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EARTH HISTORY

State shift in Deccan volcanism at the Cretaceous-Paleogene boundary, possibly induced by impact

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Bolide impact and flood volcanism compete as leading candidates for the cause of terminal-Cretaceous mass extinctions. High-precision $^{40}Ar/^{39}Ar$ data indicate that these two mechanisms may be genetically related, and neither can be considered in isolation. The existing Deccan Traps magmatic system underwent a state shift approximately coincident with the Chicxulub impact and the terminal-Cretaceous mass extinctions, after which ~70% of the Traps' total volume was extruded in more massive and more episodic eruptions. Initiation of this new regime occurred within ~50,000 years of the impact, which is consistent with transient effects of impact-induced seismic energy. Postextinction recovery of marine ecosystems was probably suppressed until after the accelerated volcanism waned.

The Deccan Traps are the most recent of several large (>10^6 km^3) continental flood basalt provinces that are circumstantially implicated in mass extinctions (*1*, *2*). The extent to which Deccan volcanism was a factor in the biotic crises that terminated the Mesozoic Era has been heavily debated, largely because the Chicxulub bolide impact provides a plausible mechanism for severe and abrupt environmental perturbations (*3*). The temporal coincidence between the impact and mass extinctions at the Cretaceous-Paleogene boundary (KPB) is well established (*4*) and implicates the bolide impact as a forcing mechanism. However, the possibility of a contributing role for volcanism, presumably through the discharge of climate-modifying gases, remains plausible in view of data showing that the immense flood basalt eruptions of the Deccan Traps spanned the KPB. A temporal correlation between other major flood volcanic events and extensive environmental transitions (*1*, *2*) illustrates the potential for the Deccan Traps alone to have caused the KPB extinctions. We combined high-precision $^{40}Ar/^{39}Ar$ dating of the lavas with previously reported U/Pb dates (*5*) and lava volume estimates (*6*) to infer that the Chicxulub impact initiated a substantial acceleration of Deccan volcanism within ~50 thousand years (ky). This probably contributed to the extinctions and moderated subsequent recovery.

The general coincidence of the Deccan Traps with the KPB, evident in geochronologic and paleomagnetic data (*7*), is not established with sufficient precision or stratigraphic control to locate the boundary within the lava stratigraphy. Limited constraints on the detailed history and tempo of volcanism obscure possible mechanisms that would relate the Deccan Traps to KPB phenomena, because these factors modulate volatile input to the atmosphere (*8*). The absence of reliable estimates of magma volume over time challenges models that suggest extrusion of the Traps in three discrete pulses (*9*, *10*). The geochemically defined stratigraphy of Deccan Group volcanics in the best-studied region, the Western Ghats, is divided into formations composing the Kalsubai, Lonavala, and Wai Subgroups, in ascending order. Each formation comprises multiple eruptive units. Paleomagnetic secular variation suggests that the eruptions were highly episodic, with a lower mean eruption frequency in the youngest and most widely distributed subgroup, the Wai (*11*, *12*). Lavas with broadly contemporaneous ages and geochemical and isotopic affinities with the Wai Subgroup occur as far north as Rajasthan (*13*), as far northeast as the Mandla lobe (~1000 km from the Western Ghats escarpment) (*14*, *15*), and as far east as Rajahmundry on the Bay of Bengal coast (*16*).

The Wai Subgroup contains numerous oxidized horizons ("red boles") between lava flows, interpreted as paleosols (*17*–*19*), which are consistent with the inference of a lower eruption frequency. Red boles are much less prevalent in the underlying Lonavala and Kalsubai Subgroups (*11*, *20*), providing possible evidence for variable long-term eruption rates during the lifetime of the Deccan magma system.

A discontinuity in lava geochemistry, flow volumes, and feeder dike orientations occurs between the Lonavala and Wai Subgroups (*6*). This discontinuity coincides with geomorphic evidence of widespread fractures and an abrupt change in susceptibility to erosion, approximately at the contact between these subgroups (*6*). It also coincides with the transition to more episodic, albeit more voluminous, eruptions in the Wai Subgroup, as inferred from paleomagnetic secular variation and the frequency of red bole horizons. Existing age constraints are compatible with the hypothesis that the KPB coincides with the transition from the Lonavala Subgroup (Bushe Formation) to the Wai Subgroup (Poladpur Formation) (*6*).

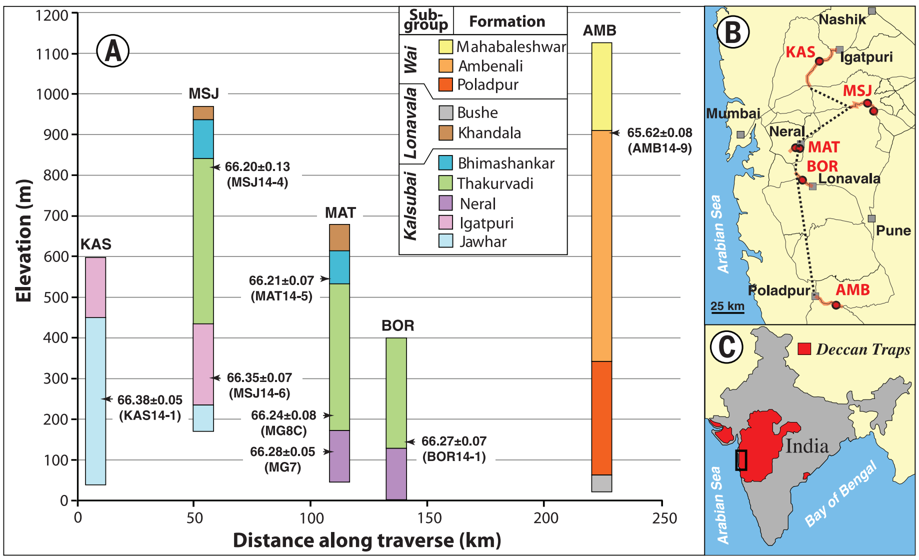

Fig. 1. Stratigraphic and geographic context of the samples. (**A**) Stratigraphic sections with dated horizons indicated, corresponding to the five traverses shown by red lines in (B). Ages (millions of years ago) are shown with uncertainties (SEM). Sample numbers for the dated horizons are given in parentheses. (**B**) Stratigraphy adapted from (*11*) for traverses KAS (Shahapur-Igatpuri section), MAT (Matheran-Neral section), BOR (Khopali-Khandala section), and AMB (Mahabaleshwar-Poladpur section). Stratigraphic data for the MSJ traverse (Malshej Ghat section) were acquired in this study. The dotted black line connects the bases of the traverses. The black rectangle in (**C**) shows the location of the area shown in (B).

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Available geochronologic data are not sufficiently precise to resolve age variations of less than 100 ky, with the exception of U/Pb zircon data (*5*). These data reveal protracted zircon age distributions, requiring subjective interpretation (*7*). Additionally, material suitable for U/Pb geochronology is reported only in rare bodies interpreted as magma segregation features and in red boles, which are sparse in both the Lonavala and Kalsubai Subgroups. These limitations restrict both the extent and the overall resolution of Deccan stratigraphy that can be determined from the U/Pb technique. Here, we report high-resolution $^{40}Ar/^{39}Ar$ dating of igneous plagioclase, which has an unambiguous genetic relationship to the host lavas and negligible retention of pre-eruptive radiogenic ^{40}Ar at basalt eruption temperatures >1100°C. We used detailed stepwise heating, dense bracketing of samples with standards during neutron irradiation, and detailed characterization of the interfering nuclear reactions to obtain data of appropriate precision and accuracy to clarify the eruptive history of the Deccan Traps (*7*).

We obtained $^{40}Ar/^{39}Ar$ plateau ages (fig. S3) for one to four aliquots of samples from each formation in the Kalsubai Subgroup and from the Ambenali Formation of the Wai Subgroup, in multiple sections across the Western Ghats region (Fig. 1). Where formation assignments were ambiguous, we analyzed samples geochemically to confirm their placement in the chemical stratigraphy by which the formations are defined (*21*). Weighted mean plateau ages placed in a composite stratigraphic section (Fig. 2) are generally consistent with previously reported U/Pb zircon data (*5*), within uncertainties.

Based on a composite stratigraphic section (*6*), our data indicate rapid eruption of no less than ~70% of the Kalsubai Subgroup before the KPB, over an interval of 173 ± 84 ky, as defined by the age difference between our samples from the Jawhar and Bhimashankar Formations (Fig. 2). The thicknesses of individual Kalsubai and Lonavala Subgroup formations vary substantially throughout the province; thus, inferences about mean magma generation rates based on values from any one section may be misleading. More meaningful inferences can be drawn from best estimates of volume (weighted by subgroup areal extent) for each formation (*6*), which indicate a volume of 71×10^3 km^3 for this time interval, corresponding to a mean magma generation rate of ~0.4 ± 0.2 km^3/year.

The KPB, dated at 66.043 ± 0.010 (without systematic sources) or ± 0.043 [with systematic sources (*7*)] million years ago (*22*), occurred less than 165 ± 68 ky after the emplacement of the Kalsubai Subgroup, within the time represented by the Khandala, Bushe, Poladpur, or possibly lower Ambenali Formations. The time interval between the eruption of the basal Bhimashankar and uppermost Ambenali Formations is 547 ± 241 ky, during which ~300×10^3 km^3 of lava was extruded at a mean rate of ~0.6 km^3/year. We determined a magma generation rate for the Wai Subgroup from U/Pb zircon dates (*5*) in the upper Ambenali and mid-Mahabaleshwar Formations, finding that a volume of 111×10^3 km^3 of lava was extruded at a mean rate of 0.9 ± 0.3 km^3/year. The mean long-term eruption rate represented by the Wai Subgroup, where it is well constrained, appears to be approximately double the rate represented by the Kalsubai Subgroup.

The increased mean magma production rate during the Wai Subgroup eruptions coincides with an abundance of red bole (weathering) horizons (Fig. 2), which first appear frequently in the Ambenali Formation and persist into the Mahabaleshwar Formation. The cumulative time represented by red boles in the Western Ghats has been estimated to be on the order of 300 ky (*11*), most of which falls in the time interval represented by the Wai Subgroup. During the Wai Subgroup time interval, it appears that the mean eruption frequency decreased dramatically, whereas the lava volume per flow field (per single eruptive event) increased, so that the mean magma eruption rate approximately doubled. Alternatively, the increased abundance of red boles in the Wai Subgroup may reflect an increase in weathering rates due to climate change (greenhouse conditions) after the KPB.

The decrease in eruption frequency coincides generally with a transition from lava fields dominated by compound pahoehoe and rare a'a flows in the Kalsubai Subgroup (*23*) to lava fields dominated by thicker, laterally extensive, inflated pahoehoe sheet lobes in the Wai Subgroup (*20*, *24*). The initiation of this transition appears to occur across the Lonavala Subgroup, with compound units absent in parts of the Khandala Formation but present in the Bushe Formation. In our study areas, sheet lobes begin to dominate near the base of the Wai Subgroup within the Poladpur Formation, where individual sheet lobes reach the greatest observed thickness of more than 60 m (*20*). The sparse occurrence of red boles in the Poladpur Formation suggests that the high eruption frequency continued until the time of the Ambenali Formation, at which point large eruptions became punctuated by longer repose intervals (represented by the red boles). During these repose intervals, occasional zircon-bearing, distally sourced silicic tephras apparently accumulated in developing paleosols (*5*).

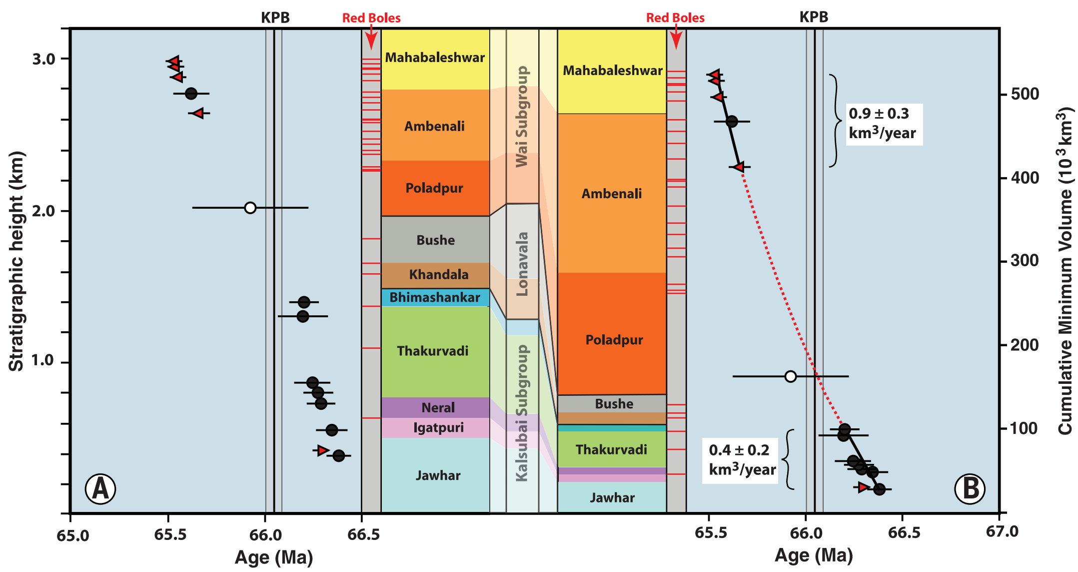

Fig. 2. Eruptive history of the Western Ghats region. (**A**) Composite stratigraphic thicknesses and (**B**) cumulative volumes, after (*6*), versus age for formations in the Western Ghats region. Included are (i) all $^{40}Ar/^{39}Ar$ plagioclase dates with uncertainties (SEM) of 300 ky or less, comprising data from this study (filled circles) and a previous study (open circles) (*35*), and (ii) previously reported U/Pb zircon dates (red triangles) (*5*). All ages are shown with 1σ uncertainties (bars), including from systematic sources. The apices of the triangles point in the direction of true age in the event of a possible bias in U/Pb ages (supplementary text). Sample positions are scaled from formation thicknesses in the sections sampled, as shown in Fig. 1A. Red boles are scaled from previous studies (*11*, *20*) and our observations. New $^{40}Ar/^{39}Ar$ dates define the mean eruption rate represented by the Kalsubai Subgroup (0.4 ± 0.2 km^3/year); previously reported U/Pb zircon dates (*5*) define the mean eruption rate represented by part of the Wai Subgroup (0.9 ± 0.3 km^3/year). The dotted red curve shows a parabolic fit, representing possible continuous change in eruption rates between the time intervals of the Kalsubai and upper Wai Subgroups. The Panhala and Desur Formations, which overlie the Mahabaleshwar Formation with limited extents, are not shown. Ma, millions of years ago.

The transition from high-frequency, low-volume eruptions to low-frequency, high-volume eruptions suggests a fundamental change in the magma plumbing system. A state shift in the threshold properties of one or more magma chambers would have been required for the latter style of eruptions to occur. The Wai Subgroup lavas mark a sharp increase in mantle contributions relative to crustal contributions, are the least crustally contaminated of the entire Deccan Group (*21*, *25*–*27*), and overlie Bushe Formation lavas that are the most crustally contaminated of the Deccan Group (*21*, *25*, *26*). This suggests a reduction in the magma-crust interface area, relative to magma volume, through an expansion of a deep-crustal magma chamber or a consolidation of multiple chambers; a shorter residence time of magma in the crust; or some combination of these factors.

A magma chamber expansion commencing with the emplacement of the Poladpur Formation, coupled with longer repose times indicated by the increased occurrence of red boles, would be associated with more extensive crystal fractionation (*28*). Wai Subgroup lavas are the most highly fractionated in the entire sequence (*21*, *25*, *27*). These and other independent lines of geochemical and tectonic evidence are all consistent with a sudden increase in magma flux from the Deccan mantle source (*6*). Larger flux rates would lead to larger magma chambers (presumably at Moho depths), longer time intervals to generate sufficient buoyancy to drive eruptions (via some combination of crystal fractionation and volatile exsolution), and hence larger and less frequent eruptions (*29*). We conclude that the Deccan magmatic system, at the source of the Western Ghats flood basalts and, by inference, the main portion of the Deccan Volcanic Province, underwent a fundamental transition upon initiation of the Wai Subgroup eruptions.

Straightforward interpolation of the age-volume data (Fig. 2B) suggests that this transition occurred within 50 ky of the Chicxulub impact and the KPB. This is an even closer temporal coincidence than indicated by previous analyses (*6*), which also suggested that strong seismic waves produced by the impact could have triggered increased volcanism. The close temporal coincidence of the impact and the accelerated volcanism makes it difficult to deconvolve the environmental perturbations attributable to each mechanism. The KPB extinctions probably resulted from the superposed effects of both phenomena.

The coincidence of widespread seismites at the Triassic-Jurassic boundary (*30*), correlated with the Central Atlantic Magmatic Province (*31*), may represent another example of seismic triggering of continental flood volcanism. The mechanisms by which seismic events trigger volcanic activity are not understood in detail (*32*), but they probably involve either a transient increase in the effective permeability of existing volcanic systems or, perhaps, induced volatile exsolution from supersaturated magma (*33*). These transient effects may not account for the subsequent episodic repetition of larger-volume, lower-frequency eruptions throughout the Wai Subgroup interval; however, the repetition of such eruptions might reflect a state change toward longer recharge times due to magma chamber enlargement, perhaps combined with other episodic seismic disturbances (such as from large regional tectonic earthquakes). Eruptions that emplaced the volumetrically dominant formations of the Wai Subgroup continued for ~500 ky after the KPB, which is comparable with the time lag between the KPB and the initial stage of ecological recovery in marine ecosystems (*34*). The effects of the Wai Subgroup eruptions may have suppressed postextinction recovery until the final stages of the time interval represented by the Mahabaleshwar Formation.

REFERENCES AND NOTES

1. V. E. Courtillot, P. R. Renne, *C. R. Geosci.* **335**, 113–140 (2003).
2. P. B. Wignall, *Earth Sci. Rev.* **53**, 1–33 (2001).
3. P. Schulte *et al*., *Science* **327**, 1214–1218 (2010).
4. P. R. Renne *et al*., *Science* **339**, 684–687 (2013).
5. B. Schoene *et al*., *Science* **347**, 182–184 (2015).
6. M. A. Richards *et al*., *Geol. Soc. Am. Bull.* (2015).
7. Materials and methods are available as supplementary materials on *Science* Online.
8. S. Self, M. Widdowson, T. Thordarson, A. E. Jay, *Earth Planet. Sci. Lett.* **248**, 518–532 (2006).
9. A. L. Chenet, X. Quidelleur, F. Fluteau, V. Courtillot, S. Bajpai, *Earth Planet. Sci. Lett.* **263**, 1–15 (2007).
10. G. Keller *et al*., *Earth Planet. Sci. Lett.* **341–344**, 211–221 (2012).
11. A. L. Chenet *et al*., *J. Geophys. Res. Solid Earth* **114**, B06103 (2009).
12. A. L. Chenet, F. Fluteau, V. Courtillot, M. Gerard, K. V. Subbarao, *J. Geophys. Res. Solid Earth* **113**, B04101 (2008).
13. A. Sen *et al*., *J. Asian Earth Sci.* **59**, 127–140 (2012).
14. J. P. Shrivastava, R. A. Duncan, M. Kashyap, *Lithos* **224-225**, 214–224 (2015).
15. Z. X. Peng, J. J. Mahoney, P. R. Hooper, J. D. Macdougall, P. Krishnamurthy, *J. Geophys. Res. Solid Earth* **103**, 29843 (1998).
16. S. Self, A. E. Jay, M. Widdowson, L. P. Keszthelyi, *J. Volcanol. Geotherm. Res.* **172**, 3–19 (2008).
17. P. Ghosh, M. R. G. Sayeed, R. Islam, S. M. Hundekari, *Palaeogeogr. Palaeoclimatol. Palaeoecol.* **242**, 90–109 (2006).
18. J. P. Shrivastava, M. Ahmad, S. Srivastava, *J. Geol. Soc. India* **80**, 177–188 (2012).
19. M. Widdowson, J. N. Walsh, K. V. Subbarao, *Geol. Soc. Spec. Publ.* **120**, 269–281 (1997).
20. A. E. Jay, thesis, The Open University, Milton Keynes, UK (2005).
21. J. E. Beane, C. A. Turner, P. R. Hooper, K. V. Subbarao, J. N. Walsh, *Bull. Volcanol.* **48**, 61–83 (1986).
22. C. J. Sprain, P. R. Renne, G. P. Wilson, W. A. Clemens, *Geol. Soc. Am. Bull.* **127**, 393–409 (2015).
23. R. J. Brown, S. Blake, N. R. Bondre, V. M. Phadnis, S. Self, *Bull. Volcanol.* **73**, 737–752 (2011).
24. N. R. Bondre, R. A. Duraiswami, G. Dole, *Bull. Volcanol.* **66**, 29–45 (2004).
25. P. C. Lightfoot, C. J. Hawkesworth, C. W. Devey, N. W. Rogers, P. W. C. Van Calsteren, *J. Petrol.* **31**, 1165–1200 (1990).
26. Z. X. Peng, J. J. Mahoney, P. Hooper, C. Harris, J. E. Beane, *Geochim. Cosmochim. Acta* **58**, 267–288 (1994).
27. J. J. Mahoney *et al*., *Earth Planet. Sci. Lett.* **60**, 47–60 (1982).
28. C. J. Hawkesworth *et al*., *J. Petrol.* **41**, 991–1006 (2000).
29. L. Karlstrom, M. Richards, *J. Geophys. Res. Solid Earth* **116**, B08216 (2011).
30. M. J. Simms, *Geology* **31**, 557 (2003).
31. A. Marzoli *et al*., *Science* **284**, 616–618 (1999).
32. M. Manga, E. Brodsky, *Annu. Rev. Earth Planet. Sci.* **34**, 263–291 (2006).
33. R. J. Carey *et al*., *J. Geophys. Res. Solid Earth* **117**, B11202 (2012).
34. H. K. Coxall, S. D'Hondt, J. C. Zachos, *Geology* **34**, 297 (2006).
35. P. Hooper, M. Widdowson, S. Kelley, *Geology* **38**, 839–842 (2010).

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SUPPLEMENTARY MATERIALS

www.sciencemag.org/content/350/6256/76/suppl/DC1
Materials and Methods
Supplementary Text
Figs. S1 to S4
Table S1
References (*36*–*69*)

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WATER STRUCTURE

Ultrafast 2D IR spectroscopy of the excess proton in liquid water

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Despite decades of study, the structures adopted to accommodate an excess proton in water and the mechanism by which they interconvert remain elusive. We used ultrafast two-dimensional infrared (2D IR) spectroscopy to investigate protons in aqueous hydrochloric acid solutions. By exciting O–H stretching vibrations and detecting the spectral response throughout the mid-IR region, we observed the interaction between the stretching and bending vibrations characteristic of the flanking waters of the Zundel complex, $[H(H_2O)_2]^+$, at 3200 and 1760 cm^{-1}, respectively. From time-dependent shifts of the stretch-bend cross peak, we determined a lower limit on the lifetime of this complex of 480 femtoseconds. These results suggest a key role for the Zundel complex in aqueous proton transfer.

Acid-base chemistry and most biological redox chemistry are governed by the transport of protons through water. Aqueous proton transfer is generally accepted to occur along hydrogen bonds through sequential hops of an excess proton from one solvating water molecule to the next. Although this widely accepted picture, known as the Grotthuss mechanism, captures the concept of long-range charge translocation without transport of a particular proton, numerous basic questions remain regarding the rapidly evolving structure of an aqueous proton (*1*).