Supplementary Table DR1: Initial Conditions

Species	Flux	Fixed Condition	Reference
CH_4	1500 Tg yr^{-1}		(Beerling et al., 2009)
CO	195 Tg yr^{-1}		(Seinfeld and Pandis, 1997)
CH_3Cl	3.5 Tg yr^{-1}		(Seinfeld and Pandis, 1997)
CH_3Br	0.15 Tg yr^{-1}		(Seinfeld and Pandis, 1997)
DMS	30 Tg yr^{-1}		(Elliott, 2009)
NO_x	15 Tg yr^{-1}		(Archibald et al., 2013)
CO_2		3550 ppm	(Kiehl and Shields, 2005)
N_2O		275 ppb	(Kiehl and Shields, 2005)
O_2		21 %	present-day O_2
S_0		1338 W m^{-2}	(Kiehl and Shields, 2005)

The species in Table DR1 are categorized as either fluxes or fixed conditions. Species listed as fluxes are released at the surface of the simulated Permian-Triassic world, with distributions as appropriate for each species. For example, DMS emissions (which derive primarily from phytoplankton) are distributed evenly over all oceanic grid cells. While Permian-Triassic CH_4 fluxes have been estimated from the rates of coal basin deposition (Beerling et al., 2009), other fluxes are drawn from estimated pre-industrial values (Archibald et al., 2013; Elliott, 2009; Seinfeld and Pandis, 1997). The concentrations of CO_2, N_2O, and O_2 are held at fixed mixing ratios as specified in Table DR1, and S_0 denotes the solar constant.

Oxidation by the hydroxyl radical is the primary sink for CH_4; this oxidation process ultimately converts between 51-100% of CH_4 into CO_2 in the Earth's atmosphere (Boucher et al., 2009; Wuebbles and Hayhoe, 2002). The contribution of CH_4 emissions to atmospheric CO_2 concentrations could be significant over the centennial to millennial timescales that may characterize metamorphism related to a large sill intrusion. Over the much shorter timescales of our simulations, however, we consider fixed CO_2 to be an appropriate assumption. We use present-day O_2 values because previous WACCM simulations suggested that Permian O_2 of 17% (Berner, 2002) does not strongly alter ozone chemistry (Lamarque et al., 2006). 2-D modeling of Siberian Traps degassing by Beerling et al. (2007) used lower atmospheric O_2 values of 15%, which may partly account for the increased rates of ozone destruction in that model (Beerling et al., 2007). Lower atmospheric O_2 values have been shown to intensify ozone loss at mid- and high-latitudes (Harfoot et al., 2007), implying that our estimates of ozone depletion are conservative. We also observe less intense stratospheric cooling from a CO_2 greenhouse relative to Beerling et al. (2007), which reduces the occurrence of polar stratospheric clouds. Because polar stratospheric clouds provide heterogeneous reaction sites for the catalytic destruction of ozone (Solomon, 1999), this reduced occurrence may also contribute to the more-resilient ozone layer we observe in our model.

Supplementary Table DR2: Simulated Emissions

Case	Run Name	Release Rate	Duration	Notes	References
0: Control	C1	Background Permian forcing	20 years chemical equilibration	See Table DR1	See Table DR1
	C2	Background Permian forcing, 10x CH_3Cl background	10 years chemical re-equilibration after y_pt_00_v3	See Table DR1	See Table DR1
	C3	Background Permian forcing, 20x CH_3Cl	10 years chemical re-equilibration after y_pt_00_v3	See Table DR1	See Table DR1
1: Aureole	A1_v1	Aureole degassing: 1.65 Gt/yr CH_3Cl 0.55 Gt/yr CH_4	10, 6, 2 years	Release at 0.15 km. 0.50 $CH_4 \rightarrow CH_3Cl$ conversion ratio.	(Aarnes et al., 2011; Svensen et al., 2009)
	A1_v2	Recovery after 10 years (background emissions only)			
	A1_v3	Recovery after 6 years (background emissions only)			
	A1_v4	Recovery after 2 years (background emissions only)			
	A2_v1	Aureole degassing: 0.87 Gt/yr CH_3Cl 0.83 Gt/yr CH_4	10, 6, 2 years	Release at 0.15 km. 0.25 $CH_4 \rightarrow CH_3Cl$ conversion ratio.	(Aarnes et al., 2011; Svensen et al., 2009)
	A2_v2	Recovery after 10 years (background emissions only)			
	A2_v3	Recovery after 6 years (background emissions only)			
	A2_v4	Recovery after 2 years (background emissions only)			
	A3_v1	Stratosphere release: 1.65 Gt/yr CH_3Cl 0.55 Gt/yr CH_4	10 years	Release at 14 km. For comparison with A1_v1.	
	A3_v2	Recovery after 10 years (background emissions only)			

2: Explosive	E1_v1	Pyroclastic eruption (240 km^3/year): 1.46 Gt SO_2/yr 48 Tg HCl/yr 160 Tg HF/yr 0.6 Tg BrO/yr 0.0014 Tg CH_3Cl/yr 1.9e-5 Tg CH_3Br/yr	5,1 years	Release at 14 km above Siberian Traps. Assumes that 75% of degassed HCl is removed from plume (Textor et al., 2003). HF is likely removed also.	(Black et al., 2012; Schwandner et al., 2004)
	E1_v2	Recovery after 5 years (background emissions only)			
	E1_v3	Recovery after 1 year (background emissions only)			
	E2_v1	Pyroclastic eruption, same emissions as E1_v1, with 10x background emissions of CH_3Cl	5 years	Release at 14 km. Background stratospheric Cl load in Beerling is higher (0.48 Tg)(Beerling et al., 2007).	(Beerling et al., 2007; Black et al., 2012; Schwandner et al., 2004)
	E2_v2	Recovery after 5 years (10x background emissions only)			
	E3_v1	Pyroclastic eruption, 3x HCl, 10x background CH_3Cl: 1.46 Gt SO_2/yr 144 Tg HCl/yr 160 Tg HF/yr 0.6 Tg BrO/yr 0.0014 Tg CH_3Cl/yr 1.9e-5 Tg CH_3Br/yr	5 years	Release at 14 km. 3x Cl release, in case 75% of Cl reaches stratosphere (Rose et al., 2006) rather than 25% (Textor et al., 2003).	(Black et al., 2012; Schwandner et al., 2004)
	E3_v2	Recovery after 5 years (10x background emissions only)			
	E4_v1	Pyroclastic eruption, 3x HCl, 20x background CH_3Cl	5 years	Release at 14 km. Background stratospheric Cl load in Beerling (2007) is higher (0.48 Tg).	(Black et al., 2012; Schwandner et al., 2004)
	E4_v2	Recovery after 5 years (20x background emissions only)			
	E5_v1	Large pyroclastic eruption (2400 km^3/year): 14.6 Gt SO_2/yr 480 Tg HCl/yr 1.6 Gt HF/yr 6 Tg BrO/yr 0.014 Tg CH_3Cl/yr 1.9e-4 Tg CH_3Br/yr	2 years	Release at 14 km.	(Black et al., 2012; Schwandner et al., 2004)

3: Pipes	P1_v1	One small pipe per year: 0.31 Gt CH_4 0.11 Gt CH_3Cl 1.9 Tg CH_3Br	5, 1 years	Release at 0.15 km. (Although delivery to the stratosphere is possible, it makes a marginal difference) Fluxes are not well-constrained.	(Svensen et al., 2009)
	P1_v2	Recovery after 5 years (background emissions only)			
	P1_v3	Recovery after 1 year (background emissions only)			
	P2_v1	One larger pipe: 4.29 Gt CH_3Cl 1.43 Gt CH_4	1 year	Release at 0.15 km. Assumes gases build up during peak production period (~260 years), before ~1% are released via a pipe.	
	P2_v2	Recovery after 1 year (background emissions only)	9 years		
	P2_v3	Second perturbation: 4.29 Gt CH_3Cl 1.43 Gt CH_4	1 year	Release at 0.15 km. A second pipe eruption, 10 years later.	
	P2_v4	Recovery after second, 1 year perturbation (background emissions only)			

Table DR2 summarizes the 27 scenarios we simulated with our model. Most emissions simulations are accompanied by a set of recovery simulations. These recovery simulations are initialized with atmospheric chemistry from a period of volcanic and/or metamorphic gas release, but the recovery scenarios themselves contain only background emissions. The fluxes as specified in the Release Rate column are provided on an annualized basis. The Duration column refers to the number of years each simulation was run. For some simulations, the Duration column contains multiple year annotations, indicating that recovery scenarios were initialized after several different emissions durations. For example, in run A1_v1 we tested the effects of metamorphic emissions lasting 10, 6, and 2 years. The recovery scenarios (A1_v2, A1_v3, and A1_v4 respectively) continued with only background emissions after 10, 6, and 2 years of the annualized emissions given in the Release Rate column. The Notes column gives the rationale for each simulation, where not explained elsewhere in the text.

The volcanic emissions we used as inputs to our model are taken from Black et al. (2012). The metamorphic emissions were drawn from Svensen et al. (2009) and Aarnes et al. (2011). As mentioned previously, Aarnes et al. (2011) employ thermochemical models to calculate gas production rates as a 5000 km[3] sill intrudes hydrocarbon- and evaporite-bearing layers. They predict peak annualized production rates (which last for the first ~260 years after the emplacement of the sill) of 1.65 Gt/yr CH_3Cl and 0.55 Gt/yr CH_4, assuming a CH_4 to CH_3Cl

conversion factor of 0.5 (run A1). A conversion factor of 0.25 translates to peak production rates of 0.87 Gt/yr CH_3Cl and 0.83 Gt/yr CH_4 (run A2). Svensen et al. (2009) estimate that a single small pipe could release 0.31 Gt CH_4, 0.11 Gt CH_3Cl, and 1.9 Tg CH_3Br (simulation P1_v1). Metamorphic gases could build up prior to release through a pipe. If a nominal 1% of gases produced during the peak production period are released through a large pipe, the release would amount to 4.29 Gt CH_3Cl and 1.43 Gt CH_4 (runs P2_v1 and P2_v3).

In general, we sought to explore the sensitivity of our results to uncertainties in the emissions estimates we used as inputs to our model. Eruption size exerts first-order control over both acid rain and ozone depletion. Acid rain during a one-year, 240 km^3 eruption is shown in Figure 1a. If this eruption continued for a second year, the most deeply acid rain would spread to cover more of the northern hemisphere. During a one-year, 2400 km^3 eruption (E5_v1), acid rain would intensify, with pH levels around 2 dominating in the northern hemisphere, and rain in the southern hemisphere would also acidify. An eruption of this size could also trigger 30-35% global ozone depletion. Runs with elevated background CH_3Cl emissions (E2, E3, and E4) were intended to test the effects of higher natural CH_3Cl fluxes from biomass burning, fungal decomposition of woody material, and tropical vegetation (Seinfeld and Pandis, 1997). These runs showed that higher background CH_3Cl reduces steady-state ozone levels (see Figure 3 in the main text). Runs that also introduce higher HCl emissions from an explosive eruption (E3, E4) test the effects of less efficient removal of HCl from the volcanic plume; airborne measurements suggest up to 75% of HCl degassed from the Hekla eruption reached the stratosphere (Rose et al., 2006). A combination of 10x higher background CH_3Cl emissions and 75% HCl delivery produces 20-40% ozone depletion. This level of ozone depletion is more comparable to that observed in Beerling et al. (2007); the higher background Cl levels in the Beerling et al. (2007) simulations may thus explain the higher rates of ozone loss from pyroclastic eruptions. Comparison runs show that the altitude of emissions strongly controls the acid rain and ozone depletion that result from pyroclastic eruptions, but exerts very little influence on the ozone depletion that results from metamorphic emissions. Finally, the simulations of pipe eruptions confront the uncertainties in the fraction of metamorphic gases that reach the atmosphere. Pipe structures provide an intriguing mechanism for gas release to the lower troposphere or even the stratosphere (Svensen et al., 2009). More detailed field, experimental, and theoretical evidence is needed to constrain the gas fluxes liberated by the pipes. However, if pipes release even a small fraction of the gases generated during sill intrusion (run P2), the ozone response could be powerful.

Supplemental References

Aarnes, I., Fristad, K., Planke, S., and Svensen, H., 2011, The Impact of Host-Rock Composition on Devolatilization of Sedimentary Rocks During Contact Metamorphism around Mafic Sheet Intrusions: Geochemistry Geophysics Geosystems, v. 12, p. Q10019.

Archibald, A., Lamarque, J.-F., Wild, O., Cionni, I., MacKenzie, I., Plummer, D., Skeie, R., and Strode, S., 2013, Pre-Industrial to End 21st Century Projections of Tropospheric Ozone from the Atmospheric Chemistry and Climate Model Intercomparison Project (Accmip): Atmospheric Chemistry and Physics, v. 13, p. 2063-2090.

Beerling, D., Berner, R.A., Mackenzie, F.T., Harfoot, M.B., and Pyle, J.A., 2009, Methane and the Ch4 Related Greenhouse Effect over the Past 400 Million Years: American Journal of Science, v. 309, p. 97-113.

Beerling, D.J., Harfoot, M., Lomax, B., and Pyle, J.A., 2007, The Stability of the Stratospheric Ozone Layer During the End-Permian Eruption of the Siberian Traps: Philosophical Transactions of the Royal Society a-Mathematical Physical and Engineering Sciences, v. 365, p. 1843-1866.

Berner, R.A., 2002, Examination of Hypotheses for the Permo–Triassic Boundary Extinction by Carbon Cycle Modeling: Proceedings of the National Academy of Sciences, v. 99, p. 4172-4177.

Black, B.A., Elkins-Tanton, L.T., Rowe, M.C., and Peate, I.U., 2012, Magnitude and Consequences of Volatile Release from the Siberian Traps: Earth and Planetary Science Letters, v. 317–318, p. 363-373.

Boucher, O., Friedlingstein, P., Collins, B., and Shine, K.P., 2009, The Indirect Global Warming Potential and Global Temperature Change Potential Due to Methane Oxidation: Environmental Research Letters, v. 4, p. 044007.

Elliott, S., 2009, Dependence of Dms Global Sea-Air Flux Distribution on Transfer Velocity and Concentration Field Type: Journal of Geophysical Research: Biogeosciences, v. 114, p. G02001.

Harfoot, M.B., Beerling, D.J., Lomax, B.H., and Pyle, J.A., 2007, A Two-Dimensional Atmospheric Chemistry Modeling Investigation of Earth's Phanerozoic O3 and near-Surface Ultraviolet Radiation History: Journal of Geophysical Research: Atmospheres (1984–2012), v. 112.

Kiehl, J.T., and Shields, C.A., 2005, Climate Simulation of the Latest Permian: Implications for Mass Extinction: Geology, v. 33, p. 757-760.

Lamarque, J.F., Kiehl, J., Shields, C., Boville, B., and Kinnison, D., 2006, Modeling the Response to Changes in Tropospheric Methane Concentration: Application to the Permian-Triassic Boundary: Paleoceanography, v. 21.

Rose, W.I., Millard, G.A., Mather, T.A., Hunton, D.E., Anderson, B., Oppenheimer, C., Thornton, B.F., Gerlach, T.M., Viggiano, A.A., Kondo, Y., Miller, T.M., and Ballenthin, J.O., 2006, Atmospheric Chemistry of a 33-34 Hour Old Volcanic Cloud from Hekla Volcano (Iceland): Insights from Direct Sampling and the Application of Chemical Box Modeling: Journal of Geophysical Research-Atmospheres, v. 111.

Schwandner, F.M., Seward, T.M., Gize, A.P., Hall, P.A., and Dietrich, V.J., 2004, Diffuse Emission of Organic Trace Gases from the Flank and Crater of a Quiescent Active Volcano (Vulcano, Aeolian Islands, Italy): J. Geophys. Res., v. 109, p. D04301.

Seinfeld, J.H., and Pandis, S.N., 1997, Atmospheric Chemistry and Physics: From Air Pollution to Climate Change, John Wiley & Sons Inc.

Solomon, S., 1999, Stratospheric Ozone Depletion: A Review of Concepts and History: Reviews of Geophysics, v. 37, p. 275-316.

Svensen, H., Planke, S., Polozov, A.G., Schmidbauer, N., Corfu, F., Podladchikov, Y.Y., and
    Jamtveit, B., 2009, Siberian Gas Venting and the End-Permian Environmental Crisis:
    Earth and Planetary Science Letters, v. 277, p. 490-500.

Textor, C., Graf, H.F., Herzog, M., and Oberhuber, J.M., 2003, Injection of Gases into the
    Stratosphere by Explosive Volcanic Eruptions: Journal of Geophysical Research-
    Atmospheres, v. 108.

Wuebbles, D.J., and Hayhoe, K., 2002, Atmospheric Methane and Global Change: Earth-Science
    Reviews, v. 57, p. 177-210.