Circum-Pacific arc flare-ups and global cooling
near the Eocene-Oligocene boundary

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ABSTRACT
Explosive eruptions from subaerial arc volcanoes can have significant environmental impact because of the discharge of ash and volatiles directly into the atmosphere and oceans. The link between climate cooling and voluminous volcanic eruptions has remained speculative due to a lack of supporting evidence. A compilation of 2814 K-Ar and \(^{40}\)Ar/\(^{39}\)Ar age determinations from four circum-Pacific arcs indicates that periods of high volcanic output (i.e., flare-ups) have been episodic and, in some cases, synchronous. Peak periods and subsequent lulls in arc magmatism over the past 50 m.y. have occurred coeval with major fluctuations in global climate, including the Eocene-Oligocene transition, one of the most prominent global climate reorganizations in the Cenozoic. Hundreds of intermediate to silicic eruptions occurred during an extremely vigorous period of circum-Pacific volcanism beginning in the late Eocene, which likely led to the production of sulfur aerosols in the stratosphere and fertilization of surface waters of the Pacific Ocean. We provide a mechanism that may have been partly responsible for the climatic preconditioning that must have preceded and ultimately promoted Antarctic ice sheet growth ~34 m.y. ago.

INTRODUCTION
Volcanic eruptions have long been considered as potential triggers of climate variations on many time scales. Volcanically induced climate cooling was first postulated by Benjamin Franklin (1784), who suggested that the unusually cold, gray winter of 1783 in Paris was associated with the eruption of Laki, Iceland. Kennett and Thunell (1975) noted that an increase in explosive circum-Pacific volcanism can be correlated with intensification of Northern Hemisphere glaciations since the late Pliocene. They also suggested that a pulse of circum-Pacific volcanism from 16 to 14 Ma may have contributed to mid-Miocene cooling. However, conclusions could not be made about Eocene or Oligocene volcano-climate interactions at that time because of the limited number of age determinations greater than 20 Ma. A decade later, Kennett et al. (1985), without much corresponding age information, suggested that a surge in volcanic activity in the circum-Pacific region during the late Eocene was responsible for climatic cooling. However, the increase in volcanism was attributed to the change in Pacific plate motion and development of an Australian-Pacific plate boundary, both of which we now know formed ca. 15 Ma, prior to the Eocene-Oligocene boundary (Sharp and Clague, 2006). Sigurðsson (2000) showed a correlation between the foraminiferal oxygen isotope record and a global compilation of tephra layers in deep-sea cores from drilling of ocean basins but did not explore the cause-and-effect relationship. We revisit this issue now that a wealth of high-precision age information is available for Eocene to Quaternary arc volcanics.

GEOCHRONOLOGIC DATA
A database containing 2814 previously published K-Ar and \(^{40}\)Ar/\(^{39}\)Ar ages of subduction-related volcanic and plutonic rocks from four circum-Pacific arcs (Izu-Bonin-Marianas, Aleutians/Alaska, Western United States and Canada, Sierra Madre Occidental/Mexican volcanic belt) (Fig. 1) was compiled based on careful screening of the NAVDAT database (http://navdat.kgs.ku.edu/) and hundreds of publications (see the GSA Data Repository1 for data and references). Several other circum-Pacific arcs (Tonga, Kuriles) have insufficient geochronologic control and were excluded. Most ages range from 50 Ma to the present, and all were calculated or recalculated using International Union of Geological Sciences (IUGS) decay constants (Steiger and Jäger, 1977).

A compilation of this type has the potential to be biased by low-quality age determinations or studies focused on particular events, episodes, or individual volcanoes. To eliminate this concern, data that did not agree with stratigraphy, had discordant \(^{40}\)Ar/\(^{39}\)Ar spectra, or lacked age uncertainties were discarded. Duplicate sampling of a specific unit was minimal, and the spatial coverage within each arc is excellent because most of the ages older than 1 Ma from these four circum-Pacific arcs came from regionally motivated studies. Abundant geochronologic data available for active arc volcanoes younger than 1 Ma have been omitted to avoid any biasing of the data set. Because we have chosen to focus on the episodic nature of arc processes in addition to their climatic influence, age information on volcanic material not related to subduction processes was not considered, even though non-subduction-related eruptions have been shown to have significant climatic impact (e.g., Laki in 1783).

Histograms and probability density curves were generated to assess age-time variations and identify periods of elevated arc magmatism (flare-ups) (Fig. 2). Even though volumetric estimates for many of these rocks are unavailable, peaks in Figure 2 likely reflect actual pulses of magmatic activity. Preservation of pre-Quaternary material in active arcs is a major concern because of erosion, rifting, and burial. Therefore, we interpret a cluster of ages at a given time period to represent a volumetrically significant period of magmatism.

EPISODIC CIRCUM-PACIFIC VOLCANISM
Circum-Pacific volcanism has been episodic, characterized by pulses of high magmatic flux lasting between 5 and 10 m.y., which is in accord with prior observations (Kennett et al., 1977; McBirney et al., 1974; Scholl et al., 1976; Jicha et al., 2006) (Fig. 2). Several, but not all, arc flare-ups have been synchronous.

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1GSA Data Repository item 2009079. Table DR1, database of K-Ar and \(^{40}\)Ar/\(^{39}\)Ar ages from circum-Pacific arcs, is available online at www.geosociety.org/pubs/ft2009.htm, or on request from editing@geosociety.org or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301, USA.

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The late Eocene to early Oligocene circum-Pacific flare-up consisted mostly of intermediate to silicic eruptions that must have been of considerable volume in order to be preserved for >25 m.y., in such dynamic tectonic settings. These eruptions undoubtedly were accompanied by enormous fluxes of gases, sulfur species (mainly \(\text{SO}_2\)), and ash into the atmosphere, although quantitative measurements of \(\text{SO}_2\) concentration in these deposits (e.g., Self et al., 2008) are lacking. Addition of \(\text{CO}_2\) and \(\text{H}_2\text{O}\) from volcanic eruptions should have had a negligible effect on the atmosphere because of the existing high atmospheric \(\text{CO}_2\) content and because the \(\text{H}_2\text{O}\) concentration is modulated via evapotranspiration and precipitation. However, the emission of \(\text{SO}_2\) into the stratosphere may have a significant climatic effect because \(\text{SO}_2\) reacts with \(\text{OH}\) and \(\text{H}_2\text{O}\) to form \(\text{H}_2\text{SO}_4\) aerosols (Robock, 2000). Partly frozen sulfate aerosol droplets in the stratosphere are about the same size (0.1–1 \(\mu\text{m}\)) as visible light and can backscatter and/or absorb solar radiation (Robock, 2000). Incoming sunlight is reflected back into space, which reduces the amount of solar energy that reaches Earth’s surface, resulting in net cooling. Climate cooling in response to individual volcanic eruptions with a total eruptive volume of a few cubic kilometers lasts for several years, as has been observed following the 1991 Pinatubo, 1982 El Chichón, 1963 Agung, 1815 Tambora, and 1600 Huaynaputina eruptions. A single large volcanic event, such as the 2800 km\(^3\) Toba eruption ~74,000 yr ago, can have a more dramatic cooling effect. Climate modeling that simulated the response to the Toba eruption indicates dramatic cooling with global temperatures dropping by as much as 10 °C, followed by a long-term recovery period of a decade or two (Jones et al., 2005). However, eruptions of this magnitude are very rare, with an average frequency of only one every ~100,000 yr (Mason et al., 2004).

Tens of arc volcanoes erupt annually, but most of these eruptions do not release enough gases or solid aerosols to have noticeable climatic impact. Our data indicate that more than 500 eruptions of considerable volume occurred between 35 and 28 Ma, which corresponds to a minimum frequency of one “large” eruption every ~13,000 yr. Although it cannot be resolved given the individual age uncertainties in our data set, it is conceivable that the shorter-term volcanic record was episodic, as in our long-term record. Consequently, a series of eruptions could have occurred more frequently on the order of every few centuries or decades. Pyle (1998) showed that >30 “large” explosive eruptions, defined as those with a volcanic explosivity index of four or more, have occurred per century in the circum-Pacific over the past 400 yr. The climatic implications of a series of volcanic eruptions closely spaced in time was highlighted by Prueher and Rea (1998), who suggested that numerous silicic eruptions in the Kurile-Kamchatka and Aleutian arcs, and cooling associated with these eruptions, brought on
full-scale Northern Hemisphere glaciation in the Pliocene. However, we suggest that the volume of material erupted into the atmosphere from the circum-Pacific during the late Eocene–early Oligocene would have had a much more severe influence on global climate.

Another by-product of explosive volcanic eruptions that has the potential to strongly influence the atmosphere and climate is the introduction of volcanic glass and ash into the ocean. When erupted volcanic ash comes in contact with seawater, salts that are adsorbed onto volcanic glass dissolve and release nutrients, metals such as iron, and anions into surface water (Frogner et al., 2001). Open-ocean iron concentrations in surface water are commonly at picomolar (10^{-12}) concentrations. Iron-seeding experiments in the equatorial Pacific and Southern Pacific Ocean have shown that addition of iron in nanomolar (10^{-9}) concentrations promotes a several-fold increase in algal biomass, resulting in a large decrease in the ocean-to-atmosphere CO2 flux (Cooper et al., 1996). Sarmiento (1993) showed that <0.1% of the total iron available in the ~4 km^3 of 1991 Pinatubo ash would have to be released to ocean surface water to provide the requisite amount to stimulate biological drawdown of CO2. Flow-through experiments of Frogner et al. (2001) using ash from the 2000 Hekla eruption yielded similar results, but they noted that a large eruption close to the equatorial Pacific, such as that of Pinatubo, may have a more profound effect on atmospheric CO2 via iron fertilization of the ocean. Recent biogeochemical experiments and satellite data also confirm that volcanic ash can excite marine algal productivity (Duggen et al., 2007). We suggest that a prolonged period of widespread Fe fertilization of the Pacific Ocean and subsequent drawdown of atmospheric CO2 likely occurred during the voluminous episode of circum-Pacific magmatism in the late Eocene–early Oligocene. The introduction of volcanic glass and ash to the Pacific Ocean was inevitable because the Aleutian and Izu-Bonin-Mariana island arcs were bounded by the Pacific, and the prevailing easterly winds in the Sierra Madre Occidental would have brought fallout and ignimbrite deposits to the ocean (Cather et al., 2003).

EOCENE-OLIGOCENE COOLING

The sudden shift toward cooler temperatures and the major expansion of the East Antarctic Ice Sheet near the Eocene-Oligocene boundary ~34 m.y. ago is considered to be one of the most prominent global climate reorganizations in the Cenozoic. One limitation of the volcanic record is that it cannot directly record climate changes such as the dramatic transition from the greenhouse world to the icehouse world near the Eocene-Oligocene boundary. However, Cenozoic climate changes are recorded in a number of marine and terrestrial sediment archives. A compilation of oxygen isotope records of deep-sea benthic foraminifera documents a >1‰ increase in δ¹⁸O at the Eocene-Oligocene boundary (Zachos et al., 2001). The pronounced increase in δ¹⁸O is synchronous with deepening of the calcite compensation depth (CCD) and the stepwise onset of Antarctic ice-sheet growth (Coxall et al., 2005). We plotted a histogram and probability density curve of all the circum-Pacific age determinations assembled in our database alongside the δ¹⁸O curve of Zachos et al. (2001) for the past 50 m.y. to evaluate the relationship between volcanism and global climate (Fig. 3). Fluctuations in δ¹⁸O since the early Eocene coincide with peaks and lulls in the circum-Pacific volcanic record. The onset of voluminous late Eocene volcanism precedes Eocene-Oligocene cooling by more than 1 m.y., which contrasts with previous suggestions that a shift toward a cooler climate promotes volcanic activity (Rampino et al., 1979). The decline in δ¹⁸O at ca. 26 Ma was also broadly concurrent with waning of circum-Pacific magmatism (Fig. 3). Recent biostratigraphic and geochemical correlations in Tibetan sediments (Pearson et al., 2008) indicate that plankton extinctions occurred during an extended phase of ecological disruption that preceded the δ¹⁸O shift by ~500 k.y. The circum-Pacific volcanic record and aforementioned ecological trend suggest that significant changes were beginning to take place well before the Eocene-Oligocene climate transition.

The origin of Eocene-Oligocene cooling has been debated for decades. A number of hypotheses have been proposed, including orbital modulation, the opening of the Southern Ocean gateways and the development of an Antarctic Circumpolar Current, and the long-term decline in atmospheric CO2 levels. Global climate modeling indicates that the 20% change in ocean heat transport associated with onset of the Antarctic Circumpolar Current had a smaller than expected effect on climate change (DeConto and Pollard, 2003). It also recognized that the increase in δ¹⁸O near the Eocene-Oligocene boundary requires a climate conditioning factor such as declining pCO2 because the 1‰ shift is too large to be explained solely by Antarctic ice-sheet growth. CO2 concentrations during the middle to late Eocene ranged between 1000 and 1500 ppm by volume (ppmv) and then rapidly decreased in the Oligocene (Pagani et al., 2005). However, CO2 concentrations were already beginning to decline from the middle to late Eocene (Pagani et al., 2005), reaching levels that could have triggered the rapid expansion of the East Antarctic Ice Sheet near the Eocene-Oligocene boundary. Even though declining atmospheric CO2 has been recognized as an important factor in global cooling and the expansion of ice in Antarctica, very few causes for a decrease in CO2 have been proposed. Enhanced continental weathering due to uplift of the Tibetan Plateau is one proposed mechanism (Raymo et al., 1988). We suggest that the prolonged period of voluminous circum-Pacific volcanism in the late Eocene provided an enormous supply of ash that fertilized the Pacific Ocean and adjacent waters, promoting algal growth and the uptake of CO2.

Repeated episodes of volcanic cooling may have provided the “kick” or additional cooling and drop in pCO2 necessary to facilitate
the transition to a cooler climate regime near the Eocene-Oligocene boundary. Our high-resolution geochronologic database is only one step toward properly understanding the influence of arc volcanism on the global climate. These data ultimately need to be combined with volumetric estimates of the eruptive products, quantitative measurements of SO₂ budgets, and additional oceanic and continental records of temperature change to further explore the relationship between volcanism and climate.

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