



Paleocene-Eocene Thermal Maximum and the Opening of the Northeast Atlantic Michael Storey, *et al. Science* **316**, 587 (2007); DOI: 10.1126/science.1135274

The following resources related to this article are available online at www.sciencemag.org (this information is current as of February 3, 2008):

Updated information and services, including high-resolution figures, can be found in the online version of this article at: http://www.sciencemag.org/cgi/content/full/316/5824/587

Supporting Online Material can be found at: http://www.sciencemag.org/cgi/content/full/316/5824/587/DC1

A list of selected additional articles on the Science Web sites **related to this article** can be found at:

http://www.sciencemag.org/cgi/content/full/316/5824/587#related-content

This article **cites 30 articles**, 9 of which can be accessed for free: http://www.sciencemag.org/cgi/content/full/316/5824/587#otherarticles

This article has been cited by 2 article(s) on the ISI Web of Science.

This article has been **cited by** 1 articles hosted by HighWire Press; see: http://www.sciencemag.org/cgi/content/full/316/5824/587#otherarticles

This article appears in the following **subject collections**: Geochemistry, Geophysics http://www.sciencemag.org/cgi/collection/geochem_phys

Information about obtaining **reprints** of this article or about obtaining **permission to reproduce this article** in whole or in part can be found at: http://www.sciencemag.org/about/permissions.dtl

Science (print ISSN 0036-8075; online ISSN 1095-9203) is published weekly, except the last week in December, by the American Association for the Advancement of Science, 1200 New York Avenue NW, Washington, DC 20005. Copyright 2007 by the American Association for the Advancement of Science; all rights reserved. The title *Science* is a registered trademark of AAAS.

- A. Volbeda et al., J. Am. Chem. Soc. 118, 12989 (1996).
- Special issue on Hydrogenases, C. J. Pickett, S. P. Best, Eds., Coord. Chem. Rev. 249, 1517–1690 (2005).
- M. Carepo et al., J. Am. Chem. Soc. 124, 281 (2002).
- M. A. Reynolds, T. B. Rauchfuss, S. R. Wilson, Organometallics 22, 1619 (2003).
- E. Bouwman, J. Reedijk, Coord. Chem. Rev. 249, 1555 (2005).
- 11. D. J. Evans, C. J. Pickett, *Chem. Soc. Rev.* **32**, 268 (2003).
- A. C. Marr, D. J. E. Spencer, M. Schröder, *Coord. Chem. Rev.* 219-221, 1055 (2001).
- M. Y. Darensbourg, E. J. Lyon, J. J. Smee, *Coord. Chem. Rev.* 206-207, 533 (2000).
- 14. Z. Li, Y. Ohki, K. Tatsumi, J. Am. Chem. Soc. 127, 8950 (2005).
- 15. W. Zhu et al., Proc. Natl. Acad. Sci. U.S.A. 102, 18280 (2005).
- 16. S. Foerster *et al.*, *J. Am. Chem. Soc.* **125**, 83 (2003). 17. M. Brecht, M. van Gastel, T. Buhrke, B. Friedrich,
- W. Lubitz, J. Am. Chem. Soc. 125, 13075 (2003).

- M. Jahncke, G. Meister, G. Rheinwald, H. Stoeckli-Evans, G. Süss-Fink, Organometallics 16, 1137 (1997).
- G. J. Colpas, M. Kumar, R. O. Day, M. J. Maroney, *Inorg. Chem.* 29, 4779 (1990).
 Materials and methods are available as supporting
- material on *Science* Online.
- 21. A. C. Ontko et al., Organometallics 17, 5467 (1998).
- S. Ogo, H. Nakai, Y. Watanabe, J. Am. Chem. Soc. 124, 597 (2002).
- 23. A. Albinati *et al., Inorg. Chim. Acta* **259**, 351 (1997). 24. M. H. Drabnis, R. Bau, S. A. Mason, J. W. Freeman,
- R. D. Ernst, Eur. J. Inorg. Chem. 1998, 851 (1998).
- 25. T. J. Marks, J. R. Kolb, Chem. Rev. 77, 263 (1977).
- 26. Y.-L. Wang, R. Cao, W.-H. Bi, *Polyhedron* 24, 585 (2005).
- H. M. Alvarez, M. Krawiec, B. T. Donovan-Merkert, M. Fouzi, D. Rabinovich, *Inorg. Chem.* 40, 5736 (2001).
- 28. R. Cammi et al., Inorg. Chem. 42, 1769 (2003).
- 29. Z. Gu et al., J. Am. Chem. Soc. **118**, 11155 (1996). 30 M. Peruzzini R. Poli *Recent Advances in Hydride*
- *Chemistry* (Elsevier, Amsterdam, ed. 1, 2001), pp. 139–188.
- A. K. Justice, R. C. Linck, T. B. Rauchfuss, S. R. Wilson, J. Am. Chem. Soc. 126, 13214 (2004).

- R. C. Linck, R. J. Pafford, T. B. Rauchfuss, J. Am. Chem. Soc. 123, 8856 (2001).
- 33. This work was supported by grants in aid 17350027, 19205009, 18033041, and 18065017 (Chemistry of Concerto Catalysis) from the Ministry of Education, Culture, Sports, Science, and Technology, Japan; and a Core Research for Evolutional Science and Technology program (Nano-Structured Catalysts and Materials) by JST. Crystallographic data for [1](OTf)₂ and [2](NO₃) have been deposited with the Cambridge Crystallographic Data Center under reference numbers CCDC-617674 (x-ray), 617675 (x-ray), and 637331 (neutron diffraction analysis).

Supporting Online Material

www.sciencemag.org/cgi/content/full/316/5824/585/DC1 Materials and Methods

Figs. S1 to S18 Tables S1 and S2 References

12 December 2006; accepted 12 March 2007 10.1126/science.1138751

Paleocene-Eocene Thermal Maximum and the Opening of the Northeast Atlantic

Michael Storey,¹ Robert A. Duncan,² Carl C. Swisher III³

The Paleocene-Eocene thermal maximum (PETM) has been attributed to a sudden release of carbon dioxide and/or methane. ${}^{40}\text{Ar}/{}^{39}\text{Ar}$ age determinations show that the Danish Ash-17 deposit, which overlies the PETM by about 450,000 years in the Atlantic, and the Skraenterne Formation Tuff, representing the end of 1 ± 0.5 million years of massive volcanism in East Greenland, are coeval. The relative age of Danish Ash-17 thus places the PETM onset after the beginning of massive flood basalt volcanism at 56.1 \pm 0.4 million years ago but within error of the estimated continental breakup time of 55.5 \pm 0.3 million years ago, marked by the eruption of mid-ocean ridge basalt—like flows. These correlations support the view that the PETM was triggered by greenhouse gas release during magma interaction with basin-filling carbon-rich sedimentary rocks proximal to the embryonic plate boundary between Greenland and Europe.

uring the Paleocene-Eocene thermal maximum (PETM) (1), the sea surface temperature rose by 5° C in the tropics (2) and more than 6°C in the Arctic (3), in conjunction with ocean acidification (4) and the extinction of 30 to 50% of deep-sea benthic formaminiferal species (5). The initiation of the PETM is marked by an abrupt decrease in the δ^{13} C proportion of marine and terrestrial sedimentary carbon (1, 6), which is consistent with the rapid addition of >1500 gigatons of 13 Cdepleted carbon, in the form of carbon dioxide and/or methane, into the hydrosphere and atmosphere (7). The PETM is thought to have lasted only 210,000 to 220,000 years, with most of the decrease in δ^{13} C occurring over a 20,000year period at the beginning of the event (8).

A possible trigger for the initiation of the PETM is a period of intense flood basalt magmatism attending the opening of the North Atlantic (9, 10), by generating metamorphic methane from sill intrusion into basin-filling carbon-rich sedimentary rocks (11). Here we present ⁴⁰Ar/³⁹Ar age determinations that allow the correlation of Early Tertiary volcanic rocks of East Greenland and the Faeroe Islands with the Danish Ash-17 deposit, which closely overlies PETM sequences in the North Atlantic. In East Greenland, a >5-kmthick sequence of plateau basalts formed in 1.0 \pm 0.5 million years (My). A surge in magma production, coupled with the eruption of mid-ocean ridge basalt (MORB)-like flows in the lower part of the flood basalt sequence, indicates the initiation of seafloor spreading at 55.5 ± 0.3 million years ago (Ma). The onset of the PETM correlates closely with this breakup-related magmatism.

The North Atlantic Igneous Province (NAIP) includes the basaltic and picritic lavas of Baffin Island and West Greenland; the ~7-km-thick, predominantly tholeiitic lava flow sequences of

the Blosseville Kyst of East Greenland; the seaward-dipping reflectors of the Greenland and northwest European volcanic rifted margins; the Faeroe Islands and British Tertiary basaltic lavas; and the aseismic ridges connecting Iceland to either margin of the central Northeast Atlantic (Fig. 1). The total area of the NAIP is 1.3×10^6 km² (*12*) and its volume is estimated to be 5×10^6 km³ to 10×10^6 km³ (*12–14*). The East Greenland (Blosseville Kyst) and Faeroe Islands flood basalts lie at opposite ends of the Greenland-Iceland-Faeroes Ridge (GIFR), the postulated Iceland hotspot track, and record volcanic activity leading up to, during, and after continental breakup between Greenland and Europe (Fig. 1).

⁴⁰Ar/³⁹Ar age determinations show that prebreakup volcanic activity in East Greenland and the Faeroes began at ~ 61 Ma (15–17). Seven lava flows cover the duration of magnetochron C25n (~500,000 years) in the uppermost part of the Faeroes lower series (FLS), indicating a very low eruption rate by ~57 Ma (18) (Fig. 2). The FLS extends into earliest C24r, as the lava flow immediately below the capping ~10-m-thick coalbearing sediment horizon (19) is reversely magnetized (18). The volcanic hiatus as represented on the Faeroes, after the end of the initial phase of volcanism, has an estimated duration of 0.6 \pm 0.4 My (Fig. 2). In East Greenland, volcaniclastic sediments overlie the FLS equivalent, the Nansen Fjord Formation (20), which includes lahars that contain coal fragments and plant imprints (21).

After the period of little or no volcanism, flood basalt eruptions commenced on a massive scale in East Greenland and the Faeroes (Fig. 2). Flood basalt activity in East Greenland is represented by four regionally extensive formations with a combined stratigraphic thickness of >5 km. The Milne Land Formation (MLF), the oldest of these four formations, includes MORBlike low-Ti basalts halfway up the succession (20) that provide correlation with the Faeroes middle series (FMS) and upper series (FUS) (Fig. 2). Paleomagnetic data suggest a high eruption

¹Quaternary Dating Laboratory, Department of Environment, Society and Spatial Change, Roskilde University Centre, Post Office Box 260, 4000 Roskilde, Denmark. ²College of Oceanic and Atmospheric Sciences, Oregon State University, Corvallis, OR 97331, USA. ³Department of Geological Sciences, Rutgers University, Piscataway, NJ 08854-8066, USA.

Fig. 1. Map of the North Atlantic region showing the distribution of igneous rocks related to the NAIP and DSDP site 550, where Danish Ash-17 closely overlies the PETM. A24, sea-floor magnetic anomaly 24r; BK, Blosseville Kyst; GC, Gardiner Complex; MAR, Mid-Atlantic Ridge.



rate at the onset of the FMS (18). In the MLF, East Greenland, lavas show a regular decrease in the Dy/Yb ratio up through the section, indicative of a progressive drop in the mean pressure of partial melting (22) and consistent with rifting and thinning of the lithosphere. A 40Ar/39Ar age determination on plagioclase from a lava flow at the base of the MLF yielded an age of 56.1 ± 0.5 Ma (16), in agreement with age determinations for MLF-equivalent lavas inland (17). The weighted mean age is 56.1 ± 0.4 Ma [2σ internal standard error (SE) used throughout; all ages are reported relative to the currently accepted age of 28.02 Ma for the ⁴⁰Ar/³⁹Ar standard Fish Canyon Tuff Sanidine (23)]. A high-precision 40 Ar/ 39 Ar age of 55.12 \pm 0.06 Ma (table S1) on sanidine from a tuff near the top of the Skraenterne Formation (SF), the uppermost of the four volcanic formations, indicates that the entire sequence was erupted in 1.0 ± 0.5 My (Fig. 2). The lowest stratigraphic occurrence of MORB-like flows, approximately 0.8 km above the base of the first flood basalts, was dated to 55.1 ± 0.5 Ma (16) on plagioclase from two samples of interlayered Fe-Ti basalts (Fig. 2). Further and more precise age constraints are provided by the Skaergaard intrusion age. The parental magma of the Skaergaard intrusion has been correlated with

Fig. 2. Correlation of a composite marine record, which encompasses the PETM, Danish Ash-17, and magnetochrons C25n and lower C24r, with the continental East Greenland (68°N) and Faeroe Islands flood basalt record. Tie points are indicated by dashed horizontal lines. Tie point 1, correlation between the SF Tuff and the marine Danish Ash-17; tie point 2, correlation of the East Greenland and Faeroes flood basalts, based on the first occurrence of MORB-like flows in the respective volcanic records (20); tie points 3 and 4, top and base of C25n correlate the Faeroes volcanic record to the marine record.



NF, Nansen Fjord Formation; RF, Rømer Fjord Formation. Faeroes: LS, lower series; MS, middle series; US, upper series. Marine record: CIE, carbon isotope excursion. ΔT , change in time. 40 Ar/ 39 Ar age determinations for SF Tuff and Danish Ash-17 are given in tables S1 and S2 and Fig. 3. The 40 Ar/ 39 Ar age for the MLF is from (16, 17). The 40 Ar/ 39 Ar ages for the RF and Faeroes US/MS are from (16). The 40 Ar/ 39 Ar-based Skaergaard intrusion age is from (26). The +1.11 My between the top of C25n and the beginning of the CIE is from (29). The +1.55 My between the top of C25n and the beginning of the top to 24t has a total duration of 2.11 My.

the top of C25n and Danish Ash-17 is based on the observation that Ash-17 occurs in the midpoint of C24r (*32*) and that C24r has a total duration of 3.11 My (*29*). The right panel shows magnetochron ages (*30*) and the estimated variation in magma productivity over time [from (*16*)]. There is a low melt production rate by the beginning of C25n and a surge in magmatism (curve 1) during early C24r. Curves 2 and 3 represent upper (6000 km³/km per My) and lower uncertainties on magma productivity during the rift-to-drift phase. Post-breakup melt production is based on seismic images of crustal thickness for the Greenland-Iceland Ridge (GIR) (*14*).

the Geike Plateau Formation (GPF) (24), which overlies the level of the MORB-like flows in East Greenland (Fig. 2). 40 Ar/ 39 Ar ages on biotite and hornblende from transgressive granophyres within the Skaergaard intrusion, in combination with models of cooling history (25), give an intrusion age of 55.75 ± 0.35 Ma (26). The weighted average of the Skaergaard intrusion age and the less precise age for the FUS/FMS is 55.5 ± 0.3 Ma. This age for the MORB-like flows allows for the possibility that the majority of flood basalts were emplaced in <300,000 years as concluded from a fluid inclusion study on late-stage granophyres from the Skaergaard intrusion (27).

The average melt production rate for the flood basalts is 3000 (+3000/–1000) km³/km of rift per My (Fig. 2), assuming that the hidden cumulates have a comparable volume to the lavas (28). Although there is a large degree of uncertainty, the figure is in accord with crustal thickness–based estimates of magmatic productivity of 1800 ± 300 km³/km of rift per My for the GIFR, proximal to the volcanic rifted margin (14) (Fig. 2). The surge in melt production after renewed volcanism in East Greenland and the Faeroes suggests a short-lived rift-to-drift phase beginning at 56.1 ± 0.4 Ma, with the eruption of MORB-like low-Ti basalts at 55.5 ± 0.3 Ma marking the opening of the northeast Atlantic at 68° N, above the ancestral Iceland hot spot.

Although the PETM has been identified globally in marine and also in some continental sedimentary sections, there has been uncertainty about its timing relative to the on-land stratigraphy of the East Greenland–Faeroes flood basalts. Orbital-based calibration for magnetochrons C24r and C25n, using cores from multiple drill holes on the Walvis Ridge in the South Atlantic, indicates



Fig. 3. Probability plot for sanidine 40 Ar/ 39 Ar ages for the SF Tuff (**top**) and Danish Ash-17 (**bottom**). With the exception of an anomalously young age, the SF Tuff ages conform to a simple Gaussian distribution. Ages are arithmetic mean \pm 2 SE. Analyses are reported in tables S2 and S3.

that the total duration of C24r is 3.12 ± 0.05 My and that the base of the PETM is 1.11 ± 0.04 My above the C24r/C25n boundary (29) (Fig. 2). This indicates an age of approximately 55.5 to 55.6 Ma for the onset of the PETM, relative to the geomagnetic polarity time scale value of 56.67 Ma for the C24r/C25n boundary (30). Further age constraints are provided by Danish Ash-17, a widespread stratigraphic marker horizon that is found in Early Tertiary marine sediments from the North Sea region and the North Atlantic. Danish Ash-17 overlies the PETM at Deep Sea Drilling Project (DSDP) site 550 in the middle of C24r (C24r.5) and has been used for the calibration of the PETM (Fig. 1) (31, 32). Danish Ash-17 has been correlated previously with an alkaline sanidine-bearing tuff in the SF near the top of the East Greenland Tertiary lava pile (Fig. 2), owing to similar mineralogy and a 40 Ar/ 39 Ar age of 55.0 ± 0.3 Ma (33). The pyroclastic deposit is believed to originate from the Early Tertiary Gardiner melanephelinite-carbonatite volcanic complex on the East Greenland margin (Fig. 1). To test the correlation, with the aim of locating the stratigraphic position of the PETM in relation to the East Greenland and Faeroes flood basalts, we have redated both Danish Ash-17 and the SF Tuff, carrying out more than 50 individual age measurements (34). Figure 3 shows that ⁴⁰Ar/³⁹Ar laser-fusion age determinations on sanidines from the SF Tuff and Ash-17 are analytically indistinguishable. Of the 15 sanidine analyses from the SF Tuff, 1 is anomalously young with an age of 54.2 Ma, possibly reflecting 40 Ar loss by alteration. The remaining 14 analyses give ages ranging between 55.0 and 55.3 Ma and conform to a simple Gaussian distribution with a mean age of 55.12 \pm 0.06 Ma (Fig. 3). Sanidine from Ash-17 is finergrained, and overall the multiple- as well as singlegrain analyses are less precise. However, the sanidine fusion ages for Ash-17 are mostly evenly distributed around 55.12 \pm 0.12 Ma. There is a smaller fraction of older ages, which cluster around 56 Ma (fig. S1) and are considered to include an inherited (xenocrystic) component.

The similar new high-precision ages for Danish Ash-17 and the SF Tuff indicate that they are coeval and, due to the rarity of sanidine-bearing tuffs in this time interval in the North Atlantic, most likely represent the same eruptive unit (33). Ash-17 occurs in the midpoint of C24r (30), which would place it approximately 450,000 years above the base of the PETM (29). Relative to the ${}^{40}\text{Ar}/{}^{39}\text{Ar}$ dates for the SF Tuff and Danish Ash-17. the start of the PETM would thus correspond to an age of 55.6 Ma. The onset of the PETM was most likely after the beginning of massive flood basalt volcanism at 56.1 \pm 0.4 Ma, but is within error of the estimated age of continental breakup at 55.5 \pm 0.3 Ma, marked by the eruption of MORB-like flows (Fig. 2). We suggest that rift propagation and magmatism (above the ancestral Iceland hot spot) during the final stages of breakup between Greenland and Europe triggered the PETM event, probably via the release of ¹²C-enriched methane though massive sill intrusion and contact metamorphism of carbon-rich sediments contained in basins proximal to the embryonic plate boundary between Greenland and Europe (11).

References and Notes

- 1. J. P. Kennett, L. D. Stott, Nature 353, 225 (1991).
- 2. J. C. Zachos et al., Science **302**, 1551 (2003).
- 3. A. Sluijs et al., Nature 441, 610 (2006).
- J. C. Zachos et al., Science 308, 1611 (2005).
 E. Thomas, N. J. Shackelton, in *Correlation of the Early* Paleogene in Northwestern Europe, R. W. O'B Knox, R. M. Corfield, R. E. Dunnay, Eds. (Geological Society of London Special Publication, Geological Society of London, 1996), vol. 101, pp. 401–441.
- P. L. Koch, J. C. Zachos, P. D. Gingerich, *Nature* 358, 319 (1992).
- G. R. Dickens, J. R. O'Neil, D. K. Rea, R. M. Owen, Paleoceanography 10, 965 (1995).
- U. Röhl, T. J. Bralower, R. D. Norris, G. Wefer, *Geology* 28, 927 (2000).
- D. K. Rea et al., Paleogeogr. Palaeoclimatol. Paleoecol. 79, 117 (1990).
- O. Eldholm, E. Thomas, *Earth Planet. Sci. Lett.* **117**, 319 (1993).
- 11. H. Svensen et al., Nature 429, 542 (2004).
- 12. O. Eldholm, K. J. Grue, J. Geophys. Res. 99, 2955 (1994).
- 13. R. S. White, D. P. McKenzie, J. Geophys. Res. 94, 7685 (1989).
- 14. W. S. Holbrook et al., Earth Planet. Sci. Lett. **190**, 251 (2001).
- C. W. Sinton, R. A. Duncan, in *Proceedings of the Ocean* Drilling Program, H. C. Larsen et al., Eds. (College Station, TX, 1998), vol. 152, pp. 387–402.
- M. Storey, R. A. Duncan, C. Tegner, *Chem. Geol.* 10.1016/ j.chemgeo.2007.01.016 (2007).
- H. Hansen et al., in The North Atlantic Igneous Province: Stratigraphy, Tectonics, Volcanic and Magmatic Processes, D. W. Jolley, B. R. Bell, Eds. (Geological Society of London Special Publication, Geological Society of London, 2002), vol. 197, pp. 183–218.
- P. Riisager, J. Riisager, N. Abrahamsen, R. Waagstein, Earth Planet. Sci. Lett. 201, 261 (2002).
- J. Rasmussen, A. Noe-Nygaard, *Geology of the Faeroe* Islands (Danmarks Geologiske Undersøgelse, Copenhagen, Denmark, 1970), series 25.
- L. M. Larsen, R. Waagstein, A. K. Pedersen, M. Storey, J. Geol. Soc. London 156, 1081 (1999).
- 21. A. K. Pedersen, M. Watt, W. S. Watt, L. M. Larsen, J. Geol. Soc. London 154, 565 (1997).
- C. Tegner, C. E. Lesher, L. M. Larsen, W. S. Watt, *Nature* 395, 591 (1998).
- 23. P. R. Renne et al., Chem. Geol. 145, 117 (1998).
- 24. T. F. D. Nielsen, J. Petrol. 45, 507 (2004).
- 25. D. Norton, H. P. Taylor, J. Petrol. 20, 421 (1979).
- 26. M. M. Hirschmann, P. R. Renne, A. R. McBirney, *Earth Planet. Sci. Lett.* **146**, 645 (1997).
- 27. R. B. Larsen, C. Tegner, Lithos 92, 181 (2006).
- 28. K. G. Cox, J. Petrol. 21, 629 (1980).
- 29. T. Westerhold et al., Paleoceanography 22, PA2201 (2007).
- J. G. Ogg, A. G. Smith, in *A Geological Time Scale*,
 F. M. Gradstein, J. G. Ogg, A. G. Smith, Eds. (Cambridge Univ. Press, Cambridge, 2004), pp. 63–86.
- R. W. O'B Knox, in *Initial Reports of the Deep Sea Drilling* Project, P. C. Graciansky et al., Eds. (U.S. Government Printing Office, Washington, DC, 1985), vol. 80, pp. 845–850.
- 32. B. S. Cramer, J. D. Wright, D. V. Kent, M.-P. Aubry, Paleoceanography 18, 1097 (2003).
- 33. L. E. Heister et al., J. Geol. Soc. London 158, 269 (2001).
- Materials, methods, and argon isotopic analyses are reported in the supporting material on *Science* Online.
- The Villum Kann Rasmussen Foundation funded the establishment of QUAD-Lab and supports its continued operation. The U.S. NSF supported the age determinations at Oregon State and Rutgers Universities.
 T. A. Becker, L. Hogan, O. Stecher, J.-O. Nielsen, O. Vagner, and R. Bitsch are thanked for technical advice and support.

18 September 2006; accepted 21 March 2007 10.1126/science.1135274