High-precision U–Pb zircon age constraints on the duration of rapid biogeochemical events during the Ludlow Epoch (Silurian Period)

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Precise determinations of the rates and durations of Palaeozoic biogeochemical events are largely unavailable. Here, we present two new high-precision U–Pb (zircon) dates from volcanic ash deposits from the Ludlow Series (Silurian System) of Podolia, Ukraine, that yielded weighted mean 206Pb/238U dates of 424.08 ± 0.20 (0.29) [0.53] Ma and 422.91 ± 0.07 (0.21) [0.49] Ma (analytical, tracer and total uncertainties). These new dates bracket the largest post-Cambrian global carbon cycle perturbation (Lau Excursion) and constrain the ‘Ludlow Rise’ in 87Sr/86Sr. These chronostatigraphically well-controlled dates improve the calibration of the Silurian time scale and provide the first determinations of the rates of biogeochemical change during the Ludlow Epoch.

Supplementary material: U–Pb geochemical methods, data and CL imagery are available at http://www.geolsoc.org.uk/SUP18798.

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Changes in the global C and Sr isotopic composition of the ocean, preserved in the stratigraphic record as changes in δ13C and δ87Sr/86Sr, can be used as tools for global chronostatigraphic correlation as well as oceanographic and global climate proxies (McArthur et al. 2012; Saltzman & Thomas 2012). Palaeozoic records of δ13C and δ87Sr contain some of the largest geochemical perturbations in Earth history, but the ultimate cause(s) of these events remain enigmatic (Munnecke et al. 2010). The general lack of precise radio-isotopic age determinations from Palaeozoic strata is a critical factor in our inability to determine the cause-and-effect relationships responsible for these intervals of significant global change. However, recent advances in radio-isotopic methods (Mattinson 2005, 2010; Condon et al. 2007), and improved chronostatigraphic correlation of radio-isotopic data, make it possible to obtain increasingly precise temporal constraints for Palaeozoic geochemical events.

The Silurian Period was one of the geochemically and biologically most dynamic intervals of Earth history (Munnecke et al. 2010; Cooper et al. 2014), and the Ludlow Epoch contains the largest perturbation of the global carbon cycle (a positive δ13C excursion known as the ‘Lau Excursion’) and one of the most rapid increases in the strontium isotopic composition (δSr) of the ocean during the past 500myr (Cramer et al. 2011a,b; McArthur et al. 2012; Saltzman & Thomas 2012). At present, five high-precision chemical abrasion–isotope dilution–thermal ionization mass spectrometry (CA-ID-TIMS) 206Pb/238U dates from zircons are available from Silurian strata, but all of those are limited to the Llandovery and Wenlock series (Cramer et al. 2012).

Here, we present new, chronostatigraphically well-controlled, high-precision isotope-dilution U–Pb (zircon) dates from two volcanic ash fall (K-bentonite) deposits from the Ludlow Series of Podolia, Ukraine. U–Pb dates were calibrated using gravimetric principles of isotope dilution combined with the chemical abrasion pretreatment method of Mattinson (2005) for the effective elimination of Pb loss (CA-ID-TIMS). These new high-precision dates improve the calibration of the Silurian time scale, effectively bracket the Lau δ13C Excursion and, when combined with recently published dates from near the Wenlock–Ludlow boundary (Cramer et al. 2012), constrain the duration of the Ludlow Rise in δ87Sr/86Sr as well.

Geological setting. The volcanic ash fall deposits sampled here come from the epicratonic succession of Podolia, southwestern Ukraine (Fig. 1). Silurian–Lower Devonian strata are well exposed throughout the Dniester (Dnister) River valley, and were deposited along the southwestern margin of the East European Platform (Tsegelynuk et al. 1983; Kaljo et al. 2007; Malkowski et al. 2009). Numerous biostratigraphic investigations have helped to constrain the timing of deposition of the generally calcareous Silurian succession of Podolia (e.g. Gritsenko et al. 1983; Tsegelynuk et al. 1983), and carbon isotope chemostratigraphy (δ13C) has further refined the global chronostatigraphic correlation of these strata by identifying the early Silurian ‘Irivken’, ‘Homian ‘Muldike’, Ludlow ‘Lau’, and Silurian–Devonian ‘Klondike’ positive δ13C excursions (Kaljo et al. 2007, 2012; Malkowski et al. 2009; Racki et al. 2012).

The volcanic ash fall deposits, now preserved as K-bentonites in Podolia, are important regional correlation tools (Tsegelynuk et al. 1983), and are the southeasternmost occurrence of lower Palaeozoic bentonites in this part of Europe (Huff et al. 2000). Chronostatigraphic correlation and REE geochemical fingerprinting of bentonites throughout NW Europe indicate that the volcanic activity recorded in the Podolia succession represents a source area distinct from those preserved in the UK, Sweden, Poland and the Baltic States (Huff et al. 2000; Cramer et al. 2012). Whereas most northwestern European explosive volcanism during the Silurian was limited to the Llandovery and Wenlock and related to the closure of the Iapetus Ocean, the Podolia bentonites are largely within the Ludlow and Pridoli and probably originated from a distinct subduction-related tectonomagmatic setting to the SE (present coordinates) within the Rheic Ocean along the Mugodzhar or Kipchak arcs (Sengör et al. 1993; Huff et al. 2000; Cramer et al. 2012).

The two bentonites studied here, M12 and C6 (Fig. 1), were collected from the outcrops Malynivtsi 150 and Ataky 117 (Fig. 1c), respectively (legacy samples from Huff et al. 2000). The nearby section, Zhvanets’ 39, also contains the M12 bentonite as well as a record of the Lau Excursion described by Kaljo et al. (2007),
which further refined the global chronostratigraphic correlation of these strata. The δ13C data of Kaljo et al. (2007) place bentonite M12 at a position immediately below the onset of the Lau Excursion within the Ludfordian Stage. Bentonite C6 comes from a position above the end of the Lau Excursion and was placed by Kaljo et al. (2014) within the upper part of the Ludfordian Stage. Whereas chronostratigraphy cannot provide a secondary confirmation of this correlation, sample C6 comes from a level just below the position of the Ludlow–Pridoli boundary at the top of the Pryhorodok Formation (Gritsenko et al. 1983; Huff et al. 2000; Kaljo et al. 2007, 2012; Malkowski et al. 2009; see discussion by Kaljo et al. 2014).

Methods and results. All zircon samples were analysed in the Isotope Geology Laboratory at Boise State University using CA-ID-TIMS methods (Schmitz & Davydov 2012). We utilized a vigorous one-step (195°C, 12h) chemical abrasion pretreatment on single CL-imaged zircon crystals prior to dissolution for the effective elimination of Pb loss (Mattinson 2005). Isotopic dilution utilized the EARTHTIME U–Pb tracer (ET535) and ages are reported with respect to the 238U decay constant of Jaffey et al. (1971). Sample ages and uncertainties (2σ) are reported as ±X(1 ± Y) [Z] Ma, where X is the internal error, Y is the internal plus tracer calibration error, and Z is the internal plus tracer plus decay constant uncertainty.

CL-imaging of zircon crystals from sample C6 revealed a homogeneous population of elongate prismatic grains with regular, planar, weakly oscillatory zoning. Occasional CL-bright, sector-zoned cores were seen in more equant grains, and these grains were avoided for their potential to contain inherited components. Eight of the elongate prismatic grains of a variety of CL brightness were selected for CA-TIMS analysis. All analyses yielded concordant and equivalent U–Pb dates with a weighted mean 206Pb/238U age of 424.08 ± 0.20 (0.29) [0.53] Ma (n = 7; MSWD = 0.76; probability of fit = 0.60), which is interpreted to estimate the eruption and depositional age of the volcanic deposit (Table 1; Fig. 2).

Table 1. Summary of interpreted U–Pb (zircon) dates

| Sample number | 206Pb/238U U date | ±X(Y) | ±(Z) | n | MSWD |
|---------------|------------------|------|------|---|------|
| C6            | 422.91 ± 0.33    | 0.17 ± 0.21 | 3.2 |
| M12           | 424.08 ± 0.20    | 0.15 ± 0.33 |
| WNH15 (Cramer et al. 2012) | 427.86 ± 0.33 | 0.17 ± 0.21 | 3.2 |

X, internal or analytical uncertainty; Y, uncertainty including quadratic addition of tracer calibration error; Z, uncertainty including quadratic addition of both tracer calibration and 238U decay constant errors.

Table 2. Calculated age difference (myr) between interpreted U–Pb (zircon) dates

| Sample | Age difference (myr) |
|--------|----------------------|
| M12    | 3.78 ± 0.38          |
| C6     | 4.95 ± 0.33          |
| WNH15  | 1.17 ± 0.21          |

Discussion. The dates from bentonites M12 and C6 provide the first precise calibration of the duration of the Lau positive δ13C excursion and demonstrate that the entire δ13C excursion was of the order of 1 myr (Table 2; Fig. 3). When the date from bentonite M12 is combined chronostratigraphically with the date from the Wren’s Nest Hill Bentonite 15 (WNH15 of Cramer et al. 2012), the duration of the 87Sr/86Sr ‘Ludlow Rise’ can be calibrated with a

Fig. 1. (a) Lithostratigraphy and carbon isotope stratigraphy of the Malynivtsi 150, Ataky 117 (after Huff et al. 2000) and Zhvanets’ 39 outcrops (after Kaljo et al. 2007), Podolia, Ukraine. Baltic graptolite zones and Podolia conodont zones from Kaljo et al. (2014). Global conodont zones after Cramer et al. (2011a). (b) Map of Eastern Europe with sample location highlighted by diagonally shaded box expanded in panel (e). (c) Locality map showing the position of outcrops within the Dniester River Valley.

Fig. 2. Single 206Pb/238U ages (sorted by uncertainty) and concordia diagrams for the M12 and C6 bentonites. Data point error ellipses are 2σ.
duration of 4 myr. These new dates are remarkably consistent with the CONOP scaling and calibration presented by Melchin et al. (2012), which was based on limited radioisotopic information from the Ludlow and Pridoli series, and they demonstrate exceptionally rapid rates of change of the magnitude of the Ludlow Rise. Conservatively, the total change in $^{87}\text{Sr}/^{86}\text{Sr}$ of 0.000025 yr$^{-1}$, making this one of the most rapid positive changes in $^{87}\text{Sr}/^{86}\text{Sr}$.

There are a few similarly exceptional rates of positive change in $^{87}\text{Sr}/^{86}\text{Sr}$ known, such as the Cambrian Rise, the Early Triassic Rise and the Cenozoic Rise (see McArthur et al. 2012). A variety of potential causative mechanisms for the Ludlow Rise were presented by Cramer et al. (2011b), including the possibility of errors in the calibration of the Ludlow Epoch. The new dates presented here, combined with the Rhenlander Series and the Ludlow Rise, limit the duration of the Ludlow Rise and effectively discount this possibility. The rapid increase in $^{87}\text{Sr}/^{86}\text{Sr}$ during the Ludlow is near the upper limit for positive rates of change in the global $^{87}\text{Sr}/^{86}\text{Sr}$ value of the oceans (McArthur et al. 2012) and was probably the result of a combination of factors acting in unison. An increase in the global Sr flux owing to the predominantly quartzofeldspathic material weathering hypothesis is probably acting in unison to produce the Ludlow Rise.

Conclusions

The two new high-precision U–Pb (zircon) dates presented here provide the first precise calibrations of the duration of the Ludlow Epoch (4.95 ± 0.33 myr), the duration of the largest post-Cambrian positive $\delta^{13}$C excursion (Lau Excursion, c. 1 myr) and the duration of one of the fastest rates of positive change in $^{87}\text{Sr}/^{86}\text{Sr}$. The Lau Excursion appears to be the largest post-Cambrian positive $\delta^{13}$C excursion in terms of absolute values as well as total change from baseline. Peak values $\geq 8.0$‰ are consistently observed in sections that contain a thick record of the excursion (Samtleben et al. 1996; Wigforss-Lange 1999; Kaljo et al. 2007; Jeppsson et al. 2007). The duration of 1.17 ± 0.21 myr (Table 2) between K-bentonites M12 and C6 provides a maximum duration for the Lau Excursion (Fig. 3). The excursion does not extend exactly to K-bentonite C6, however (Fig. 1), and a conservative estimate places the duration of the excursion at c. 1 myr. With a total duration of 1 myr, the ascending limb of the excursion is likely to have lasted no more than 500 kyr, which indicates a rate of increase of the order of $\geq 2.0$‰ per 125 kyr. This rate is very fast when compared with steady-state equations of the marine carbon cycle alone and potentially rules out hypotheses such as the carbonate weathering hypothesis (e.g. Kump & Arthur 1999) owing to the prohibitively large amount of carbonate that would need to be weathered in such a short interval of time to produce changes of the magnitude recorded here (e.g. Cramer & Saltzman 2007). However, the additional forcing of a large volcanic event that can flux thousands of Gt of CO$_2$ into the atmosphere has been modelled to produce rapid and large positive shifts in $\delta^{13}$C by promoting oceanographically induced anoxia that in turn promotes efficient remineralization and recycling of PO$_4$ (e.g. Payne & Kump 2007). Such a scenario represents both oceanographically induced anoxia owing to higher atmospheric CO$_2$ as well as increased primary productivity, which both lead to enhanced organic carbon burial. Whereas this scenario as a model can produce positive changes in $\delta^{13}$C of similar rates and magnitudes to those seen in the Ludlow, the present lack of stratigraphic evidence for such a volcanic event cannot be overlooked and this hypothesis requires substantial further investigation.

Previous age models for the Silurian included poor constraints on the duration of the Ludlow Epoch and therefore uncertain estimates of the duration of the Ludlow Rise. Wren’s Nest Hill Bentonite 15 (Cramer et al. 2012) and K-bentonite M12 (this study) bracket this interval and provide precise temporal control for the duration of the Ludlow Rise. However, the new dates presented by Cramer et al. (2011b) and K-bentonite M12 (this study) bracket this interval and provide precise temporal control for the duration of the Ludlow Rise. Conservatively, the total change in $^{87}\text{Sr}/^{86}\text{Sr}$ of 0.000025 (0.70845–0.7087, Fig. 1) took place over 4 myr (3.78 ± 0.38 myr, Table 2), which indicates a rate of change in $^{87}\text{Sr}/^{86}\text{Sr}$ of 0.0000625 myr$^{-1}$, making this one of the most rapid positive changes in $^{87}\text{Sr}/^{86}\text{Sr}$.
(Ludlow Rise, 3.78 ± 0.38 myr). The rate of positive change in δ¹³C during the Lau Excursion is calculated at c. +2.0‰ per 125 kyr, and the rate of positive change in ⁸⁷Sr/⁸⁶Sr during the Ludlow Rise is calculated at +0.0000625 myr⁻¹. A combination of events during the Ludlow Epoch could produce the changes observed in the ⁸⁷Sr/⁸⁶Sr record but the δ¹³C record remains more enigmatic and requires further investigation. These conservatively calculated rates of change provide the first calibrations of the durations of these Silurian biogeochemical events and provide important end-members for future modelling of Palaeozoic global change.

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