STRONTIUM ISOTOPES IN CONODONTS: DEVONIAN-CARBONIFEROUS TRANSITION, THE NORTHERN RHENISH SLATE MOUNTAINS, GERMANY

by

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(7 figures, 4 tables and 4 plates)

ABSTRACT.- A set of 51 $^{87}$Sr/$^{86}$Sr isotope measurements on biostratigraphically dated conodonts and brachiopods from the Devonian-Carboniferous transition of the northern Rhenish Slate Mountains yields a high resolution record for the $^{87}$Sr/$^{86}$Sr isotope curve. The sections Hasselbachtal, Oberrödinghausen, Öse and Riescheid at the Remscheid-Altena Anticline were selected because of their excellent stratigraphic control and a low degree of diagenesis. However, trace element studies and XRD analysis show that the francolite of conodonts, an unstable end-member in the system francolite-fluorapatite, is prone to diagenetic alteration. $^{87}$Sr/$^{86}$Sr of unaltered low Mg calcite of contemporaneous brachiopods corroborate a distinct enrichment in radiogenic $^{87}$Sr in the conodonts. The discussed $^{87}$Sr/$^{86}$Sr curve is therefore a secondary curve that nevertheless preserves to some degree the pattern of the original Sr paleo-seawater curve. The pattern of 3rd-order isotopic variations reaches its radiogenic maximum near the Devonian-Carboniferous boundary, coincident with a regression maximum. The biostratigraphic correlation of the sections Hasselbachtal, Oberrödinghausen and Öse is confirmed by $^{87}$Sr/$^{86}$Sr isotope stratigraphy. New conodont data show that the praesulcata Zone can be recognized in the Wockum Limestone at the Oberrödinghausen and Hasselbachtal sections.

INTRODUCTION

The Devonian-Carboniferous transition and the contemporaneous mass extinctions and overturn of the marine biosphere have been a subject of intensive studies for many years. This time interval, in many parts of the world, is characterized by a hiatus and/or a change in litho- and biofacies which may result in a lack of index fossils. Consequently, the exact position of the Devonian-Carboniferous (D/C) boundary and the precise age assessment of the hiatus are sometimes difficult to establish. Strontium isotope stratigraphy, combined with sequence stratigraphic investigation of these problematic sections (Van Steenwinkel, 1988), may therefore help with these stratigraphic assignments.

Secular variations in $^{87}$Sr/$^{86}$Sr of ancient sea water curve - as measured in carbonate or phosphatic fossils - are increasingly utilized as a new, relative dating tool in the Cenozoic. The resolution claimed is in the 10$^5$-10$^6$ years range (e.g. De Paolo & Ingram, 1985; Koepnick et al., 1985; Palmer & Elderfield, 1985; DePaolo, 1986; Hess et al., 1986; Rundberg & Smalley, 1989; Capo & DePaolo, 1990; Beets, 1991). Comparable studies for the Mesozoic and particularly for the Paleozoic are only in their infant stage (Popp et al., 1986; Brookins, 1988; Brand, 1991).

The scope and the aims of the present study are:

1. Reassessment of the conodont biostratigraphy of the Wockum Limestone, with the main emphasis on the first occurrence of Siphonodella praesulcata and Protoagnathodus meischneri;

2. Derivation of a biostratigraphically well controlled $^{87}$Sr/$^{86}$Sr isotope curve for the coeval seawater;

3. Evaluation of diagenetic alteration of conodont francolite, utilizing trace elements, XRD and comparison with $^{87}$Sr/$^{86}$Sr measurements on coeval low-Mg calcitic brachiopods;

4. High resolution correlation of the D/C boundary in sections Oberrödimghausen, Hasselbachtal and Øse, utilizing a multidisciplinary approach that combines biostratigraphy, sequence stratigraphy and Sr isotope stratigraphy.

GEOLOGY, SEQUENCE STRATIGRAPHY
AND STRUCTURAL SETTING

The Devonian-Carboniferous boundary sections of the northern limb of the Remscheid-Altena Anticline have been previously investigated by H. Schmidt (1924) and O.H. Schindewolf (1937). These authors, together with Vöhringer (1960), established the framework of litho- and ammonoid stratigraphy across the boundary in the northern Rhenish Massif. Available data on these sections have been compiled by Paproth & Strel (eds., 1982). The sedimentary succession and general stratigraphy are reviewed in Paproth (1986). Becker (1985) listed the new data that revise the ammonoid biostratigraphy and the dating for the Upper Devonian formations of the Hohenlimburg sheet. In terms of synsedimentary tectonic units, all localities are placed in the inversion structure 5 (see Paproth et al., 1986), which had been stabilized during the Givetian and subsequently experienced less thermal heating than the D/C boundary sections in the eastern Sauerland. Paleogeographically, the D/C boundary beds were deposited on a gently dipping slope north of the uplifted or emerged cores of the Remscheid-Altena and Ebbe Antclines. The southern margin of the Old Red Continent, considerably to the north of the investigated outcrop belt, had slight significance for the sedimentary history of the latter.

The Wockumian of the latest Famennian is characterized by greenish and less frequently red basinal shales, nodular shales and nodular limestones (Wockum Beds). The shale/limestone ratio decreases from Hasselbachtal to Oberrödimghausen (Wockum Limestone). The fauna is uniform and dominated by pelagic forms such as the ammonoids, nautiloids, ostracods and conodonts. The bentho is of low diversity and includes rhychnonellids (Planavatriostrium), trilobites, crinoids (Triacrinus), solitary rugose corals, gastropods and specialised pelecypods. The estimated water depth was about 100-200 m. Depending on the clay content of the limestones, there are differences in their diagenesis. At Hasselbachtal, limestones are completely recrystallized and microsparite and argonitic shells of cephalopods are dissolved. The same applies to most layers at Øse, but at Oberrödimghausen rich faunas with shells can be collected. Diagenetic differences between the three sections seem to be larger than the differences between most beds within the individual successions.

The nodular Wockum Limestone is capped by the black Wockum Shale (Kreb, 1979) with Cymaclymenia evoluta. This facies change, indicating a latest Famennian transgression, is the local expression of the global Hangenberg Event. The black shale is only
a few centimetres thick and is overlain by the greenish silty Hangenberg Shale with a very poor fauna. At Seiler, north of Iserlohn, and between Hasselbachtal and Öse, intercalations of coarser clastic channel sandstones and oolitic conglomerates are present. The Seiler Conglomerate, representing an incised valley deposit, has been deposited due to a major global regression immediately prior to the D/C boundary. At Oberfrödinghausen the equivalent strata are represented by only a few sandy shale layers. The D/C boundary at localities in the Remscheid-Altena Anticline coincides with a Type 1 unconformity or a lowstand fan deposits in the sense of Van Wagoner et al. (1988). At Hasselbachtal, a single oolitic limestone bed is present at the D/C boundary. The overlying Stockum Limestone is lithologically similar to the Carboniferous Hangenberg Limestone, the latter present in all sections. Faunal structures and biofacies of the Wockum and Hangenberg Limestones are comparable, though there is a clear change in taxonomic composition caused by the terminal Devonian global mass extinction. The Hangenberg Limestone is everywhere capped by black shales of the Lower Alum Shale Formation of Middle Tournaisian age that indicates a new major global transgression.

**CONODONT BIOSTRATIGRAPHY**

Following the early work (Voges, 1959, 1960; Ziegler, 1962, 1969), conodont zonation across the D/C boundary was revised by Sandberg et al. (1978), and Sandberg & Ziegler (1979, 1984). Dreesen et al. (1986) provide a good review. Conodont successions of the critical time interval for the sections in Sauerland have recently been described by Clausen et al. (1989a, b). Two major problems will be debated:

1. The lowermost entry of Siphonodella prae-
sulcata that defines the base of the Praesulcata Zone, and of Protonathodus meischneri, the latter an alternative index species in the Wockum Limestone facies. Also of interest is the precise dating of the Praesulcata zonal base in terms of cephalopod stratigraphy.

2. The utility of the Middle Praesulcata Zone, a zone that is defined only by the disappearance of Paltatolepis gracilis gonioclymeniae. This species seemingly disappears at various levels in terms of ammonoid zonation (Ziegler, 1962; contra Eickhoff, 1972; contra Clausen et al., 1989a).

**CONODONT GEOCHEMISTRY**

The most complete study of conodont geochemistry has been made by Pietzner et al. (1968). They concluded that conodonts consist of carbonate apatite, approximating compositionally the mineral francolite. Traces of at least 39 chemical elements have been identified in a variety of positions within the hard parts of conodonts. Some chemical features, such as the cerium anomaly for REE (Wright et al., 1984) or Nd and Sr isotope ratios (Kovach, 1980; Kato & Jacobsen, 1987; Shaw & Wasserburg, 1985), gained considerable significance for interpretation of ambient conditions for parental water bodies. Conodonts, because they yield a high resolution stratigraphy for the Paleozoic, appear to be particularly suitable material for refinement of the 87Sr/86Sr curve for coeval sea water. The 87Sr/86Sr ratio is incorporated into conodonts without any isotopic fractionation. However, diagenesis and metamorphism of organic (Epstein et al., 1977; Königshof, 1991) and inorganic (Burnett, 1988; Ebneth, 1991; Kürschner, 1991) components of conodont elements may result in significant changes to this original isotopic ratio.

**ANALYTICAL METHODS**

**PREPARATION OF CONODONT SAMPLES**

About 2000 conodonts were isolated from 61 samples collected in the four sections. All conodont samples are stored at the Geological Institute of the Ruhr University in Bochum. The conodont biostratigraphic age assignment for the Upper Devonian follows Sandberg & Ziegler (1984), and for the Lower Carboniferous follows Sandberg et al. (1978) and Lane et al. (1980). Samples were usually rich in conodonts with about 50 elements per kg. About 1-2 kg of limestone was dissolved in ≤ 10 % acetic acid (95 % tech. acetic acid plus distilled water). The insoluble residues were sieved using a 125 µm sieve, washed carefully with distilled water and dried at 50°C. Conodonts were handpicked and cleaned in an distilled water ultrasonic bath for as long as required to remove adhering sediment particles, monitored using a 64x as magnification.

**87Sr/86Sr MEASUREMENTS**

In order to exclude diagenetic effects that derive form the variable content of white matter in the
Table 1. $^{87}$Sr/$^{86}$Sr of late Devonian and early Carboniferous conodonts and brachiopods

<table>
<thead>
<tr>
<th>Sample</th>
<th>Age</th>
<th>Material</th>
<th>$^{87}$Sr/$^{86}$Sr ratio +/- 2σ</th>
</tr>
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<tbody>
<tr>
<td>I Oberrödtinghausen section</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>OR15/13*</td>
<td>Sandbergi Zone (T)</td>
<td>Polygn. sp.</td>
<td>0.708463 +/- 0.000012</td>
</tr>
<tr>
<td>OR15/13</td>
<td>Sandbergi Zone (T)</td>
<td>Polygn. sp.</td>
<td>0.708445 +/- 0.000010</td>
</tr>
<tr>
<td>OR14/8</td>
<td>Sandbergi Zone</td>
<td>Polygn. sp.</td>
<td>0.708395 +/- 0.000010</td>
</tr>
<tr>
<td>OR13/10</td>
<td>Sandbergi Zone</td>
<td>Polygn. sp.</td>
<td>0.708370 +/- 0.000017</td>
</tr>
<tr>
<td>OR13/10*</td>
<td>Sandbergi Zone</td>
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<td>0.708470 +/- 0.000014</td>
</tr>
<tr>
<td>OR12/12*</td>
<td>Sandbergi Zone</td>
<td>Polygn. sp.</td>
<td>0.708370 +/- 0.000040</td>
</tr>
<tr>
<td>OR10/5*</td>
<td>Upper Duplicata Zone</td>
<td>Polygn. sp.</td>
<td>0.708393 +/- 0.000023</td>
</tr>
<tr>
<td>OR7/18*</td>
<td>Lower Duplicata Zone (T)</td>
<td>Polygn. sp.</td>
<td>0.708464 +/- 0.000010</td>
</tr>
<tr>
<td>OR7/18</td>
<td>Lower Duplicata Zone (T)</td>
<td>Polygn. sp.</td>
<td>0.708426 +/- 0.000022</td>
</tr>
<tr>
<td>OR5/5</td>
<td>Lower Duplicata Zone</td>
<td>Polygn. sp.</td>
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</tr>
<tr>
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<td>OR2/12</td>
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<td>0.708353 +/- 0.000015</td>
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<tr>
<td>OR1/7*</td>
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<td>Polygn. sp.</td>
<td>0.708445 +/- 0.000016</td>
</tr>
<tr>
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<td>0.708432 +/- 0.000017</td>
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<td>B1.1</td>
<td>Middle Praesulcata Zone</td>
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<td>B1.3</td>
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<td>Bisp. sp.</td>
<td>0.708387 +/- 0.000016</td>
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<tr>
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<td>Middle Praesulcata Zone</td>
<td>Bisp. sp.</td>
<td>0.708367 +/- 0.000015</td>
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<td>B3</td>
<td>Middle Praesulcata Zone (B)</td>
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<td>0.708420 +/- 0.000008</td>
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<td>B4</td>
<td>Lower Praesulcata Zone (T)</td>
<td>Bisp. sp.</td>
<td>0.708473 +/- 0.000011</td>
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<td>Lower Praesulcata Zone</td>
<td>Bisp. sp.</td>
<td>0.708502 +/- 0.000017</td>
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<td>B6</td>
<td>Lower Praesulcata Zone</td>
<td>Bisp. sp.</td>
<td>0.708423 +/- 0.000019</td>
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<td>B9</td>
<td>Lower Praesulcata Zone</td>
<td>Bisp. sp.</td>
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<td>Lower Praesulcata Zone</td>
<td>Bisp. sp.</td>
<td>0.708478 +/- 0.000017</td>
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<td>B13</td>
<td>Lower Praesulcata Zone</td>
<td>Bisp. sp.</td>
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<td>B15</td>
<td>Lower Praesulcata Zone</td>
<td>Bisp. sp.</td>
<td>0.708447 +/- 0.000013</td>
</tr>
<tr>
<td>B16</td>
<td>Lower Praesulcata Zone</td>
<td>Bisp. sp.</td>
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<td>B17</td>
<td>Lower Praesulcata Zone (B)</td>
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<td>0.708443 +/- 0.000014</td>
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<td>B20</td>
<td>Upper Expanza Zone</td>
<td>Bisp. sp.</td>
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<td>B23</td>
<td>Upper Expanza Zone</td>
<td>Bisp. sp.</td>
<td>0.708561 +/- 0.000012</td>
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<td>OR6</td>
<td>Upper Expanza Zone</td>
<td>Bisp. sp.</td>
<td>0.708409 +/- 0.000018</td>
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<td>Ba55</td>
<td>Upper Postera Zone</td>
<td>Polygn. sp.</td>
<td>0.708465 +/- 0.000017</td>
</tr>
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<td>OR5</td>
<td>Lower Postera Zone</td>
<td>Polygn. sp.</td>
<td>0.708372 +/- 0.000014</td>
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<tr>
<td>Ba15</td>
<td>Lower Trachytera Zone</td>
<td>Polygn. sp.</td>
<td>0.708333 +/- 0.000013</td>
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<tr>
<td>OR3</td>
<td>Uppermost Marginifera Zone</td>
<td>Polygn. sp.</td>
<td>0.708282 +/- 0.000017</td>
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<tr>
<td>OR2</td>
<td>i. Upper Marginifera Zone</td>
<td>Polygn. sp.</td>
<td>0.708328 +/- 0.000018</td>
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<td>OR1</td>
<td>Lower Marginifera Zone</td>
<td>Polygn. sp.</td>
<td>0.708455 +/- 0.000017</td>
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</table>

II Hasselbachtal section

<table>
<thead>
<tr>
<th>Sample</th>
<th>Age</th>
<th>Material</th>
<th>$^{87}$Sr/$^{86}$Sr ratio +/- 2σ</th>
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<td>Ha69</td>
<td>Duplicata Zone</td>
<td>Polygn. sp.</td>
<td>0.708303 +/- 0.000014</td>
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<td>Ha78</td>
<td>lower Sulcata Zone</td>
<td>Polygn. sp.</td>
<td>0.708447 +/- 0.000013</td>
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<td>Ha81</td>
<td>lower Sulcata Zone</td>
<td>Polygn. sp.</td>
<td>0.708487 +/- 0.000022</td>
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<td>Ha83</td>
<td>lower Sulcata Zone</td>
<td>Polygn. sp.</td>
<td>0.708413 +/- 0.000015</td>
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<td>Ha84</td>
<td>lower Sulcata Zone</td>
<td>Polygn. sp.</td>
<td>0.708618 +/- 0.000016</td>
</tr>
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<td>HaLE</td>
<td>Middle Praesulcata Zone</td>
<td>Bisp. sp.</td>
<td>0.708384 +/- 0.000014</td>
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<td>Ha44B</td>
<td>Lower Praesulcata Zone</td>
<td>Planovariostrum richteri</td>
<td>0.708184 +/- 0.000015</td>
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sample, two to three monogenic condont elements were combined for strontium isotope analysis. Experimental procedure (Buhl et al., 1991) was as follows: Samples were dissolved in 5 ml of 2.5 N supra pure HCl for two hours at room temperature. After evaporation, strontium was extracted via 4.5 ml quartz glass exchange columns filled with Bio Rad AG50Wx8 ion-exchange resin, and eluted with 2.5 N supra pure HCl. The eluant containing most of the elemental Sr was dried and loaded on single Ta filaments using a loading liquid of Ta₂O₅, HNO₃, HF, H₃PO₄, and water (Birck, 1986). Samples were analysed on a Finnigan Mat 262 5-collector mass spectrometer. One aliquot of NBS SRM 987 was loaded with each set of twelve samples. Its mean ⁸⁷Sr/⁸⁶Sr isotope ratio during the course of this study was 0.710243±0.00005. The data were not corrected for Rb, since a realistic Rb fractionation can not be calculated. ⁸⁷Sr/⁸⁶Sr ratios were normalized to a 86Sr/⁸⁶Sr ratio of 0.1194. The 2σ for single sample varied between 8-40×10⁻⁶ with an average of 16×10⁻⁶. A set of six samples was analysed at the Isotope Geology Laboratory of the Free University Amsterdam. After a similar chemical preparation, these samples (indicated by star in Table 1) were analysed on a Finnigan MAT 261 fixed multicolonlector mass spectrometer. The measured ⁸⁷Sr/⁸⁶Sr ratio of the Amsterdam NBS SRM 987 was 0.710245±0.000013.

TRACE ELEMENT AND XRD ANALYSIS

Samples of condonts weighing 2-5 mg were prepared for trace element analyses by ICP atomic absorption spectrophotometry. The samples were analysed for Na, Sr, and Mg on a Phillips PU 7000 ICP AES at the Ruhr University (samples analysed at the Dept. of Earth Science in Utrecht are indicated by a star in Table 1). Semiquantitative CO₂ determinations were made by a method described by Gulbradsen (1970). For XRD analyses 1 to 2 mg of powdered sample were utilized and the measurements were performed at the Ruhr University.

RESULTS

SECTIONS AND THEIR CONODONT BIOSTRATIGRAPHY

The Hasselbachtal section

The Hasselbachtal section is situated at the northern flank of the Hasselbachtal Valley north of the town Hagen-Hohenlimburg (Sheet 4611 Hohenlimburg R.²⁵07000 H.²¹94220). The outcrop was described for the first time as a D/C boundary section by Schmidt (1924) and Groos-Uffenorde & Uffenorde (1974) studied its condont and ostracod fauna. This section later became important because of its mixed siliclastic/carbonate lithology that is particularly suitable for the study of miospores, ammonoids and condonts (Becker et al., 1984). Because of its rich palynoflora, the "International Working Group on the Devonian-Carboniferous Boundary", meeting in 1988 in Courtmacsherry, nominated this section for an international D/C boundary parastratotype that should enable correlation of terrestrial with marine facies. Recently, the ammonoid fauna was studied by Becker (1985, 1988) and the combination of all faunal elements yields a very detailed correlation with other boundary sections (Becker, 1992).

The condont fauna in the D/C boundary interval of the Hasselbachtal section comprises 19 taxa. Their distribution, complemented by the data from Becker et al. (1984), is depicted in Figure 1. The oldest bed, Ha18, of the Wocklum Beds yielded a rich condont fauna with Bispathodus costatus, Palmatolepis gracilis gracilis, Pa. gracilis sigmoidealis, Pa. gracilis gonioalymena, Polygnathus symmetricalus and Siphonodella praesulcata, which characterize the Early Praesulcata Zone. The top of the Wocklum Beds with Pa. gracilis gracilis, Pa. gracilis sigmoidealis, Pa. gracilis expansa, Bi. costatus, Bi. ultimus, Bi. ziegleri and Branmehla suprema indicates the lower Middle Praesulcata Zone. No condonts have been found in Bed Ha85, the uppermost, carbonate, part of the Hangenberg Shale. However, this level yielded juvenile specimen of Acutimitoceras cf. prorsum, pyritized Ammonitellas, Sphaerorhoceras sp., juvenile gastropods (Naticopsis, div. gen.), pelecypods and plant macrofossils.

In accord with the data of Becker et al. (1984), the first Siphonodella sulcata occurs together with Protognathodus kuehni in bed Ha84, thus marking the base of the Carboniferous (see Fig. 1). The rich condont fauna contains also Bi. costatus*, Bi. stabilis*, Bi. ziegleri*, Pa. gracilis gracilis*, Pa. gracilis expansa*, Pol. comm. communis, Protognathodus collinsoni, Ptogn. kockelii and Siphonodella prae- sulcata (*: reworked). Siph. praesulcata from the Bed Ha78 at the top of the metabentonite, indicates that this bed still belongs to the lower part of the Sulcata Zone. Bed Ha72, 85 cm above the D/C boundary, yielded the oldest specimen of Siph. duplicata M1 together with Pseudopol. dentilineata. Thus the boundary between the Sulcata and the Lower Duplicata Zone falls into the interval between
<table>
<thead>
<tr>
<th>Depth</th>
<th>Samples</th>
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</tr>
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<td>H281</td>
<td></td>
<td>Tourmaisian</td>
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<tr>
<td>0.6</td>
<td>H263</td>
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<td>5.5</td>
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(1) Becker et al. (1984): □
(2) Kürschner et al. (this study): ○
(1) & (2): ★

Fig. 1.: Conodont Stratigraphy of the Hasselbachthal section (complemented by Becker et al., 1984).
Fig. 2. - Conodont-Stratigraphy of the Oberrödinghausen section.
(1: Early Marginifera Zone; 2: Late Marginifera Zone; 3: Latest Marginifera Zone; 4: Trachytera Zone; 5: Early Postera Zone).
the Beds Ha72 and Ha78. The *Sulcata* Zone is about 0.7 m thick. The oldest possible age for the youngest sample from the Hangenberg Limestone, Bed Ha69 that contains *Pseudopol. triangulus inaequalis* and *Siph. duplicata* M2, is the Lower *Duplicata* Zone.

**The Obergerdinghausen section**

The section is exposed on the left bank of the Höhne Valley in a railway cut about 450 m south of the Obergerdinghausen (Sheet 4613 Balve R:25°19400 H:51°69100). Ammonoid faunas were described by Schmidt (1924), Schindewolf (1937), Vöhinger (1960) and Paproth & Streel (1970). Micropaleontological studies on conodonts were published by Bischoff (1957) and Voges (1959, 1960) and on foraminifers and conodonts by Eickhoff (1973). Paproth & Streel (1970) and Higgs & Streel (1984) investigated the miospore assemblages in this section. Ziegler (1962) established the standard for the late Devonian conodont zonation in the nearby road section. A recent paper by Weddige et al. (1990) deals with the Famennian conodont biofacies. The D/C boundary was defined at the base of the Hangenberg Limestone in the railway cut during the 1934 "First International Congress of Carboniferous Stratigraphy and Paleontology" in Heerlen, and it is coincident with the first occurrence of the ammonoid *Gattendorfia subinvoluta*.

The stratigraphic distribution of the conodont fauna, comprising in total 68 taxa, is depicted in Figure 2. In the railway cut, the base of the *Wocklumeria* Stage is located at the base of Bed 23 and yielded *Bisp. costatus*, *Brannemehla suprema*, *Pa. gracilis expansa* and *Pa. grac. gonioclymeniae*. *Protognathodus meischneri* occurs in Bed 20, 70 cm above the base of the Wocklum Limestone. *Siphonodella praesulcata* enters the record just about 40 cm higher in Bed 17 and this indicates the base of the Early *Præsulcata* Zone. Consequently, the lower part of the *Wocklumeria* Stage (Bed 23 to Bed 18) is assigned to the Late *Expansa* Zone. *Bi. ziegleri* and *Bi. ziegleri müssenbergensis* (Bed 7) as well as *Pseudopolygnathus marburgensis trigonicus* (Bed 5) follow successively the *Siphonodella praesulcata* in the upper part of the Early *Præsulcata* Zone. The last occurrence of *Pa. gracilis gonioclymeniae* in Bed 4 delineates the top of the Early *Præsulcata* Zone. The base of the Hangenberg Limestone (OR1/7) is characterized by *Siphonodella sulcata*, *Siph. præsulcata*, *Protogn. kuehni*, *Protogn. kockeli*, *Protogn. collinsoni*, *Pol. purus* and *Bi. ziegleri* (reworked). *Siph. præsulcata* has its last occurrence in the following Bed OR2/12, indicating that this is the top of the lower part of the *Sulcata* Zone. *Siph. duplicata* M1 enters the record 30 cm above the base of the Hangenberg Limestone (bed OR4/6) defining the lower limit of the Lower *Duplicata* Zone. It is followed by *Siph. duplicata* M2 and *Pseudopolygn. triangulus inaequalis* in Bed OR5/5. *Siphonodella cooperi* and *Siph. duplicata* (sensu Hass) have their first occurrence in Bed OR8/5 indicating the basis of the Upper *Duplicata* Zone. *Siph. sandbergi* marks the base of the Sandbergi Zone in Bed 13/10.

**The Öse section**

The Öse section is located in an abandoned quarry at the northern side of the Bundesstrasse B7 between Hemer and Menden (Sheet 4512 Menden R:29°27170 H:51°24200). The sedimentology and microfacies of the D/C boundary beds were studied by Keupp & Komp (1984). Higgs & Streel (1984) investigated the palynoflora.

Two samples, A1 and A2, were taken from the upper part of the Hangenberg Sandstone. The lower one yielded *Protogn. meischneri* and some pectiniform conodont elements. The upper one was somewhat richer in conodonts, with *Pol. communis* and *Protogn. kockeli*. The lowermost Bed B of the Hangenberg Limestone was characterized by *Pol. purus* and *Protogn. kuehni*, indicating its assignment to the *Sulcata* Zone.

**The Riescheid section**

The Riescheid section was chosen in order to complete the stratigraphic column into the lower Viséan. This section is located in an abandoned railroad cut in Wuppertal-Barmen (Sheet 4709 Barmen, R 83640 H 84600). It was described for the first time by Paeckelmann (1928). Franke et al. (1975), Paproth & Zimmerle (1980) and Zimmerle et al. (1980) focused their studies on sedimentological, mineralogical and geochemical aspects of the well exposed Dinantian basinal Kulm facies. The conodont fauna was studied by Lane et al. (1980). Higgs & Streel (1984) evaluated the palynology of the D/C transition. The uppermost Famennian and Dinantian sequences are characterized by a typical succession of black shales, lydites ochers, allochatic limestones, nodular limestones, and siliceous limestones, as well as tuffaceous volcanioclastics and phosphorite nodules (Zimmerle et al., 1980).

Bed 77/78 yielded *Gnathodus semiglaber* and *Scaliognathus anchoralis*, indicating the *Anchoralis*
Table II. $^{87}$Sr/$^{86}$Sr of Late Devonian and Carboniferous conodonts

<table>
<thead>
<tr>
<th>Sample</th>
<th>Age</th>
<th>Material</th>
<th>$^{87}$Sr/$^{86}$Sr ratio +/- 2σ</th>
</tr>
</thead>
<tbody>
<tr>
<td>III Öse section</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ÖseB</td>
<td>lower Sulcata Zone</td>
<td>Protagnathodus kuehni</td>
<td>0.708494 +/- 0.000020</td>
</tr>
<tr>
<td>ÖseA2</td>
<td>Upper Praesulcata Zone</td>
<td>Protagnathodus kockeli</td>
<td>0.708537 +/- 0.000017</td>
</tr>
<tr>
<td>IV Riescheid section</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R188</td>
<td>Texanus Zone</td>
<td>Gnathodus sp.</td>
<td>0.708063 +/- 0.000014</td>
</tr>
<tr>
<td>R177/78</td>
<td>Anchoralis-latus Zone</td>
<td>Gnathodus sp.</td>
<td>0.708122 +/- 0.000012</td>
</tr>
<tr>
<td>R177/78</td>
<td>Anchoralis-latus Zone</td>
<td>Gnathodus sp.</td>
<td>0.708077 +/- 0.000013</td>
</tr>
</tbody>
</table>

Table III. Wet chemical analysis of unaltered conodonts.
(Pietzner et al., 1968)

<table>
<thead>
<tr>
<th>Component</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>0.16%</td>
</tr>
<tr>
<td>Insoluble residue</td>
<td>1.59%</td>
</tr>
<tr>
<td>Loss on ignition</td>
<td>0.25%</td>
</tr>
<tr>
<td>Total-CO₃</td>
<td>2.00%</td>
</tr>
</tbody>
</table>

PO₄ | 53.30% |
Ca  | 37.28% |
Sr  | 0.40%  |
REE | 0.42%  |
Al  | 0.09%  |
Fe  | 0.04%  |
K   | 0.03%  |
Na  | 0.62%  |
H₂O | 2.95%  |
CO₃ | 1.84%  |
F   | 2.60%  |

The occurrence of Gnathodus texanus and Gnathodus semiglaber assigns the subsequent Bed 88 to the Texanus Zone of the earliest Viséan.

Isotopic and Elemental Systematics

$^{87}$Sr/$^{86}$Sr isotope data

The strontium isotope data, a set of 51 analyses with emphasis on the D/C boundary interval, are summarized in Tables I and II. In Figure 3, all measured $^{87}$Sr/$^{86}$Sr ratios are plotted and compared to the MOBIL curve (Burke et al., 1982) and the strontium isotope curve of Holser (1984). Some replicates show differences in the $^{87}$Sr/$^{86}$Sr ratio of less than 4x10⁻⁶. The overall third order trend (in the sense of Veizer, 1989) depicts a slightly curved band, with its width determined by higher order fluctuations. The inflection point is located within the latest Famennian (0.7085). In the late Famennian and early Dinantian, the depicted curve indicates fourth order oscillations, with a frequency of about 1 to 2 Ma and an amplitude of about 6x10⁻⁵. A magnification of the strontium isotope curve across the D/C boundary interval is shown in Figure 4. These high resolution measurements within the Wocklum and Hangenberg Limestone in the Oberrödinghausen section detect still higher order fluctuations, of the fifth order. Overall, the high resolution Sr isotope curve may have a fractal structure, perhaps reflecting a non-linear dynamics of a chaotic natural system (Veizer, 1989). Note, however, that the $^{87}$Sr/$^{86}$Sr of the two brachiopods (Planovatirostrum richteri), from the Bed Ha18B (base of the Early praesulcata Zone at Hasselbachtal) and the Bed Ha44B, 0.9 m higher up in the Wocklum Beds, are considerably less radiogenic at 0.70832 and 0.70818, respectively (Fig. 3). The difference between these two brachiopod values (1.3x10⁻⁵) is comparable to the amplitude of the above discussed higher order fluctuations for conodonts (Fig. 4). This brachiopod/conodont discrepancy will be discussed in greater detail in the subsequent text.

Disregarding, for the time being, the discrepancy, it appears that stratigraphically equivalent conodonts have comparable Sr isotopic ratios, regardless of the sampled section (Fig. 4). A prominent feature is the radiogenic nature (≥ 0.7085) of conodonts at the D/C transition (ÖseA2: 0.70854; Ha84: 0.70862). In order to avoid the possibility of analyzing the reworked Devonian specimens, the measured earliest Carboniferous conodonts at Hasselbachtal and Öse were only of the species Protagnathodus kuehni (Ha84; ÖseB). The measured value from the base of the Hangenberg Limestone at Oberrödinghausen (OR1/7: 0.70843) agrees well with the $^{87}$Sr/$^{86}$Sr ratio from the Bed Ha78 at Hasselbach (0.708447). The isotope curve decreases to a value of 0.70806 at the Tournaïsian/Viséan transition in the Riescheid section (Fig. 3).
Table IV.- Trace element data of conodonts

<table>
<thead>
<tr>
<th>Sample</th>
<th>Locality</th>
<th>CAI</th>
<th>Ca(%)</th>
<th>PO₄(%)</th>
<th>Na(ppm)</th>
<th>Sr(ppm)</th>
<th>Mg(ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bel'</td>
<td>Manitoban Bay</td>
<td>1</td>
<td>37.1</td>
<td>36.88</td>
<td>6044</td>
<td>3121</td>
<td>300</td>
</tr>
<tr>
<td>E105</td>
<td>Prüm/Eifel</td>
<td>1.5</td>
<td>30.5</td>
<td>41.18</td>
<td>3055</td>
<td>2896</td>
<td>55</td>
</tr>
<tr>
<td>OR'</td>
<td>Oberrödingenhausen</td>
<td>2.5</td>
<td>38.8</td>
<td>39.00</td>
<td>3387</td>
<td>3041</td>
<td>152</td>
</tr>
<tr>
<td>Ob-6-89</td>
<td>Oberscheid</td>
<td>2.5</td>
<td>37.9</td>
<td>55.69</td>
<td>3290</td>
<td>3558</td>
<td>2674</td>
</tr>
<tr>
<td>Ha-1-88</td>
<td>Hadamar</td>
<td>3</td>
<td>34.6</td>
<td>55.13</td>
<td>1938</td>
<td>2027</td>
<td>155</td>
</tr>
<tr>
<td>5514</td>
<td>Hadamar</td>
<td>3</td>
<td>37.1</td>
<td>56.09</td>
<td>1354</td>
<td>2336</td>
<td>621</td>
</tr>
<tr>
<td>R1</td>
<td>Riescheid</td>
<td>4</td>
<td>37.2</td>
<td>55.00</td>
<td>2687</td>
<td>2465</td>
<td>93</td>
</tr>
<tr>
<td>BB'</td>
<td>Burgberg. E-Sauerl.</td>
<td>5</td>
<td>39.7</td>
<td>39.42</td>
<td>2400</td>
<td>2374</td>
<td>128</td>
</tr>
<tr>
<td>Ni</td>
<td>Niederhof. E-Sauerl.</td>
<td>5</td>
<td>36.6</td>
<td>59.24</td>
<td>2620</td>
<td>2774</td>
<td>846</td>
</tr>
<tr>
<td>Me-1-89</td>
<td>Medebach</td>
<td>6</td>
<td>31.4</td>
<td>44.76</td>
<td>983</td>
<td>2975</td>
<td>1352</td>
</tr>
<tr>
<td>Rb-6-89</td>
<td>---</td>
<td>6</td>
<td>34.6</td>
<td>50.58</td>
<td>1500</td>
<td>2750</td>
<td>2385</td>
</tr>
<tr>
<td>Wei-1-89</td>
<td>Harz</td>
<td>7</td>
<td>34.5</td>
<td>50.41</td>
<td>≤50</td>
<td>2983</td>
<td>2629</td>
</tr>
</tbody>
</table>

Fig. 3.- $^{87}$Sr/$^{86}$Sr ratios of Late Devonian and Early Carboniferous conodonts and brachiopods (all data normalized to NBS SRM 987 of 0.710240). The mean 2σ of a single measurement is 1.6×10⁻⁵.
Trace element and XRD analysis

Well preserved conodonts consist of carbonate fluorapatite, approximately of the composition of the mineral francolite. Their mean chemical composition is listed in Table III. Most studies of diagenetically altered and metamorphosed conodonts concentrate on their colour variations, which are quantified by the CAI index (e.g. Epstein et al., 1977; Rejejebian et al., 1987; Königshoff, 1991). Conodont francolite is an unstable phase of the system francolite-fluorapatite and is prone to diagenetic alteration. In analogy to sedimentary phosphate, this leads to a decrease in sodium (Burnett, 1988). Our trace element data, CAI, and localities are listed in Table IV. Unaltered conodonts contain, in accordance with Pietzner et al. (1968), about 5000 ppm Na. With increase in CAI, the francolite is gradually depleted in sodium as well as strontium (Figs. 5,6), the depletion in Na being more pronounced. Note, however, that hydrothermally and contact-metamorphosed conodonts show an increase in Sr and Mg contents, a feature probably inherited from hydrothermal brines.

Unaltered conodonts contain about 1.8 weight % CO₂ (Pietzner et al., 1968; Wright et al., 1990). In analogy to sedimentary phosphates, conodonts should show gradual decarbonation with a progressive increase in diagenesis. The ΔS6 of the pck (410) and (004) has been shown by Gulbrandsen (1970) to be a linear function of the CO₃ content of the apatite. Powdered sample of conodonts were examined by X-ray diffraction and the angular difference between the two X-ray diffraction peaks (410) and (004) measured. These data show that even the conodonts of the CAI 2-3 (locality Oberördinghausen) are already strongly depleted in CO₂ (by about 1.1 weight %).

DISCUSSION AND INTERPRETATION OF GEOCHEMICAL DATA

For comparison with the previously published ⁸⁷Sr/⁶⁶Sr isotope curves, all data are normalized to NBS SRM 987 of 0.710243. The shape of the late Devonian to early Carboniferous ⁸⁷Sr/⁶⁶Sr MOBIL curve (Burke et al., 1982) and its derivative, the Holser (1984) curve, which incorporates the conodont data of Kovach (1980) is in good agreement with our trend, but the present data are generally more radiogenic. Our measurements and the MOBIL data agree well in the middle Famennian and at the Tournaisian/Viséan transition, with ⁸⁷Sr/⁶⁶Sr of 0.70835±0.00006 and 0.70806±0.00002, respectively (Fig. 3). Between these two points, the interpo-
lated MOBIL and our curves diverge. Our overall trend depicts an arc with the most radiogenic values in the latest Wockumerian Stage, exceeding the interpolated curves by about 2×10⁻⁴. On the other hand, the measurements on two well preserved contemporaneous brachiopods fall at, or below, the interpolated curves.

The above disparities are partly due to the fact that the age assignments of samples on the Mobil set cannot be read precisely from the published, stratigraphically compressed, curve. The other reason is, however, that conodonts likely incorporated some radiogenic ⁸⁷Sr during their post-depositional history, thus shifting the overall trend towards more radiogenic values. The pervasiveness of this effect is difficult to judge, but its reality has been confirmed by a representative set of Middle and lower Upper Devonian brachiopods/conodont pairs (Ebbeh, 1991; Diener, 1991; Ebneb et al., 1991). Yet, surprisingly, samples from stratigraphically contemporaneous, but physically separated Beds in the sections Hasselbachal, Oberördinghausen and Óse yield comparable Sr isotope ratios (Fig. 4). This suggests that, despite the radiogenic shift, some measure of the internal structure of the curve (or rather a band) may still be preserved, perhaps because of a comparable degree of ⁸⁷Sr enrichment in most conodont samples. Modelling of Sr isotope and elemental exchange between coeval brachiopods, conodonts and enclosing rocks (Ebbeh, 1991) suggests that conodonts are about 1/3 equilibrated with enclosing rocks. Consequently, if the isotopic difference between original sea water and the present day matrix carbonate is not to large, the conodont curve may still mimic lower order fluctuations in the original sea water curve. In contrast, for a large difference, the diagenetic shift overrides any vestiges of the original fluctuations. If this interpretation is correct, some third (and perhaps also higher) order oscillation patterns may still be real despite the overall shift of the band (Fig. 3). Similar fluctuations for the Devonian were observed also by Ebbeh et al. (1991).

The published second order - 10⁻⁷a- sea level curve (in the sense of Vail et al., 1977) (e.g. Johnson et al., 1985; Ross & Ross, 1988) shows a general Famennian regressive phase, with a maximum lowstand near the D/C boundary (van Steenwinkel, 1988). The sea level rises slightly in the lowermost Tournaissian, and a new transgressive pulse starts in the Middle Tournaissian (crenulata transgression). This sea level curve appears to correlate negatively with our third order ⁸⁷Sr/⁶⁶Sr trend, perhaps due to decreases in input of hydrothermal Sr around the D/C boundary transition. Theoretically, fast spreading causes high standing ridges, inundation of continental
$^{87}$Sr/$^{86}$Sr in conodonts

Fig. 4.- $^{87}$Sr/$^{86}$Sr ratios of the Devonian-Carboniferous transition. The upper numbers 1-7 are Beds, respectively, after Vöhringer (1960) and 1-123, the Beds after Schindewolf (1937). The Bank numbers in the Hasselbachtal section after Becker et al. (1984).
edges and high input of "mantle" strontium and vice versa (cf. Spooner, 1976).

Samples from the D/C boundary interval (Öse B: Late Praesulcata Zone, Hasselbachtal Ha 84: base of the Sulcata Zone) show extremely radiogenic $^{87}$Sr/$^{86}$Sr isotope ratios. This $^{87}$Sr/$^{86}$Sr spike correlates with a late stage of the multiphase extinction event, the Hangenberg Event, immediately below the D/C boundary. A steep sea level fall, representing a peak regressive pulse at the end of a long-term regressive trend, could have caused a short term input of radiogenic continental Sr due to strongly enhanced erosional rates. Recently, Stree1 (1992) assigned the onset of glaciation in the southern hemisphere as contemporaneous to the Middle Praesulcata Zone, coincident with the maximum lowstand prior to the D/C boundary. Consequently, this short term, third order, regression can perhaps be interpreted in terms of a glacio-eustatic signal. Erosion of Precambrian shields by large continental glaciers would be an effective means of adding radiogenic $^{87}$Sr to the oceans via riverine input (Amstrong, 1971).

Alternatively, the $^{87}$Sr peak is of post-depositional origin. This is in accord with trace element and XRD data, indicating that the francolite of conodonts is altered. A relatively high variability in trace element composition exists already within one degree of CAI. The colour index can thus be used only as first order approximation for evaluation of the quality of phosphate. The previously discussed $^{87}$Sr/$^{86}$Sr of well preserved brachiopods also argues for a diagenetic enrichment in radiogenic $^{87}$Sr for the conodonts. Pending accumulation of high resolution data for coeval brachiopods, we prefer to leave open the question of the existence and the meaning of the observed D/C strontium isotope spike.

DISCUSSION OF CONODONT BIOSTRATIGRAPHY

The new conodont data from Oberrödinghausen and Hasselbachtal contribute to resolution of some outstanding questions of conodont biostratigraphy across the D/C boundary and they also help to improve the conodont/ammonoid correlation. Two questions were listed in the introduction as awaiting resolution:

1. Base of the Praesulcata Zone in the Wocklum Limestone:

Sandberg et al. (1978), proposing that the latest Devonian Praesulcata Zone be accepted as to cover part of the range of the former Middle Costatus Zone, mentioned the association of its lower part with the Wocklum Limestone in Germany. Ziegler (1988) later placed the base of the Praesulcata Zone at Oberrödinghausen below the Bed 18 of Schindewolf (1937), but the faunal evidence for this has not yet been published. The new sampling yields a slightly different result, placing the base of this zone below Bed 17. Although the specimens identified as Siphonodella praesulcata are sometimes badly preserved, their presence in eleven younger beds in the Wocklum Limestone, together with spot sampling at Hasselbachtal suggests that the Praesulcata Zone may reliably be established in the nodular cephalopod limestone facies of the Rhenish Slate Mountains. This supports the results of Clausen et al. (1989a), who recently reported irregular and patchy occurrence of the index species in the Müssenberg section east of the Höhne Valley.
In terms of ammonoid stratigraphy, the base of the Praesulcata Zone can be correlated with the upper part of the Subarmata-/Brevispira Zone (Schindewolf, 1937; Becker, 1988), prior to the appearance of Balvia or Glatziella (Bed 15 at Oberrödinghausen: Schindewolf, 1937; Bed 32 at Hasselbachtal: Becker, 1992). Clausen et al. (1989a) correlated the base of the Praesulcata Zone with the higher part of the Upper Subarmata Zone (Korn, 1986). This level could well correspond exactly to the entries in the Oberrödinghausen and Hasselbachtal sections.

In their revision of the standard conodont zonation, Ziegler & Sandberg (1984) stated that Proton. meischneri appears at or near the base of the Praesulcata Zone. In the range chart of Sandberg & Ziegler (1979), meischneri appears prior to commencement of the Praesulcata Zone and this is confirmed by our results. Similar data were published also by Gagiev & Kononova (1990), who recorded meischneri notably earlier (topmost Bed 8) than the first praesulcata (upper part of Member XX - Bed 12 to 13) in the Kam'enka section, NE Siberia. Conodont faunas with Proton. meischneri that precede the onset of Siph. praesulcata are known also from the western North America (Utah, Nevada: Sandberg et al., 1972), but this may be related to local facies conditions. This restricts the stratigraphic utility of meischneri for precise dating in some areas. In southern Europe, at the La Serre D/C boundary stratotype, Flajs & Feist (1988) assigned the nodular limestones immediately below the Hangenberg Shale with some reservation to the Late Expansa Zone. This uncertainty in age assignment is a result of the absence of both index conodonts, praesulcata and meischneri. Yet, the presence of Wocklumeria supports the topmost Wocklumian age for these limestones, making them an equivalent of the lower Middle Praesulcata Zone. Consequently, it is not necessary to assume that the overlying Hangenberg Shale in Montagne Noire is older than its equivalent in the Rhenish Slate Mountains or that the Hangenberg Event is diachronous.

(2) The Middle Praesulcata Zone:

The middle Praesulcata Zone is defined only by the disappearance of Pa. gracilis gonioclymeniae; the published data for diverse sections imply a diachronous correlation with the established ammonoid succession. At Oberrödinghausen, Ziegler (1962, 1988) recorded the presence of the index species down to 77 cm (Bed 5), Eickhoff (1973) to 35 cm (Bed 2) and our results to 68 cm (Bed 4) below the base of the Hangenberg Shale. Correlation with the ammonoid sequence thus dates the base of the Middle Praesulcata Zone variously as the base of the Wocklumeria sphaeroides Zone, the uppermost part of the Sphaeroides Zone with Epiwocklumeria applanata, or the lower part the Sphaeroides Zone. At other localities, Pa. gracilis gonioclymeniae dissappears slightly below the entry of Wocklumeria (Kia Section, Ural: Simakov et al., 1983; Boihlen: Weyer, 1979), well below Wocklumeria (Nanjian, South China: Yu, 1988), or even below the entry of Parawocklumeria (Müsenberg: Clausen et al., 1989a). At La Serre in the Montagne Noire (Flajs & Feist, 1988) Wocklumeria and Pa. gracilis gonioclymeniae coexist. All these data shed serious doubts on the general applicability of the Middle Praesulcata Zone in its present definition.

At the base of the Carboniferous Hangenberg Limestone in the Oberrödinghausen section we have found Bispathodus ziegleri, a conodont of Upper Devonian age. This can be ascribed to the presence of reworked Devonian clasts that have been re-recognized by Van Steenwinkel (1984).

Palynological evaluation of the uppermost 50 cm of the Wocklum Limestone (Higgs & Strel, 1984) in the Hasselbachtal section yields a younger assessment (LE Biozone) than for its counterpart in the Oberrödinghausen section (LL-Biozone). However, the pelagic ammonoid fauna with Wocklumeria sphaeroides at the top of the Wocklum Limestone, and the occurrence of Cymatoclymenia evoluta in the overlying black shale horizon of both sections, suggest a synchronous turnover to anoxic conditions (Becker, 1992). The $^{87}$Sr/$^{86}$Sr isotope ratios are identical for the top of the Wocklumeria limestone in both sections (HaLE: $0.708384 \pm 0.000014$ and B1: $0.708389 \pm 0.000011$), supporting the latter correlation.

**CORRELATION OF THE SECTION**
**HASSELBACHTAL, OBERRÖDINGHAUSEN AND ÖSE**

The D/C boundary at the Remscheid-Altena Anticline in the northern Rhenish Slate Mountains is characterized by a Type 1 unconformity in the sense of Van Wagoner et al. (1988) (Van Steenwinkel, 1988). This sequence boundary is related to a major eustatic fall of sea level during the latest Famennian. After this lowstand, stratigraphically close to the extinction event that may have been associated with an anoxic environment, the relative sea level started to rise, presaging the principal transgressive phase in the Touraisian.
STRONTIIUS ISOTOPES IN CONODONTS: DEVONIAN-CARBONIFEROUS BOUNDARY TRANSITION

Fig. 7 - Correlation of the Devonian-Carboniferous boundary interval of the sections Hasselbachtal, Oberrödinghausen, Öse.

Explanations: I: Lithostratigraphy: WL, Wocklum Limestone; WB: Wocklum Beds; HSDST: Hangenberg Sandstone; HL: Hangenberg Limestone. II: Ammonoid stratigraphy: A, Upper Subarmata Zone; B, Lower Paradoxa Zone; C, Upper Paradoxa Zone; D, Prosorhizoid Zone; E, Acutum Zone; F, Dorsoplanus Zone; G, Westfalicus Zone; H, Patens Zone. III: Conodont stratigraphy: 1, Late Expansa Zone; 2, Early Praesulcata Zone; 3, Middle Praesulcata Zone; 4, Late Praesulcata Zone; 5, Sulcata Zone; 6, Lower Duplicata Zone; 7, Upper Duplicata Zone; 8, Sandbergi Zone.

A high resolution stratigraphic correlation of the D/C boundary interval of the sections Hasselbachtal, Oberrödinghausen and Öse, based on bio-, sequence-, and \(^{87}\text{Sr}/^{86}\text{Sr}\) isotopic data is depicted in Figure 7 and these new data contribute to a better correlation of the D/C sections at the Remscheid-Altena Anticline.

In the Oberrödinghausen section, the base of the Early Praesulcata Zone is located within the lower part of the Wocklum Limestone Bed 17. The \(^{87}\text{Sr}/^{86}\text{Sr}\) ratio of this horizon, derived from a Bispathodus sp. is 0.708443 ± 0.000014, comparable to the Bed Ha18 (0.708437 ± 0.000013) of the Early Praesulcata Zone in the Hasselbachtal section. The bio- and \(^{87}\text{Sr}/^{86}\text{Sr}\) isotopic data indicate that the Early Praesulcata Zone is slightly thicker at Hasselbach (about 4 m) than at Oberrödinghausen (about 3 m). The ammonoid Wocklumera sphaeroides enters the geological record in the uppermost part of the Wocklum Lime-
stone and the Cymacylenia evoluta appears in the overlying black shale horizon (Wocklum Shale sensu Krebs, 1979). These biostratigraphic data suggest an identical stratigraphic age (Becker, 1992), which is in accord with the \(^{87}\text{Sr}/^{86}\text{Sr}\) isotope ratios for the Oberrödinghausen (Bed 1: 0.708389 ± 0.000011) and Hasselbachtal (HaLE: 0.708384 ± 0.000014) sections. The Hangenberg Sandstone of the Öse section of the Remscheid-Altena Anticline, a leved channel complex in the sense of Van Wagoner et al. (1988), was deposited during a rapid sea level fall in the latest Famennian. The lower Protagnostodus fauna, extracted from the carbonate-rich top of the Hangenberg Sandstone at the Öse section, has an exceptionally radiogenic \(^{87}\text{Sr}/^{86}\text{Sr}\) ratio of 0.708537 ± 0.000017. A similar radiogenic spike has been encountered also at the base of the Carboniferous at the Hasselbachtal section (Ha84: 0.709618 ± 0.000016), suggesting a possible causal relationship with the rapid short term sea level regression.
The base of the Hangenberg Limestone is of different stratigraphic age in all three sections. The *Protognathodus-Polygonathus* biofacies of the lowermost part of the Tournaisian at the Hasselbachtal section (Ha84-Ha81) characterizes the Stockum Limestone with its autochthonous *Prorsum* fauna. The base of the *Subinvoluta* Zone is located at the Bed Ha78, at the first occurrence of *Acutimoroceras antecedens*, which appears also at the base of the Hangenberg Limestone in the Obrödöinghausen section. In contrast to Stoppel (in Becker et al., 1984), the present conodont data for the Hasselbachtal section date the horizon Ha78 with *Siphonodella paesulcata* as the lower part of the *Sulcata* Zone. Thus Ha78 is not any younger than the OR2/12 in the Obrödöinghausen section. A comparison of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios yields a correlation of the Ha78 with the OR1/7 (Ha: 0.708447 ± 0.000013; OR1/7: 0.708432 ± 0.000017).

New conodont study of the Bed B at Öse yielded typical *Protognathodus-Polygonathus* fauna, confirming the results of Higgs & Streel (1984). The presence of *Polygonathus purus purus* and *Protognathodus kuehni* at Öse as well as at Hasselbachtal, and comparable $^{87}\text{Sr}/^{86}\text{Sr}$ ratios enable correlation of Öse (Öse B: 0.708494±0.000020) with the Bed Ha81 (0.708487±0.000022) of the Hasselbachtal section. This is in agreement with the first occurrence of the trilobite *Archeogonus (M.) dreverensis* at these levels.

**CONCLUSIONS**

Conodont-apatite is prone to diagenetic alteration, which leads to decarbonation and to depletions in sodium and strontium. $^{87}\text{Sr}/^{86}\text{Sr}$ isotope data from contemporaneous well preserved brachiopods show that conodont also experience a distinct enrichment in radiogenic $^{87}\text{Sr}$.

We suggest that the pattern of the third order $^{87}\text{Sr}/^{86}\text{Sr}$ oscillations may reflect to some degree the original pattern of strontium isotope ratios in sea water, albeit shifted by some $10^{-6}$ units in the radiogenic direction. The assumption that the conodont Sr isotope curve indeed preserves some degree of the original pattern is supported also by comparable strontium isotope ratios for stratigraphically coeval samples from geographically separated sections.

The high resolution bio- and strontium isotope stratigraphy enables a detailed correlation of the sections Hasselbachtal, Obrödöinghausen and Öse, all straddling the D/C boundary. The section at Hasselbachtal contains the most complete sedimentary record, whereas the other two locations encompass hiatuses of dissimilar duration. The base of the Hangenberg Limestone at Öse correlates with the Bed Ha81 in the Hasselbachtal section. In contrast, the base of the Hangenberg Limestone at Obrödöinghausen is considerably younger and correlates with the bed Ha78.

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PLATE I

(Magnification is about 40x.)

1, 6. *Siphonodella praesulcata*, section Oberrödinghausen, OR 2/12, *Sulcata Zone*.

2. *Siphonodella praesulcata*, section Oberrödinghausen, B3, Middle *Praesulcata Zone*.

3. *Siphonodella obsoleta*, section Oberrödinghausen, OR14/8, *Sandbergi Zone*.

4, 9. *Siphonodella praesulcata*, section Oberrödinghausen, OR2/12, *Sulcata Zone*.

5. *Siphonodella praesulcata*, section Oberrödinghausen, OR2/12, *Sulcata Zone*.

7, 11. *Siphonodella praesulcata*, section Oberrödinghausen, B5, Early *Praesulcata Zone*.


10; 5. Plate 3. *Siphonodella sulcata*, section Oberrödinghausen, OR2/12, *Sulcata Zone*.

12. *Protognathodus kockeli*, section Oberrödinghausen, OR2/12, *Sulcata Zone*.

PLATE 2

(Magnification is about 40x)

1. 6. *Siphonodella praesulcata*, section Oberrödinghausen, B5, Early *Praesulcata* Zone.

2. 3. *Siphonodella praesulcata*, section Hasselbachtal, Ha78, *Sulcata* Zone.

4. *Palmatolepis gracilis expansa*, section Hasselbachtal, HaLE, Middle *Praesulcata* Zone.


7. *Siphonodella duplicata*, section Oberrödinghausen, OR7/18, Lower *Duplicata* Zone.

8. *Palmatolepis gracilis gracilis*, section Oberrödinghausen, B3, Middle *Praesulcata* Zone.

9. *Bispathodus ziegleri mussenbergensis*, section Oberrödinghausen, B1.1, Middle *Praesulcata* Zone.

10. *Siphonodella duplicata* sensu Hass, section Oberrödinghausen, OR8/5, Upper *Duplicata* Zone.

11. *Palmatolepis gracilis gomioclymeniae*, section Hasselbachtal, Ha18, Early *Praesulcata* Zone.
PLATE 3

(Magnification is about 40x)

1-2. *Siphonodella praesulcata*, section Hasselbachtal, Ha18, Early *Praesulcata* Zone.

3-4. *Siphonodella praesulcata*, section Oberrödinghausen, OR7, Early *Praesulcata* Zone.

5. Fig. 10, Pl. 1 : *Siphonodella sulcata*, section Oberrödinghausen, OR1/7, *Sulcata* Zone.

6,10. *Siphonodella praesulcata*, section Oberrödinghausen, B4, Middle *Praesulcata* Zone.

7, 8. *Siphonodella praesulcata*, section Hasselbachtal, Ha18, Early *Praesulcata* Zone.


PLATE 4

1-2. *Siphonodella sulcata*, section Hasselbachtal, Ha84 (Magn. x55)

3-6. *Siphonodella sulcata*, section Hasselbachtal, Ha84,
   3. Oral view (Magn. x55)
   4. Aboral view (Magn. x55)

5-6. Detail of the aboral view, remaining part of the removed pseudokeel,
   (Magn. 5x x240, Magn. 6: x1600)