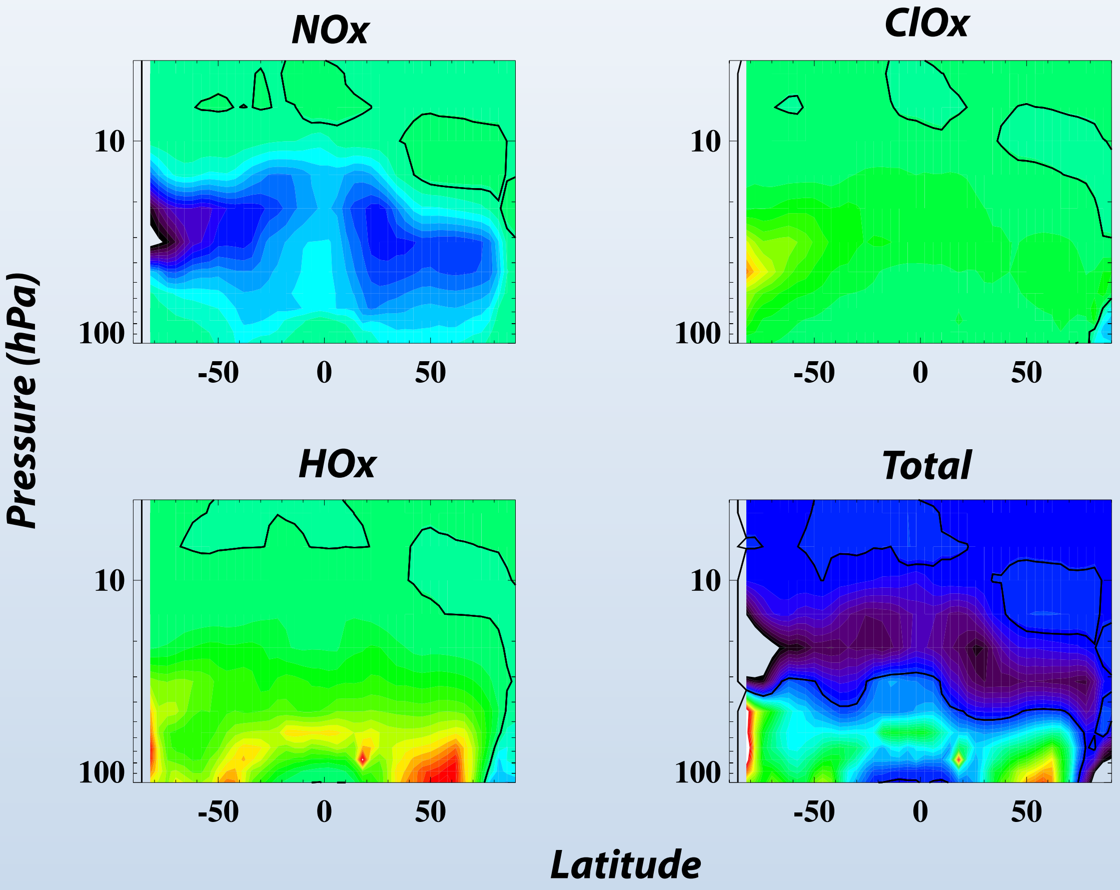
  $NO_2 + NO_3 + M \rightarrow N_2O_5 + M$
- N_2O_5 reacts on the surface of sulfate aerosols

  $N_2O_5 + H_2O \rightarrow 2\ HNO_3$
- NO_x decreases: ozone loss decreases
- Chlorine nitrate production decreases: ClO_x increases: ozone loss increases
- HO_2 + NO decreases: HO_x loss increases: ozone loss increases

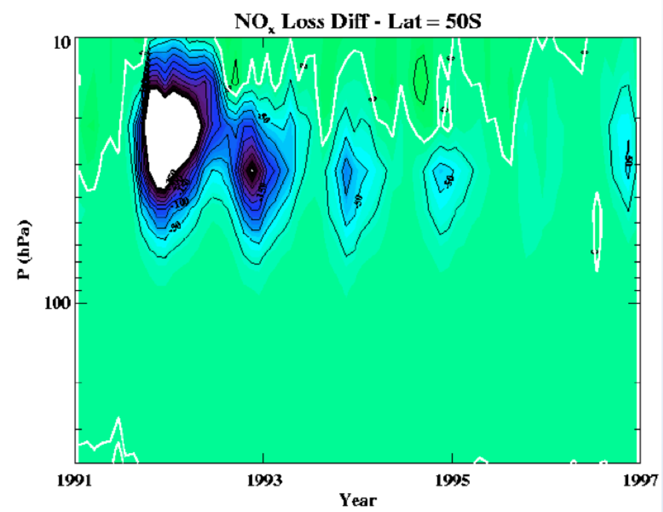
Competing effects

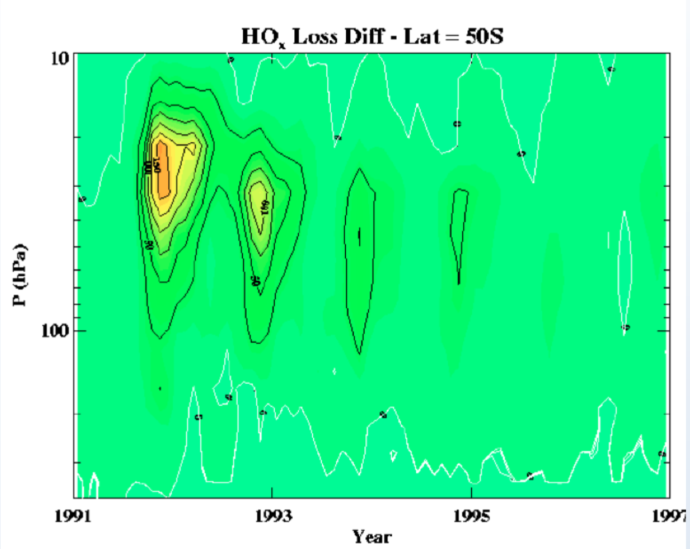
Impact of Pinatubo on Stratospheric Ozone Chemistry (at least according to a model calculation)

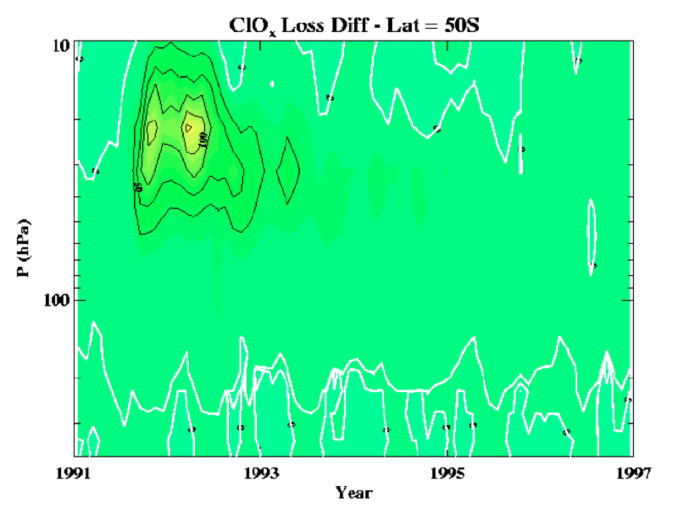
Modeled Change in Loss Terms due to Pinatubo Aerosols, March 1992

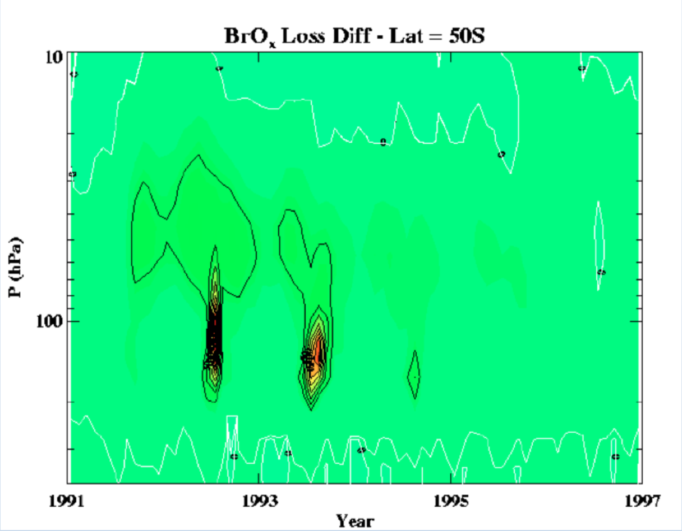


Ozone Loss Rates due to Pinatubo

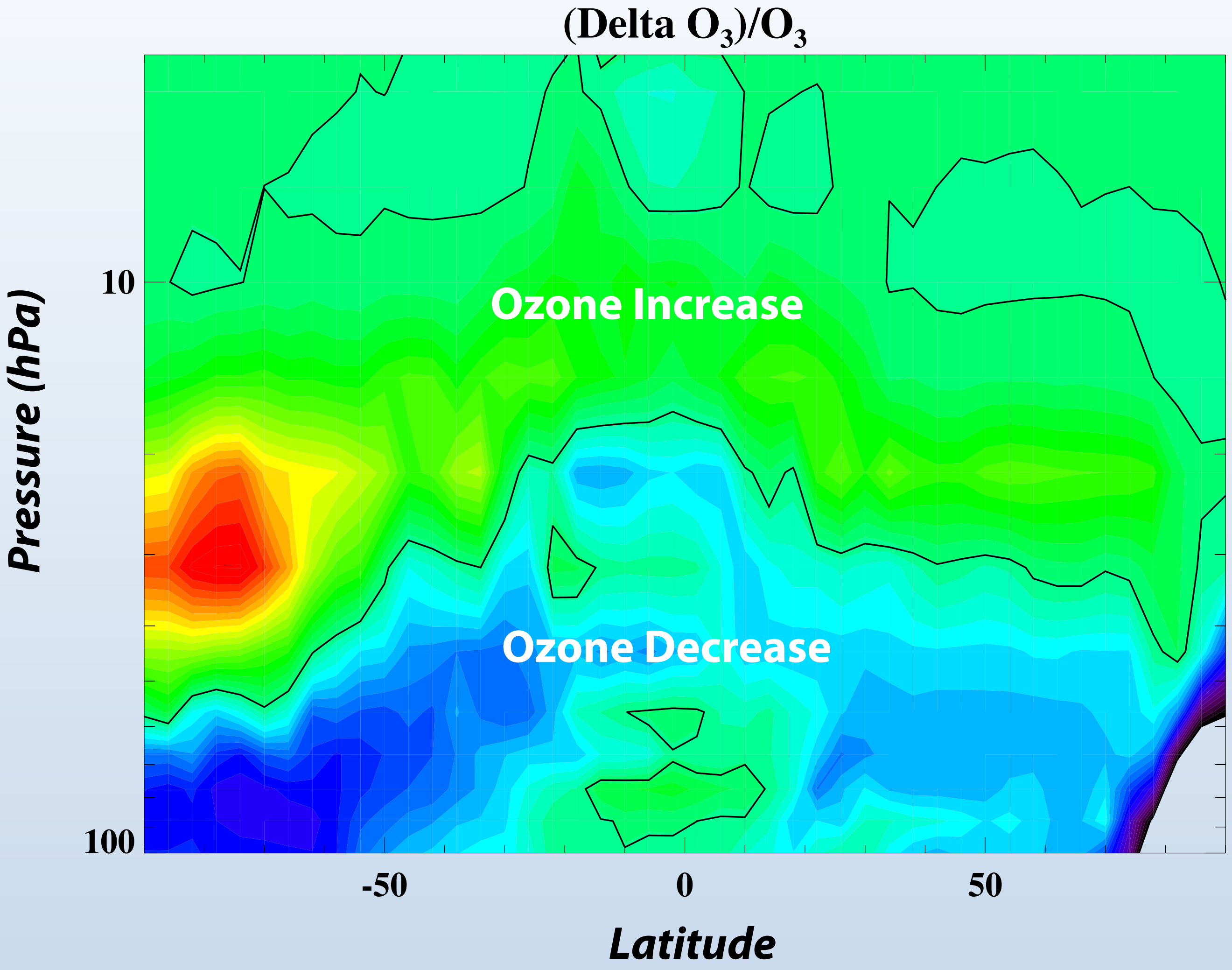




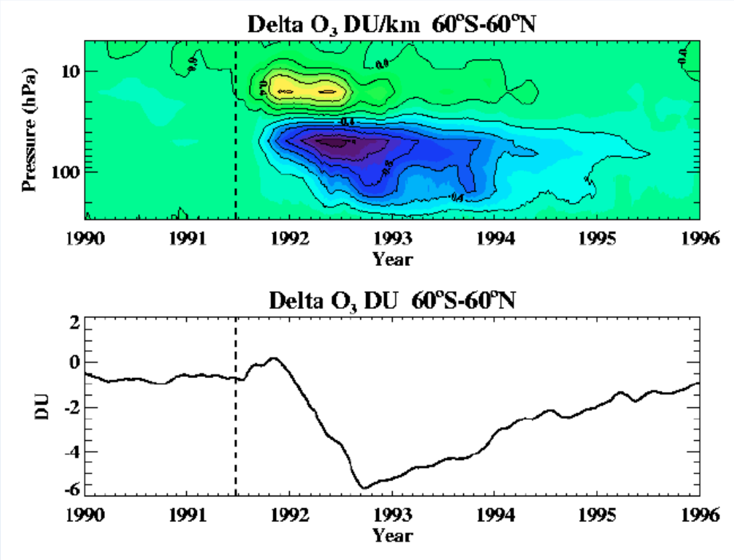


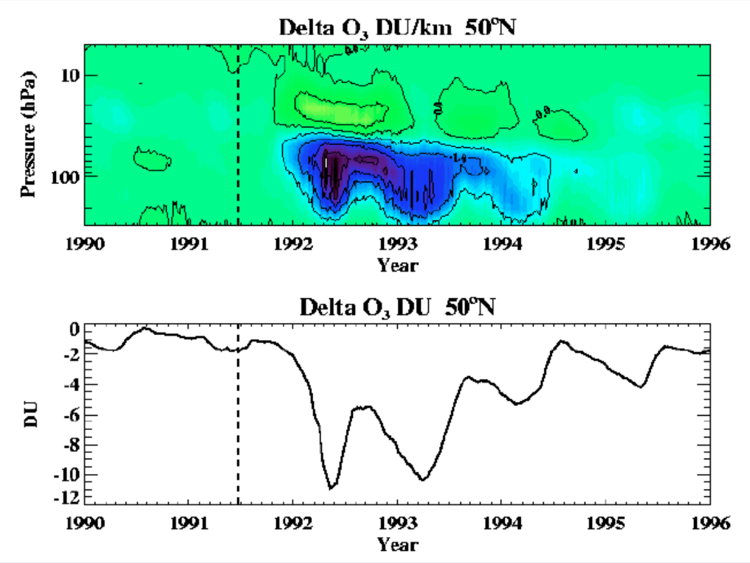


Calculated Ozone Change due to Pinatubo March, 1992 (9 months after eruption)

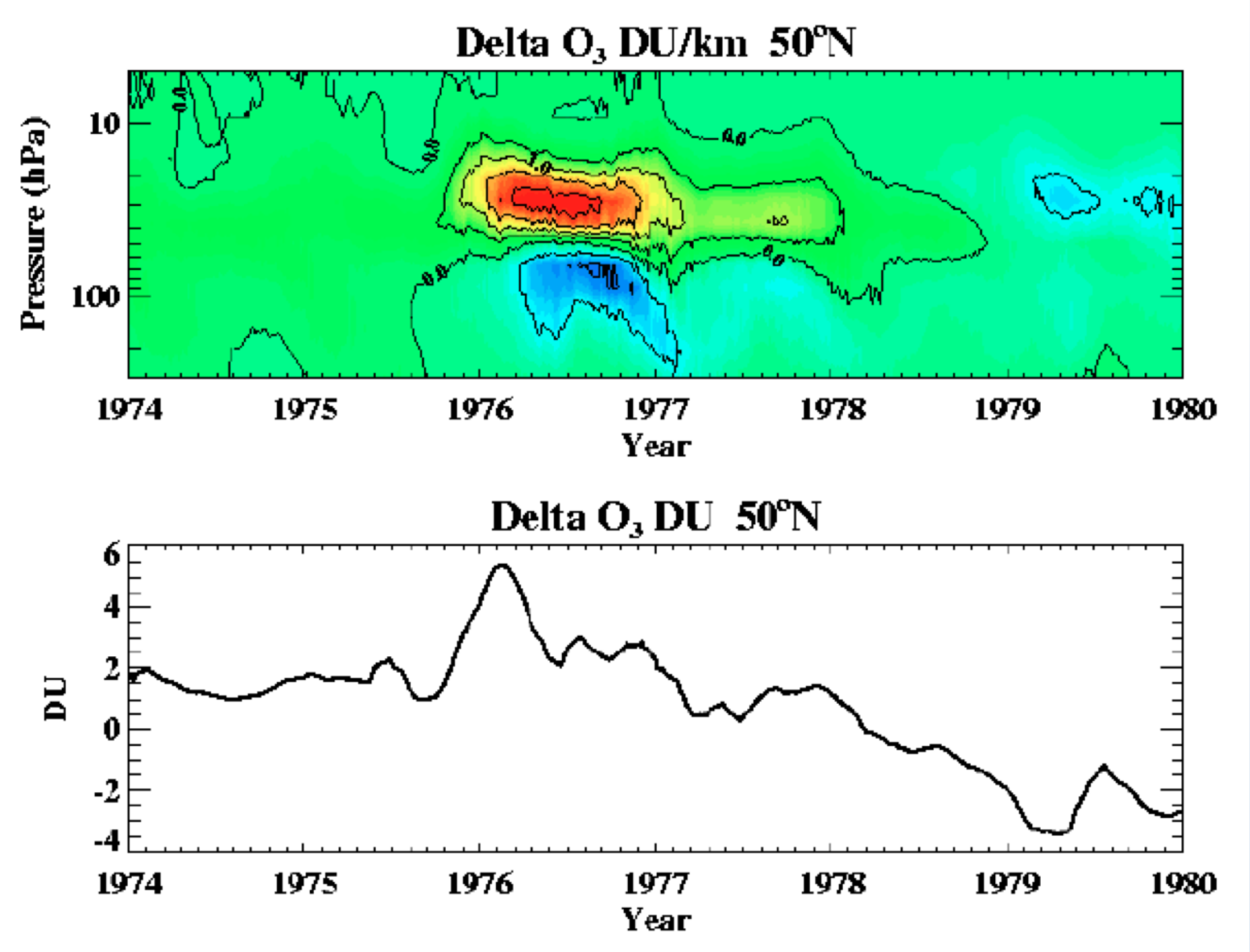


Time dependence of ozone at 50N after Pinatubo eruption

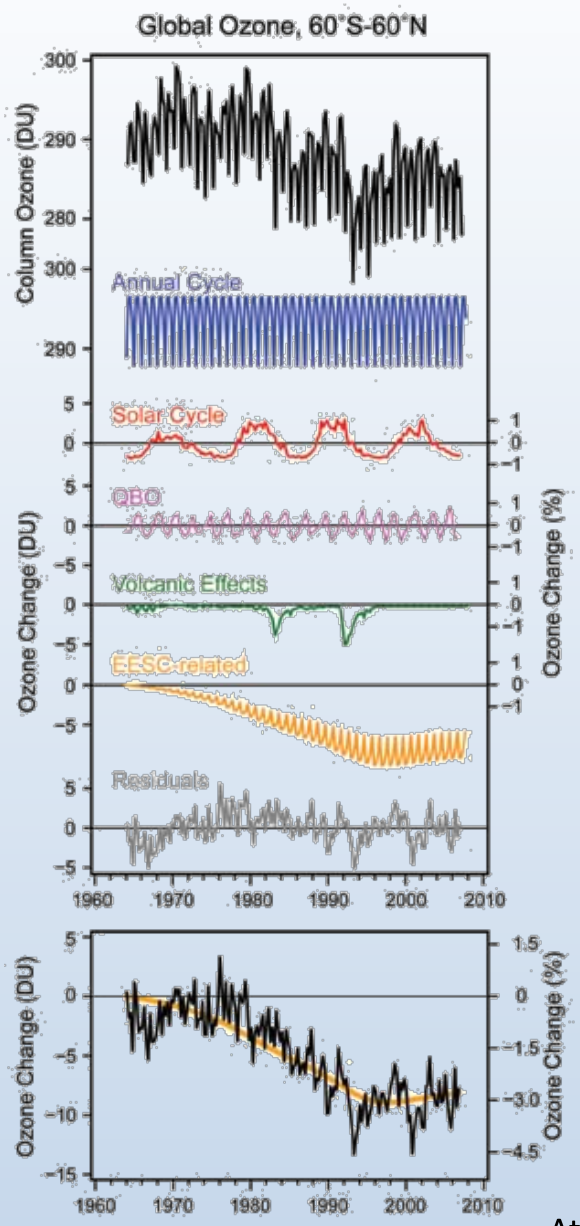




Model calculation of Pinatubo effect on ozone at low chlorine amount



What else affects the ozone record?



- Seasonal cycle
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Historical Volcanic Eruptions

Recent

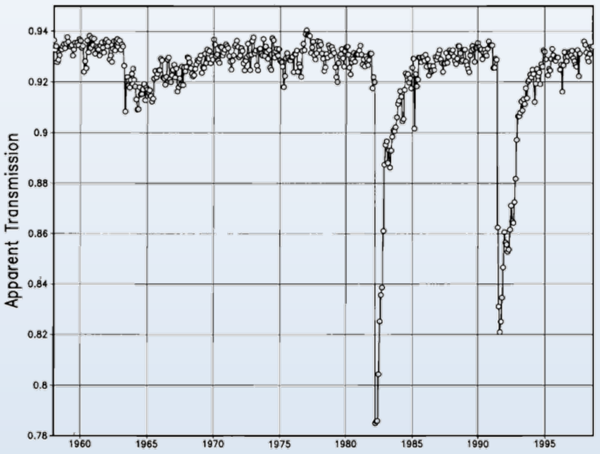


Figure 1. Broadband spectrally integrated atmospheric transmission factor, measured with the *pyrheliometer* shown in Plate 2. *Dutton et al.* [1985] and *Dutton* [1992] describe the details of the calculations, which eliminate instrument calibration and solar constant variation dependence, and show mainly the effects of aerosols. Effects of the 1963 Agung, 1982 El Chichón, and 1991 Pinatubo eruptions can clearly be seen. Years on abscissa indicate January of that year. Data courtesy of E. Dutton.

Atmospheric transmission measured at Mauna Loa

Last 400 years

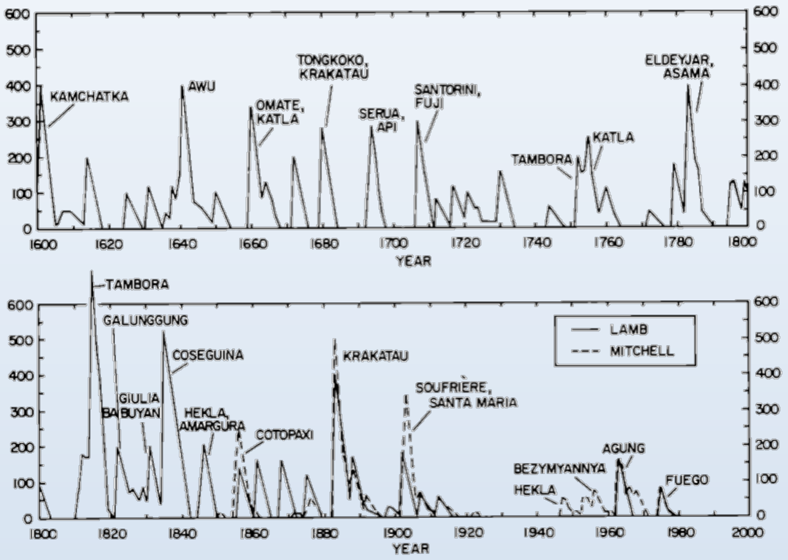


Fig.1. Northern Hemisphere average volcanic dust veil index from Lamb (1970) and Mitchell (1970).

Much larger eruptions have occurred in the past

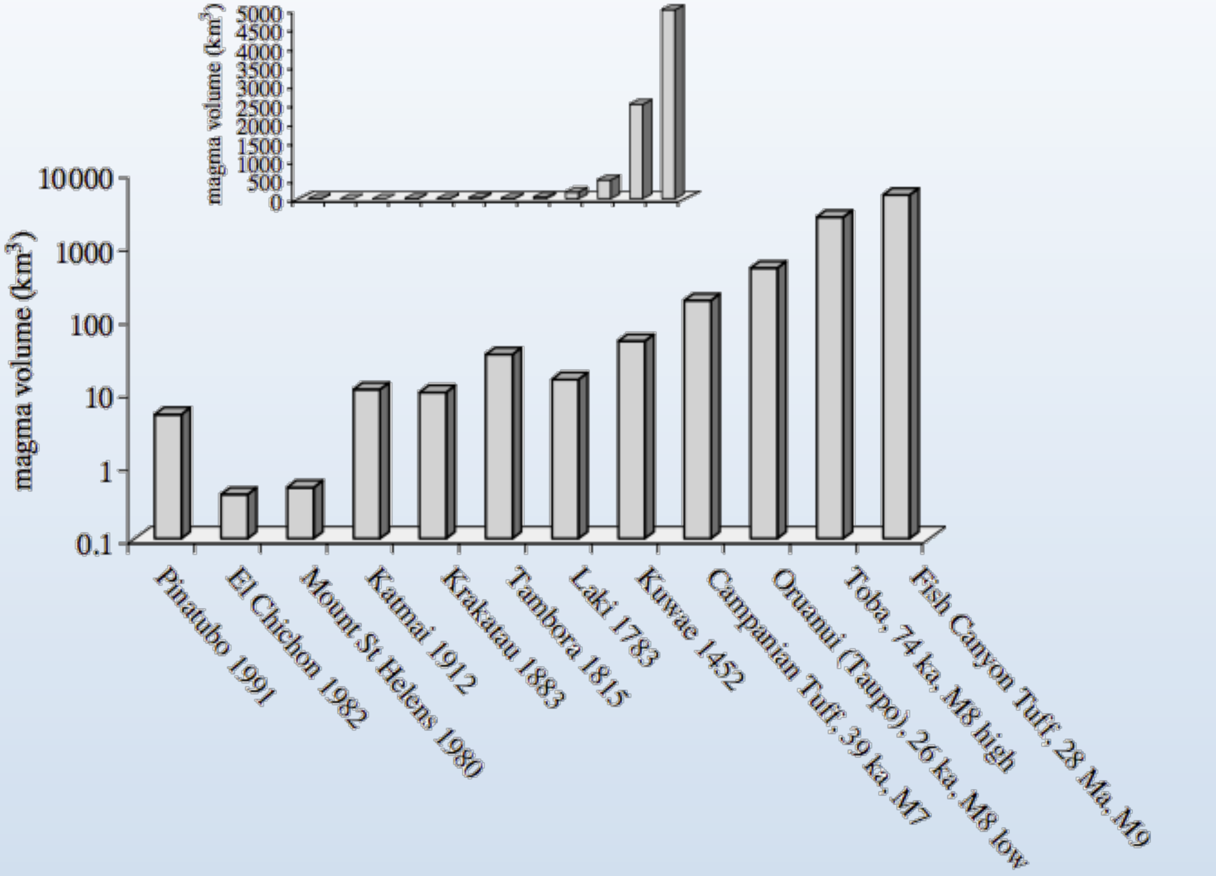


Figure 2. Volumes of magma (plotted on log scale) released by historic eruptions compared with very large eruptions; inset: same data plotted on linear scale. Historic eruptions hardly register against sizes of past very large eruptions of magnitude 7 (exemplified by Campanian Tuff) and magnitude 8 and greater (three examples at right). Ka is thousands of years (ago); Ma millions of years (ago).

Traps are sites of great lava flows that are termed Large Igneous Provinces (LIPS)

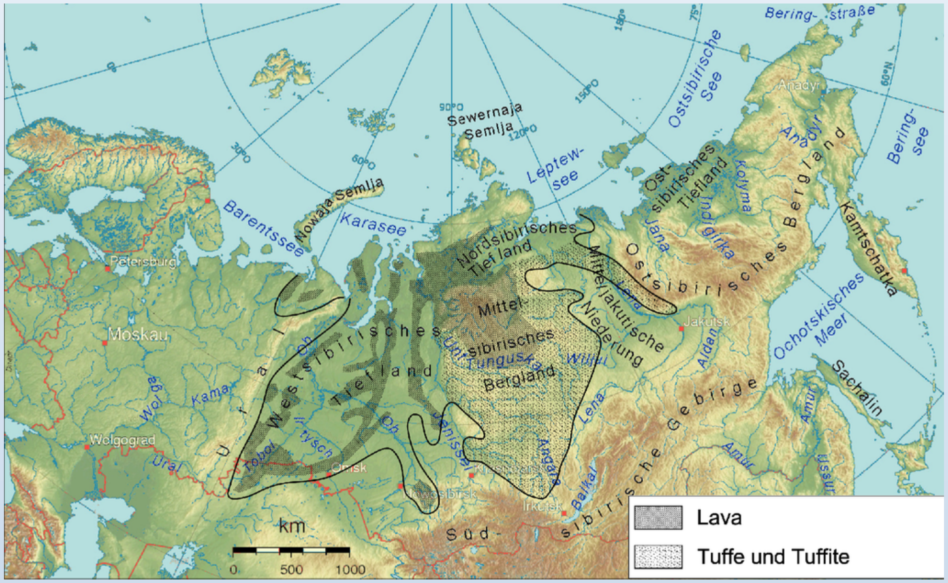
Deccan Traps

Geologic Map of the Central San Juan Caldera Cluster, Southwestern Colorado

By Peter W. Lipman

Pamphlet to accompany
Geologic Investigations Series I–2799

Wheeler Geologic Monument (Half Moon Pass quadrangle) provides exceptional exposures of three outflow tuff sheets erupted from the San Luis caldera complex. Lowest sheet is Rat Creek Tuff, which is nonwelded throughout but grades upward from light-tan rhyolite (~74% SiO_2) into pale brown dacite (~66% SiO_2) that contains sparse dark-brown andesitic scoria. Distinctive hornblende-rich middle Cebolla Creek Tuff contains basal surge beds, overlain by vitrophyre of uniform mafic dacite that becomes less welded upward. Uppermost Nelson Mountain Tuff consists of nonwelded to weakly welded, crystal-poor rhyolite, which grades upward to a densely welded caprock of crystal-rich dacite (~68% SiO_2). White arrows show contacts between outflow units.



Siberian Traps

Some provocative suggestions

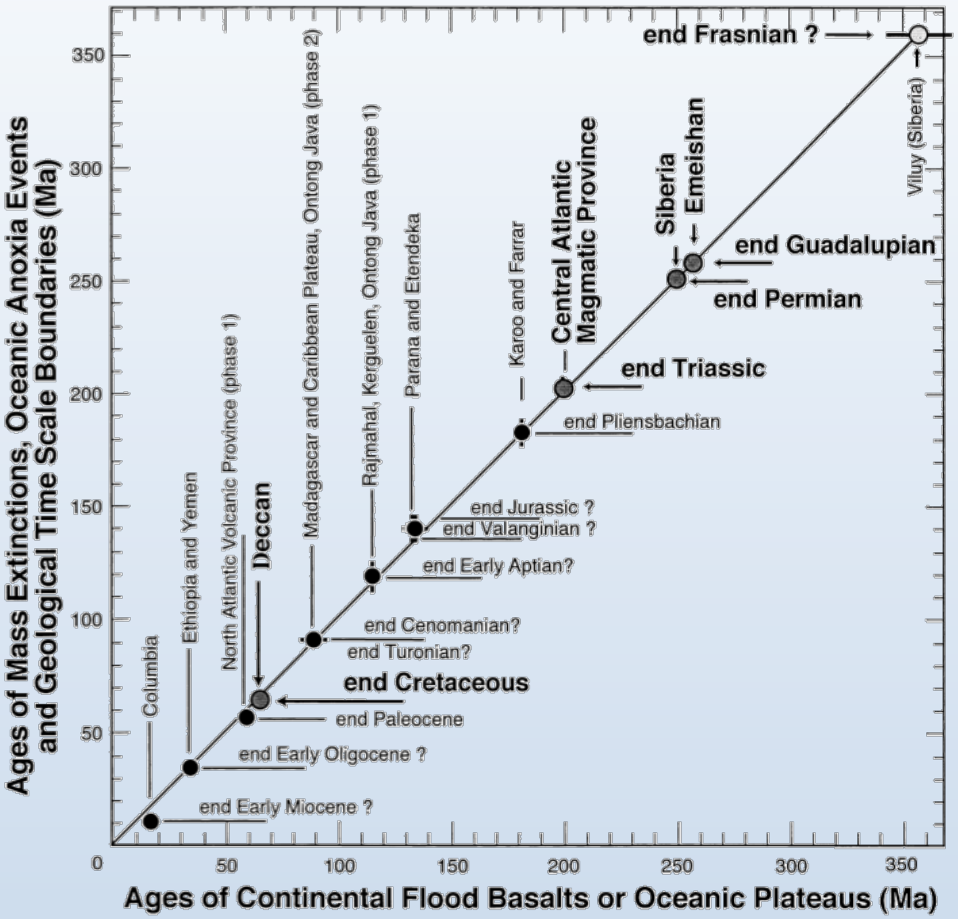
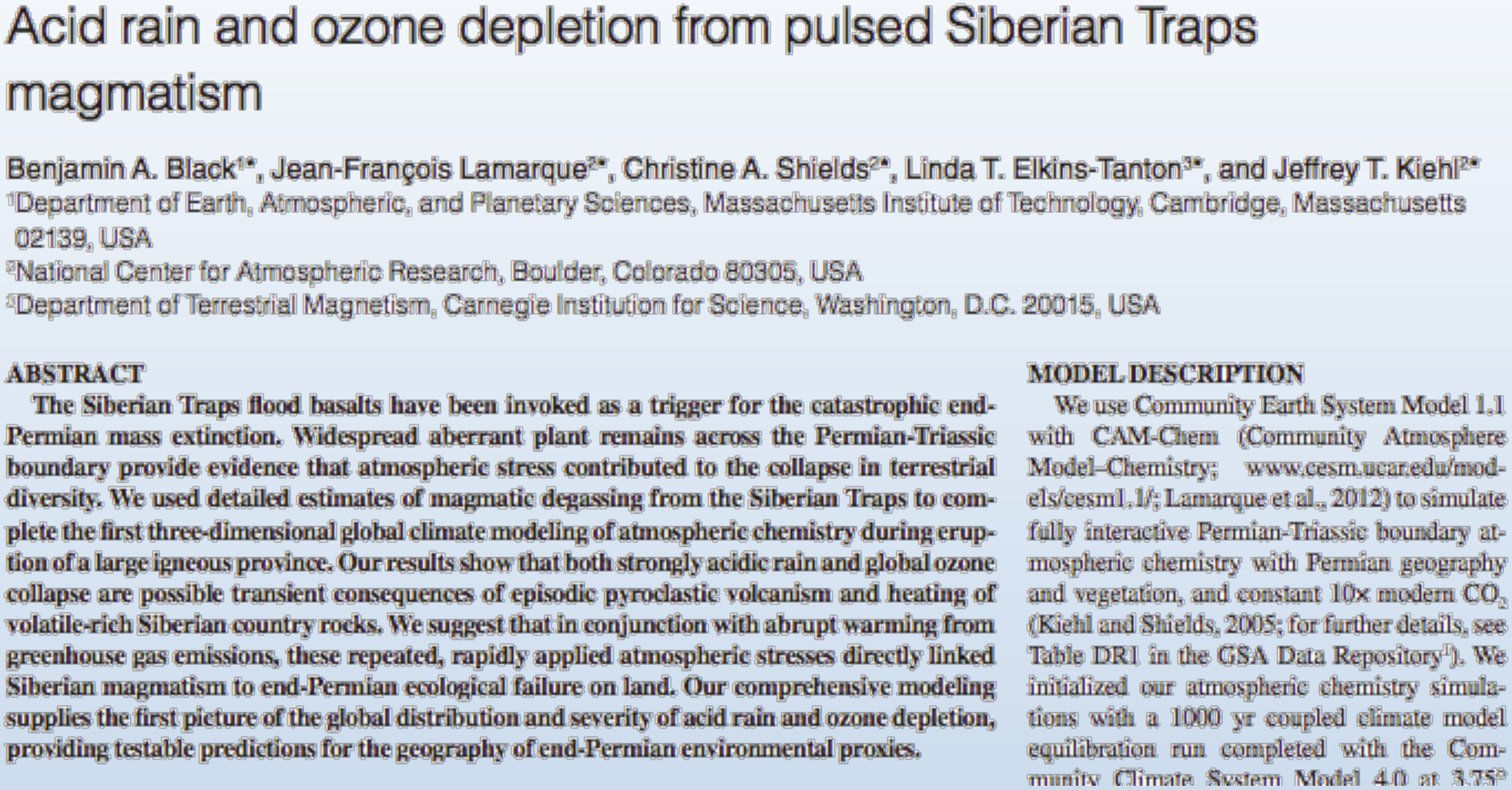


Fig. 1. Correlation between the ages of LIPs (CFBs and OPs) on one hand, and those of mass extinctions and oceanic anoxia events on the other hand (all in Ma). This figure is updated from [31] and some later versions; see also [143] for what may be the first such plot. Values are from Table 1 and are discussed in the text. Uncertainties are visible only when they are larger than the diameters of the dots corresponding to individual events. The four largest recent mass extinctions and corresponding traps are in dark grey, the previous one in light grey is being radiometrically dated.

Are Large Igneous Provinces (LIPS) responsible for mass extinctions?

Some provocative suggestions



Acid rain and ozone depletion from pulsed Siberian Traps magmatism

Benjamin A. Black[1*], Jean-François Lamarque[2*], Christine A. Shields[2*], Linda T. Elkins-Tanton[3*], and Jeffrey T. Kiehl[2*]
[1]Department of Earth, Atmospheric, and Planetary Sciences, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, USA
[2]National Center for Atmospheric Research, Boulder, Colorado 80305, USA
[3]Department of Terrestrial Magnetism, Carnegie Institution for Science, Washington, D.C. 20015, USA

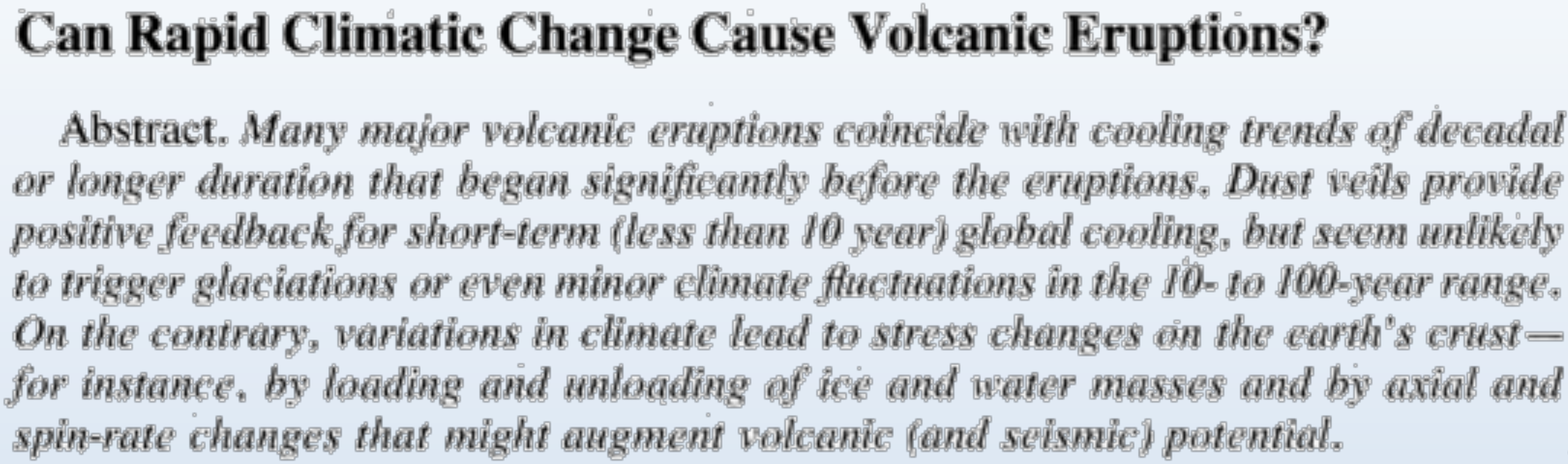
ABSTRACT

The Siberian Traps flood basalts have been invoked as a trigger for the catastrophic end-Permian mass extinction. Widespread aberrant plant remains across the Permian-Triassic boundary provide evidence that atmospheric stress contributed to the collapse in terrestrial diversity. We used detailed estimates of magmatic degassing from the Siberian Traps to complete the first three-dimensional global climate modeling of atmospheric chemistry during eruption of a large igneous province. Our results show that both strongly acidic rain and global ozone collapse are possible transient consequences of episodic pyroclastic volcanism and heating of volatile-rich Siberian country rocks. We suggest that in conjunction with abrupt warming from greenhouse gas emissions, these repeated, rapidly applied atmospheric stresses directly linked Siberian magmatism to end-Permian ecological failure on land. Our comprehensive modeling supplies the first picture of the global distribution and severity of acid rain and ozone depletion, providing testable predictions for the geography of end-Permian environmental proxies.

MODEL DESCRIPTION

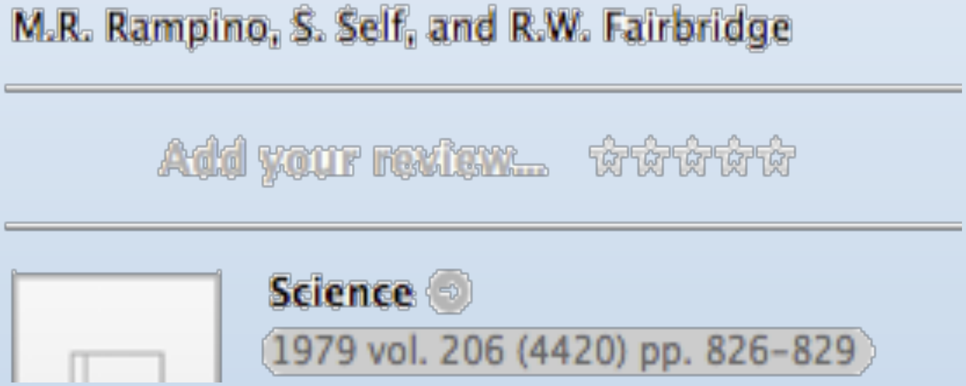
We use Community Earth System Model 1.1 with CAM-Chem (Community Atmosphere Model–Chemistry; www.cesm.ucar.edu/models/cesm1.1/; Lamarque et al., 2012) to simulate fully interactive Permian-Triassic boundary atmospheric chemistry with Permian geography and vegetation, and constant 10× modern CO_2 (Kiehl and Shields, 2005; for further details, see Table DR1 in the GSA Data Repository[1]). We initialized our atmospheric chemistry simulations with a 1000 yr coupled climate model equilibration run completed with the Community Climate System Model 4.0 at 3.75°

Some provocative suggestions



Can Rapid Climatic Change Cause Volcanic Eruptions?

Abstract. *Many major volcanic eruptions coincide with cooling trends of decadal or longer duration that began significantly before the eruptions. Dust veils provide positive feedback for short-term (less than 10 year) global cooling, but seem unlikely to trigger glaciations or even minor climate fluctuations in the 10- to 100-year range. On the contrary, variations in climate lead to stress changes on the earth's crust—for instance, by loading and unloading of ice and water masses and by axial and spin-rate changes that might augment volcanic (and seismic) potential.*



M.R. Rampino, S. Self, and R.W. Fairbridge

Science

1979 vol. 206 (4420) pp. 826–829