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GEOCHRONOMETRY AND GEOCHEMISTRY OF THE EUROPEAN MID-CARBONIFEROUS BOUNDARY GLOBAL STRATOTYPE PROPOSAL, STONEHEAD BECK, NORTH YORKSHIRE, UK.[1]

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(7 figures)

ABSTRACT.- Stonehead Beck is the only Mid-Carboniferous Boundary candidate stratotype with a refined, complete ammonoid and glacio-eustatic sequence stratigraphical calibration (65,000 years average periodicity) of the first appearance of the definitive conodont *Declinognathodus noduliferus* and its accessory conodonts. It is also the only candidate section with a terrestrial biostratigraphy, since miospores are abundant. Clay mineral studies support the sedimentology and biostratigraphy, which indicate continuous deposition in a hemipelagic, basinal environment.

Zircon $^{206}Pb/^{238}U$ dates for the Arnsbergian E2a3 and E2b2 ammonoid zones, from beneath the Mid-Carboniferous Boundary, have been obtained from K-bentonites in the Harewood Borehole, North Yorkshire, using SHRIMP analysis. They indicate respective ages of 314.4 ± 4.6 My (2σ) and 314.5 ± 4.6 My (2σ), some 5.6 to 10.6 My younger than published Pendleian/Arnsbergian dates derived from $^{40}Ar/^{39}Ar$ analysis. Namurian time was therefore short (around 5.5 My), necessitating revision of subsidence curves and Crustal Stretching Factor (β) for the Pennine Basin of northern England.

The revised Sr seawater curve plot using the new time scale and Sr values obtained from the stratotype, shows a rapid increase in the $^{87}Sr/^{86}Sr$ ratio in the early Namurian, immediately prior to the Mid-Carboniferous Boundary event, which is associated with rapid species turnover and global unconformity.

KEY WORDS: Stratotype, Namurian, ammonoid, conodont, miospore, glacio-eustacy, bentonites, geochronometry, isotopes.

RESUME. Géochronométrie et géochimie d'un stratotype européen proposé pour la limite globale mi-Carbonifère, à Stonehead Beck, nord Yorkshire, Royaume Uni. Stonehead Beck est le seul stratotype candidat pour la limite mi-Carbonifère, avec une calibration complète de la première apparition du conodonte *Declinognathodus noduliferus* et de ses conodontes accessoires, par des ammonoïdes et une séquence stratigraphique glacio-eustatique (périodicité moyenne de 65.000 ans). C'est aussi la seule coupe candidate avec une biostratigraphie terrestre puisque les miospores y sont abondants. Les études de minéraux argileux supportent la sédimentologie et la biostratigraphie, qui indiquent un dépôt continu dans un environnement de bassin, semi-pélagique.

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Des dates $^{206}Pb/^{238}U$ de zircons pour les zones d'Ammonoïdes E2a3 et E2b2 de l'Arnsbergien, situées en dessous de la limite mi-Carbonifère, ont été obtenues de K-bentonites du sondage de Harewood, nord du Yorkshire, par analyse SHRIMP. Elles indiquent des âges respectifs de 314,4 ± 4,6 Ma (2σ) et 314,5 ± 4,6 Ma (2σ), qui sont quelques 5,6 à 10,6 Ma plus jeunes que les dates publiées pour la limite Pendleien/Arnsbergien dérivées de l'analyse $^{40}Ar/^{39}Ar$. La durée du Namurien était donc courte (envirion 5,5 Ma) et une révision des courbes de subsidence et du "Crustal Stretching Factor" (β) pour le "Pennine Basin" du nord de l'Angleterre, est nécessaire.

La courbe du Sr de l'eau de mer révisée en fonction de la nouvelle échelle de temps et les valeurs de Sr obtenues dans le stratotype, montrent un accroissement rapide du rapport $^{87}Sr/^{86}Sr$ au début du Namurien, immédiatement avant l'événement de la limite mi-Carbonifère qui est associé à un brusque remplacement d'espèces et une non conformité globale.

MOTS-CLES: Stratotype, Namurien, ammonoïdés, conodontes, miospores, glacio-eustasie, bentonites, géochronométrie, isotopes.

1. INTRODUCTION

The Mid-Carboniferous Boundary Working Group met at a recent International Union of Geological Sciences (IUGS) Subcommission on Carboniferous Stratigraphy (SCCS) meeting in Liège, Belgium on June 8, 1993. It was decided that of all the candidate sections for the Mid-Carboniferous Boundary, only three should remain as candidates. These are;

i) Stonehead Beck, UK (Riley *et al.*, 1987)
ii) Arrow Canyon, Nevada, USA (Lane *et al.* 1985)
iii) Aksu-1 Section, Gissar Ridge, Uzbekistan (Nigmadganov & Nemirovsaka, 1993).

The British proposal for the Mid-Carboniferous Boundary stratotype was described in detail by Riley *et al.* (1987), Varker *et al.* (1991) and Varker (this volume). It comprises a stream section (Figures 1 & 2) running through farmland, between map co-ordinates SD 9474 4330 and SD 9470 4326 at Stonehead Beck (formerly Gill Beck), near Cowling, North Yorkshire, UK. This locality, which is also the Chokierian Stage stratotype (Ramsbottom, 1981), is a designated Site of Special Scientific Interest (SSSI) with legal protection under UK law. It is adjacent to a public road and is close to major road and rail routes through northern England and is thus easily and cheaply accessible.

Over 40m of sequence are continuously exposed, comprising a hemi-pelagic claystone succession (Sabden Shales) in which ammonoids, bivalves, conodonts and miospores are the dominant fossils. Ostracods, radiolaria and ichthyoliths also occur, but have not yet been studied, and one horizon has yielded an orthotetoid brachiopod. Ammonoids are restricted to discrete horizons, traditionally termed «marine bands». One of the most significant discoveries of recent studies is the occurrence of conodonts in strata lying between the ammonoid bands, suggesting that marine influence predominates through the Boundary interval at Stonehead Beck. The Mid-Carboniferous Boundary is placed at the first appearance of *Declinognathodus*, represented by D. *inaequalis*, 9.4m above the Arnsbergian/Chokierian Boundary (for which this section is already the stratotype) and 0.4m below the Isohomoceras subglobosum (H1a2) Marine Band; *D. noduliferus* enters 0.4m above *D. inaequalis.*

Although outcrops across the Mid-Carboniferous Boundary are ubiquitous in the UK, Stonehead Beck was studied as a potential boundary stratotype for the following reasons.

i) It has the full compliment of mid-Namurian ammonoid horizons and is the type locality for the ammonoids which straddle the Mid-Carboniferous Boundary interval (Riley, 1987). Indeed it is the only candidate section which shows both the youngest *Nuculoceras* faunas, characteristic of the early Carboniferous and oldest *Isohomoceras,* characteristic of the late Carboniferous. These ammonoid bearing bands provide the highest stratigraphical resolution in the Namurian and have lateral continuity in hemi-pelagic sequences of over 2,000 km distance, stretching from Ireland (Ramsbottom *et al.* 1978) across the UK and North Sea into Germany and Poland (Patteisky, 1959; Korejwo, 1969). Some ammonoid species e.g *Homoceras beyrichianum*, and *Isohomoceras subglobosum* appear to have an intercontinental distribution stretching from the Urals (Riley, 1987) to Nevada (Titus, 1992). Stratigraphical resolution of the marine band horizons is achieved both by the rapidly evolving ammonoid faunas, which they contain, and their constant relationship to interbedded volcanic ash bands (Trewin, 1968; Trewin & Holdsworth, 1972), resulting in a widely correlatable event stratigraphical framework,

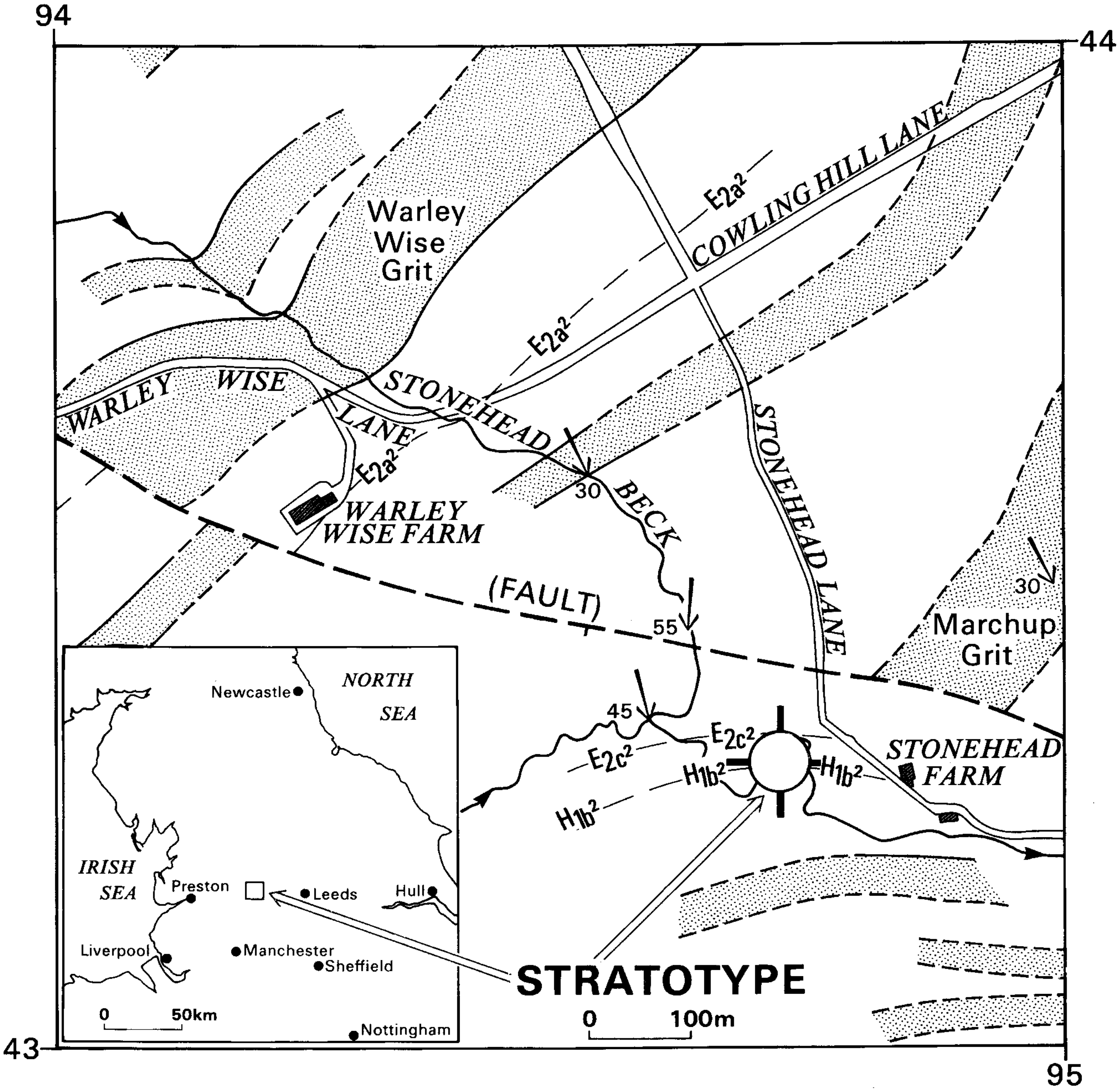

Fig. 1.- Location of the Stonehead Beck section (from Riley *et al.*, 1987 based on BGS 1:10000 Geological sheet SD 94 SE).

upon which the Namurian Series and its biozones are based (Figure 4). Indeed such ammonoid bands are considered to represent marine highstand events which were glacio-eustatically driven (Maynard & Leeder 1992) and thus are potentially correlatable throughout the Carboniferous marine realm. Furthermore the intimate association with such ash bands allows accurate geochronometric calibration of the marine bands and associated biozones, allowing cross-facies correlation into other biozones, palaeolatitudes and bioprovinces as well as into biostratigraphically barren strata.

ii) The geological setting is well known and understood. The locality lies in the Pennine Basin (Figure 3), a rapidly subsiding region of northern England which was undergoing thermal subsidence during the Namurian (Leeder, 1982), following a long period of late Devonian and Dinantian back arc rifting

iii) Because of (i) & (ii) above, it is geologically the most favourable location for a complete offshore sequence. This is particularly important as the Mid-Carboniferous Boundary interval is commonly associated with non-sequence and unconformity (Riley *et al.*, 1987). There is no biostratigraphical, sedimentological or geochemical evidence that any non-sequence, unconformity or even minor break in sequence exists at Stonehead Beck.

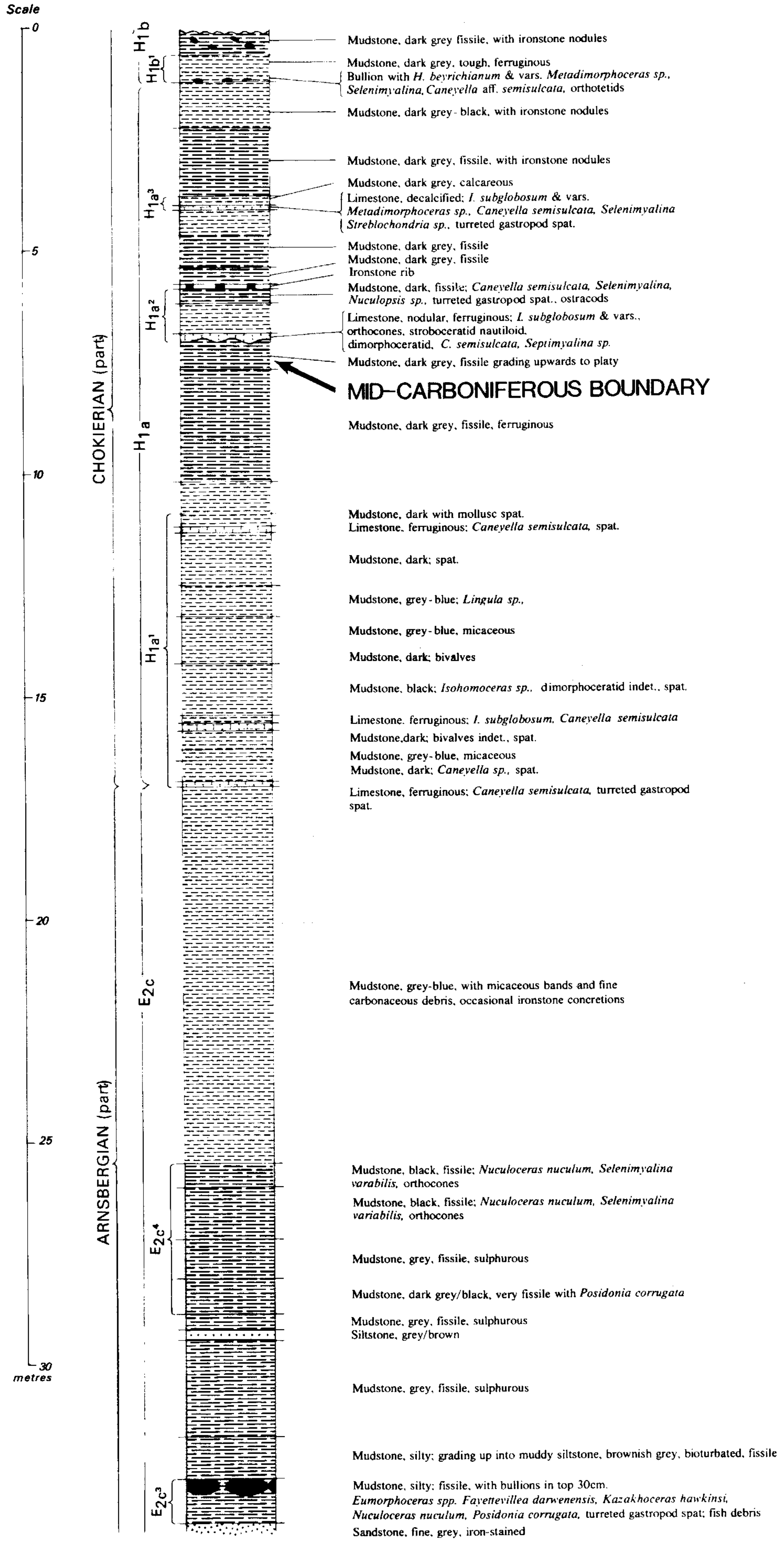
Scale
0
5
10
15
20
25
30
metres
CHOKIERIAN (part)
ARNSBERGIAN (part)
$\mathrm{H_1b}$
$\mathrm{H_1b^1}$
$\mathrm{H_1a^3}$
$\mathrm{H_1a^2}$
$\mathrm{H_1a}$
$\mathrm{H_1a^1}$
$\mathrm{E_2c}$
$\mathrm{E_2c^4}$
$\mathrm{E_2c^3}$
Mudstone, dark grey fissile, with ironstone nodules
Mudstone, dark grey, tough, ferruginous
Bullion with *H. beyrichianum* & vars. *Metadimorphoceras sp.*, *Selenimyalina, Caneyella* aff. *semisulcata*, orthotetids
Mudstone, dark grey - black, with ironstone nodules
Mudstone, dark grey, fissile, with ironstone nodules
Mudstone, dark grey, calcareous
Limestone, decalcified; *I. subglobosum* & vars. *Metadimorphoceras sp., Caneyella semisulcata, Selenimyalina* *Streblochondria sp.*, turreted gastropod spat.
Mudstone, dark grey, fissile
Mudstone, dark grey, fissile
Ironstone rib
Mudstone, dark, fissile; *Caneyella semisulcata, Selenimyalina, Nuculopsis sp.*, turreted gastropod spat., ostracods
Limestone, nodular, ferruginous; *I. subglobosum* & vars., orthocones, stroboceratid nautiloid, dimorphoceratid, *C. semisulcata, Septimyalina sp.*
Mudstone, dark grey, fissile grading upwards to platy
MID-CARBONIFEROUS BOUNDARY
Mudstone, dark grey, fissile, ferruginous
Mudstone, dark with mollusc spat.
Limestone, ferruginous; *Caneyella semisulcata*, spat.
Mudstone, dark; spat.
Mudstone, grey - blue; *Lingula sp.*,
Mudstone, grey - blue, micaceous
Mudstone, dark; bivalves
Mudstone, black; *Isohomoceras sp.*, dimorphoceratid indet., spat.
Limestone, ferruginous; *I. subglobosum, Caneyella semisulcata*
Mudstone,dark; bivalves indet., spat.
Mudstone, grey - blue, micaceous
Mudstone, dark; *Caneyella sp.*, spat.
Limestone, ferruginous; *Caneyella semisulcata*, turreted gastropod spat.
Mudstone, grey-blue, with micaceous bands and fine carbonaceous debris, occasional ironstone concretions
Mudstone, black, fissile; *Nuculoceras nuculum, Selenimyalina varabilis*, orthocones
Mudstone, black, fissile; *Nuculoceras nuculum, Selenimyalina variabilis*, orthocones
Mudstone, grey, fissile, sulphurous
Mudstone, dark grey/black, very fissile with *Posidonia corrugata*
Mudstone, grey, fissile, sulphurous
Siltstone, grey/brown
Mudstone, grey, fissile, sulphurous
Mudstone, silty; grading up into muddy siltstone, brownish grey, bioturbated, fissile
Mudstone, silty; fissile, with bullions in top 30cm.
Eumorphoceras spp. Fayettevillea darwenensis, Kazakhoceras hawkinsi, Nuculoceras nuculum, Posidonia corrugata, turreted gastropod spat; fish debris
Sandstone, fine, grey, iron-stained

Fig. 2A.

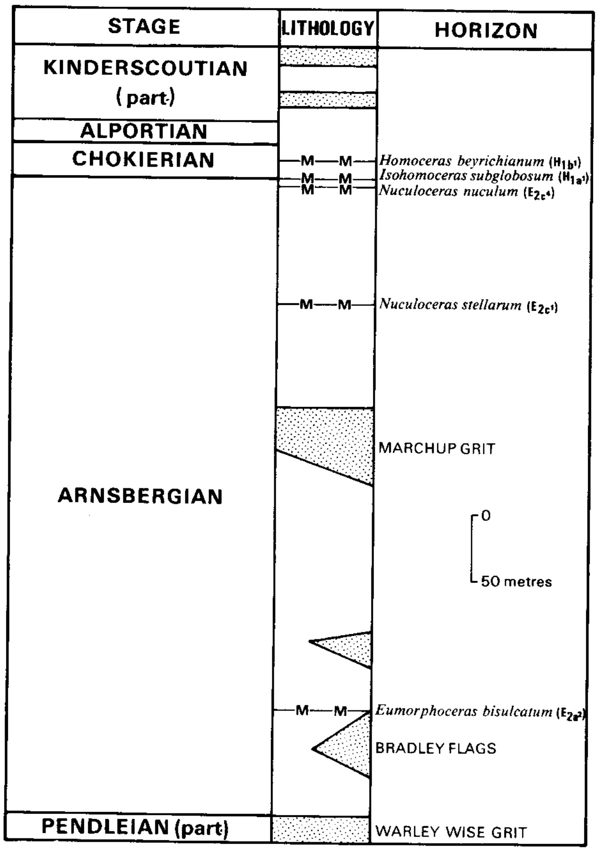

Fig. 2B. summary of the local lithostratigraphy, in which only selected marine bands are shown (from Riley *et al.* 1987).

iv) Conodonts are abundant and their ranges in the section can be calibrated independently by the much higher stratigraphical resolution of the accompanying ammonoid horizons. Futhermore there is no overlap of conodonts between the *Gnathodus bilineatus bollandensis* and *Declinognathus noduliferus* conodont zones. All sections in the UK which have been studied in detail and show such overlap (e.g. Owens *et al.*, 1991 & Riley in Brandon *et al.*, *in press*) contain a major non-sequence, the overlap resulting from reworking.

v) Miospores are abundant and provide a cross correlation between the marine and terrestrial realm. The miospore assemblages from Stonehead Beck compliment the marine biostratigraphy in that they show no evidence of non-sequence. Indeed Stonehead Beck is the only Mid-Carboniferous Boundary stratotype proposal which preserves both a marine and terrestrial biostratigraphy.

Fig. 2A. Log of Mid-Carboniferous Boundary section at Stonehead Beck (from Riley *et al.*, 1987).

vi) The sequence is tectonically undisturbed with gentle dips and shows low thermal maturity with a Conodont Alteration Index (CAI) of 2.0 (bullion in Nuculoceras nuculum E2c3 Marine Band) and vitrinite reflectance of 0.9 RM% (claystones in the overlying Kinderscoutian, some 50m above the Mid-Carboniferous boundary).

vii) Being a «tight» claystone sequence, diagenetic alteration or overprinting is probably less severe than in a carbonate or siliciclastic dominated sequence. This factor, together with vi) above, enhances the potential for the preservation of primary geochemical signatures. This has implications for future studies on the chemo-stratigraphical calibration of the Mid-Carboniferous Boundary.

viii) The section is easily and cheaply accessible, is protected by UK law, and lies close to major centres of population in a politicaly stable country. It already has stratotypic status as the stratotype for the Arnsbergian/Chokierian Stage boundary.

In chosing a stratotype it would have been desirable to find a section which also contained shallow water carbonate faunas such as corals, brachiopods and foraminifera. Sections containing these are common in northern Britain, such as in the Scottish Midland Valley, Northumberland Trough, Stainmore Trough, Alston and Askrigg Blocks. However, in all these cases the critical boundary interval is not preserved (Ramsbottom, 1977, Ramsbottom *et al.*, 1978) due to non-sequence and unconformity. Indeed it can be shown that this hiatus is present at Summersgill (Owens *et al.*, 1991) on the margin of the Pennine Basin some 36km to the west northwest of Stonehead Beck and rapidly increases in severity northwards as one rises up the systems tract from Summersgill toward the Askrigg Block (Brandon *et al., in press*). Because of this characteristic, shallow water sequences were avoided. Since non-sequences and unconformities can be demonstrated across Eurasia, North America and North Africa, over the boundary interval, we believe that this hiatus is a product of a major eustatic event and is not peculiar to North West Europe. For this reason we consider that all shallow water sequences be avoided as a potential stratotypes for the Mid-Carboniferous Boundary interval.

The following sections describe new information relevant to the Stonehead Beck section. They comprise three studies; 1) Clay mineral distribution at Stonehead Beck 2)Strontium Isotope ratios preserved in conodonts at Stonehead Beck and 3) Absolute Zircon $^{206}Pb/^{238}U$ dates for the E2a3 and E2b2 ammonoid zones, which lie in the Arnsbergian Stage

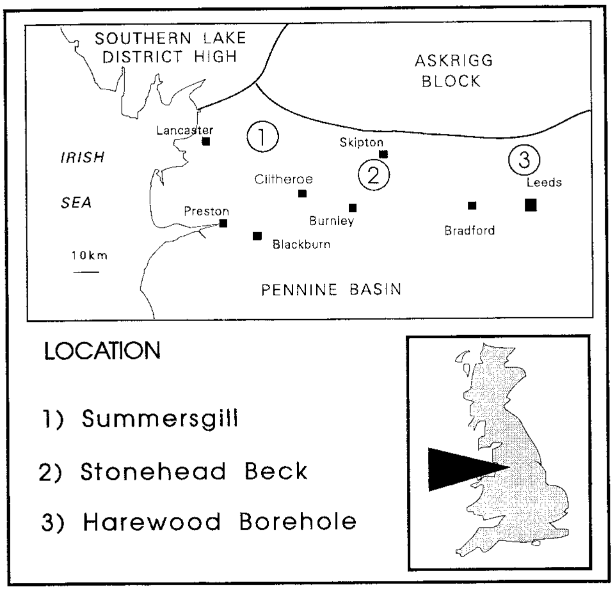

Fig. 3.- Palaeogeographic location of sections in the Pennine Basin referred to in the text.

beneath the Mid-Carboniferous Boundary, derived from K-bentonites in the Harewood Borehole, North Yorkshire, using SHRIMP analysis.

2. CLAY MINERAL DISTRIBUTION

The main purpose of the clay mineral study was to ascertain whether there was any evidence of a stratigraphical break in the Stonehead Beck section. The clay mineral profiles of marine bands in the Pennine Basin are well known and have been described by Spears (1987) and Spears & Sezgin (1985). These studies demonstrate that very high proportions of kaolinite in the total clay fraction are associated with close proximity to paleosols. High proportions of kaolinite in the clays at Stonehead Beck could therefore represent emergence, or derivation from nearby palaeosols. No such evidence has been recognised from the samples investigated.

2.1. METHODS

The clay mineralogy of the mudstones of the section at Stonehead Beck was studied using x-ray diffractometry smear mounts of clay-sized fractions which had been air-dried, treated with glycerol, and heated to 550°C for 1 hour.

In randomly orientated samples of these mudstones, reflections in the range 4.18-4.5Å could not be resolved and so indicated that these samples contain disordered kaolinite (Hinckley, 1963).

For many samples the 001 peaks were diminished in intensity while others remained at similar intensity. All samples showed a shift in 001 peak position to around 13.5-13.8Å and this could be attributed to a small proportion of vermiculite associated with chlorite. Vermiculite collapses to 10Å on heating to 550°C, but rehydrates easily and this is a possible explanation for the intermediate peak position. All chlorite peaks except 001 and 003 collapsed on heating, and composition with respect to the Fe:Mg ratio can be assumed to be fairly constant.

Percentage ratios of clay minerals peak areas measured from the samples are shown in Figure 5

Non-clay minerals that are present in the mudstones of this section are quartz, feldspar, siderite, pyrite, hematite, and in one sample only, calcite. Not all iron-bearing minerals may be found in any one sample.

2.2. DISCUSSION

A detailed interpretation of the depositional environment has not been attempted, but rather a description of general trends and changes occurring in clay mineral ratios (peak areas), especially where these could be related to possible variation in salinity levels during deposition as indicated in the biostratigraphic record. It has been assumed that there is no major change in provenance of sediment supply into the Pennine Basin during the period of sedimentation represented at Stonehead Beck. Provenance was primarily from a hinterland comprising granitic and metamorphic terrains via fluviatile systems into a euxinic marine basin.

The widely held depositional model for the Pennine Basin during the Namurian is that it was repeatedly flushed by freshwater discharge form large rivers whose deltas encroached progessively southward during successive low stands. Conversely, during marine highstands these deltas were inudated, giving rise to widespread marine band deposition, whose areal extent was dependent on the amplitude of the highstand. Stonehead Beck was too distal during the late Arnsbergian and Chokierian for its hemi-pelagic deposits to be replaced by deltaic sediment, but the hemi-pelagic clays which correspond to lowstands are located between the marine macrofaunal horizons (marine bands). It was thought, until recently, that these macrofaunally barren claystones were non-marine, however as already noted, conodonts have been recovered from them. It is therefore unclear whether the lack of macrofauna between marine bands in these hemi-

MARINE BANDS					SHRIMP DATES
INDEX		AMMONOIDS 65000 years each	CONODONTS		Bolsovian 311
G1b1		Cancelloceras cumbriense	*Idiognathoides sinuatus* - *Idiognathodus primulus (part)*		
G1a1		Cancelloceras cancellatum			
R2c2		Verneulites sigma			
R2c1		Bilinguites superbilinguis			
R2b5		Bilinguites metabilinguis			
R2b4		Bilinguites eometabilinguis			
R2b3		Bilinguites bilinguis			
R2b2		Bilinguites bilinguis			
R2b1		Bilinguites bilinguis			
R2a1		Bilinguites gracilis			
R1c4		Reticuloceras coreticulatum	*Idiognathoides corrugatus* - *Idiognathoides sulcatus*		
R1c3		Reticuloceras reticulatum			
R1c2		Reticuloceras reticulatum			
R1c1		Reticuloceras reticulatum			
R1b3		Reticuloceras stubblefieldi			
R1b2		Reticuloceras nodosum			
R1b1		Reticuloceras eoreticulatum			
R1a5		Reticuloceras dubium			
R1a4		Reticuloceras todmordenense			
R1a3		Reticuloceras subreticulatum			
R1a2		Reticuloceras circumplicatile			
R1a1		Hodsonites magistrorum			
H2c2		Homoceratoides prereticulatus	*Declinognathus noduliferus*		
H2c1		Vallites eostriolatus		spread of Boundary imprecision in sections lacking ammonoids	
H2b1		Homoceras undulatum			
H2a1		Hudsonoceras proteum			
H1b2	Stratotype	Isohomoceras sp. nov.			
H1b1		Homoceras beyrichianum			
H1a3		Isohomoceras subglobosum			
H1a2		Isohomoceras subglobosum			
H1a1		Isohomoceras subglobosum	← Mid-Carb. Boundary		
E2c4		Nuculoceras nuculum	*Gnathodus bilineatus bollandensis*		
E2c3		Nuculoceras nuculum			
E2c2		Nuculoceras nuculum			
E2c1	Harewood	Nuculoceras stellarum			
E2b3		Cravenoceratoides nititoides			
E2b2		Cravenoceratoides nitidus			314.5± 4.6
E2b1		Cravenoceratoides edalensis			
E2a3		Eumorphoceras yatesae			314.4±4.6
E2a2a		Cravenoceras gressinghamense			
E2a2		Eumorphoceras ferrimontanum			
E2a1		Cravenoceras cowlingense			
E1c1		Cravenoceras malhamense	*Kladognathus* - *Gnathodus girtyi simplex*		
E1b2		Tumulites pseudobilinguis			
E1b1		Cravenoceras brandoni			
E1a1		Cravenoceras leion			
					P1b Zone 325

Fig. 4.- Classification of western European Namurian marine bands. The position of the SHRIMP dates is shown as are the stratigraphic ranges of Harewood Bh. and the Mid-Carboniferous Boundary Stratotype section at Stonehead Beck. Note the high resolution achieved both by the glacio-eustatic marine band events and their eponymous ammonoids. The range of uncertainty in precise age of the junction between the *Gnathodus bilineatus* and *Declinognathodus noduliferus* conodont zones applies only to sections where ammonoid calibration (*Nuculoceras* and *Isohomoceras*) is lacking. These conodonts have much longer stratigraphic ranges than the ammonoids.

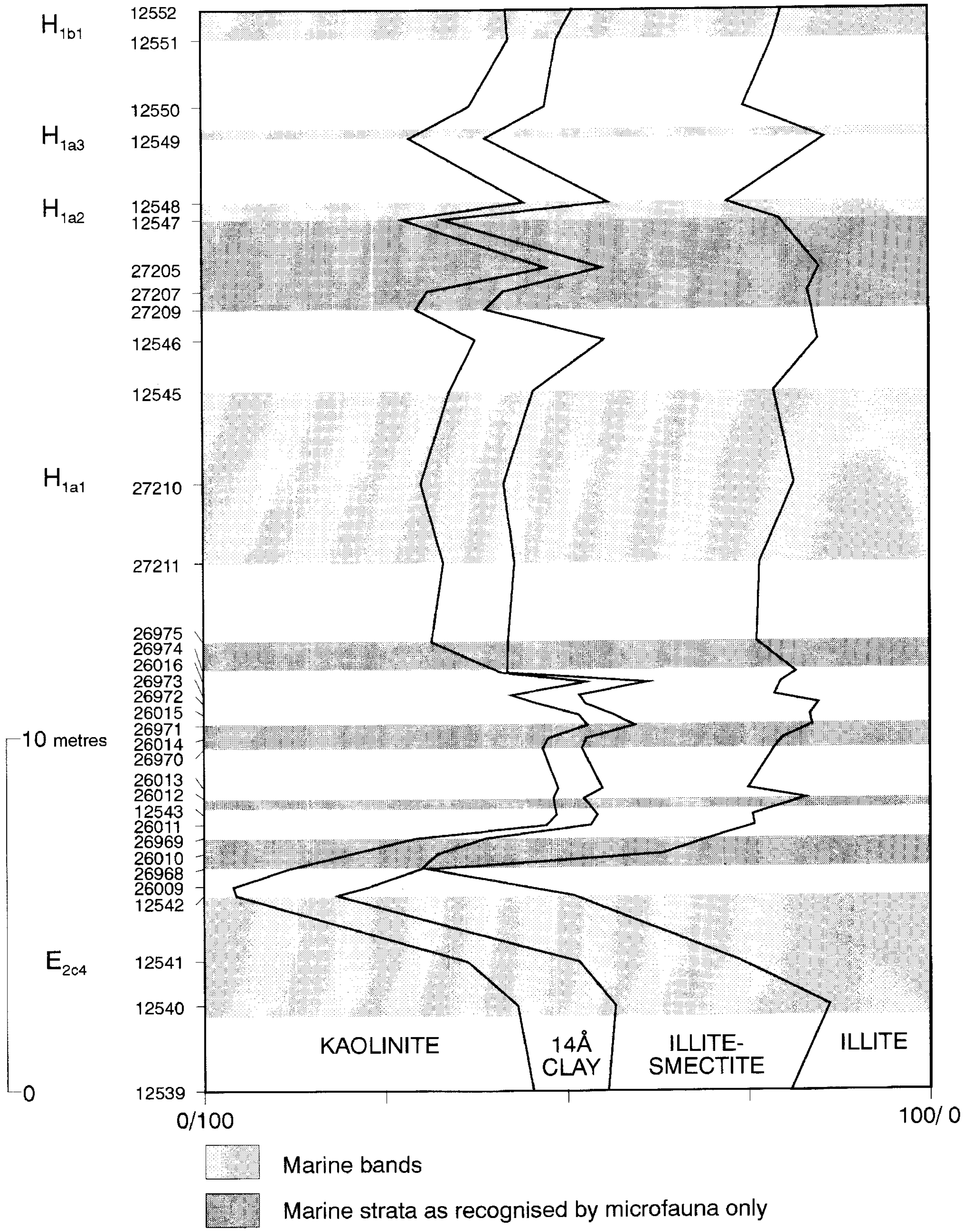

Fig. 5.- Plots of uncorrected peak area percentages of clay minerals derived from conodont and palynology samples used in Riley *et al.* (1987) and Varker *et al.* (1991).

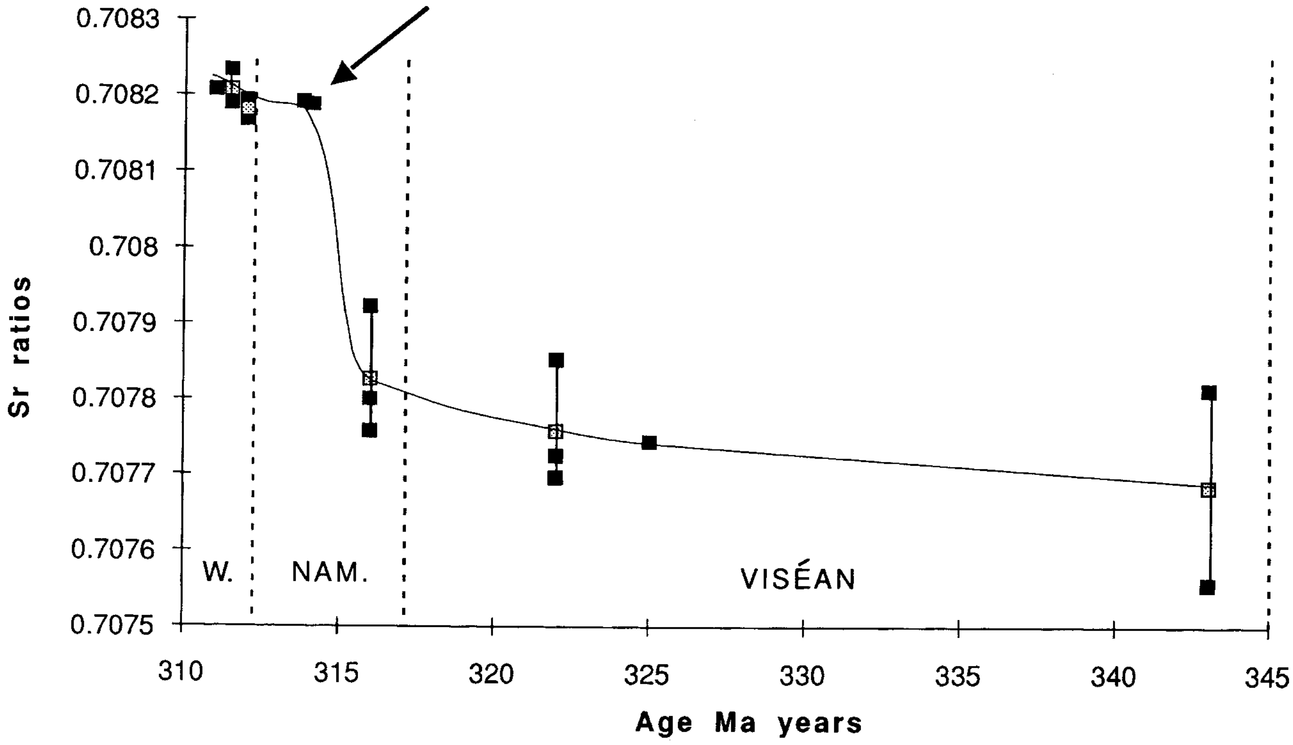

Fig. 6.- Plot of the $^{87}Sr/^{86}Sr$ isotope ratios on a Carboniferous seawater Sr curve derived from brachiopod samples analysed by Popp et al. (1986). Arrow highlights the overlapping plots of the two conodont samples from the E2c3 and H1b1 marine bands respectively across the Mid-Carboniferous Boundary in Stonehead Beck. Note the steep early Namurian gradient to the curve and close continuity of the conodont data with the Late Carboniferous brachiopod samples. Popp et al. (1986) gave their stratigraphical data in relatively broad terms. Their early Viséan samples are plotted at 343Ma. Their late Viséan samples include a sample from Scotland, which is here placed at the base of the Brigantian at 325Ma, the rest of their late Viséan samples are plotted within the Brigantian Stage at 323Ma. Early Serpukhovian samples are plotted at 316Ma within the Pendleian Stage. Bashkirian samples are placed in the earliest Westphalian (Langsettian Stage) at 312Ma, early and mid-Moscovian samples are plotted at 311.5Ma and 311Ma respectively. Vertical lines intersecting plot points show the range of values, open square plot points are the mean values. Abbreviations: W., Westphalian; NAM., Namurian

pelagic clays results exclusively from reduced salinity, much more rapid sedimentation rates or a combination of these and other factors.

The maximum proportion of kaolinite is present in the latest Alportian and the minimum in the uppermost part of the Nuculoceras nuculum (E2c4) Marine Band, suggesting that this latter horizon was the most distal from the shore, or that clays were being derived from a relatively unweathered hinterland. At no point is kaolinite of sufficient proportions to suggest close proximity to a non-sequence or palaeosol formation. Apart from the low value in the E2c4 Marine Band, the amplitude of variation in the peak areas of kaolinite (23%) lies within a 29% to 52% band throughout the rest of the samples. There is no obvious correspondence between the higher kaolinite values and the marine bands. For instance, a peak with a value of 47% occurs in the middle portion of the H1a2 Marine Band, however average kaolinite values are generally lower in the marine bands, than in the intervening clays. This is compatible with models which indicate that kaolinite is more likely to be deposited closer inshore than other clay species due to variation in grain size or differential flocculation (eg Edzwald and O'Melia, 1975; Gibbs, 1977); or due to a shift in balance from clays derived from mature soils to clays derived from less altered sediment (Spears and Segzin, 1985; Spears, 1987).

Differences in the response of the chlorite 14Å peak intensity to heat treatment were examined qualitatively and it was observed that vermiculite content (assumed to be higher with greater reduction in peak intensity) varies relatively smoothly, with gradational changes, throughout most of the section. Up to the top of E2c4, chlorite appears to be associated with a relatively high proportion of vermiculite. Over the next 2m a gradual decrease is seen and this lower proportion is maintained until an increase that occurs between 6m and 1m below the Arnsbergian-Chokierian Boundary. Higher levels of vermiculite apparently persist throughout the

H1a1 Marine Band and overlying claystone until a sharp decrease at the H1a2 Marine Band, a further increase at the H1a3 Marine Band, levels are then reduced up to the top of the section. These changes appear to occur in specific bands that are not related to marine conditions, even though the lower 14Å peaks after heat treatment are normally associated with the marine bands, and are likely to be a diagenetic effect.

3. STRONTIUM ISOTOPE RATIOS

Sr-isotope ratios were studied in order to assess whether they could provide further evidence for the completeness of the Stonehead Beck sequence and to calibrate the standard Sr seawater curve derived by Popp *et al.* (1986) for the Silesian, in particular the values for the Mid-Carboniferous Boundary. Although there is some debate, following studies on fish and inarticulate brachiopod skeletal phosphates, that Sr values may be diagenetically enriched/ depleted in conodonts, such alteration if it has occured, should not detract from the relative values of the Sr isotope ratios from the same section. Furthermore, these effects are thought to be most significant only in sediments with high CAI values or in situations where there has been considerable post depositional diagenesis (such as in carbonate or siliciclastic facies).

The values obtained (Figure 6) show continuity with the Sr curve derived from brachiopod data presented by Popp *et al.* (1986), suggesting that Sr enrichment is not significant in the Stonehead Beck samples. Furthermore the overlapping Sr values, either side of the Mid-Carboniferous Boundary at Stonehead Beck indicate that their is no evidence of a measurable time gap using this technique.

Sr-isotope stratigraphy is a valuable tool to use either to compliment biostratigraphical dating or to use where biostratigraphy is not providing the required resolution. The main sink for oceanic Sr is carbonate or phosphatic sediments, but the technique is not restricted to carbonate or phosphatic rocks because the Sr is concentrated in fossils with that composition. In most situations carbonate fossils are used, but in the Palaeozoic, conodonts having a phosphatic composition, can be used providing the CAI is low. In both carbonate and phosphatic fossils diagenetic alteration can alter the original $^{87}Sr/^{86}Sr$ ratio, particularly where such alteration is late in origin.

The results can be used in two ways: firstly the Sr ratio can be compared to a standard Sr seawater curve for a given time period, secondly, the differences between adjacent samples can indicate the extent of the time gap between them. The standard seawater curve for the Carboniferous is currently poorly known when compared to that for the Mesozoic and Cenozoic. The most comprehensive data was that of Burke *et al.* (1982) which illustrated the major trends of the seawater curve for the Carboniferous, but is not sufficiently detailed to allow its use for high resolution stratigraphy and most of the samples were whole rock ones. Peterman *et al.* (1970) and Veizer & Compston (1974) analysed calcitic fossils from a small number of samples, but did not take into account possible diagenetic alteration of the samples. Popp *et al.* (1986) summarised all of this data and added new data from carefully selected and unaltered brachiopods, although their stratigraphy was still only given in broad terms. A standard Sr seawater plot (Figure 6) can be derived from Popp *et al.* (1986) and includes data from the Stonehead Beck conodonts. This plot makes several stratigraphic assumptions and corrections which are summarised in the figure caption. The plot shows that the Carboniferous seawater Sr curve was rising steeply in the early Namurian, in contrast to the adjacent Viséan and late Namurian to Westphalian intervals. This steep rise is interesting because it immediately preceeds the Mid-Carboniferous Boundary faunal event and corresponds in time with the main onset of flysch deposits in Palaeotethys, which mark the final phases of the closure of the european part of this ancient ocean.

The Stonehead Beck samples were taken from nodular limestones (bullions) in the Nuculoceras nuculum (E2c3) and the Homoceras beyrichianum (H1b1) marine bands. These limestones are rich in conodonts and contain uncrushed ammonoids, and formed prior to the compaction of the surrounding claystone, where the ammonoids are crushed. Approximately 100 conodont specimens were analysed in total. The lower horizon (sample MPA 26024), lies 15.6m below the Arnsbergian/Chokierian boundary and contains *Gnathodus bilineatus, G. bilineatus bollandensis, Paragnathodus commutatus, P. monodosus* and *P. nodosus* (Riley *et al.*, 1987). This is a typical late Arnsbergian fauna. The higher horizon (sample MPA 26038), 15.7m above the Arnsbergian/ Chokierian boundary, has a fauna including *Declinognathodus noduliferus, D. inaequalis, D. lateralis* and *Neognathodus symmetricus* (Riley *et al.*, 1987). This is a typical early Chokierian fauna.

The $^{87}Sr/^{86}Sr$ values were 0.708188 ± 0.000008 (sample MPA 2604) and 0.708192 ± 0.000010 (sample MPA 26038). Comparison with the seawater Sr curve (Fig. 6) derived from Popp *et al.* (1986) shows that these samples are near the top of a rising curve and the slight increase in ratio from the lower to the higher sample is consistent with this feature. However, this increase is less than the margin of error, indicating a very close similarity in age, which im-

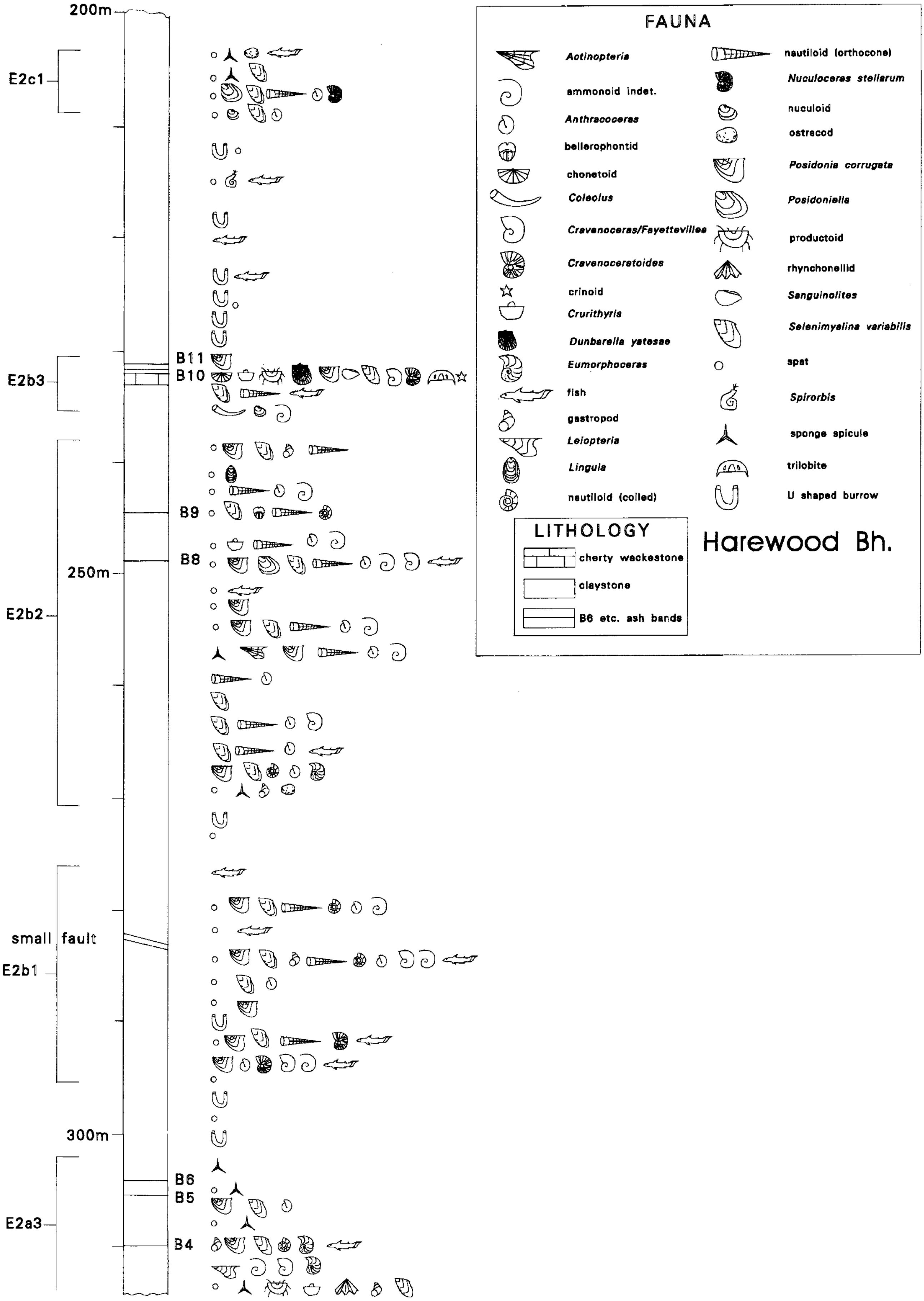

Fig. 7.- Graphic section of Harewood Bh. showing position of K-bentonites (ash bands) and marine bands.

plies that there is no evidence from this technique of a major gap across the Mid-Carboniferous Boundary at Stonehead Beck.

4. SHRIMP ZIRCON DATING

Although no suitable sources of contemporary zircons are available from the stratotypic interval exposed at Stonehead Beck, it was felt important to study such material from the closest biostratigraphically calibrated zircon sources available. A study was thus implemented on the ash bands preserved in the Arnsbergian of the Harewood Borehole [National Grid Reference SE 3220 4410], near Leeds, North Yorkshire (Figures 3 & 7). This was in order to obtain the first reliable chronometric date for the Mid-Carboniferous Boundary, and demonstrate the degree of time resolution achieved using the sequence stratigraphy derived from the ammonoid bearing marine bands. The results provide further evidence to support the importance of these marine bands as time lines and as a vehicle for calibrating the lower resolution conodont biostratigraphy upon which the Mid-Carboniferous Boundary is recognised.

The Special High Resolution Microprobe (SHRIMP) is a sophisticated analytical technique which allows the $^{206}Pb/^{238}U$ age of individual zircon crystals to be calculated. This technique is described in detail by Claoué-Long *et al.* (*in press*). One main advantage of the technique is that each growth increment in a crystal can be analysed, thus eliminating the effects of older polycyclic cores. In whole rock analytical techniques all increments are included and can give rise to an average date, which may be significantly older than the host rock which encloses the zircon.

As already noted the hemi-pelagic claystones in the British Namurian contain potassium bentonites (Trewin, 1968; Trewin & Holdsworth, 1972). These always occupy the same relative position to ammonoid horizons («marine bands») and are the result of airborne ash falls into the sea. Both A. Spears and R. Kanaris-Sotiriou (University of Sheffield) are currently studying the same samples as those submitted to the SHRIMP probe and preliminary results show that they are derived from relatively young magma chambers in an inter-plate setting. Details to support these conclusions will be presented in a forthcoming paper. The ashes are likely therefore to originate from island arc volcanics. Since northern Britain was in a back arc setting (Leader 1982, 1987) the most likely source were arcs associated with subduction on the margins of Palaeotethys, to the south of Britain. The ash bands thus contain zircons which are closely contemporaneous with the surrounding marine sediment.

No such ash bands have been located in the interval immediately adjacent to the Mid-Carboniferous Boundary as exposed at Stonehead Beck, which includes the Nuculoceras nuculum (E2c3) to Isohomoceras sp. nov. (H1b2) marine bands, or from the numerous borehole and outcrop sections known in the UK across this same interval. However, bentonites are well known in slightly older Arnsbergian rocks from around the Eumorphoceras yatesae (E2a3) Marine Band through to the Nuculoceras stellarum (E2c1) Marine Band (the type locality of *Nuculoceras stellarum* is in Stonehead Beck, upstream from the Mid-Carboniferous Boundary stratotype section). It was decided to investigate bentonites over this interval from a continuously cored borehole sequence in the same depositional basin as Stonehead Beck, in which there was absolute biostratigraphical control. The BGS Harewood Borehole [map reference SE 3220 4410], Harewood, North Yorkshire, 12km north northeast of Leeds and 36.5km east of Stonehead Beck, was chosen as a suitable source, the stratigraphy of which is given in Fig. 7. All the bentonite bands were sampled, and zircons released by heavy mineral separation techniques. Only two bentonites yielded suitable numbers of fresh zircon crystals for an accurate SHRIMP probe analysis to be made. The zircon dates obtained were as follows;

Sample BLL 1977, depth 304.10m, bentonite B6 of Trewin (1968), upper part of Eumorphoceras yatesae (E2a3) Marine Band, Arnsbergian Stage, 314.4 ± 4.6 Ma.

Sample BLL 1786, depth 248.68m, bentonite B8 of Trewin (1968), upper part of the Cravenoceratoides nitidus (E2b2) Marine Band, Arnsbergian Stage, 314.5 ± 4.6 Ma.

These dates were surprisingly younger than expected and provide the best chronometric calibration of the Mid-Carboniferous Boundary so far achieved. They contrast strongly with the most recent date suggested by Harland *et al.* (1990), who gave a date of 328 Ma for the base of the Chokierian. Indeed it now appears that it is the base of the Brigantian Stage (late Viséan) which is close to this age, based on preliminary SHRIMP probe analysis of zircons from an ash band in the P1b Ammonoid Zone of Germany, which gives an age around 325 Ma. When one considers the close tie of 311 ± 3.4 Ma for the Bolsovian (Westphalian C) Z1 Tonstein in Germany obtained both by Hess & Lippolt (1986) using 40Ar/39Ar techniques and by Claoué-Long *et al.* (*in press*) using the SHRIMP probe, it is clear that Silesian time was very short. Recalculations of subsidence curves, heat flow and stretching factors, for the Silesian of the Pennine Basin, such as those presented by Dewey (1982), are therefore necessary. The mean time interval represented by strata from the Eumorphoceras yatesae Marine Band to the Cambriense Marine Band is around 3.5 Ma. On average therefore the time interval represented between the base of each marine band in the Silesian is around 65,000 years, thus corroborating the long held view that marine bands can be treated as high resolution sequence stratigraphic time planes and that they are glacio-eustatically driven (Maynard & Leeder 1992). Clearly there is a significant advantage for a stratotype which displays marine bands, such as those at Stonehead Beck; not only do marine bands provide a high resolution sequence stratigraphical control on the first appearance of the conodont *Declinognathodus,* but they also provide significant insight into the rate of evolutionary and depositional processes across the Mid-Carboniferous Boundary. The entire outcrop at Stonehead Beck (E2c3 to H1b2) therefore represents an estimated 465,000 years and the critical boundary interval (E2c4 to H1a2) occupies 130,000 years. The marine faunal turnover across the Mid-Carboniferous Boundary appears therefore to have been astonishingly rapid and achieved within two glacio-eustatic cycles!

5. DISCUSSION

These new data presented herein, together with previously published reports, provide Stonehead Beck with the most thorough stratigraphical documentation of any of the candidate sections across the Mid-Carboniferous Boundary. It is also the only candidate section which contains a record of both the marine and terrestrial biostratigraphy.

Of the other two candidate sections, the following points are relavent:

The North American candidate section at Arrow Canyon is developed in a shallow water carbonate/clastic sequence, with depositional breaks, the stratigraphical extent of which is unclear. It also lacks ammonoid control, and as a result, refined calibration of the first appearance of the conodont *Declinognathodus noduliferus* is not possible. Furthermore there is overlap of conondonts characteristic of the *Gnathodus bilineatus* Zone with those of the *Declinognathodus noduliferus* Zone. In Britain such an overlap has only been found at basin margins (e.g. Brandon *et al.* ,*in press*) where there is known to be non-sequence and unconformity; elsewhere in the basins these conodont zones are mutually exclusive and show no overlap.

The Uzbekistan candidate sections at Gisar Ridge (Nigmadganov and Nemirovskaya, 1993), comprise two outcrops across the Mid-Carboniferous Boundary, each about 20m thick. These are termed Aksu-1 and Aksu-4, being exposed respectively on the north and south limbs of an anticline affecting a deep water, predominantly pelagic carbonate sequence. These sections have only recently been described, and only the conodonts have been described in detail. There is no information on the sedimentology or other faunal components, apart from the ammonoids. Two new conodont taxa have been described, namely *Gnathodus postbilineatus* and *Declinognathodus praenoduliferus,* which are considered by Nigmadganov and Nemirovskaya (1993) to represent part of a phylogentic continuum linking *Gnathodus bilineatus bollandensis* and *Declinognathodus noduliferus.* This evolutionary series was used as evidence that Gissar Ridge is the most complete candidate section.

Although no synonymies have been given by Nigmagdanov and Nemirovskaya (1993), this series of changes has been figured earlier on several occaisions, without the erection of new taxa. The change from *G. bilineatus bollandensis* to *G. postbilineatus,* for example, was illustrated by Higgins (1975, pl. 11, fig. 8) from the Cravenoceratoides nitidus (E2b2) Marine Band and then later from the *Nuculoceras nuculum* (E2c3 and E2c4) marine bands by Riley *et al.* (1987, p. 2 figs, 5-8, 12) and Varker *et al.* (1990, pl. 1, figs. 2-12). In each case these were described as modified *Gnathodus bilineatus bollandensis*, with much reduced platforms, which in turn had much reduced ornamentation. *Gnathodus postbilineatus* occurs in the Arnsbergian (*Eumorphoceras* Ammonoid Zone, E2) of the UK and would appear not to have the restricted range given to it by Nigmagdanov and Nemirovskaya (1993). At Stonehead Beck this species ranges from the E2c3 ammonoid horizon (the lowest available in this section) up to 2.1m below the Arnsbergian/Chokierian boundary, where forms typical of the *G. bilineatus* Zone disappear.

Declinognathodus praenoduliferus preceeds the entry of *D. noduliferus* and *D. laterlais* at both Aksu sections, where it also enters above any *Eumorphoceras* Zone ammonoids. *Declinognathodus praenoduliferus* has not been recognised at Stonehead Beck and presumably developed during the time represented by the 11.7m of the succession which occurs after the disappearance of the gnathodid faunas.

Declinognathodus praenoduliferus has, however, been seen in the *Isohomoceras subglobosum* faunas from Edale in Derbyshire, England (Higgins, 1975), from where it was included within *D. noduliferus inaequalis* and *D. (Streptognathodus) lateralis.* This new species can be regarded as the first representatives of *D. noduliferus.*

The early non-gnathodid conodont faunas in the *Homoceras* Zone (Chokierian,H1 to Alportian, H2) are so complex that a simple species concept is difficult to apply. It is necessary to consider total faunas. It is also difficult to separate the early declinognathodids, such as *D. noduliferus* and *D. lateralis* *symmetricus.* This burst of evolutionary activity subsided by Kinderscoutian times when generic and specific groups are much more distinct.

In view of the discrepencies known to occur in the range of *G. postbilineatus* and the difficulties associated with the *Homoceras* Zone conodont faunas, we conclude that the use of this evolutionary series as sole evidence for a complete boundary sequence should be treated with caution until the full stratigraphical range of all the taxa has been confirmed from other sections. In any event the Aksu sections similarly show overlap of the early and late Carboniferous conodont assemblages, which could once again suggest reworking across the boundary.

None of the Aksu ammonoids have been fully described and their preservation is poor (Nikolayeva & Nigmadganov, 1992; Nikoleyeva *in press*). They appear to show the typical syndepositional dissolution effects commonly seen in cephalopods which are preserved in condensed sequences of pelagic carbonates. Ammonoids are limited to only a few beds. Unique to Aksu-1 is the reported co-occurence of *Eumorphoceras* and *Proshumardites delepinei* Schindewolf, both early Carboniferous ammonoids, with the late Carboniferous *Isohomoceras* aff. *subglobosum* in one sample. Nikolayeva (pers comm. to NJR, 1992) suggested that this co-occurence is limited to one bedding plane. There is no precise control on the age of the *Eumorphoceras* and *Isohomoceras* faunas at Aksu-1, since the youngest early Carboniferous ammonoid, *Nuculoceras,* has not been recognised there, hence it is not possible to confirm that the *Eumorphoceras* assemblage is the youngest possible within the *Eumorphoceras* Ammonoid (E2) Zone. This co-occurence is suggestive of a reworked or condensed horizon and may account for the lack of *Nuculoceras.* From the adjacent Aksu-4 section, *Homoceras* sp., *Isohomoceras* and *Proshumardites delepinei* are reported to co-occur. *Isohomoceras* normally preceeds *Homoceras* (Riley, 1987) and their co-occurence with *Proshumardites* at Aksu 4 is also suggestive of a highly condensed or reworked assemblage. Again, as in Aksu-1, *Nuculoceras* is absent, and it is therefore not possible to determine the precise age of the early Carboniferous assemblage. Both Aksu sections fail to calibrate the upper range of *Isohomoceras,* since the position of *Reticuloceras* Zone faunas is not related to the section.

6. CONCLUSIONS

The Mid-Carboniferous Boundary Global Stratotype candidate section at Stonehead Beck is the most intensively studied candidate section over the boundary interval. The section has low thermal maturity, is tectonically undeformed and the geological setting is well known. There is no evidence of depositional breaks. It is the only candidate section where there is a combination of a marine and terrestrial biostratigraphical record and where the conodont distribution is constrained by the high resolution stratigraphical calibration of a full ammonoid and glacio-eustatic event stratigraphy (65,000 year intervals). The absolute geochronometric age is well constrained (314Ma) from the underlying K-bentonites.

When the Strontium seawater curve is plotted over the Mid-Carboniferous Boundary interval using the new geochronometric scale and Sr values obtained from the Stonehead Beck section, it shows a rapid increase in the $^{87}Sr/^{86}Sr$ ratio in the early Namurian, immediately prior to the Mid-Carboniferous Boundary event. The implications resulting from this increase in Sr ratio, which corresponds to the onset of widespread flysch depostion in the Variscan basins of Europe, have yet to be fully appraised, however, such data may provide clues to the processes governing the dramatic depositional and biostratigraphical changes associated the Mid-Carboniferous Boundary event, thus paving the way to future directions of research over this interval.

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