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

by

Wolfram KÜRSCHNER[1,2], R. Thomas BECKER[1,3], Dieter BUHL[1] & Ján VEIZER[1,4]

(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 Wocklum Limestone at the Oberrödinghausen and Hasselbachtal sections.

KURZFASSUNG.- 51 $^{87}Sr/^{86}Sr$ Isotopen-Messungen an biostratigraphisch datierten Conodonten sowie Brachiopoden des Devon-Karbon Grenzintervalls aus dem nördlichen Rechtsreinischen Schiefergebirges führen zu einer hochauflösenden Dokumentation der Sr-Isotopenkurve. Ausgewählt wurden wegen ihrer exzellenten stratigraphischen Bearbeitung und des niedrigen Diagenesegrades der Conodonten Profile am Remscheid-Altena Sattel : Hasselbachtal, Oberrödinghausen, Öse und Riescheid. Spurenelementanalysen und Röntgendiffraktometer-Untersuchungen zeigen allerdings, dass der Conodonten-Frankolith als instabiles Endglied des Systems Frankolith-Fluorapatit diagenetisch verändert ist. $^{87}Sr/^{86}Sr$ Vergleichsmessungen an nicht alterierten Brachiopodenschalen belegen eine radiogene Verschiebung der Conodonten. Diese $^{87}Sr/^{86}Sr$ Isotopenkurve ist deswegen eine sekundäre Kurve, bei der die Struktur der primären Sr Isotopen Palaeomeerwasser Kurve bis zu einem gewissen Grad bewahrt geblieben ist. Der Umschlagpunkt des übergeordneten Trends der dritten Isotopen Hierarchie fällt mit dem Regressionsmaximum an der Devon/Karbon-Grenze zusammen. Die regionale, biostratigraphische Korrelation wird durch gleiche $^{87}Sr/^{86}Sr$ Isotopenwerte bestätigt. Neue Conodonten Daten zeigen, dass die Zonierung mit *Siphonodella praesulcata* im Wocklum Kalk bei Oberrödinghausen und im Hasselbachtal anwendbar ist.

1. *Institut für Geologie, Ruhr-Universität-Bochum, Postfach 102148, 4630 Bochum, Germany.*
2. *Present address : Laboratory for Paleobotany and Palynology, State University of Utrecht, Heidelberglaan 2, 3584 CS Utrecht, The Netherlands.*
3. *present address : Paläontologisches Institut, Universität Berlin, Schwendenerstr. 8, 1000 Berlin, Germany.*
4. *Derry/Rust Research Unit, Ottawa-Carleton Geoscience Centre, University of Ottawa, Ottawa, Ontario K1N 6N5, Canada.*

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 Wocklum Limestone, with the main emphasis on the first occurrence of *Siphonodella praesulcata* and *Protognathodus 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 Oberrödinghausen, Hasselbachtal and Öse, 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 & Streel (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 Anticlines. The southern margin of the Old Red Continent, considerably to the north of the investigated outcrop belt, had little significance for the sedimentary history of the latter.

The Wocklumian of the latest Famennian is characterized by greenish and less frequently red basinal shales, nodular shales and nodular limestones (Wocklum Beds). The shale/limestone ratio decreases from Hasselbachtal to Oberrödinghausen (Wocklum Limestone). The fauna is uniform and dominated by pelagic forms such as the ammonoids, nautiloids, ostracods and conodonts. The benthos is of low diversity and includes rhynchonellids (*Planovatirostrum*), 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 to microsparite and aragonitic shells of cephalopods are dissolved. The same applies to most layers at Öse, but at Oberrödinghausen 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 Wocklum Limestone is capped by the black Wocklum Shale (Krebs, 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 oolithic conglomerates are pesent. 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 Oberrödinghausen 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 Wocklum 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 praesulcata* that defines the base of the *Praesulcata* Zone, and of *Protognathodus meischneri*, the latter an alternative index species in the Wocklum 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 *Palmatolepis 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; Keto & 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 $^{87}Sr/^{86}Sr$ curve for coeval sea water. The $^{87}Sr/^{86}Sr$ 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 % a c e t i c 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 destilled water ultrasonic bath for as long as required to remove adhering sediment particles, monitored using a 64x as magnification.

$^{87}Sr/^{86}Sr$ MEASUREMENTS

In order to exlude diagenetic effects that derive form the variable content of white matter in the

Table I.- $^{87}Sr/^{86}Sr$ of late Devonian and early Carboniferous conodonts and brachiopods

Sample	Age	Material	$^{87}Sr/^{86}Sr$ ratio +/- 2σ
I Oberrödinghausen section			
OR15/13*	*Sandbergi* Zone (T)	*Polygn.* sp.	0.708463 +/- 0.000012
OR15/13	*Sandbergi* Zone (T)	*Polygn.* sp.	0.708445 +/- 0.000010
OR14/8	*Sandbergi* Zone	*Polygn.* sp.	0.708395 +/- 0.000010
OR13/10	*Sandbergi* Zone	*Polygn.* sp.	0.708370 +/- 0.000017
OR13/10*	*Sandbergi* Zone	*Polygn.* sp.	0.708470 +/- 0.000014
OR12/12*	*Sandbergi* Zone	*Polygn.* sp.	0.708370 +/- 0.000040
OR10/5*	Upper *Duplicata* Zone	*Polygn.* sp.	0.708393 +/- 0.000023
OR7/18*	Lower *Duplicata* Zone (T)	*Polygn.* sp.	0.708464 +/- 0.000010
OR7/18	Lower *Duplicata* Zone (T)	*Polygn.* sp.	0.708426 +/- 0.000022
OR5/5	Lower *Duplicata* Zone	*Polygn.* sp.	0.708334 +/- 0.000018
OR4/6	Lower *Duplicata* Zone (B)	*Polygn.* sp.	0.708340 +/- 0.000019
OR2/12	upper *Sulcata* Zone	*Polygn.* sp.	0.708353 +/- 0.000015
OR1/7*	upper *Sulcata* Zone	*Polygn.* sp.	0.708445 +/- 0.000016
OR1/7	upper *Sulcata* Zone	*Polygn.* sp.	0.708432 +/- 0.000017
B1.1	Middle *Praesulcata* Zone	*Bisp.* sp.	0.708389 +/- 0.000011
B1.3	Middle *Praesulcata* Zone	*Bisp.* sp.	0.708387 +/- 0.000016
B2	Middle *Praesulcata* Zone	*Bisp.* sp.	0.708367 +/- 0.000015
B3	Middle *Praesulcata* Zone (B)	*Bisp.* sp.	0.708420 +/- 0.000008
B4	Lower *Praesulcata* Zone (T)	*Bisp.* sp.	0.708473 +/- 0.000011
B5	Lower *Praesulcata* Zone	*Bisp.* sp.	0.708502 +/- 0.000017
B6	Lower *Praesulcata* Zone	*Bisp.* sp.	0.708423 +/- 0.000019
B9	Lower *Praesulcata* Zone	*Bisp.* sp.	0.708387 +/- 0.000037
B12	Lower *Praesulcata* Zone	*Bisp.* sp.	0.708478 +/- 0.000017
B13	Lower *Praesulcata* Zone	*Bisp.* sp.	0.708430 +/- 0.000015
B15	Lower *Praesulcata* Zone	*Bisp.* sp.	0.708447 +/- 0.000013
B16	Lower *Praesulcata* Zone	*Bisp.* sp.	0.708465 +/- 0.000022
B17	Lower *Praesulcata* Zone (B)	*Bisp.* sp.	0.708443 +/- 0.000014
B20	Upper *Expansa* Zone	*Bisp.* sp.	0.708387 +/- 0.000020
B23	Upper *Expansa* Zone	*Bisp.* sp.	0.708561 +/- 0.000012
OR6	Upper *Expansa* Zone	*Bisp.* sp.	0.708409 +/- 0.000018
Ba55	Upper *Postera* Zone	Polygn. sp.	0.708465 +/- 0.000017
OR5	Lower *Postera* Zone	*Polygn.* sp.	0.708372 +/- 0.000014
Ba15	Lower *Trachytera* Zone	*Polygn.* sp.	0.708333 +/- 0.000013
OR3	Uppermost *Marginifera* Zone	*Polygn.* sp.	0.708282 +/- 0.000017
OR2	l. Upper *Marginifera* Zone	*Polygn.* sp.	0.708328 +/- 0.000018
OR1	Lower *Marginifera* Zone	*Polygn.* sp.	0.708435 +/- 0.000017
II Hasselbachtal section			
Ha69	*Duplicata* Zone	*Polygn.* sp.	0.708303 +/- 0.000014
Ha78	lower *Sulcata* Zone	*Polygn.* sp.	0.708447 +/- 0.000013
Ha81	lower *Sulcata* Zone	*Polygn.* sp.	0.708487 +/- 0.000022
Ha83	lower *Sulcata* Zone	*Polygn.* sp.	0.708413 +/- 0.000015
Ha84	lower *Sulcata* Zone	*Protognathodus kuehni*	0.708618 +/- 0.000016
HaLE	Middle *Praesulcata* Zone	*Bisp.* sp.	0.708384 +/- 0.000014
Ha44B	Lower *Praesulcata* Zone	*Planovatirostrum richteri*	0.708184 +/- 0.000015
Ha29	Lower *Praesulcata* Zone	*Bisp.* sp.	0.708390 +/- 0.000012
Ha18C	Lower *Praesulcata* Zone	*Bisp.* sp.	0.708437 +/- 0.000013
Ha18B	Lower *Praesulcata* Zone	*Planovatirostrum richteri*	0.708323 +/- 0.000016

sample, two to three monogeneric conodont 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 elutant containing most of the elemental Sr was dried and loaded on single Ta filaments using a loading liquid of Ta_2O_5, HNO_3, HF, H_3PO_4, 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 $^{87}Sr/^{86}Sr$ 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. $^{87}Sr/^{86}Sr$ ratios were normalized to a $86Sr/^{88}Sr$ ratio of 0.1194. The 2σ for single sample varied between $8\text{-}40\times10^{-6}$ 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 multicollector mass spectrometer. The measured $^{87}Sr/^{86}Sr$ ratio of the Amsterdam NBS SRM 987 was 0.710245± 0.000013.

TRACE ELEMENT AND XRD ANALYSIS

Samples of conodonts 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 Dep. of Earth Science in Utrecht are indicated by a star in Table 4). Semiquantitative CO_2 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:^{25}07000 H:^{51}94220). The outcrop was described for the first time as a D/C boundary section by Schmidt (1924) and Groos-Uffenorde & Uffenorde (1974) studied its conodont and ostracod fauna. This section later became important because of its mixed siliciclastic/carbonate lithology that is particularly suitable for the study of miospores, ammonoids and conodonts (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 conodont 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 conodont fauna with *Bispathodus costatus, Palmatolepis gracilis gracilis, Pa. gracilis sigmoidalis, Pa. gracilis gonioclymeniae, Polygnathus symmetricus* and *Siphonodella praesulcata,* which characterize the Early *Praesulcata* Zone. The top of the Wocklum Beds with *Pa. gracilis gracilis, Pa. gracilis sigmoidalis, Pa. gracilis expansa, Bi. costatus, Bi. ultimus, Bi. ziegleri* and *Branmehla suprema* indicates the lower Middle *Praesulcata* Zone. No conodonts 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, *Sphaerorthoceras* sp., juvenile gastropods (*Naticopsis,* div. gen.), pelecypods and plant macrofossils.

In accord with the data of Becker *et al.* (1984), the first *Siphonodella sulcata* occures together with *Protognathodus kuehni* in bed Ha84, thus marking the base of the Carboniferous (see Fig. 1). The rich conodont fauna contains also *Bi. costatus*, Bi. stabilis*, Bi. ziegleri*, Pa. grac. gracilis*, Pa. gracilis expansa*, Pol. comm. communis, Protognathodus collinsoni, Ptogn. kockeli* and *Siphonodella praesulcata* (*: 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

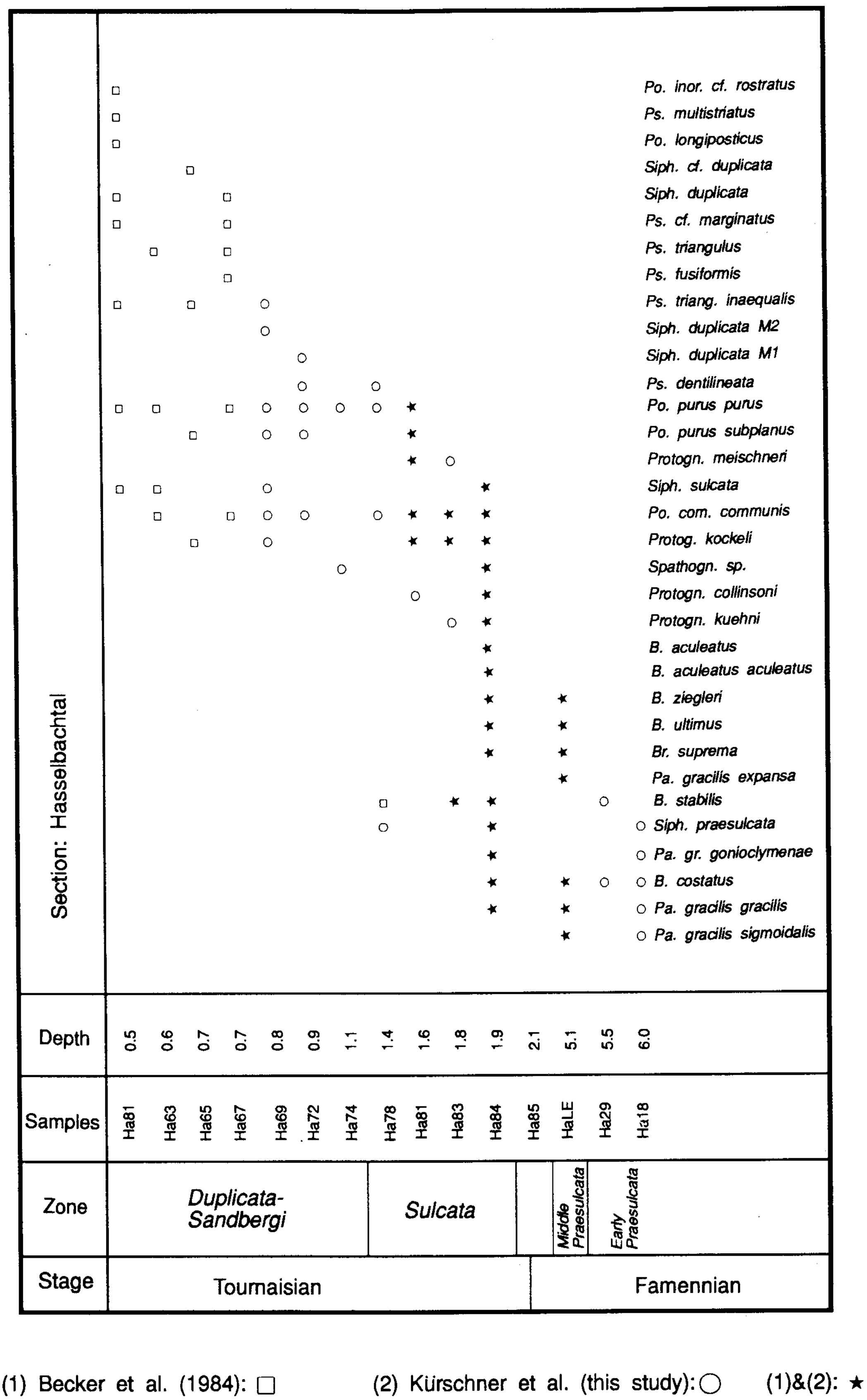

Fig. 1.- Conodont-Stratigraphy of the Hasselbachtal section (complemented by Becker *et al.*, 1984).

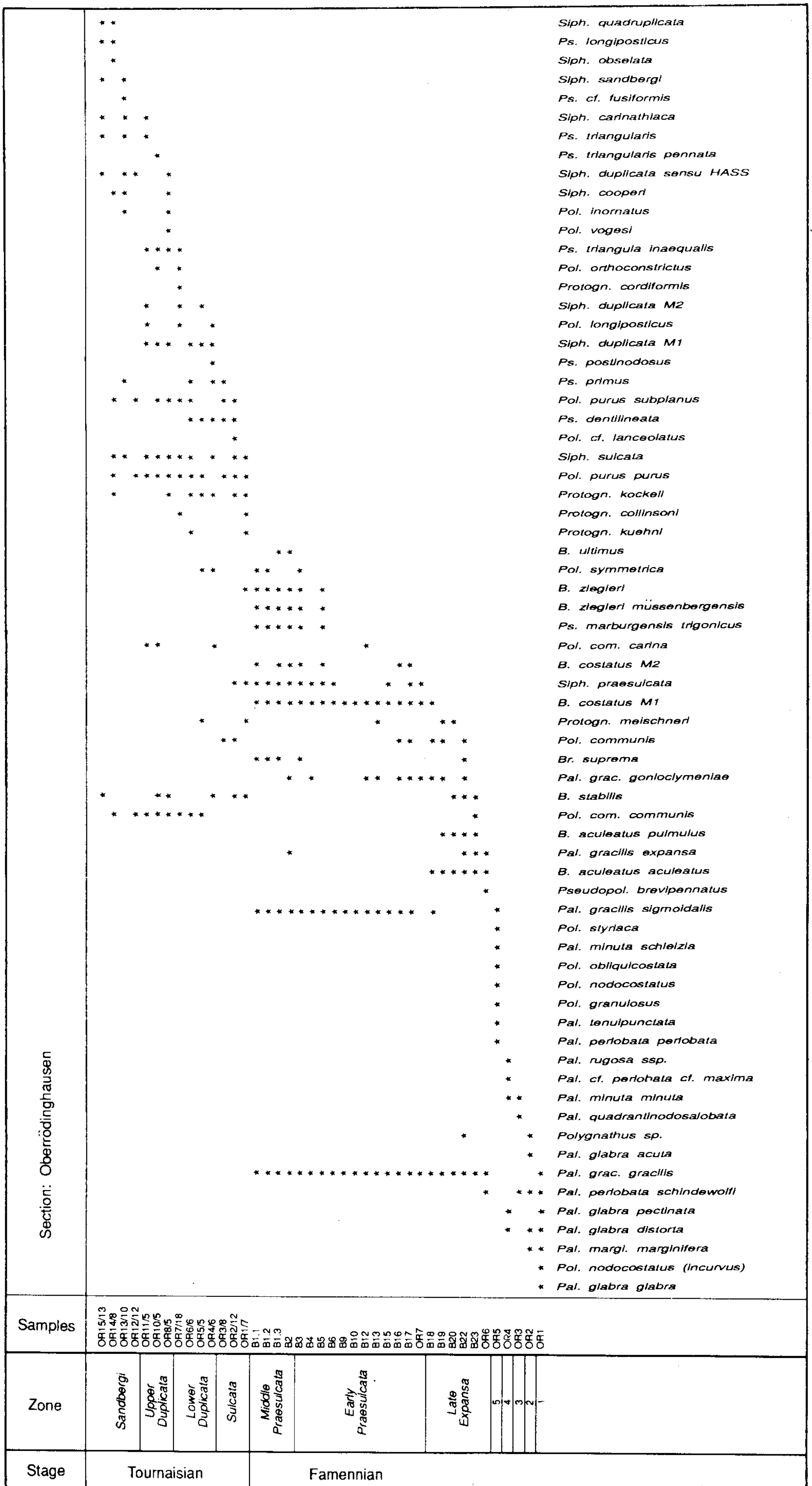

Fig. 2.- Conodont-Stratigraphy of the Oberrödinghausen section.
(1: Early *Marginifera* Zone; 2: Late *Marginifera* Zone; 3: Latest *Marginifera* Zone; 4: *Trachytera* Zone; 5: Early *Postera* Zone).

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 Oberrödinghausen section

The section is exposed on the left bank of the Hönne Valley in a railway cut about 450 m south of the Oberrödinghausen (Sheet 4613 Balve R:^{25}19400 H:^{51}69100). Ammonoid faunas were described by Schmidt (1924), Schindewolf (1937), Vöhringer (1960) and Paproth & Streel (1970). Micropaleontological studies on conodonts were published by Bischoff (1957) and Voges (1959, 1960) and on foraminiferans 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, Branmehla 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 *Praesulcata* 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 *Praesulcata* Zone. The last occurrence of *Pa. gracilis gonioclymeniae* in Bed 4 delineates the top of the Early *Praesulcata* Zone. The base of the Hangenberg Limestone (OR1/7) is characterized by *Siphonodella sulcata, Siph. praesulcata, Protogn. kuehni, Protogn. kockeli, Protogn. collinsoni, Pol. purus* and *Bi. ziegleri* (reworked). *Siph. praesulcata* 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. triangularis 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:^{25}27170 H:^{51}24200). The sedimentology and microfacies of the D/C boundary beds were studied by Keupp & Kompa (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 ocherts, allodapic limestones, nodular limestones, and siliceous limestones, as well as tuffaceous volcaniclastics 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

Sample	Age	Material	$^{87}Sr/^{86}Sr$ ratio +/- 2σ
III Öse section			
ÖseB	lower *Sulcata* Zone	*Protognathodus kuehni*	0.708494 +/- 0.000020
ÖseA2	Upper *Praesulcata* Zone	*Protognathodus kockeli*	0.708537 +/- 0.000017
IV Riescheid section			
Ri88	*Texanus* Zone	*Gnathodus* sp.	0.708063 +/- 0.000014
Ri77/78	*Anchoralis-latus* Zone	*Gnathodus* sp.	0.708122 +/- 0.000012
Ri77/78	*Anchoralis-latus* Zone	*Gnathodus* sp.	0.708077 +/- 0.000013

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

water	0.16%
insoluble residue	1.59%
loss on ignition	0.25%
total-CO_3	2.00%
PO_4	53.30%
Ca	37.28%
Sr	0.40%
REE	0.42%
Al	0.09%
Fe	0.04%
K	0.03%
Na	0.62%
H_2O	2.85%
CO_3	1.84%
F	2.60%

Zone. 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 $4x10^{-5}$. 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 ($1.3x10^{-4}$) 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 *Protognathodus 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 Tournaisian/Viséan transition in the Riescheid section (Fig. 3).

Table IV.- Trace element data of conodonts

Sample	locality	CAI	Ca[%]	PO_4[%]	Na[ppm]	Sr[ppm]	Mg[ppm]
Bel*	Manitoban Bay	1	37.1	36.88	6044	3121	300
E105	Prüm/Eifel	1.5	30.5	41.18	3055	2896	55
OR*	Oberrödinghausen	2.5	38.8	39.00	3387	3041	152
Ob-6-89	Oberscheld	2.5	37.9	55.69	3290	3558	2674
Ha-1-88	Hadamar	3	34.6	55.13	1938	2027	155
5514	Hadamar	3	37.1	56.09	1354	2336	621
RI	Riescheid	4	37.2	55.00	2687	2465	93
BB*	Burgberg. E-Sauerl.	5	39.7	39.42	2400	2374	128
Ni	Niederhof. E-Sauerl.	5	36.8	59.24	2620	2774	846
Me-1-89	Medebach	6	31.4	44.76	983	2975	1352
Rb-6-89	---	6	34.6	50.58	1500	2750	2385
Wei-1-89	Harz	7	34.5	50.41	≤50	2983	2629

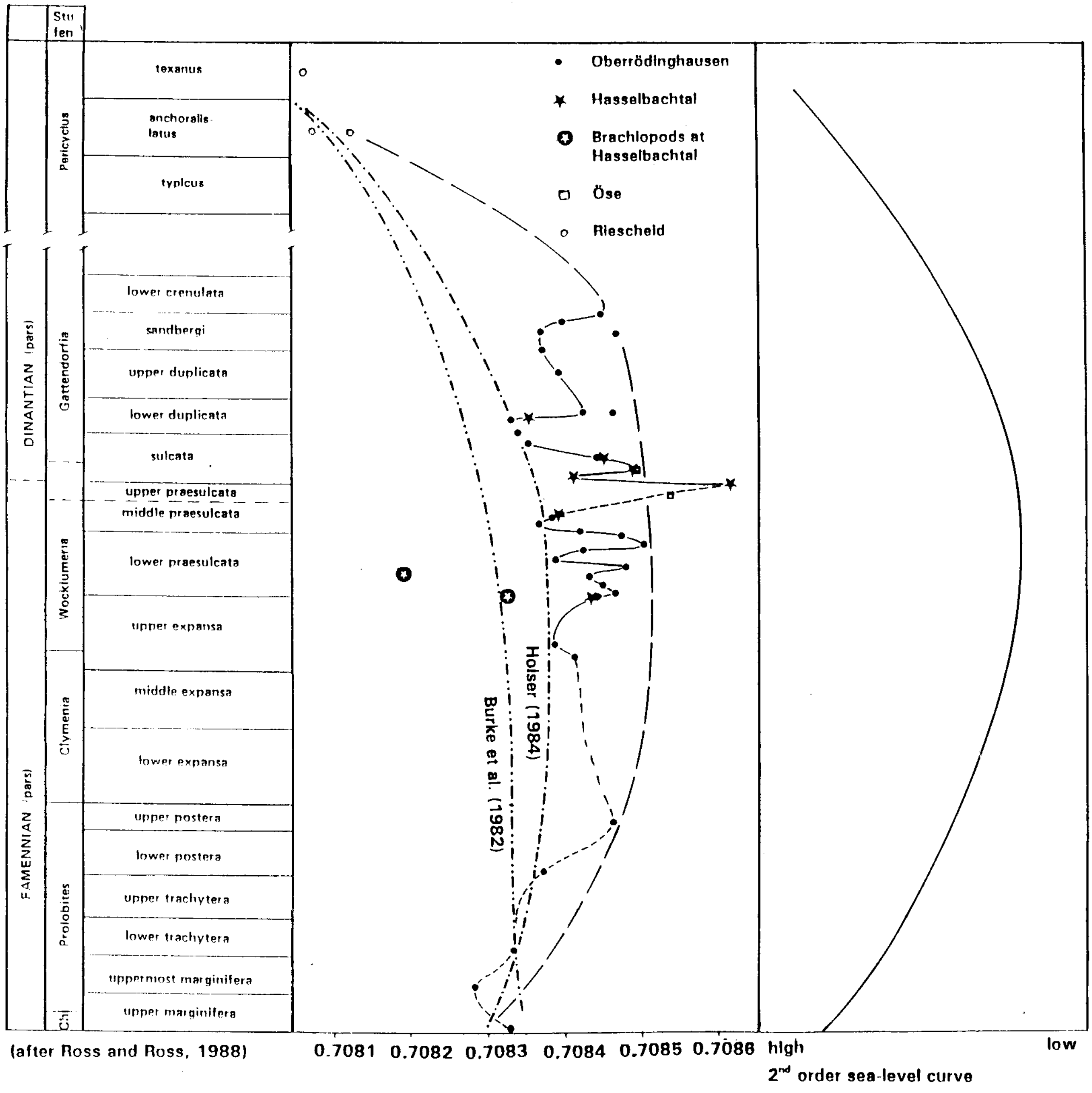

Fig. 3.- $^{87}Sr/^{86}Sr$ ratios of Late Devonian and Early Carboniferous conodonts and brachiopods (all data normalized to NBS SRM 987 of 0.710243). The mean 2σ of a single measurement is 1.6×10^{-5}.

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; Rejebian *et al.*, 1987; Königshof, 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 % CO_3 (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 $\Delta 2\Theta$ of the p e a k s (410) and (004) has been shown by Gulbrandsen (1970) to be a linear function of the CO_3 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 Oberrödinghausen) are already strongly depleted in CO_3 (by about 1.1 weight %).

DISCUSSION AND INTERPRETATION OF GEOCHEMICAL DATA

For comparison with the previously published $^{87}Sr/^{86}Sr$ isotope curves, all data are normalized to NBS SRM 987 of 0.710243. The shape of the late Devonian to early Carboniferous $^{87}Sr/^{86}Sr$ 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 $^{87}Sr/^{86}Sr$ of 0.70835±0.00006 and 0.70806±0.00002, respectively (Fig. 3). Between these two points, the interpolated MOBIL and our curves diverge. Our overall trend depicts an arc with the most radiogenic values in the latest *Wocklumerian* Stage, exceeding the interpolated curves by about $2x10^{-4}$. 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 ^{87}Sr 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 (Ebneth, 1991; Diener, 1991; Ebneth *et al.*, 1991). Yet, surprisingly, samples from stratigraphically contemporaneous, but physically separated Beds in the sections Hasselbachtal, Oberrödinghausen and Öse 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 ^{87}Sr enrichment in most conodont samples. Modelling of Sr isotope and elemental exchange between coeval brachiopods, conodonts and enclosing rocks (Ebneth, 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 Ebneth *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 Tournaisian, and a new transgressive pulse starts in the Middle Tournaisian (*crenulata* transgression). This sea level curve appears to correlate negatively with our third order $^{87}Sr/^{86}Sr$ 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

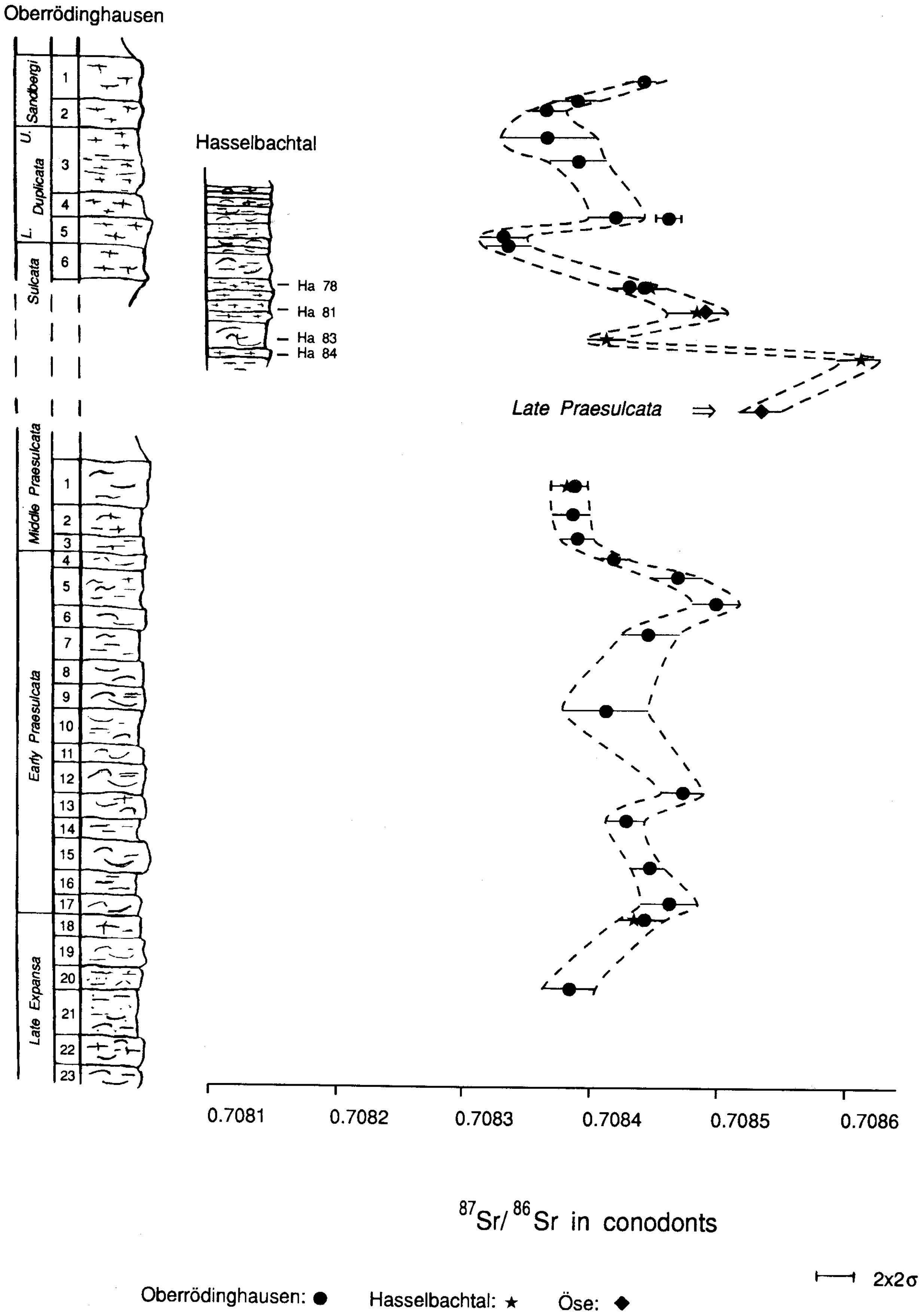

Fig. 4.- $^{87}Sr/^{86}Sr$ ratios of the Devonian-Carboniferous transition. The upper numbers 1-7 are Beds, respectively, after Vöhringer (1960) and 1-123, the Beds after Schindewolf (1937). The Bank numbers in the Hasselbachtal section after Becker *et al.* (1984).

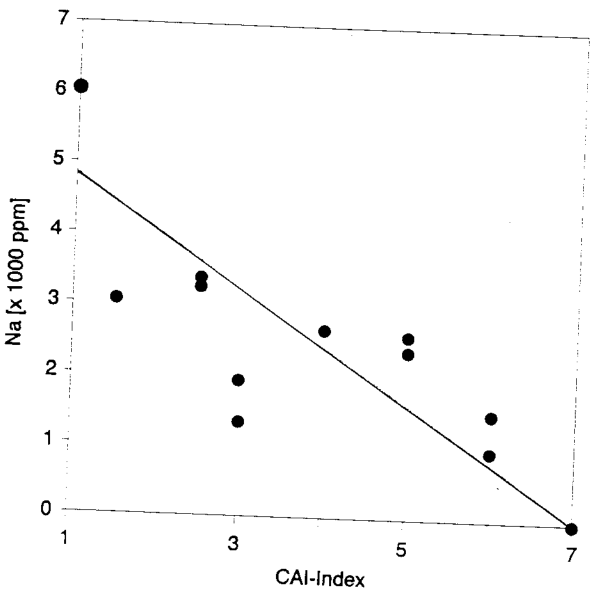

Fig. 5.- Sodium content in conodonts of different colour index.

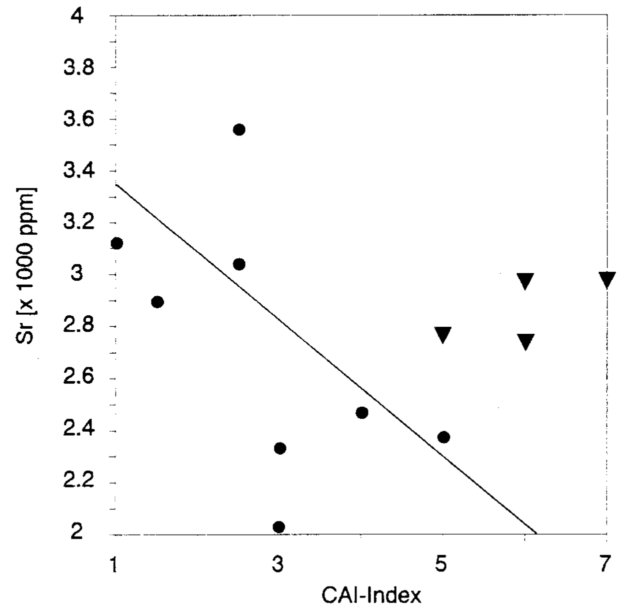

Fig. 6.- Strontium content in conodonts of different colour index. Contact-met./hydrotherm.: ▾

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, Streel (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 avaiting 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 Hönne Valley.

In terms of ammonoid stratigraphy, the base of the *Praesulcata* Zone can be correlated with the upper part of the *Subarmata-/Brevispina* 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 *Protogn. 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 Kamenka section, NE Siberia. Conodont faunas with *Protogn. 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 the *Sphaeroides* Zone. At other localities, *Pa. gracilis gonioclymeniae* dissappears slightly below the entry of *Wocklumeria* (Kia Section, Ural : Simakov *et al.*, 1983; Bohlen : Weyer, 1979), well below *Wocklumeria* (Nanbiancun, South China : Yu, 1988), or even below the entry of *Parawocklumeria* (Müssenberg : 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 recognized by Van Steenwinkel (1984).

Palynological evaluation of the uppermost 50 cm of the Wocklum Limestone (Higgs & Streel, 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 *Cymaclymenia 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 ± 0.000014 and B1 : 0.708389 ± 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 charaterized 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 Tournaisian.

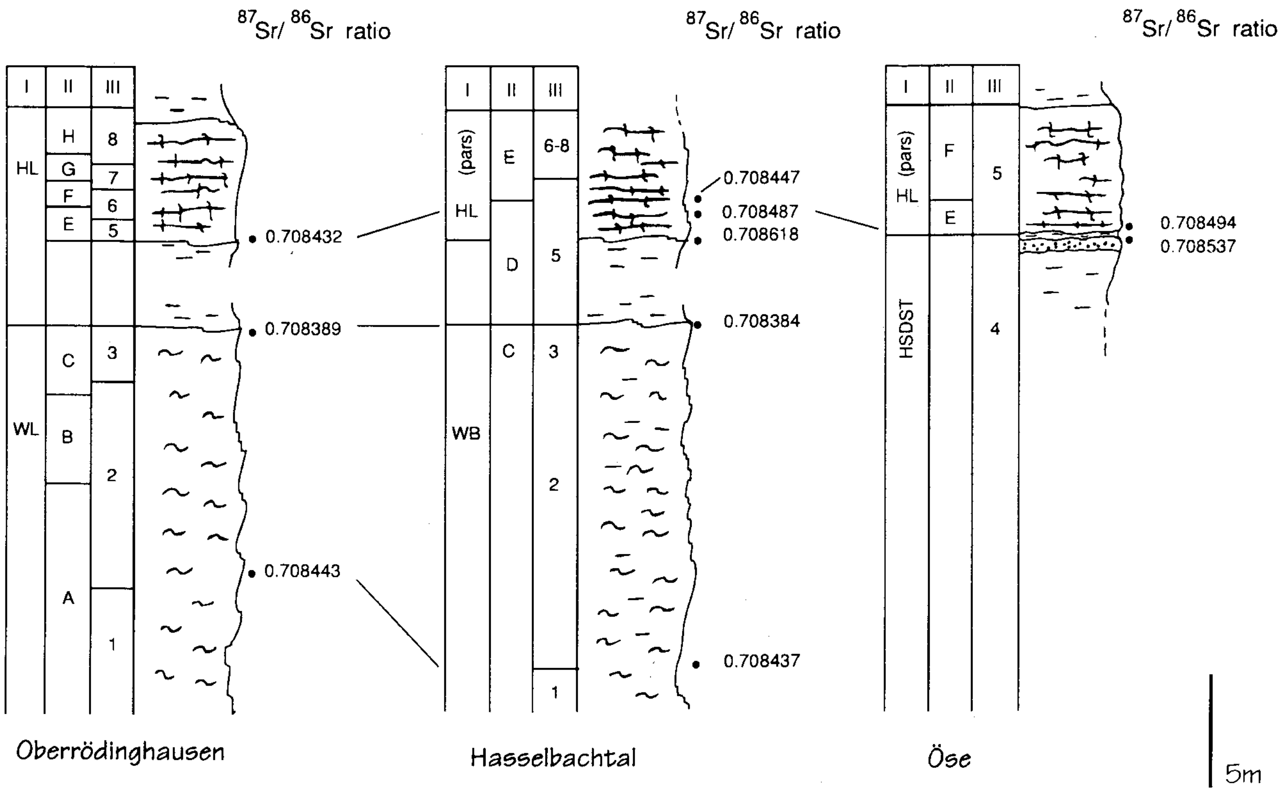

Fig. 7.- Correlation of the Devonian-Carboniferous boundary interval of the sections Hasselbachtal, Oberrödinghausen, Öse. Explanations : I. Lithostratigraphy : WL, Wocklum Limestone; WB : Wocklum Beds; HSDST : Hangenberg Sandstone; HL : Hangenberg Limestone. II: Ammonoidstratigraphy : A, Upper *Subarmata* Zone; B, Lower *Paradoxa* Zone; C, Upper *Paradoxa* Zone; D, *Prorsum* Zone; E, *Acutum* Zone; F, *Dorsoplanus* Zone; G, *Westfalicus* Zone; H, *Patens* Zone. III : Conodontstratigraphy : 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 $^{87}Sr/^{86}Sr$ 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 $^{87}Sr/^{86}Sr$ 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 $^{87}Sr/^{86}Sr$ isotopic data indicate that the Early *Praesulcata* Zone is slightly thicker at Hasselbach (about 4 m) than at Oberrödinghausen (about 3 m). The ammonoid *Wocklumeria sphaeroides* enters the geological record in the uppermost part of the Wocklum Limestone and the *Cymaclymenia 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 $^{87}Sr/^{86}Sr$ 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 leveed 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 *Protognathodus* fauna, extracted from the carbonate-rich top of the Hangenberg Sandstone at the Öse section, has an exceptionally radiogenic $^{87}Sr/^{86}Sr$ 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-Polygnathus* 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 *Acutimitoceras antecedens,* which appears also at the base of the Hangenberg Limestone in the Oberrödinghausen section. In contrast to Stoppel (in Becker *et al.*, 1984), the present conodont data for the Hasselbachtal section date the horizon Ha78 with *Siphonodella praesulcata* as the lower part of the *Sulcata* Zone. Thus Ha78 is not any younger than the OR2/12 in the Oberrödinghausen section. A comparison of the $^{87}Sr/^{86}Sr$ ratios yields a correlation of the Ha78 with the OR1/7 (Ha : 0.708447 $\pm$ 0.000013; OR1/7 : 0.708432 $\pm$ 0.000017).

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

CONCLUSIONS

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

We suggest that the pattern of the third order $^{87}Sr/^{86}Sr$ oscillations may reflect to some degree the original pattern of strontium isotope ratios in sea water, albeit shifted by some 10^{-5} 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, Oberrödinghausen 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 Oberrödinghausen 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.

8. *Siphonodella quadruplicata,* section Oberrödinghausen, OR13/10, *Sandbergi* Zone.

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

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

13. *Protognathodus kuehni,* section Oberrödinghausen, OR2/12, *Sulcata* Zone.

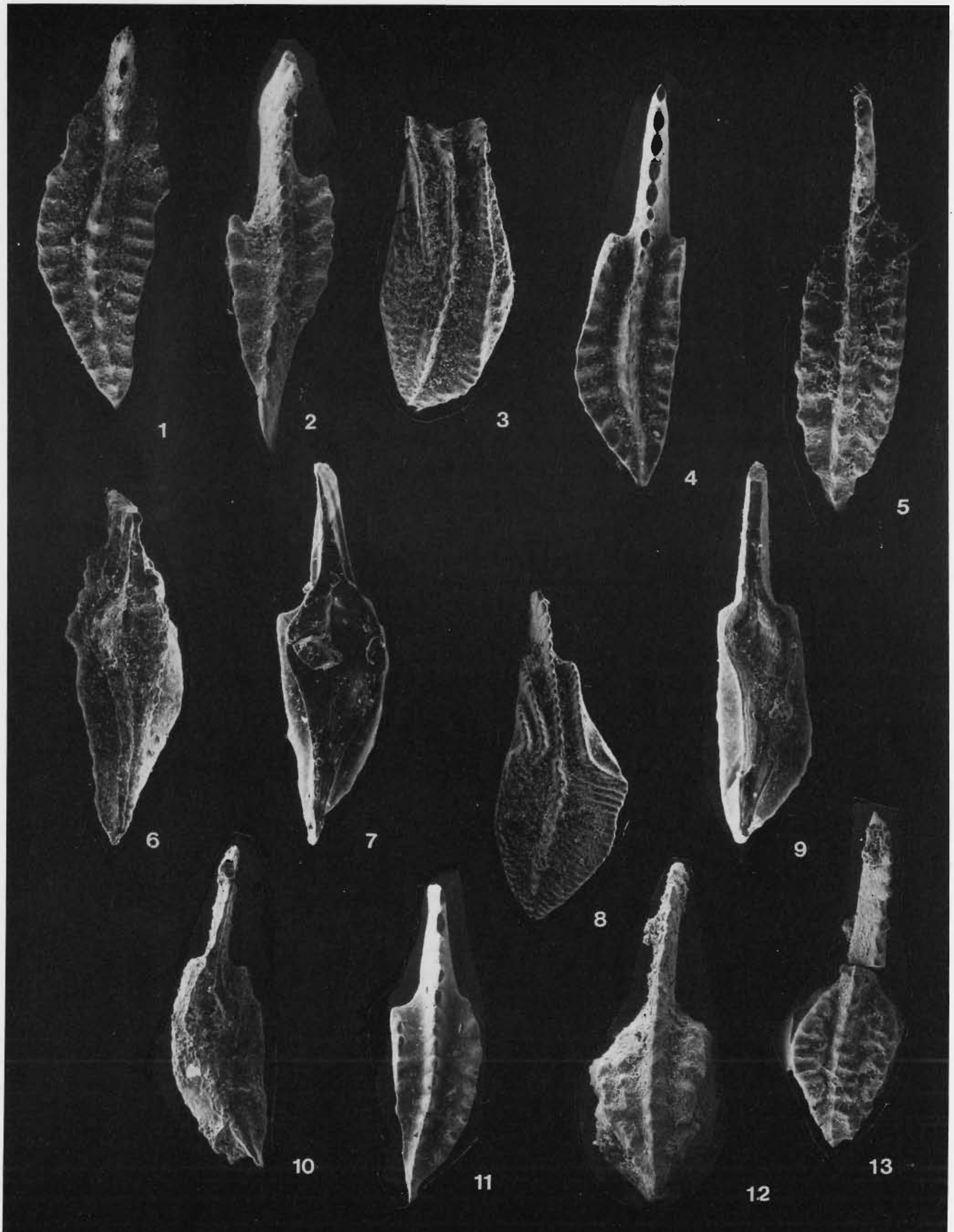
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PLATE 2

(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.

5. *Pseudopolygnathus primus,* section Oberrödinghausen, OR3/8, *Sulcata* Zone.

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

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

9. *Bispathodus ziegleri müssenbergensis,* 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.

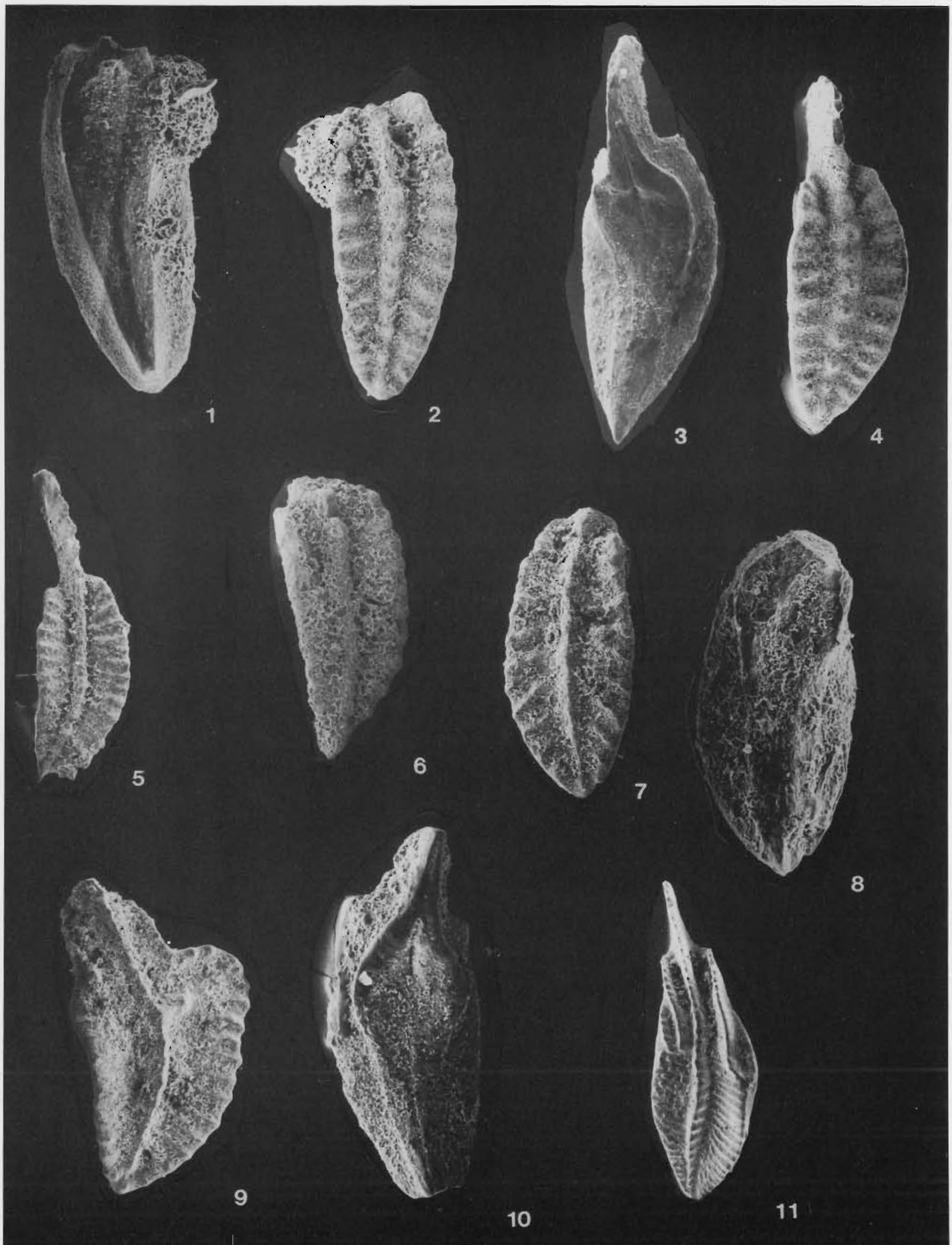
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PLATE 3

(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.

9. *Siphonodella lobata,* section Oberrödinghausen, OR15/13, *Sandbergi* Zone.

11. *Siphonodella cooperi,* section OBerrödinghausen, OR13/10, *Sandbergi* Zone.

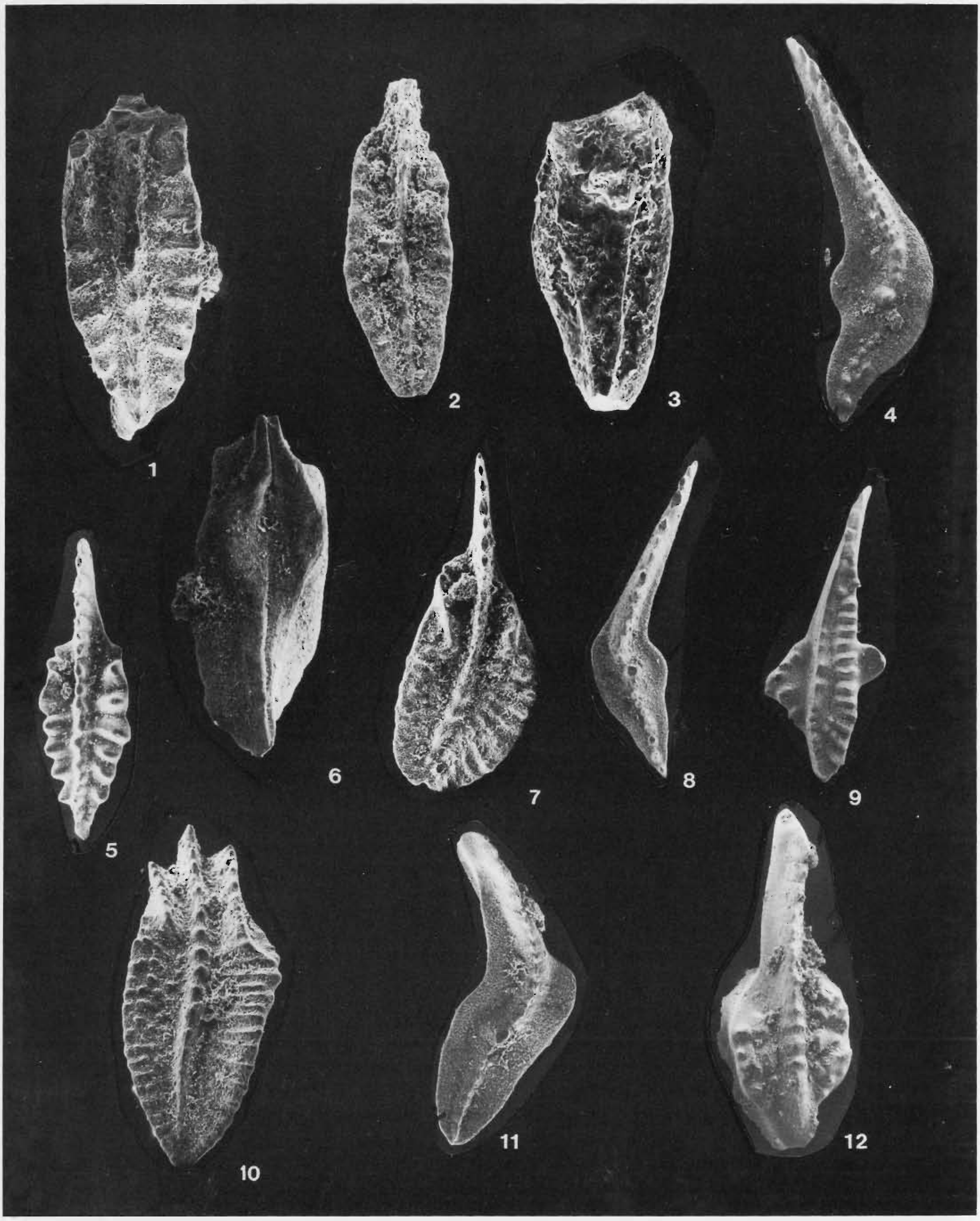
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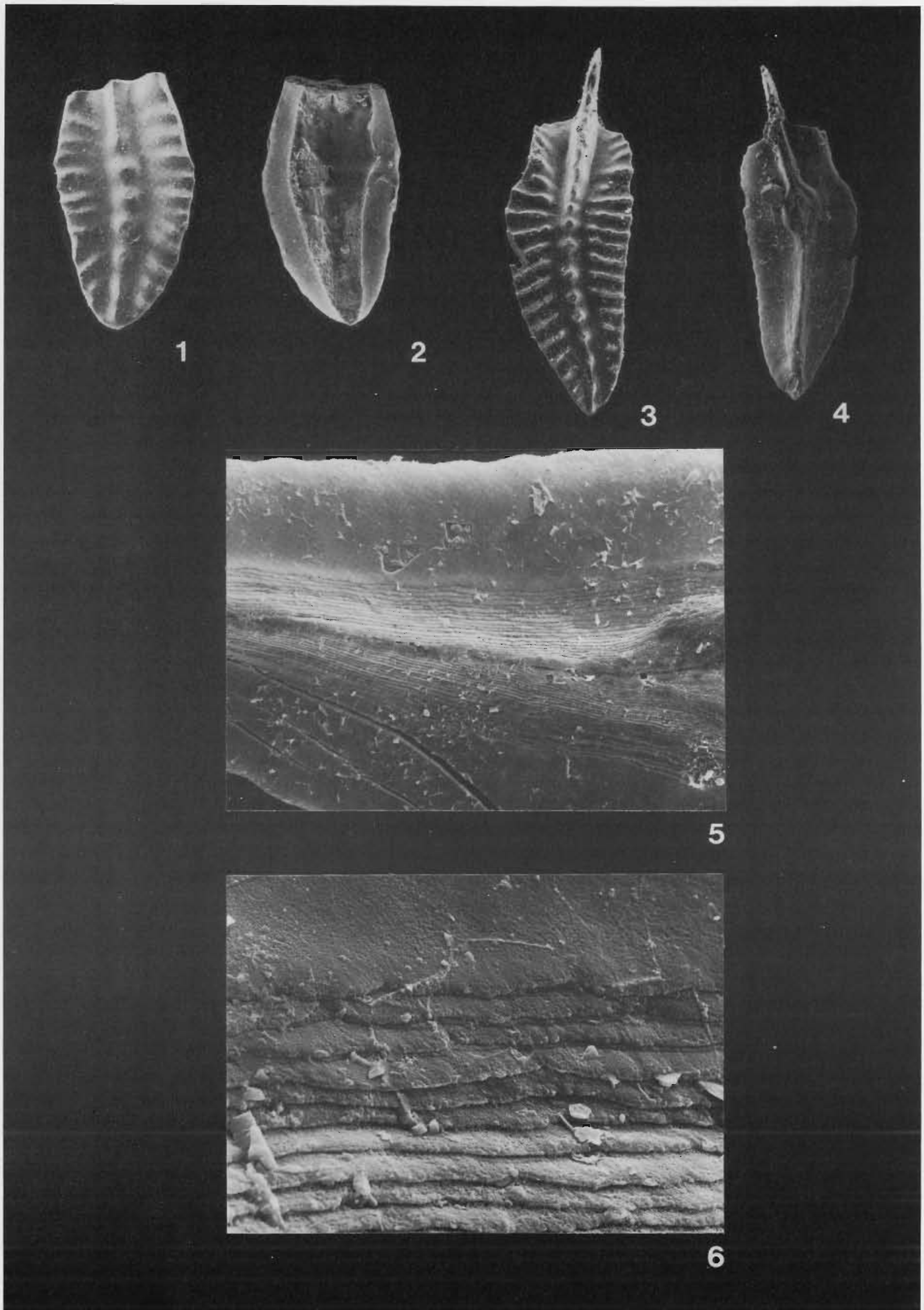
PLATE 4

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)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