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Devonian/Carboniferous boundary glacioeustatic fluctuations in a platform-to-basin direction: A geochemical approach of sequence stratigraphy in pelagic settings

Ondrej Bábek [a,*], Tomáš Kumpan [b], Jiří Kalvoda [b], Tomáš Matys Grygar [c]

[a] Department of Geology, Palacký University, Tř. Svobody 26, 77146 Olomouc, Czech Republic
[b] Department of Geological Sciences, Faculty of Science, Masaryk University, Kotlářská 267/2, 61137 Brno, Czech Republic
[c] Institute of Inorganic Chemistry, Czech Academy of Sciences, Husinec-Rez c.p. 1001, 25068 Rez, Czech Republic

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ABSTRACT

We investigated high-resolution stratigraphic distribution of selected major and trace elements and gamma-ray spectra of fourteen Devonian/Carboniferous (D/C) boundary sections of Europe located in the late Palaeozoic Laurussia and Gondwana. The aim was to trace the geochemical signature of a marked forced and normal regressive interval which was associated with rapid progradation of siliciclastics into the marine carbonate systems (Rhenish Massif) and a prominent hiatus in shallow-water ramp settings (Namur–Dinant Basin). This interval represents the late Devonian Hangenberg event (HBE) *sensu lato* (middle *praesulcata* conodont zone) as defined by previous authors. This regressive interval (FSST to LST) correlates with thin shale layers (HBE shale) sandwiched between monotonous nodular calcilutite/calcisiltite successions at five pelagic sections of Moravia, Carnic Alps, Montagne Noire, and Pyrenees. In all sections with continuous D/C sedimentation (i.e., except those of the Namur–Dinant Basin), the HBE *s.l.* interval is accompanied by elevated percentages of detrital proxies (Al, K, Rb, Zr) and changes in their ratios (Zr/Rb, K/Al, Rb/K) which are normally interpreted as indicators of increased siliciclastic input, provenance, and grain size. Zr/Rb and other proxies are traceable even without apparent lithological evidence and can, therefore, facilitate stratigraphic correlation. Paleoredox and productivity proxies (U/Th and Ni/Rb enrichment factors) only rarely show elevated values in the Hangenberg black shale interval, indicating that the associated water dysoxia/anoxia was a local rather than global phenomenon. Global correlations based on the HBE black shales should therefore be dropped in favor of the HBE *s.l.* interval. Moreover, analysis of sedimentation rates in the upper *expansa* to *kockeli* zone interval using the published radiometric ages suggests that the HBE *s.l.* was a time of significant increase in the rate of siliciclastic supply into the ocean, even in the most distal pelagic sections. Consequently, the previous interpretation of the HBE black shale as a condensed succession deposited during rapid sea-level rise seems unlikely. We interpret the HBE *s.l.* (i.e., including the HBE black shale) as a marine record of glacioeustatic sea-level drop and increased aeolian transport in connection with late Devonian climatic cooling and glaciation. The set of geochemical markers related to the late Devonian sea-level fluctuation can be used for super-regional to global correlations from platform to basin settings. Moreover, they can facilitate current efforts to determine a new D/C boundary definition.

1. Introduction

Sequence stratigraphy has proven to be an extremely useful concept in stratigraphic correlation and paleoenvironmental analysis over recent decades (Posamentier et al., 1988; Van Wagoner et al., 1990; Hunt and Tucker, 1992; Catuneanu, 2006). Studying "facies relationships and stratal architecture within a chronological framework" (Catuneanu et al., 2009), sequence stratigraphy relies on data from a broad range of scales including small-scale and large-scale outcrops, well-logs, and 3D seismic sections. Consequently, short and lithologically uniform sections are usually the least suitable working material for studying sea-level fluctuations. The Global Boundary Stratotype Sections and Points (GSSPs) of stage boundaries are typical examples of such uniformity and stratigraphic detail, yet many of them represent important overturns in the Earth's history and biotic evolution which are closely associated with sea-level fluctuations (cf., Scholle and Arthur, 1980; Ross and Ross, 1985; Brett, 1998; Hardenbol et al., 1998).

The Devonian/Carboniferous (D/C) boundary is one of such intervals, characterized by paleoenvironmental perturbations and eustatic sea-level fluctuations related to the early stages of late Paleozoic continental glaciation of Gondwana (Veevers and Powell, 1987; Fielding et al., 2008; Isaacson et al., 2008). The drop in sea level close to the D/

* Corresponding author.
E-mail address: babek@prfnw.upol.cz (O. Bábek).

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C boundary is indicated by gaps in shallow-water carbonate platform settings as well as in several deeper water sections (Korn, 1993; Kalvoda et al., 1999; Hance and Poty, 2006; Corradini, 2008; Kumpan et al., 2014b). The long duration of the gaps and scarcity of index conodont taxa in shallow water facies make it difficult to establish the exact timing and magnitude of the D/C sea-level changes. Conversely, good sections in deep-water facies yielding the necessary index conodont taxa (Flajs and Feist, 1988; Kaiser et al., 2006, 2008) are scarce, of limited thickness, and sometimes lithologically uniform. However, carbonate successions at several important D/C sections contain correlatable layers of black shales, siltstones, sandstones, and siliceous sediments which tend to concentrate at two important levels, the late Famennian Hangenberg event or crisis (HBE) (Walliser, 1984; Becker, 1993; Caplan and Bustin, 1999) and the mid-Tournaisian Lower Alum Shale event (LASE) (Becker, 1993; Zhuravlev, 1998). The HBE black shales, which are typically found in deep-water marine successions, are interpreted by many workers as a consequence of rapid transgression and establishment of oxygen-depleted or even euxinic bottom conditions (Becker, 1993; Walliser, 1996; Kump et al., 2005; Kaiser et al., 2006; Marynowski and Filipiak, 2007; Marynowski et al., 2012). The ocean anoxia associated with carbonate and biotic crisis may have been linked to the spread of vascular plants and changes in pedogenic weathering on continents (Algeo et al., 2001), the upwelling of nutrient-rich waters and the eutrophication of shelves (Caplan and Bustin, 1999), and/or global warming and increase in organic productivity (Kaiser et al., 2006). Nevertheless, at numerous locations worldwide the HBE is split into two distinct layers, the basal HBE black shale and the following gray to green shales, sometimes grading upward into sandstones and/or reworked oolites (HBE shale and sandstone) (see review in Kaiser et al., 2011). The HBE black shale is believed to reflect rapid transgression (flooding of the surface at the base of transgressive systems tract, TST) while the HBE shale/sandstone often shows progradation patterns and is generally interpreted as regressive succession (late highstand, HST, or falling stage systems tract, FSST, to lowstand systems tract, LST) (Van Steenwinkel, 1993a, 1993b; Kaiser et al., 2011; Kumpan et al., 2014b). According to several authors, this sequence of events reflects global C cycling in which enhanced organic carbon burial in the HBE black shale led to reduction of atmospheric CO_2 levels and climatic cooling, continental glaciation, and a glacioeustatic drop in sea level close to the D/C boundary proper (Caplan and Bustin, 1999; Kaiser et al., 2006; Isaacson et al., 2008). Indeed, perturbations in the global carbon cycle during the HBE have been revealed by the carbon isotopic record. Positive anomalies in both inorganic and organic $\delta^{13}C$ have been documented from the HBE interval in numerous sections from Europe, North America, and southern China (e.g., Brand et al., 2004; Buggisch and Joachimski, 2006; Kaiser et al., 2006, 2008; Cramer et al., 2008; Bojar et al., 2013; Kumpan et al., 2014a; Qie et al., 2014).

The current Global Standard Section and Point (GSSP) of the D/C boundary is a subject of considerable criticism, and there are efforts leading toward its redefinition (Ziegler and Sandberg, 1996; Kaiser, 2009; Aretz, 2011). The record of D/C glacioeustatic sea-level fluctuations may provide an alternative tool to classical biostratigraphy, but this requires establishing a clear link between the shallow- and deep-water facies realms and finding clear criteria for defining sequence stratigraphic surfaces/systems tracts in the pelagic realm. Although sequence stratigraphy of pelagic and deep-water deposits is by definition problematic, attempts have been made to link sea-level variations with subtle changes in observable lithology, such as hardgrounds and bioturbation (Martire, 1992; Lubeseder et al., 2010; Ver Straeten et al., 2011) and especially elemental, stable isotope, and organic geochemistry (Scholle and Arthur, 1980; Jarvis et al., 2001; Philip, 2004; Mabrouk et al., 2007; Halgedahl et al., 2009; Ver Straeten et al., 2011). Of particular significance are the detrital elemental proxies such as Al, Si, Rb, K, Ti, and Zr, which indicate changes in siliciclastic input in carbonate depositional settings; bottom redox proxies (total organic carbon (TOC), U, Mo, V, S, Fe^{2+}, and Fe^{3+}); and proxies related to biogenic supply and paleoproductivity (Mn, P, Sr, Cu, Zn, Ni, and Pb) (e.g., Fralick and Kronberg, 1997; Sageman and Lyons, 2005; Tribovillard et al., 2006; Śliwiński et al., 2010; Bout-Roumazeilles et al., 2013). Few of the proxies can be linked unequivocally to a particular driving factor, however, multiple lines of evidence should be examined in interpreting relative water depth (Ver Straeten et al., 2011).

In this paper, we analyze the facies successions, petrophysical patterns (gamma-ray spectra), biostratigraphy, and geochemical record (elemental composition) of fourteen D/C boundary sections of Europe (Moravo-Silesian Zone, Montagne Noire, Dinant Synclinorium, Rhenish Massif, Pyrenees, and Carnic Alps) including the current GSSP at La Serre, southern France. The sections represent a range of environmental settings including carbonate ramp, mixed carbonate–siliciclastic shelf, pelagic, and turbidite-dominated settings. The aims of this paper are twofold: to investigate various geochemical proxies as possible tools for correlation between shallow- and deep-water depositional settings, and to establish a sequence stratigraphic nomenclature for interpretation of sea-level changes in the D/C boundary interval.

2. Geological settings

2.1. Geological and geographic settings of the D/C boundary sections

Our study focused on six areas (Fig. 1). Three of them – the Namur–Dinant Basin of Belgium and northern France (3 sections); Rhenish Massif, Germany (3 sections); and Moravo-Silesian Zone, Czech Republic (3 sections) – are preserved in the Rhenohercynian Zone of the Variscan Belt of Europe (Ziegler, 1990; Oncken et al., 2000; Kalvoda et al., 2008; McCann et al., 2008). These sections constituted the southern margins of Laurussia during the late Devonian to early Carboniferous (Franke, 1999, 2000; Kalvoda et al., 2008). In contrast, Montagne Noire, Pyrenees, and Carnic Alps represent the northern tips of Gondwana in the late Devonian. Sections in the Montagne Noire and the northern Pyrenees were located on the northern Iberian margin (Gondwana), which became accreted to Armorica during the Carboniferous (Lardeaux et al., 2001; Faure et al., 2009; Ballèvre et al., 2014). Two sections in the Carnic Alps within the Eastern Alps belong to the Gondwana-derived Bosnian–Noric Terrane accreted to the intra-Alpine Mediterranean terrane during the Carboniferous (Frisch and Neubauer, 1989; Neubauer and Handler, 2000).

The D/C boundary sections in the Namur–Dinant Basin represent mixed carbonate–siliciclastic sequences deposited in shallow to deeper environments a carbonate ramp. We studied two sections in this proximal part of the carbonate ramp, the Rivage section of the Condroz sedimentation area (SA) and the Les Ardennes section of the Avesnois SA. Distal parts of the ramp system were studied at the Gendron-Celles section (Dinant SA) (Poty, 1997; Hance et al., 2001; Devuyst et al., 2005; Kumpan et al., 2014b). The Rivage section (50°29′01.6″N, 5°34′59.5″E; all coordinates corresponding to WGS 84 ellipsoid) is located 17 km S of the center of Liège, Belgium, close to the confluence of the Ourthe and Amblève rivers. The Gendron-Celles section (50°12′43.9″N, 4°57′52.4″E) is located 6.5 km ESE of the center of Dinant in a railway cut close to the Gare de Gendron-Celles train station in Belgium. The Les Ardennes section (50°7′30.9″N, 3°53′24.2″E) is located in a quarry 2.8 km W of the center of Avesnes-sur-Helpe in northern France. Three D/C boundary sections were studied in the northern part of the Rhenish Massif. The sections comprise successions of deep-water nodular carbonate with intercalations of black shales, gray shales, siltstones, and sandstones of the HBE and LASE intervals. The Oese and Oberrödinghausen sections are situated on the northern flank of the Remscheid-Altena Anticline; they constitute a part of the late Famennian-early Carboniferous turbidite-influenced basin. The Drewer section, located on the Belecke Anticline, was deposited on a deep intrabasinal swell with starved condensed basin facies (Paproth, 1986; Korn and Weyer, 2003; Korn, 2010). The Oese section (51°24′06.0″N, 7°47.15.8″E) is located on the NE outskirts of Hemer, 26 km