Precisely dating the Frasnian–Famennian boundary: implications for the cause of the Late Devonian mass extinction

L. M. E. Percival1, J. H. F. L. Davies2, U. Schaltegger6, D. De Vleeschouwer3, A.-C. Da Silva4,5 & K. B. Föllmi1

The Frasnian–Famennian boundary records one of the most catastrophic mass extinctions of the Phanerozoic Eon. Several possible causes for this extinction have been suggested, including extra-terrestrial impacts and large-scale volcanism. However, linking the extinction with these potential causes is hindered by the lack of precise dating of either the extinction or volcanic/impact events. In this study, a bentonite layer in uppermost-Frasnian sediments from Steinbruch Schmidt (Germany) is re-analysed using CA-ID-TIMS U-Pb zircon geochronology in order to constrain the date of the Frasnian–Famennian extinction. A new age of 372.36 ± 0.053 Ma is determined for this bentonite, confirming a date no older than 372.4 Ma for the Frasnian–Famennian boundary, which can be further constrained to 371.93–371.78 Ma using a pre-existing Late Devonian age model. This age is consistent with previous dates, but is significantly more precise. When compared with published ages of the Siljan impact crater and basalts produced by large-scale volcanism, there is no apparent correlation between the extinction and either phenomenon, not clearly supporting them as a direct cause for the Frasnian–Famennian event. This result highlights an urgent need for further Late Devonian geochronological and chemostratigraphic work to better understand the cause(s) of this extinction.

The Late Devonian (~383–359 Ma) marked a time of repeated environmental upheaval, featuring numerous carbon-cycle perturbations and local- to global-scale periods of marine anoxia during the Givetian (e.g., Frasnes Event), Frasnian (e.g., Punctata Event), and Famennian (e.g., Annulata Event) Stages. Two such episodes of environmental perturbation also featured major faunal extinctions, documented at the Frasnian–Famennian and Famennian–Tournasian Stage Boundaries (reviewed by e.g.1,2). The Frasnian–Famennian (FF) boundary extinction was apparently the most devastating biotic crisis of the Devonian Period, and represents one of the ‘Big Five’ mass extinctions of the Phanerozoic Eon3,4. Reef systems and especially stromatoporoids, which had enjoyed considerable ecological success and geographically widespread distribution throughout much of the preceding Devonian, were particularly affected (see5). Elevated extinction rates are also documented amongst many other benthic and planktonic marine invertebrates (reviewed by e.g.3,6). The ultimate cause(s) of this extinction remains debated, with numerous potential triggers suggested including marine anoxia, extra-terrestrial impacts, and volcanic activity (Fig. 1). However, the exact age of the Frasnian–Famennian boundary remains relatively poorly constrained, hindering any comparison of the extinction date with those of impact craters or volcanic basalts. This study presents a new precise age of the FF boundary from dating of a bentonite layer deposited 2.5 m stratigraphically below that horizon, in order to better constrain temporal correlations of the FF extinction and other Late Devonian phenomena.

The onset of the Frasnian–Famennian extinction is documented in uppermost Frasnian strata, which also record a distinct perturbation to the carbon cycle as a positive carbon-isotope excursion. Increases in δ13C values

1Institut des sciences de la Terre, Géopolis, Université de Lausanne, 1015, Lausanne, Switzerland. 2Département des sciences de la Terre, Université de Genève, 1205, Genève, Switzerland. 3MARUM—Center for Marine Environmental Sciences, University of Bremen, Leobenerstraβe, 28359, Bremen, Germany. 4Sedimentary Petrology Laboratory, Liège University, Sart Tilman B20, Allée du Six Août 12, 4000, Liège, Belgium. 5Paleomagnetic Laboratory, Utrecht University, Budapestlaan 17, 3584 CD, Utrecht, The Netherlands. Correspondence and requests for materials should be addressed to L. M. E. P. (email: lawrence.percival@unil.ch)
of up to 4‰ in both carbonates and bulk organic matter are observed in the \textit{linguiformis} conodont Zone in sedimentary records across the globe (e.g.,\textsuperscript{7,12}); see also Fig. 2). An additional positive excursion in $\delta^{13}C$ of carbonates and organic matter is also often documented in the preceding \textit{rhenana} conodont Zone or its biostratigraphic equivalent. The two $\delta^{13}C$ excursions stratigraphically correlate with the appearance of laminated black shales referred to as the Lower (LKW) and Upper (UKW) Kellwasser horizons, particularly in European records\textsuperscript{7,9}; Fig. 2). The onset of decline amongst some marine fauna (such as reef systems) is thought to have begun during the LKW Event, with such trends culminating in a more severe extinction pulse affecting numerous taxonomic groups during the UKW Event, recorded at the FF boundary (reviewed in refs\textsuperscript{1,6}). The stratigraphically correlated black shales and positive $\delta^{13}C$ excursions have been used to infer the development of widespread marine anoxia during both Kellwasser events in the latest Frasnian, which is supported by pyrite-framboid size, organic-biomarker analysis, calcite sulphur-isotope compositions, and trace-metal enrichments in sedimentary

Figure 1. Palaeogeographic map of the Late Devonian world, based on ref.\textsuperscript{77}. The location of Steinbruch Schmidt (1), the Siljan impact crater (S), the Viluy Traps (V), and the Kola, Vyatka, and Pripyat–Dniepr–Donets rift systems (K-V-PDD) are indicated.

Figure 2. Summary stratigraphic data of the Steinbruch Schmidt section (Germany). Lithological and biostratigraphic data and the stratigraphic positions of the Kellwasser horizons are from ref.\textsuperscript{49}. Carbon-isotope data are from ref.\textsuperscript{7}. The stratigraphic position of the Bed 36 bentonite is from ref.\textsuperscript{53}.
records from across the globe (e.g., 13–17). In addition to widespread marine anoxia, there is evidence for increased marine primary productivity, enhanced rates of continental weathering, and global cooling during both of the Kellwasser events11,17–22. Consequently, the marine anoxic conditions during the Kellwasser events are often attributed to enhanced primary productivity stimulated by the influx of nutrients to the marine realm during times of extreme weathering rates, potentially resulting from orogenic activity and/or the expansion of rooted vascular land plants during the Late Devonian (e.g., 23,24).

A wide range of mechanisms has been proposed as additional external triggers of the extinction, including the impact of a large extra-terrestrial body, repeated bombardment by numerous smaller extra-terrestrial objects, large-scale volcanic activity and associated gas release, and climate forcing via orbital configuration.6,12,23–31. Microtektite layers have been reported from lower Famennian strata of both Belgian and Chinese records; a Late Devonian impact crater is well known from Sweden (the ∼50 km diameter Siljan crater: e.g., 32), with another in North America indicated by an impact breccia in Upper Devonian strata of Nevada (e.g., 33). Late Devonian large-scale volcanic activity is best associated with the emplacement of the Viluy Traps, a Large Igneous Province (LIP) in eastern Siberia thought to have originally consisted of more than 1 Mkm$^3$ of basalt34–36,38,39. Additional volcanic activity linked with major rifting systems in eastern Europe has also been noted as occurring during the Late Devonian, which may have generated on the order of an additional 1 Mkm$^3$ of basaltic material30,36,37.

An excellent correlation between the determined ages of LIP volcanic events and times of mass extinction and major environmental perturbation has been established for latest-Palaeozoic through to early Cenozoic times (e.g., 35,38,39), and the end-Cretaceous extinction has additionally been linked with a large extra-terrestrial impact (e.g., 40). In this context, the record of both large-scale volcanism and extra-terrestrial impacts occurring in the Late Devonian is intriguingly suggestive of a potential causal relationship between those phenomena and the many Late Devonian biotic and environmental crises, including the FF extinction.

In order to determine whether large-scale volcanism or an extra-terrestrial impact were indeed the major cause of the FF extinction, their precise temporal relationship with the extinction must be established. This approach has been employed successfully to illustrate a precise coincidence between other extinction events, such as the end-Permian and end-Triassic, and times of major intrusive/extrusive LIP magmatism (e.g., 41–43). However, the date of the FF extinction remains poorly constrained. The current Geological Time Scale date for the FF boundary is 372.2 ± 1.6 Ma, based on Monte Carlo statistical analysis of several Devonian ash uranium-lead (U-Pb) dates44. Recalculation of this timescale based on Bayesian statistics, and independent methods such as rhenium-osmium (Re-Os) isochron dating and cyclostratigraphy anchored to the well-dated Famennian–Tournaisian boundary have all given a similar age, but with uncertainties still on the order of a million years45–48. Because major LIP magmatic events and extra-terrestrial impacts can influence the Earth’s environment on the time scale of tens of millennia or less, a much greater degree of precision is desired for the age of the FF extinction, ideally to within <100 kyr.

In this study, a bentonite layer from Bed 36 (by the numbering system of ref. 49) in the Frasnian–Famennian succession at the abandoned Steinbruch Schmidt Quarry (Germany: Figs 1 and 2) is dated using U-Pb analysis of zircons, in order to determine a precise age of the FF boundary. Recent advances in U-Pb dating have allowed for unprecedented precision in constraining the ages of deep-time volcanic eruptions, allowing geological boundary ages to be constrained to within tens to hundreds of millennia based on dating of bentonite layers stratigraphically proximal to those boundaries (e.g., 50–52). The Steinbruch Schmidt bentonite layer is just 2.5 m below the FF boundary and, crucially, lies within a thin (2.5 m) set of carbonate beds stratigraphically between the two Kellwasser horizons. The time between these two horizons is estimated as 400–450 kyr12. Thus, the age of this bentonite represents a good approximation of the ages of the FF boundary and the Upper Kellwasser extinction event. This bentonite has previously been dated to 377.2 ± 1.7 Ma by laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) techniques, from which a FF boundary age of 376.1 Ma was inferred53. However, the inconsistency between this date and more recent determinations of the FF boundary age based on Re-Os dating and statistical modelling of Devonian bentonite U-Pb ages (see below) suggests that this previous age might be erroneous44–48. Nonetheless, the previous dating by ref. 53 highlights the suitability of the zircons in this bentonite for precise dating. In this study, the Steinbruch Schmidt bentonite is re-dated using state-of-the-art chemical abrasion-isotope dilution-thermal ionization mass spectrometry (CA-ID-TIMS) analysis with the EARTHTIME 2535 spike. Such methods allow for a very precise age of the bentonite to be determined; consequently, the FF boundary age can also be constrained to a greater level of precision. This new age is compared with the determined ages of other Late Devonian phenomena such as the Siljan impact and Viluy Trap magmatic episodes in order to establish the level of coincidence between these events and the FF extinction, and to infer if they had any influence on that biotic/environmental crisis.

**Results**

The zircon crystals from the bentonite chosen for U-Pb dating were all acicular euhedral long prismatic grains. 11 grains were dated by the CA-ID-TIMS technique and 8 of these produced overlapping concordant ages from which a weighted mean age of 372.360 ± 0.053/0.11/0.41 Ma (MSWD = 1.47) was calculated (see Supplementary Table 1; Fig. 3). The three uncertainties are all at 2σ, the first (0.053 Ma) represents only the measurement uncertainty, the second (0.11 Ma) represents the measurement uncertainty plus the ET2535 tracer uncertainty, and the third (0.41 Ma) includes the measurement, tracer and also decay constant uncertainties. This last, greatest, uncertainty must be employed when making comparisons between U-Pb ages and argon–argon (Ar-Ar) ages. The three zircon ages not included in the weighted mean are all slightly older. These grains may be antecrysts that crystallized somewhere in the magmatic system significantly prior to eruption.
Discussion

The stratigraphic position of the analysed bentonite below the FF boundary means that the age of that horizon can be no older than that of the bentonite itself. Consequently, because the bentonite has a determined age of 372.36 ± 0.053 Ma, the FF boundary cannot be older than 372.4 Ma. This result is comfortably within error of the recent estimations of the FF boundary age44–48 but markedly younger than the date by ref53, supporting the hypothesis that the previous determined age of the Steinbruch Schmidt bentonite was erroneous. However, whilst a FF boundary age of 372.4 Ma is in agreement with other estimates for that horizon, its actual age will in reality be younger because the bentonite lies 2.5 m stratigraphically below that level. A recent study constructed a global cyclostratigraphic framework of geologic time during and between the two Kellwasser events12. By combining this age model with the new age of the Steinbruch Schmidt bentonite in this study, the exact age of the FF boundary can be estimated (Fig. 4). The age model in ref12 indicated that the Lower Kellwasser Event terminated 500–600 kyr prior to the end of the Frasnian, with the Upper Kellwasser Event beginning 150 kyr before the conclusion of that Stage. Consequently, approximately 350–450 kyr passed between the two events, which can be further constrained to 400–450 kyr due to the recording of an entire long-eccentricity cycle (405 kyr) between the two Kellwasser horizons12. The Bed 36 bentonite at Steinbruch Schmidt lies 42.5 cm above the top of the Lower Kellwasser Horizon, and 206 cm below the base of the Upper Kellwasser Horizon, 17% of the stratigraphic distance between the two Kellwasser beds. Assuming that the age model of ref12 is correct, that the record at Steinbruch Schmidt is stratigraphically complete, and the carbonate beds between the two Kellwasser horizons were deposited at a constant sedimentation rate, the bentonite would have been deposited ∼70–75 kyr after the end of the Lower Kellwasser Event, and consequently ∼480–525 kyr before the end of the Frasnian Stage.

For the determined bentonite age of 372.36 ± 0.053 Ma, this reasoning results in a Frasnian–Famennian boundary age of 371.93–371.78 Ma (371.86 ± 0.08 Ma).

The current Geological Time Scale (GTS) provides an age for the base of the Famennian Stage of 372.2 ± 1.6 Ma, based on Monte Carlo statistical analysis of selected U-Pb dates from volcanic materials distributed throughout the Devonian stratigraphy44. This age has subsequently been refined by Bayesian statistical analyses of the same U-Pb ages, which yielded a FF boundary age of 373.9 ± 1.4 Ma47. Such approaches are axiomatically dependent on the accuracy and precision of the U-Pb dates utilized, many of which have error bars of >1 Myr, thus hampering the precision of the Stage boundary ages output by the model. A more direct approach is to employ the decay of 187Re to 187Os in organic-rich shale records of the FF boundary to construct a Re-Os isochron age for those sediments45,46. An age of 372.4 ± 3.8 Ma for the FF boundary has been calculated using this method45. Most recently, a cyclostratigraphic timescale was constructed for the entire Famennian based on three cores from the North American Illinois Basin48. By anchoring this timescale to the well constrained date of the Famennian–Tournaisian boundary (358.9 ± 0.4 Ma), those authors determined an age of 372.4 ± 0.9 Ma for the FF boundary. Both the maximum and inferred FF boundary ages in this study of 372.4 Ma and 371.93–371.78 Ma, respectively, are consistent with the GTS date and the other previously determined ages documented.
The inferred boundary age of 371.93–371.78 Ma is also significantly more precise than the previous estimates. Moreover, because of the stratigraphic proximity of the bentonite to the FF boundary and Kellwasser horizons at Steinbruch Schmidt, cyclostratigraphic analysis of the sediments across that single record will enable the ages of both the boundary and the Kellwasser events to be constrained still more precisely and without the assumptions inherent in the date presented here. However, even without such further investigative analyses, the temporal relationships between Late Devonian volcanic and impact events and the FF boundary extinction can still be reviewed in light of the new date of the Steinbruch Schmidt bentonite, and the inferred FF boundary age of 371.93–371.78 Ma.

The most likely candidate for an extra-terrestrial impact associated with the Late Devonian extinctions is documented by the Siljan crater in Sweden. Precise dating of the Siljan crater has been substantially hindered by significant alteration of many of the crater lithologies. The most recently determined, and precise, Ar-Ar date of the crater is 377 ± 2 Ma. Even accounting for the large degree of uncertainty in this age, the results of this study confirm previous findings that the FF boundary extinction significantly post-dated the impact that formed the Siljan crater (Fig. 5). Additionally, the Siljan ring has only a ∼50 km diameter, and whilst claims have been made that the crater may well have been somewhat larger originally, even the largest estimate is well under 100 km. Thus, the Siljan impactor would have been only 30–50% of the size of the Chicxulub impactor linked with the end-Cretaceous extinction as well as being significantly smaller than other impactors not currently associated with biospheric crises (e.g., Manicouagan, Canada: Late Triassic).

The Alamo impact breccia in Nevada (USA) provides evidence for a further impact during the Late Devonian, but has been biostratigraphically dated to the punctata conodont Zone from the early Frasnian. Consequently, that impact would have substantially predated the Kellwasser events. Microtektite glasses have been reported from lower Famennian sediments in South China and Belgium as evidence for an impact but they are not known from the majority of FF boundary records worldwide. There is also little evidence for an impact-related iridium anomaly in FF boundary strata. Moreover, even if an impact did occur to produce the microtektite beds, its temporal relationship with the FF extinction is unclear, with some microtektite deposits appearing above the FF boundary and others below that horizon. This lack of stratigraphic and geographic continuity in the microtektite deposits clearly does not support a coincidence between a large-scale impact and the FF boundary extinction, although an alternative scenario of repeated bombardment by smaller extra-terrestrial objects has also been proposed (see ref. 6).

A potential link between volcanic activity and the FF extinction has long been mooted (e.g.,), but has become increasingly popular in recent years due both to dating of Viluy Trap basalts as Late Devonian in age and the clear relationship between LIP volcanism and many Mesozoic episodes of environmental perturbation and extinction. Because much of the province has been eroded, the true volume of the Viluy Traps is not well constrained, but it is estimated to have originally consisted of 0.3–1 Mkm³ of igneous material. The larger volume of which is comparable to that of several Phanerozoic LIPs associated with episodes of mass extinction and/ or environmental change. Some intrusive and extrusive magmas have been dated using Ar-Ar chronology, and indicate at least two pulses of Viluy magmatism, one in the late Frasnian, and another in the late Famennian. The first, late Frasnian, magmatic pulse was dated to 376.7 ± 1.7 Ma by ref. 31 and 374.1 ± 3.3 Ma by ref. 31. The
latter age does overlap with the FF boundary, although only because of the large error bars in the inferred age of that magmatic pulse. The given ages of individual basalts do not coincide with the FF boundary even once uncertainties in comparing the new U-Pb derived boundary age with Ar-Ar ages of volcanics are accounted for, although some may be closer in age to the Lower Kellwasser Event (∼372.6 Ma: Fig. 5). Consequently, if faunal extinctions did indeed commence during that earlier event, this may support a role for volcanism in the FF extinctions, even though there is no direct correlation between the ages of volcanism and the main extinction pulse at the FF boundary. The large uncertainties in the dates of individual basalts do overlap with the age of the FF boundary (Fig. 5); because these uncertainties are so large, more precise dating of Viluy Trap rocks are required in order to determine whether the FF boundary extinction truly coincided with major igneous activity. Interestingly, the second pulse of Viluy Trap volcanism (364.4 ± 1.7 Ma by ref.31 and 363.7 ± 0.7 Ma by ref.59) does match the age of the Fammenian Annulata Event based on the late Famennian cyclostratigraphic timescale of ref.62 (see Supplementary Figure 1).

In addition to Viluy Trap volcanism, substantial Late Devonian volcanic activity is thought to have occurred along the Kola, Vyatka, and Pripyat–Dniepr–Donets rift systems in what is now Eastern Europe (reviewed in ref.30). However, volcanic activity on these rifting margins likely represented a somewhat different style of volcanism to a Mesozoic LIP, and their impact on the Devonian palaeoenvironment may not be directly comparable with that of the large-scale volcanic episodes associated with Mesozoic extinction/climate events. Dating of the volcanism associated with these rift systems is also very poorly constrained: the Pripyat–Dniepr–Donets rifting is modelled as chiefly Famennian in age37 whilst the Kola volcanics are dated to the mid-Frasnian63. On the basis of current evidence, it appears unlikely that these rifts were the sole direct cause of the FF boundary extinction, although they may have played a contributing role in the build-up to one or more of the Late Devonian crises.

Figure 5. Summary diagram reviewing the ages of the FF boundary (from this work and previous studies), the Siljan impact crater, and the Viluy Traps. For the Viluy Trap dates, the illustrated dates indicate ages of individual LIP rocks. Biostratigraphy and the ages (where indicated) of biostratigraphic boundaries are based on the age model of ref.62. The grey bar indicates the inferred boundary age from this study after accounting for the uncertainty in calibrating between the U-Pb derived boundary age and the Ar-Ar derived ages of the Siljan impact and Viluy Trap basalts, and extends down to 372.77 Ma (the maximum age of the boundary following inclusion of the U-Pb vs Ar-Ar calibration uncertainty if negligible time is assumed to have passed between the deposition of the bentonite and the overlying boundary strata). Red dates are from ref.59, orange dates from ref.31. The blue Viluy Trap date is from ref.39 using the calibration of ref.78, the black open Viluy Trap date is that same Viluy Trap date from ref.29, using the conventional calibration. The green shaded area indicates the estimated age of the first pulse of Viluy Trap volcanism by ref.59, based on the dates of refs29,31. The red shaded area indicates the estimated age of the first pulse of Viluy Trap volcanism by ref.29, based on the dates of refs29,31,59. The FF boundary date generated in this study is also consistent with that of ref.79.
Whilst currently identified and dated episodes of large-scale volcanic activity do not appear to have clearly coincided with the Kellwasser events or the main pulse of extinction recorded at the FF boundary, such volcanism was clearly a feature of the Frasnian and Famennian Stages. It cannot be discounted that large-scale volcanic activity did occur coincident with the FF boundary extinction, but that the igneous products have not yet been identified or dated, or may not have been preserved. The application of indirect proxies of large-scale volcanism, such as sedimentary mercury concentrations (e.g. 64–67) and osmium-isotopes (e.g. 68,69), on strata from the Kellwasser horizons may give indirect evidence of the existence or absence of major volcanic activity at that time. A recent study of three FF boundary records shows mercury enrichments occurring at or near the boundary, indicating that volcanic activity may indeed have been occurring during the Upper Kellwasser Event70. Clearly, further work is needed to generate (precise) dates of more basalts from both the Viluy Traps and the Kola, Vyatka, and Pripyat–Dniepr–Donets rift-systems in order to verify the temporal relationship between large-scale volcanism and the Frasnian–Famennian extinction.

Conclusions
Precisely constraining the timing of the Frasnian–Famennian (FF) mass extinction represents a crucial step in understanding the influence of external phenomena such as large-scale volcanism and meteor impacts in causing that event. This study presents a new precise age of 372.360 ± 0.053 Ma for a bentonite stratigraphically proximal to the FF boundary, confirming an age no older than 372.4 Ma for that horizon, with an actual boundary age of 371.93–371.78 Ma reconstructed on the basis of a published age model of the Frasnian–Famennian transition. This result is consistent with other recently reported ages for the Frasnian–Famennian boundary, but is considerably more precise than these previously published works. The date also creates an anchor point for use in future cyclostratigraphic models which could establish an even more precise age for the FF boundary and associated Kellwasser events. Importantly, a greater confidence in the precise age of this horizon allows for a better understanding of the temporal relationships between the extinction event that took place at that time, and phenomena that might have contributed to the extinction such as extra-terrestrial impacts and large-scale volcanism. It is confirmed that the Siljan impact event happened significantly prior to the FF extinction, and is therefore unlikely to have played a role in that event. No individual Viluy Trap basalt matches the FF boundary date, although the timing of that horizon does fall within the age uncertainty of a late Frasnian pulse in Viluy Trap volcanism, and some individual basalts are close in age to the Lower Kellwasser Event. Thus, although there is no direct evidence of a coincidence between the extinction and large-scale volcanism based on current geochronology, major volcanic activity was likely still prevalent during the late Frasnian, highlighting the need for further geochronological and chem stratigraphic work to confirm the existence or absence of major volcanic activity during the Frasnian–Famennian extinction.

Materials and Methods
~1 kg of bentonite material was sampled from the Bed 36 layer (by the numbering of ref.49) at Steinbruch Schmidt, ~1 km north of Braunau, near the town of Bad Wildungen, Hesse, Germany (51° 5′ 12.1″ N, 9° 7′ 53.9″ E). Zircon crystals from this bentonite were separated by conventional mineral separation techniques and analysed by chemical abrasion-isotope dilution-thermal ionization mass spectrometry (CA-ID-TIMS) at the Département des sciences de la Terre, Université de Genève following the techniques described in ref.41. The bentonite contained abundant zircon crystals in many shapes and sizes, however only euhedral acicular elongated grains were selected for dating since these are least likely to be re-worked grains. 15 of the most pristine crystals were selected and annealed at 900 °C for 48 hr. The crystals were then individually cleaned with 3 Nolar HNO3 and loaded into 200 μl Savillex microcapsules for chemical abrasion to remove any areas of the grains that may have experienced Pb loss. Chemical abrasion was conducted in 3 drops of concentrated HF at 210 °C for 12 hr following the recommendation of ref.71. Eleven of the 15 grains survived the chemical abrasion procedure, these grains were then cleaned in 6 molar HCl in 3 ml Savillex beakers at 80 °C for 24 hr and then ultrasonically cleaned in 3 molar HNO3. Following cleaning, the grains were loaded into pre-cleaned 200 μl Savillex microcapsules with 3 drops of concentrated HF and trace HNO3, and one drop of the ET 202Pb + 205Pb + 233U + 235U tracer solution72,74. The microcapsules were placed in a Parr bomb, and then into an oven at 210 °C for 48 hr for dissolution. The resultant solution was dried down and the residue converted to a chloride by reaction with concentrated HCl at 210 °C for 12 hr, before being added to columns filled with pre-cleaned anion exchange resin. The Pb and U cuts were collected from the columns and dried down in cleaned 7 ml Savillex beakers with trace H3PO4 before being loaded on to outgassed zone refined Re filaments with a Si-Gel emitter and placed into a Phoenix isotop TIMS mass spectrometer. Pb was measured in dynamic mode on a daly; the U was measured as an oxide in static mode on faraday cups equipped with 10^12 Ω resistors. Mass fractionation of Pb was corrected using a known TIMS mass spectrometer. Pb was measured in dynamic mode on a daly; the U was measured as an oxide in static

References
1. Racki, G. Toward understanding Late Devonian global events: few answers, many questions. In Developments in Palaeontology and Stratigraphy 20, 5–36 (Elsevier, 2005).
2. Bond, D. P. G. & Grasby, S. E. On the causes of mass extinctions. Palaeogeogr. Palaeoclimatol. Palaeoecol. 478, 3–29 (2017).
3. McLaren, D. J. Time, life, and boundaries. J.Paleo. 44, 801–815 (1970).
4. Raup, D. M. & Sepkoski, J. J. Mass extinctions in the marine fossil record. Science 215, 1501–1503 (1982).
5. Copper, P. 100 million years of reef prosperity and collapse: Ordovician to Devonian interval. Paleontol. Soc. Pap. 17, 15–32 (2011).
6. Schmidt, K. A., Gvirtzman, H., Bard, E. & Hollert, H. U. The age of the upper Kellwasser event. Nature 402, 34–37 (1999).
7. Schmidt, K. A., Gvirtzman, H., Bard, E. & Hollert, H. U. The age of the upper Kellwasser event. Nature 402, 34–37 (1999).
8. Raup, D. M. & Sepkoski, J. J. Mass extinctions in the marine fossil record. Science 215, 1501–1503 (1982).
9. Copper, P. 100 million years of reef prosperity and collapse: Ordovician to Devonian interval. Paleontol. Soc. Pap. 17, 15–32 (2011).
10. Racki, G. Toward understanding Late Devonian global events: few answers, many questions. In Developments in Palaeontology and Stratigraphy 20, 5–36 (Elsevier, 2005).
11. Bond, D. P. G. & Grasby, S. E. On the causes of mass extinctions. Palaeogeogr. Palaeoclimatol. Palaeoecol. 478, 3–29 (2017).
12. McLaren, D. J. Time, life, and boundaries. J.Paleo. 44, 801–815 (1970).
13. Raup, D. M. & Sepkoski, J. J. Mass extinctions in the marine fossil record. Science 215, 1501–1503 (1982).
14. Copper, P. 100 million years of reef prosperity and collapse: Ordovician to Devonian interval. Paleontol. Soc. Pap. 17, 15–32 (2011).
6. McGhee, G. R. *The Late Devonian Mass Extinction: The Frasnian/Famennian Crisis* (Columbia University Press, 1996)
7. Joachimski, M. M. & Buggisch, W. Anoxic events in the late Frasnian—Causes of the Frasnian-Famennian faunal crisis? *Geology* **21**, 675–678 (1993).
8. Wang, K., Geldsetzer, H. H. J., Goodfellow, W. D. & Krouse, H. R. Carbon and sulfur isotope anomalies across the Frasnian-Famennian extinction boundary, Alberta, Canada. *Geology* **24**, 187–191 (1996).
9. Joachimski, M. M., Pancost, R. D., Freeman, K. H., Ostertag-Hening, C. & Buggisch, W. Carbon isotope geochemistry of the Frasnian–Famennian transition. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* **181**, 91–109 (2002).
10. Stephens, N. P. & Sumner, D. Y. Late Devonian carbon isotope stratigraphy and sea level fluctuations, Canning Basin, Western Australia. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* **191**, 203–219 (2003).
11. Chen, D., Qing, H. & Li, R. The Late Devonian Frasnian–Famennian (F/F) biotic crisis: insights from δ13Ccarb, δ13Corg and δ7S/δ6S isotopic systematics. *Earth Planet. Sci. Lett.* **235**, 151–166 (2005).

12. De Vleeschouwer, D. et al. Timing and pacing of the Late Devonian mass extinction event regulated by eccentricity and obliquity. *Nat. Commun.* **8**, 2268 (2017).
13. Joachimski, M. M. et al. Water column anoxia, enhanced productivity and concomitant changes in δ13C and δ34S across the Frasnian–Famennian boundary in key European sections: Chemotaxonomic constraints. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* **240**, 120–145 (2006).
14. Balter, V., Renaud, S., Girard, C. & Joachimski, M. M. Record of climate-driven morphological changes in 376 Ma Devonian fossils. *Geology* **36**, 907–910 (2008).
15. Whalen, M. T. et al. Pattern and Timing of the Late Devonian Biotic Crisis in Western Canada: Insights from Carbon Isotopes and Astronomical Calibration of Magnetic Susceptibility Data. In *New Advances in Devonian Carbonates: Outcrop Analogs, Reservoirs, and Chronostratigraphy: Tulsa, OK, USA* (eds. Platten, T., Kerans, C., Weissemberger, J., and Montgomery, P.) 283–201 (SEPM Special Publications 107, 2016).
16. Song, H. et al. Uranium and carbon isotope document global-ocean redox-productivity relationships linked to cooling during the Frasnian-Famennian mass extinction. *Geology* **45**, 887–890 (2017).
17. Algeo, T. J. & Scheckler, S. E. Terrestrial-marine teleconnections in the Devonian: links between the evolution of land plants, weathering processes, and marine anoxic events. *Phil. Trans. Royal Soc. B: Biological Sciences* **353**, 113–130 (1998).
18. Averbuch, O. et al. Mountain building–enhanced continental weathering and organic carbon burial as major causes for climatic cooling at the Frasnian–Famennian boundary (c. 376 Ma)? *Terra Nova* **17**, 25–34 (2005).
19. Wang, K. Glassy microspherules (microtektites) from an Upper Devonian limestone. *Science* **256**, 1547–1550 (1992).
20. Claey's, P. & Casier, J. G. Margolis, S. V. Microtektites and mass extinctions: evidence for a Late Devonian asteroid impact. *Science* **257**, 1102–1104 (1992).
21. Claey's, P. & Casier, J. G. Microtektite-like impact glass associated with the Frasnian-Famennian mass extinction boundary. *Earth Plant. Sci. Lett.* **122**, 303–315 (1994).
22. Ma, X. P. & Bai, S. L. Biological, depositional, microspherule, and geochemical records of the Frasnian/Famennian boundary beds, South China. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* **181**, 325–346 (2002).
23. Courtillot, V., Kravchinsky, V. A., Quideleux, X., Renne, P. R. & Gladkochub, D. P. Preliminary dating of the Viluy traps (Eastern Siberia): Eruption at the time of Late Devonian extinction events? *Earth Planet. Sci. Lett.* **300**, 239–245 (2010).
24. Kravchinsky, V. A. Paleozoic large igneous provinces of Northern Eurasia: correlation with mass extinction events. *Glob. Planet. Change* **86**, 31–36 (2012).
25. Hou, M. et al. New 40Ar/39Ar ages of the Viluy traps (Eastern Siberia): further evidence for a relationship with the Late Devonian extinction events? *Earth Planet. Sci. Lett.* **366**, 531–540 (2013).
26. Reimold, W. U., Kelley, S. P., Sherlock, S. C., Henkel, H. & Koeberl, C. Laser argon dating of melt breccias from the Siljan impact structure, Sweden: Implications for a possible relationship to Late Devonian extinction events. *Meteorit. Planet. Sci.* **40**, 591–607 (2005).
27. Missouri, J. R., Sandberg, C. A., Malkowski, K. & Joachimski, M. M. Carbon isotope chemostratigraphy and precise dating of middle Frasnian (lower Upper Devonian) Alamo Breccia, Nevada, USA. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* **282**, 105–118 (2009).
28. Kravchinsky, V. A. et al. Palaeomagnetism of East Siberian traps and kimberlites: two new poles and palaeogeographic reconstructions at about 360 and 250 Ma. *Geophys. J. Int.* **148**, 1–33 (2002).
29. Courtillot, V. & Renne, P. R. On the ages of flood basalts events. *Compt. Rend. Geosci.* **335**, 113–140 (2003).
30. Courtillot, V., Kogarko, L. N., Kononova, V. A. & Vartainen, H. The Kola Alkaline Province of the CIS and Finland: Precise Rb–Sr ages define 380–360 Ma age range for all magmatism. *Lithos* **30**, 33–44 (1993).
31. Kaiser, J. & Nanka, T. 414–422 (2013).
32. Burgess, S. D., Muirhead, J. D. & Bowring, S. A. Initial pulse of Siberian Traps sills as the trigger of the end-Permian mass extinction. *Nat. Commun.* **5**, 164 (2017).
33. Davies, I. H. F. & et al. End-Triassic mass extinction started by intrusive CAMP activity. *Nat. Commun.* **8**, 15596 (2017).
34. Becker, R. T., Gradstein, F. M. & Hammer, O. The Devonian Period. *The Geological Time Scale 2012*, 359–601 (2012).
35. Reimold, W. U., Kelley, S. P., Sherlock, S. C., Henkel, H. & Koeberl, C. Laser argon dating of melt breccias from the Siljan impact structure, Sweden: Implications for a possible relationship to Late Devonian extinction events. *Meteorit. Planet. Sci.* **40**, 591–607 (2005).
36. Gordon, G. W., Rockman, M., Turekian, K. K. & Over, J. OSIum isotope evidence against an impact at the Frasnian-Famennian boundary. *Am. J. Sci.* **309**, 420–430 (2009).
47. De Veeschouwer, D. & Parnell, A. C. Reducing time-scale uncertainty for the Devonian by integrating astrochronology and Bayesian statistics. *Geology* **42**, 491–494 (2014).
48. Pas, D. et al. Cyclostratigraphic calibration of the Famennian stage (Late Devonian, Illinois Basin, USA). *Earth Planet. Sci. Lett.* **488**, 102–114 (2018).
49. Schindler, E. D. K.-K. (Hohe Frasne-Stufe, Ober Devon). *Gött. Arb. Geol. Paläontol.* **46**, 1–115 (1990).
50. Schoene, B., Guex, J., Bartolini, A., Schaltegger, U. & Blackburn, T. J. Correlating the end-Triassic mass extinction and flood basalts volcanism at the 190ka level. *Geology* **38**, 387–390 (2010).
51. Burgess, S. D., Bowring, S. & Shen, S. Z. High-precision timeline for Earth’s most severe extinction. *Proc. Natl. Acad. Sci. USA* **111**, 3316–3321 (2014).
52. Myrow, P. M. et al. High-precision U–Pb age and duration of the latest Devonian (Famennian) Hangenberg event, and its implications. *Terra Nova* **26**, 222–229 (2014).
53. Kaufmann, B., Trapp, E. & Mezger, K. The numerical age of the upper Frasnian (Upper Devonian) Kellwasser horizons: A new U-Pb zircon date from Steinbruch Schmidt (Kellerwald, Germany). *J. Geol.* **112**, 495–501 (2004).
54. Henkel, H. & Aaro, S. Geophysical investigations of the Siljan impact structure—a short review. In: *Impact Tectonics*, 247–283 (Springer, 2005).
55. Wang, K. et al. Geochemical evidence for a catastrophic biotic event at the Frasnian/Famennian boundary in south China. *Geology* **19**, 776–779 (1991).
56. Perchgrove, F. Y. Geochemical analysis was carried out by J.H.F.L.D. with the support of U.S. All authors reviewed the results and K.B.F. Geological samples were collected by L.M.E.P. with the support of D.D.V., A.-C.D.S. L.M.E.P. wrote the main manuscript text and prepared all figures. The Results and Materials and Methods sections were written by J.H.F.L.D. and the Université de Lausanne for funding.
57. McLean, N. M. et al. An algorithm for U‐Pb isotope dilution data reduction and uncertainty propagation. *GSA Spec. Pap.* **51**, 273–276 (2017).
58. Racki, G. The Frasnian–Famennian biotic crisis: How many (if any) bolide impacts? *Geological Rundschau* **87**, 617–632 (1999).
59. Polansky, O. P. et al. Temporal correlation between dyke swarms and crustal extension in the middle Palaeozoic Vilyui rift basin, Siberian platform. *Lithos* **282**, 45–64 (2017).
60. Kuzmin, M. I., Yarmolyuk, V. V. & Kravchinsky, V. A. Phanerozoic hot spot traces and paleogeographic reconstructions of the Siberian continent based on interaction with the African large low shear velocity province. *Earth Sci. Rev.* **102**, 29–59 (2010).
61. Ganino, C. & Arndt, N. T. Climate changes caused by degassing of sediments during the emplacement of large igneous provinces. *Earth Sci. Rev.* **156**, 1–9 (2016).
62. Grasby, S. E. Geochemistry of the Frasnian-Famennian boundary in Belgium: Mass extinction, anoxic oceans and microtektite layer, but not much iridium? *Geol. Soc. Am. Spec. Pap.* **307**, 491–504 (1996).
63. Racki, G. The Frasnian–Famennian biotic crisis: How many (if any) bolide impacts? *Geological Rundschau* **87**, 617–632 (1999).
64. Percival, L. M. E. Perchgrove, F. Y. et al. Globally enhanced mercury deposition during the end-Plainsbachian and Toarcian OAE: A link to the Karoo–Ferrar Large Igneous Province. *Earth Planet. Sci. Lett.* **428**, 267–280 (2015).
65. Perchgrove, L. M. E. et al. Mercury evidence for pulsed volcanism during the end-Triassic mass extinction. *Proc. Natl. Acad. Sci. USA* **114**, 7929–7934 (2017).
66. Font, E. et al. Mercury anomaly, Deccan volcanism, and the end-Cretaceous mass extinction. *Geology* **44**, 171–174 (2016).
67. Grasby, S. E. et al. Isotopic signatures of mercury contamination in latest Permian oceans. *Geology* **45**, 55–58 (2017).
68. Robinson, N., Ravizza, G., Coccioni, R., Peucker-Ehrenbrink, B. & Norris, R. A high-resolution marine 187Os/188Os record for the late Maastrichtian: Distinguishing the chemical fingerprints of Deccan volcanism and the KP impact event. *Earth Planet. Sci. Lett.* **281**, 159–168 (2009).
69. Du Vivier, A. D. C. et al. Marine 187Os/188Os isotope stratigraphy reveals the interaction of volcanism and ocean circulation during Oceanic Anoxic Event 2. *Earth Planet. Sci. Lett.* **389**, 23–33 (2014).
70. Racki, G., Rakocinski, M., Marynowski, L. & Wignall, P. B. Mercury enrichments and the Frasnian-Famennian biotic crisis: A volcanic trigger proved? *Geology*, https://doi.org/10.1130/G40233.1 (2018).
71. Widmann, P., Davies, J. H. F. L. & Schaltegger, U. Towards a calibration of the “chemical abrasion” technique. *Goldschmidt Conference, Paris 27*, Abstract 4241 (2017).
72. Condon, D. J., Schoene, B., McLean, N. M., Bowring, S. A. & Parrish, R. R. Metrology and traceability of U–Pb isotope dilution geochronology (EARTHTIME Tracer Calibration Part I). *Geochim. Cosmochim. Acta* **164**, 464–480 (2015).
73. McLean, N. M., Condon, D. J., Schoene, B. & Bowring, S. A. Evaluating uncertainties in the calibration of isotopic reference materials and environmental isotopic tracers (EARTHTIME Tracer Calibration Part II). *Geochim. Cosmochim. Acta* **164**, 481–501 (2015).
74. Hies, J., Condon, D. J., McLean, N. & Noble, S. R. 238U/235U systematics in terrestrial uranium-bearing minerals. *Science* **335**, 1610–1614 (2012).
75. McLean, N. M., Bowring, J. F. & Bowring, S. A. An algorithm for U-Pb isotope dilution data reduction and uncertainty propagation. *Geochim. Geophys. Geosyst.* **12**, Q0A11 (2011).
76. Wotzlaw, J. F., Hüsing, S. K., Hilgen, F. J. & Schaltegger, U. High-precision zircon U–Pb geochronology of astronomically dated volcanic ash beds from the Mediterranean Miocene. *Earth Planet. Sci. Lett.* **407**, 19–34 (2014).
77. Joachimski, M. M. et al. Devonian climate and reef evolution: insights from oxygen isotopes in apatite. *Earth Planet. Sci. Lett.* **284**, 599–609 (2009).
78. Renne, P. R., Mundil, R., Balco, G., Min, K. & Ludwig, K. R. Joint determination of 40K decay constants and 40Ar+40K for the Fish Canyon sanidine standard, and improved accuracy for 40Ar/39Ar geochronology. *Geochim. Cosmochim. Acta* **74**, 5349–5367 (2010).
79. Ver Straeten, C. A., Over, D. J. & Baird G. C. Arc-to-Craton: Devonian Airfall Tephras in the Eastern United States. *GSA Spec. Pap.* (in press).

**Acknowledgements**

We thank Ronnie Guthrie for assistance in the field. We gratefully acknowledge the Swiss National Science Foundation (project no. 162341 to U.S. and J.H.F.L.D.), the European Research Council Consolidator Grant “Earthsequencing” (grant no. 617462: D.D.V.), the International Geoscience Programme Project 652 (D.D.V. and A.-C.D.S.), and the Université de Lausanne for funding.

**Author Contributions**

L.M.E.P. wrote the main manuscript text and prepared all figures. The Results and Materials and Methods sections were written by J.H.F.L.D. Geological samples were collected by L.M.E.P. with the support of D.D.V., A.-C.D.S. and K.B.F. Geochemical analysis was carried out by J.H.F.L.D. with the support of U.S. All authors reviewed the manuscript.
Additional Information
Supplementary information accompanies this paper at https://doi.org/10.1038/s41598-018-27847-7.

Competing Interests: The authors declare no competing interests.

Publisher's note: Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made. The images or other third party material in this article are included in the article’s Creative Commons license, unless indicated otherwise in a credit line to the material. If material is not included in the article’s Creative Commons license and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this license, visit http://creativecommons.org/licenses/by/4.0/.

© The Author(s) 2018