Climate forcing by iron fertilization from repeated ignimbrite eruptions: The icehouse–silicic large igneous province (SLIP) hypothesis

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ABSTRACT

During middle Eocene to middle Miocene time, development of the Cenozoic icehouse was coincident with a prolonged episode of explosive silicic volcanism, the ignimbrite flare-up of southwestern North America. We present geochronologic and biogeochemical data suggesting that, prior to the establishment of full glacial conditions with attendant increased eolian dust emission and oceanic upwelling, iron fertilization by great volumes of silicic volcanic ash was an effective climatic forcing mechanism that helped to establish the Cenozoic icehouse. Most Phanerozoic cool-climate episodes were coeval with major explosive volcanism in silicic large igneous provinces, suggesting a common link between these phenomena.

INTRODUCTION

The climate of the Earth has alternated between warm and cool regimes throughout the Phanerozoic Eon. Major continental glaciations occurred in the Late Ordovician, the Late Devonian–Permian, and in the Cenozoic. Other episodes of global cooling without evidence for polar ice caps occurred in the Middle to Late Jurassic and the Early Cretaceous. Explanations of cool climatic regimes have included the effects of continental drift, orbital variations, impact events, and changes in cosmic ray flux (Frakes et al., 1992; Shaviv and Veizer, 2003). Climatic cooling resulting from decreased atmospheric CO₂ concentration has been attributed to increased marine photosynthetic productivity or enhanced silicate weathering in orogens. Most previous studies of climate modification by volcanism have focused on the effects of increased atmospheric CO₂ from eruption of voluminous mafic lavas or the relationship between atmospheric aerosols and insolation. Here we examine the potential impact on climate of oceanic iron fertilization by volcanic ash from repeated major silicic eruptions.

Iron is a micronutrient necessary for the synthesis of chlorophyll (Martin et al., 1991), and is thus critical to primary photosynthetic productivity in the ocean. In coastal marine environments, dissolved iron is supplied mostly from nearby terrigenous sources and by upwelling circulation. In the central ocean basins, the principal source of iron to the euphotic zone is eolian dust, derived mostly from deflation of desert regions (Jickells et al., 2005; Patra et al., 2007). Large parts of the open ocean (~30% of the global ocean today) are high-nutrient, low-chlorophyll (HNLC) areas where primary photosynthetic productivity is anomalously low and is limited primarily by the availability of iron. Modern HNLC areas occur mostly in the Southern Ocean, the equatorial Pacific Ocean, and the North Pacific Ocean. The distribution of HNLC areas in ancient oceans is poorly understood. Iron-limited HNLC areas may have been more widespread during greenhouse intervals because (1) lower pole to equator temperature gradients during warm climate episodes cause diminished global wind velocities, and (2) greenhouse conditions favor warmer and wetter conditions in continental interiors (e.g., Dupont-Nivet et al., 2007). These factors favor less eolian deflation and transportation of iron-bearing dust to the open ocean.

A sporadic source of dissolved iron to HNLC areas is volcanic ash, which contains iron within reactive vitric particles and as adsorbed metal salts. These salts dissolve within minutes upon contact with seawater and thus supply critical metals directly to the euphotic zone (Frogner et al., 2001; Duggen et al., 2007). Iron fertilization may decrease oceanic (and subsequently atmospheric) CO₂ concentration by increasing the photosynthetic conversion of CO₂ to organic carbon (C₅₆) and settling and subsequent burial of a fraction of particulate C₅₆ allows for long-term reduction of atmospheric CO₂ concentration and global cooling.

Experiments have unequivocally demonstrated the effectiveness of iron fertilization to promote primary production in HNLC areas (Martin et al., 1994; Kolber et al., 1994; Boyd et al., 2000; Tsuda et al., 2003; Coale et al., 1996; Blain et al., 2007; Cassar et al., 2007). Export fluxes of particulate organic carbon from the surface mixed zone were low in several shipboard iron-addition experiments, possibly because of their small scale and short duration, and due to
dilution effects (see summaries in Buesseler et al., 2004; de Baar et al., 2005). Observation of natural iron fertilization in the Southern Ocean, however, has indicated a carbon export ratio at least ten times greater than earlier shipboard experiments (Blain et al., 2007).

A relationship between atmospheric CO$_2$ and explosive volcanic eruptions is suggested by the Mauna Loa atmospheric observatory record (Fig. 1). Two of the four largest eruptions since 1958 (Agung in 1963 and Pinatubo in 1991) were followed by pronounced decreases in CO$_2$ concentration. Only minor decreases in atmospheric CO$_2$ followed the eruptions of Mount St. Helens and El Chichón, possibly because most of the ash associated with these eruptions was deposited on land. The CO$_2$ anomaly that followed the ~5 km$^3$ eruption of Pinatubo is the largest in the record (Sarmiento, 1993) and was accompanied by an increase in atmospheric O$_2$ (Keeling et al., 1996). The post-Pinatubo increase in O$_2$ resulted from photosynthesis that may be largely the result of iron fertilization in the Southern Ocean (Watson, 1997).

Large igneous provinces (LIPs) are long-lived, intraplate volcano-plutonic provinces that have areal extents $>1 \times 10^5$ km$^2$ and igneous volumes $>1 \times 10^5$ km$^3$ (Bryan and Ernst, 2008). Most are mainly mafic in composition, but four Phanerozoic LIPs of silicic composition have so far been recognized (Bryan, 2007). These silicic large igneous provinces (SLIPs) consist mostly (>80%) of dacite and rhyolite, with rhyolite ignimbrite as the dominant volcanic rock. In contrast to their mafic counterparts, all known Phanerozoic SLIPs developed near continental margins (Bryan and Ernst, 2008; S.E. Bryan, 2008, written commun.), and thus were major sources of volcanic ash to adjacent oceanic basins.

Ignimbrite eruptions represent the largest and most explosive volcanic eruptions on Earth. Major ignimbrites have volumes of $10^2$–$10^4$ km$^3$. Plinian eruption columns and co-ignimbrite ash clouds are commonly tens of kilometers in height and can inject large volumes of volcanic ash into the stratosphere, where it persists for years and is distributed hemispherically or globally. In contrast, mafic volcanism generally is effusive, producing eruptions columns that intrude <5 km into the troposphere. The most recent major ignimbrite eruption was at Toba, Sumatra, ca. 75 ka ago. Toba erupted $\sim$2500 km$^3$ of dense rock equivalent (DRE) of ignimbrite. Cooling related to the Toba eruption lasted $\sim$1 ka or less (Zielinski et al., 1996; Huang et al. 2001). Much of the Toba ash was deposited in the Bay of Bengal (Rampino and Self, 1993), today an area in which primary productivity is not limited by the availability of iron.

Here we evaluate the potential effects of iron fertilization in relation to the youngest and best-preserved SLIP vis-à-vis the development of the global Cenozoic icehouse. We then examine the temporal relationships between cooling events and older Phanerozoic SLIPs for which age constraints and the seafloor record are less well known.

**PALEOGENE GLOBAL COOLING AND THE IGNIMBRITE FLARE-UP OF SOUTHWESTERN NORTH AMERICA**

A transition from greenhouse to icehouse conditions began in the early middle Eocene and was marked by increased δ$^18$O in calcite of benthic marine foraminifera (Fig. 2) that resulted from deep-water cooling and the accumulation of glacial ice. Approximately 15 Ma after its onset, Paleogene cooling was punctuated by the Oi-1 event (ca. 33.5 Ma ago, near the Eocene-Oligocene boundary), when major continental glaciation in Antarctica began. The Oi-1 positive carbon isotopic anomaly has been interpreted by many workers to record enhanced marine production and burial of C$_{org}$ that led to decreased atmospheric CO$_2$ and global cooling (Zachos et al., 1993; Salamy and Zachos, 1999; Diester-Haass and Zahn, 1996, 2001; Anderson and Delaney, 2005).

![Figure 1. Plot of atmospheric CO$_2$ anomaly at Mauna Loa Observatory, Hawaii, for the period 1958–1995, relative to the four largest volcanic eruptions during that period. The observed CO$_2$ anomaly is obtained by removing the seasonal signal and subtracting the industrial emissions curve from the Mauna Loa record (Keeling et al., 1995). Vertical red lines mark beginnings of eruption events, which were selected using the criteria of eruptive volume $\geq 1$ km$^3$ and Volcanic Explosivity Index of $\geq 4$ (Simkin and Siebert, 1994).](image-url)
The most intensively studied SLIP is the middle Eocene–middle Miocene ignimbrite flare-up (IFU) of southwestern North America (Fig. 3). IFU volcanism occurred ca. 50–16 Ma ago in an extensional volcanic belt ~3500 km in length in Mexico and the western USA. The volume of IFU ignimbrite was at least ~4 × 10⁵ km³ (Best and Christiansen, 1991), ~75% of which was erupted in the Sierra Madre Occidental of Mexico (Fig. 2). Within the Sierra Madre Occidental, prominent pulses of ignimbrite volcanism occurred ca. 46–43 Ma ago (~5 × 10⁴ km³ ignimbrite), 38–27 Ma ago (~2 × 10⁵ km³), and 24–18 Ma ago (~5 × 10⁴ km³) (Aguirre-Diaz and McDowell, 1991; Ferrari et al., 2002; McDowell and McIntosh, 2007; McDowell, 2007). Coeval major (>6 × 10⁴ km³) ignimbrite volcanism occurred in Afro-Arabia ca. 30–28 Ma ago (Ukstins Peate et al., 2003).

In the San Juan volcanic field of Colorado, where mapping and geochronologic analysis are reasonably complete, the average eruption volume of major ignimbrites during the IFU was ~600 km³ (Lipman, 2000). If this average ignimbrite volume is representative of the entire IFU province, then the IFU comprised ~700 major ignimbrite eruptions with an average interval between eruptions of ~40 ka. The interval between major eruptions

![Graph showing δ¹³C (%o) and δ¹⁸O (%o) with ignimbrite eruptive flux estimates for the IFU compared with deep-sea paleodepth oxygen and carbon isotopic anomalies from benthic foraminifera from more than 40 sites.](https://pubs.geoscienceworld.org/gsa/geosphere/article-pdf/5/3/315/3338739/i1553-040X-5-3-315.pdf)

Figure 2. Ignimbrite eruptive flux estimates for the ignimbrite flare-up (IFU) compared with the global deep-sea (>1000 m paleodepth) oxygen and carbon isotopic anomalies compiled from benthic foraminifera from more than 40 Deep Sea Drilling Project and Ocean Drilling Program sites (Zachos et al., 2001). Ignimbrite flux estimates for individual volcanic fields (colored lines) are derived from the age data and volume estimates of Lipman (2000), McIntosh et al. (1992), Best and Christiansen (1991), McIntosh and Bryan (2000), McDowell (2007), McDowell and McIntosh (2007), Ferrari et al. (2002), Chapin et al. (2004), Moye et al. (1988), and C.D. Henry (2008, written commun.). Black dashed line is the overall eruptive flux for the IFU. The atmospheric flux of elutriated volcanic ash during the IFU is assumed to be subequal to the ignimbrite eruptive flux.

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during peak IFU volcanism ca. 34–30 Ma ago was ~15 ka.

Crystal-enrichment studies of ignimbrites show that typically about half of the initial eruptive volume is represented by ignimbrite; thus, a similar volume of vitrically enriched ash was elutriated and dispersed by tropospheric and stratospheric winds during the eruption (Walker, 1981). Between 40 and 20 Ma ago, the location of the Intertropical Convergence Zone in the central Pacific Ocean was ~25°N (Hyeong et al., 2006, and references therein), due west of the central Sierra Madre Occidental. The Sierra Madre Occidental thus was largely within the zone of easterly trade winds, and much of the elutriated ash was blown westward into low-latitude areas of the Pacific Ocean (e.g., Ziegler et al., 2007), today an HNLC area. The average atmospheric emission of IFU ash during the interval 37–26 Ma ago was ~6 × 10¹³ g a⁻¹, assuming a volume of dispersed ash similar to the preserved ignimbrite volume (~2.7 × 10⁶ km³ DRE). This is ~3%–6% of modern annual global eolian dust emission (Zender et al., 2004). Large modern dust emissions, however, are mostly the result of post–late Miocene cooling and drying in the Northern Hemisphere (Rea, 1994) and anthropogenic effects (Neff et al., 2008). During the late Eocene and Oligocene, global eolian dust emissions were much less than in the late Neogene (Rea, 1994), and mass accumulation rates of IFU ash and eolian dust were subequal at Ocean Drilling Program (ODP) Site 1215 in the central equatorial Pacific (Ziegler et al., 2007).

Volcanic eruptions release acid gases and metals to the atmosphere as an aerosol phase. A portion of these aerosols adheres to volcanic ash as soluble metal salts. Based on the data of Frogner et al. (2001), rhyolitic ash contains ~6.0 × 10¹¹ g Fe per km³ DRE as adsorbed, rapidly soluble acid salts. In HNLC areas of the Southern Ocean, primary production from iron fertilization results in Fe/Corg ratios that vary by an order of magnitude (~2–20 µmol mol⁻¹; Cassar et al., 2007; Blain et al., 2007). This range of ratios indicates that adsorbed iron on ash deposited in iron-limited oceanic areas may cause excess production of ~2.6–26 × 10¹⁶ g Corg per km³ DRE of ash. By comparison, atmospheric emission of CO₂ during rhyolite eruptions is relatively small. Pre-eruptive rhyolite contains a few hundred ppm CO₂ (Anderson et al., 2000; Lui et al., 2006), about an order of magnitude less than basalt. Assuming complete degassing during eruption, rhyolite magmas emit ~10¹¹ g C (as CO₂) per km³ DRE.

Dissolution and alteration of vitric ash are additional potential sources of iron in marine environments. Rhyolitic glass typically contains ~1%–3% iron, as both Fe₂O₃ and FeO. Assuming (conservatively) an iron content of 1%, vitric ash contains ~2.5 × 10¹³ g Fe per km³ DRE, resulting in potential excess production of 1.1–11 × 10¹⁸ g Corg per km³ DRE of ash dissolved. Microbial etching of glass in seawater occurs within months (Staudigel et al., 1995, 1998; Brehm et al., 2005), thus some dissolution of very fine ash may occur as it settles through the ~100-m-thick euphotic zone, which may take days or weeks. Subsequent dissolution and alteration of vitric ash in the deep ocean or on the seafloor may release iron that becomes biologically available during later upwelling. We note that IFU ash at ODP Site 1215 in the central equatorial Pacific Ocean has been nearly entirely altered to smectite and zeolite (Ziegler et al., 2007).

To demonstrate the potential role of IFU volcanic iron fertilization in Paleogene cooling, we present here a biogeochemical mass balance for the prominent ~300 ka positive δ¹³C anomaly that began with the Oi-1 event. Salamy and Zachos (1999) attributed this anomaly to excess primary production and burial of 10¹⁸ g of Corg. At 33.5 Ma ago the rate of IFU ash emission was ~3 × 10⁶ km³ Ma⁻¹ (Fig. 2). In the following calculations, we assume that the modern ratio of buried Corg to primary production of Corg (~0.001;
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Ridgwell and Edwards, 2007) is applicable and scales linearly with production. Assuming a low Fe/C\text{org} ratio of 2 µmol mol\(^{-1}\) for phytoplankton (Cassar et al., 2007), burial of 10\(^2\) g of C\text{org} may be accounted for by fertilization of HNLC areas by the adsorbed iron on ~40% of the IFU ash erupted during the post-Oi-1 carbon isotopic anomaly. Using identical assumptions, burial of a similar mass of C\text{org} may result from dissolution of ~7% of the erupted IFU vitric ash. Substituting a high Fe/C\text{org} ratio of 20 µmol mol\(^{-1}\) (Blain et al., 2007), dissolution of ~10% of IFU ash would be sufficient for burial of the 10\(^8\) g of C\text{org} needed to account for the post-Oi-1 carbon isotopic anomaly. Although the volume of IFU ash deposited in Paleogene HNLC areas is unknown, these calculations demonstrate that iron fertilization by IFU ash may have contributed significantly to the post-Oi-1 carbon isotopic anomaly.

Volcanic iron fertilization also may indirectly enhance photosynthetic production in low-nutrient, low-chlorophyll areas of the ocean. These areas are extensive tropical and subtropical parts of the ocean in which fixed nitrogen is typically the growth-limiting nutrient. The principal nitrogen-fixing organisms in these areas are cyanobacteria of the genus Trichodesmium. The fixation of nitrogen by Trichodesmium is limited by the availability of iron, which is required to facilitate electron transfer reactions (Falkowski, 1997). Excretion and mortality by Trichodesmium increases the availability of fixed nitrogen to other phytoplankton, thereby boosting primary production of C\text{org} (Moore et al., 2006).

In addition to iron, volcanic ash rapidly liberates other biologically important, adsorbed nutrients upon contact with seawater (Si, Cu, Zn, PO\(_4\)\(^{3-}\), and NH\(_4\)\(^+\); Duggen et al., 2007). Silica is an important limiting element for opal production in phytoplankton (Brzezinski et al., 2007; Leblanc et al., 2005). Altered IFU ash may have played additional roles in Paleogene global cooling. The alteration products of vitric ash (smectite and zeolite) contain intercrystalline sites in which dissolved organic carbon may become sorbed, protecting it from oxidation by bacteria (e.g., Keil et al., 1994).

Temporal variations in ignimbrite eruptive flux during the IFU are closely correlated with climatic events. The Oi-1 and Mi-1 cooling events are both associated with rapid increases in IFU eruptive flux (Fig. 2). A period of late Oligocene warming (Zachos et al., 2001) coincides closely with a lull in ignimbrite volcanism ca. 26–24 Ma ago, and a warm interval in the Southern Ocean ca. 42–41 Ma ago (Bohaty and Zachos, 2003) occurred during the ca. 43–38 Ma ago ignimbrite eruptive minimum. IFU volcanism ended gradually in the middle Miocene, and thereafter played no active role in development of the late Cenozoic icehouse. Other explosive volcanic provinces, however, may have influenced late Miocene and younger cooling. These include the Altiplano-Puna in the central Andes (10–3 Ma ago, >3 × 10\(^6\) km\(^2\) ignimbrite), Taupo, New Zealand (1.6–0 Ma ago, ~2 × 10\(^6\) km\(^2\) ignimbrite), and large-volume ignimbrites associated with the Yellowstone hotspot of the northwestern United States (16–0.6 Ma ago). Rates of explosive volcanism throughout the circum-Pacific region greatly increased ca. 5 Ma ago (Sigurdsson, 2000), and deep-sea cores from the North Pacific show a tenfold increase in ash content coincident with an abrupt increase in ice-rafted debris 2.67 Ma ago (Prueher and Rea, 1998).

TEMPORAL RELATIONSHIPS BETWEEN OTHER PHANEROZOIC ICEHOUSE INTERVALS AND SLIP EVENTS

The first major icehouse event of the Phanerozoic occurred in the Late Ordovician and Early Silurian (Fig. 4). At least sporadically cold climates existed from the early Katian (middle Caradoc), ca. 456 Ma ago, to the Llandovery, which ended 428 Ma ago (Saltzman and Young, 2005; Cherns and Wheelley, 2007; Crowell, 1999; Grahn and Caputo, 1992). A short-lived (<1 Ma) episode of major continental glaciation occurred in the late Ordovician (Hirnantian, ca. 445 Ma ago) (Brenchley et al., 1994; Gibbs et al., 2000). Major explosive volcanism occurred episodically during the Early Ordovician to Late Silurian, resulting in some of the most widely dispersed ashes in the Phanerozoic (Huff et al., 1992; Huff et al., 1996). The volumes and source regions of these bentonites are poorly known. Bentonites accumulated from the Arenig (ca. 479 Ma ago) through the Pridoli (ca. 416 Ma ago) (Huff et al., 1998; Huff, 2000). The most voluminous ashes were erupted ca. 457–448 Ma ago (Min et al., 2001), about the same time as initial Late Ordovician cooling.

The great Gondwanan glaciation occurred from the Late Devonian to the Late Permian (Veivers and Powell, 1987; Crowell, 1999; Isbell et al., 2003). Glaciers achieved their maximum paleolatitudeal range between the middle Stephanian (ca. 305 Ma ago) and near the end of the Sakmarian (ca. 284 Ma ago) (Isbell et al., 2003). Three episodes of major ignimbrite volcanism occurred in the New England fold belt of eastern Australia in the Late Devonian, Carboniferous, and Early Permian. The first two of these (380–365 and 360–340 Ma ago; Bryan et al., 2004) are coeval with the early part of the Gondwanan icehouse. Explosive volcanism in the Kennedy-Connors-Auburn SLIP (ca. 320–280 Ma ago; Bryan et al., 2004, Bryan, 2007) of eastern Australia encompassed the glacial maximum. Major pulses of ignimbrite volcanism within the Kennedy-Connors-Auburn SLIP occurred ca. 320–314, 305–300, and 290–285 Ma ago (S. Bryan, 2007, written commun.). Major ignimbrite volcanism also occurred in northern Europe ca. 300–280 Ma ago (Neumann et al., 2004) and in southern South America during much of the Permian (López-Gamundí et al., 1994; Breitkreuz and Van Schmus, 1996).

Evidence for Jurassic cold climates and possible high-latitude alpine glaciation exists for the Bathonian (ca. 168–165 Ma ago) (Chumakov and Frakes, 1997; Crowell, 1999) and the latest Callovian to early Oxfordian (ca. 162–160 Ma ago) (Dromart et al., 2003). These cold climates were contemporaneous with explosive volcanism in the Early to Middle Jurassic Chon Aike SLIP of Patagonia and Antarctica. The Chon Aike province was active ca. 188–153 Ma ago, with peak pulses of ignimbrite volcanism ca. 188–178, 172–162, and 157–153 Ma ago (Pankhurst et al., 2000).

Eruption of the most voluminous SLIP of the Phanerozoic (the Whitsunday province of eastern Australia) occurred in the Cretaceous, ca. 132–95 Ma ago (Bryan et al., 1997, 2000). K/Ar data suggest that initial Whitsunday eruptions occurred ca. 145 Ma ago (Allen et al., 1998), but these ages may be too old (Bryan et al., 2000). Peak volcanism occurred ca. 120–105 Ma ago (Bryan, 2007; Bryan and Ernst, 2008). Contemporaneous with the early part of Whitsunday volcanism, major ignimbrites were erupted in the Paraná-Entendeka flood basalts province ca. 133–128 Ma ago (Peate, 1997). The timing of peak Whitsunday volcanism corresponds closely to an interval of middle Aptian–early Albian global cooling ca. 120–110 Ma ago (Crowell, 1999; Pinrri et al., 1995). Another Early Cretaceous cold period occurred during the Valanginian (ca. 138–135 Ma ago) (Stoll and Schrag, 1996; Alley and Frakes, 2003; Gröcke et al., 2005), slightly before or during the onset of Whitsunday volcanism. A short-lived (~200 ka) glaciation may have occurred ca. 91.2 Ma ago in Antarctica (Bornemann et al., 2008), ~4 Ma after the end of Whitsunday volcanism. Miller et al. (2005) invoked the presence of small glaciers in Antarctica throughout the Late Cretaceous and Eocene to account for short-term fluctuations in sea level.

DISCUSSION

Volcanic iron fertilization by IFU ash provides a plausible mechanism for atmospheric
Figure 4. Comparison of timing and volume of major silicic volcanic provinces with paleoclimate data for the Phanerozoic. Silicic large igneous provinces (red) are modified from Bryan (2007) and represent silicic volcanic provinces with documented volumes >10⁵ km³. Numbers in white boxes are minimum eruptive volumes in millions of cubic kilometers (Bryan, 2007); major silicic volcanic episodes with uncertain eruptive volumes are queried. The age range of Ordovician–Silurian episode of major explosive volcanism is from Huff et al. (1998) and Huff (2000), and that of Late Devonian–early Carboniferous silicic volcanism in Australia is from Bryan et al. (2004). Purple bands are peak pulses of volcanism showing age ranges (Ma) from Bryan (2007), Pankhurst et al. (2000), S.E. Bryan (2007, written commun.), Huff et al. (1992), and Min et al. (2001). Note that temporally overlapping episodes of major silicic volcanism in northern Europe (ca. 300–280 Ma ago; Neumann et al., 2004), in the Paraná–Etendeka province (ca. 133–128 Ma ago; Peate, 1997), and in Afro-Arabia (ca. 30–28 Ma ago; Uktstins Peate et al., 2003) are omitted for clarity. Permian ignimbrite volcanism in South America (López-Gamundí et al., 1994; Breitkreuz and Van Schmus, 1996) is not plotted for lack of adequate age and volume information. See Figure 2 for details of Cenozoic ignimbrite flare-up (IFU) volcanism. Light pink and light purple columns allow visual comparison between volcanic episodes and cold paleoclimatic intervals. Timing and paleolatitudinal distribution of glaciogenic detritus and other features (blue) and peak glacial intervals (dark blue) are from Frakes and Francis (1988), Frakes et al. (1992), Crowell (1999), Crowley (2000), Isbell et al. (2003), Brenchley et al. (1994), Saltzman and Young (2005), Chernels and Wheeleley (2007), Grahn and Caputo (1992), Dromart et al. (2003), Pirrie et al. (1995), Alley and Frakes (2003), Gröcke et al. (2005), and Zachos et al. (2001). Possible short-lived Late Cretaceous–Eocene glacial events in Antarctica (e.g., Miller et al., 2005; Bornemann et al., 2008) are not depicted. Mean tropical sea-surface temperature (black line) has been detrended and smoothed using a 50 Ma window stepping at 10 Ma increments (Veizer et al., 2000), but has not been corrected for pH of seawater (see Royer et al., 2004). Time scale is from Gradstein et al. (2004).
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CO₂ drawdown during the Cenozoic climatic transition, both in terms of timing and biogeochemical mass balance. Iron fertilization by repeated ignimbrite eruptions may have accelerated Paleogene global cooling by the stepwise forcing of the climate across a climatic threshold, via the cumulative effect of CO₂ drawdown by hundreds of volcanic fertilization events. Following initial Oi-1 glaciation, increased eolian dust deposition eventually superseded volcanogenic iron fertilization in the enhancement of primary production in HNLC areas.

Factors that may influence global climatic change are numerous and commonly interrelated. Increased glacial albedo, increased dust emission, and vigorous oceanic upwelling promote cooling, but all are positive feedbacks that follow initial cooling and glaciation, thus it is difficult to envision how such processes might initiate cooling. Volcanic forcing is independent of such feedback loops. A possible exception to this independence is the glacio-eustatic effect of falling sea level on the initiation of volcanic eruptions (e.g., Rampino and Self, 1993). Although plausible for volcanoes in coastal environments, this effect can be discounted for major continental volcanic provinces such as the IFU. Indeed, during early IFU volcanism (middle to late Eocene), eustatic sea-level fluctuations were less than a few tens of meters on million-year time scales (Miller et al., 2005), and volcanic centers were commonly many hundreds of kilometers from the sea (Fig. 3).

Pulses of IFU ignimbrite volcanism in New Mexico, Colorado, and Trans-Pecos Texas were 1.8–6.1 Ma long and are probably related to variation in far-field tectonic stresses (Chapin et al., 2004). These pulses are longer than, and show no simple relationship to, the contemporaneous eustatic fluctuations depicted by Miller et al. (2005).

Processes related to tectonism, such as changes in circulation by the opening or closing of oceanic gateways (Kennett, 1977; Diester-Haass and Zahn, 2001; Jovane et al., 2007; Allen and Armstrong, 2008) and increased silicate weathering following uplift of the Tibetan Plateau (Raymo and Ruddiman, 1992), have been invoked as important causes of Paleogene cooling. These are viable mechanisms for global climatic change, but the timing of these events is controversial, with age estimates commonly varying by many millions of years (e.g., Lawver and Gahagan, 2003; Lyle et al., 2007; McQuarrie et al., 2003; Sun et al., 2005). Unlike these tectonic processes, IFU volcanism is delimited by hundreds of radioisotopic analyses and provides a means of climatic forcing that is geologically rapid. In contrast to transient insolation effects related to volcanic-and dimethyl sulfide–derived aerosols, burial of a small portion of excess primary production of C-org following each in a series of volcanic fertilization events may produce incremental, long-term CO₂ drawdown and climatic cooling.

Initial Gondwanan glaciation has been attributed to changes in atmospheric and oceanic circulation during the assembly of Pangea (Crowell, 1999), but was also contemporaneous with the Late Devonian beginning of major explosive silicic volcanism in eastern Australia. The peak episode of Gondwanan glaciation in the late Carboniferous to Early Permian is coeval with major silicic volcanism in the Kennedy-Connors-Auburn SLIP, in northern Europe, and in South America, each of which may have contributed to the glacial expansion during the Stephanian through Sakmarian. At about the same time, eolian dust emission increased markedly in western equatorial Pangea, and may have boosted primary production via eolian iron fertilization (Soreghan and Soreghan, 2002).

Early geochemical models (Berner, 1991, 1994) and proxy studies of paleosols (Derling, 1991; Ekart et al., 1999) indicated high atmospheric CO₂ during the Late Ordovician and Mesoico cold intervals. If correct, these results imply that the temporal correlation between these cold intervals and major silicic volcanism is fortuitous, or that they are linked by a process other than iron fertilization. A later carbon-cycle model (Berner, 2006), however, predicted a CO₂ minimum during the Late Ordovician, and the usefulness of paleosol proxies for the estimation of Paleozoic atmospheric CO₂ has been questioned (Quast et al., 2006). The study of Royer et al. (2004) suggested a close link between atmospheric CO₂ concentration and temperature throughout the Phanerozoic.

A remarkable temporal correlation exists between large-volume silicic volcanism and cold climates in the Phanerozoic. A similar close correspondence is apparent with low-temperature anomalies in tropical sea-surface paleotemperatures (Veizer et al., 2000) (Fig. 4). No simple relationship, however, exists between SLIP eruptive volumes and the extent of contemporaneous global cooling. For example, the most voluminous Phanerozoic SLIP (the Early Cretaceous Whitsunday province) is temporally associated with only moderate cooling in the middle Aptian to early Albanian (ca. 120–110 Ma ago). The cooling response may have been muted by contemporaneous large CO₂ emissions from major mafic magmatism in oceanic ridges and oceanic plateaus (Ontong Java and Kerguelen) in the Early Cretaceous. Rates of mafic volcanism ca. 125–100 Ma ago are the highest known in the history of the Earth, nearly double the modern rate (Sigurdsson, 2000). Large CO₂ emissions from mafic eruptions may induce climatic warming that is largely unmitigated by iron fertilization because of the low explosivity of typical basaltic eruptions. The long-term climatic forcing effects of major mafic and silicic volcanism thus may be antithetic: silicic volcanism tends to promote cooling because of its (1) low magmatic CO₂ content and (2) highly explosive eruption style, which produces great volumes of widespread ash with large iron-fertilization potential. Mafic volcanism may promote warming for the opposite reasons.

The icehouse–SLIP hypothesis presented here, if correct, suggests that repeated episodes of oceanic iron fertilization by great volumes of rhylitic ash may be sufficient to initiate cold climatic modes. Further evaluation of this hypothesis will require a better understanding of several factors, including (1) the geographic extent and location of ancient HNLC regions; (2) the importance of volcanic iron fertilization to enhancement of nitrogen fixation in low-nutrient, low-chlorophyll waters; (3) the fraction of excess C-org produced during ancient volcanic fertilization events that became buried on the seafloor; (4) the portion of the elutriated ash from major ignimbrite eruptions that is injected into the stratosphere and subsequently hemispherically or globally distributed.

Approximately 10^12 km³ of ignimbrite were erupted during early IFU volcanism prior to initial (Oi-1) glaciation in Antarctica ca. 33.5 Ma ago. If a similar volume of ash was deposited in the ocean, then ~2.5 × 10^18 g total excess Fe were added by IFU ash to the oceanic iron inventory during the Cenozoic greenhouse-icehouse transition prior to Oi-1. This is comparable to the total global production of steel and pig iron for 2006 (3 × 10^18 g) (U.S. Geological Survey, 2007). In view of the current controversy concerning the possible remediation of global warming by anthropogenic iron fertilization of the oceans, it should be emphasized that iron fertilization by IFU volcanism proceeded for millions of years. Rapid iron fertilization on human time scales would result in limitation of primary production by the eventual drawdown of other nutrients in surface waters, such as nitrogen or phosphorus (e.g., Sarmiento and Orr, 1991). Because of the typical time interval between IFU eruptions (~15–40 ka), replenishment of these nutrients by overturning circulation may occur before the next fertilization event.

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