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THE AGE OF THE DEVONIAN-CARBONIFEROUS BOUNDARY

by

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(8 figures and 2 tables)

ABSTRACT.- The Devonian-Carboniferous boundary is now one of the most securely dated positions in the Phanerozoic column. Coincident with redefinition of the boundary, a thin volcanic layer has been identified 35 cm above the boundary in the Hasselbachtal section in Germany, now one of the auxiliary global stratotypes, and a tuff has been located at a similar biostratigraphic level in Australia. Ion microprobe zircon dating of the two horizons has yielded indistinguishable ages, and indicates 353.2 ± 4.0 Ma (2σ) as the age of the boundary.

Recent previous estimates of the age of this boundary have suggested dates with a spread of 25 Ma. A review of historical contraints shows that this uncertainty rested mainly upon biostratigraphic difficulty in correlating dated volcanics in terrestrial sediments with the type marine stratigraphy. Recognition of a dateable volcanic layer in the Hasselbachtal auxiliary stratotype eliminates this source of doubt. Future refinements of the age of the Devonian-Carboniferous boundary will depend on re-analysis of this uniquely placed volcanic, and this highlights the value of defining stratotypes in the vicinity of known dateable horizons.

1. INTRODUCTION

The numerical age of the Devonian-Carboniferous (D-C) boundary has been the subject of more speculation than investigation. Since 1982 there have been more reviews of the age of the boundary (at least nine) than there are data points (most reviewers use less than six), and no new relevant age measurements were made in this time. The 25 Ma range of boundary ages (see Figure 1) available to the stratigrapher from De Souza (1982), Odin & Gale (1982), Harland *et al.* (1982), McKerrow *et al.* (1985), Forster & Warrington (1985), Gale (1985), Odin (1985a, b), Snelling (1985), and Harland *et al.* (1990) are all based on the same scarce data, and differences between them have their origin in opinion rather than measurement. To put this in perspective, the most recent review of the age of the Precambrian-Cambrian boundary (Cowie & Harland, 1989) was able to discuss more than a hundred relevant age measurements.

The situation is now improved. Coincident with the redefinition of the D-C boundary, a very thin volcanic layer has been recognised centimetres from the boundary in the Hasselbachtal section in Germany, now one of the auxiliary global stratotypes. This has proved suited to accurate isotopic dating (Claoué-Long *et al.*, 1992), and its conjunction with stratotype biostratigraphy makes the D-C boundary now one of the most securely dated positions in the Phanerozoic column.

This contribution reviews the historical evidence for the age of the D-C boundary, and then describes the dating of the Hasselbachtal volcanic on which the age of the boundary is now based.

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2.- UNCERTAINTY IN TIMESCALE CALIBRATION

The logic of uncertainty in timescale calibration is not simple. In calibrating numerical time with biostratigraphy, magnetostratigraphy, event stratigraphy, and other measures of the progress of events, we are attempting to mesh interdependent observations. One measure necessarily moves the rest, and *vice versa.* There is, therefore, an iterative quality to the process and the notion of uncertainty must take account of this. The age measurement for the Hasselbachtal D-C boundary described in this contribution is unusual for its direct stratigraphic attribution and isotopic simplicity. More usually, the age of a stratigraphic position of interest is measured indirectly, interpolated from a measured age on the basis of some attribute of the intervening sedimentary record: a thickness of sediment, a number of fossil zones, a number of magnetic intervals. Implicit in these 'hourglass' measures of time is the assumption of a known rate of sedimentation, evolution, or sea floor spreading. These rates in their turn rely on measurements of time, and the circularity of the reasoning appears complete. The arguments are iterative rather than truly circular, however, because each new age measurement improves estimates of what are reasonable rates of geological processes, and these in turn improve interpolated stratigraphic ages. The calibration of the numerical, biostratigraphic, and other scales is therefore improved by iterative increments, and the apparent circularity of reasoning is an essential part of the iterative method.

The importance of using assumed rates of processes in measuring geological time is in part a consequence of their role in the historical preoccupation with estimating the age of the Earth. Before radioactivity was discovered and for most of this century since, measuring geological time has been seen as a legitimate goal in itself, the age of a rock the desired end of enquiry in which other quantities, such as rates of sedimentation, were used as tools. The use of sedimentation rates alone is now obsolete as a means of estimating Phanerozoic time, but it remains in use as a means of linking radiometric ages to the stratigraphic sequence. Today, however, we are in an exciting time when this situation is being reversed on itself. The dependence of timescale calibration on iterative reasoning is being reduced, in places eliminated, as new methods of isotopic measurement (interpretation of $^{40}Ar/^{39}Ar$ stepheating patterns, refinements of zircon U-Pb dating) permit reliable dating of a wider range of geological materials. This enables samples to be chosen more for their stratigraphic suitability than for the restricting criterion of chemical suitability. The stratotype Hasselbachtal date described in this contribution is an example of a stratigraphically definitive sample which could only be dated by the latest method of microbeam zircon analysis. With the uncertainty reduced to the reproducibility of the analytical method, and involving no doubt from stratigraphic interpolation, radiometric dating in the stratigraphic record is an independent scale, a tool that can be turned to direct measurement of rates of geological processes not assumed in the measurement method. The challenge now is to find and date more such samples in other parts of the Phanerozoic column. The rates of evolution, sedimentation, basin subsidence, eustatic movement, and tectonic change built into stratigraphic models will then be measured instead of inferred or assumed.

3.- THE HISTORY OF THOUGHT

This review examines the quality of data upon which successive estimates of the age of the D-C boundary have been based. The emphasis is therefore on the ages actually suggested to, and used by, successive generations of stratigraphers, and no attempt is made to recalculate previously used boundary ages to what previous reviewers might have interpreted them to be, had they applied the Steiger & Jäger (1977) decay constants now in universal usage. Renormalisation seems inappropriate in a historical review when shifting decay constants are only one of the capricious adjustments to which the age of the boundary has been subject; shifting stratigraphic correlations, for instance, are another.

Versions of the age of the D-C boundary published since 1917 are plotted with their attendant suggested uncertainties in Figure 1 and compared with the zircon U-Pb age described in this contribution for the volcanic layer in the Hasselbachtal auxiliary global stratotype. The most remarkable feature shown up by the diagram is the close approach to the boundary age measured today of the 300-370Ma bracket estimated by Barrel in 1917; this comfortably encompasses both the 345-370Ma range of the several estimates made during the 1980s, and the ±4Ma uncertainty of today's measurement.

It is often said that the numerical ages of Phanerozoic boundaries are transient quantities, shifting constantly with new correlations and measurements. This is not so. Ages are almost invariably quoted as uncertainty brackets, not single numbers; successive measurements impinge on the limits of these brackets and the central number is immaterial. Figure 1 shows clearly how the numerous **apparently** different D-C

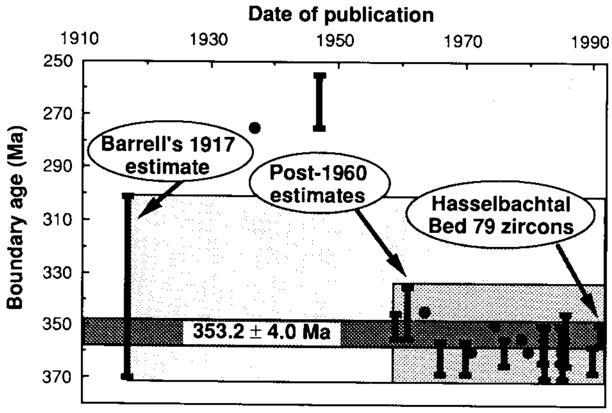


Figure 1.- Ages proposed for the Devonian-Carboniferous boundary. Successive interpretations made since 1917 have been plotted against their date of publication. Error bars are the uncertainties attributed by individual authors to their estimates, dots indicate an estimate made without an attendant uncertainty. Age estimates are plotted as originally published and are not reinterpreted on the basis of the 1977 decay constants, or updated stratigraphic correlations of the samples dated. Stippled zones indicate the progressively reducing bracket of net uncertainty.

boundary age estimates nearly all overlap, and have lain within a constant net bracket of uncertainty for the last 30 years. The significance of the Hasselbachtal age measured today is the reduction in the bracket of uncertainty, not its apparent difference from previous estimates; the object of future work must be to reduce further the envelope of debate.

3.1.- THE PIONEER PERIOD

The modern era of stratigraphic dating began soon after Becquerel detected rays emitted by uranium minerals in 1896. In 1902 Rutherford and Soddy demonstrated that atomic decay was responsible for the radioactive phenomena; in 1903 Ramsay and Soddy demonstrated that helium is a stable product of this decay; and the suggestion that lead is the final product of the uranium family was made by Boltwood in 1905. Rutherford then suggested, in a 1905 lecture, that this decay and consequent accumulation of daughter products might be used to measure the ages of geological materials, the clear advantage offered by this method being that the rate of accumulation of daughter products is constant whereas other accumulation clocks then in use, such as rates of sedimentation, demonstrably are not.

The suggestion was immediately taken up, as much to test ideas concerning atomic decay as for the interest in measuring geological time. In the first paper on the subject, Boltwood (1907) measured Pb/U ratios for uranium minerals from various localities and found that these ratios varied in sympathy with the relative ages of the minerals. Combining these and some supplementary data with early estimates of the half lives of U-Pb decay, Holmes (1913) and then Barrell (1917) formalised the first attempt to subdivide Phanerozoic time. The D-C boundary age was interpolated from the 300 Ma age of uraninite in a pegmatite associated with the post-Lower Carboniferous and pre-Triassic Portland granite in Connecticut, U.S.A.; a 355 Ma age for various minerals in granites in Norway then believed to be Devonian; and 390 Ma for uraninites in the probably Ordovician Brancheville granite also in Connecticut. Adjusting this sparse and stratigraphically uncertain evidence with relative lengths of sediment thickness attributed to each geological period, Barrell (1917) estimated the D-C boundary to lie between 300 and 370 Ma. It is remarkable that present measurements are close to the centre of this bracket.

Between the two World Wars the technology for isotopic measurement gradually improved. This period was dominated by the work of Holmes, whose 1927 book "The age of the earth", a revision of the 1913 volume but published before the isotopic composition of lead could be determined adequately, used eight Pb/U ratios for Palaeozoic minerals. He cautiously gave no specific age for the D-C boundary, placing it between 240 Ma for the Upper Carboniferous and about 440 Ma for the Upper Ordovician. In his 1937 revision, U-Pb ages were combined with numerous U-He measurements and a D-C boundary age of 275 Ma was interpreted. With hindsight, it can be seen that undue weight was given here to the U-He decay system, which is prone to leakage of He, and this resulted in reduced Palaeozoic ages. Holmes' 1947 revision of the Phanerozoic scale was based on only five U-Pb and Th-Pb measurements, but these took into consideration the isotopic composition of lead, by then measurable with Nier's new design of mass spectrometer. Interpolation of boundary ages from these five points, which themselves were not located confidently in the stratigraphic sequence, suggested a D-C boundary between 255-275 Ma, and of these the younger estimate was adopted by geologists for more than a decade.

3.2.- POST-1950

During the 1950s, with general interest in things radioactive, progress in isotopic measurements was rapid. The K-Ar and Rb-Sr methods of age determination became firmly established, and a wider range of rocks and minerals could therefore be studied. Revisions of the Phanerozoic timescale were published at the end of the decade by Holmes (1959) and Kulp (1961), the later paper including some important new measurements not available to Holmes. It was in these papers that the age of the D-C boundary was first bracketed by measurements having known, albeit interpolated, stratigraphic relationship to the boundary. Cobb & Kulp (1961) had determined a 350 ±lOMa minimum age for the uranium-rich Chattanooga Shale in Tennessee, U.S.A., a formation thought to straddle the boundary; Faul & Thomas (1959) had measured a K-Ar age of 340 ±6Ma for biotite in an altered ash layer in the same formation; and in Australia biotite in the Upper Devonian Snobs Creek Rhyolite had given a K-Ar age of 345 Ma (Evernden *et al.*, 1961; later discussed in Evernden & Richards, 1962). Holmes suggested 350 ±5Ma for the boundary, and Kulp accepted 345 ±lOMa. Although these estimates are very close to the now accepted boundary age, the uncertainties stated at this stage seem somewhat tight for what are general estimates of probabilities. Reviewing the same data in the Phanerozoic Timescale symposium of 1964, Francis & Woodland (1964) and Friend & House (1964) accepted the Kulp figure.

With several decay schemes in concurrent use, the science then entered a period of discussion about the dependence of the timescale on uncertainty in half lives, a situation only resolved much later with publication of a harmonious set of decay constants by Steiger & Jäger (1977). In a paper addressing the age of the D-C boundary, McDougall *et al.* (1966) reported K-Ar mineral ages indicating 362 ±6Ma, and Rb-Sr whole-rock and feldspar isochrons indicating 367±22Ma for the Upper Devonian Cerberean Volcanics in Australia. These volcanics overlie the previously dated Snobs Creek Rhyolite (Evernden & Richards, 1962) whose measured apparent age of 345 Ma is younger, and McDougall *et al.* (1966) attempted to reconcile these data with suggested adjustments of half lives. The Cerberean Volcanics are in poorly fossiliferous red beds, but Hills (1958) correlated freshwater fish underlying the lavas with the uppermost Famennian, suggesting the volcanics immediately underlie the D-C boundary. On this basis it was suggested that the age for the boundary be increased from Kulp's (1961) estimate of 345 ±lOMa to match the 362 ±6Ma K-Ar age for the Cerberean Volcanics, or even older depending on the true values of the half lives.

Fitch *et al.* (1970) found evidence consistent with this older boundary age when he published over fifty new K-Ar dates for British Carboniferous rocks. As with the Australian data, British volcanics relevant to the D-C boundary age are in poorly fossiliferous red beds, with consequent uncertainty of correlation to marine stratigraphy. However, minimum ages of 334 ±17Ma for basalt at Little Wenlock in Shropshire, 338 ±4Ma for basalt near Burntisland in Fife, and 347 ±5Ma for the Arthur's Seat volcano in Edinburgh were taken as constraints on the Viséan. In addition, an age of 359 ±5Ma for basalt at Campsie Fells near the base of the Clyde Plateau Lavas was taken as an Upper Tournaisian age entirely consistent with the 362 ±6Ma (Cerberean Volcanics) age for the base of the Carboniferous. Reviewing the available data, Lambert (1971) and Francis (1971) emphasised the dependence on correlation of Carboniferous terrestrial facies, but accepted that the K-Ar ages for the Cerberean volcanics and Campsie Fells basalt together justified a boundary age nearer to 360Ma than 340Ma.

Little noticed by subsequent reviewers, perhaps because discussion took place in the palaeontological rather than isotopic literature, the Victorian data base then shifted with a revision of the biostratigraphic data. Young (1974) and Talent (in Boucot, 1975) showed that the non-marine sediments overlying the Australian Cerberean Volcanics are Frasnian, probably early Frasnian, rather than late Famennian as previously supposed. This is the position accepted today (Marsden, 1988) and the age of the Cerberean Volcanics is therefore a constraint on the Givetian-Frasnian boundary, underlying the D-C boundary by a large margin. On this basis, Boucot (1975) suggested moving the age of the D-C boundary up to about 350 Ma. Supporting this notion, Halliday *et al.* (1977) reported $^{40}Ar/^{39}Ar$ stepwise heating data for the Hoy Lavas, Orkney, indicating an age close to 370Ma; these lavas postdate the Givetian part of the Middle Old Red Sandstone, and infer a Givetian-Frasnian boundary close to 370Ma. (Halliday *et al.* (1979) subsequently reported a calculation error in their data, but this was offset by the 1977 change to new decay constants giving a recalculated age of 368Ma, leaving the inferences for the Givetian-Frasnian boundary unchanged.) Armstrong (1977) included the Hoy basalt age with data for the British basalts, Cerberean lavas (which he had retained as Famennian) and the Chattanooga Shale in a computer fit of Phanerozoic stages to all available age data, and suggested that the D-C boundary must lie close to 355Ma.

3.3.- POST-1977

In 1976 a landmark was reached at the Sydney symposium on the Geologic Time Scale with the international adoption of a uniform set of decay constants (Steiger & Jäger, 1977). Until this point, isotopic ages had been susceptible to shifts as capricious as terrestrial facies correlations: since this symposium all international isotopic data have been normalised to the same constants.

The first review of the D-C boundary to recalculate all ages to the new decay constants was that of McKerrow *et al.* (1980). This used the 368Ma age of the Hoy Basalts and recalculated the age of the Cerberean Volcanics as 369 ±6Ma (but retained their superceded Upper Famennian attribution), to suggest an age of 360Ma for the D-C boundary, an estimate with which Gale *et al.* (1980) concurred. For comparison, the earlier review of the same data by Lambert (1971), giving an age of 360Ma, recalculates to 375Ma using the new decay constants, and the 355Ma estimate of Armstrong (1977) recalculates to 368Ma.

The 1980s saw an influx of new relevant age measurements at the beginning and an impressive series of reviews subsequently. A feature of the 1980s, besides stability of the decay constants used, is that the uncertainty envelope about the age of the D-C boundary expanded relative to the apparent uncertainties of the 1970s.

Three new sets of data were reported, and these have since been the dominant constraints on the interpreted age of the D-C boundary. Firstly, Richards & Singleton (1981) measured K-Ar and Rb-Sr ages for a series of plutons, some of which intrude and therefore postdate the Frasnian Cauldron Volcanics of central Victoria, Australia, among them the Cerberean Volcanics. These granites precede the Mansfield Group non-marine sediments which may be late Devonian at the base but which contain an early Carboniferous fauna and flora in higher sections. The biostratigraphic significance of these granites is taken from different areas and cannot be interlinked (Marsden, 1988), and there is no palaeontological control between the early Frasnian and an indeterminate position within the Early Carboniferous. However, ages for the plutons are in the range 365-360Ma, and Richards & Singleton (1981) concluded that the D-C boundary must therefore be younger than about 360Ma.

Subsequently, Williams *et al.* (1982) revisited the numerical age of the Cerberean Volcanics themselves with a detailed study of their K-Ar and Rb-Sr iostopic compositions. When combined with the earlier work of McDougall *et al.* (1966), the new data indicated a very precise average age of 367 ±2Ma, taken as a constraint on the early Frasnian following the reassessment of the biostratigraphic position of the lavas.

Finally, De Souza (1982) reported a number of new K-Ar ages for British Carboniferous basalts, an addition to the earlier work of Fitch *et al.* (1970). The new data included an average age of 361±7 Ma for the Kelso and Birrenswark basalts of the Scottish Border region, which are locally used to arbitrarily define the base of the Carboniferous (House *et al.*, 1977) and so have widely been quoted as a constraint on the age of the D-C boundary. Unfortunately both lavas lack precise biostratigraphic control. Both overlie Upper Old Red Sandstone beds containing a Famennian fish fauna (Westoll, 1977). The Birrenswark lavas are overlain by the Whita Sandstone, the upper limit of which is constrained by a marine fauna correlating it to the Lower Border Group or older (Day, 1970). As the age of the Lower Border Group itself is uncertain (late Tournaisian or early Viséan: Armstrong & Purnell, 1987), the Whita Sandstone could range in age from Famennian to early Visean. On the northern flank of the Cheviot Hills, the Kelso lavas are also overlain by beds whose biota is difficult to correlate with open marine successions, but miospores indicate a late Tournaisian age (Clayton, 1985). Biostratigraphic uncertainty therefore permits the Scottish Border lavas to lie within the range Famennian to late Tournaisian.

De Souza (1982) also reported an average K-Ar age of 353 ±7Ma for the early Viséan Garleton Hills lavas, comparable to the 354 ±7Ma age of the stratigraphically equivalent Arthur's Seat basalt (Fitch *et al.*, 1970). Commenting on new ages between 325-330Ma for the mid to late Viséan Clyde Plateau Lavas, De Souza (1982) pointed out that these data conflict with the apparent age of 367 ±5Ma and Tournaisian attribution of the Campsie Fells lava (basal to the Clyde Plateau Lavas) analysed by Fitch *et al.* (1970), and suggested that the Campsie Fells constraint is therefore dubious.

An addendum little noticed by subsequent reviewers was provided by Halliday *et al.* (1982) on their $^{40}Ar/^{39}Ar$ data for the Hoy basalts, a constraint on the Givetian-Frasnian boundary. Critical discussion of their two $^{40}Ar/^{39}Ar$ plateaux led to interpretation of Ar loss from one of them, leaving the best age constraint as the 379 ±lOMa plateau age of the other analysis, instead of 368Ma based on the average of the two.

In the review edited by Odin (1982), De Souza (1982) combined the available data for the 361 ±7Ma Scottish Border lavas with the Frasnian constraints of 368 ±6Ma for the Hoy basalts, and 367 ±2Ma for the Cerberean Volcanics to suggest a D-C boundary age of 360 ±5Ma. In the same volume, Odin & Gale (1982) used the same constraints in the late

Devonian but pointed out the uncertainty in the early Carboniferous brackets on the boundary, which essentially consisted of the stratigraphically ambiguous Scottish Border lavas alone. They pointed to a Rb-Sr isochron of 336 ±13Ma for the Huelgot granite which intrudes late Famennian sediments in the Massif Armorican, France, but appears not to metamorphose overlying early Tournaisian sediments. This is ambiguous stratigraphic control, but would suggest that the Scottish Border lavas are Famennian, not Carboniferous. Odin & Gale therefore placed greater uncertainty on the younger limit of the D-C boundary, estimating it as "younger than 365 and probably older than 345Ma".

The timescale review by Harland *et al.* (1982) was compiled too early to include the revision of the age of the Cerberean Volcanics (Williams *et al.*, 1982), the age of the post-Cauldron intrusives in Victoria (Richards & Singleton, 1981), and the new British basalt data of De Souza (1982), and so used a data set similar to that reviewed by Lambert (1971) and Armstrong (1977). This review used a numerical method to interpolate boundary ages from the array of constraints, and calculated a D-C boundary age of 360 +lOMa, influenced by the discrepantly old K-Ar age for the Campsie Fells basalt of the Clyde Plateau lavas.

The subsequent review volume edited by Snelling (1985) included discussions by four sets of authors on the age of the D-C boundary, each of which referred to a different subset of the available data. That by McKerrow *et al.* (1985) extrapolated an age for the D-C boundary from the Frasnian Cerberean Volcanics at 361 ±2Ma and the 361 ±7Ma Scottish Border lavas stated to lie very close to the boundary, and interpreted the boundary to be at 354 $^{+10}$Ma. Allowance of an age younger than the Scottish Border lavas (which implies them to be Devonian) was based on the well constrained base to the Frasnian, and extrapolation of the time supposed necessary for the Frasnian and Famennian stages. Gale (1985) also used an extrapolation technique but was more strongly influenced by the 361 ±7Ma age of the Scottish Border lavas and interpreted a slightly older bracket for the boundary of 360 ±5Ma.

A detailed critique of data pertaining to the D-C boundary was offered by Forster & Warrington (1985). They placed greatest weight on the 361 ±7Ma age of the Scottish Border lavas, thought to lie close to the D-C boundary. The 367 ±2Ma Cerberean Volcanics were likewise used as a minimum contraint on the Givetian-Frasnian boundary. Placing the boundary between these suggested a bracket of 365±5Ma, somewhat older than interpreted by other reviewers. This is consistent with reinterpretation of 379 Ma as the age of the post-Givetian Hoy Lavas, but would appear to conflict with the constraint posed by the post-Cauldron intrusives of Victoria, used by other reviewers to constrain the boundary to younger than 360Ma. However, Forster & Warrinton pointed out that only one of these plutons (the Barjarg granite) both intrudes the volcanics and is overlain by the Mansfield Group red beds. This has an age of 366±21Ma, an older maximum for the D-C boundary than the 360Ma age of the youngest pluton in the suite which lacks this stratigraphic control.

In commenting on these reviews, Odin (1985a,b) pointed out the permissive statigraphic constraints on the Scottish Border Lavas, which most authors take as basal Carboniferous but which could be late Devonian and so allow a boundary age younger than 360Ma. This stratigraphic interpretation would accommodate the constraint posed by the post Cauldron intrusions of Australia, whose 365-360Ma ages suggest that the D-C boundary is younger than 360Ma, and other French data cited by Odin with more doubtful stratigraphic relevance. On these grounds, Odin proposed a D-C boundary age bracket wider and younger than most others, in the range 350-365Ma.

Snelling's (1985) resume of the interpretations made by McKerrow *et al.* (1985), Gale (1985), Forster & Warrington (1985), and Odin (1985a,b), accepted a D-C boundary age at the younger end of the four suggested brackets, 355Ma, without commenting further on the degree of uncertainty.

The latest review is the geologic time scale of Harland *et al.* (1990). This applied the numerical interpolation technique introduced by Harland *et al.* (1982) to the same database available to all reviewers since 1982, but without editing of the constraints or consideration of their individual merits. Thus all published data were included, and the computer fit indicated a D-C boundary age of 362.5 $^{+5}$Ma.

This is in keeping with the estimate of Forster & Warrington (1985), but is strongly influenced by inclusion in the database of the anomalously old age of 366Ma and Tournaisian attribution for the Campsie Fells basalt near the base of the Clyde Plateau Lavas in Scotland, which De Souza (1982) had pointed out was a discrepant and dubious constraint.

4.- NEW ZIRCON AGES FOR D-C BOUNDARY VOLCANICS

This contribution refines the calibration of the D-C boundary by the study of two samples. One is from Australia, and the other is a rare occurrence of a dateable volcanic horizon in a stratotype section: a 1 cm bentonite in the auxiliary stratotype section through the D-C boundary in Germany. Both are securely bracketed by zonation of conodonts, which, in the vicinity of the D-C boundary, offer amongst the highest powers of stratigraphic resolution known in the fossil record. Use of the ion microprobe method of zircon dating has allowed possibilities of isotopic inheritance or alteration in the samples to be assessed realistically, making it unlikely that the ages obtained are seriously biased or in error. Thus, the principal limitation on the accuracy of this result is neither stratigraphic, nor the uncertainty in interpreting an age from the isotopic compositions, but is determined by the current reproducibility of Pb/U ratios measured by the SHRIMP ion microprobe.

4.1.- BED 79, HASSELBACHTAL SECTION, GERMANY

The Hasselbachtal auxiliary stratotype section through the D-C boundary is located 17 km southeast of Dortmund, at the eastern end of the Ruhr Basin, Nordrhein-Westfalen, Germany. The locality is 3 km northnortheast of Hohenlimburg (sheet 4611 Hohenlimburg, R 07000, H 94220) and is a stream section in the valley of the Hasselbach (Hassel brook), an eastern tributary of the River Lenne (Becker *et al.*, 1984). The section contains a rich biota of spores, conodonts, ammonoids, ostracods and trilobites. These form the basis of a detailed sequence of biozones which allow direct correlation with other D-C boundary sections nearby (e.g. Hönnetal, Stockum, Seiler (Bless *et al.*, 1988) and in other continents (Ziegler & Sandberg, 1984). Although it lacks the complete evolutionary conodont lineage from *Siphonodella praesulcata* to *S. sulcata*, the otherwise rich biota has led to its selection as a global auxiliary stratotype.

The detailed biostratigraphy of the Hasselbachtal section is compiled in Figure 2. Sample Z822 for zircon dating was obtained from bentonite Bed 79. Its biostratigraphic position is very tightly constrained by conodonts, trilobites, ammonoids and spores, both directly within the Hasselbachtal section, and by cross reference to the succession of these fossils in the important Hönnetal and Stockum sections.

The Hasselbachtal section begins with nodular limestone and minor shale (Wocklum Limestone) containing the transition between the middle and upper *costatus* conodont faunas, the boundary between the *hemisphaerica/dichotoma* and *hemisphaerica/latior Interregnum* ostracod Zones (Groos-Uffenorde & Uffenorde, 1974), ammonoids of the *Wocklumeria sphaeroides* Zone (Becker, 1988) and spores of the LE Biozone (Higgs & Streel, 1984). The Wocklum Limestone is succeeded by about 5 m of the Hangenberg Shale, with the zonal ammonoid *Clymenia evoluta* at the base - the last indication of the *Wocklumeria* Stufen. The upper levels of the Hangenberg Shale contain spores of the LN Biozone and an ammonoid fauna with *Acutimitoceras* cf. *prorsum prorsum* in the interval 36-46 cm below the top of the shale (Becker, 1988). Above this interval the boundary between the LN and the VI Biozones lies 14 cm below the top of the Hangenberg Shale (i.e., at the top of bed 85, see Fig. 1), and below the level of the first appearance of *S. sulcata.* which is in the upper, turbidite, part of bed 84.

The succeeding argillaceous limestones and thin shales constitute the Hangenberg Limestone. The D-C boundary lies at the base of the Hangenberg Limestone with the first appearance of *S. sulcata*, and the lowest two beds of the Hangenberg Limestone (beds 84 and 83) contain conodont faunas of the *S. sulcata* Zone (Groos-Uffenorde & Uffenorde, 1974). A conodont fauna in the uppermost limestone bed, 1.9 m above the base of the Hangenberg Limestone, includes *S. carinthiaca.* which infers that the top of the Hangenberg Limestone is at a level between the Upper *duplicata* Zone and the lower part of the *S. sandbergi* Zone of Sandberg *et al.* (1978). The conodont zonation between these limits (based on the conodont determinations by Stoppel, in Becker *et al.* (1984)) can be calibrated with the trilobite (Braukmann & Hahn, 1984) and ammonoid (Becker, 1988) biozonations in Figures 2 and 4.

The Bed 79 bentonite is 1 cm thick, and lies 35 cm above the first appearance of *S. sulcata*, which is in the upper part of Bed 84. Conodonts in Bed 81, immediately below the bentonite, are within the range of the *sulcata* to *sandbergi* Zones (Becker *et al.*. 1984). The first occurrence of the trilobite *Archegonus (Phillilobe)* cf. *drewerensis.* also in Bed 81 (Braukmann & Hahn, 1984), suggests that Bed 81 is within the *sulcata* Zone and below the base of the *G. subinvoluta* Zone of the Hönnetal section (Paproth & Streel, 1984). This is confirmed in Bed 78, an 8 cm thick nodular limestone overlying the bentonite, in which Becker (1988) identified *"Acutimitoceras" antecedens.* In the Hönnetal section this ammonoid first appears at the base of the *G. subinvoluta* Zone

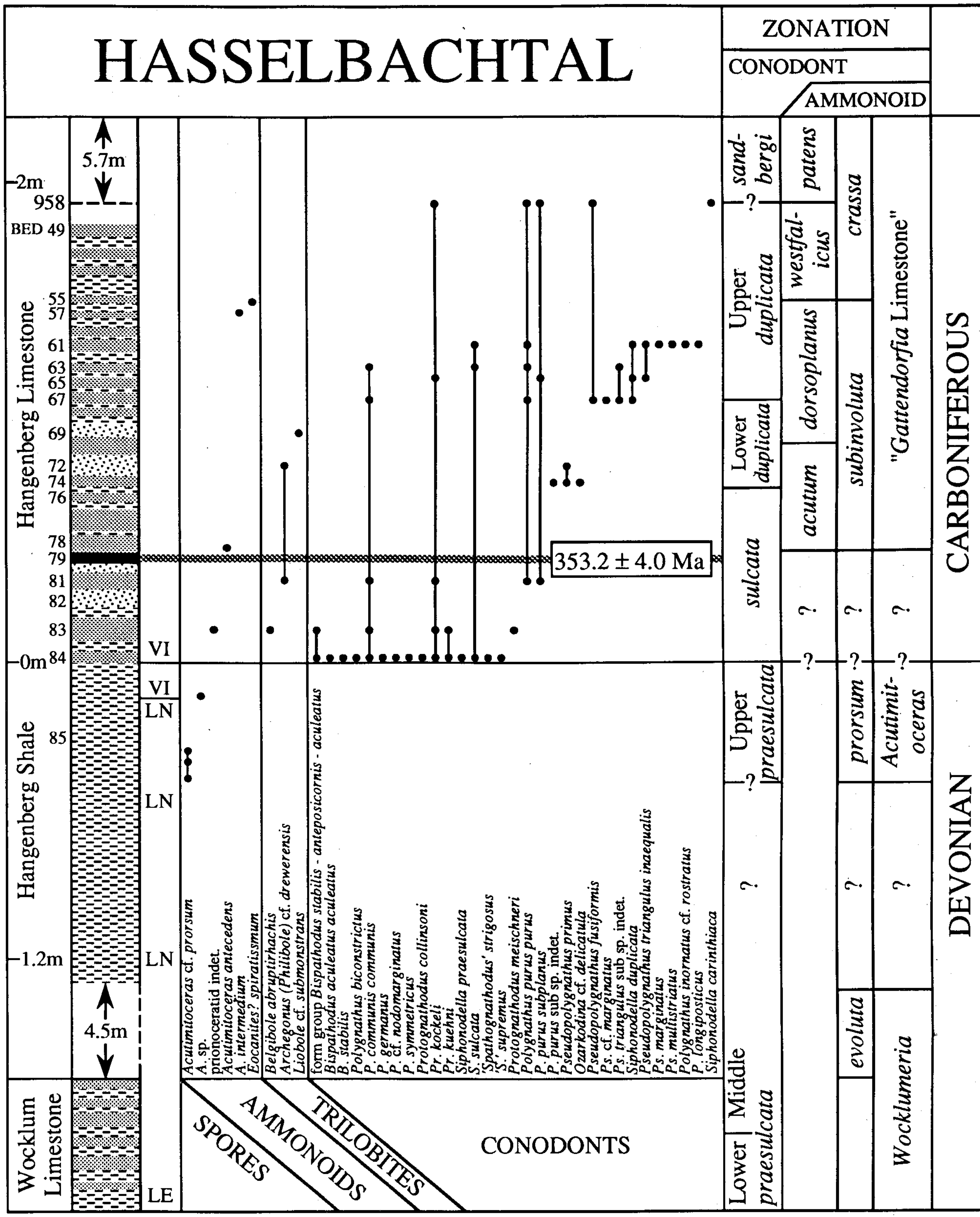


Figure 2.- Detail of the Hasselbachtal auxiliary stratotype section through the Devonian-Carboniferous boundary. The Bed 79 bentonite is indicated in black in the lithology column, and the D-C boundary definition 35 cm below is indicated by the Om line. Positions and ranges about the D-C boundary of spore assemblages, ammonoid, trilobite, and conodont species are from Higgs & Streel (1984), Becker (1988), Braukrnann & Hahn (1984), Becker *et al.* (1984), and Groos-Uffenorde & Uffenorde (1974). Only those elements significant for biozone determination of Bed 79 are cited; endemic pectiniform elements and elements known to be derived from the Devonian have been omitted. Lithologies as follows: Shale = dashes; limestone = dense stipple; sandstone = light stipple.

with the first species of *Gattendorfia* and conodonts of the *sulcata* Zone (Sandberg *et al.*, 1978). *A. antecedens* is known to range into the base of the *G. crassa* ammonoid Zone (Vohringer, 1960) and into the Upper *duplicata* conodont Zone. Bed 67, which is 60 cm above the bentonite, has conodonts of Upper *duplicata-sandbergi* range (Becker *et al.*, 1984), and Bed 55, which is 35cm higher, has the ammonoid *Eocanites? spiratissimum* (Becker, 1988), which in the Hönnetal section is found at the base of the *G. crassa* Zone with conodonts of the Upper *duplicata* Zone (Vohringer, 1960; Voges, 1959,1960; Sandberg *et al.*, 1978). *A. antecedens* in Bed 78 is therefore at the lower end of its range, within the *sulcata* Zone.

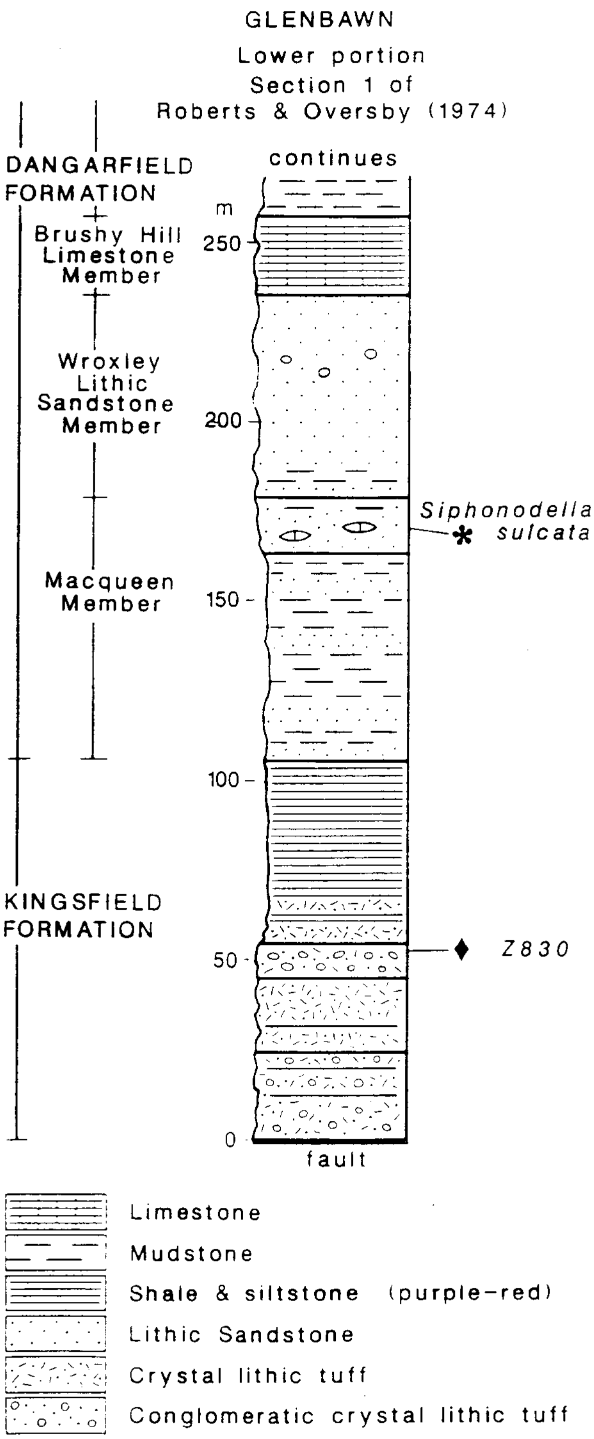


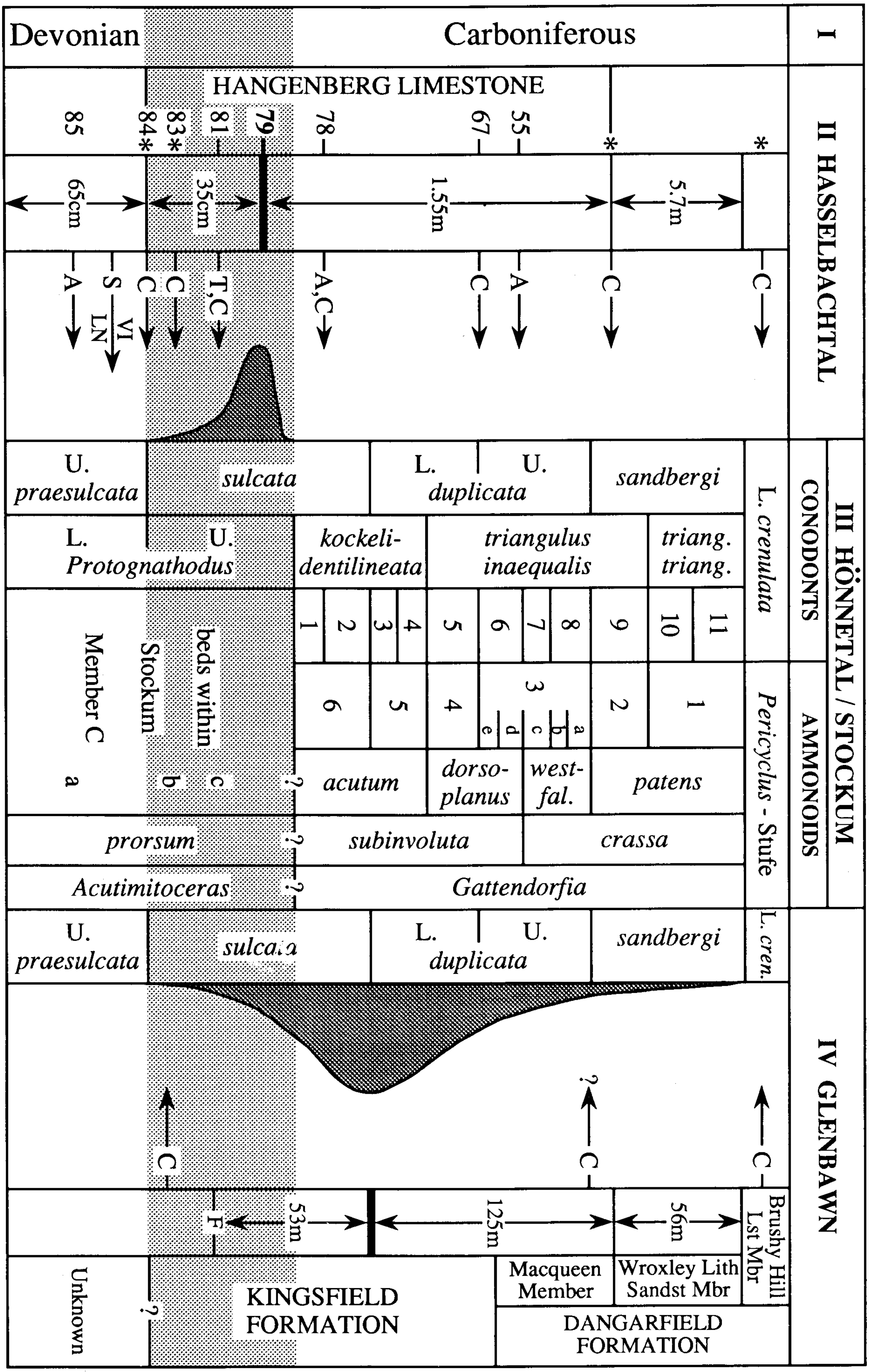
Figure 3.- A portion of Glenbawn Section 1 measured by Roberts and Oversby (1974) showing the position of the volcanic sample obtained for dating.

Analysis of a recently reported conodont fauna in Hasselbachtal Bed 78 (Becker, 1988) may further refine this biostratigraphic calibration, but the conclusion that the Bed 79 bentonite lies within the *S. sulcata* conodont Zone is inescapable. A further constraint arises from observation that Bed 79 is within 8 cm below the base of the *G. subinvoluta* ammonoid Zone of the Hönnetal section, and this restricts the bentonite to the lower part of the *S. sulcata* conodont Zone. The schematic "probability curve" in Figure 4 shows how this brackets the volcanic horizon between the ammonoid and conodont definitions of the D-C boundary, within the lower part of the conodont zone whose base 35 cm below is now the definition of the boundary.

4.2.- GLENBAWN SECTION, HUNTER VALLEY, AUSTRALIA

The Glenbawn section in Australia is less fossiliferous than the exceptional Hasselbachtal section, but the biostratigraphy is controlled by conodonts (Roberts & Oversby, 1974; Mory, 1978) and this zonation is shown in Figures 3 and 4. The Kingsfield Formation contains the oldest Carboniferous volcanogenic rocks in the Tamworth Belt of New South Wales, and crops out near Glenbawn Dam, 14 km SE of Scone. The lowest units are volcanics, and a basal sandstone containing calcareous nodules with *S. sulcata* (locality L57 in Mory & Crane (1982)). Higher units are volcanics and volcaniclastics, from which sample Z830 of crystal-lithic tuff was obtained for dating (Fig. 3), and these are overlain by shale and siltstone.

Purple shales of the Kingsfield Formation pass apparently conformably into the overlying Dangarfield Formation, a shallow marine succession that grades from possibly estuarine, through beach, to shallow and then deeper marine conditions. The shallow water succession at the base is subdivided into the Macqueen Member (Mory, 1978; Roberts *et al.*, in press), the Wroxley Lithic Sandstone Member and the Brushy Hill Limestone Member. The latter is overlain by a thick succession of mudstone, lithic sandstone and minor limestone (Roberts & Oversby, 1974). Calcareous concretions within the upper part of the Macqueen Member, approximately 168 m


Devonian
Carboniferous
I
HANGENBERG LIMESTONE
85
84*
83*
81
79
78
67
55
65cm
35cm
1.55m
5.7m
A
S
C
C
T,C
A,C
C
A
C
C
VI
LN
II HASSELBACHTAL
U. praesulcata
sulcata
L. duplicata
U. duplicata
sandbergi
L. Protognathodus
U. Protognathodus
kockeli-dentilineata
triangulus inaequalis
triang. triang.
L. crenulata
CONODONTS
1
2
3
4
5
6
7
8
9
10
11
6
5
4
3
2
1
a
b
c
d
e
Member C
Stockum
beds within
a
b
c
?
acutum
dorso-planus
west-fal.
patens
Pericyclus - Stufe
AMMONOIDS
III HÖNNETAL / STOCKUM
prorsum
subinvoluta
crassa
Acutimitoceras
Gattendorfia
U. praesulcata
sulcata
L. duplicata
U. duplicata
sandbergi
L. cren.
C
?
C
C
F
53m
125m
56m
Unknown
?
KINGSFIELD FORMATION
Macqueen Member
Wroxley Lith Sandst Mbr
Brushy Hill Lst Mbr
DANGARFIELD FORMATION
IV GLENBAWN

above the base of Section 1 of Roberts & Oversby (1974), have yielded the conodont *S. sulcata* (locations L55 and L54 of Mory & Crane (1982)). The Brushy Hill Limestone Member contains conodonts of the lower *S. crenulata* Zone (Mory & Crane, 1982).

As shown in Figure 3, Sample Z830 was taken 53 m above the base of Kingsfield Formation Section 1 measured by Roberts & Oversby (1974) along the Hunter River (GR111454 Scone 1:25000 Sheet). Despite local faulting, it is clear that sample Z830 is bracketed by *S. sulcata,* whose range extends from the base of the Carboniferous to the Lower *crenulata* Zone. The sample is constrained to the lower part of that range by the 180 m of sediment separating the tuff from the Lower *crenulata* Zone in the Brushy Hill Limestone Member, suggesting a position similar to, but slightly less certain than, the Hasselbachtal Bed 79, within either the *sulcata* or Lower *duplicata* Zones. This biostratigraphic location and its uncertainty is indicated by the schematic "probability curve" in Figure 4.

5.- SHRIMP ZIRCON DATING

5.1.- ANALYTICAL PROCEDURES

Zircon is the only remnant igneous phase suitable for isotopic dating in both the Hasselbachtal Bed 79 bentonite and the Kingsfield Formation tuff. Zircons were separated using standard heavy liquid and magnetic techniques, mounted on the surface of epoxy plugs, and sectioned in half to reveal grain interiors. U-Th-Pb isotopic compositions were measured for 30 µm diameter areas of the sectioned zircons using the SHRIMP ion-microprobe. By this means, cracks and inclusions in the grains were avoided. A cold trap was employed in the sample chamber to minimise any hydride interferences. Each analysis comprises 5 cycles through the mass stations, data were reduced in the manner described by Compston *et al.* (1984), decay constants used are those recommended by Steiger & Jäger (1977), and the isotopic data for each sample are listed in Tables 1 and 2.

The most useful age information in Phanerozoic zircons comes from $^{206}Pb^*/^{238}U$ ratios ($^{206}Pb^*$ is radiogenic ^{206}Pb), which have good measurement precision and are insensitive to correction for initial Pb. Uncertainty in $^{207}Pb^*$ measurement frustrates definitive testing for concordance, and the incidence of Pb loss is assessed instead from grouping of $^{206}Pb^*/^{238}U$ data. The primary control on the accuracy of SHRIMP $^{206}Pb^*/^{238}U$ ages is the accuracy of calibration of Pb/U ratios to the known composition of a standard zircon. Ratios of $^{206}Pb^*/^{238}U$ are referenced to a value of 0.0928 for $^{206}Pb^*/^{238}U$ (equivalent to an age of 572Ma) in our standard zircon SL13, a chip of which was mounted with the unknown zircons to minimise any possible bias in the conditions of analysis between the standard and unknowns. Uncertainties in calibration of Pb/U ratios are included in the tabulated errors, and details of the calibration upon which each age calculation depends are discussed in the sections on the individual samples below.

Corrections for initial Pb have been made using average common Pb of the same age as the zircons (Cumming & Richards, 1975), and have been calculated using one of two methods as appropriate. Direct calculation by reference to the amount of ^{204}Pb in each zircon (^{204}Pb method), is imprecise because counting precision on the small ^{204}Pb peak is poor. More precise calculation is possible from the difference between measured $^{208}Pb^*/^{206}Pb^*$ and that calculated from Th/U (^{208}Pb method of Compston *et*

Figure 4. - Summary chart showing biostratigraphic positions of zircon samples in relation to the Hönnetal and Stockum reference sections.
Column I : Definitions of the D-C boundary. The top of the grey zone indicates the previous (ammonoid) definition (Jongmans & Gothan, 1937), and the bottom of the grey zone indicates the now accepted conodont definition (Paproth, 1980).
Column II: Hasselbachtal section - unit numbers, thicknesses, and positions of ammonoids (A) (Becker, 1988); conodonts (C: those from Groos-Uffenorde & Uffenorde (1974) denoted*, those from Becker *et al.* (1984), denoted with bed numbers); spores (S) (Higgs & Streel, 1984); and trilobites (T) (Braukmann & Hahn, 1984). The schematic "probability curve" is a representation of the biostratigraphic location of the Bed 79 bentonite (thick line) and its attendant uncertainty, and indicates that its position is within the lower part of the *Siphonodella sulcata* Zone, between the conodont and ammonoid definitions of the D-C boundary.
Column III: A composite of standard zonations based on Hönnetal and Stockum sections. Conodonts after the zonation and sampling intervals of Voges (1959, 1960) in the Hönnetal, the *Protognathodus* Fauna of Ziegler (1969) at Stockum (Alberti *et al.*, 1974), and the standard siphonodellid zonation (Sandberg *et al.*, 1978). Ammonoids after the zonation and sampling intervals of Vohringer (1960) in the Hönnetal and the *Acutimitoceras* Fauna at Stockum (Alberti *et al.*, 1974; Korn, 1984).
Column IV: Glenbawn section - units and thicknesses (Roberts & Oversby, 1974; Mory, 1978), and positions of conodonts (Mory & Crane, 1982). F = local fault. The schematic "probability curve" is a representation of the biostratigraphic range within which the tuff sample (thick line) must lie, and indicates that its position is slightly less certain than that of the Hasselbachtal Bed 79.

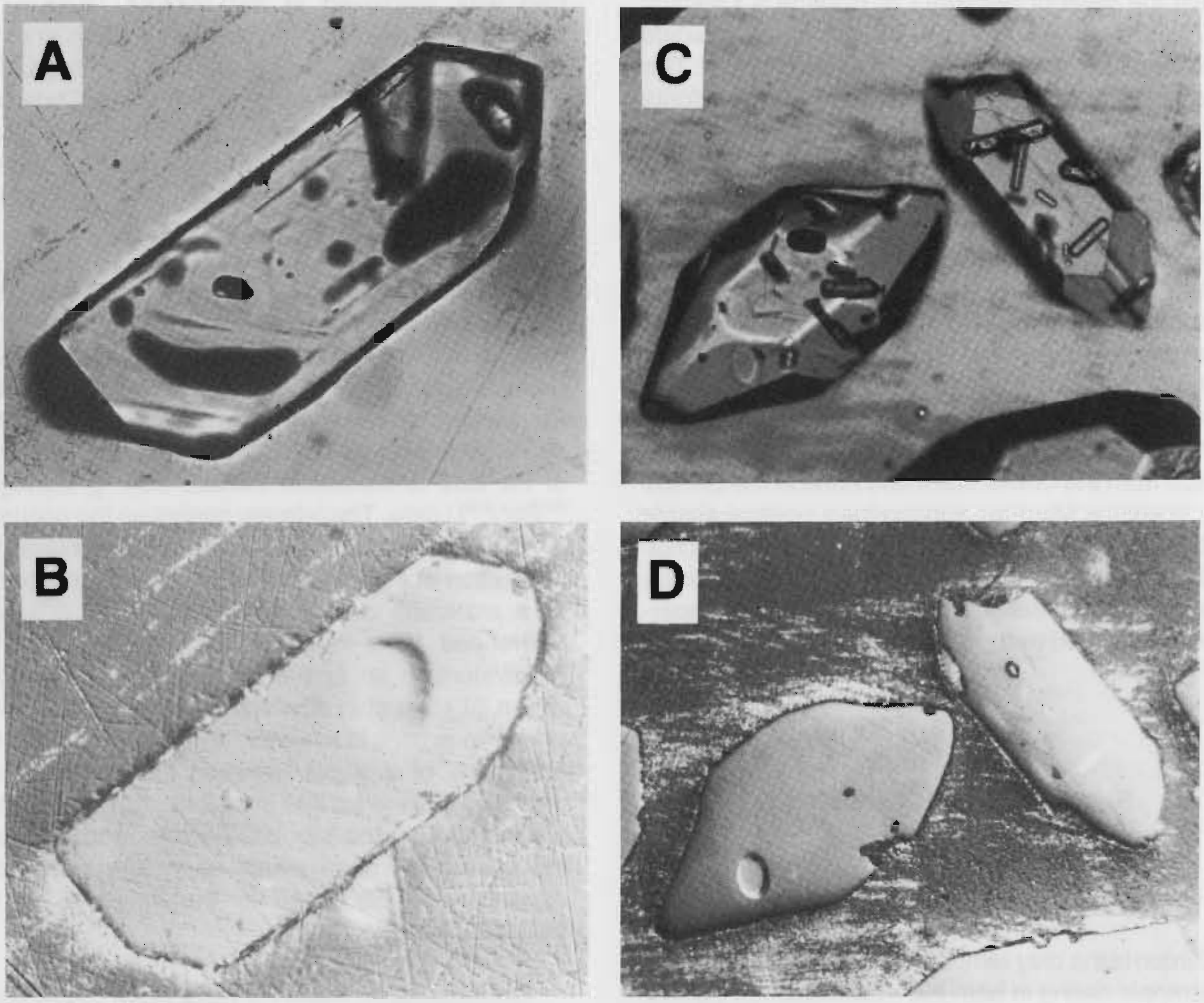


Figure 5.- Photomicrographs of zircons in the two samples. Scale is indicated by the 25 μm diameter crater excavated by the ion microprobe, which has been used to target areas of pure zircon in the inclusion rich crystals. **A (transmitted) and B (reflected)** paired views of zircon #2 from the Hasselbachtal Bed 79 bentonite showing the simple prismatic form and abundance of large inclusions typical of zircons in this sample. The amorphous dark shapes appear to be voids enclosing altered volcanic glass, an indication of rapid, skeletal crystal growth. **C (transmitted) & D (reflected)** paired views of zircons (including analysed grain #7) in the Kingsfield Formation tuff, which are also of simple magmatic form and rich in inclusions of other phases.

al. (1984)), provided there is concordance of the ^{232}Th and ^{238}U systems: radiogenic isotopic ratios calculated in this way are listed in Tables 1 and 2, and used in plotting the Concordia diagrams. A related method uses the difference between measured ^{207}Pb /^{206}Pb and that calculated from ^{235}U/^{238}U (^{207}Pb method). This method cannot yield the ^{207}Pb /^{206}Pb and ^{207}Pb /^{235}U ratios needed to plot Concordia diagrams, but offers the advantage that precise ^{206}Pb /^{238}U ages can be calculated independently from uncertainty and/or bias in Th/U and ^{208}Pb/^{206}Pb measurement. ^{207}Pb-corrected data have therefore been used in ^{206}Pb*/^{238}U age calculations in this paper and are listed separately in Tables 1 and 2. Uncertainties quoted in Tables 1 and 2 include the uncertainties of common Pb correction.

5.2.- HASSELBACHTAL SECTION, BED 79

Zircons in the Bed 79 bentonite have the uniformity of morphology, simple prismatic shapes, and oscillatory growth zoning expected of zircons grown in an eruptive event. A typical example is photographed in Figure 5. Large inclusions form up to 25% of some crystals and include anhedral shapes filled with amorphous material interpreted as altered volcanic glass. This high abundance of included material would render conventional zircon analysis prone to analysing material other than zircon, but the 30 μm analysing beam of SHRIMP was able to avoid the inclusions and target pure zircon.

Table I.- Ion microprobe U-Th-Pb isotopic data for zircons in Hasselbachtal Bed 79 bentonite sample Z822.

Grain -area	U (ppm)	Th (ppm)	Th/U	^{204}Pb (ppb)	f^{206}Pb[a] (%)	^{208}Pb corrected data: ^{206}Pb/^{238}U ±1σ	^{208}Pb corrected data: ^{207}Pb/^{235}U ±1σ	^{208}Pb corrected data: ^{207}Pb/^{206}Pb ±1σ	^{207}Pb corrected data: ^{206}Pb/^{238}U ±1σ	^{207}Pb corrected data: Apparent age[b] (Ma) ±1σ
1.1	128	63	.50	4	1.12	0.0564 ±12	0.462 ±28	0.0595 ±32	0.0560 ±12	351 ±7
2.1	41	26	.62	4	3.64	0.0559 ±13	0.493 ±58	0.0640 ±72	0.0552 ±13	346 ±8
3.1	93	46	.49	4	1.54	0.0554 ±12	0.496 ±33	0.0650 ±39	0.0546 ±12	342 ±7
5.1	433	176	.41	128	9.80	0.0578 ±13	0.419 ±23	0.0526 ±25	0.0578 ±13	362 ±8
5.2	331	149	.45	7	.72	0.0596 ±13	0.475 ±22	0.0578 ±21	0.0593 ±13	371 ±8
5.3	333	469	1.41	30	2.92	0.0649 ±15	1.340 ±57	0.1497 ±50	0.0571 ±13	358 ±8
5.4	551	326	.59	14	1.01	0.0541 ±12	0.532 ±20	0.0713 ±21	0.0529 ±12	333 ±7
6.1	91	49	.54	10	3.96	0.0574 ±13	0.440 ±39	0.0556 ±46	0.0573 ±13	359 ±8
7.1	111	53	.48	8	2.79	0.0532 ±12	0.397 ±34	0.0542 ±43	0.0532 ±12	334 ±7
8.1	238	93	.39	6	.95	0.057 ±12	0.431 ±21	0.0548 ±22	0.0569 ±12	357 ±8
8.2	311	117	.38	3	.42	0.0573 ±13	0.424 ±19	0.0537 ±20	0.0573 ±13	359 ±8
9.1	267	112	.42	8	1.15	0.0552 ±12	0.417 ±20	0.0549 ±22	0.0551 ±12	346 ±7
10.1	164	84	.51	12	2.53	0.0599 ±13	0.431 ±30	0.0522 ±33	0.0600 ±13	375 ±8
11.1	146	61	.42	5	1.41	0.0558 ±12	0.431 ±26	0.0560 ±30	0.0556 ±12	349 ±7
12.1	102	45	.44	3	1.17	0.0539 ±12	0.382 ±31	0.0515 ±38	0.0540 ±12	339 ±7
13.1	381	141	.37	2	.21	0.0542 ±12	0.433 ±17	0.0579 ±17	0.0540 ±12	339 ±7
13.2	99	43	.43	4	1.64	0.0536 ±12	0.416 ±31	0.0563 ±39	0.0534 ±12	336 ±7
13.3	608	303	.50	8	.46	0.0588 ±13	0.441 ±17	0.0545 ±16	0.0587 ±13	368 ±8
13.4	498	148	.30	5	.40	0.0566 ±12	0.445 ±16	0.0570 ±15	0.0563 ±12	353 ±7
13.5	452	174	.38	9	.77	0.0573 ±13	0.434 ±18	0.0550 ±19	0.0572 ±12	358 ±8
14.1	60	36	.60	10	6.27	0.0541 ±13	0.295 ±55	0.0396 ±73	0.0550 ±13	345 ±8
15.1	48	27	.56	4	2.79	0.0547 ±13	0.417 ±51	0.0553 ±65	0.0546 ±12	343 ±8
16.1	137	61	.45	6	1.72	0.0573 ±13	0.413 ±28	0.0523 ±32	0.0574 ±13	360 ±8
17.1	65	51	.79	4	2.30	0.0575 ±13	0.451 ±51	0.0569 ±61	0.0573 ±13	359 ±8
18.1	73	36	.50	3	1.31	0.0568 ±13	0.442 ±37	0.0564 ±44	0.0566 ±13	355 ±8
19.1	52	45	.86	5	3.24	0.0564 ±13	0.465 ±61	0.0598 ±75	0.0559 ±13	351 ±8
20.1	31	22	.70	4	4.58	0.0606 ±15	0.421 ±82	0.0504 ±96	0.0608 ±14	381 ±9
21.1	368	197	.53	15	1.45	0.0577 ±13	0.384 ±19	0.0483 ±20	0.0581 ±13	364 ±8
22.1	61	36	.60	5	3.33	0.0543 ±13	0.339 ±48	0.0453 ±62	0.0548 ±12	344 ±8
23.1	90	45	.50	5	1.99	0.0547 ±12	0.408 ±35	0.0541 ±43	0.0547 ±12	343 ±7
24.1	154	67	.44	6	1.51	0.057 ±13	0.416 ±27	0.0529 ±31	0.0570 ±13	357 ±8
25.1	58	32	.56	4	2.47	0.0563 ±13	0.384 ±46	0.0494 ±56	0.0566 ±13	355 ±8
26.1	198	76	.38	4	.68	0.0559 ±12	0.405 ±21	0.0525 ±23	0.0560 ±12	351 ±7
29.1	243	136	.56	12	1.70	0.0594 ±13	0.488 ±25	0.0595 ±26	0.0590 ±13	370 ±8
30.1	72	64	.89	3	1.46	0.0572 ±13	0.469 ±52	0.0595 ±63	0.0568 ±13	356 ±8
30.2	67	61	.91	8	3.97	0.0603 ±14	0.730 ±64	0.0879 ±72	0.0577 ±13	362 ±8

[a] f^{206}Pb indicates the percentage common ^{206}Pb in the total measured ^{206}Pb

[b] Apparent age is the ^{206}Pb*/^{238}U age

The ion microprobe provides a large number of analyses of minute subvolumes within single zircons. Only if the subvolumes prove to be of identical composition are they combined as an average representing the total analysed volume of zircon. This is an improvement over conventional zircon analysis in which the homogeneity of the zircons analysed has to be assumed, and their total Pb and U is combined during the chemical dissolution process prior to analysis. The basis for deciding whether the ion microprobe analyses indicate a homogeneous ^{206}Pb /^{238}U composition is the scatter of data observed for the homogeneous standard zircon. This is a direct measure of the reproducibility of a known constant Pb/U target achieved during the analytical run, and provides a direct comparitive basis for assessing data for the unknown zircon compositions collected at the same time.

During the period when the Hasselbachtal zircons were analysed, 23 measurements of standard zircon SL13 were alternated with those of the unknowns. The analyses are compared in Figure 5a with the SHRIMP calibration relationship, which is a well established quadratic curve relating variations in the measured ionic ratio of Pb^+/U^+ to the measured ratio of UO^+/U^+ (Williams & Claesson, 1987). Figure 6a illustrates the close adherence of the analyses of the standard to the expected curve. The reproducibility of the standard composition, 2.13% (σ), is included in the uncertainty in Pb/U of each of the unknowns, and the 0.45% (σ) uncertainty in the mean position of the calibration data is included in the error on the mean age of the unknowns.

Table 2.- Ion microprobe U-Th-Pb isotopic data for zircons in the Kingsfield Formation tuff sample Z822.

Grain -area	U (ppm)	Th (ppm)	Th/U	^{208}Pb corrected data: ^{204}Pb (ppb)	f^{206}Pb[a] (%)	^{206}Pb/^{238}U ±1σ	^{207}Pb/^{235}U ±1σ	^{207}Pb/^{206}Pb ±1σ	^{207}Pb corrected data: ^{206}Pb/^{238}U ±1σ	Apparent age[b] (Ma) ±1σ
1.1	75	45	.60	8	3.80	0.0536 ±12	0.462 ±54	0.0625 ±71	0.0530 ±12	333 ±7
2.1	62	29	.47	12	7.51	0.0503 ±11	0.463 ±66	0.0668 ±93	0.0495 ±12	311 ±7
3.1	93	62	.67	12	4.88	0.0557 ±12	0.445 ±55	0.0579 ±69	0.0554 ±13	348 ±8
4.1	65	41	.63	12	6.60	0.0538 ±12	0.495 ±70	0.0668 ±92	0.0529 ±13	332 ±8
5.2	87	43	.49	7	3.13	0.0527 ±11	0.507 ±53	0.0698 ±70	0.0516 ±12	325 ±7
6.1	111	54	.49	16	5.21	0.0564 ±12	0.464 ±49	0.0597 ±60	0.0560 ±13	351 ±8
7.1	75	34	.46	14	7.33	0.0511 ±11	0.367 ±58	0.0520 ±81	0.0512 ±12	322 ±7
8.1	111	58	.53	19	5.97	0.0568 ±12	0.530 ±52	0.0676 ±63	0.0559 ±13	350 ±8
9.1	60	26	.43	21	11.96	0.0551 ±12	0.486 ±84	0.0640±108	0.0544 ±14	341 ±8
10.1	86	33	.38	21	8.85	0.0528 ±12	0.392 ±58	0.0539 ±77	0.0528 ±12	332 ±7
11.1	49	25	.52	18	11.65	0.0583 ±13	0.575 ±99	0.0715±120	0.0570 ±15	357 ±9
12.1	63	27	.42	20	11.23	0.0538 ±12	0.578 ±82	0.0780±107	0.0522 ±13	328 ±8
13.1	83	40	.48	27	10.68	0.0589 ±13	0.597 ±76	0.0736 ±91	0.0574 ±14	360 ±8
14.1	186	136	.73	32	5.91	0.0585 ±13	0.487 ±43	0.0604 ±51	0.0580 ±13	363 ±8
14.3	225	163	.73	22	3.50	0.0584 ±12	0.413 ±36	0.0513 ±41	0.0586 ±13	367 ±8
14.4	205	171	.84	28	4.63	0.0603 ±13	0.425 ±42	0.0511 ±48	0.0605 ±13	379 ±8
14.5	233	201	.86	20	2.90	0.0597 ±13	0.467 ±42	0.0567 ±48	0.0594 ±13	372 ±8
15.1	168	84	.50	3	.55	0.0583 ±12	0.465 ±34	0.0579 ±39	0.0580 ±13	363 ±8
15.2	176	101	.57	36	7.51	0.0540 ±12	0.440 ±50	0.0591 ±65	0.0537 ±12	337 ±7
16.1	82	68	.82	6	2.75	0.0569 ±12	0.439 ±52	0.0560 ±64	0.0567 ±13	355 ±8
17.1	42	23	.54	9	7.34	0.0542 ±12	0.390 ±90	0.0522±118	0.0543 ±14	341 ±8
19.1	87	37	.43	3	1.45	0.0549 ±12	0.448 ±44	0.0591 ±55	0.0546 ±12	343 ±7
20.1	66	34	.52	13	7.23	0.0534 ±12	0.454 ±67	0.0616 ±89	0.0529 ±13	332 ±8
21.1	127	92	.73	12	3.35	0.0576 ±13	0.496 ±54	0.0625 ±65	0.0569 ±13	357 ±8
22.1	71	35	.49	18	8.75	0.0560 ±13	0.577 ±93	0.0746±117	0.0546 ±14	342 ±9

[a] f^{206}Pb indicates the percentage common ^{206}Pb in the total measured ^{206}Pb
[b] Apparent age is the ^{206}Pb*/^{238}U age

Also shown in Figure 6a are the measured compositions of the Hasselbachtal zircons, all of which were targetted *a priori* as simple magmatic zircons likely to give the crystallisation age of the volcanic ash. These adhere closely to a quadratic curve of the same form as that through the standard analyses, but at lower ratios of Pb/U appropriate to their younger age. The ^{206}Pb /^{238}U ratio (and age) of each unknown zircon is given by the difference between its measured ^{206}Pb /^{238}U and that of the standard taken at the same UO/U. To first order, and without further number processing, it can be seen directly from the raw data on the calibration graph that the Hasselbachtal zircons have coherent ^{206}Pb /^{238}U with a reproducibility similar to that obtained for the homogeneous standard zircon.

Plotted on a Concordia diagram in Figure 7 the simple grouping of data for the Hasselbachtal zircons stands out clearly. The 36 separate analyses of 30 zircons cluster on Concordia and there is no scatter of Pb/U ratios detectable beyond the analytical reproducibility monitored by the repeat analyses of the standard. There is no evidence for Pb loss or other forms of isotopic complexity in the sample. The weighted mean ^{206}Pb* /^{238}U ratio of the group is 0.05632 ± 00067 (2σδ), equivalent to an age of 353.2 ± 4.0 Ma (2σ), and this is interpreted as the age of crystallisation of the volcanic horizon.

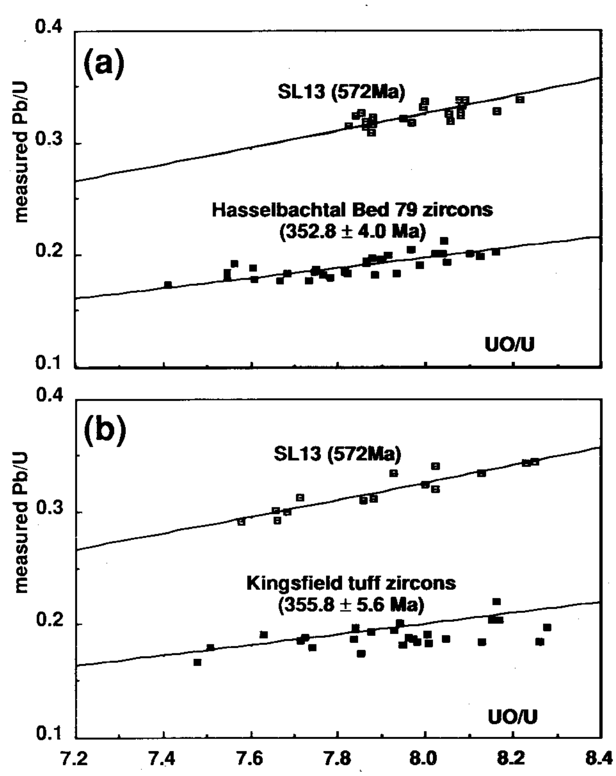


Figure 6.- Data for zircons in (a) Bed 79 bentonite and (b) Kingsfield Formation tuff compared with the SHRIMP calibration curve and concurrently collected data for standard zircon SL13. Scatter of Bed 79 data is similar to that of SL13, inferring a homogeneous composition. The Kingsfield data scatter slightly more than concurrent analyses of SL13, inferring Pb loss in the lower Pb/U compositions.

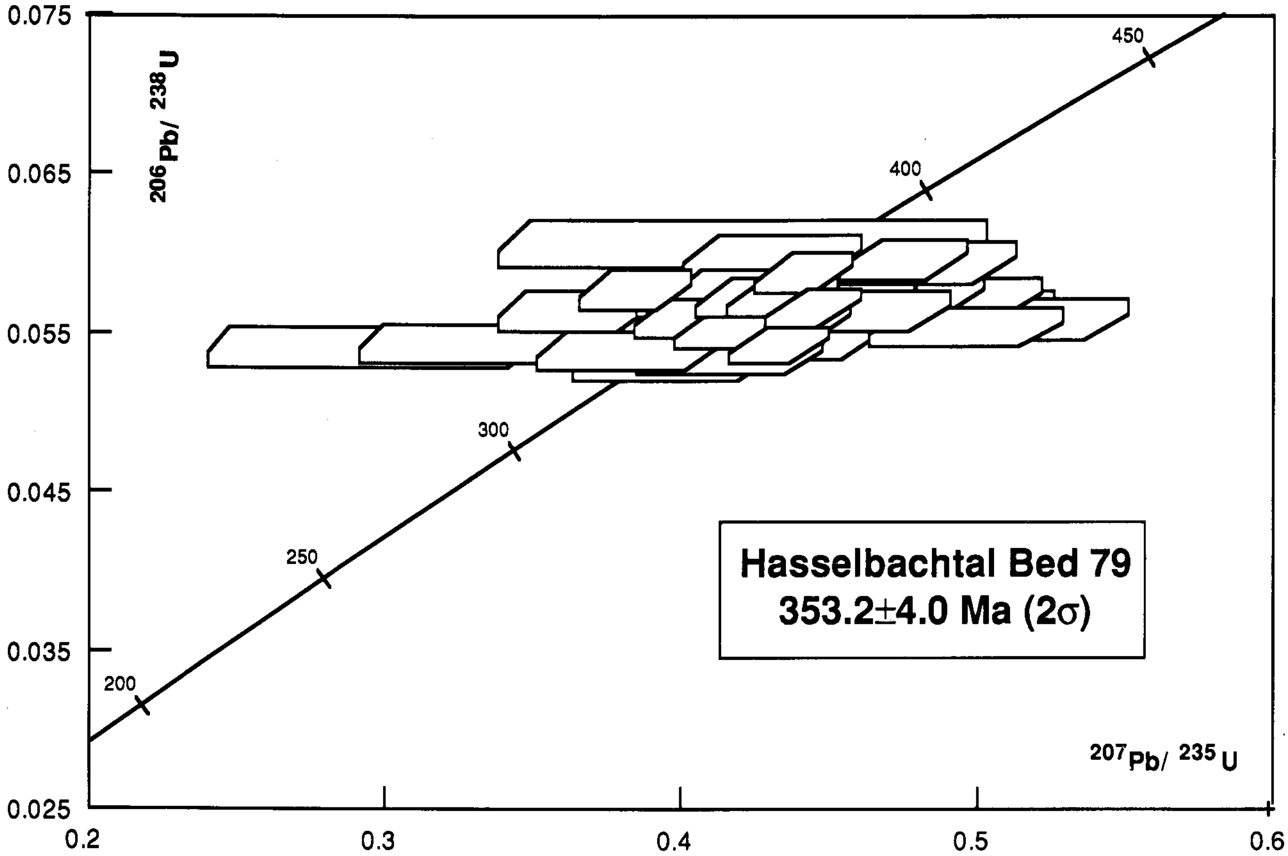


Figure 7.- Concordia diagram for zircons in the Hasselbachtal bentonite

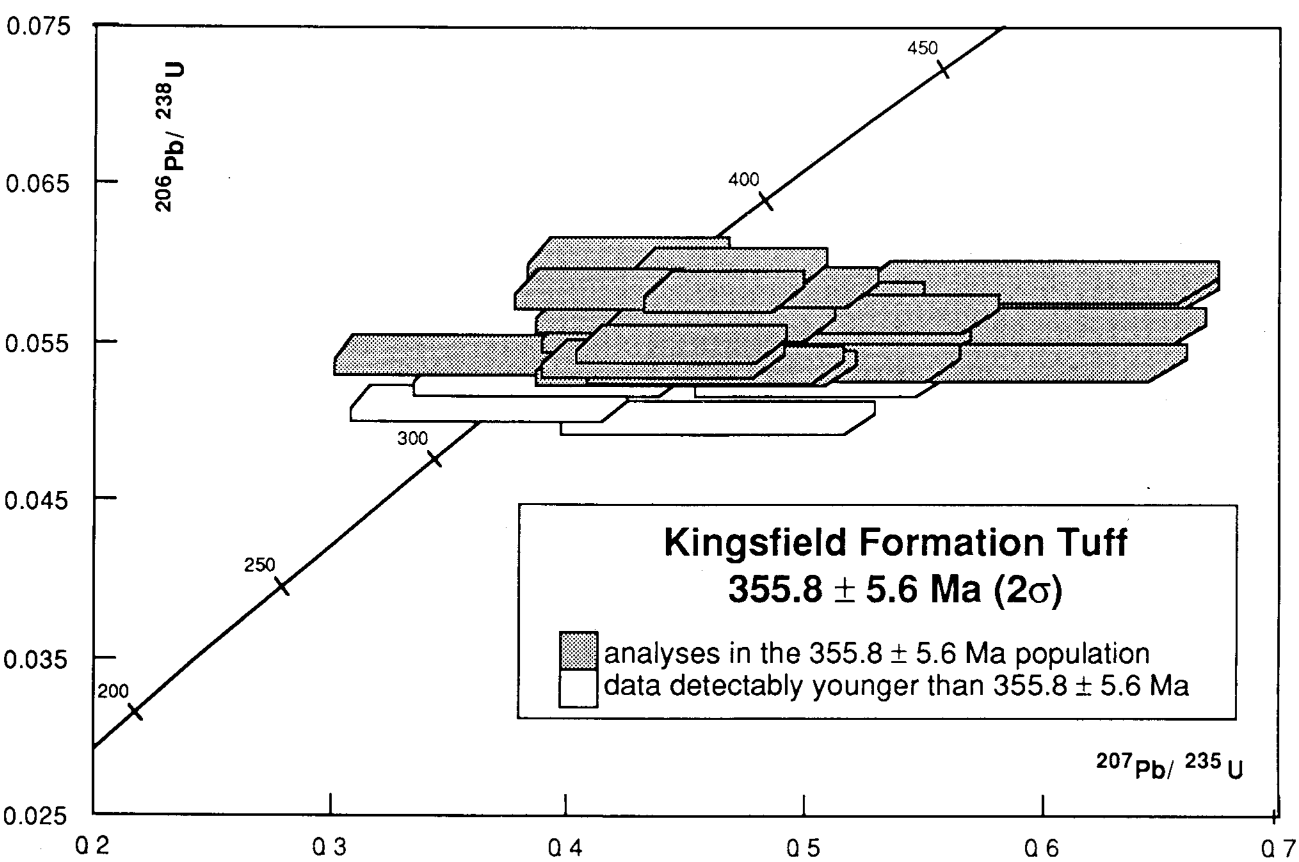


Figure 8.- Concordia diagram for zircons in the Kingsfield Formation tuff.

5.3.- CONVENTIONAL ANALYSIS OF HASSELBACHTAL BED 79 ZIRCONS

Attempts have been made to date the Hasselbachtal Bed 79 zircons using conventional methods of zircon analysis. At the time of writing the full results of this are not available to the present authors, but a resume has been published by Kramm (1991), who kindly provided his zircon sample for the ion microprobe study described in this contribution. This deserves comment for the comparison between conventional and microbeam analysis of the same zircon sample.

The conventional analysis involved dissolving several zircon grains together, and analysing U and Pb extracted from that dissolution. Despite careful hand picking and washing of the zircons, the principal feature of the analyses was very high abundances of non-radiogenic Pb, more than 60% of the total measured Pb. Age interpretation is therefore dependent on the >60% correction for common Pb. Discordant apparent ages clearly younger than the D-C boundary (336.1±4.0 and 339.2±4.4Ma, respectively, for two fractions) were interpreted by assuming 350Ma common Pb; according to Kramm (1991) the interpreted age can be shifted closer to 350Ma by assumption of a different composition of common Pb in the correction procedure. Abrasion of the zircons and etching in acid reduced the common Pb component to one-third of the measured Pb and yielded an apparent age of 346.6 ±1.6Ma, but this is also clearly younger than the D-C boundary.

The common Pb dependance of the conventional analyses is in marked contrast to compositions measured by ion microprobe on the same zircon sample; these have common Pb contents generally less than 5%, often less than 1% (Table 1). The influence of common Pb correction on the ion microprobe age measurements is therefore trivial.

Zircon photographs in Figure 5 show up the reason for this difference. The Hasselbachtal Bed 79 zircons are characterised by very high abundances of inclusions, up to 25% of many crystals; these comprise other minerals, and devitrified and altered volcanic glass. Dissolution of several such grains in a beaker unavoidably includes in the conventional analysis a high proportion of material other than zircon. The reflected light photographs show how the 30 μm analysing beam of the SHRIMP ion microprobe was able to avoid the inclusions and target pure zircon. This effectively eliminated the dependence of age measurement on modelling of the Pb content in the included material, and has made it possible to date accurately a sample not amenable to conventional methods of analysis.

5.4.- KINGSFIELD FORMATION TUFF

Zircons in the Kingsfield formation tuff are all of simple magmatic form, examples are photographed in Figure 5. As in the Hasselbachtal sample, the crystals are very rich in inclusions of other phases, but the SHRIMP analysing beam was able to avoid these and target pure zircon.

During analysis of the Kingsfield Formation zircons, fourteen analyses of standard SL13 were alternated with 25 analyses of the unknowns. These data are compared with the SHRIMP calibration curve in Figure 6b and plotted on a Concordia diagram in Figure 8. Data for the homogeneous standard zircon adhere closely to the expected calibration curve. The 2.09% (σ) reproducibility of the standard composition is included in the error in Pb/U of each of the unknowns, and the 0.56% (σ) uncertainty in the mean position of the calibration is included in the error on the mean age of the unknowns.

In contrast to the coherent grouping of Hasselbachtal zircon compositions, ratios of Pb/U in the Kingsfield zircons scatter more than can be attributed to analytical uncertainty. In the calibration graph (Figure 5b) this is evident as a dispersion of data about the calibration curve greater than the dispersion of concurrent measurements of the standard zircon. This inhomogeneity is interpreted to indicate that some of the zircons have lost radiogenic Pb, and consequently have lowered Pb/U ratios. The excess scatter is contributed by 5 of the 21 individual analyses which have Pb/U ratios lower than that of the population mean by more than 2σ (95% confidence). Elimination of these analyses, as shown in Figure 7, leaves a group of 16 analyses in which the scatter of Pb/U ratios is comparable to that of the standard zircon, indicating a homogeneous Pb/U ratio within error. The weighted mean $^{206}Pb^{*}/^{238}U$ ratio of this group is 0.05674 $\pm$ .00091(2σ), equivalent to an age of 355.8 $\pm$ 5.6 Ma (2σ). This age of a majority subset of the analysed zircons is the best estimate available of the crystallisation age of the Kingsfield Formation tuff. The process of interpreting an age from these zircons has involved an interpretation stage not necessary in the homogeneous Hasselbachtal sample, and this must make the age determination slightly less secure. Attention is drawn to two features of this interpretation process. Firstly, it is possible to make this interpretation of Pb loss, and attempt to assess its consequences for the interpreted age, because within-grain ion microprobe data was obtained; conventional zircon analysis might have hidden this complexity in the process of combining whole zircons in the dissolution. Secondly, it should be noted that the interpreted age may have been driven to too high a level by elimination of the apparently younger data, or it may be that insufficient elimination of low Pb/U analyses has left a component of Pb loss in the group from which the age is interpreted. The quoted analytical precision may not, therefore, encompass any error introduced through the interpretation process.

6.- DISCUSSION AND CONCLUSIONS

Historical uncertainty in the age of the D-C boundary has been founded principally on stratigraphic uncertainty among the samples used for isotopic dating. The most relevant dates have been for volcanics in poorly fossiliferous terrestrial red beds of uncertain correlation to the marine sequence. Refinements of the methods of isotopic analysis now make it possible to study samples which are of greater stratigraphic relevance, and which were not amenable to older analytical techniques.

The rich biota of the Hasselbachtal section allows the Bed 79 bentonite to be located biostratigraphically with confidence and fine resolution. It lies within the lower part of the *Siphonodella sulcata* conodont Zone whose base defines the D-C boundary, and just 35 cm above the boundary definition. The horizon is also at or immediately below the base of the *Gattendorfia subinvoluta* ammonoid Zone which was the previous ammonoid definition of the boundary. The zircon U-Pb age for the bentonite is also securely constrained: 33 analyses of 27 zircons failed to find evidence of isotopic complexity, and there is every reason to believe that the age of the sample is encompassed by the ± 4 Ma analytical reproducibility. Conodont zones in this section of the fossil record almost certainly represent less than 4 Ma, and we therefore consider that the Devonian-Carboniferous boundary lies within the error on the 353.2 ± 4.0 Ma (2σ) age.

This conclusion is lent strong support by the age obtained for the Kingsfield Formation tuff. Biostratigraphic constraints for the Australian sample are slightly less tight, but it is certainly within the range of the conodont *S. sulcata* and probably is close to the stratigraphic level of the German bentonite because 180 m of sediment intervenes before the Lower *crenulata* Zone. The zircon age is also slightly less secure because there is evidence for isotopic disturbance of the sample. However, the ion microprobe data have allowed the affected zircons to be identified and eliminated from calculation, and the 355.8 ± 5.6 Ma (2σ) age is indistinguishable from the age of the German sample.

Finally, we note that the confidence of this determination of the age of the D-C boundary rests on the chance existence of a thin bentonite near the boundary in the richly fossiliferous Hasselbachtal auxiliary stratotype section. Future refinements of the age of the D-C boundary may well depend on reanalysis of this uniquely placed volcanic horizon. The conjunction of fossils and zircons has afforded a rare opportunity of directly matching the biostratigraphic and numerical time scales in a stratotype section, and this highlights the value of defining biostratigraphic stratotypes in the vicinity of known dateable horizons.

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