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Calibrating the Devonian Time Scale: A synthesis of U–Pb ID–TIMS ages and conodont stratigraphy

Bernd Kaufmann *

Institut für Geowissenschaften, Universität Tübingen, Sigwartstrasse 10, 72076 Tübingen, Germany

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Abstract

The recalibrated Devonian time scale represents an important improvement of Devonian chronology regarding two aspects. Firstly, a data set of 13 biostratigraphically well-bracketed U–Pb ID–TIMS zircon and monazite ages constitutes the framework of the scale. Secondly, approximately time-linear biostratigraphic scales have been used for the interpolation between the isotopic ages. The new construction thus represents a 'biochronometric' time scale, which allows the assignment of numeric ages not only to stage boundaries but also to each biozone boundary. The method of interpolation applied also enables the projection of the geochronological error onto the time scale. According to the newly calibrated scale, the Devonian lasted 57.4±5.7 Ma from 418.1±3.0 to 360.7±2.7 Ma. This is, compared to previously published time scales, the longest time span ever calculated for this period. The age interpolations for the eight stage boundaries are:

Famennian–Tournaisian (=Devonian–Carboniferous)	360.7±2.7 Ma
Frasnian–Famennian	376.1±3.6 Ma
Givetian–Frasnian	383.7±3.1 Ma
Eifelian–Givetian	388.1±2.6 Ma
Emsian–Eifelian	391.9±3.4 Ma
Pragian–Emsian	409.1±3.8 Ma
Lochkovian–Pragian	412.3±3.5 Ma
Pridolian–Lochkovian (=Silurian–Devonian)	418.1±3.0 Ma

The duration of the Middle Devonian is calibrated here as quite short with 8.2 Ma and the Emsian and the Famennian are the longest stages with interpolated durations of 17.2 and 15.4 Ma, respectively. Together, all Devonian stages contain 57 conodont zones (including subzones, according to the standard conodont zonation) giving a mean duration of about 1 Ma. In the highly resolved part of the time scale (mid-Eifelian to the Devonian–Carboniferous boundary), zonal resolution averages 0.6 Ma. In contrast, the lowest resolution is shown in the early Emsian to mid-Eifelian interval with zonal durations of up to 5.5 Ma (*serotinus* Zone).

Keywords: Devonian; time scales; U/Pb; absolute age; biostratigraphy; conodont zonations

* Fax: +49 7071 292757.
E-mail address: bernd.kaufmann@uni-tuebingen.de.

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1. Introduction

The Devonian was an extraordinary eventful period for the biosphere. It comprises the radiation of fish and the appearance of the first ammonoids, the first amphibians and the first insects. Plants took over the land and became so abundant that the first coal deposits formed in tropical swamps that covered much of the Canadian Arctic Islands, Northern Greenland, Spitsbergen and Scandinavia. Due to greenhouse climate and sea-level highstand, global reef growth reached an acme in the Middle Devonian followed in the Late Devonian by one of the most important extinction events (Kellwasser Crisis) of Earth history. The assignment of the timing, the sequence and the rates of these events requires an accurate numerical Devonian time scale with a high resolution to the biozone level. Therefore, such different disciplines as biostratigraphy and geochronology have to be combined. The relative biostratigraphic time, as documented by fossils in the sedimentary record, is calibrated here with the absolute time given by isotopic ages obtained from intercalated volcaniclastic layers. Such an integration of the chronologic dimension into the sedimentary record is required to determine the duration of processes like extinction events or the growth of reefs and carbonate platforms. Particularly, the geochronological evaluation of sedimentary cyclicity regarding possible Milankovitch signatures depends on an accurate time scale as an essential tool.

2. Devonian geochronology

The construction of accurate numerical time scales requires a sufficient data set of reliable and biostratigraphically well-bracketed isotopic ages. Not even twenty years ago, only a few were available for the Devonian period (Boucot, 1975; Ziegler, 1978; Harland et al., 1990). These ages were derived from different isotopic decay schemes; they were quite imprecise and rarely met the requirement of a close biostratigraphic constraint. Accordingly, time-scale constructions based on these isotopic ages show considerable divergence (Fig. 1). In the 1990s, new, highly precise U–Pb monazite and zircon ages (Roden et al., 1990; Tucker et al., 1998) considerably improved the situation. These new U–Pb ages were derived from volcanic ashes

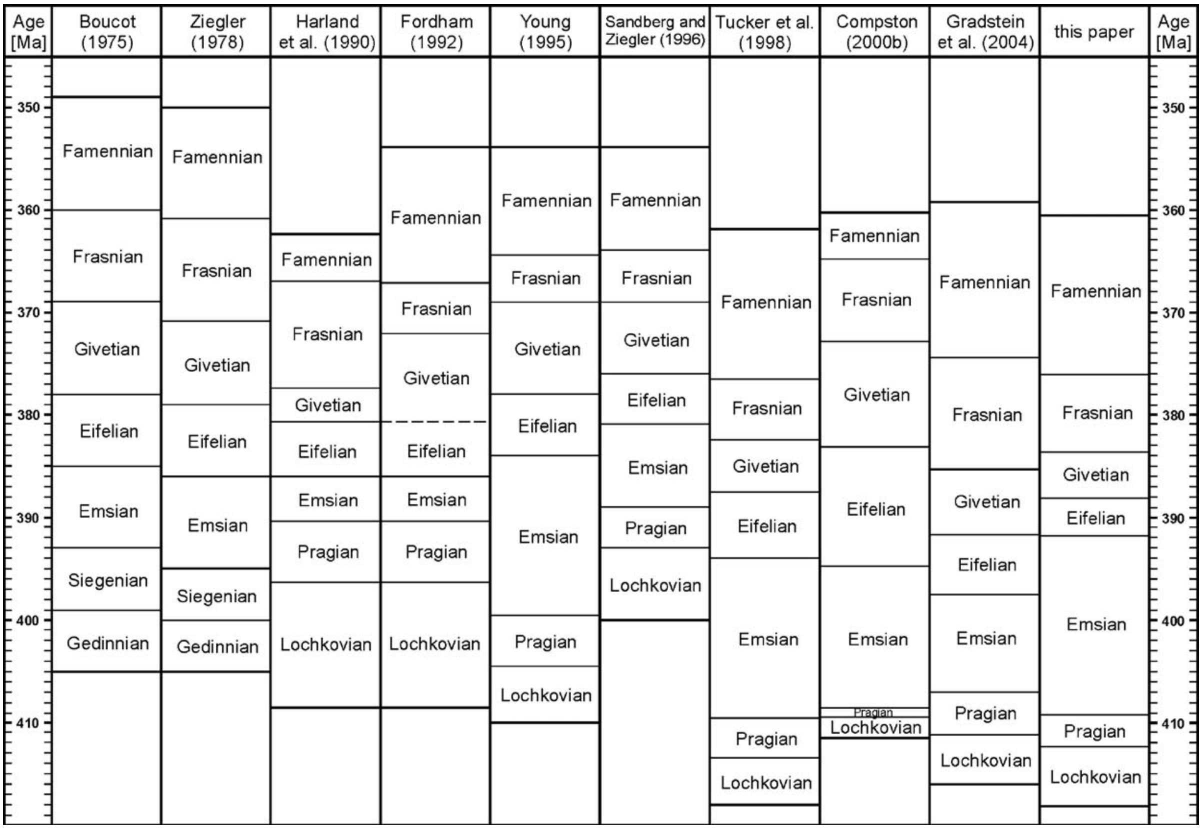

Fig. 1. Comparison of Devonian time scales (selection).

(essentially K-bentonites) intercalated in biostratigraphically well-documented marine sedimentary successions.

The U–Pb method, due to precisely measured decay constants, high initial parent–daughter element ratios and a dual decay scheme, is a precise and reliable isotopic system. Ages derived from other isotopic systems, due to their scarcity and their mostly lower precision and much poorer biostratigraphic control, play a minor role in the Devonian period. However, within the U–Pb system, different analytical methods (isotope dilution–thermal ionization mass spectrometry (ID–TIMS) versus sensitive high-mass resolution ion microprobe (SHRIMP)), applied to identical zircon material, may yield different ages (see detailed discussions in Tucker and McKerrow, 1995; Compston, 2000a,b; Williams et al., 2000). Consequently, the time-scale construction of Compston (2000b), based on SHRIMP and reassessed ID–TIMS zircon ages, differs significantly from the time scale of Tucker et al. (1998) which is based exclusively on ID–TIMS zircon ages (Fig. 1). SHRIMP ages 1–2% younger than ID–TIMS ages have turned out to be caused by a recently detected heterogeneity in the SL 13 zircon reference material and by the erroneous inclusion of youngest data points (later assumed to have lost Pb) in the weighted mean ages (Compston, 2000a,b). These problems have been resolved meanwhile. However, SHRIMP ages are typically less precise (0.5–1.4%) than ID–TIMS ages (0.2–0.5%) and there are merely four reliable Devonian SHRIMP ages available (Jagodzinski and Black, 1999; Nesbitt et al., 1999; Compston, 2004), of which some lack a close biostratigraphic control. Thus, the time scale of Tucker et al. (1998), based on six biostratigraphically well-bracketed U–Pb ID–TIMS ages, represents hitherto the most reliable Devonian geochronology. There are, however, still many problems left with Tuckers' scale that have inspired the initiation of this project. First of all, the network of only six U–Pb ages is still quite fragmentary for a period with a length of about 55 to 60 Ma. Another problem is that Tucker et al. (1998) used a quite conservative and subjective method for time-scale construction (see Section 4 below). And lastly, the time scale of Tucker et al. (1998) focused on the interpolation of the Devonian stage boundaries while an integration of a reproducible, time-linear biostratigraphy was not attempted.

2.1. Data set of U–PB ID–TIMS zircon and monazite ages

Meanwhile, supplementary to the six U–Pb ID–TIMS ages of Tucker et al. (1998) and the one of Roden et al. (1990), six more biostratigraphically well-constrained Devonian U–Pb ID–TIMS zircon and monazite ages have been published (Richards et al., 2002; Kaufmann et al., 2004; Trapp et al., 2004; Kaufmann et al., 2005). A total of 13 ID–TIMS ages is thus available now to recalibrate the Devonian time scale. Such a dense framework of isotopic data is unique in the Palaeozoic era. However, the consistency of this data set raises problems that must be taken into consideration. Although all 13 ages have been acquired by the U–Pb ID–TIMS method, the different authors have used not less than five methodologies for the interpretation of the magmatic crystallisation age of individual zircon or monazite populations: the approaches in Kaufmann et al. (2004), Trapp et al. (2004), and Kaufmann et al. (2005) usually draw on one decay scheme ($^{206}Pb/^{238}U$), but apply three different ways of choosing which $^{206}Pb/^{238}U$ age to use. (1) At Bundenbach (Kaufmann et al., 2005; see Section 2.1.3 below) and Hasselbachtal (Trapp et al., 2004; see Section 2.1.11 below), the weighted mean of a group of $^{206}Pb/^{238}U$ analyses; (2) at Wetteldorf (Kaufmann et al., 2005; see Section 2.1.4 below), the youngest end of a cluster of $^{206}Pb/^{238}U$ analyses; and (3) at Steinbruch Schmidt (Kaufmann et al., 2004; see Section 2.1.8 below), the oldest end of another such cluster. In the first, concordance is assumed but the other two approaches (though well-founded) are methodologically inconsistent and other interpretations are possible. A fourth approach to U–Pb data is contained in the ages of Tucker et al. (1998, see Sections 2.1.1, 2.1.2, 2.1.5, 2.1.7, and 2.1.9 below), which proposed upper intercept $^{207}Pb/^{206}Pb$ ages of multi-grain zircon analyses as the preferred age estimator. $^{207}Pb/^{206}Pb$ ages are commonly shifted older relative to $^{206}Pb/^{238}U$ measurements and the interpretation of multi-grain analyses is inherently more ambiguous than single-grain data. Moreover, Compston (2000b) has discussed alternative age interpretations of the data of Tucker et al. Finally, the fifth approach is the reliance on $^{207}Pb/^{235}U$ data when calculating monazite ages (Roden et al., 1990; Richards et al., 2002; see Sections 2.1.6 and 2.1.10, respectively). Here, the meaning of concordance is doubtful in view of the possible effects of disequilibrium on the ^{206}Pb.

Supplementary to the problems arising from the different methodologies for interpreting U–Pb measurements mentioned above, there are four sources of error understatement which cannot be ignored. (1) The interpretation uncertainty in each individual age is certainly larger than the attractively small laboratory error: with the true uncertainty thus understated, the 'real' age of some dated volcaniclastic rocks may well lie outside the quoted error. (2) Comparison of $^{207}Pb/^{206}Pb$ data with other ages from $^{206}Pb/^{238}U$ and $^{207}Pb/^{235}U$ ratios requires the uncertainty in the two U–Pb half lives to be considered (Ludwig, 1998). (3) The ways of choosing which data population to incorporate in a mean age are all very different and difficult to relate to each other. (4) The 13 U–Pb ID–TIMS ages used here are the product of different laboratories. The total uncertainty of measurement should thus include a measure of inter-laboratory variance in isotopic analysis.

To give consideration to all the above mentioned factors diminishing the consistency of the data set of U–Pb ID–TIMS ages, an additional uncertainty of 2 Ma is added to the 2σ error of individual ages (in the heading of the following chapters and in Figs. 8 and 9). This is in fact a quite inelegant solution but all that can be done according to the present state of time-scale research. The approach remains unsatisfying because each published age has its individual pathway of interpretation and a unique set of uncertainties. A goal of future research must be to narrow the scope for debate in this area, because this source of error is a major barrier in the way of constructing more accurate and reproducible time scales.

2.1.1. Kalkberg Formation (New York, USA), 417.6 ± 3.0 Ma, postwoschmidti/woschmidti conodont zone (lower Lochkovian)

Ten multi-grain analyses (4–12 grains each) of long-prismatic zircons obtained from an 8 cm thick K-bentonite of the Kalkberg Formation (Helderberg Group, Cherry Valley, New York) yielded four concordant and five slightly discordant (2–3%) $^{207}Pb/^{206}Pb$ ages with a weighted mean of 417.6 ± 1.0 Ma (Tucker et al., 1998). The Kalkberg Formation contains *Icriodus woschmidti*, the index conodont of the lowermost Devonian conodont zone. The dated K-bentonite is situated in the higher part of this zone because younger units of the Helderberg Group (Becraft and Alsen Formations) contain conodonts of the superjacent *Ozarkodina delta* and *Pedavis pesavis* zones (Kirchgasser et al., 1985; Tucker et al., 1998).

2.1.2. Esopus Formation (New York, USA), 408.3 ± 3.9 Ma, kitabicus to excavatus conodont zones (Lower Emsian)

At Sprout Brook (Cherry Valley, New York), two K-bentonites occur 3.0 and 3.6 m above the base of the Esopus Formation. Five multi-grain analyses (2–17 grains each) of long-prismatic zircons of the lower ash bed were concordant with a weighted mean $^{207}Pb/^{206}Pb$ age of 408.3 ± 1.9 Ma (Tucker et al., 1998). Hitherto, the biostratigraphic age of the basal Esopus Formation was, due to the paucity of fossils, only roughly constrained to the lower half of the Emsian stage (Tucker et al., 1998). However, conodonts (determined as *Icriodus curvicauda* or *I. celtibericus* by José Valenzuela-Rios) have been obtained from the Carlisle Center, a stratigraphic unit that is younger than the basal Esopus Formation (J. Ebert, personal communication). The conodonts can be precisely assigned to the Lower *Polygnathus excavatus* conodont zone (P. Carls, personal communication) giving a new upper biostratigraphic age limit for the Sprout Brook K-bentonites.

2.1.3. Bundenbach (Hunsrück, Germany), 407.7 ± 2.7 Ma, excavatus conodont zone (Lower Emsian)

The Eschenbach quarry near Bundenbach exposes a type section of the famous Lower Emsian Hunsrück Slate. Ten analyses of single zircons extracted from an intercalated pyroclastic layer, the so-called Hans-Platte, have yielded five concordant results, which form a tightly grouped cluster with a weighted mean $^{206}Pb/^{238}U$ age of 407.7 ± 0.7 Ma (Kaufmann et al., 2005). Tentaculites (dacryoconarids) allow a biostratigraphic assignment to the upper part of the *Nowakia zlíchovensis* dacryoconarid zone (Alberti, 1982) correlated to the middle to upper part of the *Polygnathus excavatus* conodont zone (Bultynck and Hollard, 1980; Alberti, 1981; Schönlaub, 1985).

2.1.4. Wetteldorf 'Hercules I' (Eifel, Germany), 392.2 ± 3.5 Ma, patulus conodont zone (Upper Emsian)

The Wetteldorf section is the Global Stratotype Section and Point (GSSP) locality of the Lower–Middle Devonian boundary. The K-bentonite 'Hercules I' is situated 13 m below the boundary in the uppermost part of the *Polygnathus costatus patulus* conodont zone. Some of the 19 single-zircon analyses obtained from this bentonite appear to document significant influences of inheritance. The 13 youngest points are, however, concordant and form an elongated cluster along concordia with $^{206}Pb/^{238}U$ ages between 392.2 and 407.7 Ma (Kaufmann et al., 2005). Given the (risky) assumption that this age scattering is exclusively caused by varying amounts of inheritance, the youngest point of this cluster represents the analysis with the lowest or no inheritance. In this case, its $^{206}Pb/^{238}U$ age of 392.2 ± 1.5 Ma should approach the eruption age of the bentonite (Kaufmann et al., 2005).

2.1.5. Tioga Middle Coarse Zone (Virginia, USA), 391.4±3.8 Ma, costatus conodont zone (lower to mid-Eifelian)

The K-bentonite from the Tioga Middle Coarse Zone (MCZ) of the southern Appalachian Basin (Wytheville, Virginia) was erroneously indicated as Tioga ash bed F by Tucker et al. (1998). Ver Straeten (2001) has shown that the Tioga ash bed F was misidentified and should be the Tioga MCZ positioned significantly below the Tioga ash bed zone sensu stricto (see Section 2.1.6 below). Five multi- and single-grain analyses (1–4 grains each) of zircons obtained from the Tioga MCZ K-bentonite yielded concordant results with a weighted mean $^{207}Pb/^{206}Pb$ age of 391.4±1.8 Ma (Tucker et al., 1998). The dated K-bentonite occurs in a relatively biostratigraphically barren section. It is, however, based on correlation of a number of widely correlatable marker beds, laterally equivalent to the upper Nedrow and/or the lower Moorehouse Members of the Onondaga Formation of New York (Ver Straeten, 2001). These strata are well documented by conodonts and are, based on the common occurrence of *Polygnathus costatus patulus* and *P. costatus costatus* (Klapper, 1971), constrained to the lower half of the *P. costatus costatus* Zone.

2.1.6. Tioga ash bed B (Pennsylvania, USA), 390.0±2.5 Ma, costatus conodont zone (mid-Eifelian)

The Tioga ash bed zone consists of eight ash beds numbered according to their stratigraphic order from A (oldest) to H (youngest) (Way et al., 1986). They can be correlated over wide areas of the Appalachian Basin from Virginia to New York. Three of four multi-grain analyses (<10 grains) of monazites extracted from ash bed B of the Zeigler pit locality (Union County, Pennsylvania) gave nearly concordant results with a weighted mean $^{207}Pb/^{235}U$ age of 390.0±0.5 Ma (Roden et al., 1990). To the north in New York state, the Tioga ash bed B marks the boundary between the Moorehouse and Seneca Members of the Onondaga Formation. Stratigraphically, the ash bed is constrained by conodonts to the upper half of the *Polygnathus costatus costatus* Zone (Klapper, 1971).

2.1.7. Belpre Ash (Tennessee, USA), 381.1±3.3 Ma, Frasnian Zone 8 (mid-Frasnian)

The Belpre Ash dated by Tucker et al. (1998) is the lowest layer of the Belpre ash suite, a 0.8 m thick interval comprising six ash beds in the Chattanooga Shale at Little War Gap (Tennessee) (Rotondo and Over, 2000). In Tucker et al. (1998), it is erroneously indicated as Center Hill Ash, which is situated much higher in the section, near the Frasnian–Famennian boundary (Over, 1999). Nine multi- and single-grain analyses (1–25 grains each) of the Belpre Ash gave two concordant and seven discordant results, which, however, share a common $^{207}Pb/^{206}Pb$ age of 381.1±1.3 Ma (Tucker et al., 1998). Dark shales between the two youngest of the Belpre ash beds contain the conodonts *Palmatolepis punctata* and *Ancyrognathus barba* (Rotondo and Over, 2000). *A. barba* restricts the biostratigraphic age to the lower two-thirds of Frasnian Zone 8 (Klapper, 1997) corresponding to an interval in the middle to upper part of the Lower *hassi* Zone of the standard conodont zonation (Ziegler and Sandberg, 1990; Klapper and Becker, 1999).

2.1.8. Steinbruch Schmidt (Kellerwald, Germany), 377.2±3.7 Ma, Upper rhenana conodont zone (upper Frasnian)

Steinbruch Schmidt is a famous locality that exposes the upper Frasnian Kellwasser horizons. Twenty-four single-zircon analyses extracted from a three cm thick bentonite layer (bed 36) intercalated between the two Kellwasser horizons yielded 17 concordant results, which form an elongated cluster along concordia (Kaufmann et al., 2004). Age scattering in the cluster from 359.2 to 377.2 Ma is interpreted to result from varying amounts of Pb loss with the oldest point suggested to represent the lowest or no Pb loss. Therefore, the $^{206}Pb/^{238}U$ age of 377.2±1.7 Ma of the oldest concordant analysis is regarded to represent the eruption age of the bentonite (Kaufmann et al., 2004). Biostratigraphically, bed 36 bentonite occurs in the middle part of the Upper *Palmatolepis rhenana* conodont zone (Schindler, 1990; Ziegler and Sandberg, 1990).

2.1.9. Piskahegan Group (New Brunswick, Canada), 363.8±4.2 and 363.4±3.8 Ma, Uppermost marginifera to Upper expansa conodont zone (upper Famennian)

Volcanic rocks of the Mount Pleasant Caldera Complex are intruded into the Upper Devonian Carrow Formation of the Piskahegan Group (McCutcheon et al., 1997). Four multi- and single-grain analyses (1–15 grains each) of the pumiceous tuff member intercalated in the Carrow Formation yielded concordant results with a weighted mean $^{207}Pb/^{206}Pb$ age of 363.8±2.2 Ma (Tucker et al., 1998). The pumiceous tuff member predates a miospore horizon that is overlain by the Bailey Rock Rhyolite (McCutcheon et al., 1997). Five multi-grain analyses (2–25 grains each) of zircons extracted from this rhyolite gave concordant results with a weighted mean $^{207}Pb/^{206}Pb$ age of 363.4±1.8 Ma

(Tucker et al., 1998). Therefore, the miospore-bearing level is bracketed between two analytically indistinguishable volcanic rocks. Tucker et al. (1998) grouped the two ages to a single, more precise average $^{207}Pb/^{206}Pb$ age of 363.6±1.6 Ma. However, because these are two independently measured volcanic units, it is preferred in the time-scale calibration of this study to treat the two ages separately. According to McGregor and McCutcheon (1988), the miospores belong most likely to the *pusillites–lepidophyta*, or less likely to the upper *flexuosa–cornuta* miospore zone (upper Famennian) correlating with the Upper *Palmatolepis expansa* conodont zone. This miospore dating was questioned by Streel (2000) because McGregor and McCutcheon (1988: Table 2; Figs. 15 and 16) found only one doubtful specimen (*Retizonomonoletes lepidophyta*?) of the index fossil of the *pusillites–lepidophyta* Zone. Moreover, that specimen is attributed rather to *R. cassicula* (now *R. macroreticulata*) by Steemans et al. (1996) and it appears earlier in the Uppermost *P. marginifera* conodont zone in Belgium (Streel and Loboziak, 1996). Therefore, the biostratigraphic range of the two dated volcanic rocks of Mount Pleasant Caldera Complex must be extended downward and comprises now the interval from the Uppermost *P. marginifera* to the Upper *P. expansa* conodont zone (Streel, 2000).

2.1.10. Nordegg Tuff (Alberta, Canada), 363.3±2.4 Ma, Middle expansa to Lower praesulcata conodont zone (upper Famennian)

Silicic tuffs are intercalated in the Exshaw Formation of southwestern Canada. Four multi-grain analyses of monazites extracted from the Nordegg Tuff (SW-Alberta) yielded extraordinary precise results with a weighted mean $^{207}Pb/^{235}U$ age of 363.3±0.4 Ma (Richards et al., 2002). Nodular limestone beds from below and above the Nordegg Tuff contain conodonts of the Middle *Palmatolepis expansa* to the Lower *Siphonodella praesulcata* Zone (Savoy et al., 1999).

2.1.11. Hasselbachtal beds 79 and 70 (Sauerland, Germany), 360.5±2.8 and 360.2±2.7 Ma, sulcata and Lower duplicata conodont zones (basal Tournaisian)

The well-known bed 79 bentonite of the Hasselbachtal auxiliary stratotype section is situated only 43 cm above the Devonian–Carboniferous (D–C) boundary within the *Siphonodella sulcata* conodont zone (Korn and Weyer, 2003). U–Pb SHRIMP analyses of zircons extracted from this ash bed yielded a mean $^{206}Pb/^{238}U$ age of 353.2±4.0 Ma (Claoué-Long et al., 1992, later slightly changed to 353.7±4.2 Ma by Claoué-Long et al., 1995) that has defined the absolute reference age of the D–C boundary at 354 Ma (Fordham, 1992; Young, 1995; Sandberg and Ziegler, 1996) (Fig. 1). This age, however, is significantly younger than the boundary age of 362 Ma based on U–Pb ID–TIMS data extrapolated by Tucker et al. (1998) from the age of the Piskahegan Group (see Section 2.1.9 above). The reasons for younger SHRIMP than ID–TIMS ages are discussed in Section 2.

ID–TIMS analyses have also been acquired on the bed 79 bentonite. The first attempt was made by Kramm et al. (1991) whose multi-grain analyses of abraded crystals yielded a maximum $^{206}Pb/^{238}U$ age of 346.6±1.6 Ma. However, due to high amounts of common Pb (mainly derived from apatite inclusions) and low amounts of radiogenic Pb, the analytical uncertainties of the $^{207}Pb/^{235}U$ ages were so high that the observed concordancy could not be taken as a useful criterion. The $^{206}Pb/^{238}U$ age of 346.6±1.6 Ma is regarded as a minimum age attributed to Pb loss. Trapp et al. (2004) made a new attempt and performed single-grain analyses on zircons and zircon fragments. Five concordant points formed a tightly grouped cluster with a $^{206}Pb/^{238}U$ concordia age of 360.5±0.8 Ma. Zircons were also analyzed from the next younger bentonite layer (bed 70, Lower *S. duplicata* conodont zone) positioned 57 cm above bed 79. Seventeen single-zircon analyses yielded concordant results, of which ten form a tightly grouped cluster with a $^{206}Pb/^{238}U$ concordia age of 360.2±0.7 Ma. These are the first U–Pb ID–TIMS ages from basal Tournaisian strata, which have been used for the re-interpolation of the Devonian–Carboniferous boundary (Trapp et al., 2004).

2.2. Overlapping ages — a new qualifier of geochronological tie-points

Some of the above reported U–Pb ID–TIMS ages overlap not only within their analytical errors but also in their biostratigraphic uncertainties. As these overlapping ages meet the isotopic as well as the biostratigraphic constraints of two dated volcanic rocks (often acquired in different laboratories) they can be regarded as highly reliable geochronological tie-points. Compared to isolated and non-confirmed ID–TIMS datings, these ages substantiate the accuracy of each other. There are three of these overlapping ages available now:

(1) Tioga Middle Coarse Zone/Tioga ash bed B: overlapping U–Pb ID–TIMS ages at 390.05±2.45 Ma, overlapping biostratigraphic age in the

middle of the *Polygnathus costatus costatus* conodont zone.

(2) Nordegg Tuff/Piskahegan Group: overlapping U–Pb ID–TIMS ages at 363.3 ± 2.4 Ma, overlapping biostratigraphic age in the Middle to Upper *Palmatolepis expansa* conodont zone.

(3) Hasselbachtal bed 79 and 70: overlapping U–Pb ID–TIMS ages at 360.3 ± 2.6 Ma, overlapping biostratigraphic age at the *Siphonodella sulcata*–Lower *S. duplicata* zonal boundary.

3. Quantified Devonian conodont stratigraphy

The internationally established biostratigraphic subdivision of the Devonian is based on conodont biozones defined by the first appearances of index taxa (Ziegler and Klapper, 1985). Conodonts are small, phosphatic skeletal remains of an extinct group of nektonic marine animals, which are regarded as the earliest jawless vertebrates (Donoghue et al., 2000).

The second part of this study was the compilation of a quantified Devonian conodont stratigraphy resulting in approximately time-linear biostratigraphic scales used for interpolation between the isotopic ages. Sedimentary successions, well-documented by conodonts and lithologically as homogeneous as possible, are the basis of this work. Lithological homogeneity is regarded to represent a uniform stratal accumulation rate required for an approximately linear record of time. In several former time-scale constructions, biostratigraphy is often displayed as non-proportionate schemes with biozones of equal length, an approach which, though convenient, lacks justification (Fordham, 1992). Variables like sea-level curves or stable-isotope curves, plotted against such scales must be inevitably biased and do not allow any interpretations, e.g. regarding possible periodicities.

The pioneering studies of Fordham (1992), Cooper (1999), Cooper and Sadler (2004), and Melchin et al. (2004) for the Palaeozoic era exemplify the geochronological calibration of time-linear biostratigraphic scales. Cooper (1999), Cooper and Sadler (2004) and Melchin et al. (2004) based their calibrations on the graptolite stratigraphy of pelagic successions regarded as essentially missing gaps and unconformities and displaying approximately constant rock accumulation rates (Cooper, 1992). With the application of the newly developed Constrained Optimization (CONOP) software (Sadler, 2001), a further development of the graphic-correlation method (Shaw, 1964), 1356 graptolite species from 236 sections were computed to a scaled, high-resolution composite sequence. The result of the calculation was a relative time scale that plots by means of a fitted curve against the data set of isotopic ages and that enables the conversion of the scaled composite into a numerical time scale for the Ordovician and Silurian periods (Cooper and Sadler, 2004; Melchin et al., 2004). Unfortunately, Devonian conodont stratigraphy does not offer any opportunities for the application of the CONOP software because this period lacks a sufficient number of conodont sections, which fit the requirement of lithological homogeneity

Table 1
Stratigraphic data of Devonian conodont sections used for calibration of the time scale

Conodont section (author)	Calibrated stratigraphic interval	Thickness [m]	Time span [Ma] (according to Fig. 9)	m/Ma
Lali, Guangxi (Ji and Ziegler, 1993)	Basal Famennian to lower Tournaisian (Lower *triangularis* to Upper *duplicata* Zone)	88.3	16.6	5.3
Frasnian Composite Standard (Klapper, 1997)	Mid-to uppermost Frasnian (Frasnian Zone 8 to 13)	26.2	5.1	5.1
CPS-E, F and H, Montagne Noire (Feist and Klapper, 1985; Klapper, 1985, 1989)	Uppermost Givetian to mid-Frasnian (*norrisi* Zone to Frasnian Zone 8)	11.0	3.1	3.5
Pic de Bissous VS–W, Montagne Noire (Feist and Klapper, 1985)	Upper Givetian (*latifossatus* to *norrisi* Zone)	7.7	2.7	2.9
Bou Tchrafine, Anti-Atlas (Bultynck and Holland, 1980)	Basal to mid-Givetian (*hemiansatus* to *latifossatus* Zone)	13.7	2.7	5.1
Eifel sections, Rhenish Massif (Weddige, 1977; Bultynck et al., 1988)	Mid-Eifelian to basal Givetian (*costatus* to *hemiansatus* Zone)	350.8	2.8	125.3
Tizi n' Ikiouâch, Anti-Atlas (Bultynck, 1985)	Uppermost Emsian to mid-Eifelian (*patulus* to *costatus* Zone)	30.7	3.4	9.0
Zinzilban, Uzbekistan (Yolkin et al., 1994)	Basal to mid-Emsian (*kitabicus* to *serotinus* Zone)	330.0	9.4	35.1
Nevada, USA (Murphy, 2000)	Uppermost Pridolian to basal Emsian (*hesperius* to *kitabicus*, *sulcatus* μ Zone)	268.8	9.4	28.6

and conodont-stratigraphical documentation. Virtually all published Devonian conodont sections (much more than 100) were evaluated regarding their suitability for time-scale calibration. Extremely condensed sections (<1 m/Ma) were not considered because their homogeneous accumulation is regarded as being strongly distorted. Several cephalopod limestone sections of the Rhenish Massif (often reference sections for the standard conodont zonation) have stratal accumulations rates below the 1 m/Ma limit (e.g., Sessacker Trench I and II (Ziegler, 1962), Aeketal (Ziegler, 1962), Enkeberg (Korn and Ziegler, 2002), Martenberg (Ziegler and Sandberg, 1990), Diana C (Buggisch et al., 1983) and Rhenert (Ziegler et al., 1976). Aside from stratigraphic condensation, many other investigated sections turned out as lithologically heterogeneous or incompletely documented by conodonts. Therefore, these sections are, because of their non-time-linear stratigraphic record unsuitable for calibration. In some intervals of the Devonian time, it was not possible to find even one section meeting the above

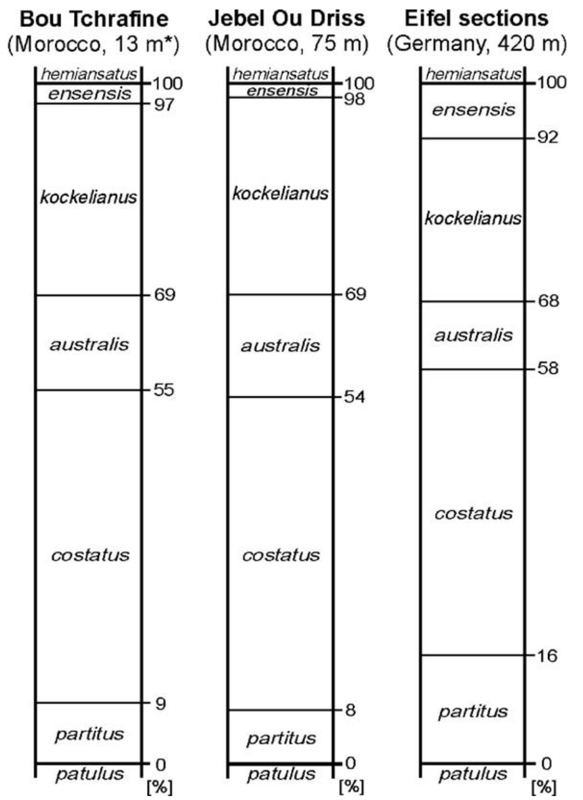

Fig. 2. Comparison of the chronological distribution pattern of conodont zones of the Eifelian stage. Based on Bultynck (1985, 1987, 1989, 1991), Bultynck and Hollard (1980), Bultynck and Jacobs (1981), and Weddige (1977). *Note the extremely different thicknesses of the investigated sections.

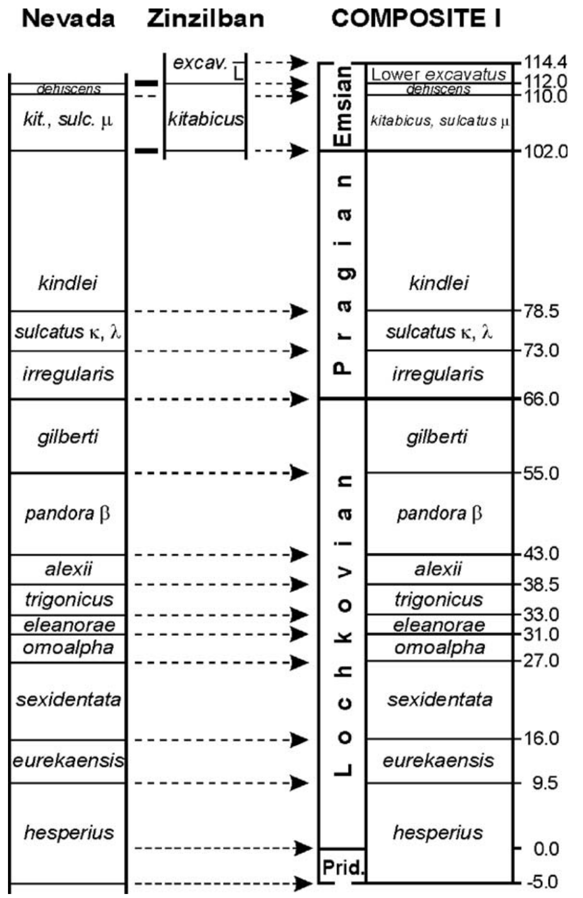

Fig. 3. Composite I, a compilation of the conodonts first occurrences in Nevada (Murphy, 2000) and the Zinzilban section (Yolkin et al., 1994). Bold solid lines between the sections mark the stratigraphic intervals used for the proportional adjustment. The scale of the composite is adopted and extended from Murphy (2000).

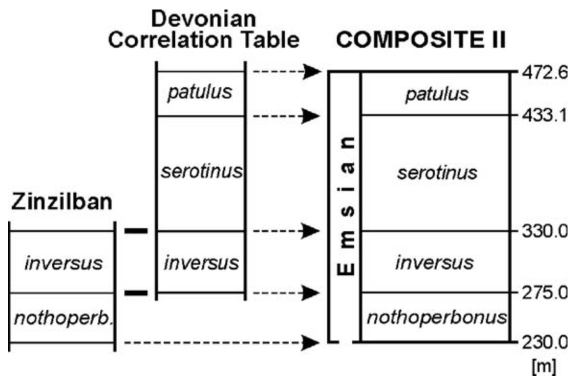

Fig. 4. Composite II, a compilation of the Zinzilban section (Yolkin et al., 1994) and the Devonian Correlation Table (Weddige, 1996: p. 274). Bold solid lines between the sections mark the stratigraphic intervals used for the proportional adjustment. The scale of the composite is adopted and extended from the Zinzilban section (Yolkin et al., 1994).

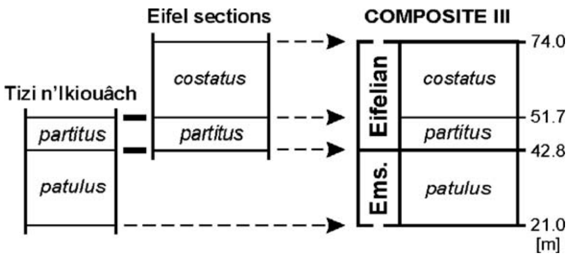

Fig. 5. Composite III, a compilation of the section Tizi n' Ikiouâch (Bultynck, 1985) and the Eifel sections (Weddige, 1977). Bold solid lines between the sections mark the stratigraphic intervals used for the proportional adjustment. The scale of the composite is adopted and extended from the section Tizi n' Ikiouâch (Bultynck, 1985).

mentioned criteria. Therefore, selection of each the best-suitable section representing the relative time for a certain biostratigraphic interval, was regarded to offer the most pragmatic solution. The application of modern software (e.g., GRAPHCOR or CONOP, see above) for a mathematical integration of other sections (if these exist at all) which hardly meet the requirement of lithological homogeneity had rather caused bias than more accuracy in the linearity of the resulting biostratigraphic scales.

Devonian conodont sections selected for time-scale calibration are shown in Table 1. Some of these sections are stratigraphically condensed, though not as extreme

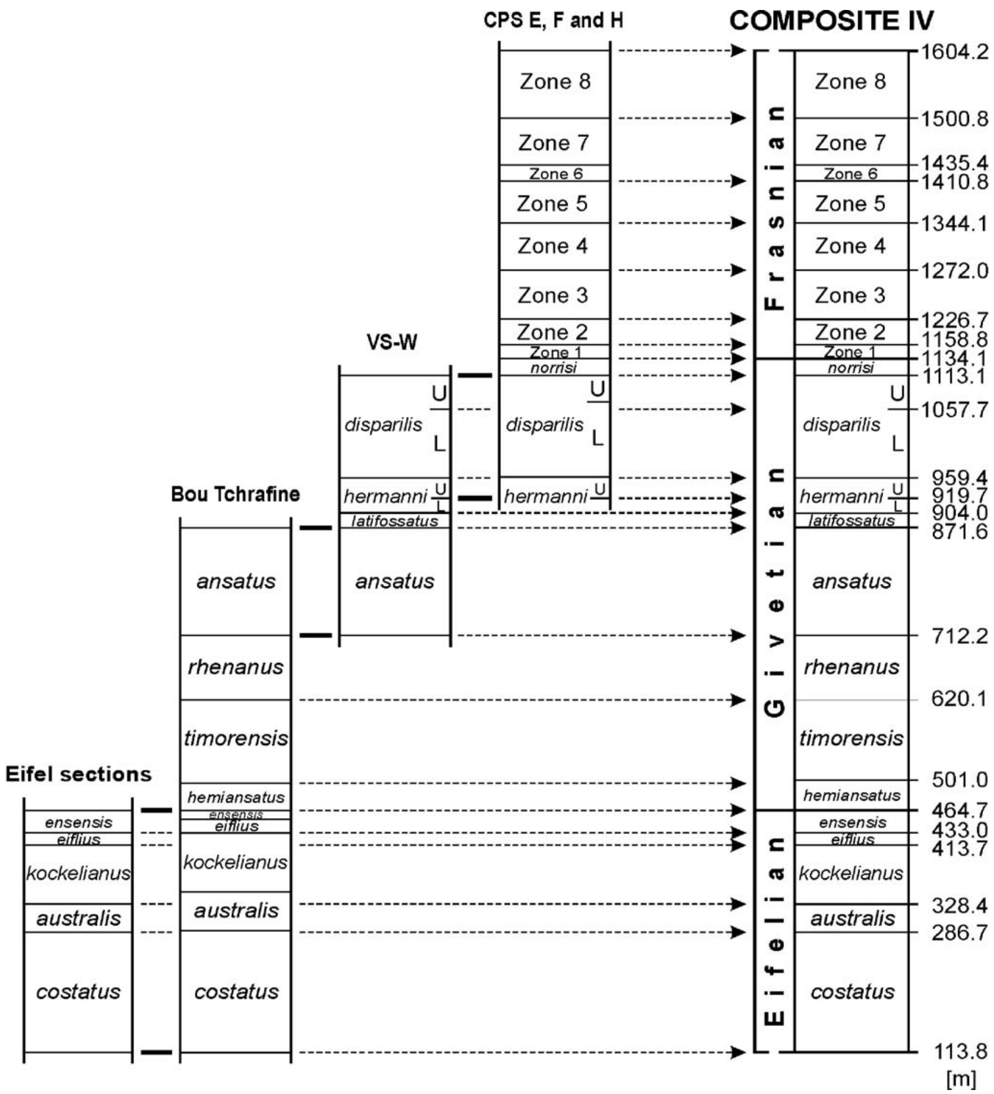

Fig. 6. Composite IV, a compilation of the Eifel sections (Weddige, 1977; Bultynck et al., 1988), the sections of Bou Tchrafine (Bultynck and Hollard, 1980), Pic de Bissous VS–W (Feist and Klapper, 1985) and Col de Puech de la Suque CPS E, F and H (Feist and Klapper, 1985; Klapper, 1985, 1989). Bold solid lines between the sections mark the stratigraphic intervals used for the proportional adjustment. The scale of the composite is adopted and extended from the Eifel sections (Weddige, 1977).

as these sections from the Rhenish Massif, which were sorted out before (see above). Although selected sections are lithologically more or less homogeneous, there was concern about the distorting effect of condensation regarding hiatuses and bias of time-linear stratal accumulation. But surprisingly, it has turned out to be less problematic as originally assumed. Fig. 2 illustrates the chronological distribution pattern of Eifelian conodont zones in the condensed Bou Tchrafine section (Tafilalt Platform, Morocco) and in the much thicker neritic section of Jebel Ou Driss (Mader Basin, Morocco) and in the Eifel Mountains. The sections show extremely variable sedimentary thicknesses and they were deposited under different palaeoenvironmental conditions. The proportional lengths of conodont zones are, however, remarkably similar. This illustration suggests that lithological homogeneous sections show an, at least approximately, time-linear stratigraphic record. However, one should never forget that relative, biostratigraphic scales derived in this manner have incorporated many sources of error as there are varying stratal accumulation rates, incomplete sampling, taxonomic confusion and diachronism of index taxa. But these scales have the enormous advantage that they can be reproduced by other workers and, if required, be recalculated by means of more adequate sections. Anyway, proportionate biostratigraphic scales are certainly more reliable than bioschemes based on the erroneous assumption that biozones represent equal time intervals.

Unfortunately, no adequate section for the upper Emsian stage (*serotinus* to *patulus* Zone) could be obtained from the literature and the biostratigraphic scale of this interval has thus been adopted from the Devonian Correlation Table (Weddige, 1996: p. 274), which also claims for time-linear biozonal proportions. The Frasnian Composite Standard of Klapper (1997) was chosen to represent the interval between the mid- to upper Frasnian Zones 8 to 13 because it was derived from graphic correlation of more than 70 sections in North America, Europe and Western Australia. Linear correlations of these sections suggest that they meet the requirement of uniform stratal accumulation rates (Klapper, 1997). The Lali section (Guangxi, China)

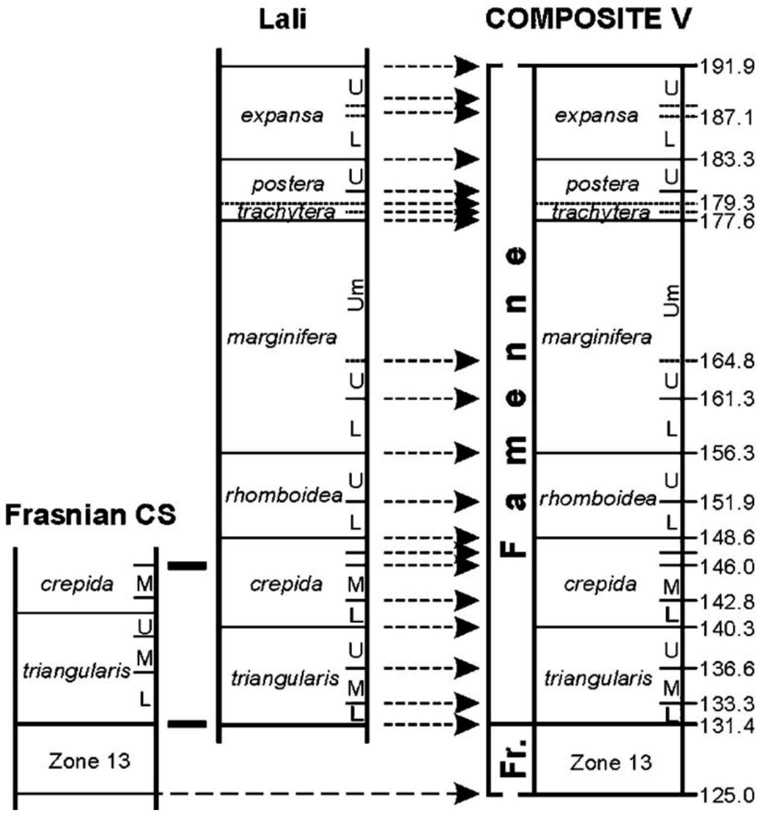

Fig. 7. Composite V, a compilation of the Frasnian Composite Standard (Klapper, 1997) and the Lali section (Ji and Ziegler, 1993). Bold solid lines between the sections mark the stratigraphic intervals used for the proportional adjustment. The scale of the composite is adopted and extended from the Frasnian Composite Standard (Klapper, 1997).

(Ji and Ziegler, 1993) was selected to represent the interval from the basal Famennian Lower *Palmatolepis triangularis* Zone to the lower Tournaisian Upper *Siphonodella duplicata* Zone. Due to missing index taxa, the bases of six conodont zones (Uppermost *P. marginifera* Zone, Upper *P. trachytera* Zone, Lower *P. postera* Zone, Middle *P. expansa* Zone, Upper *P. expansa* Zone and Upper *S. praesulcata* Zone) can only roughly be positioned in this section by alternative taxa (Ji and Ziegler, 1993). The Lali section was also selected for the interpolation of the D–C boundary (see also Trapp et al., 2004).

4. Calibration of the Devonian time scale

The construction of a time-scale line is a frequently utilized procedure for the combination of biostratigraphic and isotopic ages (e.g., McKerrow et al., 1985; Gale, 1985; Tucker et al., 1998). In a Cartesian coordinate system, isotopic ages (*x*-axis), including their errors, are adjusted by their biostratigraphic ages (*y*-axis) in such a manner that they are connected by a regression line. Subsequently, the biostratigraphic gaps on the *y*-axis are filled and the numeric ages of stage and period boundaries are determined by the intersection with the regression line. It is an iterative method and the adjustment is repeated until a satisfactory correspondence (best-fit) of points is achieved. The disadvantage is the low reproducibility, i.e. the positioning of the time-scale line is rather subjective and may differ from author to author. Furthermore, the integration of relative biostratigraphic scales is often quite arbitrary and, if at all, only based on estimations of biostratigraphers.

In this study, another approach avoiding the above mentioned disadvantages is followed: it is suggested to adhere strictly to the isotopic data set and to interpolate between each two successive U–Pb ID–TIMS ages. However, selected conodont sections for interpolation, or more precise, these parts of the sections, which show a homogeneous lithology, span time intervals of 2.7 to 16.6 Ma (Table 1). This is often too short even to bridgeover between two successive U–Pb ID–TIMS ages, which differ from each other by up to 16 Ma. Therefore, composite sections made of up to four sections had to be compiled in these cases. To achieve this, two or more sections were correlated and subsequently combined by proportional adjustment of their overlapping stratigraphic intervals (Figs. 3–7). The result are five composite sections stratigraphically extended enough to bridgeover between successive

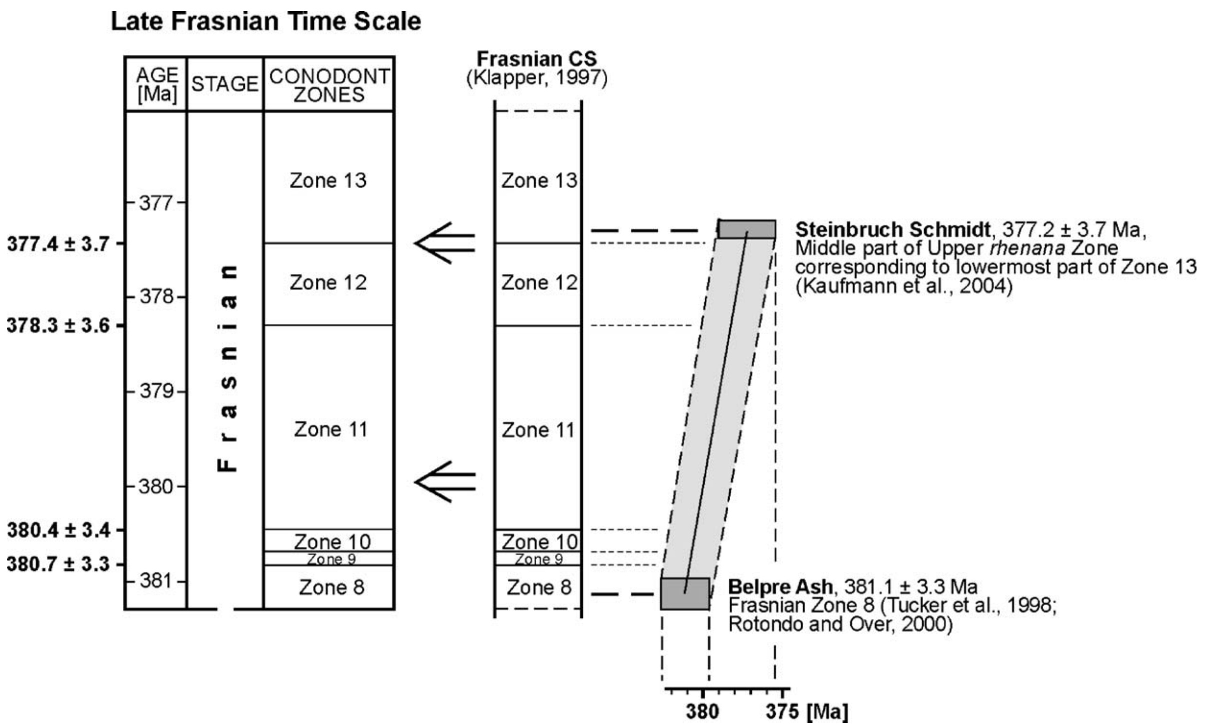

Fig. 8. Example for the calibration of a biostratigraphic scale by two successive U–Pb ID–TIMS zircon ages in a Cartesian coordinate system. The Frasnian Composite Standard (CS) represents an approximately time-linear biostratigraphic scale which is converted by a regression line to a numerical scale. Note the error channel which enables the assignment of an error to each calibrated biozone boundary.

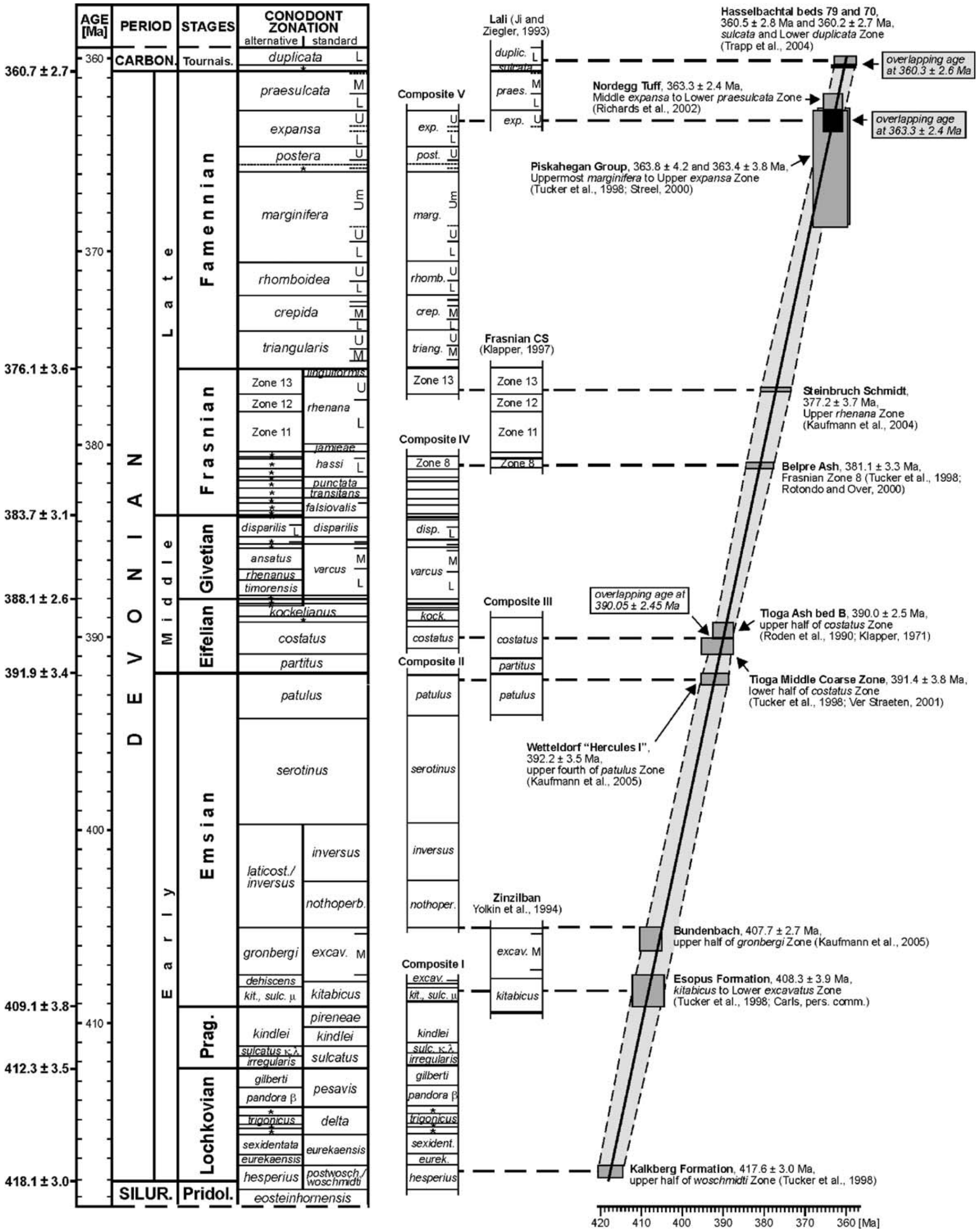

Fig. 9. Calibration of the Devonian time scale. Each U–Pb ID–TIMS age (shaded rectangles) is represented by its biostratigraphic range and its 2σ error plus 2 Ma additional uncertainty (see Section 2.1 above). *Conodont zones not labelled are (in ascending order): Lochkovian: *omoalpha*, *eleanorae*, *alexii*; Eifelian: *australis*, *eiflius*, *ensensis*; Givetian: *hemiansatus*, *latifossatus*, *hermanni*, *norrisi*; Frasnian: Zones 1–10; Famennian: *trachytera*; Tournaisian: *sulcata*. Correlation of Frasnian zones with the standard conodont zonation is based on Sandberg et al. (1989) and Klapper and Becker (1999). Alternative conodont zonation is based on Belka et al. (1997), Klapper (1997), and Murphy (2000).

U–Pb ID–TIMS ages. This procedure of segmented calibration (as already applied by Fordham, 1992) is suggested here as being more accurate than plotting a complete Devonian biostratigraphic scale by straight line fitting against the isotopic data set as made by most other time-scale constructors. Such a complete Devonian relative scale had to be composited by several conodont–stratigraphic fragments. Even if compiled by modern quantitative methods (e.g., graphic correlation, ranking/scaling, constrained optimization), it would have incorporated much higher uncertainties than predetermined by the U–Pb ID–TIMS geochronological framework. The accuracy of such a composite scale would probably not even exceed the reliability of a subjective estimate, as made by M.R. House (see Section 5 below).

For calibration, similar to the above described time-scale line method, the two isotopic ages are plotted in a Cartesian coordinate system according to their numerical ages on the x-axis and then spanned between the biostratigraphic scale (y-axis) obtained from the composite sections (see above). The ages (usually the centers of the error rectangles) are then connected by a regression line that enables the conversion of the composites to a numerical time scale (Fig. 8). In addition, an error channel between the two isotopic ages is constructed by a line connection of the outer margins of the error rectangles. This allows the assignment of an error to each numerical calibration (Fig. 8). It is assumed here, that the uncertainty given by the error channel is sufficiently enough to include also the (mathematically not attestable) inaccuracy of the biostratigraphic scale. The final result of all numerically calibrated composites, the new calibrated Devonian time scale, is shown in Fig. 9.

5. Comparison to the new Cambridge time scale (Geologic Time Scale 2004)

House and Gradstein (2004) based the Devonian part of the 'Geologic Time Scale 2004' (Gradstein et al., 2004) on a relative stage/zone scale developed by M.R. House (deceased), one of the most experienced Devonian researchers and stratigraphers. His scale was plotted against a data set of isotopic ages using the 'spline-fitting method' that combines the biostratigraphic uncertainties with the analytical errors of the isotopic ages. The problems arising from the resulting time-scale construction are as follows. (1) Unfortunately, in House and Gradstein (2004), and also in previous works (e.g. House, 2002), there are no details given about how the relative scaling of stages and zones of the 'House scale' was calculated. The author thus concludes that it is a subjective estimate based on stratigraphic experience. However, the scale has been integrated into the calibration of Devonian time without any variations of its proportions leading to an over emphasis of the biostratigraphic scale with respect to the more substantiated isotopic data. The use of stratigraphers' experience continues a tradition that was already questioned and regarded as poorly justifiable by Fordham (1992). (2) Although preference was given to U–Pb ID–TIMS datings, the data set of isotopic ages was compiled from different isotopic systems that might lead to inconsistent results. (3) The calculated 'spline-fitting curve' does not intersect the two overlapping U–Pb ID–TIMS isotopic ages of the mid-Eifelian Tioga ashes (Roden et al., 1990; Tucker et al., 1998) (see Section 2.1.5 and 6 above). This is the main objection because the datings of the Tioga ashes represent one of the few cases of biostratigraphically and isotopically concordant ages (see Section 2.2 above) obtained from widely separated localities and acquired in two different laboratories. Therefore, these ages should be regarded as representing a securely established numerical age of ca. 390 Ma for the mid-Eifelian stage.

6. Future works

The longest geochronological gap left in the Devonian time scale is the early to latest Emsian interval (ca. 16 Ma). In this interval, the biostratigraphic resolution is quite crude with only four conodont zones. However, even if a further U–PB ID–TIMS age within this interval could be acquired and constrained to one conodont zone only, its biostratigraphic error would average 4 Ma. Therefore, the establishment of a much higher resolved biozonation by the integration of other fossil groups, namely ammonoids, dacryoconarids, trilobites and brachiopods appears just as mandatory for the Emsian stage.

More important is an accurate calibration of the Silurian–Devonian boundary based on U–PB ID–TIMS ages from above and below the boundary (as also performed for the Devonian–Carboniferous boundary by Trapp et al., 2004). Although the extrapolation of the isotopic age of the Kalkberg Formation provides a good approach to the boundary age (Fig. 9), it should be more securely established by bracketing with another date from the late Pridolian stage. This additional U–Pb age could be obtained from K-bentonites of the Carnic Alps in Austria (section Dr. Steinwender Hutte, Histon and Schönlaub, 2001) or from Podolia in the Ukraine (Huff et al., 2000).

7. Conclusions

A time scale as constructed here never represents an end-product. It is composited by a hardly manageable multitude of variables requiring recalibration from time to time. It can only be the closest approach to the 'true' Devonian chronology that can be achieved based on the presently available data. Certainly, further biostratigraphically well-bracketed isotopic ages and elaborated methods of interpolation as well as methods to linearize the stratigraphic record will provide more accurate calibrations in the future.

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