Volatiles and the tempo of flood basalt magmatism

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Abstract

Individual flood basalt lavas often exceed 10^3 km^3 in volume, and many such lavas erupt during emplacement of flood basalt provinces. The large volume of individual flood basalt lavas implies correspondingly large magma reservoirs within or at the base of the crust. To erupt, some fraction of this magma must become buoyant and overpressure must be sufficient to encourage failure and dike propagation. The overpressure associated with a new injection of magma is inversely proportional to the total reservoir volume, and as a large magma body heats the surrounding rocks thermally activated creep will relax isotropic overpressure more rapidly. Here, we examine the viability of buoyancy overpressure as a trigger for continental flood basalt eruptions. We employ a new one-dimensional model that combines volatile exsolution, bubble growth and rise, assimilation, and permeable fluid escape from Moho-depth and crustal chambers. We investigate the temporal evolution of degassing and the eruptibility of magmas using the Siberian Traps flood basalts as a test case. We suggest that the volatile inventory set during mantle melting and redistributed via bubble motion controls ascent of magma into and through the crust, thereby regulating the tempo of flood basalt magmatism. Volatile-rich melts from low degrees of partial melting of the mantle are buoyant and erupt to the surface with little staging or crustal interaction. Melts with moderate volatile budgets accumulate in large, mostly molten magma chambers at the Moho or in the lower crust. These large magma bodies may remain buoyant and poised to erupt—triggered by volatile-rich recharge or external stresses—for $10^5 - 10^6$ years. If and when such chambers fail, enormous volumes of magma can ascend into the upper crust, staging at shallow levels and initiating substantial assimilation that contributes to pulses of large-volume flood basalt eruption. Our model further predicts that the Siberian Traps may have released $10^{19} - 10^{20} \text{ g}$ of CO_2 during a number of brief ($\sim 10^4$ year) pulses, providing a plausible trigger for warming and ocean acidification during the end-Permian mass extinction. The assimilation of carbon-rich crustal rocks strongly enhances both flood basalt eruptibility and CO_2 release, and the tempo of eruptions influences the

45 environmental effects of CO₂, SO₂, and halogen degassing. The eruptive dynamics of
46 flood basalts are thus intertwined with their environmental consequences.

1. Introduction

Flood basalts are voluminous outpourings of basaltic lava that likely erupt as a result of magmatic processes that are distinct from those occurring at plate boundaries (Richards *et al.*, 1989). Flood basalt provinces can encompass several million cubic kilometers of magma, with hundreds of stacked flows that reach kilometers of total thickness (e.g., Bryan *et al.*, 2010). Individual eruptive episodes during flood basalt emplacement last decades or more (Self *et al.*, 2014), separated by hiatuses of 10^3 - 10^5 years (Self *et al.*, 2014); in total, flood basalt provinces can span 10^5 - 10^7 years (e.g. Kamo *et al.*, 2003; Blackburn *et al.*, 2013; Schoene *et al.*, 2015), with active flood basalt provinces recurring at intervals of $\sim 10^7$ years somewhere on Earth (Courtillot and Renne, 2003).

Even as debate continues regarding the deep genesis of flood basalt magmas (e.g. Richards *et al.*, 1989; Campbell and Griffiths, 1990; Elkins-Tanton and Hager, 2000; DePaolo and Manga, 2003; Foulger and Natland, 2003), a clearer picture of flood basalt lithospheric plumbing systems is gradually emerging. Abundant physical and geochemical evidence supports widespread interaction with crustal material (e.g., Cox, 1980; Wooden *et al.*, 1993; Kontorovich *et al.*, 1997; Bryan *et al.*, 2010; Black *et al.*, 2014a). On the other hand, most flood basalt provinces also host alkaline lavas that may have interacted with mantle lithosphere but show little evidence for protracted crustal residence (Arndt *et al.*, 1998).

Many flows within flood basalt provinces are highly homogeneous and combine to form coherent geochemical sequences, consistent with eruption from a large centralized magmatic system (Wolff *et al.*, 2008). This geochemical homogeneity has been interpreted as evidence for processing in long-lived magma reservoirs undergoing Recharge, Tapping via eruptions, Fractionation, and Assimilation (O'Hara, 1977; Cox, 1988; Arndt *et al.*, 1993; Wooden *et al.*, 1993), also known as RTFA processes. Intercalated low-Ti and high-Ti lavas in the Siberian Traps have been interpreted as the result of dual plumbing systems (Arndt *et al.*, 1998), each erupting repeatedly. The evidence for large, well-integrated, episodically erupting plumbing systems underscores a fundamental question: how and why do flood basalts erupt?

Eruptions occur when magmas are buoyant and mobile (e.g., Marsh, 1981), and when external stresses or magmatically-generated stresses around an overpressured chamber are sufficiently large to allow dike propagation (e.g., Tait *et al.*, 1989). Large volume magma chambers resist eruption, for at least two reasons. First, the overpressure associated with injection of a new volume of magma—a process thought to be key to relatively small volcanic eruptions—is inversely proportional to the total reservoir volume (Jellinek and DePaolo, 2003; Karlstrom *et al.*, 2010; Caricchi *et al.*, 2014). Second, large masses of resident magma will heat the crust, expediting viscoelastic relaxation and relieving overpressures from volume change (Jellinek and DePaolo, 2003). Consequently, injection alone is probably an inadequate trigger for rare, explosive super-eruptions. Instead, roof failure (e.g., de Silva and Gregg, 2014) and buoyancy overpressure (e.g., Caricchi *et al.*, 2014) have been invoked to trigger caldera-forming silicic eruptions.

In some respects, continental flood basalt eruptions are even more difficult to explain than large silicic eruptions. The episodic tempo of flood basalt volcanism and the large volumes attained by individual lava flows and magmatic pulses (e.g., Chenet *et al.*, 2008; Chenet *et al.*, 2009; Bryan *et al.*, 2010; Pavlov *et al.*, 2011) are consistent with accumulation in immense reservoirs prior to main phase eruptions. While the factors that control the inception of magma reservoirs are poorly understood, we expect the rheological structure of the continental lithosphere to influence the depths of magma accumulation. If the geothermal gradient is shallow and the lower crust is fluid-saturated, the lower crust will be weaker than both the upper crust and lithospheric mantle (e.g., Bürgmann and Dresen, 2008), encouraging growth of lower crustal magma reservoirs. If the lower crust is dry and the geothermal gradient is steep (as expected when a mantle plume arrives), the uppermost mantle may be much weaker than the crust (e.g., Bürgmann and Dresen, 2008), encouraging growth of magma reservoirs at the Moho. In either case, continental flood basalt magmas encounter a mechanical barrier to ascent at the base of the crust or in the lower to middle crust, which is compounded by a possible density barrier due to the high densities of volatile-free flood basalt magmas (relative to the upper continental crust).

Lange (2002) and Karlstrom and Richards (2011) have invoked gas exsolution and the resulting buoyancy to overcome this density barrier. H₂O, sulfur species, and halogens are relatively soluble in basaltic melts up until shallow crustal pressures (e.g. Gerlach, 1986). However, significant quantities of CO₂ may exsolve even at Moho depths (Karlstrom and Richards, 2011).

In this study, we build on ideas proposed by Lange (2002) to investigate buoyancy produced through magmatic volatile exsolution at depth. We propose that, in addition to allowing mafic magmas to surmount the crustal density barrier, such buoyancy may also be an important trigger for failure of large magma reservoirs surrounded by warm wall rocks at lower crustal or Moho depth. To explore the consequences of magmatic volatile exsolution for the tempo of flood basalt eruptions, we couple one-dimensional models for thermal evolution, assimilation, gas exsolution and bubble population dynamics in a magma chamber with permeable gas transfer through the overlying crust. While our model is designed to capture the eruptive dynamics of flood basalts generally, we consider the Siberian Traps as a useful case study. Our model can explain the most distinctive features of flood basalt eruptions in the Siberian Traps and elsewhere, including eruptibility despite large magma chamber volumes, the buoyancy of mafic magmas, and repeated, sustained eruptive episodes punctuated by long hiatuses.

Flood basalt eruptions and volatile degassing have been hypothesized to have severe environmental repercussions. Geochronologic evidence suggests that flood basalt eruptions overlapped temporally with the end-Guadalupian, end-Permian, end-Triassic, and end-Cretaceous mass extinctions (Zhou *et al.*, 2002; Courtillot and Renne, 2003; Blackburn *et al.*, 2013; Burgess *et al.*, 2014; Schoene *et al.*, 2015; Renne *et al.*, 2015; Burgess and Bowring, 2015). The flux of gases to the atmosphere critically determines the severity of magmatically-induced acid rain, ozone depletion, and surface temperature changes (e.g., Caldeira and Rampino, 1990; Black *et al.*, 2012; Black *et al.*, 2014b; Schmidt *et al.*, 2015). Most studies of volatiles in melt inclusions focus on degassing at

the vent and in shallow conduits and chambers (Métrich and Wallace, 2008). However, the preponderance of CO₂ will exsolve at depth. In some cases large quantities of CO₂ may also be released in the subsurface through metamorphism of carbon-rich sedimentary rocks (Svensen *et al.*, 2009). Such CO₂ may be trapped at depth as a fluid, or it may react with water and feldspars in the crust to form hydrated minerals (Bredehoeft and Ingebritsen, 1990). Alternatively, CO₂ can be dissolved in groundwater (e.g., James *et al.*, 1999), or may reach the atmosphere through permeation and passive degassing or during an eruption that breaches a magma chamber that hosts a significant mass of exsolved CO₂. This exsolved CO₂, which would not be recorded directly in melt inclusions (Wallace *et al.*, 2015), may be distilled from larger volumes of magma than those of the lavas that erupt. The total flux of CO₂ to the atmosphere or surface environments—a critical variable for understanding the climatic consequences of flood basalts—is therefore difficult to determine.

Here, we propose that the evolution of magmatic CO₂, eruption tempo, and environmental consequences are all interrelated. Episodic surface volcanism reflects rheological and density barriers to magma ascent into the crust, and results in expulsion of CO₂ and SO₂ to the atmosphere in brief pulses. These dynamics may help to explain the profound climate and carbon cycle perturbations that seem to coincide with the emplacement of some flood basalt provinces.

2. Model Description

2.1 Overview

160 The features of flood basalt plumbing systems dictate the structure of our model.
161 Flood basalt magmas originate in the mantle, most likely where mantle plumes arrive at
162 the base of the lithosphere (Richards *et al.*, 1989). The arrival of a plume may lead to a
163 swell in melt production (Richards *et al.*, 1989; Hooper *et al.*, 2007). As described in the
164 previous section, we expect this melt to rise towards the base of the crust, where
165 rheological and density contrasts may cause the melt to pond and form large primitive
166 magma chambers (Ridley and Richards, 2010; Farnetani *et al.*, 1996). The number of
167 such chambers will be governed in part by the compaction length, which describes the
168 volume of crystalline matrix from which melt can be extracted (Keller *et al.*, 2013).
169 When the magma in these lower crustal or Moho-depth chambers is buoyant and
170 overpressures are high enough to cause the overlying crust to fail, magmas will ascend
171 via dikes. We expect magmas to fall into two broad categories: volatile rich magmas that
172 are buoyant and that spend little time in magma chambers, and magmas that are initially
173 less rich in volatiles, and which therefore must ascend in stages, accruing volatiles
174 through magma replenishment and bubble rise and from the country rocks. Crustal
175 heating from magmas residing in shallow chambers can lead to significant assimilation.
176 We illustrate this system of coupled lower crustal to Moho-depth and upper crustal
177 magma chambers schematically in Figure 1.

178 We consider the Siberian Traps flood basalt province as a test case. The eruption
179 of the Siberian Traps has been invoked as a trigger for the catastrophic end-Permian mass
180 extinction (e.g. Renne and Basu, 1991; Campbell *et al.*, 1992; Courtillot and Renne,
181 2003; Reichow *et al.*, 2009; Black *et al.*, 2012; Burgess and Bowring, 2015), and the
182 crustal and volcanic stratigraphies have been the subject of extensive study (e.g.

Meyerhoff, 1980; Zharkov, 1984; Renne and Basu, 1991; Fedorenko *et al.*, 2000). The present-day areal extent of the Siberian Traps is $\sim 340,000 \text{ km}^2$ (Reichow *et al.*, 2009), though the area prior to erosion may have been much larger.

In cases where flood basalt magmas are stored prior to eruption, the sheer volume of individual eruption episodes implies that reservoirs must be laterally extensive to accommodate storage of 10^3 - 10^4 km^3 of magma. We therefore choose to model the magmatic systems that feed flood basalts in one dimension. Since exsolving CO_2 and water dominate the production of buoyancy in relatively primitive magmas (Karlstrom and Richards, 2011), we expect volatile solubility and fluid movements to regulate the eruptibility of flood basalt magmas. We thus focus particular attention in our model on processes that control the fate of volatiles, including bubble growth, rise, and coalescence; viscous compaction, porosity, and permeable fluid escape; assimilation; and degassing (Figure 2).

2.2 Mantle melt production

Trace element data from the Siberian Traps (Wooden *et al.*, 1993) indicate that early melting occurred in the garnet stability field, whereas later melting extended to shallower depths (Figure 3). The decreasing depth of melting may reflect thermal and mechanical erosion of the lithosphere during magmatism (Wooden *et al.*, 1993; Elkins-Tanton and Hager, 2000; Sobolev *et al.*, 2011). For fixed mantle potential temperature, an expanded melting column will produce larger degrees of partial melting and consequently less volatile enrichment (Figure 4). We parameterize this Siberian partial melting history

through an arctangent function that begins at small degrees of partial melting and reaches $F=0.1\pm0.0125$ (1-sigma) after several hundred thousand years. We note that alkaline magmas such as meichmechites (which are thought to be the last Siberian Traps magmas to erupt) depart from this idealized history (e.g., Elkins-Tanton *et al.*, 2007). We use a Weibull function to model the expected peak in melt production in the mantle as a plume head arrives, followed by a gradual decline (Hooper *et al.*, 2007). These functions are simple approximations for the mantle melting history deduced from geochemical and petrologic data from the Siberian Traps. We stress that the actual melting history may vary from province to province and even within a given province. Our goal is to interpret the predicted eruptive regimes across a range of melting conditions.

We assume a mantle source composition (X_{mantle}) with 500 ppm water and CO₂ concentrations of 100-500 ppm. While these values are at the upper end of mantle estimates (e.g., Halliday, 2013), they may be appropriate for a mantle source that contains a large component of enriched or recycled material (e.g., Dasgupta and Hirschmann, 2010; Sobolev *et al.*, 2011). For a given degree of partial melting (F), we then calculate the initial concentrations of water and CO₂ in the melts (X_{melt}) from

$$X_{melt} = \frac{X_{mantle}}{D+F(1-D)}, \quad (1)$$

where the bulk partition coefficient D is approximately 0.01 for water (Katz *et al.*, 2003) and strongly incompatible ($<10^{-4}$) for CO₂ (Hauri *et al.*, 2006). Our assumption that magmas originate from a mantle source with constant composition is a simplification that neglects possible mantle lithospheric melting (e.g., Lightfoot *et al.*, 1993) and heterogeneous plume material (e.g., Arndt *et al.*, 1993; Sobolev *et al.*, 2009; Sobolev *et al.*, 2011). Variations in mantle composition may yield a more complex intrusive and

volcanic history, though the fundamental processes that control eruption dynamics should remain unchanged.

We link prescribed histories of mantle melting and melt fraction (based on the trace element stratigraphy of the Siberian Traps) with chambers near the base of the crust, which in turn either erupt directly to the surface or feed chambers at 8-12 km depth (Figure 1B and Figure 2). In order to supply melt from the mantle to deep reservoirs, we assume that melt is extracted over a distance controlled by the compaction length l_c (Keller *et al.*, 2013), with

$$l_c = \sqrt{\eta k_m \varphi^3 / \mu}, \quad (2)$$

where $\eta \approx 10^{21}$ Pa-s is the viscosity of the mantle, $k_m \approx 10^{-6}$ m² is the permeability prefactor (Keller *et al.*, 2013), φ is melt fraction, and $\mu \approx 10$ Pa-s is the viscosity of the melt at Moho conditions. For melt fractions F between 5–10%, the compaction length ranges from approximately 100–300 km. If the present-day basalts are centered above the main region of melt production and extraction, compaction radii of 100-300 km imply that 1–10 extraction centers may have comprised the Siberian Traps. In order to translate our one-dimensional model to a two-dimensional surface we therefore consider ensembles of 10 individual model realizations, scaled to reproduce an overall extrusive volume of 2×10^6 km³ (Reichow *et al.*, 2009).

2.3 Magma reservoirs

Thermal evolution, thermodynamics, bubble ascent and coalescence, and country rock porosity and permeability all influence conditions in and around magma reservoirs.

We describe our treatment of these magmatic processes in detail in the Supplementary Materials and in Black and Manga (2016). We model equilibrium crystallization of an initial melt with constant composition using Rhyolite-MELTS (Ghiorso and Sack, 1995; Gualda *et al.*, 2012). In our Rhyolite-MELTS calculations, we adopt the most magnesian primary melt composition computed by Sobolev *et al.* (2009) from picritic Siberian Traps melt inclusions (see Supplementary Table 1). We use our Rhyolite-MELTS modeling to generate an enthalpic lookup table in order to account for latent heat. We numerically solve the one-dimensional heat equation with latent heat. We assume that magma bodies are well-mixed (with the exception of ascending bubbles) and that therefore temperatures within chambers are vertically isothermal. We use a fixed surface temperature and a flux boundary condition at depth. Future work including temperature and compositional gradients within the chamber could account for the contributions of crystal segregation to differentiation and increased buoyancy. We compute bubble size distributions using empirically and theoretically validated expressions for collision frequency (Manga and Stone, 1995), and from the bubble size distributions obtain rise velocities and the vertical distribution of exsolved volatiles within the chamber (Black and Manga, 2016). The fluid densities are calculated with a parameterized equation of state (Degruyter and Huber, 2014). In conjunction with melt and crystal densities from Rhyolite-MELTS, this fluid density yields an overall magma density. The buoyancy-related chamber overpressure (ΔP_b) is then (Caricchi *et al.*, 2014):

$$\Delta P_b = (\rho_{surrounding} - \rho_{magma})g h \quad (3)$$

where h is the thickness of the chamber in meters, $g=9.81 \text{ m/s}^2$, and we assume that the magma has ascended to a level of neutral buoyancy and that therefore the density of the country rocks at that depth ($\rho_{surrounding}$) is equivalent to the initial density of the magma (ρ_{magma}).

2.4 Volatiles and assimilation

We implement the joint H_2O - CO_2 solubility model of Iacono-Marziano et al. (2012), which accounts for melt composition and is experimentally constrained to 10 kbar, to calculate volatile solubilities. As magmas ascend we recalculate solubility and allow fluids to exsolve. Further exsolution occurs as magmas cool and crystallize.

In the case of magma bodies in the upper crust, we investigate the end-member case where the country rocks are all carbonates. We consider assimilation of impure Ca-Mg carbonates with a latent heat of 59 kJ/mol distributed across a melting interval from 1273–1373 K (Haynes, 2013). During assimilation, we add stoichiometric quantities of CO_2 to the magma chamber, but neglect the compositional effects of MgO and CaO addition. Because the East and West Siberian basins contain up to ~12 km of Proterozoic to Permian sedimentary rocks (Meyerhoff, 1980), including several kilometers of Proterozoic and Paleozoic carbonates (Meyerhoff, 1980; Zharkov, 1984), large-scale carbonate assimilation is a reasonable scenario. However, the sedimentary stratigraphy also contains abundant shales, evaporites, hydrocarbon-bearing rocks, coals, siltstones and marls (Meyerhoff, 1980; Zharkov, 1984; Svensen *et al.*, 2009; Grasby *et al.*, 2011; Black *et al.*, 2012). Examination of drill core and geochemical evidence suggests some magmas also interacted to varying degrees with these other lithologies (e.g., Kontorovich

et al., 1997; Svensen *et al.*, 2009; Black *et al.*, 2014a). The volatile contribution, melting properties, and carbon isotopic composition associated with assimilation will thus depend on the crustal lithologies within which large magma bodies reside.

Fluids can escape from magma reservoirs through pore spaces or fractures in the surrounding rocks. We assume that this process can be described by Darcy's Law (e.g., Manning and Ingebritsen, 1999) and that permeability gradually decreases with time as the country rocks undergo viscous compaction and porosity loss (e.g., Bredehoeft and Ingebritsen, 1990; Weis *et al.*, 2012). We do not consider local hydraulic fracturing due to elevated pore pressures (e.g., Weis *et al.*, 2012), which may elevate permeability and expedite volatile egress from the magma chamber. This process will trade off with the critical overpressure at which the reservoir fails. If fracturing is pervasive, fluids will escape and buoyancy overpressure will build up more slowly, but the strength of the country rock may also drop, encouraging dike propagation and magma ascent (e.g., Rubin, 1995).

2.4 Magma ascent

When the buoyancy overpressure exceeds 10 MPa (Rubin, 1995), we assume that the chamber fails. We further assume that the fraction of a body that is both buoyant and molten at this critical buoyancy overpressure is eruptible. Eruptible magmas at the Moho or in the lower crust then ascend into the upper crust and magmas already in the upper crust erupt to the surface. We do not explicitly model dike propagation, but we assume that magma chamber failure occurs via fracturing and dike formation, and that this

process will also fracture the surrounding rocks, increasing their bulk permeability and facilitating fluid egress (Bredehoeft and Ingebritsen, 1990). Therefore we reset the porosity and permeability in the country rocks following each eruption (Manning and Ingebritsen, 1999). A more detailed treatment of magma ascent could in future yield insights into why flood basalt magma chambers form when and where they do, and how connections among multiple chambers evolve over time.

3. Results

We demonstrate the roles of mantle CO₂ concentrations, bubble coalescence and rise, and coupling between deep and shallow magma reservoirs in Figure 5. Figure 5A shows the evolution of buoyancy overpressure in an upper crustal reservoir for a range of mantle CO₂ concentrations, with and without accounting for bubble rise. Figure 5B shows the same for a magma reservoir at 36 km depth, representing a reservoir at the Moho or in the lower crust. The interval between pulses of magma ascent is sensitive both to CO₂ concentrations and to whether the volatile phase efficiently segregates at the top of the reservoir. A limited magmatic CO₂ budget inhibits ascent from the Moho or lower crust, resulting in less frequent eruptions.

Our model suggests that flood basalt provinces progress through three fundamental eruptive regimes, depending on the evolution of melt production in the mantle.

First, volatile-rich low-degree melts create a regime in which buoyancy accumulates rapidly, driving frequent, smaller eruptions (Figures 5 and 6). Magmas that

ascend from the base of the crust continue to exsolve large quantities of volatiles during decompression. They are consequently highly buoyant and reside very briefly, if at all, in the crust prior to erupting to the surface.

Second, higher-degree melts with moderate volatiles create a regime in which large quantities of hot, crystal-poor melt accumulate at the Moho or in the lower crust as buoyancy slowly builds towards the failure threshold, accompanied by a hiatus in surface volcanism for 10^5 – 10^6 years. When failure does occur, immense volumes of magma can be injected into the middle to upper crust. However, the initially high porosity and permeability of the upper crust encourage volatile escape from the magma. As the country rocks surrounding the magma body grow warmer, thermal annealing and compaction seal fractures and reduce porosity, leading to decreased permeability and trapping more volatiles in the chamber. Assimilation of upper crustal sedimentary rocks can further increase the mass of volatiles in the reservoir. For sufficiently large injections of magma into the upper crust, a series of large-volume eruptions can result. The entire pulse of volcanism can last 10^3 – 10^5 years. While we consider idealized magma bodies in the crust, the injection of the same volume of magma in a more realistic configuration with multiple interconnected or isolated magma lenses (e.g., Bryan *et al.*, 2010; Cashman and Giordano, 2014) should lead to comparable thermal effects and therefore a similar extent of assimilation.

Third, melts that contain modest volatile concentrations may never quite achieve eruptibility, because crystallization proceeds slowly in a large magma body at lower crustal and Moho depths, and consequently permeable fluid escape provides a release valve for exsolving volatiles. We find that such gradually cooling magma bodies can

reside in mostly molten states with near-critical overpressure for 10^5 – 10^6 years (Figure 5A).

The percentage of magmas that erupt ranges from 5% to 30% in our simulations; the majority of the magma typically remains at Moho or lower crustal depths, with less than 20% of magmas freezing in the upper crust (Figure 6).

In simulations in which we consider assimilation of carbonate rocks into magma bodies emplaced at depths less than 12 km, the total CO_2 release can exceed 10^5 Gt CO_2 (Figure 8). For comparison, the present-day atmosphere contains approximately 3×10^3 Gt CO_2 , and the ocean-atmosphere system contains 1.4×10^5 Gt CO_2 (e.g., Houghton, 2007). If most of the flood basalt CO_2 is released during eruptions, it would enter the atmosphere during brief volcanic pulses. In simulations in which we do not consider assimilation, the total CO_2 release is an order of magnitude lower.

4. Discussion

4.1 Flood basalt eruption dynamics and comparison with observations

Our model suggests that flood basalt provinces progress through three fundamental eruptive regimes, depending on the evolution of melt production in the mantle: 1) rapid eruption of volatile-rich, low-degree melts with little crustal interaction, 2) sporadic pulses of voluminous magmatism accompanied by large-scale assimilation, and 3) slow freezing of large volumes of almost-eruptible melt at Moho or lower crustal depth. We describe each of these regimes in more detail in the prior section, and we

discuss the implications for the tempo of volcanism below. As noted previously, the time evolution of the degree of melting and volatile enrichment may vary from flood basalt province to flood basalt province, which would not alter these three thermo-mechanically distinct regimes but could lead to a different progression than we expect for the Siberian Traps.

The predicted eruptive dynamics depend on the rate of buoyancy addition relative to the rate of melt addition. The rate of buoyancy addition is governed by bubble exsolution and expansion from depressurization, crystallization, and bubble rise counterbalanced by volatile escape through permeable country rocks. We develop new scalings for overpressure in laterally extensive, laccolith-shaped magma reservoirs, and we find that as magma injection heats the crust the magmatic system rapidly evolves towards a viscous regime (Figure 7) in which buoyancy dominates, though deviatoric stresses do not relax entirely (Karlstrom *et al.*, 2010).

Geologic and geochemical observations from Phanerozoic flood basalt eruptions yield a number of consistency tests for the validity of our results, including the fraction of magmas that erupt, the tempo of surface volcanism, and the composition of erupted rocks. Our model predicts that 70-90% of the magma by mass should freeze at the Moho or in the lower crust, which is consistent with the presence of high-velocity structures ~5-15 km thick just above the Moho in the Emeishan, Deccan, Siberian, and Columbia River flood basalt provinces (Ridley and Richards, 2010). Slow crystallization of deep magma bodies is expected to yield olivine- and clinopyroxene-rich cumulates with high seismic velocities (Farnetani *et al.*, 1996). Gravity data has also been interpreted as evidence for several kilometers of cumulates or basalt frozen in the crust beneath the West Siberian

Basin (Braitenberg and Ebbing, 2009). Perhaps most importantly, we find that buoyancy from exsolved volatiles (in particular CO₂) is sufficient to erupt melt from the subcontinental Moho, causing repeated pulses of voluminous basaltic volcanism (Figures 5, 6 and 8). The predicted tempo agrees well with recent paleomagnetic and geochronologic results, which favor brief episodes of intense volcanism separated by hiatuses. Paleomagnetic directional groups within the Siberian Traps and Deccan Traps lava piles imply that—excluding periods of quiescence—the bulk of the volcanic stratigraphy in each flood basalt province may have been emplaced in a total of 10³-10⁴ years (Chenet *et al.*, 2009; Pavlov *et al.*, 2011). U-Pb dates reveal a hiatus of 420 ± 149 kyr within the Delkansky formation of the Siberian Traps across only ~135 meters of stratigraphic separation (Burgess and Bowring, 2015). Significantly, this hiatus occurs directly after the end-Permian mass extinction (Figure 9); the model predicts that in general hiatuses should follow large pulses of magmatism. Because eruptibility depends on the magmatic volatile budget, slight changes in the degree of melting may shift the eruptive regime, providing one plausible explanation for the apparent state change in the midst of Deccan volcanism (Renne *et al.*, 2015). The unsteady supply of magma from a constellation of Moho or lower crustal-depth reservoirs leads to multiple suites of geochemically and petrologically related eruptions that evoke the distinct volcanic formations found in flood basalt provinces (Figure 6A and 6B).

At the inception of Moho-depth or deep crustal magma reservoirs, melt fractions are low. However, after 10⁵ years or less, as they receive copious supplies of melt from the mantle (Figure 6D) and continuing for several Myr after mantle melt supply declines, deep reservoirs can maintain melt fractions of tens of percent. The overall lifetimes of the

largest magma reservoirs depend strongly on variations in the flux and temperature of melt arriving from the mantle and on the temperature of the upper mantle, but can reach 5-10 Myr. Siberian Traps picrobasalts and basalts commonly contain 5 to 15 wt% MgO (Sobolev *et al.*, 2009; Fedorenko *et al.*, 2000). Primary mantle melts at sublithospheric depth will be mafic or ultramafic (Farnetani *et al.*, 1996; Karlstrom and Richards, 2011). To obtain the more evolved lava compositions, >25% crystallization may be required (Karlstrom and Richards, 2011). The model predicts typical crystal fractions in lower crustal or Moho-depth chambers of ~20-50%; further crystallization occurs during staging in the upper crust. We expect upper crustal flood basalt reservoirs to more closely resemble modern upper crustal magmatic systems that are cold and melt-poor most of the time (e.g., Glazner *et al.*, 2004).

Previous efforts to model compositional evolution in flood basalt provinces have combined mantle melting with Recharge, Tapping, Fractionation, and Assimilation (RTFA) in magma chambers within or at the base of the crust (e.g., Cox, 1980; Cox, 1988; Wooden *et al.*, 1993; Arndt *et al.*, 1993). Wooden *et al.* (1993) interpreted variable but widespread Nb-Ta depletion, low ϵ_{Nd} values, and elevated $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in Siberian Traps lavas as evidence for contamination of RTFA magma bodies at multiple levels in the crust. In our model, the increasing thermal stability of magma reservoirs with increasing depth suggests that the predominant locus for long-lived RTFA processes may be at or near the base of the crust, with the potential for further assimilation and isotopic imprinting during staging at upper crustal depths.

Geochemical tracers suggest that the primitiveness of flood basalt magmas in some provinces increased over time (Yu *et al.*, 2015), contrary to our expectation that

assimilation should increase with time as magmas heat the crust (Karlstrom *et al.*, 2010). Yu et al. (2015) propose that this discrepancy may result from the development of cumulate rinds that separate the wall rock from hot magma. Although we do not model this process here, we do not expect such cumulate rinds to impede assimilation of roof rocks unless crystallization of relatively low-density plagioclase predominates.

One defining feature of continental flood basalt provinces is the cessation of eruptions after 10^5 - 10^6 years. Volcanism often includes a main phase that is brief relative to the timescale for arrival of a plume head and that can encompass multiple distinct episodes of exceptionally intense magmatism (e.g., Hooper *et al.*, 2007; Chenet *et al.*, 2008; Karlstrom and Richards, 2011; Burgess and Bowring, 2015). Consequently variations in melt supply from partial melting of the mantle cannot fully explain onset and cessation of main phase volcanism (Karlstrom and Richards, 2011). Karlstrom and Richards (2011) proposed that heating of the country rocks and onset of thermally activated creep might set the timescale during which magmas are eruptible. Viscous creep cannot alleviate buoyancy overpressure. However, because exsolving volatiles can escape into the permeable country rock, either high rates of buoyancy addition or external perturbations are required to render deep flood basalt magmas eruptible. As melt injection and buoyancy addition decline, large volumes of molten and buoyant magma may be stranded at the Moho or in the lower crust in a near-eruptible state. Relatively small external stresses such as shifting regional tectonic stresses (e.g., White and McKenzie, 1989) may then be sufficient to cause ascent and eruption of magmas that would otherwise freeze at the Moho or in the lower crust.

4.2 Implications for environmental consequences of flood basalt magmatism

Some flood basalt eruptions coincide with periods of major environmental deterioration (Zhou *et al.*, 2002; Blackburn *et al.*, 2013; Burgess *et al.*, 2014; Schoene *et al.*, 2015; Renne *et al.*, 2015; Burgess and Bowring, 2015), but the severity of environmental stress appears to vary widely (Wignall, 2001). Siberian Traps volcanism coincided within geochronologic uncertainty with the end-Permian mass extinction (Burgess *et al.*, 2014; Burgess and Bowring, 2015). The tempo of volcanism, which controls the rate of degassing, is a key determinant of climate and chemical perturbation (e.g., Burgess and Bowring, 2015; Schmidt *et al.*, 2015). Our modeling suggests that the dynamics of flood basalt eruptions may favor brief pulses of voluminous volcanism. These pulses could release large masses of carbon, sulfur, halogen, and trace metal species to the atmosphere, with a range of potential consequences for Earth systems (Figure 9). In this section we therefore summarize recent constraints on the tempo of Siberian Traps volcanism and the chronology of the Permo-Triassic environmental crisis in order to evaluate links between mantle and crustal magmatic processes, the tempo of degassing, and Permo-Triassic climate.

The marine end-Permian extinction was particularly severe among poorly buffered or heavily calcified organisms, implying that ocean acidification, warming, and anoxia contributed to the extinction (Knoll *et al.*, 2007; Payne and Clapham, 2012). Oxygen isotope measurements in conodonts suggest that low-latitude sea surface temperatures increased by 6–10 °C during the extinction interval (Chen *et al.*, 2015). A major negative carbon isotope excursion has been attributed to injection of isotopically

light carbon (Payne and Clapham, 2012), perhaps from sedimentary rocks intruded by the Siberian Traps (Svensen *et al.*, 2009; Cui *et al.*, 2015) or from recycled material in a Siberian mantle plume (Sobolev *et al.*, 2011). Clarkson *et al.* (2015) report a drop in ocean pH recorded in a carbonate section in the United Arab Emirates about 40 meters above the initial carbon isotope excursion; they suggest that assimilation of isotopically neutral Siberian carbonates contributed to a ~10,000 year pulse of CO₂ outgassing and ocean acidification with little perturbation of the carbon isotope record (Figure 9).

Our model predicts that if Siberian Traps magmas staged within carbon-rich upper crustal rocks, they could have released $10^{19} - 10^{20}$ g CO₂ (one to two orders of magnitude greater than the total mass of CO₂ in the present-day atmosphere) within ~10⁴ years. This predicted outgassing is consistent with the magnitude and timescale of CO₂ release necessary to cause short-lived but severe greenhouse conditions and ocean acidification as inferred from the geochemical proxy record (Cui *et al.*, 2015; Clarkson *et al.*, 2015).

The chronology predicted by our model underscores several outstanding questions. First, it is difficult to reconcile the negative carbon isotope excursion that immediately preceded the onset of the extinction with release of carbonate carbon $\delta^{13}\text{C}$ close to zero or mantle carbon with $\delta^{13}\text{C} \approx -5$ ‰ (Cui *et al.*, 2015). Second, as shown in Figure 9, the initial negative carbon isotope excursion occurred ~32 kyr prior to a rapid 10°C increase in global sea surface temperatures and ocean acidification (Clarkson *et al.*, 2015; Chen *et al.*, 2015). Thus the carbon, oxygen, and boron isotope records are consistent with an initial carbon cycle perturbation followed by subsequent large-scale carbon release and global warming (Cao *et al.*, 2009; Chen *et al.*, 2015). If carbon

injection is responsible for both the negative $\delta^{13}\text{C}$ excursion and the subsequent pulse of warming and ocean acidification (during an interval with stable carbonate $\delta^{13}\text{C}$), the $\delta^{13}\text{C}$ of the injected carbon must have varied from very negative values initially to carbon with $\delta^{13}\text{C} \approx 0$ ‰ driving ocean acidification (Clarkson *et al.*, 2015).

One set of explanations for the negative carbon isotope excursion invokes liberation of carbon from mantle reservoirs depleted in ^{13}C (Sobolev *et al.*, 2011; Paris *et al.*, 2016). An alternative explanation for the carbon, oxygen, and boron isotope data is that during Siberian Traps magmatism, thermogenic gases were released first because halocarbon generation occurs at temperatures of only 275 °C (Svensen *et al.*, 2009). It is thus reasonable to expect that thermogenic production of low $\delta^{13}\text{C}$ gas could begin quickly once basaltic magmas intrude hydrocarbon-bearing source rocks (Svensen *et al.*, 2009). In contrast, because carbonate assimilation requires much higher temperatures and latent heat to drive melting (Haynes, 2013), large-scale degassing of neutral carbon is expected after more prolonged magmatism, crustal heating, and injection of large volumes of magma.

Caldeira and Rampino (1990) relied on typical basaltic CO_2 concentrations to estimate flood basalt outgassing totaling $\sim 9 \times 10^{18}$ g, and predicted that the climate effects of flood basalt CO_2 should be modest. However, the diminishing solubility of CO_2 at crustal depths challenges petrologic attempts to quantify the total CO_2 budget (Wallace *et al.*, 2015). Melt inclusions do not faithfully record exsolved volatiles. Therefore if a magma is already CO_2 saturated, additional carbon introduced through assimilation may be difficult to detect (Black *et al.*, 2012). Finally, our results emphasize that fluids may decouple from their source melts, implying that even originally volatile-poor tholeiitic

magmas might potentially release large quantities of CO₂ and halogens when they erupt. We suggest that CO₂ estimates based on the volatile budget required to cause eruptions may provide a useful and independent perspective (Lange, 2002), though such estimates also incorporate uncertainties related to assimilated lithologies, mechanical properties limiting chamber overpressure, and the composition of the mantle source. Future carbon cycle and climate modeling should consider rapid carbon release that may reach or exceed 10²⁰ g CO₂.

5. Conclusions

We present results from a one-dimensional model of flood basalt plumbing systems in which we focus on the fate of volatiles and their role in determining magmatic eruptibility. We consider the linked evolution of mantle melting, melt accumulation at the Moho or in the lower crust, and upper crustal magma chambers. We find that buoyancy from volatile exsolution is sufficient to cause eruption of magmas from Moho or lower crustal depth, and that the rate at which buoyancy accumulates relative to the rate at which magma accumulates regulates the eruptive tempo at the surface. For less buoyant magmas, upper crustal staging and assimilation further modulate eruptibility.

We suggest a framework for understanding how mantle melting histories that vary from flood basalt province to flood basalt province result in diverse eruption dynamics and consequent impacts on climate. Specifically, we predict that low degrees of partial melting will result in frequent eruptions of smaller volumes of alkaline magmas that experience limited interaction with crustal material. Higher degrees of partial melting will

result in episodes of voluminous, relatively homogeneous volcanism, separated by
hiatuses. In the Siberian Traps, we suggest that this voluminous magmatism was
accompanied by extensive crustal staging, assimilation, and intense pulses of degassing
of CO₂ and other assimilated volatiles. We expect volatile-poor melts to remain at the
Moho or in the lower crust as near-eruptible, primed, but slowly freezing magma bodies.
The eruptive dynamics predicted by our model are broadly consistent with available
constraints on the tempo, extrusive fraction, and petrogenesis of Phanerozoic flood
basalts.

Although petrologic resources such as melt inclusions record snapshots of
dissolved volatile concentrations at the time of entrapment (Black *et al.*, 2012), they
yield incomplete information about coexisting fluid or vapor phases (e.g., Métrich and
Wallace, 2008; Wallace *et al.*, 2015). The eruptibility of flood basalt magmas provides an
independent lower bound on the abundance of pre-eruptive volatiles (Lange, 2002). The
fate and budget of volatiles (especially CO₂) governs both flood basalt eruptibility and
environmental consequences. Furthermore, the environmental effects of CO₂ and SO₂
degassing depend crucially on the tempo of magmatism as well as the magnitude of
degassing (Figure 9). We therefore suggest that understanding how eruptions occur may
place an important constraint on the ecological ramifications of flood basalt magmatism.

Acknowledgments

The authors acknowledge support from the Open Earth Systems project funded by
National Science Foundation grant EAR-1135382.

FIGURES AND CAPTIONS

Figure 1. A) Schematic diagram of the lithospheric plumbing of a flood basalt province, modified from Richards et al. (2015). B) The processes considered in the model.

Figure 3. Normalized Gd/Yb ratio for Noril'sk lavas; data from Wooden et al. (1993) normalized to Hofmann (1988). The decline in Gd/Yb implies a decrease in the depth of melting. The black line is a moving average.

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Figure 4. Peridotite melt fraction calculated with the parameterization of Katz et al. (2003). Note that the mantle source for the Siberian Traps has been hypothesized to contain a significant pyroxenite component (e.g., Sobolev et al., 2011), which could melt at lower temperatures and/or higher pressures than those shown here. The white circle indicates the onset of melting and the black arrow indicates the approximate trajectory with time. Siberian meimechites (green oval) have been experimentally constrained to an origin at 5.5 GPa and 1550-1700 °C (Elkins-Tanton *et al.*, 2007).

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Figure 5. Evolution of buoyancy overpressure in coupled A) upper crustal chambers and B) Moho-depth or lower crustal chambers with variable assumed mantle CO₂ and with versus without accounting for bubble coalescence and rise.

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Figure 6. The thickness of magma A) erupted to the surface, B) in the upper crust, and C) residing near the base of the crust, for ten model realizations, including the thickness of frozen or immobile magma. D) Melt production (black curve) and melt fraction (gray curve) produced in the mantle, for a single representative simulation. The maximum melt fraction in each simulation is selected from a Gaussian distribution with a mean of 0.1 ± 0.0125 .

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Figure 7. Overpressure regimes in a laccolith-shaped magma reservoir at 36 km depth. Dashed and solid black lines indicate recharge and country rock conditions at which the reservoir can reach 10 MPa overpressure due to elastic stresses in the overlying crust, for a range of laccolith diameters from 10 to 100 km. Assuming a reservoir diameter of 10 km or more, the magma reservoirs in our simulations evolve quickly towards the viscous regime. Here we show the evolution of a chamber at 36 km depth from a single representative simulation.

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Figure 8. A) Cumulative erupted volume across ten simulations, scaled to achieve a total erupted volume of 2×10^6 km³. B) Cumulative CO₂ release; light gray shaded area denotes fraction of CO₂ from carbonate assimilation, dark gray shaded area denotes fraction of CO₂ from the mantle.

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Figure 9. Earth system consequences of volcanic eruptions across a range of eruption magnitudes and durations. During pulses of flood basalt volcanism, release of carbon, halogen, and trace metal species in conjunction with sulfur may trigger a range of perturbations in climate, atmospheric and ocean chemistry, weathering, and hydrology. Among these, the most ecologically consequential processes remain to be determined. Here, maximum plume heights for fissure eruptions are estimated using equations from Stothers et al. (1986), and for brief explosive eruptions are approximated after Newhall and Self (1982). Toba mass and duration are from Costa et al. (2014). Pinatubo mass and climactic duration are from Self (2006). Laki mass and duration are from Thordarson and Self (1993). Mass and duration for the Deccan DG6 directional group are from Chenet et al. (2008). Campanian Ignimbrite mass and duration are from Costa et al. (2012).

Figure 10. A) Permo-Triassic boundary temperature record from oxygen isotopes in conodonts (Chen et al., 2015; with temperatures calculated according to Lecuyer et al., 2013), ocean acidification record derived from boron isotopes (Clarkson et al., 2015), carbon isotope record (Cao et al., 2009), and geochronologic data from the Siberian Traps (Burgess and Bowring, 2015). Modified from Burgess and Bowring (2015). B) Proposed flood basalt eruptive regimes, which we offer as a partial explanation for the tempo and sequence of environmental perturbations during the Permo-Triassic.

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References

- 639 Arndt, N. T., Czamanske, G. K., Wooden, J. L., Fedorenko, V. A., 1993. Mantle and crustal
640 contributions to continental flood volcanism. *Tectonophysics*. 223, 39-52.
- 641 Arndt, N., Chauvel, C., Czamanske, G., Fedorenko, V., 1998. Two mantle sources, two plumbing
642 systems: tholeiitic and alkaline magmatism of the Maymecha River basin, Siberian flood volcanic
643 province. *Contributions to Mineralogy and Petrology*. 133, 297-313.
- 644 Black, B. A., Elkins-Tanton, L. T., Rowe, M. C., Peate, I. U., 2012. Magnitude and consequences
645 of volatile release from the Siberian Traps. *Earth and Planetary Science Letters*. 317, 363-373.
- 646 Black, B. A., Hauri, E. H., Elkins-Tanton, L. T., Brown, S. M., 2014a. Sulfur isotopic evidence
647 for sources of volatiles in Siberian Traps magmas. *Earth and Planetary Science Letters*. 394, 58-
648 69.
- 649 Black, B. A., Lamarque, J., Shields, C. A., Elkins-Tanton, L. T., Kiehl, J. T., 2014b. Acid rain
650 and ozone depletion from pulsed Siberian Traps magmatism. *Geology*. 42, 67-70.
- 651 Black, B. A. and Manga, M., 2016. The eruptibility of magmas at Tharsis and Syrtis Major on
652 Mars. *Journal of Geophysical Research: Planets*.
- 653 Blackburn, T. J., Olsen, P. E., Bowring, S. A., McLean, N. M., Kent, D. V., Puffer, J., McHone,
654 G., Rasbury, E. T., Et-Touhami, M., 2013. Zircon U-Pb geochronology links the end-Triassic
655 extinction with the Central Atlantic Magmatic Province. *Science (New York, N.Y.)*. 340, 941-
656 945.
- 657 Braitenberg, C. and Ebbing, J., 2009. New insights into the basement structure of the West
658 Siberian Basin from forward and inverse modeling of GRACE satellite gravity data. *Journal of*
659 *Geophysical Research: Solid Earth*. 114, .
- 660 Bredehoeft, J. D. and Ingebritsen, S. E., 1990. Degassing of carbon dioxide as a possible source
661 of high pore pressures in the crust. *The Role of Fluids in Crustal Processes*. 158-164.
- 662 Bryan, S. E., Peate, I. U., Peate, D. W., Self, S., Jerram, D. A., Mawby, M. R., Marsh, J. G.,
663 Miller, J. A., 2010. The largest volcanic eruptions on Earth. *Earth-Science Reviews*. 102, 207-
664 229.
- 665 Burgess, S. D. and Bowring, S. A., 2015. High-precision geochronology confirms voluminous
666 magmatism before, during, and after Earth's most severe extinction. *Science Advances*. 1,
667 e1500470.
- 668 Burgess, S. D., Bowring, S., Shen, S., 2014. High-precision timeline for Earth's most severe
669 extinction. *Proceedings of the National Academy of Sciences*. 111, 3316.

- 670 Bürgmann, R. and Dresen, G., 2008. Rheology of the lower crust and upper mantle: Evidence
671 from rock mechanics, geodesy, and field observations. *Annual Review of Earth and Planetary*
672 *Sciences*. 36, 531.
- 673 Caldeira, K. and Rampino, M. R., 1990. Carbon dioxide emissions from Deccan volcanism and a
674 K/T boundary greenhouse effect. *Geophysical Research Letters*. 17, 1299-1302.
- 675 Campbell, I. H. and Griffiths, R. W., 1990. Implications of mantle plume structure for the
676 evolution of flood basalts. *Earth and Planetary Science Letters*. 99, 79-93.
- 677 Campbell, I. H., Czamanske, G. K., Fedorenko, V. A., Hill, R. I., Stepanov, V., 1992.
678 Synchronism of the Siberian Traps and the Permian-Triassic Boundary. *Science*. 258, 1760-1763.
- 679 Cao, C., Love, G. D., Hays, L. E., Wang, W., Shen, S., Summons, R. E., 2009. Biogeochemical
680 evidence for euxinic oceans and ecological disturbance presaging the end-Permian mass
681 extinction event. *Earth and Planetary Science Letters*. 281, 188-201.
- 682 Caricchi, L., Annen, C., Blundy, J., Simpson, G., Pinel, V., 2014. Frequency and magnitude of
683 volcanic eruptions controlled by magma injection and buoyancy. *Nature Geoscience*. 7, 126-130.
- 684 Cashman, K. V. and Giordano, G., 2014. Calderas and magma reservoirs. *Journal of Volcanology*
685 *and Geothermal Research*. 288, 28-45.
- 686 Chen, J., Shen, S., Li, X., Xu, Y., Joachimski, M. M., Bowring, S. A., Erwin, D. H., Yuan, D.,
687 Chen, B., Zhang, H., 2015. High-resolution SIMS oxygen isotope analysis on conodont apatite
688 from South China and implications for the end-Permian mass extinction. *Palaeogeography,*
689 *Palaeoclimatology, Palaeoecology*.
- 690 Chenet, A., Courtillot, V., Fluteau, F., Gérard, M., Quidelleur, X., Khadri, S., Subbarao, K.,
691 Thordarson, T., 2009. Determination of rapid Deccan eruptions across the Cretaceous- Tertiary
692 boundary using paleomagnetic secular variation: 2. Constraints from analysis of eight new
693 sections and synthesis for a 3500- m- thick composite section. *Journal of Geophysical Research:*
694 *Solid Earth* (1978–2012). 114, .
- 695 Chenet, A., Fluteau, F., Courtillot, V., Gérard, M., Subbarao, K., 2008. Determination of rapid
696 Deccan eruptions across the Cretaceous- Tertiary boundary using paleomagnetic secular
697 variation: Results from a 1200- m- thick section in the Mahabaleshwar escarpment. *Journal of*
698 *Geophysical Research: Solid Earth*. 113, .
- 699 Clarkson, M. O., Kasemann, S. A., Wood, R. A., Lenton, T. M., Daines, S. J., Richoz, S.,
700 Ohnemüller, F., Meixner, A., Poulton, S. W., Tipper, E. T., 2015. Ocean acidification and the
701 Permo-Triassic mass extinction. *Science* (New York, N.Y.). 348, 229-232.
- 702 Costa, A., Folch, A., Macedonio, G., Giaccio, B., Isaia, R., Smith, V., 2012. Quantifying volcanic
703 ash dispersal and impact of the Campanian Ignimbrite super- eruption. *Geophysical Research*
704 *Letters*. 39, .

705 Costa, A., Smith, V. C., Macedonio, G., Matthews, N. E., 2014. The magnitude and impact of the
706 Youngest Toba Tuff super-eruption. *Frontiers in Earth Science*. 2, 16.

707 Courtillot, V. E. and Renne, P. R., 2003. On the ages of flood basalt events. *Comptes Rendus*
708 *Geoscience*. 335, 113-140.

709 Cox, K., 1988. Numerical modelling of a randomized RTF magma chamber: a comparison with
710 continental flood basalt sequences. *Journal of Petrology*. 29, 681-697.

711 Cox, K., 1980. A model for flood basalt vulcanism. *Journal of Petrology*. 21, 629-650.

712 Cui, Y., Kump, L., Ridgwell, A., 2015. Spatial and Temporal Patterns of Ocean Acidification
713 During the End-Permian Mass Extinction—An Earth System Model Evaluation.

714 Dasgupta, R. and Hirschmann, M. M., 2010. The deep carbon cycle and melting in Earth's
715 interior. *Earth and Planetary Science Letters*. 298, 1-13.

716 de Silva, S. L. and Gregg, P. M., 2014. Thermomechanical feedbacks in magmatic systems:
717 Implications for growth, longevity, and evolution of large caldera-forming magma reservoirs and
718 their supereruptions. *Journal of Volcanology and Geothermal Research*. 282, 77-91.

719 Degruyter, W. and Huber, C., 2014. A model for eruption frequency of upper crustal silicic
720 magma chambers. *Earth and Planetary Science Letters*. 403, 117-130.

721 DePaolo, D. J. and Manga, M., 2003. Deep origin of hotspots-the mantle plume model.
722 *SCIENCE-NEW YORK THEN WASHINGTON*-. 920-920.

723 Elkins-Tanton, L. T., Draper, D. S., Agee, C. B., Jewell, J., Thorpe, A., Hess, P., 2007. The last
724 lavas erupted during the main phase of the Siberian flood volcanic province: results from
725 experimental petrology. *Contributions to Mineralogy and Petrology*. 153, 191-209.

726 Elkins-Tanton, L. T. and Hager, B. H., 2000. Melt intrusion as a trigger for lithospheric
727 foundering and the eruption of the Siberian flood basalts. *Geophysical Research Letters*. 27,
728 3937-3940.

729 Farnetani, C. G., Richards, M. A., Ghiorso, M. S., 1996. Petrological models of magma evolution
730 and deep crustal structure beneath hotspots and flood basalt provinces. *Earth and Planetary*
731 *Science Letters*. 143, 81-94.

732 Fedorenko, V., Czamanske, G., Zen'ko, T., Budahn, J., Siems, D., 2000. Field and geochemical
733 studies of the melilite-bearing Arydzhangsky Suite, and an overall perspective on the Siberian
734 alkaline-ultramafic flood-volcanic rocks. *International Geology Review*. 42, 769-804.

735 Foulger, G. R. and Natland, J. H., 2003. *Geology*. Is "hotspot" volcanism a consequence of plate
736 tectonics? *Science (New York, N.Y.)*. 300, 921-922.

737 Gerlach, T. M., 1986. Exsolution of H₂O, CO₂, and S during eruptive episodes at Kilauea
738 Volcano, Hawaii. *Journal of Geophysical Research: Solid Earth (1978–2012)*. 91, 12177-12185.

739 Ghiorso, M. S. and Sack, R. O., 1995. Chemical mass transfer in magmatic processes IV. A
740 revised and internally consistent thermodynamic model for the interpolation and extrapolation of
741 liquid-solid equilibria in magmatic systems at elevated temperatures and pressures. *Contributions*
742 *to Mineralogy and Petrology*. 119, 197-212.

743 Glazner, A. F., Bartley, J. M., Coleman, D. S., Gray, W., Taylor, R. Z., 2004. Are plutons
744 assembled over millions of years by amalgamation from small magma chambers? *GSA Today*.
745 14, 4-12.

746 Grasby, S. E., Sanei, H., Beauchamp, B., 2011. Catastrophic dispersion of coal fly ash into oceans
747 during the latest Permian extinction. *Nature Geoscience*. 4, 104-107.

748 Gualda, G. A., Ghiorso, M. S., Lemons, R. V., Carley, T. L., 2012. Rhyolite-MELTS: a modified
749 calibration of MELTS optimized for silica-rich, fluid-bearing magmatic systems. *Journal of*
750 *Petrology*. 53, 875-890.

751 Halliday, A. N., 2013. The origins of volatiles in the terrestrial planets. *Geochimica Et*
752 *Cosmochimica Acta*. 105, 146-171.

753 Hauri, E. H., Gaetani, G. A., Green, T. H., 2006. Partitioning of water during melting of the
754 Earth's upper mantle at H₂O-undersaturated conditions. *Earth and Planetary Science Letters*.
755 248, 715-734.

756 Haynes, W.M., 2013. *CRC handbook of chemistry and physics*. CRC press, .

757 Hofmann, A. W., 1988. Chemical differentiation of the Earth: the relationship between mantle,
758 continental crust, and oceanic crust. *Earth and Planetary Science Letters*. 90, 297-314.

759 Hooper, P. R., Camp, V. E., Reidel, S. P., Ross, M. E., 2007. The origin of the Columbia River
760 flood basalt province: Plume versus nonplume models. *Geological Society of America Special*
761 *Papers*. 430, 635-668.

762 Houghton, R., 2007. Balancing the global carbon budget. *Annu.Rev.Earth Planet.Sci.* 35, 313-
763 347.

764 Iacono-Marziano, G., Morizet, Y., Le Trong, E., Gaillard, F., 2012. New experimental data and
765 semi-empirical parameterization of H₂O–CO₂ solubility in mafic melts. *Geochimica Et*
766 *Cosmochimica Acta*. 97, 1-23.

767 James, E. R., Manga, M., Rose, T. P., 1999. CO₂ degassing in the Oregon Cascades. *Geology*.
768 27, 823-826.

769 Jellinek, A. M. and DePaolo, D. J., 2003. A model for the origin of large silicic magma chambers:
770 precursors of caldera-forming eruptions. *Bulletin of Volcanology*. 65, 363-381.

771 Kamo, S. L., Czamanske, G. K., Amelin, Y., Fedorenko, V. A., Davis, D. W., Trofimov, V. R.,
772 2003. Rapid eruption of Siberian flood-volcanic rocks and evidence for coincidence with the
773 Permian-Triassic boundary and mass extinction at 251 Ma. *Earth and Planetary Science Letters*.
774 214, 75-91.

775 Karlstrom, L., Dufek, J., Manga, M., 2010. Magma chamber stability in arc and continental crust.
776 *Journal of Volcanology and Geothermal Research*. 190, 249-270.

777 Karlstrom, L. and Richards, M., 2011. On the evolution of large ultramafic magma chambers and
778 timescales for flood basalt eruptions. *Journal of Geophysical Research: Solid Earth* (1978–2012).
779 116, .

780 Katz, R. F., Spiegelman, M., Langmuir, C. H., 2003. A new parameterization of hydrous mantle
781 melting. *Geochemistry, Geophysics, Geosystems*. 4, .

782 Keller, T., May, D. A., Kaus, B. J., 2013. Numerical modelling of magma dynamics coupled to
783 tectonic deformation of lithosphere and crust. *Geophysical Journal International*. 195, 1406-1442.

784 Knoll, A. H., Bambach, R. K., Payne, J. L., Pruss, S., Fischer, W. W., 2007. Paleophysiology and
785 end-Permian mass extinction. *Earth and Planetary Science Letters*. 256, 295-313.

786 Kontorovich, A., Khomenko, A., Burshtein, L., Likhanov, I., Pavlov, A., Staroseltsev, V., Ten,
787 A., 1997. Intense basic magmatism in the Tunguska petroleum basin, eastern Siberia, Russia.
788 *Petroleum Geoscience*. 3, 359-369.

789 Lange, R. A., 2002. Constraints on the preeruptive volatile concentrations in the Columbia River
790 flood basalts. *Geology*. 30, 179-182.

791 Lightfoot, P. C., Hawkesworth, C. J., Hergt, J., Naldrett, A. J., Gorbachev, N. S., Fedorenko, V.
792 A., Doherty, W., 1993. Remobilization of the continental lithosphere by a mantle plume: Major-,
793 trace-element, and Sr-, Nd- and Pb-isotopic evidence from picritic and tholeiitic lavas of the
794 Noril'sk district, Siberia. *Contributions to Mineralogy and Petrology*. 114, 171-188.

795 Manga, M. and Stone, H., 1995. Low Reynolds number motion of bubbles, drops and rigid
796 spheres through fluid–fluid interfaces. *Journal of Fluid Mechanics*. 287, 279-298.

797 Manning, C. and Ingebritsen, S., 1999. Permeability of the continental crust: Implications of
798 geothermal data and metamorphic systems. *Reviews of Geophysics*. 37, 127-150.

799 Marsh, B., 1981. On the crystallinity, probability of occurrence, and rheology of lava and magma.
800 *Contributions to Mineralogy and Petrology*. 78, 85-98.

801 Métrich, N. and Wallace, P. J., 2008. Volatile abundances in basaltic magmas and their degassing
802 paths tracked by melt inclusions. *Reviews in Mineralogy and Geochemistry*. 69, 363-402.

803 Meyerhoff, A. A., 1980. Geology and petroleum fields in Proterozoic and Lower Cambrian strata,
804 Lena-Tunguska petroleum province, eastern Siberia, USSR.

805 Newhall, C. G. and Self, S., 1982. The volcanic explosivity index (VEI) an estimate of explosive
806 magnitude for historical volcanism. *Journal of Geophysical Research: Oceans*. 87, 1231-1238.

807 O'Hara, M., 1977. Geochemical evolution during fractional crystallisation of a periodically
808 refilled magma chamber. *Nature*. 266, 503-507.

809 Paris, G., Donnadieu, Y., Beaumont, V., Fluteau, F., Goddris, Y., 2016. Geochemical
810 consequences of intense pulse-like degassing during the onset of the Central Atlantic Magmatic
811 Province. *Palaeogeography, Palaeoclimatology, Palaeoecology*. 441, 74-82.

812 Pavlov, V., Fluteau, F., Veselovskiy, R., Fetisova, A., Latyshev, A., 2011. Secular geomagnetic
813 variations and volcanic pulses in the Permian-Triassic traps of the Norilsk and Maimecha-Kotui
814 provinces. *Izvestiya, Physics of the Solid Earth*. 47, 402-417.

815 Payne, J. L. and Clapham, M. E., 2012. End-Permian mass extinction in the oceans: An ancient
816 analog for the twenty-first century? *Annual Review of Earth and Planetary Sciences*. 40, 89-111.

817 Reichow, M. K., Pringle, M. S., Al'Mukhamedov, A. I., Allen, M. B., Andreichev, V. L., Buslov,
818 M. M., Davies, C. E., Fedoseev, G. S., Fitton, J. G., Inger, S., Medvedev, A. Y., Mitchell, C.,
819 Puchkov, V. N., Safonova, I. Y., Scott, R. A., Saunders, A. D., 2009. The timing and extent of the
820 eruption of the Siberian Traps large igneous province: Implications for the end-Permian
821 environmental crisis. *Earth and Planetary Science Letters*. 277, 9-20.

822 Renne, P. R., Sprain, C. J., Richards, M. A., Self, S., Vanderkluysen, L., Pande, K., 2015. State
823 shift in Deccan volcanism at the Cretaceous-Paleogene boundary, possibly induced by impact.
824 *Science*. 350, 76-78.

825 Renne, P. R. and Basu, A. R., 1991. Rapid eruption of the siberian traps flood basalts at the
826 permo-triassic boundary. *Science (New York, N.Y.)*. 253, 176-179.

827 Richards, M. A., Alvarez, W., Self, S., Karlstrom, L., Renne, P. R., Manga, M., Sprain, C. J.,
828 Smit, J., Vanderkluysen, L., Gibson, S. A., 2015. Triggering of the largest Deccan eruptions by
829 the Chicxulub impact. *Geological Society of America Bulletin*. B31167. 1.

830 Richards, M. A., Duncan, R. A., Courtillot, V. E., 1989. Flood basalts and hot-spot tracks: plume
831 heads and tails. *Science (New York, N.Y.)*. 246, 103-107.

832 Ridley, V. A. and Richards, M. A., 2010. Deep crustal structure beneath large igneous provinces
833 and the petrologic evolution of flood basalts. *Geochemistry, Geophysics, Geosystems*. 11, .

834 Rubin, A. M., 1995. Propagation of magma-filled cracks. *Annual Review of Earth and Planetary
835 Sciences*. 23, 287-336.

836 Schmidt, A., Skeffington, R. A., Thordarson, T., Self, S., Forster, P. M., Rap, A., Ridgwell, A.,
837 Fowler, D., Wilson, M., Mann, G. W., 2015. Selective environmental stress from sulphur emitted
838 by continental flood basalt eruptions. *Nature Geoscience*.

839 Schoene, B., Samperton, K. M., Eddy, M. P., Keller, G., Adatte, T., Bowring, S. A., Khadri, S. F.,
840 Gertsch, B., 2015. Earth history. U-Pb geochronology of the Deccan Traps and relation to the
841 end-Cretaceous mass extinction. *Science (New York, N.Y.)*. 347, 182-184.

842 Self, S., Schmidt, A., Mather, T., 2014. Emplacement characteristics, time scales, and volcanic
843 gas release rates of continental flood basalt eruptions on Earth. *Geological Society of America
844 Special Papers*. 505, SPE505-16.

- 845 Self, S., 2006. The effects and consequences of very large explosive volcanic eruptions.
846 Philosophical Transactions. Series A, Mathematical, Physical, and Engineering Sciences. 364,
847 2073-2097.
- 848 Sobolev, A., Krivolutsкая, N., Kuzmin, D., 2009. Petrology of the parental melts and mantle
849 sources of Siberian trap magmatism. *Petrology*. 17, 253-286.
- 850 Sobolev, S. V., Sobolev, A. V., Kuzmin, D. V., Krivolutsкая, N. A., Petrunin, A. G., Arndt, N.
851 T., Radko, V. A., Vasiliev, Y. R., 2011. Linking mantle plumes, large igneous provinces and
852 environmental catastrophes. *Nature*. 477, 312-U80.
- 853 Stothers, R. B., Wolff, J. A., Self, S., Rampino, M. R., 1986. Basaltic fissure eruptions, plume
854 heights, and atmospheric aerosols. *Geophysical Research Letters*. 13, 725-728.
- 855 Svensen, H., Planke, S., Polozov, A. G., Schmidbauer, N., Corfu, F., Podladchikov, Y. Y.,
856 Jamtveit, B., 2009. Siberian gas venting and the end-Permian environmental crisis. *Earth and*
857 *Planetary Science Letters*. 277, 490-500.
- 858 Tait, S., Jaupart, C., Vergnolle, S., 1989. Pressure, gas content and eruption periodicity of a
859 shallow, crystallising magma chamber. *Earth and Planetary Science Letters*. 92, 107-123.
- 860 Thordarson, T. and Self, S., 1993. The Laki (Skaftár Fires) and Grímsvötn eruptions in 1783–
861 1785. *Bulletin of Volcanology*. 55, 233-263.
- 862 Wallace, P. J., Kamenetsky, V. S., Cervantes, P., 2015. Melt inclusion CO₂ contents, pressures of
863 olivine crystallization, and the problem of shrinkage bubbles. *American Mineralogist*. 100, 787-
864 794.
- 865 Weis, P., Driesner, T., Heinrich, C. A., 2012. Porphyry-copper ore shells form at stable pressure-
866 temperature fronts within dynamic fluid plumes. *Science (New York, N.Y.)*. 338, 1613-1616.
- 867 White, R. and McKenzie, D., 1989. Magmatism at rift zones: the generation of volcanic
868 continental margins and flood basalts. *Journal of Geophysical Research: Solid Earth (1978–*
869 *2012)*. 94, 7685-7729.
- 870 Wignall, P., 2001. Large igneous provinces and mass extinctions. *Earth-Science Reviews*. 53, 1-
871 33.
- 872 Wolff, J., Ramos, F., Hart, G., Patterson, J., Brandon, A., 2008. Columbia River flood basalts
873 from a centralized crustal magmatic system. *Nature Geoscience*. 1, 177-180.
- 874 Wooden, J. L., Czamanske, G. K., Fedorenko, V. A., Arndt, N. T., Chauvel, C., Bouse, R. M.,
875 King, B. W., Knight, R. J., Siems, D. F., 1993. Isotopic and trace-element constraints on mantle
876 and crustal contributions to Siberian continental flood basalts, Noril'sk area, Siberia. *Geochimica*
877 *Et Cosmochimica Acta*. 57, 3677-3704.
- 878 Yu, X., Lee, C. A., Chen, L., Zeng, G., 2015. Magmatic recharge in continental flood basalts:
879 Insights from the Chifeng igneous province in Inner Mongolia. *Geochemistry, Geophysics,*
880 *Geosystems*. 16, 2082-2096.

- 881 Zharkov, M.A., 1984. Paleozoic salt bearing formations of the world. Springer-Verlag, Berlin.
- 882 Zhou, M., Malpas, J., Song, X., Robinson, P. T., Sun, M., Kennedy, A. K., Leshner, C. M., Keays,
883 R. R., 2002. A temporal link between the Emeishan large igneous province (SW China) and the
884 end-Guadalupian mass extinction. *Earth and Planetary Science Letters*. 196, 113-122.
- 885
- 886