Palaeobiodiversity and Palaeoenvironments (2023) 103:711–731
https://doi.org/10.1007/s12549-023-00578-y

SENCKENBERG

ORIGINAL PAPER

Palaeozoic (Silurian–Devonian) cherts from the Balkan Terrane, western Bulgaria: geochemistry, biostratigraphy and depositional settings

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Received: 27 October 2022 / Revised: 20 February 2023 / Accepted: 23 February 2023 / Published online: 25 April 2023

Abstract

Palaeozoic (Silurian and Devonian) bedded cherts from the Balkan Terrane in western Bulgaria occur in three tectonic units: Svoge, Lyubash-Golo Bardo, and Morava. The Silurian and Devonian ages of the chert-bearing lithostratigraphic successions have been determined by conodonts and graptolite macrofauna. The silica source and depositional settings of the cherts have been interpreted based on the received mineralogical, petrographic, and geochemical (major, trace, and rare earth elements) data. The presence of radiolarian tests, the Si/Si+Al+Fe+Ca ratios, and Al–Fe–Mn diagram plotting at the non-hydrothermal field, testify that the source of silica in the studied rocks is mostly biogenic or both biogenic and terrigenous in origin. Differential thermal analysis results suggest that the Silurian and Devonian siliceous rocks were presumably formed in predominating anoxic oceanic conditions and only sporadically in oxic waters. The MnO/TiO_2 ratio and received Al_2O_3, Fe_2O_3, TiO_2, La_n, and Ce_n contents indicate that the studied cherts have been deposited in continental margin environments. Most probably, they have been formed in slope and outer-shelf settings on the passive margin of northern peri-Gondwana.

Keywords Palaeozoic · Cherts · Biostratigraphy · Geochemistry · Depositional settings · Western Bulgaria

Introduction

Silurian and Devonian bedded cherts are cropping out in the Srednogorie (Svoge and Lyubash-Golo Bardo units) and the Morava-Rhodope (Morava Unit) zones (Dabovski and Zagorchev 2009) of the Balkan Terrane (Yanev 1997a, 2000) in western Bulgaria (Fig. 1a, b). In these units, the siliceous deposits commonly occur in close association with shales, sandstones, siltstones and rare carbonates. Litho- and biostratigraphy of the Palaeozoic chert-bearing successions have been studied and described by numerous authors (Tenčov 1965; Parvanov 1967; Spassov 1960a, b, 1973; Yanev 1985; Yanev and Spassov 1985; Sačanski 1993; Boncheva and Yanev 1993; Sachanski and Tenchov 1993; Zagorchev 2001; Sachanski and Boncheva 2002; Lakova and Sachanski 2004; Milovanov et al. 2006a, b, c; Angelov et al. 2010a, b; Boncheva et al. 2010; Boncheva and Sachanski 2016; Sachanski 2017). Most of these Palaeozoic siliceous sediments are regarded as biochemical marine deposits (Yanev 1985, 1991a, b). A hydrothermal origin has also been suggested for some of the cherts from Svoge and Lyubash-Golo Bardo units (cf. Yanev 1991a). Macro- and micro-petrographic features of the Palaeozoic cherts from western Bulgaria have been previously described by Spassov (1960a, b) and Yanev (1985). The only published geochemical data (major element geochemistry) of Silurian and Devonian siliceous rocks are also presented in these works (Spassov

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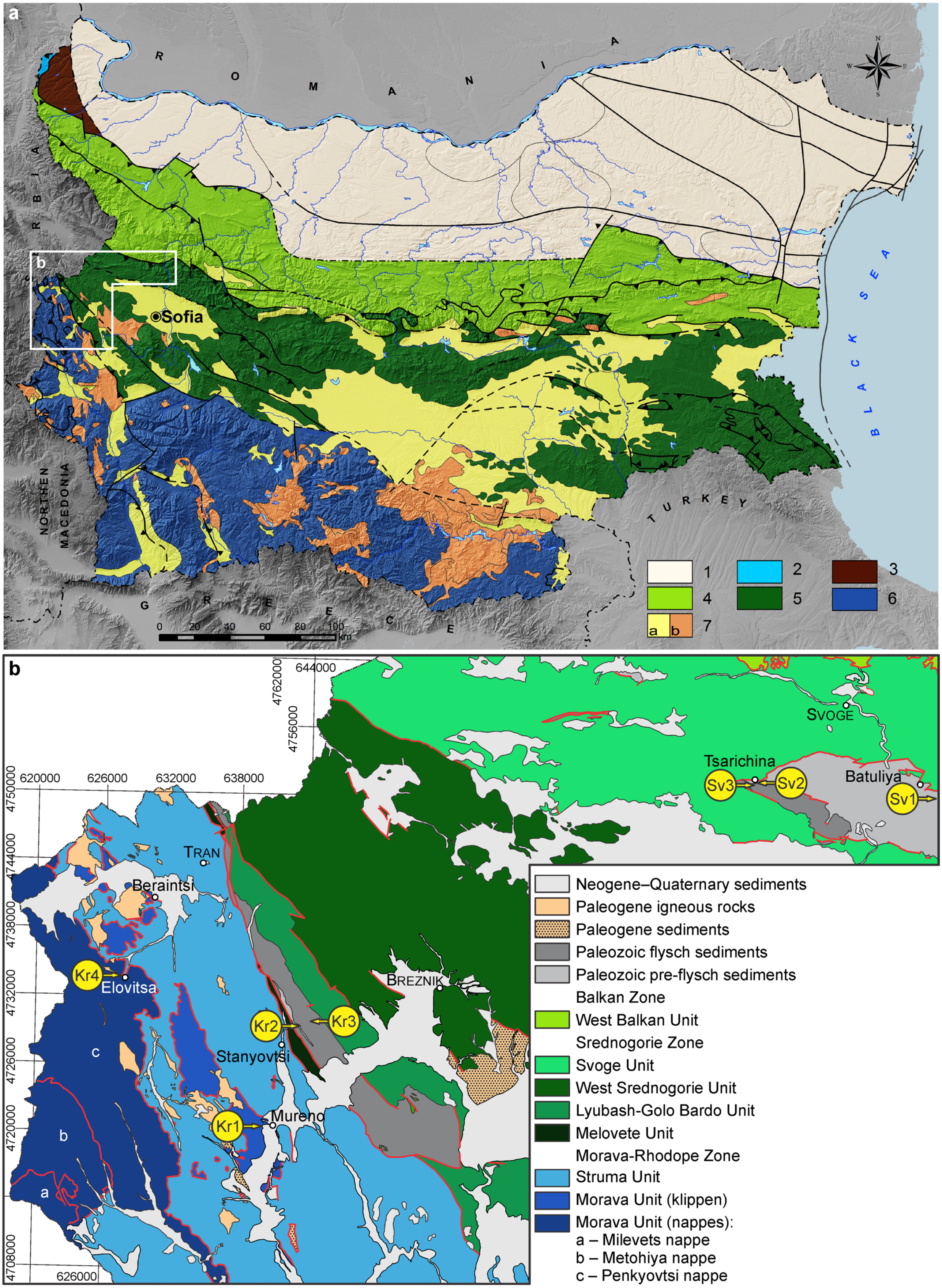

a
ROMANIA
SERBIA
NORTHERN MACEDONIA
GREECE
TURKEY
BLACK SEA
Sofia
b
1
2
3
4
5
6
7
a b
0 20 40 60 80 100 km
b
644000
4762000
4756000
4750000
620000
626000
632000
638000
4744000
4738000
4732000
4726000
4720000
4708000
626000
SVOGE
Tsarichina
Batuliya
Sv1
Sv2
Sv3
TRAN
Beraintsi
BREZNIK
Kr1
Kr2
Kr3
Kr4
Elovitsa
Stanyovtsi
Mureno
a
b
c
Neogene–Quaternary sediments
Paleogene igneous rocks
Paleogene sediments
Paleozoic flysch sediments
Paleozoic pre-flysch sediments
Balkan Zone
West Balkan Unit
Srednogorie Zone
Svoge Unit
West Srednogorie Unit
Lyubash-Golo Bardo Unit
Melovete Unit
Morava-Rhodope Zone
Struma Unit
Morava Unit (klippen)
Morava Unit (nappes):
a – Milevets nappe
b – Metohiya nappe
c – Penkyovtsi nappe

◂**Fig. 1** **a** Alpine tectonic subdivision of Bulgaria by Dabovski and Zagorchev (2009) with location of the study area: *1* Moesian Platform; South Carpathian orogenic system: *2* Kraynenska Zone; *3* Kula Zone; Balkan orogenic system: *4* Balkan Zone; *5* Srednogorie Zone; *6* Moravo-Rhodope Zone; *7* Intra-orogenic basins (post-tectonic): *a* Neogene–Quaternary; *b* Paleogene; **b** Simplified tectonic map with location of the studied samples (after Angelov et al. 2010a, b, 2011; Marinova et al. 2010a,b; Milovanov et al. 2006b,c): coordinates WGS84 Sv1 – N 42°53′10.8″, E 023°26′17.0″; Sv2 – N 42°53′54.5″, E 023°14′38.1″; Sv3 – N 42°53′46.7″, E 023°14′30.9″; Kr1 – N 42°37′28.9″, E 022°42′34.5″; Kr2 – N 42°42′18.5″, E 022°45′02.4″; Kr3 – N 42°42′18.4″, E 022°45′02.8″; Kr4 – N 42°44′43.8″, E 022°33′35.5″

1960a, b; Yanev 1985). However, the interpretations of the obtained geochemical results are very scarce.

The aims of this study are to investigate the source of silica and the depositional environment (continental margin, pelagic, or ridge-proximal) of the Siliurian-Devonian cherts, based on the received mineralogical, petrographic, DTA, and geochemical (major, trace, and rare earth elements) data. Additionally, some new conodont and graptolite data are also recorded from the chert-bearing successions in Lyubash-Golo Bardo and Svoge units.

Geological background

The Palaeozoic rock successions from western Bulgaria are referred by Yanev (1997a, 2000) to the Balkan Terrane. The latter consists of Palaeozoic volcano-sedimentary and marine deposits as well as continental sediments (Yanev et al. 2005). The studied chert-bearing sequences are cropping out in the Srednogorie Zone and the Moravo-Rodope Zone of the Alpine Orogenic Belt (after the tectonic scheme of Dabovski and Zagorchev 2009) in three tectonic units: Svoge, Lyubash-Golo Bardo and Morava units (Fig. 1a, b). The lower Palaeozoic deposits of these units have been affected by tectonic events during the Variscan (Hercynian) and Alpine orogenies.

The description of the tectonic units in this work follows Ivanov (2017), Dabovski et al. (2002), and Dabovski and Zagorchev (2009).

Svoge Unit

The Svoge Unit is a relatively wide, north-vergent allochthonous plate. It is composed of lower Palaeozoic (Ordovician, Silurian, and Devonian) marine sediments (shales, siltstones, quartzites, and cherts) covered by transgressive alluvial and coal-bearing upper Carboniferous and Permian siliciclastic deposits. The Palaeozoic basement of the Svoge Unit displays several NW-vergent fold structures that have been formed in pre-Westphalian times.

The Mesozoic cover of this unit consists of Triassic, Jurassic, and Lower Cretaceous epicontinental shallow-water sediments. Rare Upper Cretaceous siliciclastic, clayey-carbonate, and carbonate sedimentary successions interbedded with volcano-sedimentary and volcanic rocks occur as well. The Mesozoic sedimentary cover is characterised by numerous kilometer-scale north-vergent fold structures with east-west axis direction.

Lyubash-Golo Bardo Unit

The Lyubash-Golo Bardo Unit is a fault-bounded structure also belonging to the Srednogorie Zone. This unit consists of Silurian and Devonian dark grey or black shales (locally containing graptolite macrofauna), marls, thin-bedded cherts, and flysch deposits. The Upper Devonian flysch succession is unconformably overlain by Stephanian-Permian continental sediments (breccias, conglomerates, sandstones, and siltstones). The Silurian–Devonian, and Stephanian-Permian deposits have been strongly deformed forming a number of SW-vergent fold structures.

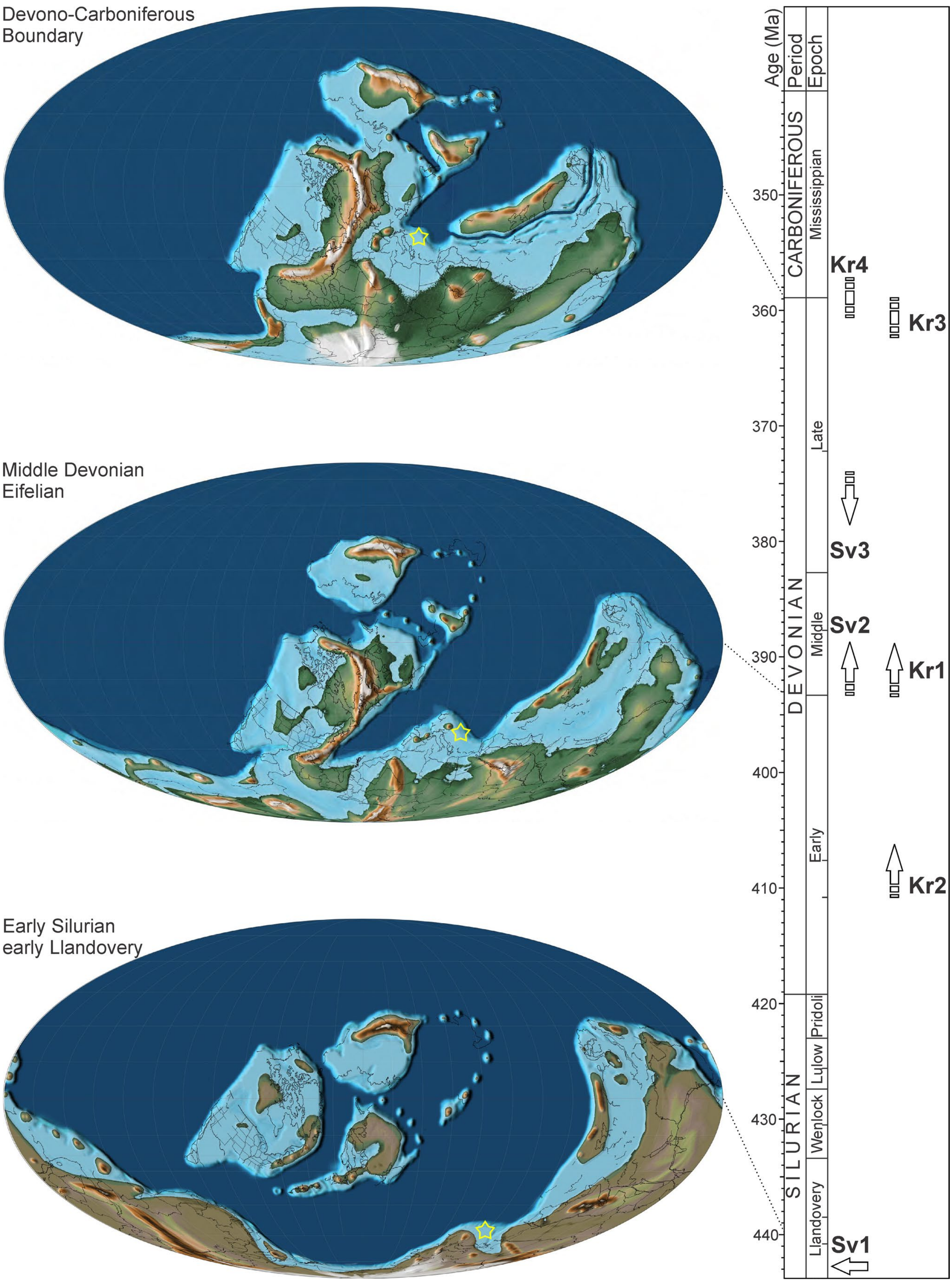
The Mesozoic cover (Triassic, Jurassic, and Lower Cretaceous sequences) is composed of shallow-water continental and marine siliciclastic and carbonate deposits. The Upper Cretaceous rocks are rarely exposed and include Turonian coal-bearing siliciclastic sediments and Coniancian-Santonian marls and limestones.

Morava Unit

The Morava Unit represents a system of nappes. The latter were trusted over the Struma Unit of the Moravo-Rodope Zone during the mid-Cretaceous time. This unit is composed of a Precambrian basement of metamorphites (gneisses and migmatites) which is overlain by Silurian–Devonian successions (shales, cherts, carbonates, and flysch siliciclastic deposits). The pre-Mesozoic basement is covered by Eocene-Oligocene volcano-sedimentary sequences.

Silurian–Devonian depositional setting and palaeogeography of the Balkan Terrane

The previous sedimentological and palaeogeographic interpretations concerning the Silurian and Devonian sequences from the Balkan Terrane in western Bulgaria suggest that they have been formed on a passive shelf margin of northern peri-Gondwana (cf. Yanev 1985, 1993, 1996, 1997a, b, 2000; Lakova and Sachanski 2004; Yanev et al. 2005; Boncheva et al. 2007; Boncheva et al. 2010, Fig. 2), where the chert deposits were part of flysch and open-shelf facies associations. According to these authors, the Silurian chert succession of Svoge Unit is regarded as deposited in a deep marine setting during the upper Hirnantian post-glacial



Devono-Carboniferous Boundary
Middle Devonian Eifelian
Early Silurian early Llandovery
Age (Ma)
Period
Epoch
CARBONIFEROUS
Mississippian
DEVONIAN
Late
Middle
Early
SILURIAN
Pridoli
Ludlow
Wenlock
Llandovery
350
360
370
380
390
400
410
420
430
440
Kr4
Kr3
Sv3
Sv2
Kr1
Kr2
Sv1

◂**Fig. 2** Silurian–Devonian palaeogeographic reconstruction by Scotese (2014a, b) with the location of the Balkan Terrane and chronostratigraphic positions of the studied cherts

sea-level rise. A continuous sedimentation took place from the Silurian to the Devonian (Boncheva et al. 2007; Boncheva et al. 2010). During the Lochkovian and Pragian, sedimentation took place in an open-shelf environment. The Emsian age is characterised by the differentiation of the depositional settings. Open-shelf settings predominated in Svoge Unit whereas turbiditic sedimentation started in Lyubash-Golo Bardo Unit and continued until the end of the Devonian. In Svoge Unit turbiditic successions have been deposited during Givetian age. A thick flysch sequence was formed during the Late Devonian. In the Mora Unit, Early Devonian sedimentation is characterised by the deposition of nodular limestones formed in a shelf settings (cf. Boncheva et al. 2010). There, flysch sedimentation occurred during the Givetian and continued to the Late Devonian. A carbonate flysch sequence has been deposited during Famennian and Tournaisian.

Material and methods

Samples

In the present work, we have studied Palaeozoic cherts from Svoge Unit (Saltar Formation – Sv1 and Katina Formation – Sv2 and Sv3), Lyubash-Golo Bardo Unit (Parchar Formation – Kr2 and Tumba Formation – Kr3) and Morava Unit (Kosovo Formation – Kr4 and Zdravkovtsi Formation – Kr1). The sampling locations are shown in Fig. 1b and Fig. 3. Conodont samples have been prepared by standard preparation methods, described in details by Ta et al. (2022). Sample material is stored in the Geological Institute of the Bulgarian Academy of Sciences under repository numbers: SR.1.2023.1.1–SR.1.2023.1.7.

Analytical methods

X-ray diffraction analysis (XRD)

The mineral composition of the cherts was determined by X-ray diffraction analysis (XRD). It was carried out on an X-ray diffractometer BRUKER D2 Phaser in the University of Mining and Geology "St. Ivan Rilski", Sofia.

Differential thermal analysis (DTA)

Differential thermal analysis (DTA) and Thermogravimetric analysis (TGA) of the cherts have been carried out in the Geological Institute of the Bulgarian Academy of Sciences on 500 mg samples heated in air at a programmed rate of 10 °C/min up to 1000 °C, TG sensitivity 200 mg.

Geochemical analysis

Whole-rock major element analyses of the cherts by X-ray fluorescence (XRF) were performed on EDXRF, Epsilon 3XLE, Omnian 3SW instrument at the University of Sofia "St Kliment Ohridski". XRF analyses were conducted on fused disks of powdered material from the chert samples. The fused pellets were prepared by mixing approximately 1g of sample with 3g of lithium metaborate ($LiBO_2$) and 6g of lithium tetraborate ($Li_2B_4O_7$) flux. Analytical errors for major oxides are within the range of 1 %.

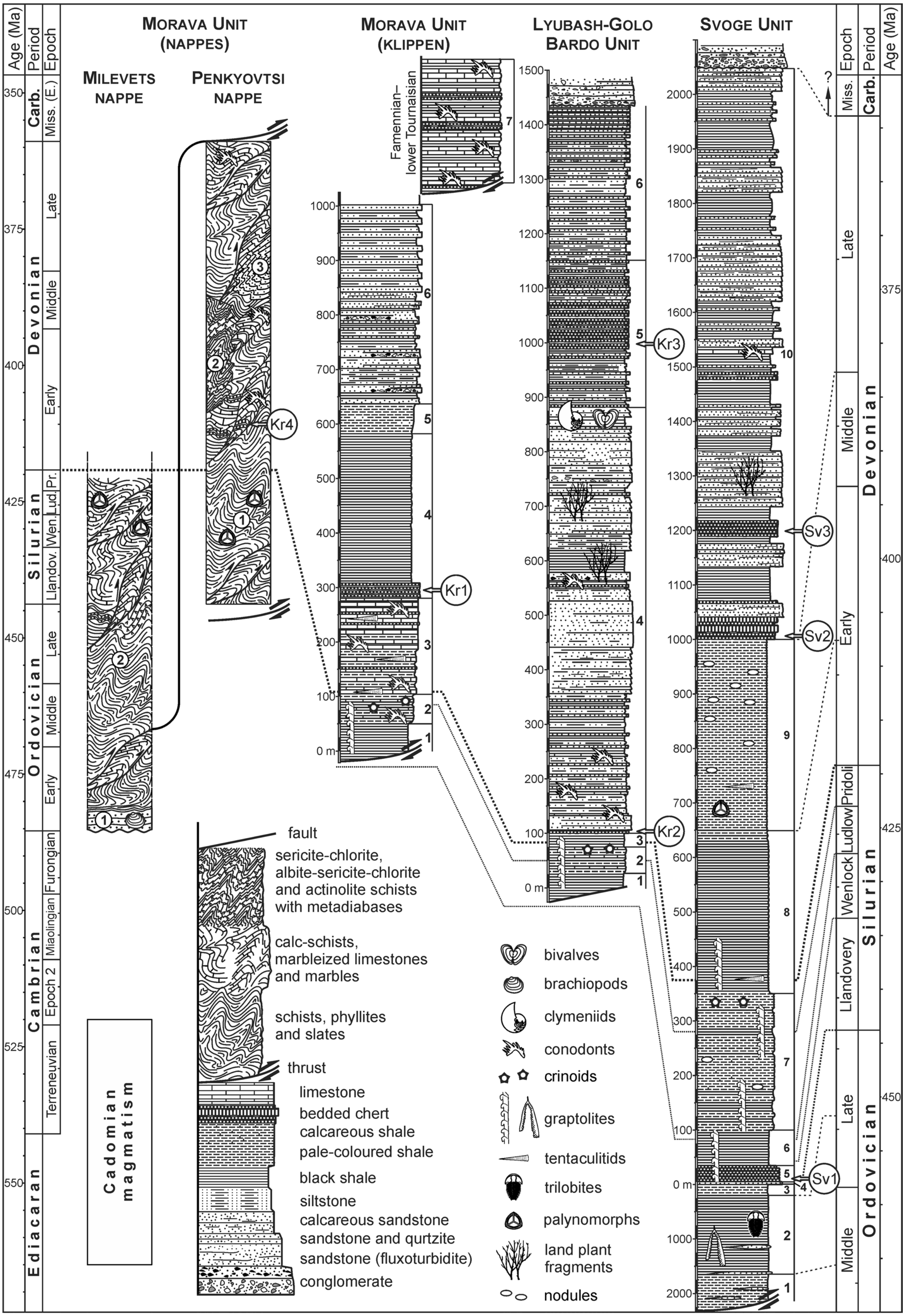
Trace elements and rare earth elements (REE) were performed on broken and polished fragments of the same fused pellets, using the laser ablation system New Wave UP193FX coupled with an ICP-MS PerkinElmer ELAN DRC at the Geological Institute of Bulgarian Academy of Sciences, Sofia. Every analytical block consisted of measuring two external standards (NIST-610) at the beginning and end, and unknown analyses in-between. Every sample was measured with three spot analyses and the average was taken as the result. The diameter of the crater was 100 μm, with a frequency of 10 Hz. The measured specters were recalculated to element concentrations using the software of Guillong et al. (2008) with SiO_2 as an internal standard from the XRF major element analyses.

Stratigraphy of the Silurian and Devonian siliceous successions from western Bulgaria

In the present work, we have studied siliceous successions from several lithostratigraphic units: Saltar and Katina formations (Svoge Unit), Parchar, and Tumba formations (Lyubash-Golo Bardo Unit), and Kosovo and Zdravkovtsi formations (Morava Unit) (Fig. 1b, Fig. 3 and Fig. 4a–g).

Saltar Formation (Svoge Unit)

The sediments of the Saltar Formation (Sachanski and Tenchov 1993) are cropping out in a section near the village of Batouliya, Sofia Region (Fig. 1b). It consists of a 30 m-thick sequence of dark grey to black shales containing common graptolite macrofauna and black thin-bedded cherts (Fig. 3 and Fig. 4f). The siliceous rocks predominate in the lower parts of the unit. Rich and diverse graptolite fauna clearly determined a late Hirnantian–early Telychian age (*Metabolograptus persculptus–Torquigraptus tullbergi* graptolite zones) of the Saltar Formation (Sačanski 1993; Sachanski and Tenchov 1993).


Morava Unit (nappes)
Milevets nappe
Penkyovtsi nappe
Morava Unit (klippen)
Famennian–lower Tournaisian
Lyubash-Golo Bardo Unit
Svoge Unit
Age (Ma)
Period
Epoch
Carb.
Miss. (E.)
Devonian
Late
Middle
Early
Silurian
Pr.
Lud.
Wen.
Llandov.
Ordovician
Cambrian
Furongian
Miaolingian
Epoch 2
Terreneuvian
Ediacaran
Cadomian magmatism
Kr1
Kr2
Kr3
Kr4
Sv1
Sv2
Sv3
Pridoli
Ludlow
Wenlock
Llandovery
fault
sericite-chlorite, albite-sericite-chlorite and actinolite schists with metadiabases
calc-schists, marbleized limestones and marbles
schists, phyllites and slates
thrust
limestone
bedded chert
calcareous shale
pale-coloured shale
black shale
siltstone
calcareous sandstone
sandstone and qurtzite
sandstone (fluxoturbidite)
conglomerate
bivalves
brachiopods
clymeniids
conodonts
crinoids
graptolites
tentaculitids
trilobites
palynomorphs
land plant fragments
nodules

◂**Fig. 3** Lithological logs of the marine Paleozoic rocks of the studied tectonic units with stratigraphic position of the chert samples: Milevets nappe *1* basal psammites, 2 Cheshlyantsi metamorphic complex (Parvanov 1967; Zagorchev 1993, 2001) or Cheshlyantsi Metasediments (Milovanov et al. 2006a); Penkyovtsi nappe *1* Kosovo Formation (Parvanov 1967; Zagorchev 2001) or Kosovo Metasediments (Milovanov et al. 2006a), *2* Bazovitsa Formation (Parvanov 1967; Zagorchev 2001) or Bazovitsa Metasediments (Milovanov et al. 2006a), *3* Tranovdol (Melna) Formation (Parvanov 1967; Zagorchev 2001); Palaeozoic in the klippen (Spassov 1973; Milovanov et al. 2006a and references therein) *1* argillite formation, *2* argillite-carbonate formation, *3* Vrabcha Formation, *4* Zdravkovtsi Formation, *5* Staychovtsi Formation, *6* Tranovdol Formation, *7* Beraintsi Formation; Lyubash-Golo Bardo Unit (Spassov 1973; Yanev and Spassov 1985; Sachanski 2015) *1* argillite formation, *2* argillite-carbonate formation, *3* Gradishte Formation, *4* Parchar Formation, *5* Tumba Formation, *6* Propalnitsa Formation; Svoge Unit (Sachanski 2015 and references therein) *1* silty-clayey metaformation, *2* Grohoten Formation, *3* Tseretsel Formation, *4* Sirman Formation, *5* Saltar Formation, *6* Mala Reka Formation, *7* Yabukov Dol Formation, *8* Ogradishte Formation, *9* Romcha Formation, *10* Katina Formation. Abbreviations: *Llandov.* Llandovery; *Wen.* Wenlock; *Lud.* Ludlow; *Pr.* Pridoli; *Carb.* Carboniferous; *Miss.* Mississippian; *E.* Early

We have studied the lowermost parts of the *Akidograptus ascensus* graptolite Zone (Fig. 5). The first occurrence (FO) of *Ak. ascensus* Davies has been recorded 1 m above the boundary between the Sirman and Saltar formations, together with the FOs of *Neodiplograptus lanceolatus* Štorch and Serpagli, (1993) and *Normalograptus trifilis* (Manck). The latter species are characteristic of the uppermost part of the *ascensus* Zone and the lower part of *acuminatus* Zone. *Metabolograptus persculptus* (Elles and Wood) and has been recorded 50 cm below them, and the FO of *Parakidograptus acuminatus* (Nicholson) was found 20 cm higher (Sačanski 1993; Lakova and Sachanski 2004). A new sampling of the section has documented that the first occurrence of *Ak. ascensus* Davies is 20 cm lower than previously known, i.e. at 80 cm above the boundary between the Sirman and Saltar formations.

Katina Formation (Svoge Unit)

The Katina Formation (Tenčov 1965) is represented by flysch deposits which have a total thickness of 700 m. Light grey bedded cherts, siltstones, sandstones, and shales built up the lower part of the unit. The upper part of the Katina Formation consists of shales, sandstones, bedded cherts, conglomerates, and rare carbonates. Two intervals of siliceous rocks have been studied from the Katina Formation from section Tzarichina (Fig. 1b). The first interval (Fig. 3 and Fig. 4d) is from the base of the unit and has a thickness of 40 m. The second chert sequence (30 m in thickness) crops out 150 m higher in the section (Fig. 4a). The age of the unit is Late Devonian (Boncheva and Yanev 1993; Yanev et al. 2005; Angelov et al. 2010a). Conodont fauna extracted from two limestone layers indicate the upper *linguiformis* Zone (uppermost Frasnian) and the lower *triangualris* Zone (lowermost Famennian).

Parchar Formation (Lyubash-Golo Bardo Unit)

The Parchar Formation (Yanev 1985; Yanev and Spassov 1985) represents a flysch succession (>700 m thick) composed of an alternation of siliciclastic deposits (siltstones, sandstones and shales). A bedded chert sequence (5 m in thickness) occurs at the base of the unit (Fig. 3 and Fig. 4e) and overlies black shales containing Lochkovian graptolites (Yanev and Spassov 1985; Sachanski 2017). Sporadic limestone layers are also presented in the lower part of the unit. They contain conodonts with Emsian–early Eifelian to early Famennian age (Yanev and Spassov 1985; Sachanski and Boncheva 2002; Boncheva et al. 2010). The established conodont fauna (upper *linguiformis* Zone and *triangularis* Zone) indicate the late Frasnian and early Famennian age (Frasnian/Famennian boundary) (Sachanski and Boncheva 2002).

In this study, two sections of the Parchar Formation were sampled for conodonts: Berende and Stanyovtsi (Fig. 1b). The section near the village of Berende contains a conodont fauna dominated by the genus *Ancyrodella*. The presence of *Ancyrodella joides* and *Ancyrodella africana* indicates the end of the Frasnian stage according Liao and Valenzuela-Rios (2012). The extracted conodont fauna from the lower part of the Parchar Formation in section Stanyovtsi belongs to *expansus* Zone, while in the upper part of the unit the lowermost Famennian stage – *triangularis* Zone was recorded (Fig. 6).

Tumba Formation (Lyubash-Golo Bardo Unit)

The Tumba Formation (Yanev and Spassov 1985) consists of bedded cherts alternating with shales, siltstones, and sandstones. The thickness of this unit varies from 170 m to 250 m. The age of the sediments of the Tumba Formation is most probably Famennian (Yanev and Spassov 1985), post-*Annulata* Event (Boncheva et al. 2015). In this work, the chert sediments from the section near Stanyovtsi village were sampled (Fig. 1b, Fig. 3, and Fig. 4c).

Penkyovtsi nappe (Morava Unit)

The siliceous deposits of the Penkyovtsi nappe from the allochthonous Morava Unit are assigned to Vrabcha Formation (Spassov 1973) by Marinova et al. (2010a, b). This sequence is 185 m thick and consists of an alternation of shales, black bedded cherts, and light grey argillaceous limestones. Based on conodonts and tentaculites the age of this unit is determined as Ludlow to Early Devonian and


a
b
c
d
e
f
g

◂**Fig. 4** Field photos of the studied intervals with bedded cherts: **a** Katina Formation, sample Sv3; **b** Kosovo Formation, sample Kr4; **c** Tumba Formation, sample Kr3; **d** Katina Formation, sample Sv2; **e** Parchar Formation, sample Kr2; **f** Saltar Formation, sample Sv1; **g** Zdravkovtsi Formation, sample Kr1

early Eifelian (Spassov 1973; Boncheva 1991; Sachanski et al. 2005; Boncheva et al. 2007, 2010). The late Silurian (Ludlow and Pridoli) have been proven by graptolites (*parultimus-ultimus* Zone) and conodonts (*siluricus* Zone) (Boncheva et al. 2007). The Silurian/Devonian boundary has also been identified by conodont fauna (the last occurrence of *Ozarkodina remscheidensis eosteinhornensis* and the first occurrence of *Icriodus woschmidti* (Boncheva et al. 2007, 2010) (Fig. 6). Other recognied Early Devonian and earliest Eifelian conodont zones include *postwoschmidti, deltapesavis, sulcatus, dehiscens, gronbergi-perbonus, laticostatus, serotinus, costatus patulus* and *costatus partitus* zones by Klapper and Johnson (1975; cf. Boncheva et al. 2007; 2010).

According to other authors, the strongly deformed sediments of the Penkyovtsi nappe are referred to the Kosovo Formation (Parvanov 1967; Zagorchev 2001) or Kosovo metasediments by Milovanov et al. (2006a, b, c). Their lithostratigraphic subdivisions are applied in this work. These metasediments contain carbonate layers of Early Devonian, Late Devonian, and Carboniferous ages (Spassov 1973). The siliceous deposits in section Elovitsa are studied herein (Fig 1b, Fig. 3, and Fig. 4b). The conodont associations indicating the upper Famennian *expansa* Zone, the last Famennian *praesulcata* Zone, and the first Carboniferous *sulcata* Zone, according the standard conodont zonation by Ziegler and Sandberg (1990). The *sulcata* Zone corresponds in part to the *Protognathodus kockeli* Zone (Corradini et al. 2017; Spalletta et al. 2017).

The dating of Devonian sediments in the studied sections is based on the dominant presence of three characteristic conodont genera *Polygnathus, Palmatolepis,* and *Siphonodella.* Three taxa have been identified within the early range of the genus *Siphonodella*: *Siphonodella praesulcata*, *Siphonodella duplicata*, and *Siphonodella sulcata.* These species are used in the conodont zonal divisions as the main markers in the definition of the Early Carboniferous.

Zdravkovtsi Formation (Morava Unit – klippen)

The Zdravkovtsi Formation (Spassov 1973) has a thickness up to 100 m and is composed of dark grey to black shales interbedded with thick packages of folded cherts. The Eifelian age of this unit is based on its lithostratigraphic position, rather than base on well-defined biostratigraphy. The chert deposits from the Vonski klippe near Mureno village are studied in this work (Fig. 1b, Fig. 3, and Fig. 4g).

Mineralogy and petrography of cherts

X-ray diffraction analyses

X-ray diffraction analyses of whole rocks show that the cherts of the studied sections are mainly comprised of quartz and muscovite (sericite) (Fig. 7), which confirms microscopic observations. Feldspars (plagioclases and one case of potassium feldspar) are represented in samples Sv1, Sv3, Kr1, and Kr3. Clinochlore appears in samples Kr2 and Sv2, and hematite only in sample Kr1. A minimum amount of kaolinite occurs in the samples Kr2 and Kr3.

Petrography

Based on the type and abundance of siliceous organic constituents the investigated cherts are referred to bedded radiolarian cherts (cf. Boggs 1995). Two main petrographic varieties can be distinguished based on microscopic observation: non-laminated radiolarian cherts and laminated radiolarian cherts.

Non-laminated radiolarian cherts

These cherts are represented in all studied units: Svoge (samples Sv1 and Sv3), Lyubash-Golo Bardo (samples Kr2), and Morava (samples Kr1 and Kr4), (Fig. 1b). They are composed of microcrystalline quartz groundmass with dark brown or black colour and various amounts of radiolarian tests (Fig. 8a–e). The latter consist of chalcedony, or rarely of polycrystalline quartz. A part of them are strongly deformed (Fig. 8e) or replaced by black opaque minerals. In some samples, the rock matrix is characterised by higher organic content. Silt- to sand-sized clastic quartz and feldspar grains are also locally observed.

Laminated radiolarian cherts

The laminated cherts occur only in two samples from Svoge (sample Sv2) and Lyubash-Golo Bardo (samples Kr3) units (Fig. 8b). Under the microscope, these cherts display clear millimeter-scale lamination (Fig. 8f–h), consisting of an alternation of fine-grained (dark brown) and more coarse-grainy (light grey) laminas. The fine-grain laminas are composed predominantly of microcrystalline quartz and sericite. Silt-sized clastic quartz and feldspar grains as well as muscovite (sericite) are observed within coarse-grained laminas. Radiolarians are variably presented and some of them are characterised by deformed chalcedonic tests. Sometimes some laminas consist almost completely of concentrated chalcedonic radiolarian tests. Black or dark brown opaque minerals are also locally noted.

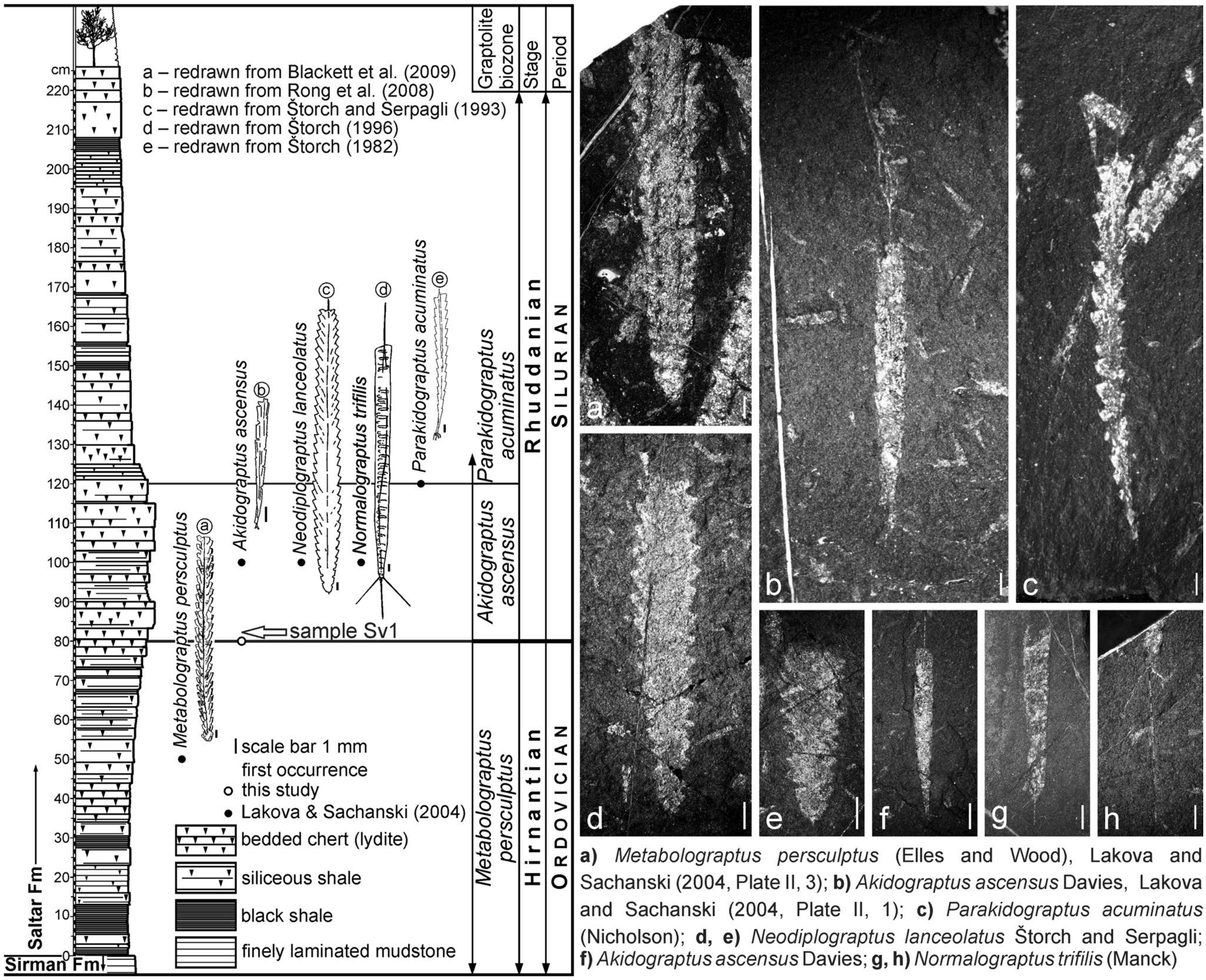


Fig. 5 Lithostratigraphic column of the Ordovician/Silurian boundary sedimentary succession in Saltarski Dol section with position of the sample Sv1 and first occurrence of some important graptolite species

Differential thermal analysis (DTA) data

Cherts have been submitted to Differential Thermal analysis (DTA) to assess the presence and ignition temperature of the organic matter. Following exothermic peaks are registered on the DTA curves (Fig. 9) – at temperatures 280 °C–390 °C (Kr2 and Kr3) and the interval 490 °C–560 °C (Kr4, Sv1, and Sv3). These peaks represent the ignition temperature of the organic matter (OM).

The endothermic peaks at 110 °C and the interval of 480 °C to 560 °C could be referred to the weight loss respectively of unbounded water (dehydration) and bounded or constituent water (dehydroxilation) of clay minerals and chlorites (Phillips 1963; Jozanikohan et al. 2015).

Comparing the loss on ignition after chemical analysis with weight loss on the TG curve after Thermal analysis shows similar quantities. The weight loss is referred to the exclusion of H_2O, loss of hydroxyl group (OH) from clay minerals, and the oxidation of the organic matter. The higher ignition temperatures of the organic matter reflect the higher degree of it's diagenetic alteration. Thus, the amount of organic matter in the cherts from the Svoge Unit is higher than in the other units, and is more diagenetically altered.

Geochemical data

Geochemical characteristics of cherts are typically used for interpretation of their origin, material provenance, and depositional setting (Murry et al. 1991; Murry 1994; Halamic et al. 2005; Yan et al. 2009; Hara et al. 2010; Thassanapak et al. 2017; Lu et al. 2019; Men et al. 2020; Xu et al. 2021). In this work, we analysed major, trace, and rare earth elements.

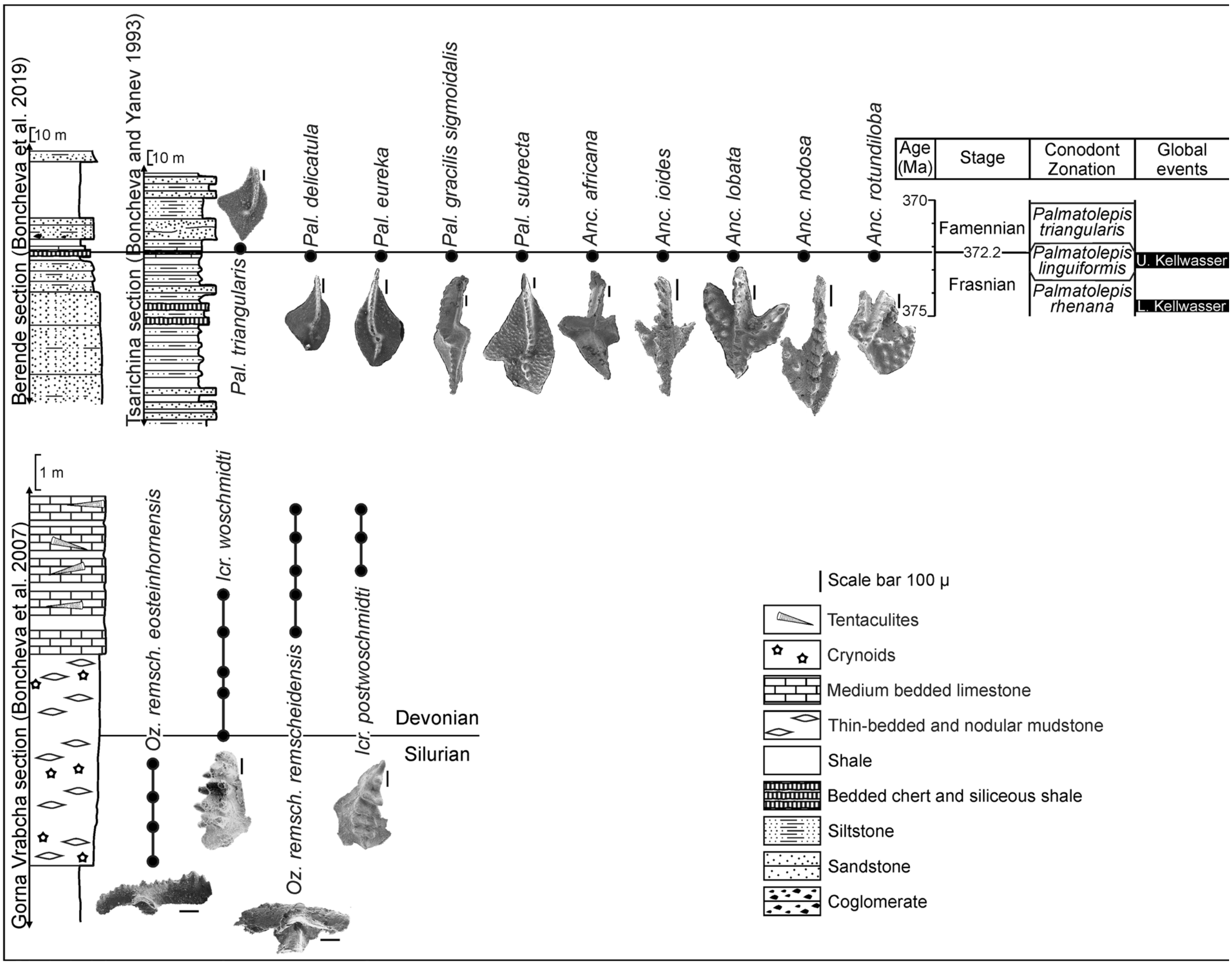


Fig. 6 Part of the stratigraphic important conodont taxa related to Silurian/Devonian boundary interval and to Frasnian/Famennian boundary (Upper Kelwasser event) by Boncheva et al. (2019), Boncheva et al. (2007), Boncheva and Yanev (1993)

Major elements

The results of geochemical analyses of the Silurian and Devonian cherts from western Bulgaria are listed in Table 1. The SiO_2 content varies from 76.06% to 96.02%. It is lower in laminated cherts in samples Sv2 and Kr3 (76.06% and 78.04%) and higher in the non-laminated radiolarian cherts in samples Sv1, Sv3, Kr1, Kr2, and Kr4, which range from 89.86% to 96.09% (average 92.13%). SiO_2 content shows a negative correlation with the other major elements. Al_2O_3 content ranges from 1.95% to 10.92%, with an average of 5.23%, and demonstrates a positive correlation with TiO_2 and K_2O. It should be noted, that the laminated radiolarian cherts have higher Al_2O_3 (8.72% and 10.92%), TiO_2 (0.41% and 0.49%) and K_2O (1.15% and 1.85%) values in comparison with the non-laminated radiolarian cherts - Al_2O_3 (1.95–4.48%), TiO_2 (0.08–0.20%) and K_2O (0.32–0.89%). The total Fe_2O_3 content (TFe_2O_3) of the laminated radiolarian cherts is 4.87% and 5.84% and varies from 0.34% to 2.13% in the non-laminated radiolarian cherts. Other major elements show similarities in chert samples and are less concentrated: MgO (0.11–2.11%, average 0.63%) MnO (0.00–0.13%, average 0.04%) and Na_2O (0.02–0.38%, average 0.19%). Only the Kr1 chert sample is distinguished with a higher concentration of CaO (1.11%) and P_2O_5 (0.63%) in comparison with the other cherts, where CaO varies from 0.01% to 0.09%, and P_2O_5 ranges from 0.01% to 0.04%. Most probably, it is related to the carbonate component in the bedded radiolarian cherts, because in the section they are closely associated with limestones (Fig. 3).

The Si/(Si+Fe+Al+Ca) ratio is often used to determine the content of non-detrital (biogenic) silica in comparison with aluminosilicates, ferruginous and calcium minerals (Ruiz-Ortiz et al. 1989). In the studied cherts Si/(Si+Fe+Al+Ca) ratio ranges from 0.79 to 0.97 (average 0.90). Laminated radiolarian cherts (Sv2 and Kr3) are characterised by lower Si/(Si+Fe+Al+Ca) values (0.79 and 0.81) than the non-laminated radiolarian cherts (0.92–0.97).

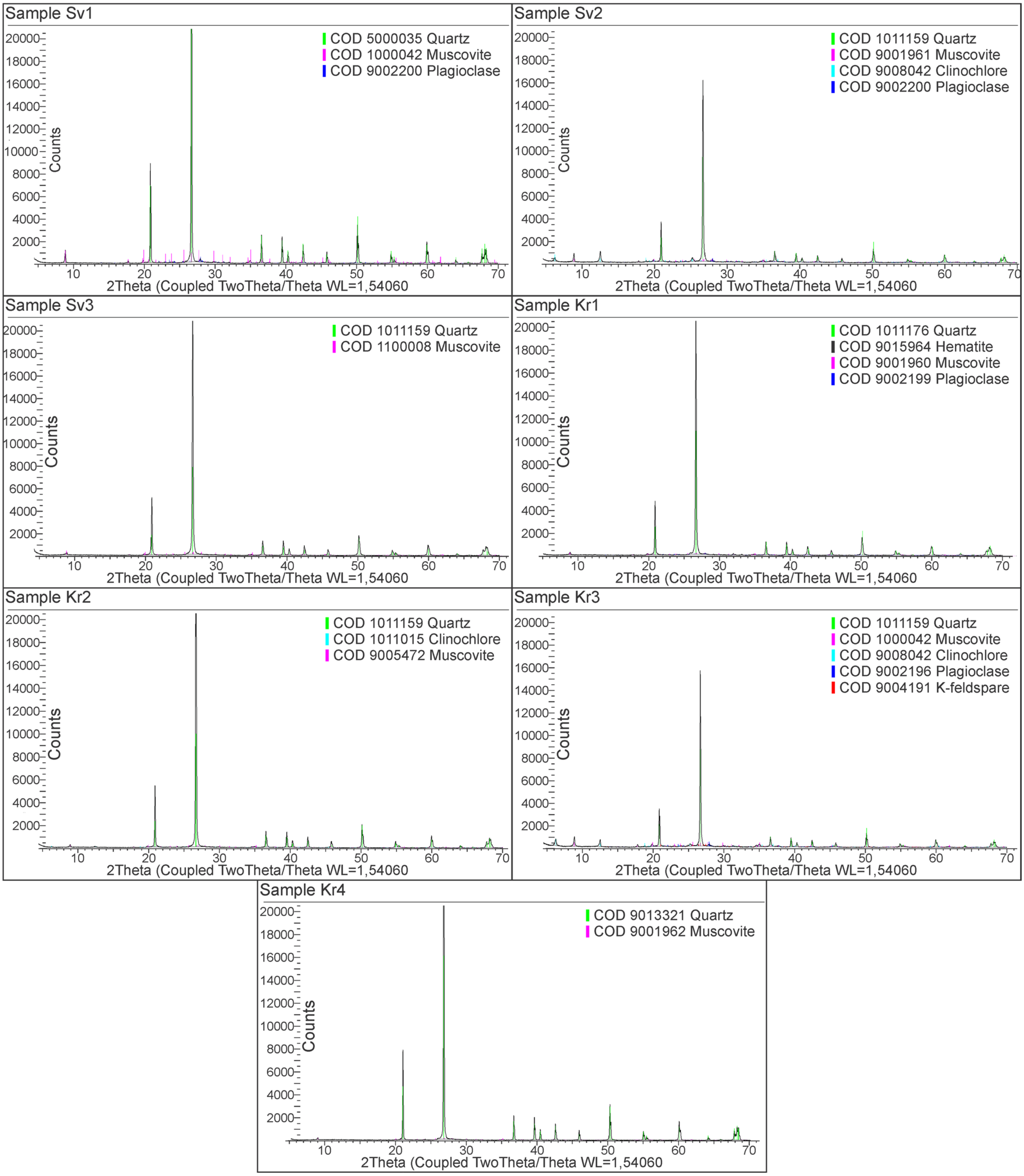


Fig. 7 X-ray diffraction patterns of studied chert samples

Trace elements

Geochemical results of analysed trace elements of Silurian and Devonian cherts from western Bulgaria are presented in Table 2. A positive correlation consists of lithophile elements Rb, Zr, Th, Nb, and Hf with TiO_2 and Al_2O_3. These elements are mostly related to the supply of clastic material and their concentration could be used as an indicator of the distance of the depositional setting from the continent (cf. Marchig et al. 1982; Halamic et al. 2005). Co and Ni also show a positive correlation with Rb, Zr, Th, Nb, Hf, TiO_2, and Al_2O_3. Sr is most probably connected with carbonate components (cf. Halamic et al. 2005) and has the highest concentrations in sample Kr 1 from Kosovo Formation.

Rare Earth Elements (REE)

The REE data obtained from the radiolarian cherts are listed in Table 3. The total REE content (∑REE) is variable and is relatively high in laminated radiolarian cherts (101.68 ppm and 117.28 ppm) and lower in non-laminated radiolarian cherts which ranges from 22.89 ppm to 70.39 ppm. REE analytical data are shown as Chondrite and PAAS (Post-Archean Australian shales)-normalized plots in Fig. 10.

The studied cherts exhibit a slightly negative or no Ce anomaly (Ce/Ce*) from 0.82 to 1.11, (average 0.95). The Ce anomaly was calculated following Taylor and McLennan (1985): Ce/Ce* = (Cen)/[(Lan × Prn)1/2], where REE were normalized to PAAS (Post-Archean Australian shales) (McLennan 1989).

The estimated ratios of La_n/Ce_n in the cherts vary from 0.91 to 1.07. The La_n/Ce_n concentrations in the chert samples were normalized to NASC (North American shale composite) using values given by Gromet et al. (1984).

Discussion

Sources of Silica

Under the microscope, all studied cherts contain various amounts of radiolarian tests which suggest the non-hydrothermal (biogenic) origin of these rocks. The received geochemical data also support this assumption. The calculated Si/(Si+Fe+Al+Ca) ratio in the Silurian and Devonian cherts ranges from 0.79 to 0.97 (average 0.90, Table 1) and indicate that most silica is biogenic in origin. According to Ruiz-Ortiz et al. (1989), typical radiolarian cherts have Si/(Si+Fe+Al+Ca) ratio values between 0.8 and 0.9. In this study, laminated radiolarian cherts (Sv2 and K3) from Svoge and Lyubash-Golo Bardo units) are distinguished with lower Si/(Si+Fe+Al+Ca) ratio values in comparison with the non-laminated radiolarian cherts (see Table 1). These values could be explained by a possible mixed biogenic and terrigenous (clastic) source of silica in these samples.

Generally, the contents of Al_2O_3 and TiO_2 in siliceous sediments are supplied from terrigenous input (Murry 1994). K_2O, Na_2O, Rb, Zr, Hf, Nb, and Th are also good indicators of a clastic supply in the rocks (cf. Murry et al. 1991; Hara et al. 2010). The received values of these elements are relatively high in laminated radiolarian cherts of samples Sv2 and Kr3 (Table 1 and Table 2) and testify that terrigenous components were important during their formation. The well-distinguished lamination fabric (Fig. 8f–h) is also interpreted as a result of fluctuating input of detrital material.

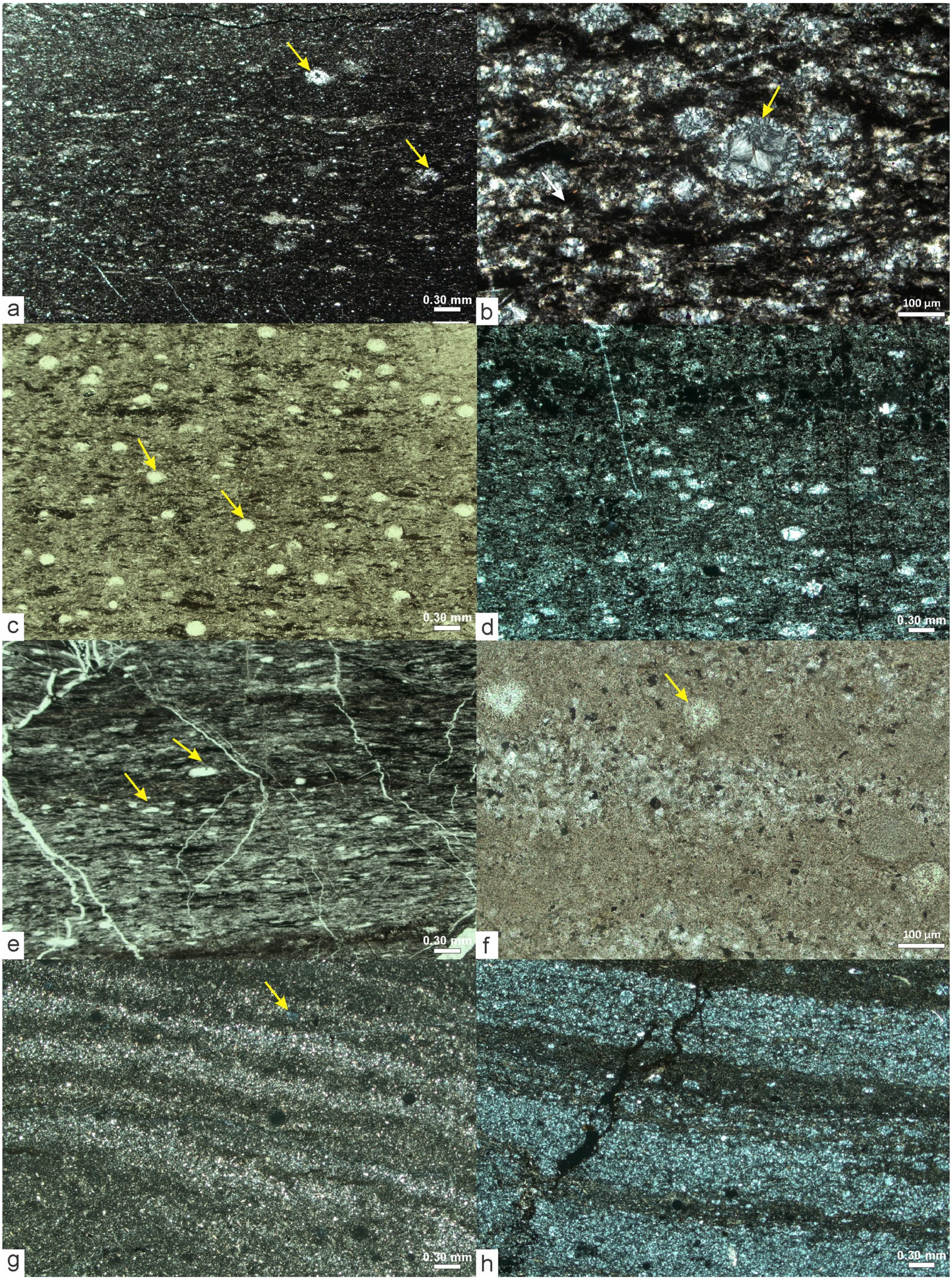
The Al/(Al+Fe+Mn) ratio is another indicator of the hydrothermal or non-hydrothermal origin of the cherts (Adachi et al. 1986). According to Adachi et al. (1986), the Al/(Al+Fe+Mn) > 0.5 are indicative of terrigenous provenance of siliceous rocks and lower values (less than 0.35) testify hydrothermal influence on the chert formation. The Silurian and Devonian cherts from western Bulgaria are characterised by values from 0.52 to 0.85 (Table 1) and are interpreted as non-hydrothermal in origin.

The Al–Fe–Mn ternary diagram is proposed by Adachi et al. (1986) and Yamamoto (1987) for the characterisation of the origin (hydrothermal and non-hydrothermal) of siliceous rocks. All of the studied chert samples are plotted in the field of non-hydrothermal cherts or close to Al-apex (Fig. 11).

Based on the received petrographic, mineralogical, and geochemical data we can conclude that the source of silica in the studied cherts is mostly biogenic in origin. In laminated radiolarian cherts (from Svoge and Lyubash-Golo Bardo Units) the input of terrigenous material was also important and a mixed biogenic/clastic source of silica can be suggested. A part of the cherts contains clastic quartz, feldspars, and clinochlore grains. The latter is formed during low metamorphic or hydrothermal processes (Bevins and Rowbotham 1983). However, the geochemical calculations plotted on Al–Fe–Mn triangle diagram (Fig. 11) by Adachi et al. (1986) show that the cherts are not hydrothermally influenced. Thus, the origin of clinochlore in these sediments is interpreted to be a result of weathering effects of older rocks.

Depositional environments

A set of depositional chemical criteria have been proposed for recognising continental margin, pelagic, and ridge-proximal chert environments (Murry et al. 1991; Murry 1994). The variations in the concentration of Al_2O_3, TiO_2, and Fe_2O_3 in cherts are used as important indicators because they remain relatively unaffected by diagenesis (Murry 1994). As mentioned above, Al_2O_3 and TiO_2 contents are indicative of terrigenous input and Fe_2O_3 is enriched in metalliferous ridge-proximal sediment settings. However, on the Fe_2O_3/TiO_2 vs. $Al_2O_3/(Al_2O_3+Fe_2O_3)$ discrimination diagram continental margin field overlapped with the pelagic setting field (Murry 1994). On the other hand, the three depositional regimes can be distinguished by their rare earth elements geochemistry (Murry 1994). Thus, the proposed La_n/Ce_n vs. $Al_2O_3/(Al_2O_3+Fe_2O_3)$ diagram has the best resolution and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◂**Fig. 8** **a** Non-laminated chert with dark brown organic-rich matrix containing radiolarian tests (*yellow arrows*). Sample Sv1, Svoge Unit, PPL; **b** Non-laminated chert with organic-rich matrix and common radiolarians (*yellow arrow*) composed of chalcedony aggregates. Sample Sv3, Svoge Unit, CPL; **c** Non-laminated chert with common radiolarians (*yellow arrows*). Sample Kr2, Lyubash-Golo Bardo Unit, PPL; **d** Non-laminated chert containing radiolarians with deformed tests. Sample Kr1, Morava Unit, CPL; **e** Strongly deformed chert cross-catted by quartz veins with various thickness and orientation. All radiolarian tests are strongly deformed (*yellow arrows*). Sample Kr4, Morava Unit, PPL; **f** Laminated chert composed of alternation of fine-grainy (dark brown) and more coarse-grainy (*light grey*) laminas. Rare radiolarians (*yellow arrow*) are also observed. Sample Sv2, Svoge Unit, PPL; **g** Laminated argillaceous chert. Some radiolarian tests consist of chalcedony (*yellow arrow*). Sample Sv2, Svoge Unit, CPL; **h** Laminated chert composed of fine-grainy dark brown laminas and lighter chalcedony laminas. Some radiolarian test can be distinguished (*yellow arrow*). Sample Kr3, Lyubash-Golo Bardo Unit, CPL. Note: *PPL* plane polarized light; *CPL* crossed polarized light

allows differentiating of continental margin from pelagic environments.

In this study, all cherts plot into the field of the continental margin sediment settings on both Fe_2O_3/TiO_2 vs. $Al_2O_3/(Al_2O_3+Fe_2O_3)$ and La_n/Ce_n vs. $Al_2O_3/(Al_2O_3+Fe_2O_3)$ diagrams (Fig. 12a, b).

Murry et al. (1991) studied numerous chert samples from different marine depositional settings and concluded that siliceous sediments deposited near spreading ridges have low Ce/Ce* average values (~0.29) and these deposited in a pelagic setting without metalliferous or terrigenous influence have Ce/Ce*average values ~0.58. The highest Ce/Ce* average values (~1.03) have been recorded in chert samples originating from marine settings located close to the continents. Silurian and Devonian cherts from the Balkan Terrane are characterised by Ce/Ce* values ranging from 0.82 to 1.11 (average 0.95) (Table 3) suggesting deposition on a continental marginal setting.

A comparison with the total REE content of the Post-Archean Australian Shale average (183 mg/kg; Taylor and McLennan 1985) and the North American Shale Composite (173 mg/kg; Gromet et al. 1984) demonstrate that the studied cherts are characterised with considerably lower ΣREE values (Table 3). They are higher in laminated radiolarian cherts (101.68 ppm and 117.28 ppm) and lower in non-laminated cherts, which range from 22.89 ppm to 70.39 ppm. These values most probably reflect a stronger terrigenous influence over laminated radiolarian cherts in comparison with non-laminated radiolarian cherts.

According to Sugisaki et al. (1982) and Kunimaru et al. (1998), the MnO/TiO_2 ratio in cherts lower than 0.5 is related to the continental shelf and slope deposits, while the values higher than 0.5 are characteristic

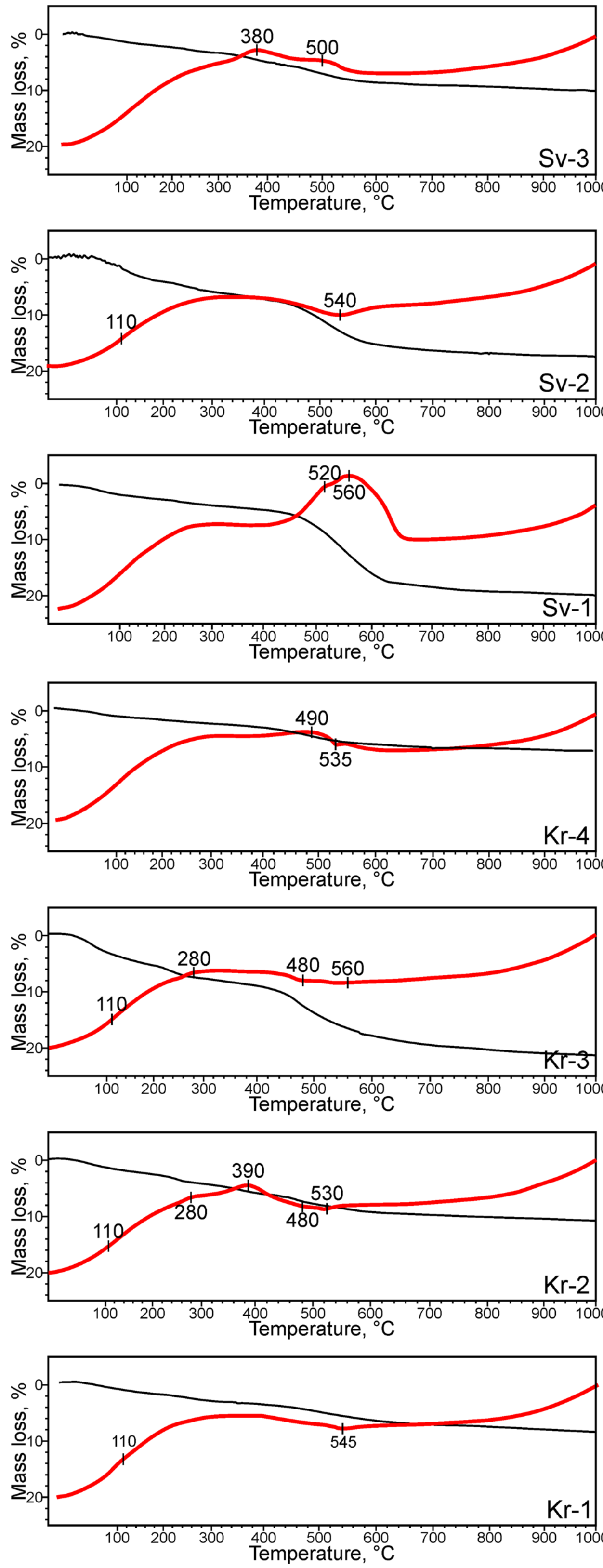

Fig. 9 TG–DTA curves of the analysed chert samples

Table 1 Major element data (wt. %) of the analysed cherts from western Bulgaria and major element ratio values used in this study

Major element (wt.%)	Sv1	Sv2	Sv3	Kr1	Kr2	Kr3	Kr4
SiO_2	89.86	78.04	92.9	91.01	90.81	76.06	96.09
TiO_2	0.20	0.41	0.12	0.15	0.14	0.49	0.08
Al_2O_3	4.48	8.72	3.34	3.41	3.79	10.92	1.95
Fe_2O_3	0.15	2.73	0.07	0.88	1.80	3.29	0.04
FeO	0.56	2.80	0.32	0.38	0.30	1.43	0.27
MgO	0.21	2.11	0.13	0.20	0.37	1.31	0.11
MnO	0.00	0.13	0.00	0.04	0.01	0.11	0.00
CaO	0.01	0.08	0.03	1.11	0.07	0.09	0.03
K2O	0.89	1.15	0.59	0.60	0.67	1.85	0.32
Na_2O	0.28	0.38	0.10	0.16	0.04	0.36	0.02
P_2O_5	0.02	0.02	0.02	0.63	0.04	0.04	0.01
LOI	3.27	3.11	2.34	1.39	1.93	3.87	1.05
Sum	99.94	99.69	99.96	99.95	99.96	99.82	99.97
Fe_2O_3 (Total)	0.77	5.84	0.42	1.30	2.13	4.87	0.34
$Al_2O_3/(Al_2O_3 + Fe_2O_3)$	0.85	0.60	0.89	0.72	0.64	0.69	0.85
Fe_2O_3/TiO_2	3.85	14.24	3.50	8.67	15.21	9.94	4.25
Si/(Si+Fe+Al+Ca)	0.94	0.81	0.95	0.92	0.92	0.79	0.97
Al/(Al+Fe+Mn)	0.81	0.52	0.85	0.66	0.57	0.62	0.81
MnO/TiO2	0.00	0.32	0.00	0.27	0.07	0.22	0.00

Table 2 Trace element data (ppm) of the studied cherts from western Bulgaria

Trace element (ppm)	SV1	SV2	SV3	Kr1	Kr2	Kr3	Kr4
Be	<28.84	<55.41	<67.41	<51.99	<62.90	<65.15	<42.67
Sc	6.28	9.69	<6.43	<7.25	<7.66	13.13	<6.00
V	230.71	79.87	163.79	70.94	68.04	112.56	122.67
Cr	322.31	297.18	213.23	197.48	252.51	350.52	213.51
Co	<2.22	20.27	<2.09	15.16	6.23	22.93	<2.67
Ni	<13.45	77.41	20.06	55.15	53.29	44.35	<18.60
Cu	18.15	39.99	7.86	52.57	56.48	46.48	12.32
Zn	<17.80	108.17	17.86	60.41	91.62	65.31	26.92
As	17.84	8.19	<7.23	<11.24	<9.13	<11.95	<12.86
Rb	39.89	55.05	29.63	30.95	33.93	80.02	13.94
Sr	13.12	61.50	30.87	78.36	19.33	42.61	10.49
Y	18.97	15.75	2.88	9.95	4.68	17.48	8.48
Zr	39.16	103.24	17.25	20.28	21.55	89.04	14.34
Nb	5.86	10.07	2.20	2.55	3.40	7.62	3.46
Mo	<5.67	<5.00	<6.80	<9.02	<7.52	6.69	<9.10
Ag	2.61	<1.14	<2.49	<2.69	<2.75	<1.83	2.41
Cd	<10.59	7.17	13.35	<8.48	<13.12	<10.15	<13.59
Cs	1.57	3.69	3.35	1.36	1.12	2.77	1.81
Ba	275.50	269.75	201.80	782.34	493.27	405.69	107.84
Hf	1.29	2.31	<1.87	<2.10	2.34	3.18	<2.13
Ta	<0.72	0.85	0.62	0.68	0.45	0.67	<0.56
W	<2.76	6.78	<2.64	<2.3064	2.53	3.03	3.52
Pb	24.48	13.92	11.56	9.49	7.68	15.79	9.66
Bi	0.46	0.42	<0.56	<0.48	<0.43	<0.63	<0.65
Th	1.71	7.14	1.40	1.27	1.43	5.42	1.02
U	2.91	1.40	1.95	1.23	1.26	1.42	1.65

Table 3 Rare earth elements (ppm) of the analysed chert samples from western Bulgaria and REE ratio values used in this study

REE (ppm)	Sv1	Sv2	Sv3	Kr1	Kr2	Kr3	Kr4
La	12.57	23.39	4.62	8.92	5.14	20.69	6.25
Ce	25.28	52.32	10.93	20.36	10.89	41.99	13.12
Pr	3.58	5.03	1.22	2.86	1.38	4.88	2.09
Nd	15.49	18.14	4.50	11.54	4.44	15.69	5.81
Sm	<2.25	4.92	<2.40	3.14	<3.71	3.53	<2.05
Eu	0.91	0.95	<0.53	<0.70	0.60	0.89	1.02
Gd	4.35	4.43	<1.84	<3.63	2.66	4.14	<3.71
Tb	0.43	0.44	<0.45	<0.42	<0.50	0.59	0.52
Dy	3.04	2.29	<1.62	1.82	2.46	2.69	1.43
Ho	0.56	0.63	<0.46	<0.44	<0.58	0.59	<0.433
Er	1.67	2.27	<1.01	1.21	<1.98	2.29	1.36
Tm	0.50	0.25	<0.31	<0.39	<0.51	0.45	<0.29
Yb	2.02	1.80	1.62	1.73	1.72	3.27	2.14
Lu	<0.37	0.41	<0.27	<0.34	<0.40	<0.37	<0.52
REE Sum	70.39	117.28	22.89	51.58	29.30	101.68	33.74
$(La/Ce)_N$	1.07	0.96	0.91	0.94	1.02	1.06	1.03
Ce/Ce*	0.86	1.11	1.06	0.91	0.98	0.96	0.82

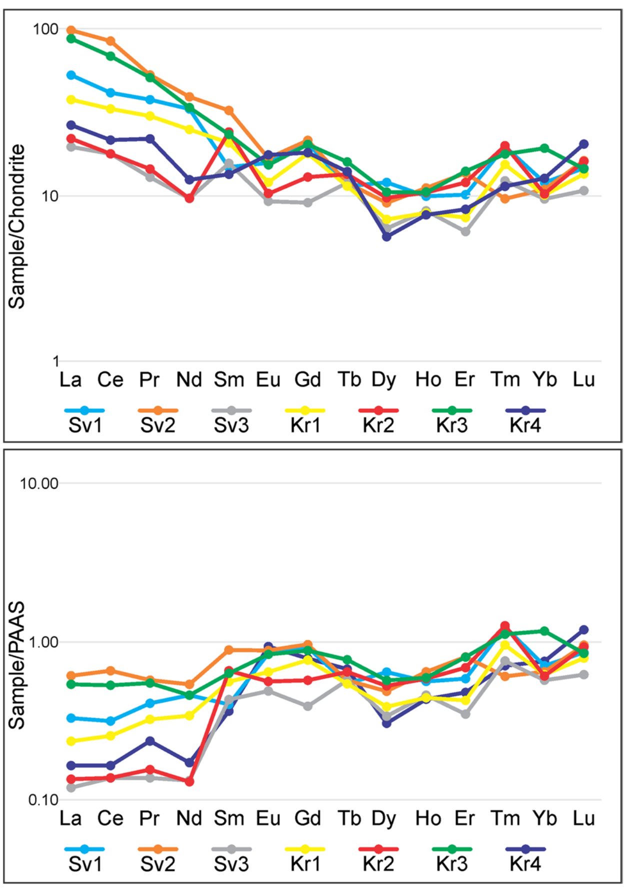

Fig. 10 Chondrite and PAAS normalized REE distribution diagrams for analysed bedded cherts (PAAS values are after McLennan 1989)

of deep basin settings. All studied cherts have MnO/TiO_2 lower than 0.5 (Table 1), indicating deposition in continental shelf or slope environments. The obtained DTA data show that most of the cherts (Sv1, Sv3, Kr2, Kr3 and Kr4) contain preserved organic matter suggesting deposition in predominating anoxic oceanic water conditions. On the other hand, two chert samples (Sv2 and Kr1) do not contain organic matter and most probably were formed in a mainly oxic oceanic water environment.

We can only presume that a part of the Silurian cherts from the Balkan Terrane could be formed under anoxic oceanic conditions related with global climatic and extinction events. As mentioned above, the Silurian cherts of Saltar Formation (Svoge Unit) have been deposited during the upper Hirnantian post-glacial sea-level rise (after the Hirnantian glacial event) (cf. Lakova and Sachanski 2004). The latest Hirnantian–early Rhuddanin is also widely recognised as a period of rapid global warming and widespread oxygen depletion (cf. Wilde et al. 1991; Melchin et al. 2013). According to Melchin et al. (2013) during this time the oceanic anoxia in the peri-Gondwana region resulted from several main factors: melting ice sheets, increased nutrient input and changes in moisture transport. On the other hand, the organic-rich Devonian cherts can be a result of various factors: hydrographical setting of the marine basin, changes in sea level and climate, rate of nutrient input into oceans, rate of nutrient recycling within oceans, atmospheric oxygen levels and changes in the biosphere are among them (Melchin et al. 2013). However, considerably more research is needed for more precise interpretation of the occurrence of the Devonian anoxic depositional settings in the Balkan Terrane.

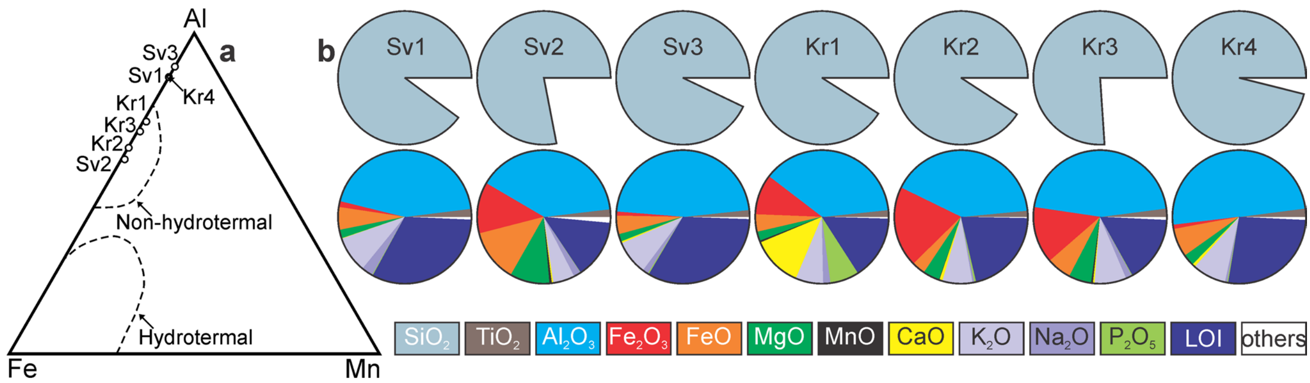

Fig. 11 **a** Al–Fe–Mn diagram (after Adachi et al. 1986) of the Silurian and Devonian cherts from western Bulgaria; **b** Major element contents of the studied siliceous rocks

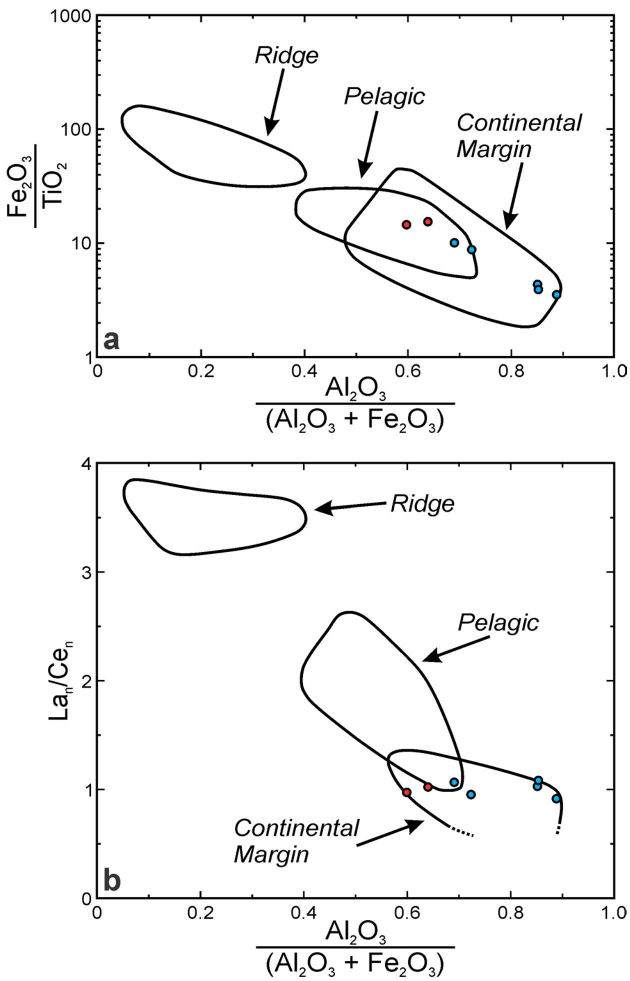

Fig. 12 **a** Fe_2O_3 /TiO_2 versus Al_2O_3/(Al_2O_3 + Fe_2O_3) and **b** La_n/Ce_n versus Al_2O_3/(Al_2O_3 + Fe_2O_3) discrimination diagrams (after Murray 1994). In both diagrams the Silurian-Devonian radiolarian cherts are plotted in continental margin field. Note: *red circles* laminated radiolarian cherts; *blue circles* non-laminated cherts

Conclusions

Present biostratigraphic, petrographic, mineralogical, DTA and geochemical data of the Silurian and Devonian bedded radiolarian cherts from the Balkan Terrane suggest the following interpretations:

1. The section of the Parchar Formation near the village of Berende contains conodont fauna (mostly the genus *Ancyrodella*) indicating the end of the Frasnian stage. The determined conodont fauna from the lower part of the Parchar Formation in section Stanyovtsi belongs to the *expansus* Zone, while the upper part of the unit to the *triangularis* Zone (the lowermost Famennian stage);
2. A new sampling of the section near the Batouliya village indicates that the first occurrence of *Ak. ascensus* Davies is 20 cm lower than previously known, i.e. at 80 cm above the boundary between the Sirman and Saltar formations.
3. The non-laminated radiolarian cherts of Svoge, Lyubash-Golo Bardo, and Morava units have a high content of SiO_2 (average 92.13%) indicating that most silica is biogenic in origin. The presence of radiolarian tests, the estimated Si/Si+Al+Fe+Ca ratios, and Al–Fe–Mn diagram plotting in a non-hydrothermal field, also support this suggestion. In laminated radiolarian cherts (from Svoge and Lyubash-Golo Bardo units) the input of terrigenous material was also important and a mixed biogenic/clastic source of silica can be suggested. The well-distinguished lamination fabric of these cherts is also interpreted as a result of fluctuating input of detrital material;
4. Ce anomalies as well as Fe_2O_3/TiO_2 vs. Al_2O_3/(Al_2O_3+Fe_2O_3) and La_n/Ce_n vs. Al_2O_3/(Al_2O_3+Fe_2O_3) diagrams indicate sedimentation in the continental

margin environment. The estimated MnO/TiO_2 ratios are typical for the continental shelf and slope deposits;

5. The obtained DTA data suggest that the Silurian and Devonian siliceous rocks were presumably formed in predominating anoxic oceanic conditions and only sporadically in oxic waters. It could be only supposing that a part of the Silurian cherts from the Balkan Terrane were formed under anoxic oceanic settings related with the rapid global warming and widespread oxygen depletion after the Hirnantian glacial event;
6. Based on the received geological data and the previously published studies we can conclude that the Silurian and Devonian cherts from the Balkan Terrane in western Bulgaria were deposited in continental shelf and slope settings on the passive margin of northern peri-Gondwana.

Acknowledgements This work has been carried out in the framework of the National Science Program "Environmental Protection and Reduction of Risks of Adverse Events and Natural Disasters", approved by the Resolution of the Council of Ministers № 577/17.08.2018 and supported by the Ministry of Education and Science (MES) of Bulgaria (Agreement № Д01-279/03.12.2021). The authors are grateful to Dr Peter Königshof and Dr Petr Štorch for their valuable scientific comments, which helped to improve the paper.

Data availability The studied specimens (thin sections and rock material) are deposited at the Geological Institute, Bulgarian Academy of Sciences, Sofia, Bulgaria. All mineralogical, petrographic, DTA, trace element and REE data generated during or analysed during the current study are included in this paper.

Declaration

Conflict of interest The authors declare that they have no conflict of interest.

References

Adachi, M., Yamamoto, K., & Sugisaki, R. (1986). Hydrothermal chert and associated siliceous rocks from the northern Pacific their geological significance as indication of ocean ridge activity. *Sedimentary Geology*, *47*, 125–148. https://doi.org/10.1016/0037-0738(86)90075-8.

Angelov, V., Antonov, M., Gerdzhikov, S., Sirakov, V., Tanatsiev, S., Sachanski, V., & Valev, V. (2010a). *Geological map of the Republic of Bulgaria 1:50 000, Svoge map sheet*. Sofia: Ministry of Environment and Water, Bulgarian National Geological Survey.

Angelov, V., Marinova, R., Grozdev, V., Antonov, M., Sinnyovsky, D., Ivanova, D., Petrov, I., Metodiev, L., Milovanov, P., Popov, A. Valev, V., & Aydanliyski, G. (2010b). *Geological map of the Republic of Bulgaria 1:50 000, Dragoman map sheet*. Sofia: Ministry of Environment and Water, Bulgarian National Geological Survey.

Angelov, V., Gerdzhikov, S., Sirakov, V., Marinova, R., Valev, V., Tanatsiev, S., Metodiev, L., & Aydanliyski, G. (2011). *Geological map of the Republic of Bulgaria 1:50 000, Slivnitsa map sheet*. Sofia: Ministry of Environment and Water, Bulgarian National Geological Survey.

Bevins, R. E., & Rowbotham, G. (1983). Low-grade metamorphism within the Welsh sector of the paratectonic Caledonides. *Geological Journal*, *18*, 2, 141–167. https://doi.org/10.1002/gj.3350180206.

Boggs, S. J. (1995). *Principles of Sedimentology and Stratigraphy* (pp. 1–774). New Jersey: Prentice Hall.

Boncheva, I. (1991). Conodont biostratigraphy of the Lower Devonian in Southwest Bulgaria. *Geologica Balcanica*, *21*(4), 55–72.

Boncheva, I., & Sachanski, V. (2016). New data on the age of the rocks of Rizovtsi allochthone (Moravian Unit) at Stradalovo village, Kyustendil district. *Review of the Bulgarian Geological Society, 77 (1),* 19–25. [in Bulgarian, with English abstract]

Boncheva, I., & Yanev, S. (1993). New data on the Paleozoic flysch of the Sofiyska Stara Planina Mountain. *Geologica Balcanica, 23(5),* 15–22.

Boncheva, I., Sachanski, V., Lakova, I., & Yaneva, M. (2007). Facial transition and biostratigraphic correlation of the Upper Silurian and Lower Devonian in West Bulgaria. *Geological Quarterly, 51* (4), 7–17.

Boncheva, I., Sachanski, V., Lakova, I., & Koenigshof, P. (2010). Devonian stratigraphy, correlations and basin development in the Balkan Terrane, western Bulgaria. *Gondwana Research, 17*(2–3), 573–582. https://doi.org/10.1016/j.gr.2009.11.012.

Boncheva, I., Sachanski, V. & Becker, R.T. (2015). Sedimentary and faunal evidence for the Late Devonian Kellwasser and *Annulata* events in the Balkan Terrane (Bulgaria). *Geologica Balcanica, 44*(1–3), 17–24.

Boncheva, I., Sachanski, V., Andreeva, P., & Tanatsiev, S. (2019). Evidence for the presence of the global Late Devonian Kellwasser event in the Berende section (Parchar formation, Western Bulgaria). *Review of the Bulgarian Geological Society*, *80*(3) 113–115.

Corradini, C., Spalleta, C., Mossoni, A., Matyja, H., & Over, J. (2017). Conodonts across Devonian/Carboniferous boundary: a review and implication for the redefinition of the boundary and proposal for an updated conodont zonation. *Geological Magazine*, *154*(4), 888–902. https://doi.org/10.1017/S001675681600039X.

Dabovski, Ch., Boyanov, I., Khrischev, K., Nikolov, T., Sapounov, I., Yanev, Y., & Zagorchev, I. (2002). Structure and Alpine evolution of Bulgaria. *Geologica Balcanica, 32*(2–4), 9–17.

Dabovski, Ch., & Zagorchev, I. (2009). Introduction: Mesozoic evolution and Alpine structure. Alpine structure. In I. Zagorchev, Ch. Dabovski, & T. Nikolov (Eds.), *Geology of Bulgaria, Vol. II, Mesozoic geology* (pp. 30–37). "Prof. M. Drinov". Sofia: Academic Press. [in Bulgarian, with English abstract]

Gromet, L. P., Haskin, L. A., Korotev, R. L., & Dymek, R. F. (1984). The "North American shale composite": Its compilation, major and trace element characteristics. *Geochimica et Cosmochimica Acta*, *48*, 2469–2482. https://doi.org/10.1016/0016-7037(84)90298-9.

Guillong, M., Meier, D. L., Allan, M., Heinrich, A. C., & Yardley, B. (2008). SILLS: a Matlab-based program for reduction of laser ablation ICPMS data of homogeneous materials and inclusions. In P. Sylvester (Ed.), *Laser-Ablation-ICP-MS in the earth sciences, current practices and outstanding issues* (pp. 328–222). Vancouver: Mineralogical Association of Canada, Short Course.

Halamic, J., Marchig, V., & Gorican, Š. (2005). Jurassic radiolarian cherts in north-western Croatia: geochemistry, material provenance and depositional environment. *Geologica Carpathica, 56*(2), 123–136.

Hara, H., Kurihara, T., Kuroda, J., Adachi, Y., Kurita, H., Wakita, K., Hisada, K., Charusiri, P., Charoentitir, T., & Chaodumrong, P. (2010). Geological and geochemical aspects of a Devonian siliceous succession in northern Thailand: implications for the opening of the Paleo-Tethys. *Palaeogeography, Palaeoclimatology, Palaeoecology, 297*, 452–464. https://doi.org/10.1016/j.palaeo.2010.08.029

Ivanov, Zh. (2017). *Tectonics of Bulgaria* (pp. 1–331). Sofia: University Press "St. Kliment Ohridski".

Jozanikohan, G., Sahabi, F., Norouzi, G., & Memarian, H. (2015). Thermal Analysis: A Complementary Method to Study the Shurijeh Clay Minerals. *International Journal of Mining and Geo-Engineering, 49*(1), 33–45. https://doi.org/10.22059/IJMGE.2015.54362.

Klapper, G. & Johnson, D. (1975). Sequence in conodont genus *Polygnathus* in Lower Devonian et Lone Mountain, Nevada. *Geologica et Palaeontologica*, *9*, 65–83.

Kunimaru, T., Shimizu, H., Takahashi, K., & Yabuki, S. (1998). Differences in geochemical features between Permian and Triassic cherts from the Southern Chichibu terrane, southwest Japan: REE abundances, major element compositions and Sr isotopic ratios. *Sedimentary Geology, 119*(3-4), 195–217. https://doi.org/10.1016/S0037-0738(98)00046-3.

Lakova, I. & Sachanski, V. 2004. Cryptospores and trilite spores in oceanic graptolite-bearing sediments (Saltar Formation) across the Ordovician–Silurian boundary in the West Balkan Mountains, Bulgaria. *Review of the Bulgarian Geological Society, 65*(1-3), 151–156.

Liao, J. & Valenzuela-Rios, J.I. (2012). Upper Givetian and Frasnian (Middle and Upper Devonian) conodonts from Ampriu (Aragonian Pyrenees, Spain): Global correlations and palaeogeographical relations. *Palaeontology, 55*(4), 819–842.

Lu, B., Qiu, Z., Zhang, B., & Li, J. (2019).Geochemical characteristics and geological significance of the bedded chert during the Ordovician and Silurian transition in the Shizhu area, Chongqing, South China. *Canadian Journal of Earth Sciences*, *56*(4), 419 – 430. https://doi.org/10.1139/cjes-2018-0160.

Marchig, V., Gundlach, H., Möller, P., & Schley, F. (1982). Some Geochemical Indicators for Discrimination between Diagenetic and Hydrothermal Metalliferous Sediments. *Marine Geology*, *50*(3), 241–256. https://doi.org/10.1016/0025-3227(82)90141-4.

Marinova, R., Grozdev, V., Ivanova, D., Sinnyovsky, D., Milovanov, P., Petrov, I., & Popov, A. (2010a). *Geological map of the Republic of Bulgaria 1:50 000, Tsravena yabuka, Vlasotintse, Tran-north, Tran-south map sheets*. Sofia: Ministry of Environment and Water, Bulgarian National Geological Survey.

Marinova, R., Grozdev, V., Ivanova, D., Sinnyovsky, D., Petrov, I., Milovanov, P., & Popov, A. (2010b). *Geological map of the Republic of Bulgaria 1:50 000, Breznik map sheet*. Sofia: Ministry of Environment and Water, Bulgarian National Geological Survey.

Melchin M.J., Mitchell, C.E., Holmden, C., & Štorch, P (2013). Environmental changes in the Late Ordovician–early Silurian: review and new insights from black shales and nitrogen isotopes. *Geological Society of America Bulletin*, *125*(11-12), 1635–1670. https://doi.org/10.1130/B30812.1.

Men, X., Mou, C., Ge, X., & Wang, Y. (2020). Geochemical characteristics of siliceous rocks of Wufeng Formation in the Late Ordovician, South China: Assessing provenance, depositional environment, and formation model. *Geological Journal, 55*(4), 2930–2950. https://doi.org/10.1002/gj.3553

McLennan, S. M. (1989). Rare earth elements in sedimentary rocks: Influence of provenance and sedimentary processes. *Reviews in Mineralogy and Geochemistry*, *21*, 169–200. https://doi.org/10.1515/9781501509032-010.

Milovanov, P., Goranov, E., Zhelev, V., Valev, V., Petrov, I., & Ilieva, E. (2006a). *Explanatory note to the geological map of the Republic of Bulgaria 1:50 000, Bosilegrad and Treklyano map sheets* (pp. 1–59). Sofia: Ministry of Environment and Water, Bulgarian Geological Survey.

Milovanov, P., Goranov, E., Zhelev, V., Valev, V., Petrov, I., & Ilieva, E. (2006b). *Geological map of the Republic of Bulgaria 1:50 000, Bosilegrad and Treklyano map sheets*. Sofia: Ministry of Environment and Water, Bulgarian National Geological Survey.

Milovanov, P., Goranov, E., Zhelev, V., Valev, V., Petrov, I., & Ilieva, E. (2006c). *Geological map of the Republic of Bulgaria 1:50 000, Radomir map sheet*. Sofia: Ministry of Environment and Water, Bulgarian National Geological Survey.

Murray, R.W. (1994). Chemical criteria to identify the depositional environment of chert: general principles and applications. *Sedimentary Geology, 90*, 213–232. https://doi.org/10.1016/0037-0738(94)90039-6.

Murray, R.W., Buchholtz ten Brink, M.R., Gerlach, D.C., Russ III, G.P., & Jones, D.L. (1991). Rare earth, major, and trace elements in chert from the Franciscan Complex and Monterey Group, California: assessing REE sources to fine-grained marine sediments. *Geochimica et Cosmochimica Acta, 55*, 1875–1895. https://doi.org/10.1016/0016-7037(91)90030-9.

Parvanov, B. (1967). Attempt for a stratigraphic subdivision of the metamorphic rocks in the central and southern part of the Kraishte. In *Jubilee Volume on Geology* (pp. 317–323). Sofia: Committee of Geology. [in Bulgarian]

Phillips, W. (1963). A differential thermal study of the chlorites. *Mineralogical Magazine and Journal of the Mineralogical Society, 33*(260), 404–414. https://doi.org/10.1180/minmag.1963.033.260.06.

Ruiz-Ortiz, P. A., Bustillo, M. A., & Molina, J. M. (1989). Radiolarite sequences of the Subbetic, Betic Cordillera, Southern Spain. In J. R. Hein & J. Obradović (Eds.), *Siliceous deposits of the Tethys and Pacific regions* (pp. 107–127). New York, NY: Springer. https://doi.org/10.1007/978-1-4612-3494-4_8.

Sačanski, V. (1993). Boundaries of the Silurian System in Bulgaria on graptolites. *Geologica Balcanica 23*(1), 25–33.

Sachanski, V. (2015). The Silurian in the West Balkan Mts. (Svoge Unit, Srednogorie Zone) – 110 years later. *Geologica Balcanica*, *44*(1–3), 3–15.

Sachanski, V. (2017). The first fossil eurypterids (sea scorpions) discovered in Bulgaria. *National Conference with international participation "Geosciences 2017"*, 95–96. [in Bulgarian, with English abstract]

Sachanski, V., & Boncheva, I. (2002). Geological events and process dating by the rate of sedimentation in the area of Cherna Gora Height. *Geologica Balcanica 32*(2–4), 127–129.

Sachanski, V., & Tenchov, Y. (1993). Lithostratigraphic subdivision of the Silurian sediments in the Svoge anticline. *Review of the Bulgarian Geological Society, 54(1)*, 71–81. [in Bulgarian with an English abstract]

Sachanski, V., Boncheva, I., & Lakova, I. (2005). A continuous section across the Silurian–Devonian boundary in the Kraishte region: graptolite and conodont biostratigraphy. In Y. Yanev & R. Nedialkov (Eds.), *Proceedings of the Jubilee International Conference "80 years Bulgarian Geological Society",* (pp. 18–20). Sofia: Bulgarian Geological Society.

Scotese, C. R. (2014a). *Atlas of Silurian and Middle-Late Ordovician Paleogeographic Maps (Mollweide Projection)*, Maps 73–80, 5, The Early Paleozoic, PALEOMAP Atlas for ArcGIS, PALEOMAP Project, Evanston, IL.

Scotese, C. R. (2014b). *Atlas of Devonian Paleogeographic Maps,* PALEOMAP Atlas for ArcGIS, 4, The Late Paleozoic, Maps 65–72, Mollweide Projection, PALEOMAP Project, Evanston, IL.

Spalleta, C. Perri, M.C., Over, D.J., & Corradini, C. (2017). Famennian (Upper Devonian) conodont zonztion: revised global standard. *Bulletin of Geosciences,* 92(1), 31–57.

Spassov, Ch. (1960a). Stratigraphie der paläozoische Sedimente zwischen Tran und Temelkovo in Südwestbulgarien. *Travaux sur la Géologie de Bulgarie, Serie Stratigraphie et Tectonique, 1,* 93–102. [in Bulgarian, with Russian and German abstracts]

Spassov, Ch. (1960b). Stratigraphie des Ordoviziums und Silurs im Kern der Svoge-Antiklinale. *Travaux sur la Géologie de Bulgarie,* *Serie Stratigraphie et Tectonique*, *1,* 161–202. [in Bulgarian, with Russian and German abstracts]

Spassov, H. (1973). Stratigraphy of the Devonian in SW Bulgaria. *Buletin of the Geological Institute, Series Straigraphy and Lithology, Sofia, 22,* 5–38. [in Bulgarian]

Štorch, P., & Serpagli, E. (1993). Lower Silurian graptolites from southwestern Sardinia. *Bollettino della Societa Paleontologica Italiana, 32*, 3–57.

Sugisaki, R., Yamamoto, K., & Adachi, M. (1982). Triassic bedded cherts in central Japan are not pelagic. *Nature*, *298*(5875), 644–647.

Ta, H.P., Königshof, P., Ellwood, B.B., Nguyen, T.C., Luu, P.L.T., Doan, D.H. & Munkhjargal, A. (2022). Facies, magnetic susceptibility and timing of the Late Devonian Frasnian/Famennian boundary interval (Xom Nha Formation, Central Vietnam). *Palaeobiodiversity and Palaeoenvironments*, *102*(1), 129–146. https://doi.org/10.1007/s12549-021-00506-y.

Taylor, S. R., & McLennan, S. M. (1985). *The Continental Crust: Its Composition and Evolution* (pp. 1–312). Oxford: Blackwell.

Tenčov, J. (1965). Ober Devon im Kern der Svoge-Antikline. *Review of the Bulgarian Geological Society, 26*(1), 109–112. [in Bulgarian, with German abstract]

Thassanapak, H., Udchachon, M., Burrett, C., & Feng, Q. (2017). Geochemistry of Radiolarian Cherts from a Late Devonian Continental Margin Basin, Loei Fold Belt, Indo-China Terrane. *Journal of Earth Science*, *28*(1), 29–50. https://doi.org/10.1007/s12583-017-0738-4.

Wilde, P., Berry, W.B.N., & Quinby-Hunt, M.S. (1991). Silurian oceanic and atmospheric circulation and chemistry. In M. G. Bassett, P. D. Lane, & D. Edwards (Eds.), *The Murchison Symposium. Special Papers in Paleontology, 44,* 123–143.

Xu, L., Wang, X., Feng, M., & Liu, X. (2021). Deciphering the upper Ordovician Wufeng siliceous shale depositional environments (Wuxi, NE Chongqing) based on multi-proxy record. *Petroleum, 7*, 10–20. https://doi.org/10.1016/j.petlm.2020.06.001.

Yan, D., Chen, D., Wang, Q., & Wang, J. (2009). Geochemical changes across the Ordovician-Silurian transition on the Yangtze Platform, South China. *Science in China Series D: Earth Sciences*, *52*(1), 38–54. https://doi.org/10.1007/s11430-008-0143-z.

Yamamoto, K. (1987). Geochemical characteristics and depositional environments of cherts and associated rocks in the Franciscan and Shimanto Terranes. *Sedimentary Geology*, *52*, 65–108. https://doi.org/10.1016/0037-0738(87)90017-0.

Yanev, S. (1985). Devonian flysch in the Černogorie (Southwest Bulgaria). *Palaeontolgy, Stratigraphy, Lithology, 21,* 76–87. [in Bulgarian]

Yanev, S. (1991a). Genetic environments of chert formations in the Paleozoic sections in Bulgaria. *Abstracts of the VI International Flint Symposium*. October 1991, Spain, 26–28.

Yanev, S. (1991b). Paleozoic cherts in Bulgaria. *Abstracts of the VI International Flint Symposium*. October 1991, Spain, 61–64.

Yanev, S. (1993). Gondwana Palaeozoic terranes in the Alpine Collage System on the Balkans. *Journal of Himalayan Geology, 4*(2), 257–270.

Yanev, S. (1996). A sedimentological study of Paleozoic siliciclastic rocks from Western Bulgaria- implications for long-term tectonic evolution. *Beitrage zur Geologie von Thubingen, Neue Floge, 3*, 19–31.

Yanev, S. (1997a). Palaeozoic migration of terranes from the basement of the eastern part of the Balkan peninsula from peri-Gondwana to Laurussia. In M. C. Göncüoğlu & A. S. Derman (Eds.), *Early Palaeozoic Evolution in NW Gondwana, Turkish Association of Petroleum Geologists, Special Publication, 3*, 89–100.

Yanev, S. (1997b). Paleoclimatic data on terrane movements from Bulgaria during Paleozoic. In A. K. Sinha,, F. P. Sassi, & D. Papanikolaou, (Eds.), *Geodynamic domains in Alpine–Himalayan Tethys* (pp. 347–368). Rotterdam, Brookfield: A.A. Balkema.

Yanev, S. (2000). Palaeozoic terrans of the Balkan Peninsula in the framework of Pangea assembly. *Palaeogeography, Palaeoclimatology, Palaeoecology, 161*(1–2), 151–177. https://doi.org/10.1016/S0031-0182(00)00121-8.

Yanev, S. & Spassov, Ch. (1985). Lithostratigraphy of the Devonian flysh between Tran and Temelkovo. *Paleontology, Stratigraphy*, *Lithology, 21,* 82–86.

Yanev, S., Lakova, I., Boncheva, I., & Sachanski, V. (2005). The Moesian and Balkan Terranes in Bulgaria: Palaeozoic basin development, plaeogeography and tectonic evolution. *Geologica Belgica, 8*(4), 185–192.

Zagorchev, I. (1993). *Explanatory note to the geological map of Bulgaria 1:100 000, Bosilegrad and Radomir map sheet* (pp. 1–77). Sofia: Geology and Geophysics Ltd.

Zagorchev, I. (2001). Introduction to the geology of SW Bulgaria. *Geologica Balcanica, 31* (1–2), 3–52.

Ziegler, W. & Sandberg, Ch. (1990). The Late Devonian Standard Conodont Zonation. *Courier Forschungsinstitut Senchenberg*, *121*, 1–115.