High-precision U–Pb zircon CA-ID-TIMS dates from western European late Viséan bentonites

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Abstract: Three new U–Pb zircon chemical abrasion isotope dilution thermal ionization mass spectrometry dates obtained from late Viséan Belgian bentonites are reported and are used to estimate the periodicity of early Warnantian shallowing-upwards carbonate parasequences that are interbedded with the dated bentonites. Early Warnantian parasequences exhibit mean cycle periodicity values that are consistent with the c. 100 ka Milankovitch cycle, which is the dominant Milankovitch frequency recognized from recent Pleistocene glacial records, and thus strengthen the arguments for (1) these sedimentary cycles being of glacio-eustatic origin and (2) the initiation of the main phase of late Palaeozoic glaciation before the start of or during earliest Warnantian times. The new dates also provide additional high-precision age constraints for the improved calibration of the Mississippian time scale. Using the new dates, the stratigraphical age of the Clydes Plateau Volcanic Formation, Midland Valley of Scotland, is revised from Holkerian to early Asbian.

Supplementary material: U–Pb zircon CA-ID-TIMS data tables and the method of the mean cycle periodicity calculations are available at www.geolsoc.org.uk/SUP18747.

In recent years, calibration of the Pennsylvanian (Late Carboniferous) time scale has been improved greatly by the publication of several high-precision U–Pb dates obtained from eastern European and Russian tuffs and tonsteins (Davydov et al. 2010; Schmitz & Davydov 2012). In contrast, the early to middle parts of the Mississippian time scale (Tourmaisian and Viséan stages) are poorly constrained: only eight high-precision U–Pb dates from the Tournaisian and Viséan were presented in the latest version of the Geologic Time Scale (Davydov et al. 2012). These are unevenly distributed within a stratigraphical interval that is estimated to span c. 29 Ma (Davydov et al. 2012). In this study, we present new high-precision U–Pb zircon chemical abrasion isotope dilution thermal ionization mass spectrometry (CA-ID-TIMS) dates from several biostratigraphically well-constrained, diagenetically altered volcanic ash layers (bentonites; Fig. 1) within the Namur–Dinant Basin, Belgium (Fig. 2). The bentonites occur interbedded with cyclically bedded carbonates of the Livian and Warnantian regional substages (Figs 1 and 3).

The new U–Pb dates are used to calculate the mean periodicity of late Viséan Belgian sedimentary cycles to test previous suggestions that late Viséan cyclic sedimentation in western Europe was controlled by Milankovitch orbital forcing and preserves a record of glacio-eustasy (e.g. Wright & Vanstone 2001). We also discuss the implications that the new U–Pb zircon CA-ID-TIMS dates have for calibration of the Mississippian time scale and for the stratigraphical age of the Clydes Plateau Volcanic Formation, Midland Valley, Scotland.

Belgian Mississippian stratigraphy

The Mississippian Subsystem consists of the Tourmaisian, Viséan and Serpukhovian stages (Heckel & Clayton 2006), the first two originally defined in Belgium, where they constituted the Dinantian Subsystem (now abandoned). Whereas the Tournaisian and Viséan stages (formerly series) have now been defined by the ratification of Global Boundary Stratotype Section and Points (GSSPs), the base of the Serpukhovian has yet to be selected; however, it is clear that its base will be at a level that formerly would have been regarded as being within the late Viséan (Sevastopulo & Barham 2014).

Conil et al. (1976) proposed chronostratigraphical divisions of the Tournaisian and Viséan series (as formerly understood) of Belgium into five stages: Hastarian, Ivorian, Moliniacian, Livian and Warnantian (now regional substages). Of these, the two youngest, the Livian and Warnantian regional substages, are relevant to the current investigation. Details of the Livian and Warnantian regional substages were given by Poty & Hance (2006a) and Poty & Hance (2006b) respectively. The current lithostratigraphical framework for the Livian and Warnantian strata of the Namur–Dinant Basin was established by Poty et al. (2001; Fig. 1). In brief, the Warnantian Substage comprises the Banne River Formation (with constituent Thon-Samson and Poilvache members) and the Anhée Formation (divided into Lower and Upper members; Figs 1 and 3). Biostratigraphical division of the Warnantian has been achieved through the use of foraminifers and corals; Conil et al. (1991) proposed a biozonal scheme based on foraminifers using the notation Cßα, Cßβ, etc. (Fig. 1). This has been superseded by a set of interval zones proposed by Poty et al. (2006; Fig. 1). The Neoarchaedicus interval zone (MFZ 13) and Howchinia bradyana interval zone (MFZ 14) span the early part of the Warnantian, and the Janischewskina typica interval zone (MFZ 15) the younger part (Fig. 1). Coral zones spanning the Warnantian (Poty et al. 2006) are the Dibunophyllum interval zone (RC7) and the Lonsdaleia interval zone (RC8; Fig. 1). Details of the distribution of conodonts
in the Warnantian of Belgium, which are important for the correlation of the base of the Serpukhovian Stage, have been provided by Higgins & Bouckaert (1968) and Groessens (1974). The determinations of species of *Lochria* [formerly *Gnathodus*] reported by those workers require revision in the light of more recent taxonomic work (see Nemirovskaya et al. 1994). The first occurrence of *Lochria ziegleri* has been agreed as the primary tool for the definition and correlation of the base of the Serpukhovian (Richards & Task Group 2006). Based on the occurrences of the conodonts *Lochria* [*Gnathodus*] nodosa and *Lochria* [*Gnathodus*] cruciiformis (Higgins & Bouckaert 1968), which are likely to straddle the first occurrence of *Lochria ziegleri*, the base of the Serpukhovian probably lies at the base of or within the Upper Member of the Anhée Formation. This is consistent with the suggestion by Groves et al. (2012) that *Janischewskina delicata*, the index taxon for MFZ 15, first occurs close to the base of the Lower Member of the Anhée Formation.

**Bentonite samples**

Interbedded with limestones of Livian and Warnantian age in the Namur–Dinant Basin are several clay-rich horizons that consist of predominantly polymineralic clays, including ordered illite–smectite mixed-layer clays, illite, sodoite, kaolinite and chlorite–smectite mixed-layer clays (Thorez & Pirlet 1979; Anceau 1992, 1996; Delcambre 1996). The clay-rich horizons have been interpreted as diagenetically altered volcanic ash layers (Thorez & Pirlet 1979; Delcambre 1996) and are commonly termed bentonites or cinerites. Many of these horizons contain trace amounts of coarser euhedral zircon and apatite, splinter quartz and biotite, which are inferred to be original volcanic phenocrysts (Thorez & Pirlet 1979; Delcambre 1996). U–Pb zircon CA-ID-TIMS dating was undertaken on zircon grains separated from four bentonite horizons (Figs 1 and 3) that were sampled from outcrop sections within the Namur–Dinant Basin.

Samples of bentonites W1 and W8 were collected from a long-abandoned quarry to the north of the village of Anhée (Figs 2 and 3), a locality that has been previously referred to as Yvoir (Pirlet 1968) and Anhée Nord (Delcambre 1996). Several bentonite horizons and partings have been identified in the lowermost c. 23 m of section exposed at Anhée Nord; bentonite W1 is the lowest and bentonite W8 is the highest (Fig. 3). In outcrop, bentonite W1 is c. 10 cm thick, orange and poorly consolidated. At this locality the stratigraphical position of bentonite W1 relative to the base of the Warnantian is not clear; bentonite W1 rests upon the Grande Brèche Viséenne (a diachronous, laterally extensive breccia unit) and is succeeded by a thin (20 cm) karstic limestone, which is infilled and overlain by bentonite W2 (Fig. 3). However, Delcambre (1996) showed, using zircon typology, that bentonite W1 of Anhée Nord correlates with a bentonite exposed, but now inaccessible, in the Transcar Quarry at Maizeret (Fig. 2), which occurs within the upper part of the Maizeret Member, c. 22 m below the base of the Warnantian Substage. Bentonite W1 is thus of late Livian age. Bentonite W8 at Anhée Nord is c. 18 cm thick, red–brown, homogeneous and well consolidated. It occurs c. 18 m above bentonite W1, within the Poilvache Member (Figs 1 and 3), and is of early Warnantian age.

Two further bentonites (W12 and W13), which occur in close stratigraphic proximity, were collected from the disused Watrisse Quarry (Figs 2 and 3), a locality previously referred to as Anhée Sud (Pirlet 1968; Delcambre 1996). Bentonite W12 was the youngest Viséan bentonite reported by Delcambre (1996). In outcrop it is c. 5 cm thick, black and poorly consolidated, and rests on a strongly undulose, palaeokarstic(?) surface. U–Pb zircon CA-ID-TIMS dating of zircon grains from bentonite W12 was undertaken but yielded complex and inconclusive results (see below). However, better results were obtained from bentonite W13, a previously undescribed bentonite, which has been named following the nomenclatural scheme of Delcambre (1989, 1996). Bentonite W13...
occurs at the base of a 20 cm thick recessive mudstone bed, c. 0.5 m above bentonite W12 (Fig. 3), and is c. 1 cm thick, pale grey and internally massive.

Zircon separates

The sample of bentonite W1 yielded mostly euhedral to subhedral zircon grains (80–280 μm in length) with aspect ratios of 2–4, although rare euhedral, elongate grains (aspect ratios up to six) are also present. Most grains are heavily fractured and/or exhibit oscillatory zonation that is visible under a petrographic microscope. The sample of bentonite W8 yielded a small zircon population of notably finer grain size (50–150 μm in length). Zircons in bentonite W8 are predominantly euhedral with aspect ratios of 3–9. Most grains are relatively clear and contain few fractures or inclusions, although a few grains contain melt inclusions parallel to the c-axis. A few rounded, cloudy and fractured grains were also recovered from this bentonite. Bentonite W12 yielded an abundant zircon population, comprising a diverse range of grain morphologies (anhedral to euhedral, sub-spherical to acicular). Anhedral grains are typically 40–100 μm in length and have low aspect ratios (less than three). Subhedral and euhedral grains are 40–150 μm in length and exhibit a wider range of aspect ratios (1.5–8). Some elongate subhedral and euhedral grains contain melt inclusions parallel to the c-axis. A few subhedral grains contain melt inclusions oriented parallel to the c-axis; whereas some of the more equant grains contain rounded cores and/or radial fractures. Bentonite W13 also yielded an abundant and diverse zircon population; grains are anhedral to euhedral, 50–220 μm long and have aspect ratios of 1.5–4.5 (mostly less than four). Subhedral grains are the most common morphology in this sample.

Analytical methods

Zircon grains were separated from the bentonite samples using the facilities at the Department of Geology, Trinity College Dublin. Poorly consolidated samples (bentonites W1, W12, W13) were disaggregated using a pestle and mortar, and then sieved using a 300 μm sieve. The indurated bentonite W8 was disaggregated using a Retsch jaw crusher, sieved and the sub-300 μm fraction was then processed for zircon. Zircons were concentrated by standard methods, using heavy liquid separation with methylene iodide, followed by magnetic separation using a Chas. W. Cook & Sons magnetic separator. Zircons from the non-magnetic fractions were subsequently hand-picked in alcohol at high magnification using a Nikon SMZ 1500 binocular microscope.

U–Pb CA-ID-TIMS dating of sample zircon grains was undertaken at the University of Geneva, Switzerland. Only the salient aspects of the U–Pb CA-ID-TIMS method are described here; full details of the analytical method employed have been given by Pointon et al. (2012). All U–Pb CA-ID-TIMS analyses were of single grains that were chemically abraded (sensu Mattinson 2005) prior to dissolution. All analyses were spiked with the EARTHTIME tracer solution. Results were corrected for initial 207Pb–206Pb–233U–238U isotopic tracer solution. Concordia diagrams were constructed using Isoplot v. 3.0 (Ludwig 2003).

Weighted mean 206Pb/238U dates were calculated from several overlapping, concordant analyses (within analytical and decay constant uncertainties; calculated using Isoplot v. 3.0; Ludwig 2003) and are used to define the ages of the bentonite horizons. Date uncertainties on weighted mean calculations are given in the ±XYYZ notation of Schoene et al. (2006), where X is the internal error, Y is the internal error plus tracer calibration uncertainties and Z is the internal error plus tracer calibration and 238U decay constant uncertainties. Systematic uncertainties arising from tracer calibration and the 238U decay constant were added in quadrature. In this study, the same EARTHTIME tracer was used for all U–Pb CA-ID-TIMS analyses, allowing systematic uncertainties in the tracer calibration (0.05%, 2σ) and the 238U decay constant (0.107%, 2σ; Jaffey et al. 1971) to be disregarded when undertaking internal comparisons of our data. Systematic uncertainties in tracer composition need to be considered only where our data are compared with (1) other ID-TIMS dates calibrated against a non-EARTHTIME tracer or (2) U–Pb dates derived using a different analytical method (e.g. laser ablation inductively coupled plasma mass spectrometry, secondary ion mass spectrometry). Tracer calibration and decay
constant uncertainties must be propagated in full where our data are compared with data obtained using a different decay system (e.g. K–Ar, Re–Os).

Results

**Bentonite W1 (late Livian)**

Eight single-grain analyses were undertaken from the sample of bentonite W1 (Fig. 4a). One analysis yielded a distinctly older age than all other analyses (W1/4; Fig. 4a) and is interpreted to represent inheritance, possibly of antecrystic origin (sensu Miller et al. 2007). This analysis is accordingly excluded from the weighted mean calculation. The weighted mean $^{206}\text{Pb}^{238}\text{U}$ date of all other analyses is 336.22 ± 0.06 Ma (95% confidence, MSWD = 0.83; Fig. 4a); this is taken as the best estimate of the eruption age of this bentonite.

**Bentonite W8 (early Warnantian)**

Nine U–Pb CA-ID-TIMS analyses were undertaken on single, euhedral, elongate grains (Fig. 4b). The data from this sample show some complexity: there is one imprecise analysis (W8/5; Fig. 4b and c), which yielded a relatively old age; a cluster of analyses yielding $^{206}\text{Pb}^{238}\text{U}$ dates of c. 336.3 Ma (W8/6, 8, 11, 12, 14; Fig. 4b and c); and three analyses yielding younger $^{206}\text{Pb}^{238}\text{U}$ dates of c. 335.6 Ma (W8/4, 7, 9; Fig. 4b and c). Analysis W8/5 is interpreted to represent a grain with an inherited core. The cluster of analyses yielding $^{206}\text{Pb}^{238}\text{U}$ dates of c. 336.3 Ma are equivalent and concordant within analytical uncertainties and yield a weighted mean $^{206}\text{Pb}^{238}\text{U}$ date of 336.35 ± 0.13 Ma (95% confidence, MSWD = 0.62; Fig. 4c). This date, however, is inconsistent with the weighted mean $^{206}\text{Pb}^{238}\text{U}$ date from the underlying W1 bentonite (336.22 ± 0.06 Ma; Fig. 4a; see above), and therefore these grains are interpreted to represent antecrystic inheritance. The three younger grains in this sample are equivalent and concordant within analytical and decay constant uncertainties and yield a weighted mean $^{206}\text{Pb}^{238}\text{U}$ date of 335.59 ± 0.19 Ma (95% confidence, MSWD = 0.16, Fig. 4c). This latter date is taken to approximate the eruption age of this bentonite.

**Bentonites W12 and W13 (early Warnantian)**

Fifteen single-grain zircon analyses were undertaken from the sample of bentonite W12, all of which are concordant within analytical and decay constant uncertainties (Fig. 4d). Most of the analyses cluster between c. 332 and 333 Ma (Fig. 4d), with the exception of two analyses (W12/4, W12/8; Fig. 4d) that yielded significantly younger dates ($^{206}\text{Pb}^{238}\text{U}$ dates of c. 331.4 Ma). It is not clear from these data alone whether the two analyses that yielded relatively young dates record late-stage growth of magmatic zircon or were affected by residual lead loss that was not completely removed by the chemical abrasion technique. U–Pb zircon CA-ID-TIMS dating of grains from the underlying W13 bentonite was undertaken because of the complexity of the W12 data. In contrast to the data from bentonite W12, no grains of c. 331.4 Ma age were observed in the bentonite W13 dataset (Fig. 4e; see below). Instead, the data from the W13 horizon mostly cluster around 332.5 Ma (Fig. 4e). Thus, we infer that the two anomalously young (c. 331.4 Ma) analyses in the bentonite W12 sample were affected by residual lead loss and that the true age of this bentonite lies within the c. 332–333 Ma data cluster. Unfortunately, it is not possible to refine the age of bentonite W12 further: there is too much dispersion within the c. 332–333 Ma data cluster for these data to represent a single age population and the cause(s) of the data scatter are not certain. Some of the complexity in the results may arise from subtle residual lead loss and/or antecrystic inheritance.

Six single-grain U–Pb zircon CA-ID-TIMS analyses were undertaken from bentonite W13; five of the analyses cluster around 332.5 Ma (Fig. 4e). Analysis W13/3 yielded a significantly older age (Fig. 4e) and may represent a grain with an unresolved xenocrystic core or an antecrystic grain. The weighted mean $^{206}\text{Pb}^{238}\text{U}$ date of all analyses except W13/3 is 332.50 ± 0.07 Ma (95% confidence, MSWD = 2.4, Fig. 4e).

Discussion

Robust U–Pb dates were obtained from three out of the four dated Viséan bentonites (Table 1), and these are the focus of the following discussion. Using the new U–Pb zircon CA-ID-TIMS dates, periodicity estimates are calculated for early Warnantian sedimentary cycles that occur interbedded with the dated bentonite horizons. These periodicity estimates are compared with Milankovitch cycle frequencies, which have been demonstrated to modulate Pleistocene glacial ice volumes (e.g. Hays et al. 1976; Imbrie et al. 1993), to evaluate whether the late Viséan cycles of the Namur–Dinant Basin could be an expression of glacio-eustacy. There have been previous suggestions of Milankovitch and glacio-eustatic controls for other time-equivalent sedimentary cycles within western Europe (e.g. British Asbian cycles; Walkden 1987; Wright & Vanstone 2001); however, previous attempts to determine the periodicity of these cycles (e.g. Wright & Vanstone 2001) have been thwarted by a lack of precise age control.

**Periodicity of Belgian early Warnantian sedimentary cycles**

Late Viséan (Livian and Warnantian) cyclic sedimentation within the Namur–Dinant Basin has been described previously (Pirlet 1963, 1968; Poty & Hance 2006a,b) and therefore only a brief introduction is given here. Cyclic sedimentation is manifest as the alternation of bioclastic and micritic limestones (Pirlet 1963). Cycle boundaries have traditionally been defined at the base of the first bioclastic limestone bed overlying a micritic limestone bed of the underlying cycle and are typically sharp, undulose and erosive. The transition from bioclastic to micritic limestone is gradational within a bed or occurs across a bedding plane. The lower bioclastic facies typically contain a diverse faunal assemblage, including brachiopods, corals, crinoids and foraminiferans, whereas the overlying micritic facies are barren or contain an impoverished fauna. Warnantian cycles are c. 0.5–15 m thick, show no clear systematic trends in cycle thickness upwards through the stratigraphy, and have been correlated laterally within the basin (Pirlet 1963, 1968). The cycles were interpreted by Pirlet (1963, 1968) to record the

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**Fig. 3.** Early Warnantian sedimentary cycles. The records of sedimentary cycles at Anhée Nord (except for the lowermost 20 m of Warnantian strata), De Jaiffe Quarry and Anhée Sud are all simplified from the sedimentary logs of Pirlet (1968). For the lowermost 20 m of Warnantian strata exposed at Anhée Nord (i.e. the length of the section that is still accessible), we prefer to reinterpret the record of sedimentary cycles rather than use the interpretations of Pirlet (1968). This is because within this interval Pirlet (1968) subdivided sets of micritic beds into separate cycles. The significance of the micritic cycles is uncertain and we prefer to use only cycles containing both micritic and bioclastic beds in the mean cycle periodicity calculations. Correlations between Anhée Nord, De Jaiffe Quarry and Anhée Sud follow Pirlet (1968). Mbr, Member.
Fig. 4. (a, b, d, e) New U–Pb zircon CA-ID-TIMS data from bentonites W1, W8, W12 and W13 presented as Wetherill concordia diagrams. The concordia curve is drawn as a continuous black line. The grey band surrounding the concordia reflects the uncertainty in the position of the concordia arising from U and Pb decay constant uncertainties (Jaffey et al., 1971). Bold numbers are concordant dates (Ma). Error ellipses are drawn at the 2σ confidence level. Continuous- and dashed-line error ellipses represent data points included in and excluded from the weighted mean 206Pb/238U date calculations respectively. Date uncertainties are quoted at the 95% confidence level and exclude systematic uncertainties arising from the calibration of the EARTHTIME isotopic tracer solution and the decay constant of the $^{238}\text{U}$ decay constant. (c) Ranked single-grain 206Pb/238U dates from bentonite W8. Box heights (representing date uncertainties) are drawn at the 2σ confidence level. The grey bands represent the uncertainties of the weighted mean 206Pb/238U date calculations (95% confidence).
upward shallowing of water depth, from a subtidal environment with good ocean connectivity (bioclastic facies), to a restricted (lagoonal) intertidal to supratidal environment (micritic facies). Subsequent studies (Hance et al. 2001; Chevalier & Aretz 2005; Poty & Hance 2006a,b) have supported this interpretation and have described the cycles as shallowing-upwards parasequences.

Warnantian cycles are well exposed in the Dinant and Namur sedimentation areas of the basin (sensu Hance et al. 2001; Fig. 2). The record of early Warnantian sedimentary cycles used in the calculations of mean cycle periodicity (Fig. 3) has been compiled from outcrop localities in the Dinant Sedimentation Area, where the stratigraphic record is most complete and where the dated bentonites were sampled.

Between bentonites W8 and W13 there are 25.5–28.5 sedimentary cycles (Fig. 3). The uncertainty in the number of cycles arises because two of the parasequences are locally subdivided into multiple cycles: cycle 1 at De Jaiffe Quarry (cycles 1 and 1′) and cycle 3 at Anhée Sud (cycles 3a and 3b; Fig. 3). In both instances, the extra cycles occur at only a single locality. Whether these extra cycles reflect basin-wide eustatic events that are not preserved elsewhere or represent more a localized flooding phenomenon is unclear and this is taken into consideration in the periodicity calculations. Additionally, it is unclear from the sedimentary logs of Pirlet (1968) whether cycle B at Anhée Nord contains any bioclastic beds, and therefore this cycle is treated as uncertain. Using the new U–Pb zircon dates from bentonites W8 and W13 (Table 1), the mean periodicity of the intervening sedimentary cycles is between 108 ± 7 and 121 ± 8 ka per cycle, which can be simplified to 101–129 ka per cycle.

Unfortunately, it is not possible to estimate with confidence the average cycle periodicity of the 3.5 earliest Warnantian cycles that occur between bentonites W1 and W8 at Anhée Nord (Fig. 3). This is because it is unclear how much time resides within the Livian strata between bentonite W1 and the base of the first Warnantian cycle. The situation is further complicated by a marked palaeokarst surface between bentonites W1 and W2 at Anhée Nord, which according to the bentonite correlations of Delcambre (1996) represents a stratigraphical gap equivalent to the upper part of the Maizeret Member and lower part of the Bay Bonnet Member (Fig. 1).

The above periodicity calculation for the sedimentary cycles between bentonites W8 and W13 demonstrates that the mean periodicity of early Warnantian sedimentary cycles of the Namur–Dinant Basin is compatible with the Milankovitch c. 100 ka eccentricity frequency (Fig. 5), which is the dominant Milankovitch frequency identified in recent Pleistocene glacial records (e.g. Hays et al. 1976; Imbrie et al. 1993; Lisiecki 2010). The mean periodicity of Belgian early Warnantian sedimentary cycles is also similar to that of younger, Serpukhovian to Bashkirian, siliciclastic cycles preserved within western Europe (Fig. 5; Pointon et al. 2012), which post-date the appearance of widespread glacial deposits on

### Table 1. U–Pb zircon CA-ID-TIMS dates from the Belgian late Viséan bentonite samples

| Bentonite horizon | Stratigraphical age | Weighted mean 206Pb/238U date (Ma) | Date uncertainties (95% confidence)* | MSWD | Probability-of-fit | Number of analyses† |
|-------------------|--------------------|------------------------------------|--------------------------------------|------|-------------------|--------------------|
| W1                | Late Livian        | 336.22                             | 0.06/0.18/0.40                       | 0.83 | 0.54              | 7/8                |
| W8                | Early Warnantian   | 335.59                             | 0.19/0.25/0.44                       | 0.16 | 0.86              | 3/9                |
| W13               | Early Warnantian   | 332.50                             | 0.07/0.18/0.40                       | 2.4  | 0.051             | 5/6                |

*XYZ uncertainty levels follow Schoene et al. (2006).
†Number of analyses used in the weighted mean 206Pb/238U date calculations relative to the total number of analyses undertaken.
Gondwana during early Serpukhovian times (Veevers & Powell 1987; Frakes et al. 1992; Fielding et al. 2008) and are interpreted to be of glacio-eustatic origin (Maynard & Leeder 1992; Martinsen et al. 1995; Davies et al. 1999; Pointon et al. 2012). Thus, the available periodicity calculations strengthen the argument for the early Warnantian cycles also being of glacio-eustatic origin. Furthermore, these data support that the main phase of late Palaeozoic glaciation commenced before or during earliest Warnantian times, which is consistent with the conclusions of several other studies of far-field proxy records (Wright & Vanstone 2001; Rygel et al. 2008; Barham 2010; Barham et al. 2012).

**Calibration of the Mississippian time scale**

The new U–Pb zircon CA-ID-TIMS dates provide additional age constraints for the improved calibration of the Mississippian time scale. In particular, bentonite W13 has yielded the youngest high-precision U–Pb date (332.50 ± 0.07 Ma) below the base of the Serpukhovian Stage. Our new U–Pb zircon CA-ID-TIMS dates are also consistent (within uncertainty) with recently published U–Pb dates from other late Viséan bentonites and ash layers (Kryza et al. 2010; Schmitz & Davydov 2012; Fig. 1). Kryza et al. (2010) reported a U–Pb zircon sensitive high-resolution ion microprobe (SHRIMP) date of 333.7 ± 3.4 Ma (2σ; Fig. 1) for a bentonite within the Paprotinia Beds, Poland, of late Asbian age (Goniatiates crenistria ammonoid biozone), which is stratigraphically younger than the base of the Asbian and Brigantian (correlated with the early and late Warnantian respectively; Poty & Hance 2006b) and was not differentiated in the time scale of Davydov et al. (2012). The global Viséan–Serpukhovian boundary is drawn following Davydov et al. (2012).

**Base of the Warnantian Substage**

The global Viséan–Serpukhovian boundary is drawn following Davydov et al. (2012).
Conclusions

Three new U–Pb zircon CA-ID-TIMS dates from Belgian late Viséan bentonites are used to estimate the periodicity of early Warningian shallowing-upwards carbonate cycles that occur interbedded with the dated bentonites. Early Warningian sedimentary cycles yield mean cycle periodicities that are consistent with the c. 100 ka Milankovitch cycle, which is the dominant Milankovitch frequency recognized from recent Pleistocene glacial records, strengthening the argument for these cycles being of glacio-eustatic origin. Furthermore, the recognition of glacio-eustatic Warningian sedimentary cycles suggests that the late Palaeozoic glaciation commenced before the start of or during earliest Warningian times, which is consistent with several other studies of far-field, indirect glacial records. The new dates also provide additional high-precision age constraints for the improved calibration of the Mississippian time scale. The correlation of U–Pb isotopic dates from the Clyde Plateau Volcanic Formation (Monaghan & Parrish 2006) with the new U–Pb zircon CA-ID-TIMS dates suggests that the Clyde Plateau Volcanic Formation, Scotland, is of early Asbian age.

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