New high-precision U–Pb dates from western European Carboniferous tuffs; implications for timescale calibration, the periodicity of late Carboniferous cycles and stratigraphical correlation

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Supplementary material: Zircon separation and concentration procedures, U–Pb zircon CA-ID-TIMS methodology and data table, average periodicity calculations for western and central European Namurian and Westphalian sedimentary cycles, and procedures for recalibrating legacy ⁴⁰Ar/³⁹Ar dates are available at www.geolsoc.org.uk/SUP00000.

Abstract

We present three new high-precision U–Pb zircon CA-ID-TIMS dates from western European Carboniferous diagenetically altered volcanic ash layers (bentonites and
tonsteins) that occur interbedded with cyclic siliciclastic sedimentary rocks. The dates constrain the average periodicity of western European late Carboniferous (Arnsbergian to early Langsettian) cyclic sedimentation to between 89 and 124 ka / cycle. This is consistent with the 100 ka ‘short’ eccentricity Milankovitch cycle and supports previous suggestions that the cycles are the product of glacio-eustasy. Cyclostratigraphic tuning of Namurian cycles to the 100 ka eccentricity cycle revises the timing of the global Mississippian-Pennsylvanian boundary to c. 323.9 Ma. CA-ID-TIMS dates also facilitate correlation between different facies belts where biostratigraphical correlations are difficult. Correlation between eastern and western European sequences confirms that the base of the Moscovian stage is located within the Duckmantian (Westphalian B) western European regional substage.

**Introduction**

The timescale for late Mississippian and Pennsylvanian strata of western and central Europe assigned to the Namurian and Westphalian regional stages is poorly constrained because of the paucity of precise isotopic ages. With the exception of four recent U–Pb zircon chemical abrasion – isotope dilution – thermal ionization mass spectrometry (CA-ID-TIMS) age determinations (Gastaldo *et al.* 2009; Waters & Condon 2012), the dataset consists predominantly of dates determined by the $^{40}$Ar/$^{39}$Ar sanidine technique, mostly acquired during the 1980s (e.g. Lippolt *et al.* 1984; Hess & Lippolt 1986), and by the U–Pb zircon Sensitive High Resolution Ion Microprobe (SHRIMP) method, from the 1990s (e.g. Riley *et al.* 1993; Claoué-Long *et al.* 1995). These data have large analytical uncertainties (c. 0.3 – 4.2 %, 2σ; equivalent to 0.9 - 15.3 Ma uncertainty for Carboniferous rocks) and are imprecise by present day standards. Modern U–Pb zircon CA-ID-TIMS dating can yield ages with
precision better than 0.1 % (2σ, 300-360 ka on a Carboniferous aged sample), as
demonstrated by Davydov et al. (2010).

We present new high-precision dates determined by the U–Pb zircon CA-ID-TIMS
technique from three western European diagenetically altered volcanic ash horizons
(bentonites and tonsteins). These dates are used to determine the average periodicity
of western European late Carboniferous (Arnsbergian to Duckmantian) sedimentary
cycles. In addition, the new data yield dates bracketing the global Mississippian-
Pennsylvanian (Mid-Carboniferous) boundary and, in conjunction with recently
published dates from Eastern Europe (Davydov et al. 2010), enable correlation of the
base of the Moscovian stage with Westphalian strata of Western Europe.

Stratigraphical levels of the samples analysed
Bentonite B9 corresponds to the middle K-bentonite horizon of Trewin & Holdsworth
(1972) and was collected from Oakenclough Brook, Staffordshire, Pennine Basin,
England [SK0501 6369], from the upper sedimentary cycle of the Namurian E2b2
ammonoid sub-zone (cycle E2b2ii; Fig. 1). Samples from two Westphalian tonsteins
(T75 and Z1) were supplied by Dr Bernard Delcambre (Université Catholique de
Louvain). Tonstein T75, sampled from the Zwartberg Coal Mine (now disused) in the
Campine Basin, Belgium, occurs between the Wasserfall and Quaregnon marine
bands (Fig. 1) and is of Langsettian (Westphalian A) age. Tonstein Z1 was sampled
from the Furst Leopold Coal Mine, Dorsten, in the Ruhr Basin, Germany, and occurs
10 – 12 m beneath the Ägir marine band (Fiebig 1969), which defines the base of the
Bolsovian (Westphalian C) substage and is thus of latest Duckmantian (Westphalian
B) age (Fig. 1).
Zircon populations separated from the studied samples

The sample of bentonite B9 yielded a population of small (mostly < 120 μm in length), euhedral zircons possessing low aspect ratios (typically 1.5 – 3). Grains from bentonite B9 are relatively clear, containing few inclusions or fractures. The sample of tonstein T75 yielded a zircon separate of predominantly euhedral grains, with lengths of 50 – 260 μm and aspect ratios of c. 2 – 8. Some grains, particularly those with longer aspect ratios, contain melt inclusions parallel to the c-axis. A few grains display evidence of xenocrystic inheritance (small, round, high-relief cores and radial fractures). The sample of tonstein Z1 yielded a bimodal population, comprising both rounded and euhedral zircons. The rounded sub-population accounts for c. 80 % of the total zircon separate and is typically finer grained than the euhedral sub-population, which is comprised of crystals 100 – 250 μm in length with aspect ratios of 2 – 6. Some of the euhedral zircons contain melt inclusions orientated parallel to the c-axis.

Methodology

Full details of the sample preparation and analytical methods used are given in the online supplementary material (www.geolsoc.org.uk/SUP00000). Zircon grains were separated from the bentonite and tonstein samples using the facilities at the Department of Geology, Trinity College Dublin. U–Pb zircon CA-ID-TIMS dating of sample grains was undertaken at the University of Geneva. All analyses were of single grains that were chemically abraded (sensu Mattinson 2005) prior to dissolution and spiked with the EARTHTIME $^{202}\text{Pb}$-$^{205}\text{Pb}$-$^{233}\text{U}$-$^{235}\text{U}$ isotopic tracer solution. Results were corrected for initial $^{230}\text{Th}$ disequilibrium and subtractions were
made for blank and isotopic tracer contributions. Isotopic dates were calculated using the U decay constants of Jaffey et al. (1971). Concordia diagrams were constructed using Isoplot v. 3.0 (Ludwig 2003).

Weighted mean $^{206}\text{Pb}/^{238}\text{U}$ dates of overlapping, concordant analyses (within analytical and decay constant uncertainties) are used to define the ages of the bentonite and tonstein horizons. Errors on weighted mean calculations are given in the ± X/ Y/ Z format 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 $^{238}\text{U}$ decay constant uncertainties. Systematic uncertainties arising from tracer calibration and the U decay constants were added in quadrature. In this study the same EARTHTIME tracer was used for all CA-ID-TIMS analyses, allowing systematic uncertainties in tracer calibration (0.05%, 2σ) and the U decay constants (0.107%, 2σ; Jaffey et al. 1971) to be disregarded during internal comparisons of our sample data. Systematic uncertainties in tracer composition need to be considered only where our data are compared with other ID-TIMS dates calibrated against a non-EARTHTIME tracer, or to U–Pb dates derived using a different analytical method (e.g. SHRIMP, LA-ICP-MS). 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. Re–Os, K–Ar).

**Results**

**Age of bentonite B9 (Arnsbergian, E2b2 ammonoid sub-zone)**

U–Pb zircon CA-ID-TIMS data from bentonite B9 are plotted in Fig. 2a. Nine single grains were dated. One analysis (B9/3) yielded significantly older dates and is
interpreted to reflect inheritance, possibly from a grain core. The remaining eight analyses yield comparable $^{206}\text{Pb}/^{238}\text{U}$ ratios. There is some dispersion in $^{207}\text{Pb}/^{235}\text{U}$ ratios, particularly between analyses with high analytical blanks (> 3 pg common Pb; analyses B9/2, 5, 9, 16). The $^{207}\text{Pb}/^{235}\text{U}$ ratio is more sensitive to the composition of the analytical blank and we attribute the shifting of high-blank analyses to the right of concordia to slight inaccuracies in the common lead correction.

The high-blank analyses are excluded from the weighted mean $^{206}\text{Pb}/^{238}\text{U}$ date calculation. However, these data have very little effect on the calculated $^{206}\text{Pb}/^{238}\text{U}$ date because they are significantly less precise than the four analyses with lower analytical blanks (Fig. 2b). The weighted mean $^{206}\text{Pb}/^{238}\text{U}$ date of the four analyses with lower analytical blanks (analyses B9/10, 11, 14, 15; Fig. 2b) is $324.54 \pm 0.26/0.31/0.46$ Ma (95% conf., MSWD = 0.94, p = 0.42), and this is taken to approximate the age of this bentonite horizon. This differs substantially from the U-Pb zircon CA-ID-TIMS date of $328.34 \pm 0.30/0.43/0.55$ Ma (95% conf.) of Waters & Condon (2012) for bentonite B6 of Trewin (1968) which occurs within the upper part of the *Eumorphoceras yatesae* (E2a3) Marine Band (Fig. 1). The reasons for this significant age difference are uncertain and are beyond the intended scope of this paper.

**Age of tonstein T75 (Langsettian)**

Eleven single grain U–Pb zircon CA-ID-TIMS analyses were undertaken from the sample of tonstein T75. Ten analyses are shown in Fig. 2c; one data point was not drawn (analysis T75/5) because it is substantially older than the others. This sample shows some age complexity: there are four analyses yielding relatively old ages (analyses T75/5, 7, 8, 11); a cluster of data points that overlap and are concordant
within analytical and decay constant uncertainties (solid ellipses in Fig. 2c; analyses T75/1, 2, 3, 6, 13); and two analyses with high analytical blanks (> 3 pg; T75/4, 9), which yield relatively young ages. The latter analyses (T75/4, 9) only marginally overlap (at the 2σ confidence level) with each other and with the concordia band (Fig. 2c). We interpret these to contain residual lead loss that was not completely removed by chemical abrasion. The efficiency of the chemical abrasion method (Mattinson 2005) is unquestionably better than air abrasion, but evidently it is not always entirely effective as there are instances within several recent studies that employed chemical abrasion where anomalously young dates have been attributed to residual lead loss (e.g. Gastaldo et al. 2009; Davydov et al. 2010; Gulbranson et al. 2010; Schoene et al. 2010). These two data points (T75/4, 9) are therefore not included in the calculation of weighted mean 206Pb/238U date.

Analysis T75/5 is substantially older than the rest (206Pb/238U date of 321.53 ± 0.83 Ma, 2σ) and is considered to represent an inherited grain. Analyses T75/7, T75/8 and T75/11 are marginally older (< 1 Ma) than the main concordant cluster and may represent antecrystic grains (sensu Miller et al. 2007).

We consider the five analyses that are equivalent and concordant within analytical and decay constant uncertainties (analyses T75/1, 2, 3, 6, 13; solid ellipses in Fig. 2c) to provide the best estimate for the age of this tonstein. The weighted mean 206Pb/238U date of these is 317.63 ± 0.12/ 0.20/ 0.39 Ma (95 % conf., MSWD = 0.70, p = 0.59).

**Age of tonstein Z1 (late Duckmantian)**
Seven single grain analyses were undertaken from the sample of tonstein Z1 (Fig. 2d). One analysis has an unacceptably high analytical blank (11.45 pg common Pb; analysis Z1/1) and is not illustrated, nor is it included in further interpretations. The remaining six analyses yield a simple age population (Fig. 2d) and a weighted mean $^{206}\text{Pb}/^{238}\text{U}$ date of 313.78 ± 0.08/ 0.18/ 0.38 Ma (95% conf., MSWD = 2.2, p = 0.056). This is within error of (but substantially more precise than) previous age determinations from tonstein Z1 (Fig. 1) which used the $^{40}\text{Ar}/^{39}\text{Ar}$ sanidine (Hess & Lippolt 1986) and U–Pb zircon SHRIMP methods (Claoué-Long et al. 1995). This date is also very close to the U-Pb zircon CA-ID-TIMS date of 314.37 ± 0.25/ 0.40/ 0.53 Ma (95 % conf.) of Waters & Condon (2012) for the Sub-High Main Tonstein, a tonstein of earliest Bolsovian age from the Pennine Basin, northern England.

**Periodicity of late Carboniferous cyclic sedimentation**

The Namurian and Westphalian regional stages of western Europe are characterised by siliciclastic facies that demonstrate simple cyclicity in the form of rocks which are barren of marine fossils alternating with thin bands of shale, mudstone or limestone that contain an abundant marine fauna (Holdsworth & Collinson 1988). The latter are commonly termed ‘marine bands’ and are thought to reflect eustatic highstands (Holdsworth & Collinson 1988; Martinsen et al. 1995).

The marine bands have long been argued to be glacio-eustatic in origin on the basis of their regional extent and the known occurrence of coeval ice centres on Gondwana (Veevers & Powell 1987). An alternative approach to evaluating potential glacio-eustatic control of cyclic sedimentation is to estimate cycle periodicities and compare them to the Milankovitch cycles (e.g. Heckel 1986), which have been shown to
modulate ice volumes during recent Pleistocene glaciations (Hays et al. 1976). For
Palaeozoic-aged strata, such comparisons are normally restricted to the eccentricity
frequencies (c. 100 ka and c. 400 ka), which are thought to be stable over geological
time unlike the shorter obliquity and precession frequencies (Berger et al. 1992).
There have been several previous attempts to apply this methodology to the late
Carboniferous of western Europe using published isotopic age data (e.g. Riley et al.
1993). However, the imprecision of existing isotopic age data (\(^{40}\)Ar/\(^{39}\)Ar, U–Pb
SHRIMP data) propagates through as large uncertainties in the periodicity estimates,
preventing a robust comparison to the Milankovitch cycles.

Arnsbergian to early Langsettian cycles

Combining the Namurian stratigraphic record from the Pennine Basin, northern
England, and the Langsettian record from the Ruhr Basin, Germany (both illustrated
in the online supplementary material), 58 marine bands are recognised between
bentonite B9 and tonstein T75 (correlated with tonstein Wilhelm of the Ruhr Basin;
Paproth et al. 1983; Delambre 1996). Within the Langsettian of the Ruhr Basin there
are also 16 faunal bands that contain ostracodes of the genus Jonesina, the trace fossil
Planolites ophthalmoides, arenaceous foraminifera and/or brachiopods (Lingula)
(Fiebig 1969; Bachmann et al. 1970). These are thought to be indicative of brackish
(near-marine) conditions (Rabitz 1966; Calver 1968; Bless et al. 1988; Paproth et al.
1994; Dusar et al. 2000). Because it is difficult to trace these bands to regions away
from the Ruhr Basin, their lateral continuity is not known and thus the likelihood that
they reflect eustatic oscillations is difficult to assess. The uncertainty as to whether the
brackish horizons reflect eustatic highstands has been taken into consideration in the
periodicity calculations: the total number of faunal bands between bentonite B9 and
tonstein T75 that are attributable to eustatic processes is between a minimum of 58
(marine bands only) and a maximum of 74 (marine and brackish bands).

Using the new CA-ID-TIMS dates from bentonite B9 and tonstein T75 presented
here, the average periodicity of Namurian (Arnsbergian) to early Langsettian
sedimentary cycles is between 89 and 124 ka / cycle (95 % confidence; the periodicity
calculations are shown in the online supplemental material). This is comparable
(within uncertainty) to the dominant c.100 ka cycle frequency observed in late
Pleistocene glacial records (e.g. Hays et al. 1976), which is widely attributed to result
from Milankovitch 100 ka eccentricity orbital-forcing (Hays et al. 1976; Imbrie et al.
1993; Lisiecki 2010). We suggest that similarities between the periodicity of
Pleistocene glacial cycles and the Arnsbergian to early Langsettian sedimentary
cycles of western Europe strengthens the argument that these late Carboniferous
sedimentary cycles were the product of glacio-eustatic fluctuations.

Late Langsettian to Duckmantian sedimentary cycles
The Westphalian stage of western Europe contains notably fewer marine bands than
the Namurian stage. Only 19 bands are recognised from the Pennine Basin (Calver
1968; Ramsbottom et al. 1978); most occur in the early Langsettian and the late
Duckmantian to early Bolsovian (Calver 1968, 1969; shown in the online
supplementary material). The reduction in the number of marine bands during mid to
late Langsettian times is coincident with an increased prevalence of non-marine
mussel bands (Calver 1968, 1969) and sedimentological changes that suggest a
landward shift in the depositional environment from a lower to an upper delta plain
(Guion & Fielding 1988; Guion et al. 1995).
A similar reduction in the number of marine bands is found in the Campine Basin, Belgium, and the Ruhr Basin, Germany. Early Langsettian strata contain numerous marine bands but few have been found in younger rocks (Fiebig 1969; Paproth et al. 1994). There are, however, numerous late Langsettian- and Duckmantian-aged brackish faunal and trace fossil bands. In the Ruhr Basin, between tonsteins Wilhelm and Z1 there are only two fully marine bands (Katharina and Domina horizons in Fig. 1), whereas 34 bands containing ostracodes of the genus *Jonesina*, the trace fossil *Planolites ophthalmoideas*, arenaceous foraminifera and/or *Lingula* have been recognised (Fiebig 1969; Bachmann et al. 1970). Thus within this stratigraphic interval there are between two and 36 faunal bands that could be eustatic. Using the same methodology as employed to Arnsbergian to early Langsettian cycles yields periodicity values for late Langsettian to Duckmantian sedimentary cycles of between 103 and 1995 ka / cycle (95 % confidence).

Using the same tonstein dates (T75 and Z1) but applying them to the stratigraphic record from the Pennine Basin, where the same stratigraphic interval contains between five and eleven faunal and trace fossil bands (see the online supplementary material for details), yields periodicities of between 337 and 798 ka / cycle (95 % confidence).

The above periodicity calculations highlight differences in the amount of time between Pennine and Ruhr Basin faunal bands. There are a sufficient number of brackish and marine faunal bands preserved within the Ruhr Basin to yield an average periodicity that is similar to the older Namurian cycles and the c. 100 ka Milankovitch
eccentricity cycle. The periodicity calculations are consistent with the hypothesis that the brackish faunal bands in the Ruhr Basin could represent the distal expression of glacio-eustasy. However, this is not definitive proof and further research is necessary to confirm this hypothesis. More tonstein horizons are reported from the Ruhr Basin (e.g. Fiebig 1969; Burger et al. 2005) interbedded with these cryptic brackish faunal bands. Additional U–Pb zircon CA-ID-TIMS dates from such horizons would evaluate whether our calculated average periodicity is representative at a finer scale of analysis.

The longer average periodicities of the Pennine marine and trace fossil bands probably reflects the waning of marine influence in Britain, resulting in several sea-level oscillations of late Langsettian and early Duckmantian age being unrepresented in the British record, so that the periodicity calculation is biased by the occurrence of missing “beats”.

Carboniferous timescale calibration and astronomical tuning

Until recently, Carboniferous timescales (e.g. Menning et al. 2000) have primarily been constructed by fitting isotopic age data to composite standard (thickness-based) stratigraphic scales and using interpolation to derive the timings of stratigraphic boundaries. Such an approach assumes stratigraphic thickness is linearly proportional to time duration and is thus an idealised situation, unlikely to be fulfilled in real sedimentary basins. This limitation is mitigated to some extent by integrating a number of stratigraphic sections and computing an average (or composite) section.
An alternative approach, which circumvents the need for a composite standard stratigraphic scale, is astronomical (or orbital) tuning (Hinnov & Ogg 2007). Where sedimentary strata contain evidence of cyclicity that can be demonstrated to correspond to a known Milankovitch orbital-forcing cycle, it is possible to tune the stratigraphic record to such an orbital beat and interpolate the ages of stratigraphic boundaries against it. This method offers continuous temporal calibration of stratigraphic sequences (Hinnov & Ogg 2007) but it is based on assumptions of constancy of cycle frequency.

Astronomical tuning has been applied to late Carboniferous stratigraphy in several studies. Heckel (2008) utilised the c. 400 ka Milankovitch ‘long’ eccentricity cycle to derive ages for late Pennsylvanian strata from the midcontinent of North America and Davydov et al. (2010) and Peterson (2011) applied similar techniques to the Pennsylvanian stratigraphy of the Donets Basin, Ukraine.

As shown in previous sections, the periodicity of Arnsbergian to early Langsettian cycles is consistent with the Milankovitch c. 100 ka eccentricity frequency. We employ this Milankovitch frequency and astronomically tune the upper part of the Namurian stratigraphy of the Pennine Basin, northern England. This enables the global Mid-Carboniferous boundary and the base of the regional Westphalian stage to be constrained in time. Extrapolation of this cyclostratigraphic approach to the base of the regional Namurian stage, which is outside of the stratigraphic interval bracketed by our new U–Pb CA-ID-TIMS age constraints, is problematic and is discussed below. Our astronomically tuned estimates are then compared to published timescale calibrations (Menning et al. 2000; Davydov et al. 2004, 2010; Peterson 2011).
We do not extend astronomical tuning into the Westphalian stage because it is uncertain whether the numerous late Langsettian to Duckmantian brackish faunal and trace fossil bands preserve a record of Milankovitch orbital forcing. However, tonstein Z1 occurs adjacent to the base of the Bolsovian regional substage and its new U–Pb zircon CA-ID-TIMS date approximates the age of this boundary, enabling us to comment on the duration of the Langsettian and Duckmantian regional substages combined.

**Temporal constraints on the Namurian regional stage**

**Base of the Namurian stage**

The basal boundary of the Namurian western European regional stage is defined as at the base of strata containing the earliest occurrence of the ammonoid *Cravenoceras leion* (van Leckwijck 1960). In the Pennine Basin, this corresponds to the base of the E1a1 (*C. leion*) marine band, which occurs 15.5 sedimentary cycles below bentonite B9 (shown in the online supplementary material; the half cycle corresponds to the part of a cycle between bentonite B9 and the underlying E2b2ii marine band). If it is assumed that these cycles reflect the 100 ka eccentricity cycle then the age of the base of the Namurian regional stage is calculated as c. 326.1 Ma. This value is close to that reported by Davydov *et al.* (2004; 326.4 ± 1.6 Ma; Fig. 3) and Menning *et al.* (2000, 326.5 Ma; Fig. 3), but is substantially younger than was estimated by Davydov *et al.* (2010, 329.2 Ma; Fig. 3) and Gastaldo *et al.* (2009; 329.7 Ma). The true date of the base of the Namurian stage is almost certainly older than 326.1 Ma because Davydov *et al.* (2010) reported the age of a tonstein within the C11 coal of the Donets Basin, which is correlated with a horizon in the Pendleian regional substage of western
Europe, as 328.14 ± 0.1 Ma (2σ). Gastaldo et al. (2009) similarly reported an age of 328.84 ± 0.16 Ma (2σ) for a tonstein correlated with the Pendleian regional substage in the Ostrava Formation of the Upper Silesian Basin of the Czech Republic. Using the estimate of 329.2 Ma in Davydov (2010) for the age of the base of the Namurian stage, together with the new U–Pb zircon CA-ID-TIMS date from bentonite B9, the average duration of the cycles in the Pendleian and Arnsbergian below the B9 bentonite is calculated to be c. 300 ka. The data available at present are not sufficient to explore possibilities such as the combination of long eccentricity (c. 400 ka) and short eccentricity (c. 100 ka) frequencies controlling sedimentary cycles within this stratigraphic interval, or a change from long to short eccentricity, several cycles above the base of the Namurian stage. The former possibility has been suggested by Waters & Condon (2012).

Age of the Mississippian-Pennsylvanian (Mid-Carboniferous) boundary

The Mississippian-Pennsylvanian boundary was correlated with the base of the H1a2 marine band in the European parastratotype at Stonehead Beck, northern England (Riley et al. 1993, p. 281, fig. 4). In recent Carboniferous Timescale compilations, the age of this boundary has been successively revised towards older dates (Fig. 3) by c. 6 Ma (from 318.1 ± 1.3 Ma to 324.42 ± 0.54 Ma; Davydov et al. 2004 and Peterson 2011 respectively). The substantial age shift reflects the paucity of precise isotopic age constraints from near to this boundary.

Part of the confusion surrounding the age of this boundary arises because of inconsistencies within the published isotopic dataset. The isotopic age constraints from closest to the Mid-Carboniferous boundary, i.e. two U–Pb SHRIMP
determinations from the Pennine Basin, northern England (Riley et al. 1993), and a
\(^{40}\text{Ar}/^{39}\text{Ar}\) sanidine date from tonstein 479 of the Upper Silesian Basin, Czech
Republic (Fig. 1; Lippolt et al. 1984; Hess & Lippolt 1986), diverge significantly. The
two bentonites from the Pennine Basin dated by the U–Pb SHRIMP method are
equivalent to bentonites B6 and B8 of Trewin (1968) and Trewin & Holdsworth (1972) (Fig. 1) and yielded weighted mean \(^{206}\text{Pb}/^{238}\text{U}\) dates of 314.4 ± 4.6 Ma and
314.5 ± 4.6 Ma respectively (Riley et al. 1993). Originally, Hess & Lippolt (1986)
determined a plateau age of 319.5 ± 2.4 / 7.8 Ma (2\(\sigma\), internal error/ internal error plus
standard uncertainties) for tonstein 479. However, this isotopic date requires revision
before comparison with the U–Pb SHRIMP data. The internal error of the \(^{40}\text{Ar}/^{39}\text{Ar}\)
date is recalculated to express it as the standard deviation of the weighted mean,
which is how U–Pb internal errors are routinely expressed (Claoué-Long et al. 1995).
Additionally, the \(^{40}\text{Ar}/^{39}\text{Ar}\) date is recalibrated against astronomically tuned Fish
Canyon Tuff sanidine (Kuiper et al. 2008) and an updated \(^{40}\text{K}\) decay constant (Min et
al. 2000). Following these recalibration steps, the \(^{40}\text{Ar}/^{39}\text{Ar}\) sanidine date of tonstein
479 is revised to 323.7 ± 1.0 / 3.6 Ma (2\(\sigma\); internal error/ internal error plus standard
and decay constant uncertainties). Full details of this recalibration are presented in the
online supplemental information. The recalibrated \(^{40}\text{Ar}/^{39}\text{Ar}\) date and U–Pb SHRIMP
dates are statistically distinct at the 95% confidence level.

Our new CA-ID-TIMS date from bentonite B9 provides additional information that
can clarify the discrepancy between the two sets of published data. Although
bentonite B9 is a different (younger) horizon to those dated by Riley et al. (1993) and
Hess & Lippolt (1986), it occupies a similar stratigraphic position based on
ammonoid biostratigraphy (Fig. 1). Ammonoid radiation rates during Namurian times
were such that the majority of marine bands in the Pennine Basin have a different characteristic ammonoid fauna (Ramsbottom et al. 1978; Holdsworth & Collinson 1988). Five ammonoid-bearing marine bands are recognised in the Pennine Basin between bentonites B6 and B9 (Fig. 1). This would imply, based on our calculated average periodicity (c. 100 ka / cycle), that there should be no more than a c. 0.5 Ma age difference between these altered ash layers. As illustrated in Fig. 4 this is not the case, as the U–Pb SHReMP dates from bentonites B6 and B8 are significantly younger than the U–Pb zircon CA-ID-TIMS date from bentonite B9 and the recalibrated ⁴⁰Ar/³⁹Ar sanidine date from tonstein 479.

Using the CA-ID-TIMS date for bentonite B9 as an anchor point and astronomically tuning the cycle record between bentonite B9 and the Mid-Carboniferous boundary (6.5 sedimentary cycles; the half cycle corresponds to the part of cycle E2b2ii between bentonite B9 and the overlying E2b3 marine band; Fig. 1), the age of this boundary is c. 323.9 Ma. Our estimate is consistent with the date of 324.42 ± 0.54 Ma calculated by Peterson (2011).

**Base of the Westphalian regional stage**

The Namurian – Westphalian boundary (Fig. 3) is defined as at the base of the marine band containing the earliest occurrence of *Gastrioceras subcrenatum* (Waters & Davies 2006). In recent timescale calibrations the age of this boundary has been progressively revised towards older dates, shifting by c. 4 Ma over the last decade (c.f. Davydov et al. 2004 and Davydov et al. 2010 in Fig. 3). This reflects a lack of precise isotopic dates from near to this boundary. There are 46.5 sedimentary cycles between B9 and the base of Westphalian stage (the half cycle corresponds to the top part of
cycle E2b2ii between bentonite B9 and the overlying E2b3 marine band; Fig. 1).

Using the CA-ID-TIMS date of bentonite B9 and tuning the intervening cycles to the 100 ka eccentricity cycle yields an age of c. 319.9 Ma for the base of the Westphalian stage. This is the oldest estimate for the base of the Westphalian stage to date (Fig. 3).

Base of the Bolsovian regional substage

Tonstein Z1 occurs 10 – 12 m below the Ägir marine band (Fiebig 1969), which identifies the base of the Bolsovian substage. It is sufficiently close to this boundary that the new CA-ID-TIMS age approximates a boundary age (313.78 ± 0.08 Ma; Fig. 3). Our boundary estimate is older than that estimated by Davydov et al. (2004) and Menning et al. (2000), and younger than the estimate of Davydov et al. (2010; Fig. 3).

Time durations of Chokierian to Duckmantian regional substages

Using the astronomically-tuned boundary ages for the base of the Chokierian regional substage and the Westphalian stage (Fig. 3), the duration of the intervening stratigraphic interval is estimated to be c. 4.1 Ma, which is comparable to the durations presented in all of the published timescales illustrated in Fig. 3. Similarly, taking the astronomically-tuned age for the base of the Westphalian stage (319.9 Ma; see above) and the new U–Pb CA-ID-TIMS date from tonstein Z1, the duration of Langsettian and Duckmantian substages combined is revised to c. 6.1 Ma. This compares favourably with the c. 5.5 Ma duration shown in Menning et al. (2000; Fig. 3) but it is substantially longer than was suggested by Davydov et al. (2004, 2010; Fig. 3).
It is noteworthy that the three new U–Pb zircon CA-ID-TIMS dates yield similar time duration relationships for the intervening stratigraphic intervals compared to the timescale B of Menning et al. (2000). Between bentonite B9 and tonstein T75 there is a duration of c. 6.9 Ma, compared to the c. 7.4 Ma duration shown in timescale B of Menning et al. (2000). Likewise, between tonsteins T75 and Z1 there is a c. 3.9 Ma duration compared to 3.2 Ma shown in Menning et al. (2000). Both the timescale B of Menning et al. (2000) and the duration estimates herein are based upon isotopic age data obtained from a single (albeit different) decay system and standard (\(^{40}\text{Ar}/^{39}\text{Ar}\) data and U–Pb CA-ID-TIMS data respectively) and thus isotopic age data from different decay systems and standards yield similar time duration relationships for the studied stratigraphic interval. Whilst the time durations calculated in this study are similar to the values presented in Menning et al. (2000) there is a 3 – 4 Ma systematic offset between the stratigraphic boundary ages determined in this study (Fig. 3) and those of Menning et al. (2000; Fig. 3). This discrepancy is likely to arise because the \(^{40}\text{Ar}/^{39}\text{Ar}\) dates that underpin the Menning et al. (2000) timescale B were calibrated against values for the age of the monitor standard and \(^{40}\text{K}\) decay constant that are now considered obsolete. Recalibrating these legacy \(^{40}\text{Ar}/^{39}\text{Ar}\) data against recent estimates for the age of the monitor standard and \(^{40}\text{K}\) decay constant increases the sample ages by c. 4 Ma (see online supplementary material), which is similar in magnitude to the observed systematic offset.

**Correlation of the base of the Moscovian stage with regional stages of western Europe**

The Moscovian stage is the second oldest of the four global stages of the Pennsylvanian subsystem (Heckel & Clayton 2006). Heckel & Clayton (2006)
showed the base of the stage as being equivalent to a level in the younger part of the Duckmantian regional substage of western Europe (Fig. 1). However, Wagner & Álvarez-Vázquez (2010; and references therein) contended that the base of the Moscovian should be correlated with a level slightly below the base of the Langsettian in western Europe (Fig. 1). Correlation of the base of the Moscovian cannot yet be precise because a GSSP for the base of the stage has yet to be selected. It seems probable, however, that the base will be chosen to coincide with the evolutionary first occurrence of the conodonts Declinognathodus donetzianus, Idiognathoides postsulcatus or Diplognathodus ellesmerensis. Within the Donets Basin these taxa first occur in limestones K1, K2 and K3, respectively (Davydov et al. 2010), all of which are contained within a single orbitally-tuned 400 ka cycle (Davydov et al. 2010).

Taking the base of the K1 limestone as a preliminary base for the Moscovian, and utilising astronomical tuning tied to precise U–Pb zircon CA-ID-TIMS of tuff horizons, Davydov et al. (2010) and Peterson (2011) estimated the boundary at 314.6 Ma and 314.61 ± 0.33 Ma respectively. This is very close to the 313.78 Ma date from the Z1 tonstein established in this study and confirms that the base of the Moscovian should be correlated with a level in the younger part of the Duckmantian regional substage of western Europe. The base is certainly younger than the horizon of the late Langsettian tonstein T75 (317.63 Ma). High-precision U–Pb zircon CA-ID-TIMS data thus have the potential to aid biostratigraphical correlation between different facies belts with non-equivalent faunas.

Conclusions
Based on three new high-precision U–Pb zircon CA-ID-TIMS dates from bentonites and tonsteins interbedded with late Carboniferous western European sedimentary rocks the periodicity of western European Arnsbergian to early Langsettian cyclic sedimentation is revised to between 89 and 124 ka / cycle. This is consistent with the Milankovitch 100 ka eccentricity cycle. Tuning of Namurian cycles to this astronomical beat revises the timing of the global Mid-Carboniferous boundary to c. 323.9 Ma and the base of the regional Westphalian stage to c. 319.9 Ma. Additionally, the base of the global Moscovian stage can be correlated to within the younger part of the Duckmantian western European substage.

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**Figure Captions**

Fig. 1. A stratigraphic column showing the positions of bentonites and tonsteins discussed and/or dated herein. ‘B’ bentonite nomenclature and stratigraphic positions are from Trewin (1968), Trewin & Holdsworth (1972) and Riley *et al.* (1993).
Tonstein 479 (within the Max coal seam; Lippolt et al. 1984) is located above the Enna marine horizon (contains *Cravenoceratoides* (*Ct.* *edalensis*; E2b1; Dzik 1997) and below the Roemer marine horizon (contains *Ct. nitidus* and *Ct. nitidoides*; E2b2–E2b3; Dzik 1997; Hartung & Patteisky 1960), and is therefore within the E2b1 ammonoid sub-zone. The biostratigraphic constraints on tonstein 479 mean it could correlate to within either of the three sedimentary cycles of the E2b1 ammonoid sub-zone (E2b1i – iii cycles; Holdsworth & Collinson 1988). Westphalian tonstein positions are from Delambre (1996). Local names are given for the Westphalian marine bands, followed in brackets by the standard names suggested by Ramsbottom et al. (1978). The position of the Mississippian-Pennsylvanian (Mid-Carboniferous) boundary is from Riley et al. (1993). Cited isotopic dates: 1) Hess & Lippolt (1986) dates recalibrated against modern estimates for the age of the monitor standard and the \(^{40}\text{K}\) decay constant; see the online supplementary material for details; 2) Claoué-Long et al. (1995); 3) Riley et al. (1993); 4) Waters & Condon (2012). All date uncertainties are at the 95% or 2\(\sigma\) confidence level. CA-ID-TIMS date uncertainties are given in ± X/ Y/ Z notation (sensu Schoene et al. 2006; see the methodology section for an explanation).

Fig. 2. New U–Pb zircon CA-ID-TIMS data from bentonite B9 and tonsteins T75 and Z1. (a, c, d) Conventional (Wetherill) concordia diagrams of U-Pb zircon CA-ID-TIMS data from bentonite B9 and tonsteins T75 and Z1. The Concordia curve is shown as a solid black line with increments of 2 Ma (a), 0.5 Ma (c) and 0.2 Ma (d). The grey band surrounding the Concordia reflects the uncertainty in the position of the Concordia arising from \(^{235}\text{U}\) and \(^{238}\text{U}\) decay constant uncertainties (Jaffey et al. 1971). Solid and dashed error ellipses represent data points included in and excluded
from the weighted mean $^{206}\text{Pb}/^{238}\text{U}$ date calculations respectively. Error ellipses are drawn at the 2σ level. (b) A weighted mean $^{206}\text{Pb}/^{238}\text{U}$ date plot of data from bentonite B9. Box heights are drawn at the 2σ confidence level. Pbc = common lead. All dates presented in this figure are weighted mean $^{206}\text{Pb}/^{238}\text{U}$ dates. Date uncertainties are quoted at the 95% confidence level and exclude systematic uncertainties arising from isotopic tracer calibration and the $^{238}\text{U}$ decay constant.

Fig. 3. Revised estimates for some western European regional stage and substage boundaries based on astronomical tuning and the new U–Pb CA-ID-TIMS dates. These are compared to published timescales (timescale B of Menning et al. 2000; Davydov et al. 2004, 2010). U–Pb CA-ID-TIMS dates shown are weighted mean $^{206}\text{Pb}/^{238}\text{U}$ dates. Date uncertainties are at the 95% confidence level and exclude systematic uncertainties arising from the calibration of the isotopic tracer solution and the $^{238}\text{U}$ decay constant. MCB = Mid-Carboniferous (Mississippian-Pennsylvanian) boundary. Namurian stage boundaries, and the substage boundaries therein, are astronomically tuned to the 100 ka eccentricity cycle. The base of the Bolsovian substage is constrained by the CA-ID-TIMS date from tonstein Z1. The timing of the base of the Duckmantian substage cannot presently be precisely constrained. Global stage boundary ages and their associated uncertainties (illustrated as grey bands) are from Peterson (2011).

Fig. 4. Comparison of isotopic dates from several Arnsbergian bentonites and tonsteins that constrain the Mississippian-Pennsylvanian (Mid-Carboniferous) boundary. All date uncertainties are at the 95% or 2σ confidence level. U-Pb SHRIMP and $^{40}\text{Ar}/^{39}\text{Ar}$ date uncertainties include systematic uncertainties arising
from the age of standard materials and decay constants. For the CA-ID-TIMS B9 date
the ± X/Y/Z uncertainty levels (*sensu* Schoene *et al.* 2006) are shown. The U–Pb
SHRIMP data are from Riley *et al.* (1993). The $^{40}\text{Ar}/^{39}\text{Ar}$ sanidine date is recalibrated
from data presented in Lippolt *et al.* (1984). Sample data are colour-coded based on
their biostratigraphic position, which is constrained by thick-shelled ammonoids.
A) B9

B) B9

C) T75

D) Z1

Mean $^{206}\text{Pb}/^{238}\text{U}$ date = $317.63 \pm 0.12$ Ma

(95% conf., MSWD = 0.70)

Mean $^{206}\text{Pb}/^{238}\text{U}$ date = $313.78 \pm 0.08$ Ma

(95% conf., MSWD = 2.2)
### Subsystem

#### Global Stage
- **Westphalian**
  - **Moscovian**
  - **Bashkirian**

#### Regional Stage
- **Namurian**
  - **Marsdenian**
  - **Kinderscoutian**
  - **Alportian**
  - **Chokierian**

#### Base of Namurian Stage
- **Base of Westphalian Stage**
- **MCB**

#### This study
- **Base of Namurian Stage**
- **U-Pb zircon CA-ID-TIMS dates**
- **B9 = 324.54 ± 0.26 Ma**
- **T75 = 317.63 ± 0.12 Ma**
- **Z1 = 313.78 ± 0.08 Ma**

### Recent Published Timescales

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### Recent Published Timescales

- **Age (Ma)**
  - **Mississippian**
  - **Pennsylvanian**
  - **Namurian**
  - **Westphalian**
  - **Duckmantian**
  - **Langsettian**
  - **Bolsovian**
  - **Base of Namurian Stage**
  - **Base of Westphalian Stage**
  - **MCB**

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**U-Pb zircon CA-ID-TIMS dates**

- **Z1 = 313.78 ± 0.08 Ma**
- **T75 = 317.63 ± 0.12 Ma**
- **B9 = 324.54 ± 0.26 Ma**

**Recent Published Timescales**

- **Davydov et al. (2010)**
- **Menning et al. (2000)**
- **Davydov et al. (2004)**