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Geochemical decoupling of water masses in the Variscan oceanic system during Late Devonian times

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Abstract

Neodymium isotope data obtained from conodonts collected in Morocco and Poland attest a geochemical decoupling of seawater in the Variscan realm during the Late Devonian. The water masses on the shelves were characterized by unradiogenic ε_{Nd} values, from about −7 to −12. The surface water in the bordering oceans (the Rheic Ocean and the Variscan Sea) yielded more radiogenic ε_{Nd} values, ranging from about −1 to −6. A compilation of Nd and C isotope signatures from the Moroccan Meseta suggests that the shelf and the surface oceanic water differed also in their carbon isotope evolution. The geochemical decoupling constrains a restricted water exchange between shelves and the ocean. Oceanic waters entered far into the shelf areas only during the *semichatovae* transgression in the Frasnian Zone 11. Sea-level fluctuations constituted the major force that modified circulation, and thus controlled the mixing of shelf and surface oceanic seawater. The Nd conodont data reveal that the surface water of the Variscan oceanic water resembled the seawater of the modern Pacific Ocean rather than those of the Atlantic and Indian oceans. The geochemical character of the Variscan oceanic water is consistent with the geotectonic regime of the Variscan realm in Late Devonian and Carboniferous times.
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Keywords: Neodymium isotopes; Conodonts; Seawater geochemistry; Variscan realm; Late Devonian

1. Introduction

Over the last two decades, the usage of Nd isotope signatures of biogenic phosphates to track changes in ocean geochemistry and circulation became a standard method of palaeoceanography (Grandjean et al., 1988; Stille, 1992; Holmden et al., 1996; Stille et al., 1996; Thomas et al., 2003; Scher and Martin, 2004). Neodymium is the ideal seawater tracer because of short residence time (shorter than the global ocean mixing time) and because its isotopic composition in seawater is controlled by the weathering flux of Nd from surrounding continents (e.g., Elderfield and Greaves, 1982; Goldstein and Jacobsen, 1988; Elderfield et al., 1990; Jeandel et al., 1995). All this creates distinct differences in the Nd isotope composition between waters masses in the oceans (e.g., Piepgras and Wasserburg, 1980; Bertram and Elderfield, 1993; Jeandel, 1993). Biogenic phosphates are regarded as very suitable for palaeoceanographic studies because they are less susceptible to diagenetic alteration than other marine precipitates (e.g., Wright et al., 1987; Grandjean et al., 1987; Schmitz et al., 1991; Martin and Haley, 2000; Martin and Scher, 2004).

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Although biogenic phosphates, and especially conodonts, are generally quite common in the Palaeozoic, records of the geochemistry of the Palaeozoic oceans are still very few (Felitsyn et al., 1998; Holmden et al., 1998). This is because the Palaeozoic sediment record is dominated by epeiric sea deposits, and sediments that deposited on the oceanic crust are rare and mostly represented by metamorphosed rocks.

Conodont elements are small skeletal remains of an extinct group of the earliest jawless vertebrates. There are several advantages of using these microfossils as archives of the neodymium isotope composition of ancient seawater. They occur frequently in marine sedimentary rocks of Late Cambrian to Late Triassic age. Their rapid evolution combined with worldwide distribution makes these microfossils very effective stratigraphic tools, providing high-resolution biostratigraphic data. Thus, as a rule, conodont samples are stratigraphically well constrained. Conodont elements are constructed from fluorapatite which exhibits a very high thermal and chemical stability under the conditions prevailing at the earth's surface (Wright, 1990; Holmden et al., 1996; Armstrong et al., 2001). In fact, the conodont fluorapatite represented a stable mineral phase already during the growth of conodont elements, almost immune to oxidation, and thus, not susceptible to weathering (Belka, 1993).

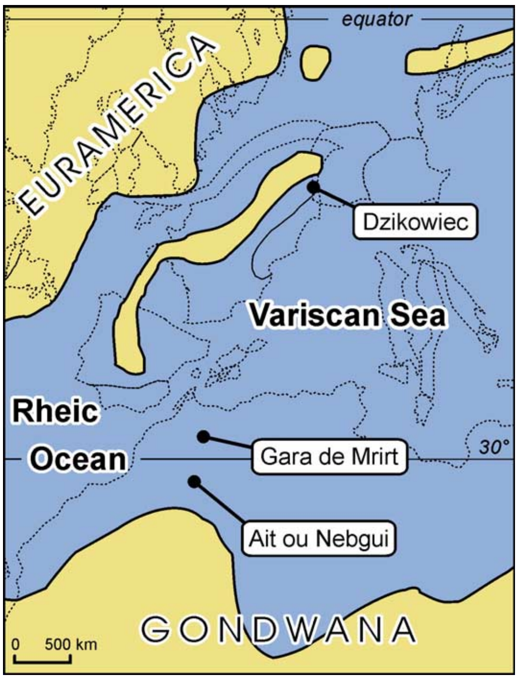

Fig. 1. Palaeogeographic location of the studied sections during the Late Devonian. The palaeogeographic reconstruction is taken from Atlas (Version 3.2), an interactive software developed for the PC by Cambridge Paleomap Services Ltd. For coordinates of investigated localities see Table 1.

Conodont elements yield a relatively high Nd content, from tens to more than a thousand ppm (e.g., Girard and Albarède, 1996; Holmden et al., 1996), acquired during very short time after deposition (Dopieralska, 2003). Belka et al. (2000) showed that the Nd concentration in the conodont crowns depends on their morphology; the higher the surface/volume ratio of conodont elements the higher is their Nd content. Consequently, the Nd concentration varies significantly within each conodont sample but all conodonts in the sample show identical Nd isotope composition. Recent studies revealed also that the Nd content in conodonts was not modified by secondary (diagenetic) processes (Belka et al., 2000; Armstrong et al., 2001). All this indicates that ε_{Nd} values of conodonts represent a signature of a single reservoir, namely that of seawater. Recently, Dopieralska (2003) showed that conodont apatite is much more stable und useful as a tool in palaeoceanographic studies than shark teeth and placoderm fish remains.

In this paper, we present the first extensive isotope dataset for Nd in Late Devonian conodonts collected in western and eastern parts of the Variscan realm (Fig. 1). These data will show that water masses on the shelves and surface water in the bordering oceans were geochemically distinct. The shelf and the surface oceanic waters differed not only in their Nd signatures but each exhibited also individual carbon isotope evolutions. Furthermore, we will also show that fluctuations of the sea level played the most significant role in controlling the water exchange between shelves and the oceans.

2. Outline of the Late Devonian palaeogeography and sea level changes

In the past, several palaeogeographical reconstructions for the Late Devonian were presented (see Dopieralska, 2003 for review). Although they differ in details, all show two large palaeocontinents, Gondwana and Euramerica, separated by a marine space (Fig. 1). Gondwana was located in the Southern hemisphere at intermediate to high latitudes. It formed the largest landmass of the Devonian world and only its margins were covered by epeiric seas. The palaeocontinent of Euramerica, termed also as Laurussia or the Old Red Continent, originated by amalgamation of Laurentia, Baltica and Avalonia during Late Ordovician to Silurian times, as a result of the Caledonian orogenic events (Torsvik et al., 1996; McKerrow et al., 2000). Euramerica was positioned in equatorial latitudes during the Late Devonian and possessed extremely wide shelf areas along its western and eastern margins.

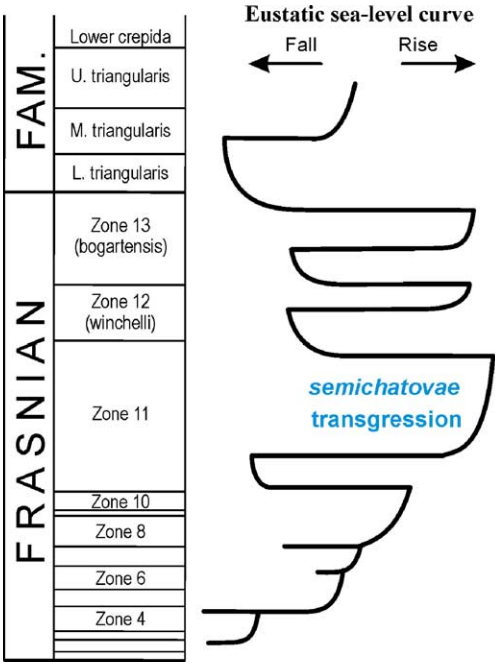

Fig. 2. Frasnian (Late Devonian) eustatic sea-level curve inferred from facies data (adopted from Johnson and Sandberg, 1988; and Sandberg et al., 1992). The curve is plotted against the quantitative biostratigraphic framework of the Frasnian (Klapper, 1977).

Palaeomagnetic data show that several small Variscan terranes occurred between Gondwana and Euramerica. There is still a debate whether some of these Gondwana-derived crustal blocks, i.e., Saxo-Thuringia, Bohemia, Moldanubia, Iberia, and the Armorican Massif, constituted individual terranes or whether they formed a coherent microplate termed the Armorican Terrane Assemblage (Tait et al., 1997). Stampfli and Borel (2002) suggested recently a more radical scenario and merged all crustal blocks between Gondwana and Euramerica into one large superterrane, the European Hunic Terrane.

A serious difficulty in palaeogeographic reconstructions of the Palaeozoic is that outlines of the oceans and seas cannot be directly reconstructed. They arise from the positions of continental crustal units constrained by palaeolatitude data. During the Devonian, Gondwana continued its northward movement but its palaeogeographic position is poorly constrained by palaeomagnetics (see Tait et al., 2000, for discussion). As a result multiple palaeogeographies have been proposed, including a very narrow ocean between Gondwana and Euramerica, and reconstructions showing a wide separation. The first scenario was suggested in reconstructions based predominantly on biogeographic data (Dalziel et al., 1994; McKerrow et al., 2000), whereas palaeomagnetism provided rather evidence for a wide ocean (Tait et al., 2000; Stampfli and Borel, 2002; Lewandowski, 2003). The western part of the ocean is mostly termed the Rheic Ocean, which was originally defined to describe only the space between Avalonia and Armorica (Cocks and Fortey, 1982). More to the east, for the space separating the Armorican Terrane Assemblage (ATA) from the Gondwana margin, Neugebauer (1988) introduced the name the Variscan Sea (Fig. 1).

The Late Devonian was a time of many significant sea-level changes. The widely accepted eustatic sea-level curve was constructed by Johnson et al. (1985) on the basis of coastal onlap and deepening events recognized in the Devonian sequences of Euramerica. Although this curve was later modified (Johnson and Sandberg, 1988; Sandberg et al., 1992; Sandberg et al., 2002), its original version is sometimes erroneously used as a standard up to

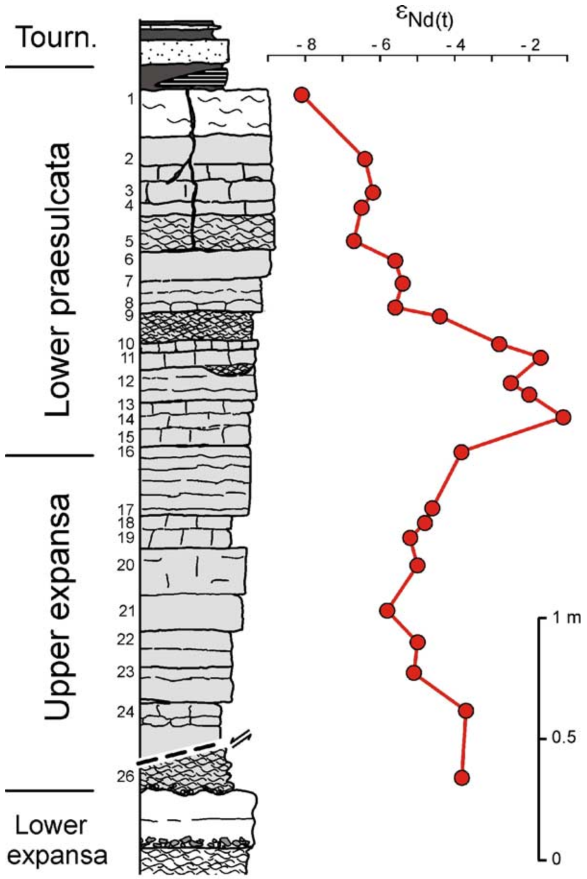

Fig. 3. Variation of ε_{Nd} values of conodonts in the upper Famennian of Dzikowiec (Sudetes), a pelagic sequence deposited on the Devonian oceanic crust. The deep-water carbonates (indicated in gray) are predominantly composed of red, micritic and nodular limestones. With exception of three samples (see Table 1) the analytical error is less than the size of the symbols (=0.4 epsilon unit). Numbers to the left of lithological column correspond to sample numbers.

now (e.g., Streel et al., 2000; Filer, 2002; Chen and Tucker, 2003). The most pronounced Devonian eustatic rise, the cycle IId *sensu* Johnson et al. (1985), happened during the middle Frasnian (Fig. 2). This event is also known as the *semichatovae* transgression because the conodont species *Palmatolepis semichatovae* expanded rapidly at that time throughout Euramerica (e.g., Sandberg et al., 1992). The *semichatovae* transgression marks the culmination point of the general sea-level rise during the Devonian. It was followed by a generally falling Famennian sea level related to glaciations in the Southern Hemisphere.

3. Geological background

In order to provide first insights into the Nd isotope composition of seawater in the Variscan realm during the Late Devonian, three carbonate sequences from different palaeoceanographic and tectonic settings have been selected for the study.

One of very few fragments of the Devonian sedimentary cover that were deposited directly on the oceanic crust and remained unmetamorphosed in the Variscan Belt is the sequence of Dzikowiec (Ebersdorf in the old German literature) in the West Sudetes, southern Poland (Figs. 1 and 3; see Berkowski, 2002 for details of location). It belongs to the Sudetic Ophiolite complex which is a part of the Saxo-Thuringian Terrane (Franke and Zelazniewicz, 2000). This complex comprises gabbros covered by carbonates, Frasnian to Early Mississippian in age. The late Famennian part of the section, which is still well exposed, attracted interest of palaeontologists since the end of the nineteenth century because of the occurrence of cephalopods and a unique fauna of deep-water colonial corals (see Berkowski, 2002 for a review). Conodonts were studied by Freyer (1968), Chorowska

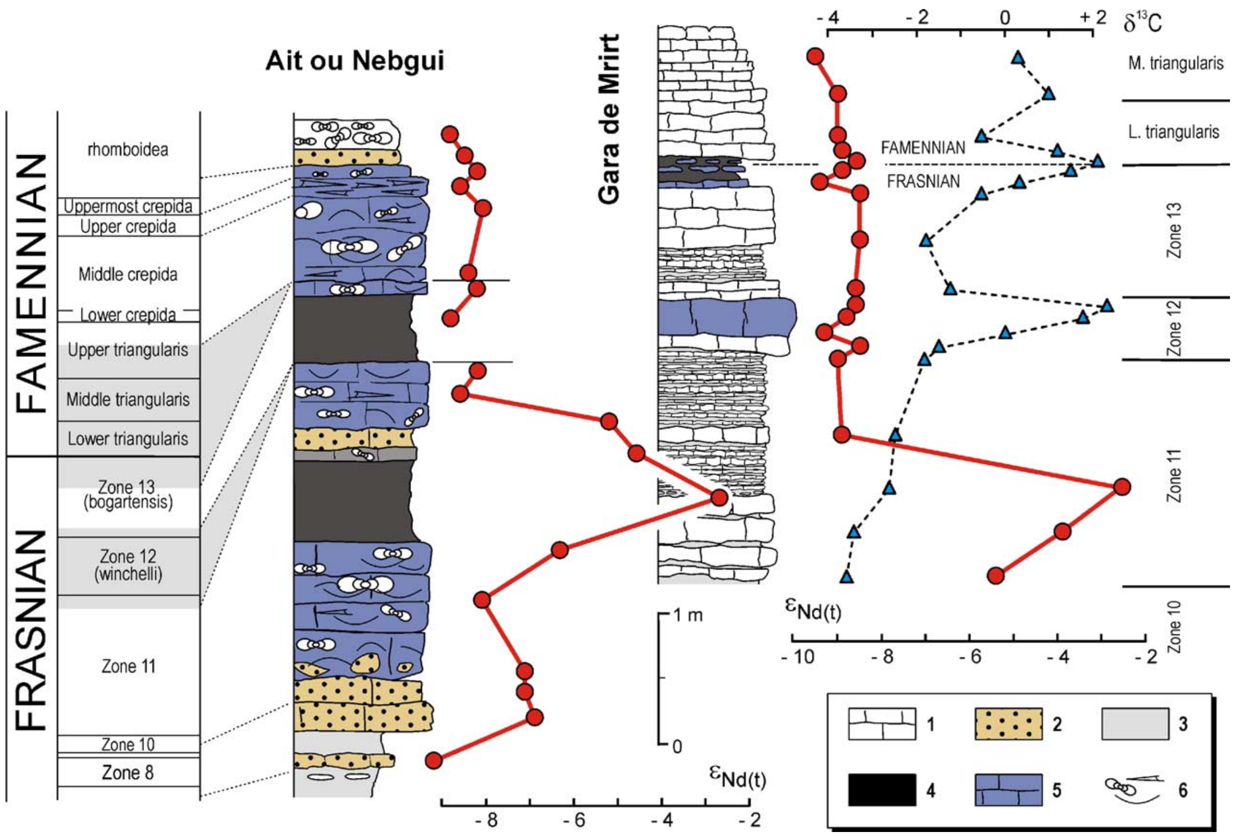

Fig. 4. Variation of ε_{Nd} values (circles) of conodonts in the Upper Devonian of Ait ou Nebgui (Anti-Atlas) and of Gara de Mrirt (Moroccan Meseta). Note the significant positive excursion in ε_{Nd} values within the Zone 11 related to the *semichatovae* transgression. With exception of five samples (see Table 1) the error is less than the size of the symbols (=0.4 epsilon unit). $\delta^{13}C_{carb}$ record (triangles) of the Gara de Mrirt section taken from Joachimski et al. (2002); $\delta^{13}C$ values in ‰ relative to V-PDB. Stratigraphic gaps are indicated in gray in the stratigraphic column; 1 = micritic limestones, 2 = crinoidal limestones, 3 = shales, 4 = black shales, 5 = Kellwasser limestones, 6 = goniatites, orthoconic cephalopods, and ammonoid shell debris. For more details on samples and geology see Table 1 and Dopieralska (2003).

and Radlicz (1987), and Dzik (1997). The so-called "*Wocklumeria* Limestone" is composed of red, micritic limestones, wackestones and mudstones in texture, having a typical nodular appearance in several layers. Conodont fauna recovered during the present study revealed a stratigraphic gap between the "*Wocklumeria* Limestone" and underlying carbonates of the Lower *expansa* Zone (Fig. 3). It allowed also to define the stratigraphic range of the unit, as comprising the Upper *expansa* and the Lower *praesulcata* zones (Streel et al., 2004). Conodonts are quite abundant in the "*Wocklumeria* Limestone", about 50 platform elements per kilogram of dissolved rock, on average. The fauna shows high diversity and is very similar in its taxonomic composition to faunas known from the Rhenohercynian shelf. The striking difference, however, is that the conodont elements in the Dzikowiec section are predominantly small-sized. They show a constant CAI (Colour Alteration Index) value of 2.5, indicating that the rocks have not been exposed to temperatures higher than about 100 °C.

A sequence representing a shelf environment was sampled at Ait ou Nebgui in the eastern Anti-Atlas (Figs. 1 and 4). The Anti-Atlas of southern Morocco is a broad, NE–SW trending Variscan anticlinorium developed at the northern margin of the West African Craton (Piqué and Michard, 1989). Its Palaeozoic sedimentary cover represents sediments deposited on the northern, passive margin of Gondwana. During the Early to Middle Devonian a regional transtension regime stimulated a differential subsidence in this shelf area and led to the formation of carbonate platforms and small basins (Wendt, 1988; Belka et al., 1997; Kaufmann, 1998). The Upper Devonian, perfectly exposed over an area of about 20000 km^2, reaches a maximum thickness of about 1200 m (Belka, 1991). The thickness varies strongly depending on the depositional setting. On the platforms, it ranges from only a few metres to 50 m of fossiliferous wackestones and packstones, whereas thick monotonous shale accumulated in the basins. Black, and organic-rich facies forms the most conspicuous part of the Upper Devonian. It constitutes an equivalent to the Kellwasser sediments of the Rhenohercynian Zone (Wendt and Belka, 1991; Belka and Wendt, 1992). In contrast to the German counterparts, the Kellwasser deposits in the Anti-Atlas contain a more extensive spectrum of lithology and represent a much longer stratigraphic interval that comprises the upper Frasnian and the lower Famennian (Fig. 4 and Belka et al., 2002).

The section Ait ou Nebgui is located in the central part of the Mader Platform (see Dopieralska, 2003 for details of location) and only 5 m thick. The lowest part of the exposed succession consists of shales with some interbeds of yellowish crinoidal limestones. Overlying is the Kellwasser facies composed of three complexes of fossiliferous, cephalopod packstones separated by intervals of black shales. The latter are very rich in conodonts. Although the basal Kellwasser layer rests on an erosional surface there is no evidence for any stratigraphic gap in this part of the section. The conodont fauna recovered from this layer is characteristic for the middle part of the Frasnian Zone 11. Two significant gaps have been recognized in the middle part of the sequence (Fig. 4). These gaps have a regional character and were also identified in other carbonate platform sections (Dopieralska, 2003). Deposition of black, organic-rich sediments terminated within the *rhomboidea* Zone, with a layer of cephalopod packstone bearing very abundant cheiloceratids. Overlying is a thin layer of red crinoidal packstone, followed by brown-coloured cephalopod wackestone. In the whole sequence conodont elements exhibit CAI values from 3.5 to 4 suggesting burial temperatures of 150 °C to 200 °C (Belka, 1991).

The sequence Gara de Mrirt from the Moroccan Meseta (Figs. 1 and 4) was selected to represent sediments deposited on a continental terrane which was distant from margins of Euramerica and Gondwana during Late Devonian times. The Moroccan Meseta forms the westernmost termination of the Variscan Belt. Its tectonometamorphic evolution is still poorly constrained. The exposed Palaeozoic succession ranges in age from the Cambrian to the Westphalian. It is strongly deformed due to NW–SE compression, resulting from the collision of Gondwana with Euramerica during Late Carboniferous time. The Palaeozoic rocks display a thermal overprint that ranges from supramature level to metamorphic amphibolite facies. Devonian rocks investigated during the present study have been collected in the Mrirt nappe, which includes Ordovician to Carboniferous sedimentary sequence overthrusted on the autochthonous unit of Tandara–Bou Tazart (Huvelin, 1973; Allary et al., 1976). Because of lack of detailed information regarding stratigraphy, facies, and tectonics, the original location of the Mrirt nappe sequence remains unknown.

The sampled succession, which is also termed the Bou–Ounebdou section in the literature, is exposed in numerous sections at the southern slope of the Gara de Mrirt, about 5 km southeast of Mrirt (see Dopieralska, 2003 for details of location). During the present study the samples were collected very close to the section line of Lazreq (1999). The sampled interval ranges from the Frasnian conodont Zone 10 to the Middle *triangularis* Zone of the Famennian (Fig. 4). The sequence is about 4 m thick and consists predominantly of gray micritic to bioclastic limestones, mudstone to wackestone in texture,

Table 1
Sm–Nd isotopic data of conodont samples from the Dzikowiec section (Sudetes, Poland), from the Ait ou Nebgui section (eastern Anti-Atlas, Morocco), and from the Gara de Mrirt section (Moroccan Meseta)

Sample	Weight (mg)	Sm (ppm)	Nd (ppm)	$^{147}Sm/^{144}Nd$	$^{143}Nd/^{144}Nd$ (measured)	$^{143}Nd/^{144}Nd$ (365 Ma)	ε_{Nd} (365 Ma)
Dzikowiec section (N 50°34′253 / E 1634′830)							
DZ-1	5.29	42.1	117.0	0.2176	0.512273±12	0.511753	−8.10±0.23
DZ-2	6.40	34.7	111.2	0.1887	0.512289±5	0.511838	−6.44±0.10
DZ-3	6.00	113.9	34.2	0.1816	0.512284±7	0.511850	−6.20±0.14
DZ-4	7.65	112.6	33.5	0.1799	0.512264±5	0.511834	−6.52±0.10
DZ-5	2.62	34.6	119.0	0.1760	0.512248±8	0.511827	−6.65±0.16
DZ-6	8.84	31.8	112.8	0.1704	0.512291±8	0.511884	−5.55±0.16
DZ-7	6.51	32.6	112.6	0.1751	0.512311±8	0.511892	−5.38±0.16
DZ-8	7.08	36.5	125.9	0.1751	0.512299±9	0.511881	−5.61±0.18
DZ-9	11.11	43.9	157.6	0.1683	0.512345±6	0.511943	−4.39±0.12
DZ-10	7.18	35.7	134.8	0.1604	0.512410±7	0.512027	−2.76±0.14
DZ-11	11.09	34.9	142.6	0.1481	0.512433±6	0.512079	−1.74±0.12
DZ-12A	9.52	33.6	138.3	0.1468	0.512417±7	0.512066	−1.99±0.14
DZ-12B	7.80	33.3	135.6	0.1486	0.512395±5	0.512040	−2.50±0.10
DZ-14	3.14	29.2	124.5	0.1416	0.512448±9	0.512110	−1.14±0.18
DZ-16	4.62	21.4	86.5	0.1498	0.512331±8	0.511973	−3.80±0.16
DZ-17	12.25	21.2	88.0	0.1454	0.512282±10	0.511935	−4.55±0.20
DZ-18	9.39	20.1	81.2	0.1499	0.512281±8	0.511923	−4.79±0.16
DZ-19	10.00	21.5	86.5	0.1502	0.512262±6	0.511903	−5.16±0.12
DZ-20	5.36	19.1	76.3	0.1510	0.512271±10	0.511911	−5.02±0.20
DZ-21	6.08	32.8	123.4	0.1605	0.512256±12	0.511872	−5.78±0.23
DZ-22[a]	9.93	35.6	135.4	0.1592	0.512293±11	0.511913	−4.98±0.21
DZ-23	11.56	31.5	118.0	0.1614	0.512292±7	0.511906	−5.12±0.14
DZ-24	4.04	28.5	109.1	0.1577	0.512357±14	0.511981	−3.66±0.27
DZ-26	7.46	30.3	116.1	0.1576	0.512351±7	0.511974	−3.78±0.14
Ait ou Nebgui section (N 30°45′294, W 4°54′958)							
AN-1	8.64	32.7	97.7	0.2025	0.512182±7	0.511697	−9.18±0.14
AN-2	6.23	26.8	88.1	0.1839	0.512252±10	0.511813	−6.94±0.20
AN-3[a]	3.59	45.7	110.3	0.2506	0.512401±12	0.511802	−7.14±0.23
AN-4B[a]	2.36	28.5	102.7	0.1679	0.512205±9	0.511804	−7.11±0.18
AN-4M	6.39	27.9	106.2	0.1589	0.512132±6	0.511752	−8.12±0.12
AN-4T[a]	3.98	26.3	68.5	0.2318	0.512401±11	0.511847	−6.26±0.21
AN-5	2.23	37.4	72.8	0.3103	0.512772±10	0.512031	−2.68±0.20
AN-6	8.53	33.1	78.1	0.2558	0.512543±9	0.511931	−4.62±0.18
AN-8	7.01	23.4	73.0	0.1941	0.512366±10	0.511902	−5.20±0.20
AN-8a	6.01	23.6	81.1	0.1761	0.512148±7	0.511727	−8.61±0.14
AN-9T[a]	2.05	28.9	86.6	0.2015	0.512229±10	0.511748	−8.21±0.20
AN-10	8.10	30.5	90.2	0.2044	0.512203±8	0.511715	−8.85±0.16
AN-11[a]	3.80	26.3	97.5	0.1629	0.512138±10	0.511749	−8.18±0.20
AN-12B	3.44	20.9	96.9	0.1307	0.512050±9	0.511738	−8.39±0.18
AN-12T	3.62	37.5	115.2	0.1970	0.512221±10	0.511750	−8.15±0.20
AN-12T-1[a]	1.13	45.9	173.4	0.1598	0.512111±10	0.511729	−8.58±0.20
AN-12T-2	1.61	41.2	153.9	0.1618	0.512140±9	0.511754	−8.09±0.18
AN-13B[a]	1.90	154.7	501.0	0.1867	0.512181±10	0.511735	−8.45±0.20
AN-14[a]	1.86	78.9	272.0	0.1753	0.512137±10	0.511718	−8.79±0.20
Gara de Mrirt section (N 33°08′831, W 5°31′391)							
MR-96	5.08	38.1	133.0	0.1733	0.512303±7	0.511889	−5.45±0.14
MR-97	9.10	33.0	132.7	0.1504	0.512326±8	0.511967	−3.93±0.16
MR-98	7.94	48.1	153.0	0.1899	0.512491±8	0.512037	−2.55±0.16
MR-99	7.41	32.6	112.6	0.1751	0.512130±12	0.511675	−8.91±0.23
MR-0	6.62	33.8	115.9	0.1760	0.512128±7	0.511708	−8.99±0.14
MR-1T[a]	2.61	23.7	96.8	0.1480	0.512085±10	0.511731	−8.52±0.20
MR-2B[a]	1.79	40.6	131.5	0.1866	0.512137±15	0.511691	−9.30±0.29
MR-2M	11.52	15.8	75.8	0.1256	0.512020±8	0.511720	−8.75±0.16
MR-2T[a]	2.27	11.9	57.8	0.1242	0.512024±10	0.511727	−8.60±0.20

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Table 1 (*continued*)

Sample	Weight (mg)	Sm (ppm)	Nd (ppm)	$^{147}Sm/^{144}Nd$	$^{143}Nd/^{144}Nd$ (measured)	$^{143}Nd/^{144}Nd$ (365 Ma)	ε_{Nd} (365 Ma)
Gara de Mrirt section (N 33°08′831, W 5°31′391)							
MR-3B	8.28	27.1	102.4	0.1598	0.512110±8	0.511728	−8.59±0.16
MR-3M	3.89	29.4	120.7	0.1475	0.512084±12	0.511731	−8.52±0.23
MR-3T	9.12	41.9	124.6	0.2034	0.512217±8	0.511731	−8.53±0.16
MR-4A	8.67	68.5	158.9	0.2606	0.512311±9	0.511688	−9.37±0.18
MR-4B	4.36	55.5	136.3	0.2459	0.512300±7	0.511713	−8.89±0.14
MR-4C	8.27	41.6	122.9	0.2046	0.512216±8	0.511727	−8.61±0.16
MR-5B	5.78	50.5	198.4	0.1534	0.512079±9	0.511712	−8.90±0.18
MR-5B2	5.37	59.8	235.2	0.1539	0.512073±12	0.511705	−9.04±0.23
MR-5T	6.06	33.6	140.6	0.1444	0.512053±9	0.511708	−8.98±0.18
MR-6A	6.92	43.6	150.6	0.1749	0.512100±10	0.511682	−9.49±0.20
MR-6C	8.55	53.5	159.0	0.2034	0.512133±14	0.511647	−10.17±0.27
MR-6D	7.74	44.0	153.7	0.1731	0.512096±8	0.511683	−9.47±0.16

[a] Samples measured in Munich.

which alternate with gray shales. The Kellwasser facies forms two horizons; the lower one is a 25 cm thick layer of black wackestone that comprises most of the conodont Zone 12 (*winchelli*), whereas the Upper Kellwasser horizon is developed as lenses and layers of black limestone, alternating with black shales. Conodonts sampled during the present study document that the deposition of black Upper Kellwasser sediments did not terminate at the Frasnian–Famennian boundary, as was reported by Lazreq (1992, 1999) and subsequently adopted by other authors, but it continued into the Famennian (Fig. 4). The uppermost black carbonate layer contains already a fauna characteristic for the Lower *triangularis* Zone. Both Kellwasser horizons yield fauna that is dominated by *Buchiola* (bivalve) and styliolinids. These fossils are accompanied by less frequent orthoconic cephalopods and rare ammonoids. Conodonts are very frequent in the whole section. They yield CAI values of 4.5 to 5, indicating burial temperatures up to 300 °C (Epstein et al., 1977).

4. Material and methods

Rock samples, each between 1–2 kg, were predominantly limestones and marly limestones; only a few samples were taken from shales. Conodont elements were recovered from the host rock by dissolution in 10% acetic acid followed by wet-sieving. To avoid input of additional, unknown chemical components, a pure (99.7–100%) acetic acid was used. The biogenic fluorapatite was separated from the insoluble residue with a Frantz isodynamic magnetic separator. Final selection of conodont elements was accomplished by handpicking under a binocular microscope. In order to remove any adhering mineral detritus from the conodont surface, the samples were shortly (~ 2 min) treated with 1% HCl and washed with deionised water. Conodont sample weights used for Nd isotope analysis were from 1.1 to 12.2 mg, i.e., the samples contained from 10 to 150 conodont elements. Conodont stratigraphy of the studied sections was performed by one of us (Z.B.). The biostratigraphic framework as shown in Figs. 3 and 4 has already been presented by Belka et al. (2002) and Streel et al. (2004).

The isotope analyses were carried out in the Isotope Laboratories at the Munich University and at the Giessen University, Germany. The samples were spiked with a ^{150}Nd–^{149}Sm tracer solution and dissolved on a hot plate (~ 100 °C, overnight) in closed PFA vials using concentrated nitric acid (~ 14 N).

At Munich, the LREE were separated on 5 ml quartz columns using an AG 50W-X12 resin, while at Giessen EICHROM TRU resin and 50 µl teflon columns were used for the same purpose (cf. Pin et al., 1994). Separation of Nd and Sm was achieved by reverse-phase ion-exchange chromatography on 2 ml quartz columns packed with Teflon powder coated with HDEHP (Hexyl di-ethyl hydrogen phosphate). Details of the analytical procedures are described in Dopieralska (2003). Samarium and neodymium were measured in a double filament configuration on a FINNIGAN MAT 261 mass spectrometer running in static (Sm, Nd) and dynamic (Nd) mode. Repeated measurements of the AMES standard over the duration of this study yielded $^{143}Nd/^{144}Nd=0.512073\pm10$ (2σ, $n=31$, static collection mode) and 0.512135 ± 11 (2σ, $n=23$, dynamic collection mode) in Munich, and 0.512135 ± 8 (2σ, $n=27$, static collection mode) in Giessen. When necessary, instrumental bias was suitably corrected according to those standard values. External reproducibility of $^{143}Nd/^{144}Nd=1.9\times10^{-5}$ (2σ) for measurements performed in Munich and 1.6×10^{-5} (2σ) for those performed in Giessen.

$^{143}Nd/^{144}Nd$ ratios were normalized to $^{146}Nd/^{144}Nd = 0.7219$, and Sm isotope ratios to $^{147}Sm/^{152}Sm = 0.56081$. Total procedure blanks for Nd and Sm were <30 pg and were found to be negligible with respect to the results. Nd isotope data are reported in the standard epsilon notation (å) calculated using $^{143}Nd/^{144}Nd = 0.512638$ and $^{147}Sm/^{144}Nd = 0.1967$ for present-day CHUR (Jacobsen and Wasserburg, 1980). All ε_{Nd} values are recalculated according to the measured $^{147}Sm/^{144}Nd$ ratios for the time of deposition (365 Ma). Although the stratigraphic age of the measured samples spans approximately 8 Ma, the maximum error introduced by using a single age for all samples is 0.1 epsilon units only.

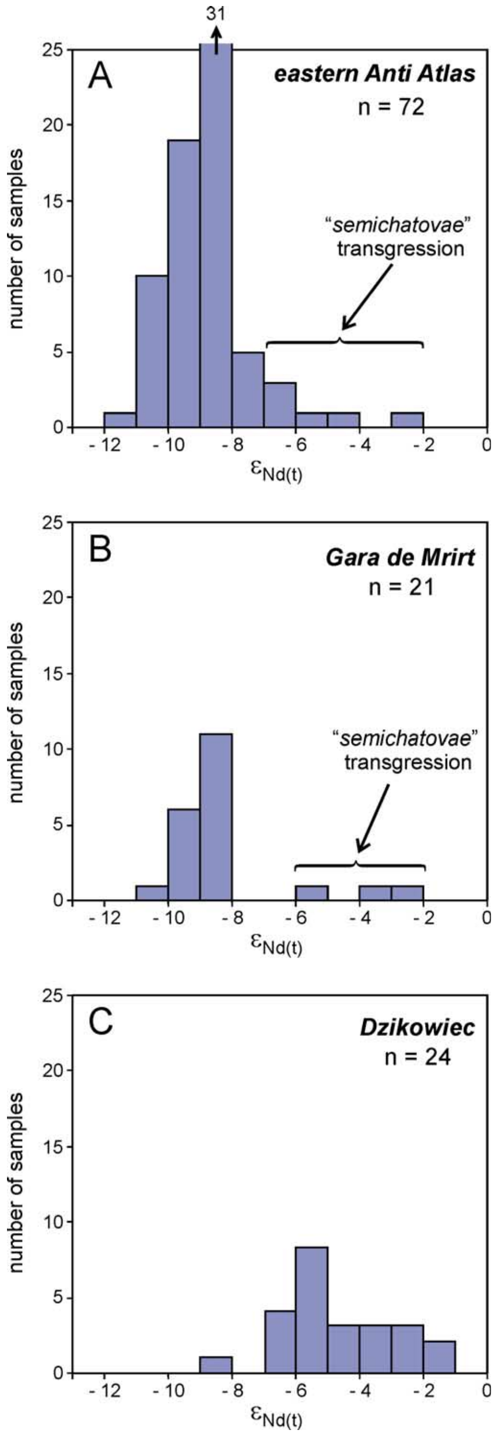

Fig. 5. Histograms showing of ε_{Nd} values of seawater of the Variscan realm recorded in Late Devonian conodonts collected in different oceanographic and tectonic settings. A — The Anti-Atlas data are taken from Dopieralska (2003). They include Nd isotope measurements performed on conodonts from three successions, Mech Irdane, Ait ou Nebgui, and Lahmida, located on the Moroccan shelf of Gondwana. The shelf water is characterized by low radiogenic ε_{Nd} values. The high radiogenic ε_{Nd} values of the surface oceanic water were identified only during the *semichatovae* transgression of the conodont Zone 11. B — Histogram of ε_{Nd} values of seawater in the Moroccan Meseta (southwestern part of the Variscan Orogen). Note the presence of the shelf water with an input of surface oceanic waters during the *semichatovae* transgression. C — Histogram of ε_{Nd} values of seawater in the eastern part of the Variscan Sea (Dzikowiec section). The range of ε_{Nd} values is indicative of the oceanic seawater.

5. Results

5.1. Variation in Nd isotope composition

Results of Nd isotope measurements are presented in Table 1. They reveal a significant difference in Nd isotope signatures between seawater in the Sudetes and that recorded in the Moroccan localities. In the Dzikowiec section conodonts are characterized by high radiogenic ε_{Nd} values from -1.1 to about -6.5 (Fig. 3). There is only a single sample, taken from the topmost layer of the carbonate succession, with ε_{Nd} value of -8.1. It is remarkable that this is the only one bed in this generally deep-water carbonate sequence containing shallow-water sedimentary features. In contrast to Dzikowiec, in both Moroccan localities the seawater was less radiogenic with ε_{Nd} values of about -9 in average (Figs. 4 and 5). The most conspicuous features, however, are prominent positive excursions in ε_{Nd} values (up to -2.6) during the Frasnian Zone 11 in both sections. Their synchronous appearance and similar level of ε_{Nd} value suggest a relation to the same event. It is important to note that these successions were located in different geotectonic settings and were distant more than 500 km from each other during the Late Devonian. The peaks in ε_{Nd} coincide with the *semichatovae* transgression (Fig. 2). Dopieralska (2003) observed the *semichatovae* peaks in ε_{Nd} values also in two other sections of the eastern Anti-Atlas. She showed

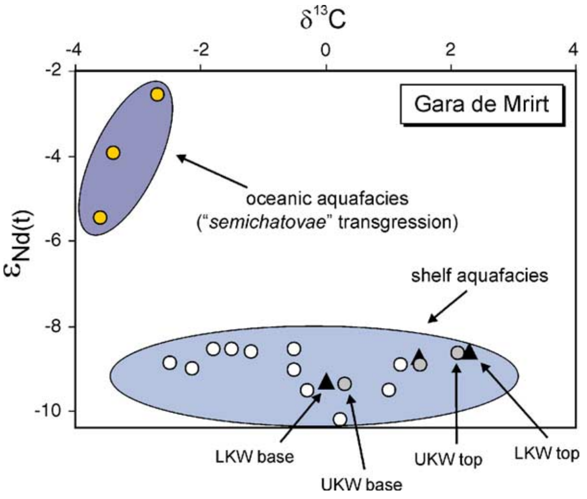

Fig. 6. Diagram showing contrasting geochemical characteristics for the Variscan oceanic seawater and shelf waters recorded in the Upper Devonian sequence of Gara de Mrirt. The ε_{Nd} values of conodonts are plotted against $\delta^{13}C$ values of carbonate host rocks. The carbon data are taken from Joachimski et al. (2002). The data points of the Lower Kellwasser (LKW) are marked as black triangles, those of the Upper Kellwasser (UKW) as gray circles.

that seawater in this shelf area was characterized by ε_{Nd} values between −7 and −12 (Fig. 5), with exception of the time of the *semichatovae* transgression when high radiogenic waters entered the Anti-Atlas from the north and from the southwest.

5.2. Nd versus C isotopic composition

Joachimski et al. (2002) provided carbon isotope data for carbonate rocks of the Gara de Mrirt section. $\delta^{13}C_{carb}$ values increase from around −3 during the Zone 11 up to positive values in the early Famennian (Fig. 4). There are two significant positive excursions in $\delta^{13}C_{carb}$ with amplitudes of +3‰ during the deposition of the Lower and Upper Kellwasser sediments. A compilation of carbon isotope data with the ε_{Nd} values of conodonts, shown in Fig. 6, emphasises clearly a distinct geochemical character of seawater during the *semichatovae* transgression, characterized by high ε_{Nd} values and strongly negative $\delta^{13}C$ signatures. The diagram reveals also a peculiar relation between the Nd and C isotope composition during the deposition of the Kellwasser sediments. The onsets of both Kellwasser horizons exhibit almost identical Nd and C isotope signatures, and a similar consistence is also observed by the termination of this organic-rich facies. Such correlation within a single seawater reservoir is very enigmatic and needs additional investigations of other Kellwasser occurrences.

6. Discussion and conclusions

Conodonts recovered from different locations in Poland and Morocco provide a strong evidence for significant differences in seawater geochemistry within the Variscan realm during Late Devonian times. We suggest that two geochemically distinct water masses can be distinguished, the shelf and the surface oceanic waters. This duality is expressed by distinct ranges of Nd isotope signatures. In addition, the data suggest also an individual carbon isotope evolution of these seawater reservoirs. The geochemical decoupling attests a restricted water exchange between shelves and the ocean.

Surface oceanic water, characterized by high radiogenic ε_{Nd} signatures (Fig. 5C), is documented in the Variscan Sea during the late Famennian by this study. Nd isotope data from the Anti-Atlas and the Moroccan Meseta testify similar geochemical characteristics of surface seawater in the Rheic Ocean during the Frasnian (Fig. 5A, B). But records of high radiogenic waters in these areas originated from an ingression of oceanic waters onto the shelves where the oceanic waters were mixed with the shelf water. Therefore, it is very likely that pristine Rheic Ocean surface water may presumably have displayed even more radiogenic Nd isotopic signatures than the highest ε_{Nd} values measured at Gara de Mrirt and at Ait ou Nebgui. Considering the range of ε_{Nd} values, from −1.1 to about −6.5, it can be concluded that the Variscan oceanic water (both in the Rheic Ocean and the Variscan Sea) resembled the seawater of the modern Pacific Ocean (with average ε_{Nd} value level of −3.5) rather than those of the Atlantic and Indian oceans, having average ε_{Nd} values of −12.1 and −8.3, respectively (see Bertram and Elderfield, 1993, for summary). This geochemical character is consistent with the geotectonic regime of the Variscan realm with several active magmatic arc systems and subduction zones, and a mosaic of terranes predominantly built from relatively young Cadomian crust (Franke, 2000). Thus, the Variscan realm exhibited strong geotectonic similarity to the present structure of the western Pacific and the Philippine and Indonesian Archipelago.

Various shelves that rimmed the Rheic Ocean and the Variscan Sea as well as at least some terranes within the Variscan space were covered by unradiogenic shelf waters that displayed a range of ε_{Nd} values, from −7 to −12. Besides of the Anti-Atlas and the Moroccan Meseta, seawater with a similar Nd isotope composition was also recorded in the Montagne Noire (southern France) and on the Baltic shelf of Euramerica in southern Poland (Dopieralska, 2003). This suggests a generally similar age of continental source rocks for the riverine Nd input from the surrounding land areas. The largest Nd dataset, available from the Devonian of the Anti-Atlas, reveals clear lateral trends in ε_{Nd} values on the northern shelf of Gondwana (Dopieralska, 2003). The lowest ε_{Nd} values occurred close to the coast and correspond well with the input of clastic material from the West African Craton. The most radiogenic signatures, however, were recorded in the distant seaward settings. Temporal trends in ε_{Nd} values observed at any given point on the shelf were first of all results of sea-level fluctuations. A rise in sea-level generated a positive shift in ε_{Nd} values, during regression phases ε_{Nd} values decreased. The oceanic waters entered far into the shelf areas only during the *semichatovae* transgression. It seems that sea-level changes constituted the most critical factor that controlled the mixing of shelf and oceanic waters in the marginal parts of the Variscan shelves (Dopieralska et al., 2003).

As mentioned above, seawater on the shelves and in the ocean differed not only in their Nd isotopic signatures but very probably also in their carbon isotopic evolution. Geochemical decoupling between various water masses in marine environments is known both from the past and the present time. Holmden et al. (1998) provided Nd and C isotopic evidence for geochemical decoupling between the epicontinental Mohawkian Sea in the Midcontinent region of North America and the bordering Iapetus Ocean during the Ordovician. Recently, Immenhauser et al. (2002) demonstrated positive shifts in the C isotope record, created by an eustatic deepening event, in the Atokan shallow-water carbonate platform from northern Spain. The carbon isotope composition of modern surface seawater is relatively uniform and shows variations smaller than 1.5‰ (Charles and Fairbanks, 1992), but differences as high as 4‰ can occur in certain oceanographic situations. In particular, a scenario with shallow-water carbonate platforms covered by seawater depleted in $\delta^{13}C$ compared to open-ocean surface water might be the rule rather than the exception in epeiric seas (e.g., Lloyd, 1964; Patterson and Walter, 1994; Immenhauser et al., 2003).

Considering restricted water exchange between shelves and the ocean in the Variscan realm care must be taken when interpreting trends in C isotope composition in the Late Devonian epeiric seas. This is because exchange and mixing of shelf and ocean seawater reservoirs could produce considerable excursions in the carbon isotope record. In addition, the C isotope data identified for the Rheic Ocean seawater appear to indicate that this ocean was characterized by a very low phytoplankton productivity and a low total carbon burial rate during the time of the Zone 11. Under such conditions respiration might have controlled surface water $\delta^{13}C$ values, rather than photosynthetic processes. Hsü and McKenzie (1990) termed this scenario the postcatastrophic "Respiring Ocean" in which dead phytoplankton is being decayed by bacterial activity within the surface waters and thus this influx of ^{12}C drives the $\delta^{13}C$ toward lighter values. The cessation of organic export from the surface ocean leads to an isotopically homogeneous ocean. If this condition persists, the ocean's isotopic composition approaches that of the riverine weathering input (Kump, 1991).

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