Acid rain and ozone depletion from pulsed Siberian Traps magmatism

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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.

INTRODUCTION
Gas release from Siberian Traps magmatism and thermal metamorphism of hydrocarbon- and evaporite-rich country rocks is a leading candidate to have driven end-Permian ecological upheaval (Payne and Clapham, 2012). We present new results from a comprehensive model of global chemistry and climate (Kiehl and Shields, 2005; Lamarque et al., 2012) that reveal the global patterns of environmental stress that could have emanated from pulses of Siberian Traps magmatism. The end-Permian mass extinction marked the death knell for a vast majority of global species, and set the stage for the rise of the dinosaurs. While the extinction was particularly severe in the oceans, where organisms that were most vulnerable to changes in CO2 died preferentially (Knoll et al., 2007) and overall only 10% of species survived into the Triassic (Erwin, 1994), terrestrial plants and animals also were affected. Numerous reptile, amphibian, and insect genera vanished (Erwin, 1994). An abrupt depositional shift in several locations from meandering to braided river systems has been interpreted as a result of accelerated die-off of terrestrial vegetation (Ward et al., 2000).

The precise onset of Siberian magmatism is geochronologically uncertain, though emplacement of the lava pile was almost complete by 251.4 ± 0.3 Ma (Kamo et al., 2003). The peak marine extinction interval is well constrained to have begun at 252.17 ± 0.06 Ma with a duration of <200 ± 100 k.y.; the global timing of the terrestrial extinction is more tentative, but appears to have been synchronous (Shen et al., 2011). Although the coincidence of the marine and terrestrial mass extinctions suggests that they were related, perhaps by a common trigger such as the Siberian Traps, the specific environmental conditions that led to declines in diversity may have included distinct elements on land and in the oceans. In this work we investigate two kill mechanisms that have been linked (Maruoka et al., 2003; Visscher et al., 2004) to the terrestrial mass extinction, i.e., acid rain and ozone depletion.

Here we use comprehensive estimates of sulfur release from the Siberian Traps (Black et al., 2012) to carry out the first three-dimensional (3-D) global climate modeling of atmospheric chemistry during flood volcanism. These results provide the first data-driven demonstration of the extent and intensity of acid rain in the latest Permian and early Triassic. We also present results from simulations of ozone chemistry. Previous 2-D modeling has shown that emissions of HCl and CH3Cl related to Siberian magmatism could have caused ozone depletion (Beerling et al., 2005). However, the wealth of paleontological data from different Permian-Triassic boundary sections provides a key resource for understanding the patterns of the mass extinction. In particular, palynological data record episodes of high atmospheric stress that produced spikes in abnormal pollen abundance (Visscher et al., 2004; Foster and Afonin, 2005). These worldwide patterns of magmatism-induced ecological stress and associated global severity of acid rain and ozone depletion are best understood through a comparison of 3-D chemistry-climate simulations with the paleontological record.

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 10x modern CO2 (Kiehl and Shields, 2005; for further details, see Table DR1 in the GSA Data Repository1). We initialized our atmospheric chemistry simulations with a 1000 yr coupled climate model equilibrium run completed with the Community Climate System Model 4.0 at 3.75° × 3.75° and interpolated to the model resolution. Detailed initial conditions are provided in Table DR1. Our model atmosphere includes 26 vertical levels and a horizontal resolution of 1.9° × 2.5°, and is coupled to prescribed sea-surface temperatures from the initial equilibrium run and to an active land model with end-Permian vegetation (from Kiehl and Shields, 2005). Gases are released into the lowermost troposphere (at 0.15 km) or the lower stratosphere (at 14 km).

The environmental effects of volcanism depend on the rates of volatile emission from degassing magmas (Black et al., 2012) and heated and metamorphosed country rocks (Svensen et al., 2009). In the end-Permian atmosphere, the lifetime of methylated halogens is ∼1 yr, the lifetime of methane is slightly more than 10 yr, and stratospheric sulfate has a residence time of ∼1 yr. U-Pb geochronology suggests that the total emplacement of the ∼4 × 106 km3 Siberian Traps occurred in <1 m.y. (Kamo et al., 2003), but paleomagnetic secular variation implies that some large lava suites were erupted in pulses lasting <10 k.y. (Pavlov et al., 2011). In addition to the long-term effects of CO2 release, these eruptions could have produced severe but geologically short-lived environmental deterioration. We focus on the transient effects of sulfur, halogen, organohalogen, and methane release over time scales of years to tens of years.

We simulated 27 perturbation and recovery scenarios (summarized in Table DR2). Each was

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1GSA Data Repository item 2014016, Table DR1 (initial conditions), Table DR2 (simulated emissions), and supplemental information on modeling is available online at www.geosociety.org/pubs/fl2014.htm, or on request from editing@geosociety.org or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301, USA.
chosen to approximate volatile release from a plausible magmatic episode, including a large pyroclastic eruption (Black et al., 2012), contact heating and metamorphism of hydrocarbon-bearing evaporite salts (Aarnes et al., 2011), and one or more explosive pipes (Svensen et al., 2009). We also considered the effects of stratospheric versus tropospheric release and background emissions of methyl chloride. We included a wide range of gas emissions in our 27 scenarios because the eruptive fluxes and durations are subject to significant uncertainty. The gas fluxes in Table DR2 were selected on the basis of petrologic estimates (Black et al., 2012), experiments and volumetric estimates (Svensen et al., 2009), thermal modeling (Aarnes et al., 2011), and modern volcanological measurements of trace gases.

We track the water contents of each parcel of air, and include the interrelated effects of SO$_2$, SO$_3$, HS$_2$O, NO$_x$, HCO$_3^-$, OH, CO$_2$, and NH$_3$ in order to calculate the pH of rainwater. Because solubilities depend on pH, we determine the pH iteratively.

Our model does not include gravitational settling of stratospheric sulfates. For very large sulfur fluxes, larger sulfate aerosols will form (Timmreck et al., 2009). These larger particles settle more quickly from the atmosphere and may also enter less readily into aqueous solutions. As a result, our simulations may overestimate the acuteness and longevity of acid rain following large eruptions. We modified CAM-Chem to include the effects of stratospheric sulfate aerosols on polar stratospheric cloud formation, and therefore on the surface-area density available to facilitate heterogeneous reactions involving Cl and ozone. For this calculation, we use aerosol sizes based on simulations of a 100x Mount Pinatubo sulfur release (Timmreck et al., 2009), similar in magnitude to the sulfur release in our E1–E4 simulation cases (see Table DR2).

**RESULTS**

**Acid Rain**

Our simulations show that both CO$_2$ and SO$_2$ released from the Siberian Traps could have strongly affected the acidity of rain. The contribution of volcanic CO$_2$ release is included in the 3550 ppm fixed CO$_2$ concentration we assume in our model. Oxygen isotopic data record a rapid increase in temperatures coincident with the marine extinction interval (Sun et al., 2012), consistent with an order of magnitude increase in atmospheric CO$_2$. In addition to producing global warming (Kiehl and Shields, 2005), in our model a tenfold increase in CO$_2$ leads to more acidic rain ($\text{pH} \approx 4$) globally. This background acidity of rain during the Permain-Triassic transition is similar in both the Northern and Southern Hemispheres. Sulfur injected into the stratosphere during pyroclastic eruptions can further shift pH of rain by one or more log units; pH rebounds quickly after the eruptions cease. Because the Siberian Traps were located at ~60°N in the Permian, volcanogenic acid rain is particularly intense in the Northern Hemisphere. Within the Northern Hemisphere, the intensity of acid rain is modulated by regional precipitation totals (increased precipitation dilutes the sulfuric acid) and by atmospheric transport and removal of SO$_3$. In a broad swath between the equator and 60°N, the annually averaged acidity during a 1 yr, ~240 km$^3$ eruption (simulation E1) drops to $\text{pH} = 2$–3, similar to undiluted lemon juice (Fig. 1). A 1 yr, ~2400 km$^3$ eruption (simulation E5) yields acid rain that is even deeper and more prevalent, with extensive areas of the Northern Hemisphere receiving rainfall with annually averaged $\text{pH} = 2$; in this scenario, pH levels also begin to drop in the southern low latitudes.

Local precipitation on a given day may be significantly more acidic than the annual averages described here. In addition, our model does not include the acidity produced by HCl and HF. Because HCl and HF are preferentially removed proximal to the vent through dissolution or adsorption onto particulates, these gases may have intermittently enhanced acidity in the region of the Siberian Traps.

**Ozone Depletion**

Volatiles release associated with Siberian Traps magmatism can produce ozone depletion ranging from moderate reduction to nearly total collapse in both the Northern and Southern Hemispheres. The fluxes of halogen and halocarbons compounds to the stratosphere critically determine the rate of catalytic ozone loss. In the Tunguska Basin, Proterozoic hydrocarbons coexist with halites (Svensen et al., 2009). Depending on the total organic carbon contents of Siberian halite layers, and conversion efficiency of methane to CH$_3$Cl, thermal metamorphism related to emplacement of a flat ~5000 km$^3$ sill could result in peak annualized production (over 10$^6$ yr) of 0.55–0.83 Gt CH$_4$ and 0.87–1.65 Gt CH$_3$Cl (Aarnes et al., 2011), which may be released passively or through widely dispersed pipe structures (Svensen et al., 2009).

Methane and methyl chloride fluxes in this range produce steady-state ozone depletion of 60%–70% globally (Figs. 2 and 3). If gases accumulate during the peak production period prior to release through a pipe, ozone depletion can reach 55%–60%, assuming that ~1% of aureole gases mobilize into the pipe. Recovery typically takes ~10 yr after the cessation of emissions. Because more than 100 pipes are associated with widespread and voluminous Siberian Traps sills (Svensen et al., 2009), ozone levels could have undergone multiple cycles of collapse and recovery. The lifetime of CH$_3$Cl in the troposphere is sufficiently long (>1 yr) that CH$_3$Cl released...
in the lower troposphere reaches the stratosphere (Fig. 2A). Consequently, the magnitude of ozone depletion is similar for either tropospheric or stratospheric release of CH$_3$Cl gas (Fig. 3).

In the case of magmatic HCl, stratospheric release during an explosive episode is critical, because HCl is soluble and quickly washes out of the troposphere (Textor et al., 2003). A Siberian Traps eruption that injects 48 Tg HCl per year into the stratosphere produces only 5%–20% ozone depletion (Fig. 3), in contrast to previous results suggesting that <10% of the HCl flux over long time scales would produce ~30% ozone depletion (Beerring et al., 2007). The comparative resilience of the end-Permian ozone layer in our model is consistent with the limited ozone response to hydrogen sulfide emissions observed in global climate-chemistry simulations (Lamarque et al., 2007), and may result from more realistic simulation of polar stratospheric clouds, less severe CO$_2$-driven stratospheric cooling, and different background O$_3$ and Cl levels (see Table DR1).

**DISCUSSION**

The scale of Siberian Traps tuff deposits suggests that multiple explosive eruptions of >$10^3$ km$^3$ probably occurred (Black et al., 2012), generating repeated intervals of highly acidic rain comparable to that shown in Figure 1A. The effects of acid rain on Permian ecosystems are poorly constrained, and depend on species physiology and local buffering capacity (Fig. 1B). Elevated background CO$_2$ leads to long-term acidification of rain that could have leached soil nutrients. During pyroclastic eruptions, sulfur-rich rain with pH $\sim 2$ in the Northern Hemisphere is sufficient to disfigure plants and stunt growth (Howells, 1990); sustained sulfur release could damage weakly buffered aquatic ecosystems. Paleontological and pollen studies indicate that plant communities in the Southern Hemisphere also were affected during the end-Permian mass extinction (Rees, 2002; Visscher et al., 2004). Although increased sulfide concentrations across the Permian-Triassic boundary in the Karoo Basin, South Africa (Fig. 1A) have been interpreted as a record of sulfur rainout from volcanic sources (Maruoka et al., 2003), sedimentation and the patterns of tropospheric and stratospheric circulation limit the overall flux of SO$_2$ from the Siberian Traps to the Southern Hemisphere.

Whereas sulfuric acid rain is muted in the Southern Hemisphere, metamorphic CH$_3$Cl emissions can ravage the ozone layer at all latitudes (Fig. 2B), with potentially severe consequences for Permian terrestrial biota. The extent of ozone deterioration varies among our model results (Fig. 3): we observe a modest 5%–30% depletion for volcanic HCl release, and 55%–67% depletion for metamorphic emissions from a 5000 km$^3$ sill, assuming that these emissions reach the atmosphere. In all scenarios, the most intense depletion occurs at high latitudes. In run A1, the high-latitude ozone column depth dwindles to <15% of Permian background levels. Based on power-law scaling of biologically active ultraviolet (UV) radiation with ozone (Madrornich et al., 1998), this 85% reduction equates to a maximum 4900% increase in mutagenic ultraviolet (UV)-B flux (Fig. 4). Elevated UV-B fluxes have been shown to produce an increase in genetic recombination rates and stunting of Arabidopsis seedlings in laboratory experiments (Ries et al., 2000). Absolute ozone levels are slightly lower in the Northern Hemisphere (Fig. 2B), but the
percentage depletion is greatest at the South Pole (Fig. 4). Thermodynamic modeling predicts that large methane fluxes will accompany release of metamorphic CH$_3$Cl (Aarnes et al., 2011), which could have exacerbated the end-Permian greenhouse (Sun et al., 2012). Results from our simulations are limited by uncertainties in metamorphic emissions and eruptive time scales, the CO$_2$ mixing ratio, CH$_3$Cl release efficiency, and pre-eruptive background emissions (Table DR1). Whereas some degree of acid rain seems inevitable, the fluctuations in pH and UV flux, coupled with a acid rain relents within 1 yr after the end of gas (Pavlov et al., 2011), pulses of deeply acidic rain (Jump and Peñuelas, 2005). Because conditions can outpace the biological capacity for adaptation (Jump and Peñuelas, 2005), the rate of environmental change is arguably as important as the magnitude of change.

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