Journal of the Geological Society, *London*, Vol. **167**, 2010, pp. 433–436. doi: 10.1144/0016-76492009-125.

SPECIAL

Zircon dating ties NE Atlantic sill emplacement to initial Eocene global warming

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The Earth experienced rapid greenhouse gas induced global warming during the Palaeocene–Eocene thermal maximum (PETM). The source of the gas is, however, debated. We have, for the first time, determined the ages of magmatic sills in the Vøring Basin offshore Norway. Zircon U–Pb ages of 55.6 ± 0.3 and 56.3 ± 0.4 Ma demonstrate that sill emplacement was synchronous with the PETM within small errors. This discovery strengthens the hypothesis that global warming was triggered by rapid release of greenhouse gases generated by heating of organic-rich sediments around intrusions in the NE Atlantic rather than from dissociation of gas hydrates.

Supplementary material: U–Pb data are available at http://www.geolsoc.org.uk/SUP18392.

The geological record shows that an abrupt environmental change occurred in the earliest Eocene. This event, the Palaeocene–Eocene thermal maximum (PETM), lasted for about 170 ka and was characterized by pronounced global warming of 5–9 °C and mass extinction among benthic oganisms (e.g. Kennett & Stott 1991; Kelly *et al*. 1996; Zachos *et al*. 2005; Röhl *et al*. 2007). The greenhouse conditions resulted from the release of several thousand gigatons of ^{12}C-enriched carbon gases to the atmosphere (e.g. Dickens *et al*. 1997; Zachos *et al*. 2005; Zeebe *et al*. 2009).

Although the sedimentary deposits spanning the PETM have been thoroughly studied, there is currently no consensus about the source of the emitted carbon. Carbon dioxide degassing from the lavas of North Atlantic volcanic province was initially proposed as the source, in line with similar scenarios from other large igneous provinces that were emplaced synchronously with global environmental changes (e.g. Caldeira & Rampino 1990). More recently, dissociation of marine gas hydrates has been favoured as a carbon source compared with lava degassing, as the content of isotopically light carbon in magmatic gases is too low (e.g. Dickens *et al*. 1997; Thomas *et al*. 2002; Lourens *et al*. 2005; Maclennan & Jones 2006). Recent carbon cycle modelling has suggested that CO_2 alone, regardless of its source, is insufficient to explain the warming and suggests that methane degassing is a possible mechanism (Zeebe *et al*. 2009). Alternatively, unknown feedback mechanisms contributed to a significant part of the warming, with a lesser component (1–3.5 °C) from carbon gases (Zeebe *et al*. 2009).

Magma intruded the Møre and Vøring basins offshore Norway during the initial stages of the continental break-up in the NE Atlantic. Svensen *et al*. (2004) suggested that the PETM was triggered by the release of carbon gases generated by contact metamorphism of organic-rich sediments around the intrusions. The strength of this hypothesis is that it has a firm basis in geological observations of the presence of sills and associated hydrothermal vent complexes (e.g. Planke *et al*. 2005) and it is supported by recent dating of tuffs and lavas of the North Atlantic volcanic province (Storey *et al*. 2007). However, a challenge has been the lack of radiometric ages of the sill intrusions offshore Norway. In this paper, we present new ages from zircons found in two sills drilled by a commercial borehole on the Utgard High in the Vøring Basin (well 6607/5-2). These new data allow us to compare the sill emplacement ages with the timing of the PETM.

Sill intrusions in the Vøring and Møre basins. The Vøring and Møre basins offshore Norway contain a voluminous magmatic complex of dominantly subhorizontal sheets (sills) that intruded Cretaceous sedimentary rocks during opening of the NE Atlantic (e.g. Berndt *et al*. 2000; Brekke 2000; Planke *et al*. 2005; Cartwright & Møller Hansen 2006). Sill intrusions are identified as high-amplitude reflections on seismic profiles, and are present within the pre-Cenozoic stratigraphy in a >85 000 km^2 large area offshore mid-Norway (Fig. 1a). The sills have been drilled by a few industrial boreholes on structural highs. The best example is the Utgard borehole (6607/5-2), which intersects two prominent dolerite sills with thicknesses of 91 m (Utgard Upper Sill) and >50 m (Utgard Lower Sill) present in Upper Cretaceous mudstones (Fig. 1b) (e.g. Berndt *et al*. 2000). Drilling terminated 50 m into the lower sill, thus its thickness remains unknown. The upper sill is very well imaged on seismic profiles and can be followed for more than 100 km westward (Fig. 2). Hydrothermal vent complexes are also abundant in the basins and more than 700 craters up to 12 km in diameter have been mapped on the Palaeocene–Eocene palaeo-sea floor (Fig. 1), providing evidence for violent release of gas generated within the contact aureoles around the sills (Svensen *et al*. 2004; Planke *et al*. 2005).

Methods. The 6607/5-2 borehole was drilled by Esso in 1991, and sampled at the core storage of the Norwegian Petroleum Directorate in Stavanger, Norway, in 2007. A maximum of 40 g of material (i.e. rock chips retrieved during drilling) was granted per sample. We merged 10 of the samples collected from various levels within the Utgard Upper Sill and three from the Utgard Lower Sill for mineral separation.

After enrichment in heavy liquid and by magnetic separation, zircon and baddeleyite were selected for dating by hand-picking. Zircon is generally rare or absent in mafic rocks but when present it tends to occur as long-prismatic, euhedral or skeletal crystals. The search for zircons in the sills was therefore focused on this type of crystals (Fig. 3b and c), as they are less likely to represent detrital grains from the surrounding sediments. The chosen crystals were generally broken and characterized by brownish, elongate interiors that may represent thin cores of baddeleyite or, more likely, altered cavities. These grains were

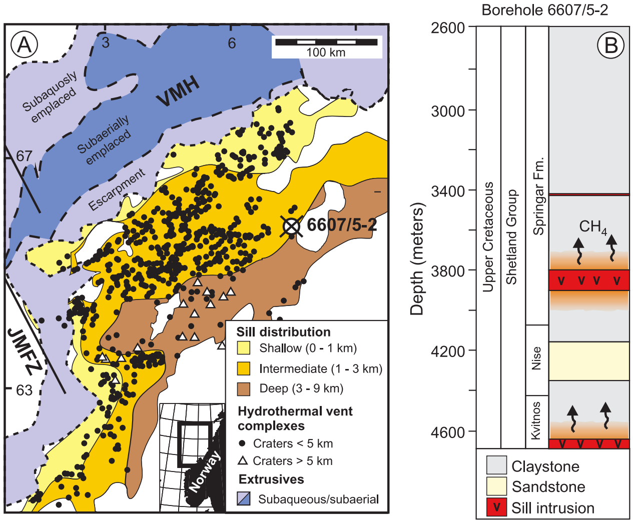

Fig. 1. (**a**) Sill complexes and hydrothermal vent complexes in the Vøring Basin offshore Norway, based on Planke *et al*. (2005). The location of the studied 6607/5-2 Utgard borehole is shown. JMFZ, Jan Mayen Fracture Zone; VMH, Vøring Margin High. (**b**) Simplified stratigraphy of the Utgard borehole. Two prominent sill intrusions were drilled, with extensive contact aureoles in which the original claystone minerals have been replaced by high-temperature minerals. The organic carbon content has been lowered as a result of greenhouse gas generation and subsequent migration (symbolized by arrows).

then abraded (Krogh 1982), a process that generally also led to further fragmentation, to remove external and altered outer domains affected by Pb loss. Baddeleyite fragments were all thin and tabular (Fig. 3a) and could not be abraded. The U–Pb analyses were carried out at the University of Oslo by isotope dilution thermal ionization mass spectrometry (Krogh 1973) using a mixed ^{235}U–^{205}Pb–^{202}Pb spike. Pb and U were measured directly without chemical purification. Blank correction was 2 pg or less for Pb and 0.1 pg for U. Only two analyses had some excess common Pb, which was corrected using the Stacey & Kramers (1975) model. All uncertainties in the presented ages represent 2σ. The external uncertainty of the ages related to spike calibration is estimated to be less than 2‰ on the basis of a comparison with various calibration solutions, including ‘Earthtime’ solutions (http://www.earth-time.org/), corresponding to roughly 0.1 Ma. Other details of the procedure have been given by Corfu (2004).

Age of sill intrusions. Six zircon analyses from the Utgard Upper Sill gave ages clustering between 56 and 55 Ma (Fig. 3). Because of the high surface to volume ratio of such long prisms, and the presence of internal cavities and alteration, it is assumed that the slight dispersion of the data reflects some residual Pb loss effects in the two analyses with the lowest $^{206}Pb/^{238}U$ ages. These were excluded from the calculation of the concordia age of 55.6 ± 0.3 Ma, which is interpreted as the age of emplacement of the Utgard Upper Sill. Baddeleyite yields a slightly lower age, probably because of Pb loss promoted by its tabular shape. Two other zircon grains yielded ages of 412 and about 1600 Ma, indicating a detrital origin for these two. The attempt to find zircon crystals in the Utgard Lower Sill was less successful. One zircon analysis defines a concordia age of 56.3 ± 0.4 Ma, which overlaps, within error, the age of the Utgard Upper Sill. A second zircon and a baddeleyite analysis are slightly younger, probably due to Pb loss, whereas another two yielded ages of more than 70 Ma, indicating that they are xenocrystic.

Our results show that subvolcanic mafic rocks have the potential to yield zircon suited for U–Pb dating. This method has yielded high-precision ages for mafic sills in other volcanic basins (Svensen *et al*. 2007, 2009), increasing the reliability of the ages compared with the more widely applied $^{40}Ar/^{39}Ar$ method on plagioclase. The U–Pb system in zircon can be biased by the presence of xenocrystic components and by Pb loss. To avoid xenocrystic zircons the measurements were made on long, slender prisms, especially such crystals with longitudinal cavities or inclusions of melts and/or other minerals that leave no space for old zircon cores. These features are typical for zircons that have grown rapidly in oversaturated magmas (Corfu *et al*. 2003). The strategy was reasonably successful and only three of the zircon grains, including only one long prism, were found to have older ages. The disadvantage of such crystals is that they have high surface to volume ratios and hence a greater propensity to lose Pb. To reduce this effect, the grains were very strongly abraded at the expense of considerable volume reduction. Although this also reduced the precision of the single analyses,

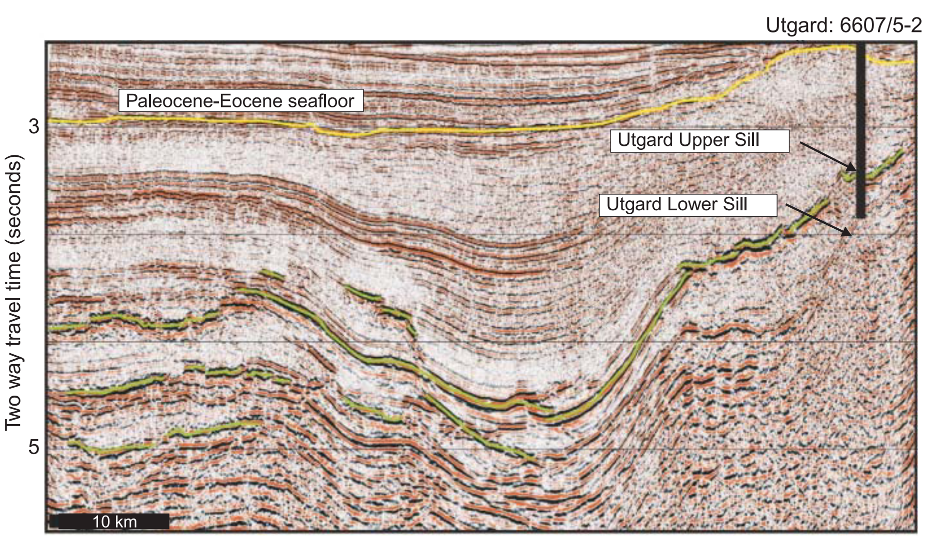

Fig. 2. Seismic reflection profile from the Vøring Basin and the Utgard borehole 6607/5-2. A noteworthy feature is the abundant high-amplitude reflections interpreted as sill intrusions (green). This interpretation is validated by the borehole. It should be noted also that the Utgard Upper Sill is partly masking the reflections from the Utgard Lower Sill. Hydrothermal vent complexes are not present in the profile. The profile is from an east–west section and covers a distance of about 80 km.

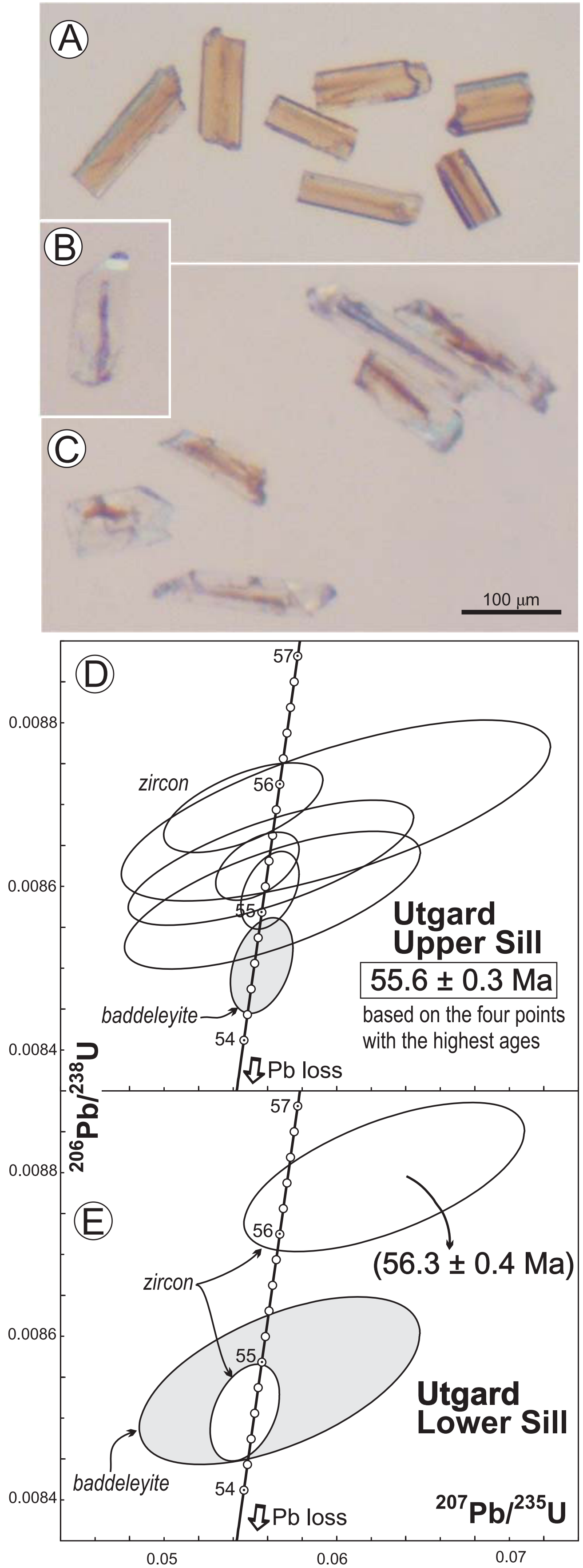

Fig. 3. (**a**) Baddeleyite blades. (**b**) Euhedral zircon prism with longitudinal inclusion or cavity. (**c**) Long-prismatic zircon crystals, with or without pyramidal ends, and with prominent longitudinal inclusions or cavities, generally rusty. These are typical morphologies of zircon in mafic rocks and are representative for most zircon grains analysed. The scale also applies to (**a**) and (**b**). (**d**, **e**) U–Pb concordia diagrams: (**d**) for the Utgard Upper Sill; (**e**) for the Utgard Lower Sill. The ages are interpreted to represent the sill emplacement ages.

the fact that a number of data points overlap is a good indication that Pb loss was minimal in these grains.

Correlation between sill ages and the PETM. A causal relationship between methane generation around sill intrusions and the environmental changes during the PETM requires identical timing within the uncertainties of the methods used. The initiation of the PETM, and hence the Palaeocene–Eocene boundary, is defined by a negative carbon isotope excursion (Gradstein *et al*. 2004). However, because the negative carbon isotope excursion commonly is asymptotic and gradual, other geochemical signals have been adopted (i.e. Ba, Fe, Ca; Röhl *et al*. 2007). An absolute age of the excursion itself is not available. Currently, the PETM is dated using a combination of $^{40}Ar/^{39}Ar$ dates of ash layers within magnetochron C24r and recalculations of that age to match the position of the excursion (see Westerhold *et al*. 2008). With this approach, it is suggested that the PETM most probably started at either *c*. 55.53 Ma or *c*. 55.93 Ma and lasted about 170 ka (Röhl *et al*. 2007; Westerhold *et al*. 2008). The unresolved timing of the PETM is due to uncertainties in the $^{40}Ar/^{39}Ar$ method and the cyclostratigraphy (Westerhold *et al*. 2008). Of importance is that both ages overlap the age of the Utgard Upper Sill (55.6 ± 0.3 Ma) within small errors. This strengthens a causal relationship between sill emplacement, generation and venting of thermogenic ^{12}C-enriched methane, and the PETM.

Regional implications. How representative are the ages of the Utgard sills when considering sill emplacement on a basin scale? Several lines of evidence suggest that sill emplacement in the Vøring and Møre basins was rapid, and that the major part of the sill complex was emplaced close to the time of the intrusion of the Utgard sills. (1) Seismic mapping shows that the Utgard Upper Sill is a part of the Vøring sill complex (Fig. 2; Planke *et al*. 2005). To construct the bulk of the mapped sill complex would require only a relatively small volume of melt to form the entire intrusive complex, and a few intrusive episodes (2000–10 000 km^3) (Svensen *et al*. 2004). (2) Biostratigraphy from one of the hydrothermal vent complexes in the Vøring Basin suggests their formation during the PETM (Svensen *et al*. 2004), and 95% of the degassing craters associated with the sill intrusions are confined to the Top Palaeocene horizon (Planke *et al*. 2005). (3) Sill intrusions in the Faeroe–Shetland Basin have been indirectly dated by biostratigraphy from sediments onlapping structures uplifted during sill emplacement, further linking sill emplacement to the PETM (Trude *et al*. 2003). Moreover, hydrothermal vent complexes have also been identified in the Faeroe–Shetland Basin (e.g. Møller Hansen 2006). (4) The ages of the Utgard sills fit well with other radiometric age determinations of volcanic rocks from the North Atlantic volcanic province (e.g. Storey *et al*. 2007).

To conclude, a few batches of melt can be responsible for constructing the bulk of the sill complex present in the Vøring and Møre basins. This conclusion is particularly important when assessing the climate implications of sill emplacement and contact metamorphism. For instance, a single 5000 km^3 dolerite sill may in a decade generate 125–450 Gt carbon in greenhouse gases if intruded as a 100 m thick sill in a black shale sequence with 1–3 wt.% total organic carbon transferred to carbon gas (see Svensen *et al*. 2007). The generated gas corresponds to up to 60 years of anthropogenic greenhouse gas emission at today's rates. Methane would be the dominant gas formed during contact metamorphism in the Vøring Basin, having a climate warming effect of more than 10 times that of carbon dioxide.

Conclusions. Zircons have been found in two sill intrusions emplaced into Cretaceous sedimentary rocks in the Vøring Basin offshore mid-Norway, yielding U–Pb zircon ages of 55.6 ± 0.3 Ma for the Utgard Upper Sill and 56.3 ± 0.4 Ma for the Utgard Lower Sill. The ages overlap within errors the time of the PETM. Seismic and borehole data show that, within the uncertainty of the methods, the bulk of the Vøring sill complex was emplaced at the same time as the Utgard sills. The new dates strengthen the hypothesis that contact metamorphism of organic-rich sediments around sill intrusions, and subsequent methane venting to the atmosphere, were the key processes that triggered the PETM.

We thank the Norwegian Petroleum Directorate for access to samples, TGS-NOPEC for access to seismic data, and the Norwegian Research Council for funding (SFF grant to PGP and a PetroMaks grant to H.S.). M. Schjoldager is thanked for careful zircon separation. Discussions with T. Pedersen and constructive comments on the manuscript by M. Huber, V.R. Troll and an anonymous referee are appreciated.

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Received 24 August 2009; revised typescript accepted 16 November 2009.
Scientific editing by Martin Whitehouse.