Mineralogic evidences of a mid-Paleozoic tectono-thermal event in the Zonguldak terrane, northwest Turkey: implications for the dynamics of some Gondwana-derived terranes during the closure of the Rheic Ocean

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Abstract: The Zonguldak terrane is a Gondwana-derived continental microplate along the Black Sea coast in northwest Anatolia. It includes a Cadomian basement, with oceanic- and island-arc sequences, unconformably overlain by siliciclastic rocks of Ordovician to Middle Silurian age. After a period of deformation and erosion, late Lower Devonian (Emsian) quartzites and shallow-marine limestones unconformably cover Middle Silurian (Wenlock) graptolitic shales. Along several cross sections across the unconformity plane, the mineralogical characteristics of the Paleozoic sedimentary rocks in the Zonguldak terrane are studied to check whether this regional unconformity is only of epeirogenic nature or the result of a thermal event. In addition to the appearance of kaolinite in Devonian units, crystal-chemical data of illites show a sudden jump at the unconformity plane. The *b* cell dimension values of illites of Ordovician–Silurian units are somewhat higher than those of Devonian–Carboniferous units and show a drastic drop between the Silurian and Devonian units. The new mineralogic data indicate that the pre-Emsian rocks in the Zonguldak terrane experienced a thermodynamo event, prior to the Emsian transgression. This Caledonian-time event is also reported in east Moesian terrane but not noticed in the neighboring Istanbul–Zonguldak and in the west Moesian – Balkan – Kreishte terranes. By this, it is suggested that Zonguldak and east Moesian terranes behaved independently from the Istanbul–Balkan terranes during the closure of the Rheic Ocean. They very likely docked to Laurussia during Emsian by strike-slip faults and remained thereon at its platform margin, where the Middle–Late Devonian shallow-platform conditions were followed by fluvial (lagoon and delta) conditions and deposition of coal during Late Carboniferous.

Résumé : Le terrane de Zonguldak est une microplaque continentale provenant de Gondwana, situé le long de la côte de la mer Noire dans le nord-ouest de l'Anatolie. Il comprend un socle cadomien avec des séquences d'arcs océaniques et d'arcs insulaires, il est recouvert de manière discordante par des roches silicoclastiques datant de l'Ordovicien au Silurien moyen. Après une période de déformation et d'érosion, des quartzites et des calcaires marins peu profonds du Dévonien inférieur tardif (Emsien) recouvrent de manière discordante des shales à graptolites du Silurien moyen (Wenlockien). Le long de plusieurs coupes transversales à travers le plan de discordance, les caractéristiques minéralogiques des roches sédimentaires du Paléozoïque dans le terrane de Zonguldak ont été étudiées afin de vérifier si cette discordance était de nature seulement épeirogénique ou si elle était accompagnée d'un événement thermique. En plus de la venue de kaolinite dans les unités du Dévonien, les données chimiques et cristallines des illites montrent un accroissement soudain au plan de la discordance. Les valeurs de la dimension *b* des illites des unités de l'Ordovicien–Silurien sont quelque peu plus élevées que celles des unités du Dévonien–Carbonifère et montrent une baisse importante entre les unités du Silurien et du Dévonien. Les nouvelles données minéralogiques indiquent que dans le terrane de Zonguldak les roches pré-emsiennes ont subi un événement thermodynamique avant la transgression à l'Emsien. Cet événement de l'époque calédonienne est aussi enregistré dans le terrane de Moesie Est mais il n'a pas été remarqué dans les terranes avoisinants d'Istanbul–Zonguldak et de Moesie Ouest – Balkan – Kreishte. Selon ces faits, les terranes de Zonguldak et de Moesie Est se comportaient de manière indépendante des terranes Istanbul Balkan durant la fermeture de l'océan Rhéique. Ils se sont très probablement arrimés au continent Laurussia durant l'Emsien par des failles de décrochement et sont restés à la plate-forme/bordure, où les conditions de la plate-forme peu profonde au Dévonien moyen tardif ont été suivies de conditions fluviales (lagunes et deltas) et la déposition de charbon au Carbonifère tardif.

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Introduction

The Istanbul–Zonguldak terrane comprising the classical (e.g., de Verneuil 1836–1837) successions of Variscan "Paleozoic of Istanbul" is a Variscan terrane assemblage (Fig. 1) or a composite terrane (sensu Howell 1989). Its original position and assemblage to the Western and Central European terrane groups (e.g., Baltica, Avalonia, Armorica) during the Paleozoic is a matter of debate (e.g., Kalvoda and Babek 2010). One of the suggestions is that it was part of the south Laurussian platform margin in a similar setting to Moesia, until late Mesozoic (e.g., Görür et al. 1997; Stampfli 2000; von Raumer et al. 2003) and obtained its present location by southward drift owing to the opening of the western Black Sea basin (e.g., Okay and Tüysüz 1999). Another idea is that this terrane assemblage actually consists of two different Gondwanan microplates: Istanbul terrane (IT), recently located to the west in Istanbul, Gebze, and south Camdağ regions; and Zonguldak terrane (ZT) in north Camdag, Zonguldak, and Safranbolu regions (Göncüoglu and Kozur 1998, 1999; Göncüoglu and Kozlu 2000; Kozur and Göncüoglu 2000; Yanev et al. 2006). The main differences between Zonguldak and Istanbul terranes were elucidated on account of stratigraphic variations and the presence of a Caledonian-time event in ZT (Göncüoglu 1997; Yanev et al. 2006). These differences cannot be explained simply by lateral facies changes; hence, they were considered (Göncüoglu et al. 1997) as two different Variscan terranes. In the Safranbolu area of the ZT, Paleozoic successions include a low-grade angular unconformity between Wenlock graptolitic shales (Sachanski et al. 2010) and late Early Devonian (Emsian) (Göncüoglu et al. 2004) carbonates. On the contrary, IT is characterized by continuous deposition during the same time interval.

In several detailed studies, textural and mineralogical configurations were used (e.g., Merriman and Frey 1999; Merriman and Peacor 1999; Bozkaya et al. 2002, 2006) for the interpretations in terms of various thermal maturities in these types of thick sedimentary sequences. To find out whether this unconformity is only of epeirogenic character or the result of a tectonothermal event, we studied several sections by means of petrographic and X-ray diffraction (XRD) methods (bulk and clay mineralogy, Kübler index (KI) value, *b* cell dimension, and polytype of illites).

Geological framework

The Istanbul and Zonguldak terranes in northwest Anatolia (Fig. 2) comprise more or less similar basement rocks, consisting of a crystalline series covering gneisses of continental crust origin, an oceanic assemblage (ultramafics, gabbros, and basalts), and an island-arc complex (granites, felsic volcanites, and pyroclastics) in the ZT. The radiometric age data from neighboring Bolu (Ustaömer and Rogers 1999) and Safranbolu Karadere areas (570–590 Ma, Chen et al. 2002) suggest that the basement is of Cadomian age. It is unconformably overlain by Ordovician rocks (Dean et al. 2000; Lakova et al. 2006), which include greenish grey siltstones and mudstones (Bakacak formation) and dark-red conglomerates and sandstones (Kurtköy and Aydos formations) (Fig. 3), with the dark-grey mudstones and siltstones including Darriwilian (Middle Ordovician) graptolites and trilobites; and the lithostratigraphic differences between the Zonguldak and Istanbul areas commence. Following a thick package of Upper Ordovician limestones, the Early to Middle Silurian period is mainly characterized by graptolitic black and gray shales and siltstones (Fındıklı formation). By this, the shelf-type deposition in ZT completely differs from the coeval fluvial to coastal–lagoonal sediments of the IT. In the former area, late Lower Devonian conglomeratic sandstones and quartzites (Ferizli formation) rest with a low-angle unconformity on different levels of Silurian and earliest Devonian rocks (Boncheva et al. 2009). The conglomerates are dominated by Kurtköy and Aydos-type pebbles, with subordinate amounts of clasts from the pre-Ordovician crystalline basement. They are followed by 800 m thick shallow-marine dolomites and limestones (Yılanlı formation) of Emsian (late Early Devonian) to Sephukovian (late Early Carboniferous) age. In the IT, however, the deposition is continuous and characterized from Middle Devonian onwards by slope and then by basin-type sediments of latest Devonian – Early Carboniferous. Significantly, the post-Silurian – pre-Emsian unconformity does not exist in the IT. In ZT (Fig. 3), the platform carbonates are followed by a thick succession of fluvial sediments, with coal stems of Late Carboniferous (Westphalian G) age.

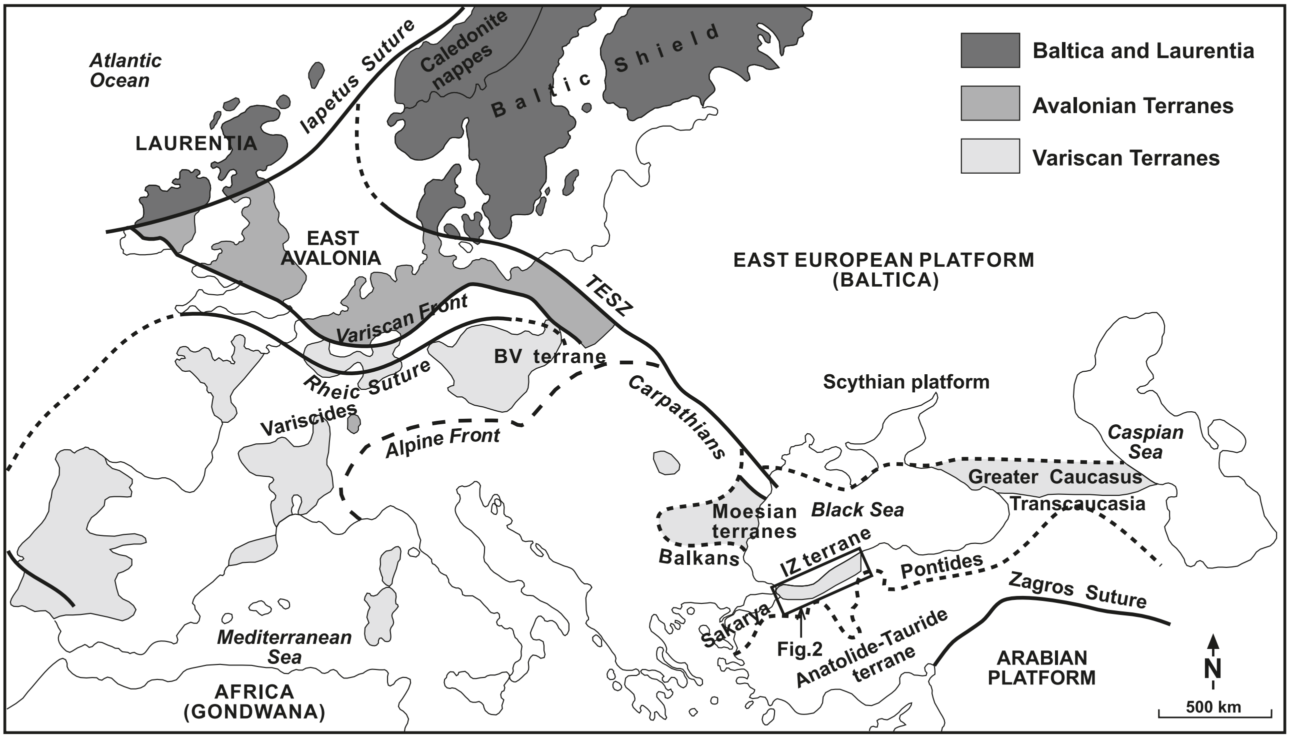
In this study, Paleozoic units in the Eflani–Çatak (section 1), Araç–Karadere–Ovacık–Karasu (sections 2–4), and Karasu–Yayladere–Madendere (sections 5 and 6), shown on Figs. 2*a*–2*d*, were measured and sampled. From these, disregarding the variations in thickness, the successions are very similar. In the Karasu–Yayladere–Madendere (sections 5 and 6) in north Çamdağ, the coarse clastics of Kurtköy formation are well developed, whereas the Middle Ordovician graptolite-bearing black shales are not encountered yet.

Material and method

A total of 222 rock samples not affected by Alpine deformation were collected from the measured sections and analyzed by optical and XRD methods.

The XRD studies were performed in the X-ray diffractometer (Rigaku DMAX IIIC) at the Geological Engineering Department of Cumhuriyet University in Sivas, Turkey. The analysis was made using CuKα (λ = 1.541 871 Å) irradiation, Ni filter or monochromator, 35 kV and 20 mA voltage and current, respectively, slits (divergence, 1°; scatter, 1°; receiving, 0.3 mm; receiving monochromator, 0.8 mm). Scan speed was set as 2° 2θ/min (where θ represents the diffraction angle) in the range from 5° to 35° 2θ for the whole rock, and 1° 2θ/min in the range from 2° to 30° 2θ for oriented clay fractions. The clay fraction (<2 μm) was separated by centrifuge after dispersion with the sedimentation method. Carbonate and organic matter were eliminated by HCl and H_2O_2 acid treatments. In addition to air-dried samples, clay fractions are also saturated with ethylene glycol (EG) at 60 °C for 16 h, and heated to 490 °C for 4 h. After sample preparation and clay separation processes, the semiquantitative percentages of the rock-forming minerals and clay-size fractions were calculated using the external standard method of Brindley (1980). The determinations of the mixed-layered clays, such as C–S, I–C, and I–S, and proportions of the interlayer components were identified by using the methods of Moore and Reynolds (1997). NEWMOD (Reynolds

Fig. 1. Location of the Istanbul–Zonguldak terrane within the Western and Central European terrane assemblages.



1985) and WINFIT (Krumm 1996) computer programs were also applied for the interpretation of mixed-layer clay minerals.

Illite crystallinity values, the widths of the 10 Å illite peaks at half-height (KI, in degrees $\Delta 2\theta$; Kübler 1968) were used for the determination of diagenetic to low-grade metamorphic grades. The KI values were calibrated by means of both polished-slate standards (Kisch 1980) and crystallinity index standards (CIS; Warr and Rice 1994). The details of calibration lines and linear regression equations were given in Bozkaya et al. (2006). In this study, CIS calibrated values were preferred because of the widespread usage in the literature. The limits of the early and late diagenesis, and lower and upper anchizone correspond to 1.00°, 0.42°, and 0.25° $\Delta 2\theta$, respectively (e.g., Kübler 1969; Merriman and Frey 1999; Merriman and Peacor 1999). KI values were measured from fitted peaks by the WINFIT program to minimize the individual measurement errors.

The reflections, $d_{(060,331)}$, of illites were measured on unoriented powder clay fractions using the (211) peak of quartz (2θ = 59.982°, d = 1.541 Å, where d represents interplanar lattice spacing) as an internal standard. b cell dimensions of illites, reflecting octahedral Mg + Fe + Mn composition (e.g., Guidotti et al. 1992), were utilized as an empirical indicator of pressure (e.g., Sassi and Scolari 1974; Guidotti and Sassi 1986). For b cell dimension determinations, samples rich in white K-mica but lacking in paragonite were evaluated as the Y assemblage in the AKNa diagram of Guidotti and Sassi (1976).

Illite polytype samples were scanned in the range of 16°–36° 2θ on the random powder mounts. WINFIT decomposition by profile fitting was used for determination of areas and intensities of the specific peaks of $1M$ and $2M_1$ (crystal-chemical parameters) polytypes for quantification of individual ones with the equations of Grathoff and Moore (1996).

Petrography

Paleozoic units are represented mainly by shale, siltstone, sandstone, and limestone–dolomite. Siliciclastic rocks contain monocrystalline and polycrystalline quartz, polysynthetic and zoned plagioclase, calcite, biotite, muscovite and chlorite, and secondarily of metamorphic and magmatic rock fragments, orthoclase, dolomite, zircon, tourmaline, apatite, goethite, and opaque minerals. The amount of polycrystalline quartz, feldspar, and biotite are high in the Ordovician–Silurian formations, whereas biotite, chlorite, and feldspar minerals are scarce or not found in the Devonian formations. Besides, Devonian sandstones comprise relatively lower amounts of clay matrix than those of the Ordovician–Silurian formations.

Shale samples from the Ordovician units show rough cleavage planes (S_1) in addition to bedding planes (S_0) (Fig. 4*a*), whereas shales from the Devonian and younger units display weakly oriented bedding planes. White K-micas are rarely found as medium- to coarse-grained muscovite sheets or flakes and fine-grained occurrences in the matrix. Chlorites were observed as authigenic products within the micropores and (or) fissures and as alteration products of detrital biotites in the siltstones and sandstones. In the Ordovician units, chloritic minerals in C–S-rich samples are marked both as authigenic ones in the pores (Fig. 4*b*) and as alteration products, whereas in I–C-rich samples, chlorites are dominantly transformed from biotites (Fig. 4*c*). Silurian biomicritic limestones exhibit weakly developed orientation and include carbonate-filled fissures that are nearly perpendicular to bedding planes in some samples (Fig. 4*d*). In contrast, there is no orientation or widespread carbonate-filled fissures, which were observed in limestones from the Devonian and younger formations. Metamorphic rock fragments as lithoclastic fragments were detected in some limestone samples. Devonian siltstones and sandstones with quartz-arenite com-

Fig. 2. (*a*) Distribution of the Paleozoic rock units in the Istanbul and Zonguldak terranes. (*b–d*) Geological maps and section locations of the studied units.

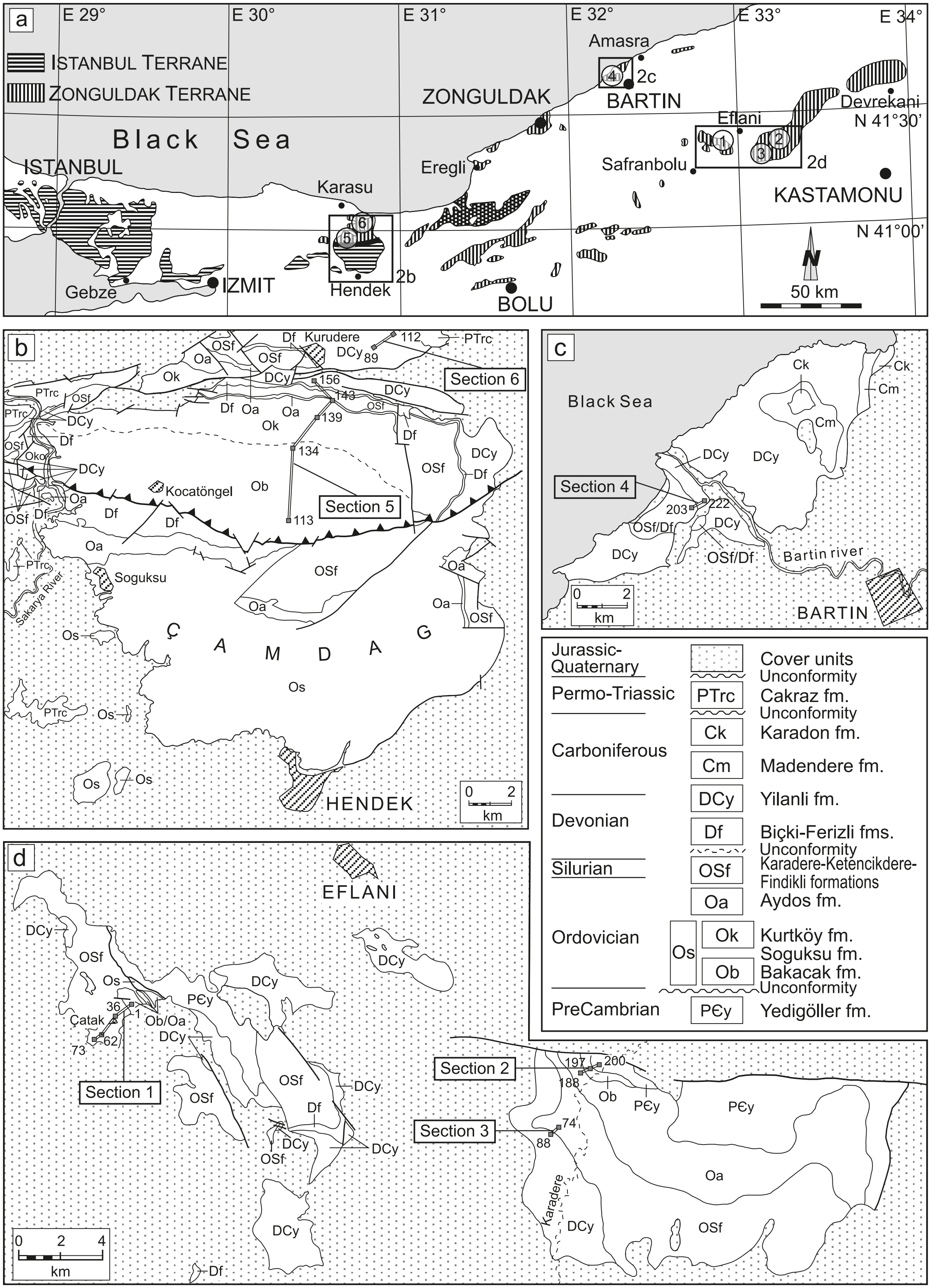
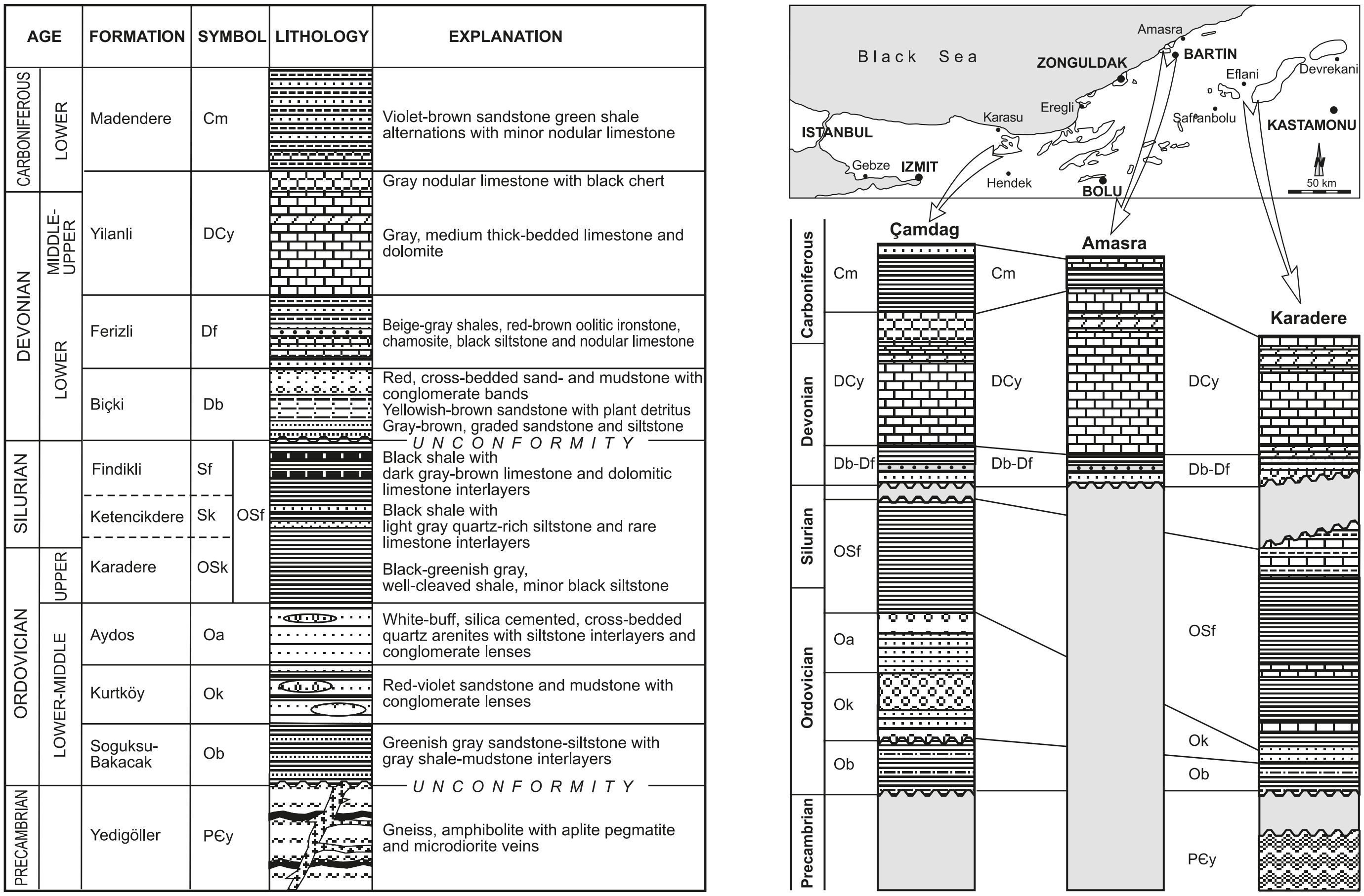


Fig. 3. Generalized lithostratigraphic section of the Zonguldak terrane and its lateral and vertical correlation with sections in neighboring areas.



position have low amounts of fine-grained micaceous matrix and show weakly developed orientation, defined by thin muscovite flakes (Fig. 4*e*). Authigenic kaolinites with spherulitic texture were also identified within the pores and fissures in the Devonian sandstones (Fig. 4*f*).

X-ray mineralogy

Bulk and clay mineralogy

Ordovician to Carboniferous rocks of the ZT mainly contain phyllosilicates, quartz, feldspar, calcite, dolomite, hematite, and goethite. Phyllosilicate minerals are represented by illite, chlorite, kaolinite, mixed-layered chlorite–vermiculite (C–V), chlorite–smectite (C–S), and illite–chlorite (I–C) (Fig. 5).

In general, quartz and phyllosilicate minerals are common in all formations, but the abundances of feldspar, calcite, and dolomite increase in some levels. Phyllosilicate minerals display some similarities and differences with respect to the underlying and overlying formations (Table 1; Figs. 6–8).

Granitic gneisses of the pre-Ordovician Yedigöller formation are rich in feldspar, quartz, and mica, whereas mafic metamorphic rocks are mainly made up of amphibole, feldspar, and phyllosilicate minerals, which are represented by chlorite, C–S, and illite–muscovite.

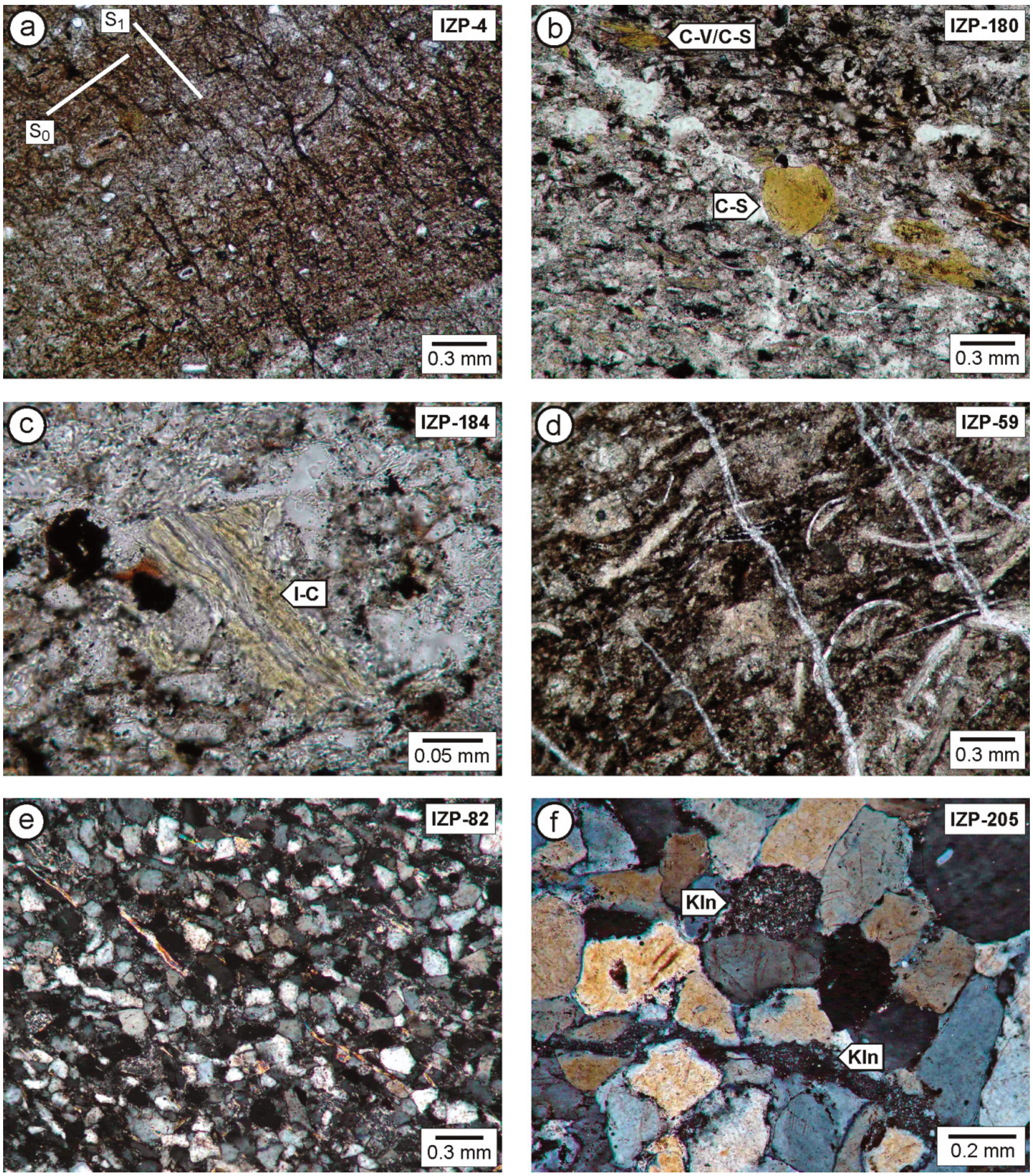
Bakacak formation, the lowermost unit of Ordovician, is exemplified by relatively higher amounts chlorite and I–C in the Karadere and Çatak regions (Figs. 6, 7), whereas C–V and C–S are high in the north Çamdağ region (Fig. 8). In addition, hematite and feldspar contents of clastic rocks increase in the Karadere and Çamdağ regions, respectively.

The siliciclastic rocks of the Ordovician Aydos and Kurtköy formations contain more quartz and illite and less feldspar than those of Bakacak formation. These units comprise, respectively, illite + chlorite + I–C and illite + chlorite or C–S in the Çatak and Çamdağ regions.

Ordovician to Silurian Karadere, Ketencikdere, and Fındıklı formations involve clayey and sandy clastic rocks, with limestone intercalations. They include calcite and dolomite in addition to quartz and feldspar, and the phyllosilicate minerals are illite + chlorite + I–C ± C–S and illite ± I–C ± chlorite associations.

Devonian Ferizli and Yılanlı formations were characterized by fairly different mineralogic compositions, such as the abundance of dolomite, calcite, and illite, scarcity of feldspar, and the first appearance of kaolinite in the Çatak and Karadere sections (Figs. 6, 7). However, Devonian and Carboniferous units show similar associations to those of Ordovician and Silurian units in the Çamdağ section (Fig. 8). The presence of bulk and clay mineralogical differences between eastern (Çatak and Karadere) and western (Çamdağ) areas could be originated from differences in their respective source areas.

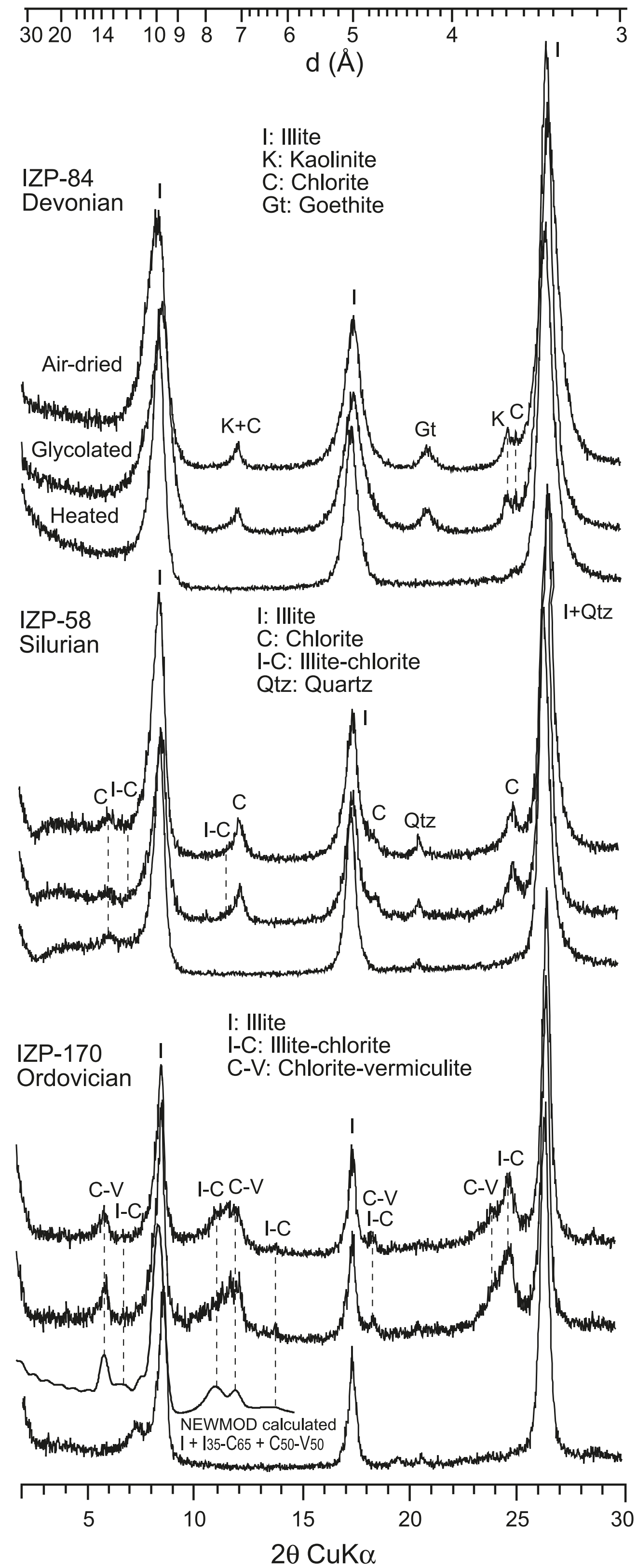
Fig. 4. Characteristic textural features of the Ordovician–Devonian units in the Zonguldak terrane. (*a*) Bedding planes (S_0) and weakly developed cleavage planes (S_1) in the shales of the Bakacak formation (plane polarized light, ppl). (*b*) Chloritic minerals (C–S and C–V) as authigenetic in pores and transformed from biotites in siltstones of the Bakacak formation (ppl). (*c*) Chloritic minerals (I–C) derived from detrital biotites as diagenetic transformation in sandstones of the Bakacak formation (ppl). (*d*) Weakly developed orientation and postsedimentary carbonate-filling fissures in the biomicritic limestones of the Fındıklı formation (ppl). (*e*) Weakly developed orientation formed by mica flakes in the siltstone of the Ferizli formation (crossed nicols, cn). (*f*) Authigenetic pore- and crack-filled kaolinite (Kln) occurrences in the sandstone of the Ferizli formation (cn).



Kübler index

KI values of illites refer to different degrees of diagenetic–metamorphic grades through both vertical and lateral distributions (Table 1; Figs. 6–8). In general, Ordovician–Silurian formations have late diagenetic KI values, but Devonian formations have early diagenetic KI values in the eastern part of the region (Çatak and Karadere). However, KI values of the Ordovician–Silurian and Devonian–Carboniferous formations in some sections (e.g., sections 5 and 6 in Fig. 2) from the western part of the region (Çamdağ) indicate relatively higher diagenetic–metamorphic grades as anchimetamorphism and late diagenesis, respectively. In the vertical distributions of different formations, KI values change suddenly between some formation boundaries, such as the boundary between the Silurian Fındıklı and Devonian Ferizli formations in sections 1 and 3 (Figs. 6–8, 9*a*). In addition, KI

Fig. 5. Typical clay mineralogic assemblages in the Ordovician–Devonian units of the Zonguldak terrane. The computer program NEWMOD (Reynolds 1985) was used for the calculation of one-dimensional diffraction patterns of mixed-layered clays. *d*, interplanar lattice spacing; θ, diffraction angle.



values of the Ordovician Bakacak and Kurtköy formations also reflect a sharp boundary in section 5. In the diagrams showing KI and *b* cell dimension values (Fig. 9*b*), and intensity ratios of glycolated and air-dried peaks of illites (Ir; Środoń 1984), Silurian units clearly differ from the Devonian units (Fig. 9*c*).

b cell dimensions of illites

The *b* cell dimension values of illites show wide ranges, from 8.975 to 9.036 Å, for a total of 67 samples. *b* values of illites from Ordovician–Silurian formations (9.012 ± 0.013 Å) are generally higher than those of the Devonian–Carboniferous formations (8.998 ± 0.012 Å) (Table 1; Figs. 6–8, 9*b*). According to *b* or d_{060} (d_{060}, reflections of illites) values, octahedral Mg + Fe contents of illites are 0.37 and 0.13 (atoms per formula unit) for Ordovician–Silurian and Devonian–Carboniferous formations, respectively. Sudden changes of *b* values from Silurian to Devonian formations were clearly determined in sections 1 and 2 in the eastern part of the region where the angular unconformity is clearly observed (Figs. 6, 7).

Octahedral compositions of illites change from muscovite to phengite. Illites from Silurian–Ordovician and Devonian–Carboniferous formations have, respectively, phengite- and muscovite-rich compositions. When the measured *b* values of illites were evaluated as a monitoring of pressure conditions (Sassi and Scolari 1974; Guidotti and Sassi 1986), Silurian and older formations were exposed to relatively higher pressure conditions than Devonian and younger formations.

Polytypes

Illites reflect the mixed nature of three or two polytypes as $2M_1$ + $1M$ + $1M_d$ and $2M_1$ + $1M_d$ (Table 1; Figs. 6–8). $2M_1$ proportions of the illites from Ordovician–Silurian formations are relatively higher than those of Devonian–Carboniferous formations. The presence of $1M$ polytype could be used as a discrimination factor for Silurian and Devonian formations near the boundary zone, as seen in sections 1 and 3 (Figs. 6, 7, 9*d*), except for sections 5 and 6 (Fig. 8). Thus, the polytype data indicate considerable mineralogical differences between Ordovician–Silurian and Devonian–Carboniferous in the Bartın and Eflani regions, similar to the KI and *b* values of illites. As to chlorites, they completely represent the II*b* polytype.

Conodont alteration index (CAI)

The Ordovician–Silurian formations (Bakacak, Aydos, and Fındıklı) have CAI values around 5–6. Devonian–Carboniferous units (Yılanlı and Madendere), however, have a distinctly lower CAI (2–2.5) value (Göncüoglu and Kozur 1998; Boncheva et al. 2009).

Discussion and conclusions

Lithologic and compositional variations in depositional environment

The vertical distribution of lithologies and their mineralogic compositions may reflect the corresponding depositional environments of the sedimentary rocks that constantly vary on account of time. In the study area, the Early Ordovician Bakacak formation unconformably overlaying the Cadomian basement is characterized by conglomerates, greywacke,

Table 1. Bulk and clay mineralogic composition and some crystal-chemical properties of illites of Ordovician–Carboniferous units from the Zonguldak terrane.

	Mineralogic composition		Crystal-chemical characteristics of illites		
Formations (age)	Bulk	Clay	KI (Δ° 2θ)	b_0 (Å)	Polytype
Çatak (1) section					
Ferizli–Yılanlı (Devonian)	Qtz+Cal+Fel+Phl	I+Kln	0.72–1.36 (1.08)	8.984–9.022 (9.011)	$2M_1$+1M+1M_d
Fındıklı (Ordovician–Silurian)	Qtz+Phl+Cal+Fel+Dol	I+C+I–C+C–S	0.56–1.01 (0.76)	9.008–9.022 (9.015)	$2M_1$+1M_d
Aydos–Kurtköy (Ordovician)	Qtz+Phl+Fel	I+C+I–C	0.55–0.92 (0.71)	8.982–9.010 (8.993)	$2M_1$+1M+1M_d
Bakacak (Ordovician)	Qtz+Phl+Fel	I+C+I–C	0.61–0.95 (0.74)	9.011–9.014 (9.013)	—
Ovacık (2) – Karadere (3) – Karasu (4) sections					
Ferizli–Yılanlı (Devonian)	Qtz+Phl+Cal+Dol+Fel	I+K+C	0.66–1.54 (1.09)	8.975–9.008 (8.991)	$2M_1$+1M+1M_d $2M_1$+1M_d
Fındıklı (Ordovician–Silurian)	Qtz+Phl+Cal+Fel+Dol	I+I–C+C	0.63–0.86 (0.74)	9.019–9.031 (9.024)	$2M_1$+1M_d
Aydos (Ordovician)	Qtz+Fel+Phl	I+C+I–C	0.47	—	—
Bakacak (Ordovician)	Qtz +Fel+Phl	I+C+I–C	0.38–0.75 (0.53)	—	—
Karasu – Yayladere (5) – Madendere (6) sections					
Harem (Carboniferous)	Qtz+Phl+Fel+Cal	I+C+I–C+C–S	0.46–0.70 (0.60)	8.990–9.011 (9.003)	$2M_1$+1M+1M_d
Ferizli–Yılanlı (Devonian)	Dol+Cal+Qtz+Phl+Fel	I+I–C+C+C–V	0.51–0.65 (0.60)	8.993–9.005 (9.000)	$2M_1$+1M+1M_d
Fındıklı (Ordovician–Silurian)	Qtz+Phl+Fel+Cal+Hem	I+C+I–C	0.45–0.63 (0.46)	—	—
Aydos–Kurtköy (Ordovician)	Qtz+Phl+Fel+Hem	I+C+C–S	0.58–0.70 (0.66)	8.999–9.021 (9.012)	$2M_1$+1M+1M_d
Bakacak (Ordovician)	Fel+Qtz+Phl+Hem	I+C+C–S+ I–C+C–V	0.32–0.58 (0.42)	9.036	$2M_1$+1M+1M_d

Note: Section location numbers were stated in Fig. 2. Qtz, quartz; Fel, feldspar; Phl, phyllosilicate; Dol, dolomite; Cal, calcite; Hem, hematite; I, illite; C, chlorite; Kln, kaolinite; I–C, mixed-layered illite–chlorite; C–V, mixed-layered chlorite–vermiculite; C–S, mixed-layered chlorite–smectite; b_0, cell dimension values; KI, Kübler index; M, M_1, M_d, crystal-chemical parameters.

shallow-marine siltstones, and mudstones with graptolites and acritarchs (Lakova et al. 2006). It is followed by variegated fluvial sediments (Kurtköy formation). The Aydos Formation is typically made of beach-type quartzites and quartz arenites. Middle Ordovician (Karadere), Late Ordovician Ketencikdere, and Silurian Fındıklı formations mainly comprise greenish siltstones, black shales with graptolites, and black limestone–shale alternations. The dominance of the black shales is typical for accommodation of large amounts of decomposing organic material, lack of bottom currents, and reducing conditions. By this, it is suggested that the Karadere, Ketencikdere, and Fındıklı formations were laid down in a restricted shallow-marine and anoxic environment. The Emsian transgression represented by quartzitic conglomerates and quartzites are again typical for beach facies. The fossil content and the petrographical features of the Middle Devonian – late Lower Carboniferous carbonates are characteristic of lagoon and restricted shelf conditions. The Serpukhovian – Late Carboniferous coal-bearing clastics are indicative of a fluvial to coastal plain depositional environment.

In addition to lithology, the mineralogic compositions of the Ordovician–Silurian clastic rocks differ from the Devonian–Carboniferous successions. The abundances of polysynthetic and zoned plagioclase, biotite, and chlorite in the former group seem to be related to volcanogenic input. High quartz contents but low amount of clay matrix and relatively well-sorted sandstones of the latter group are criterion for a higher energy environment.

Paleogeographic and (or) paleoclimatic implications of clay minerals

In general, clay mineral assemblages in ancient sequences are controlled by preburial and postburial conditions. Preburial controls are indicative of the source area, lithology, depositional environments, paleoclimate, and topography (e.g., Chamley 1989; Inglès and Anadón 1991; Inglès and Ramos-Guerrero 1995). As a postburial control, diagenetic processes, on the other hand, can modify the original detrital composition of clays, or allow precipitation of new minerals from the diagenetic or pore fluids (authigenesis). Therefore, in sequences that had not suffered intense diagenesis–metamorphism, the lateral and vertical changes of clay minerals can be used as a significant tool to decipher the depositional history of the sedimentary rocks (e.g., Bozkaya et al. 2002, 2006; Bozkaya and Yalçın 2004).

Clay mineral assemblages in Paleozoic sequences in the ZT point out both dominantly preburial and partly postburial conditions. There are chlorite-bearing mixed layers in the Ordovician–Silurian formations, whereas kaolinite in the Devonian formations were presumably related not only to the source area but also to paleoclimatic controls. Chlorite and chlorite-bearing mixed layers should be associated with metamorphic and (or) volcanic provenances with mafic composition under the high-latitude geographic setting during the Ordovician–Silurian. However, the presence of kaolinite seems to be related to changes of depositional environment or to formation in a different paleogeographic setting close

Fig. 6. Vertical distributions of bulk- and clay-fraction-forming minerals and some crystal-chemical parameters in the Çatak section (section number was stated in Fig. 2). C–S, chlorite–smectite; C–V, chlorite–vermiculite; I–C, illite–chlorite; *M*, M_1, M_d, crystal-chemical parameters.

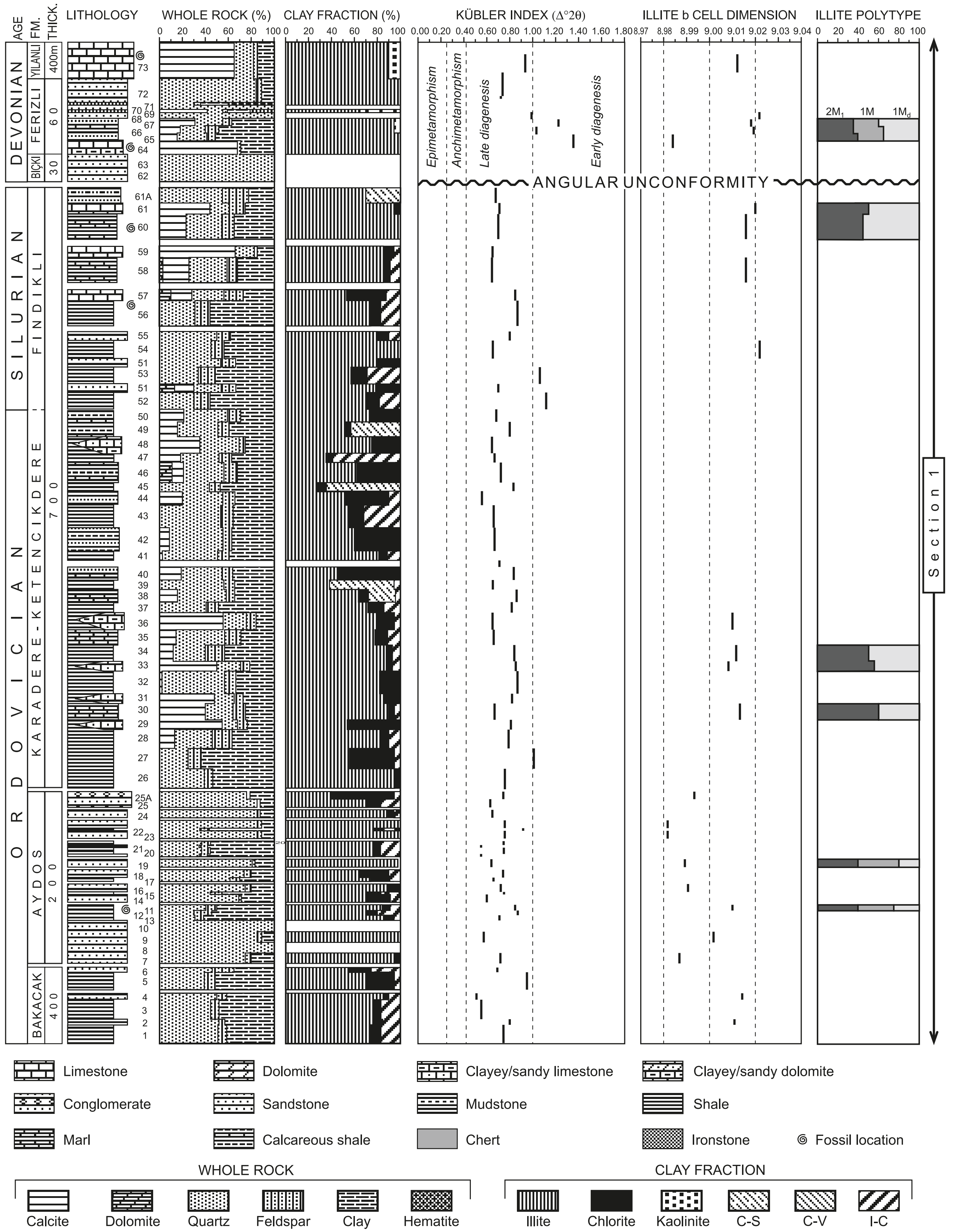
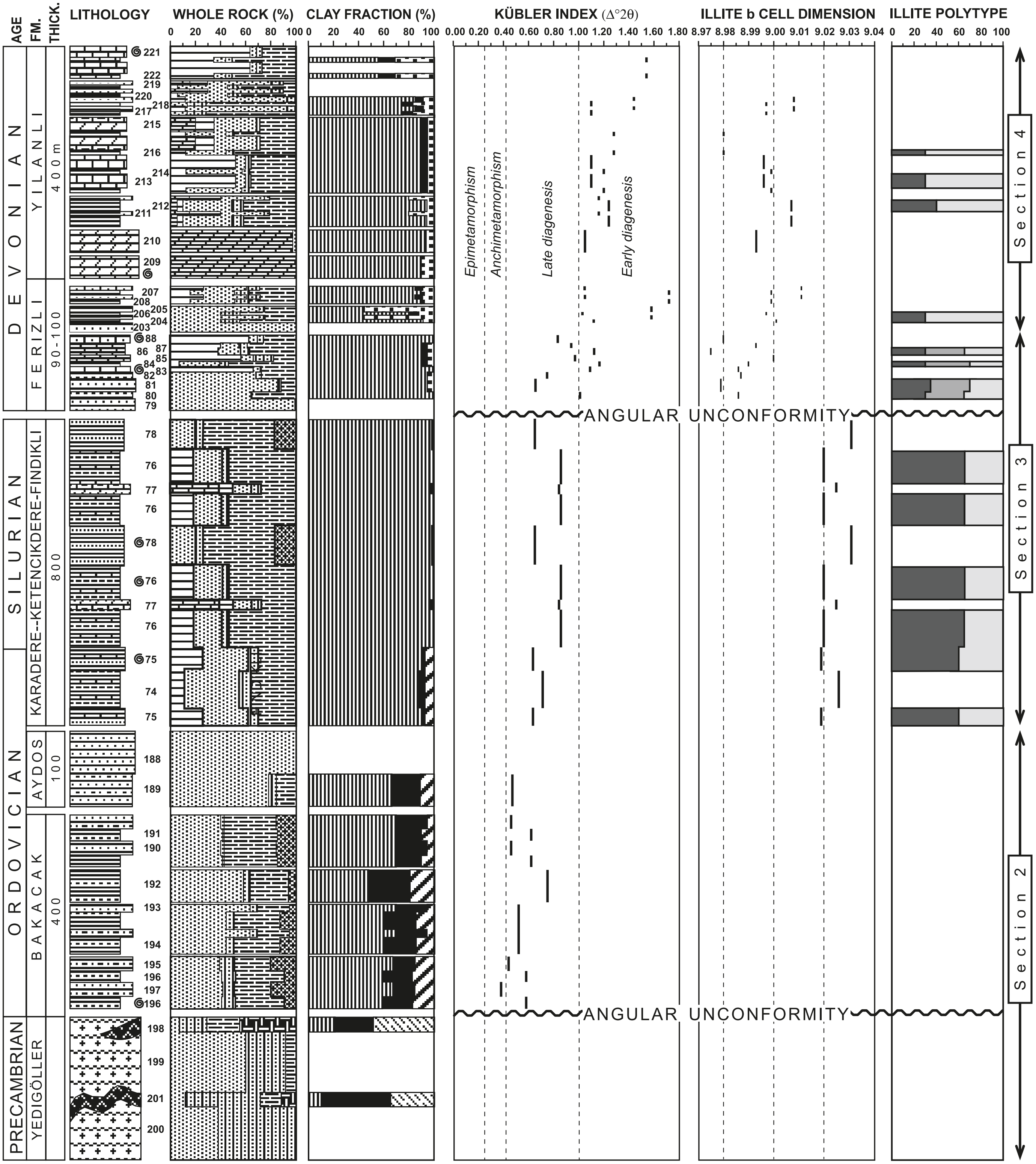


Fig. 7. Vertical distributions of bulk- and clay-fraction-forming minerals and some crystal-chemical parameters in the Karadere–Ovacık and Karasu sections (section numbers were stated in Fig. 2). Legend as in Fig. 6.



to low latitudes under tropic conditions during the Late Devonian. According to petrographic observations, chlorite and chlorite-bearing mixed-layer clays mainly depend upon detrital minerals, partly of authigenetic origin. Kaolinite, however, is completely of authigenetic origin, which was precipitated within the pores during diagenesis, and it was generally observed as very fine-grained filling minerals in quartz sandstones. Feldspar is rare or absent in kaolinite-rich samples, excluding formation of kaolinite from argillized detrital feldspars.

Fig. 8. Vertical distributions of bulk- and clay-fraction-forming minerals and some crystal-chemical parameters in the Karasu–Yayladere–Madendere sections (section numbers were stated in Fig. 2). Legend as in Fig. 6.

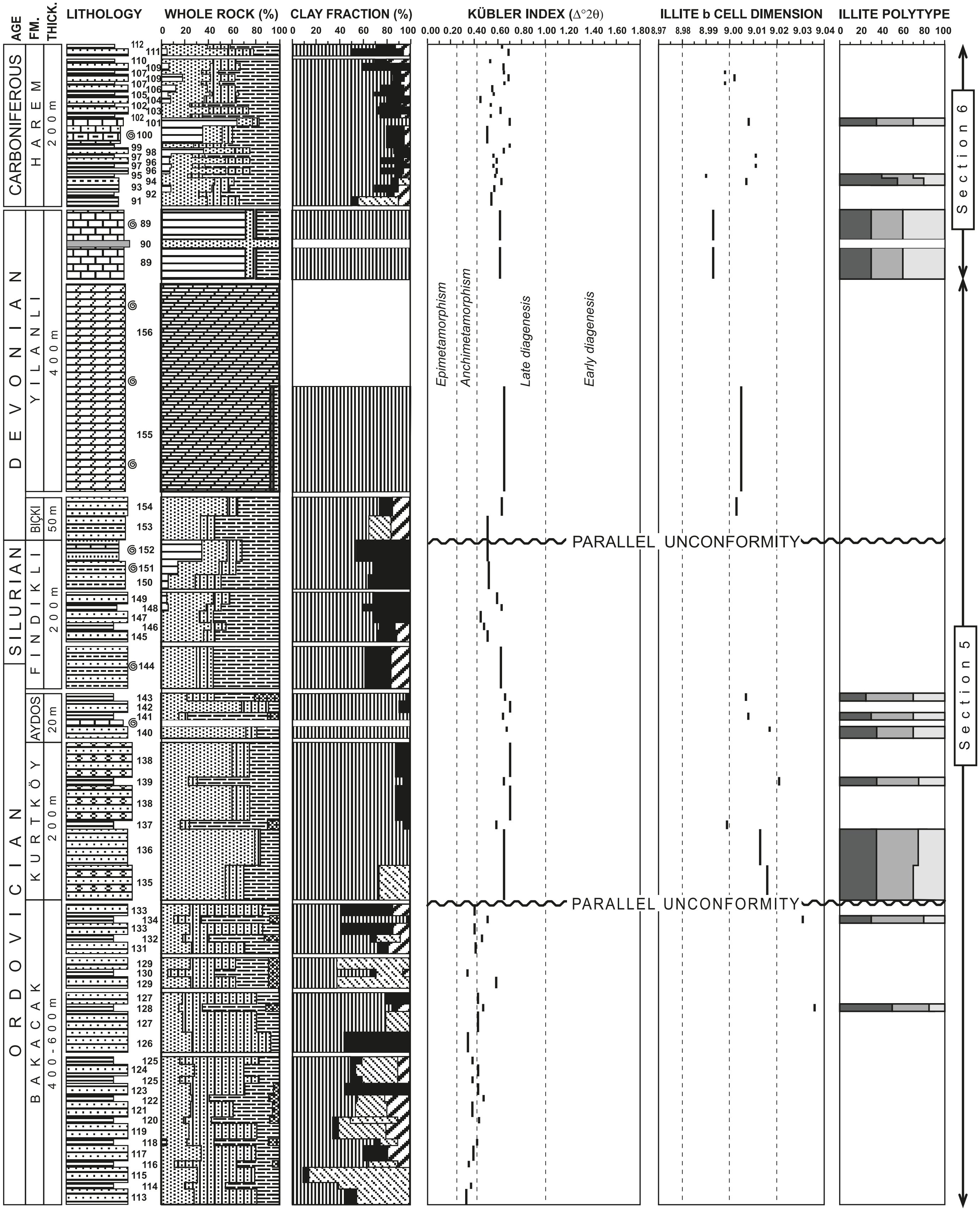
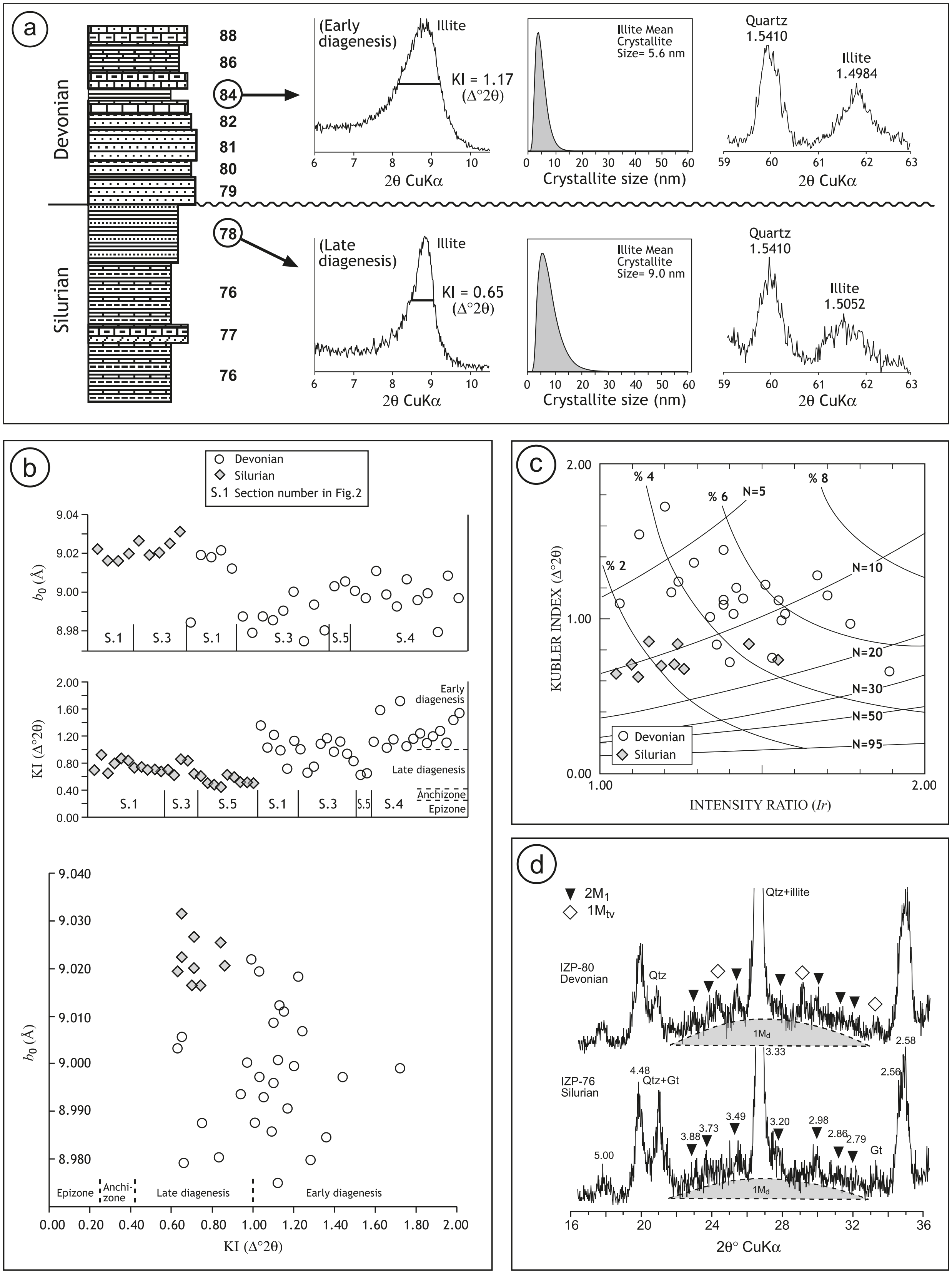


Fig. 9. (*a*) Differences between the values of the Kübler index (KI), crystallite size, and *b* cell dimension values of illites in Silurian and Devonian units (crystallite size values were determined by WINFIT (Krumm 1996) computer program); (*b*) distribution of KI and *b* (b_0) cell dimensions of illites; (*c*) crystallite size and smectite % contents of illites in the crystallinity (KI) – intensity ratio (Ir) diagram of Eberl and Velde (1989); (*d*) polytype characteristics of illites. Legend as in Fig. 6. Gt, goethite; *M*, M_1, M_d, M_{tv}, crystal-chemical parameters; *N*, number of samples; Qtz, quartz; θ, diffraction angle.



Regional tectonothermal implications of clay minerals

The drastic changes in associations with crystal-chemical characteristics of clay minerals within the diagenetic – very low-grade metamorphic Paleozoic sequences could be evaluated as fingerprints of the earlier tectonothermal events rather than local differences in the source area or climatic conditions (e.g., Bozkaya et al. 2002, 2006; Bozkaya and Yalçın 2004).

The variations of KI and *b* values of illites across the Emsian unconformity together with the appearance of kaolinite in clay mineral associations in only Devonian parts indicate the presence of a metamorphic hiatus between Silurian and Devonian. Higher grade diagenetic–metamorphic maturation of Silurian and older units compared with Devonian–Carboniferous rocks also suggest that they were affected by a tectonothermal event, prior to the deposition of Devonian formations. This type of metamorphic hiatus is marked by the continuity of diagenetic–metamorphic grades, which is interrupted by the absence of one or more diagenetic–metamorphic zone from a sequence (e.g., Merriman and Frey 1999). On regional scale, a metamorphic hiatus should be associated with a major unconformity rather than local depositional varieties. The dissimilarity of the KI and *b* cell dimensions of illites in Silurian and Devonian sections, where the former one shows greater degree of diagenesis–metamorphism, characterizes a difference exemplified by a hiatus in diagenesis–metamorphism.

Mixed-layered C–S, C–V, and I–C occurrences in the study area are observed in both late diagenetic and anchimetamorphic series, and their amount and types are unrelated to diagenetic grades. Thus, the vertical distribution and amounts of mixed-layer clays were mainly controlled by source material and lithology. C–S, C–V, and I–C seem to be formed at the intermediate stages of transformation of detrital biotite to vermiculite, smectite, or chlorite, rather than by progressive transformation during burial diagenesis (Hoffman and Hower 1979; Chang et al. 1986; Nieto et al. 1996). C–S appears generally in graywackes with volcanic fragments in the Ordovician Bakacak formation, as a result of an alteration process from volcanic biotite to C–S, as previously described by Inoue et al. (1984) and Inoue and Utada (1991). The appearance of mixed layers C–V and C–S in the anchizonal rocks are inconsistent with metamorphic grade; therefore, these may represent the retrograde alteration products (e.g., Nieto et al. 1994, 2005; Bozkaya and Yalçın 2004). The increase of C–V and C–S in the trioctahedral mica-rich levels exhibit the mixed layers derived from biotite during retrogression. Additionally, I–C is mostly originated from low- to medium-grade metamorphic rocks, such as metagranite, mica–schist, and mica–gneiss, by the reaction of chloritization of biotite (e.g., Veblen and Ferry 1983; Eggleton and Banfield 1985) during the burial diagenetic–metamorphic processes.

Siliciclastic and calcareous rocks of the ZT comprise mainly phyllosilicates (illite, chlorite, kaolinite, C–V, C–S, and I–C), quartz, feldspar, calcite, dolomite, hematite, and goethite minerals. Phyllosilicate assemblages of Ordovician–Silurian and Devonian–Carboniferous formations are illite + chlorite + I–C ± C–V ± C–S and illite + kaolinite + chlorite, respectively. Chlorite and chlorite-bearing mixed-layered minerals seem to be derived from both authigenetic and detrital origin as pore-filling and transformed from trioctahedral micas, respectively. The presence of authigenetic kaolinite and a decrease in chlorite bearing mixed-layers in the Devonian units are the main diversities for clay mineral associations. Late diagenetic KI values of Silurian rocks suddenly jump to early diagenetic KI values in the Devonian units. This also supports the sudden jump in the CAI data (Göncüoglu and Kozur 1998). Similar changes were also observed in *b* cell dimension values of illites, as *b* values drop across the Emsian unconformity. Another mineralogic disparity for Silurian and Devonian was observed in illite polytype variations, where Ordovician–Silurian units contain generally $2M_1 + 1M_d$, whereas Devonian–Carboniferous units include $2M_1 + 1M + 1M_d$.

Regional correlation and comments on Variscan geological evolution

To conclude, the obtained mineralogic data point out that the Ordovician–Silurian rocks in the ZT were subjected to a tectonothermal event prior to the late Lower Devonian transgression and angular unconformity. The possible cause of this event in the ZT (and the corresponding one in east Moesia as described later in the text) is speculative. Some authors (e.g., Aydın et al. 1987; Derman 1997) suggest that it may be due to epeirogenic movements. Göncüoglu (1997), in contrast, puts forward that this event should be related to a collision of the ZT with Laurussia, prior to the final closure of the southeast European Variscan ocean (Rheic, e.g., Nance and Linnemann 2009). Whatever the cause, the information accommodated in the last years clearly shows that this problem cannot be solved without considering the geological features of the other Paleozoic terranes at the southeast edge of the Eastern European craton, where a complex mosaic of Gondwanan and Laurussian terranes meet across the Trans-European Suture Zone (e.g., Winchester et al. 2002). By this, the geological features of four tectonic units (terranes) in this specific area and their equivalents, namely the Istanbul, west Moesian – Balkan – Kreishte, and east Moesian, will be evaluated and correlated with the ZT.

In the neighboring IT, which shares the same Cadomian basement and its Early Ordovician fluvial cover with Zonguldak, the regional unconformity associated with a tectonothermal event is not encountered (Bozkaya et al. 2011). According to detailed conodont data, the Wenlock – early Emsian interval to the east of Bosporus is characterized by a complete succession of neritic carbonates, followed by late Emsian – early Eifelian sandstones and finally late Eifelian – mid-Tournaisian nodular limestones and radiolarian cherts (Haas 1968; Boncheva et al. 2005). The succession is interpreted as a depositional environment transitional from shelf to continental slope conditions during the Middle Devonian and finally from slope to deep basin conditions at the end of Devonian. By this, obviously, IT was in a dissimilar tectonic position and has not been affected by this event. As noticed previously, this dissimilar tectonic and probably also paleogeographic setting is underlain by the differences in the Devonian to Early Carboniferous sediments, which cannot be explained simply by lateral facies changes (e.g., Kalvoda et al. 2003).

Based on its lithostratigraphical similarities, IT is considered as the eastward continuation of the Balkan terrane (e.g., Yanev et al. 2006). The Balkan terrane is a piece of continental crust of Gondwanan origin (Yanev et al. 1995). It actually includes different successions in the Kraishte region to the west of Sofia and in the Balkan Mountains. In the former area, the pre-Silurian rock units are not observed. The Late Silurian – Early Carboniferous interval includes preflysch and flysch-type deposits, with lydite and limestone intervals. By this, the succession of events in Kraishte is similar to the IT, with the restriction that the flysch formation starts considerably earlier. In the Balkan Mountains, which may include a part of the west Moesian terrane, the basement is characterized by Neoproterozoic – Early Cambrian ophiolites and volcanic arc, very similar to the Cadomian basement of the Istanbul and Zonguldak terranes in northwest Turkey. The Ordovician–Silurian successions are mainly made of siliciclastics and shales, more akin to the ZT. No deformation or stratigraphical break is observed in Early Devonian, and the Devonian – Early Carboniferous rock units are again preflysch and flysch type. Late Carboniferous – Permian sediments are posttectonic fluvial in character and coal-bearing. In brief, the stratigraphy of the Balkan terrane shows similarities both to Istanbul and Zonguldak terranes but lacks the Emsian angular unconformity and related thermal event, characteristic of the ZT. Moreover, the onset of deposition of flyschoidal sediments in foredeeps already in late Middle Devonian is indicative of its proximity to the Variscan accretional prism.

The last Paleozoic terrane with Ordovician to Late Carboniferous stratigraphy similar to Zonguldak is the Moesian terrane to the north of the east Black Sea Basin on the east continuation of the eastern European Platform (Yanev et al. 2006). In the eastern part of the Moesian terrane in the Dobrogea Highlands, the Neoproterozoic to Cambrian basement is disconformably overlain by quartzitic sandstones of Early Ordovician age. The Middle Ordovician to Late Silurian interval is characterized by graptolite-bearing black shales and argillites (Seghedi et al. 2005). A thick quartzite formation (Simirna quartzites) transgressively covers the Silurian successions. This boundary is described as an angular unconformity between the Late Silurian and Devonian successions on the northern and western Moesian Platform margin and in several boreholes in South Dobrogea (Paraschiv 1974 in Seghedi et al. 2005). The following Middle Devonian to Early Carboniferous succession is represented by black limestones and dolomites of shallow-marine environment, grading into coal-bearing fluvial (delta and lagoon; Kerey 1984 for Zonguldak, Pană 1997 for east Moesia) sediments of Middle and Late Carboniferous. This Ordovician to Carboniferous lithostratigraphic development is almost identical to the stratigraphy of the ZT. Unfortunately, no mineralogical data is available across the Emsian unconformity from the east Moesian sections. However, the deformation of the argillites below the Eifelian Simirna Quartzites is attributed to the "Ardennian phase" in the classical sense by Seghedi et al. (2005).

Another common and critical feature of the Zonguldak and east Moesian terranes is that they do not include the Variscan flysch deposits, the typical compounds of the Istanbul – west Moesian – Balkan – Kreishte terranes. In contrast, both the shallow-marine Middle Devonian – Early Carboniferous carbonates and the conformably overlying fluvial sediments with coal measures are indicative of a quiet platform-margin deposition. These may constrain the paleogeographic setting of the Zonguldak and east Moesian terranes to a completely different area, away from the Variscan orogenic front.

To conclude, as commonly accepted, all terranes under consideration (e.g., Yanev 1993; Göncüoglu 1997; Seghedi et al. 2005; Okay et al. 2008) were originally located at the northwest Gondwanan margin and drifted northward to collide with the Laurussian margin across the closing Paleozoic oceanic branches (Iapetus and Rheic oceans). From these, the Zonguldak and east Moesian terranes were in close association since Middle Ordovician, from whereon the lithostratigraphical differences to Istanbul – west Moesian – Balkan – Kreishte areas initiated. This difference may be caused by the opening of a restricted basin between the Zonguldak – east Moesian terrane and the rest, considering the deposition of graptolitic shales during Middle Ordovician to Middle Silurian in the Zonguldak–Moesian part. The absence of a thermal event in the pre-Emsian rocks in the Istanbul area excludes a heating, induced by extension-related thermal upwelding of mantle material and, hence, a separation of the Zonguldak – east Moesian terrane from the rest by a completed or aborted rifting. The differentiation of these tectonic units and the deformational event described in this study may indicate the presence of strike-slip faults, which would tear off Zonguldak – east Moesia from the Istanbul–Balkan terrane and penecontemporaneously give way to a low-temperature deformation by collision with a northerly located terrane. Such regional-scale faults are described in east Moesia (Seghedi et al. 2005) and in the Camdag area (Gedik and Önalan 2001), northwest Turkey. However, their structural features are largely obscured by post-Variscan strike-slip displacements and Cimmerian and Alpine compressional tectonic events.

The juxtaposition of the Zonguldak – east Moesian and the Istanbul–Balkan terranes must have been realized prior to Late Permian, considering their earliest common cover in northwest Anatolia. According to present knowledge, no Paleozoic oceanic lithologies or remnants of a Variscan subduction–accretion prism representing a suture were known in northwest Anatolia. By this, Göncüoglu (1997) suggested that the juxtaposition of these terranes was also realized by oblique collision. Then again, the recent finding of a number of arc-type Late Carboniferous (Nzegge et al. 2006) rocks in north Anatolia and Late Devonian – Early Carboniferous detrital magmatic zircons in the Lower Carboniferous flysch of IT (Okay et al. 2010) clearly indicates that a Variscan arc of yet unknown origin is also involved in this collisional orogen.

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References

Aydın, M., Şahintürk, Ö., Serdar, H.S., Özçelik, Y., Akarsu, İ., Çokuğraş, R., and Kasar, S. 1987. Geology of Çamdağ (Sakarya) - Sünnücedağı (Bolu) area. Bulletin of the Geological Society of Turkey, **30**: 1–14.

Boncheva, I., Sachanski, V., Gedik, I., Özgül, N., Göncüoğlu, M.C., Okuyucu, C., Saydam, DG., Lakova I., and Yanev, S. 2005. Devonian in the Keishte and Istanbul Units in Bulgaria and Turkey: Review and recent data. Depositional Environments of the Gondwanan and Laurasian Devonian (DEVEC) IGCP 499, Abstracts and Guide Book, 9–10.

Boncheva, I., Göncüoglu, M.C., Leslie, S.A., Lakova, I., Sachanski, V., Saydam, G., Gedik, I., and Konigshof, P. 2009. New conodont and palynological data from the Lower Palaeozoic in Northern Camdag, NW Anatolia, Turkey. Acta Geologica Polonica, **59**: 157–171.

Bozkaya, Ö., and Yalçın, H. 2004. Diagenetic to low-grade metamorphic evolution of clay mineral assemblages in Palaeozoic to early Mesozoic rocks of the Eastern Taurides, Turkey. Clay Minerals, **39**(4): 481–500. doi:10.1180/0009855043940149.

Bozkaya, Ö., Yalçın, H., and Göncüoglu, M.C. 2002. Mineralogic and organic responses to the stratigraphic irregularities: An example from the Lower Paleozoic very low-grade metamorphic units of the Eastern Taurus Autochthon, Turkey. Schweizerische Mineralogische und Petrographische Mitteilungen, **82**: 355–373.

Bozkaya, Ö., Gürsu, S., and Göncüoglu, M.C. 2006. Textural and mineralogical evidence for a Cadomian tectonothermal event in the eastern Mediterranean (Sandıklı-Afyon area, western Taurides, Turkey). Gondwana Research, **10**(3–4): 301–315. doi:10.1016/j.gr.2006.04.009.

Bozkaya, Ö., Yalçın, H., and Göncüoglu, M.C. 2011. Diagenetic and very low-grade metamorphic characteristics of the Paleozoic units of the Istanbul Terrane (NW Turkey). European Clay Conference-EUROCLAY 2011, 26 June–01 July 2011, Antalya, Turkey. Abstract book, p. 11.

Brindley, G.W. 1980. Quantitative X-ray mineral analysis of clays. *In* Crystal Structures of Clay Minerals and their X-ray Identifications. *Edited by* G.W. Brindley and G. Brown. Mineralogical Society, London. pp. 411–438.

Chamley, H. 1989. Clay Sedimentology. Springer, Berlin, 623 pp.

Chang, H.K., Mackenzie, F.T., and Schoonmaker, J. 1986. Comparisons between the diagenesis of dioctahedral and trioctahedral smectite, Brazilian offshore basins. Clays and Clay Minerals, **34** (4): 407–423. doi:10.1346/CCMN.1986.0340408.

Chen, F., Siebel, W., Satır, M., Terzioğlu, M.N., and Saka, K. 2002. Geochronology of the Karadere basement (NW Turkey) and implications for the geological evolution of the Istanbul zone. International Journal of Earth Sciences, **91**(3): 469–481. doi:10.1007/s00531-001-0239-6.

de Verneuil, M. 1836–1837. Notice géologique sur les environs de Constantinople. Bulletin de la Société Géologique de France, **1/8**: 268–278. [Paris.]

Dean, W.T., Monod, O., Rickards, R.B., Demir, O., and Bultynck, P. 2000. Lower Paleozoic stratigraphy and paleontology, Karadere-Zirze area, Pontus Mountains, Northern Turkey. Geological Magazine, **137**(5): 555–582. doi:10.1017/S0016756800004635.

Derman, A.S. 1997. Sedimentary characteristics of early Paleozoic rocks in the western Black Sea region. *In* Early Paleozoic in NW Gondwana. *Edited by* M.C. Göncüoglu and A.S. Derman, Turkish Association of Petroleum Geologists Special Publication, 3, pp. 24–31.

Eberl, D.D., and Velde, B. 1989. Beyond the Kübler index. Clay Minerals, **24**(4): 571–577. doi:10.1180/claymin.1989.024.4.01.

Eggleton, R.A., and Banfield, J.F. 1985. The alteration of granitic biotite to chlorite. The American Mineralogist, **70**: 902–910.

Gedik, I., and Önalan, M. 2001. New observations on the Paleozoic stratigraphy of Çamdağ (Sakarya Province). Istanbul University Earth Sciences, **14**: 61–76.

Göncüoglu, M.C. 1997. Distribution of Lower Paleozoic rocks in the Alpine terranes of Turkey. *In* Early Paleozoic in NW Gondwana. *Edited by* M.C. Göncüoglu and A.S. Derman, Turkish Association of Petroleum Geologists Special Publication, 3, pp. 13–23.

Göncüoglu, M.C., and Kozlu, H. 2000. Early Paleozoic evolution of the NW Gondwanaland: data from southern Turkey and surrounding regions. Gondwana Research, **3**(3): 315–324. doi:10.1016/S1342-937X(05)70290-2.

Göncüoglu, M.C., and Kozur, H.W. 1998. Facial development and thermal alteration of Silurian rocks in Turkey. *In* Proceedings of the 1998 Silurian Field-Meeting, *Edited by* J.C. Gutierrez-Marco and I. Rabano. Temas Geologico-Mineros ITGE, **23:** 87–90.

Göncüoglu, M.C., and Kozur, H.W. 1999. Remarks on the pre-Variscan development in Turkey. *In* Prevariscan Terrane Analyses of Gondwanean Europa. *Edited by* U. Linnemann, T. Heuse, O. Fatka, P. Kraft, R. Brocke and B.T. Erdtmann. Schriften des Staatlichen Museums, Mineralogie, Geologie, Dresden. 9, pp. 137–138.

Göncüoglu, M.C., Dirik, K., and Kozlu, H. 1997. Pre-Alpine and Alpine Terranes in Turkey: Explanatory notes to the terrane map of Turkey. Annales Géologique Pays Hellénique, **37**: 515–536.

Göncüoglu, M.C., Saydam, D.G., Gedik, İ., Okuyucu, C., Özgül, N., Timur, E., et al. 2004. Correlation of the Paleozoic units in Bulgaria and Turkey. MTA-BAS-TUBITAK 2004–16B4 Project Report, 44 p.

Görür, N., Monod, O., Okay, A.I., Şengör, A.M.C., Tüysüz, O., Yiğitbaş, E., Sakınç, M., and Akkok, R. 1997. Palaeogeographic and tectonic position of the Carboniferous rocks of the western Pontides (Turkey) in the frame of the Variscan belt. Bulletin de la Société Géologique de France, **168**: 197–205.

Grathoff, G.H., and Moore, D.M. 1996. Illite polytype quantification using Wildfire© calculated X-ray diffraction patterns. Clays and Clay Minerals, **44**(6): 835–842. doi:10.1346/CCMN.1996.0440615.

Guidotti, C.V., and Sassi, F.P. 1976. Muscovite as a petrogenetic indicator mineral in pelitic schists. Neues Jahrbuch fur Mineralogie-Abhandlungen, **127**: 97–142.

Guidotti, C.V., and Sassi, F.P. 1986. Classification and correlation of metamorphic facies series by means of muscovite b0 data from low-grade metapelites. Neues Jahrbuch fur Mineralogie-Abhandlungen, **153**: 363–380.

Guidotti, C.V., Mazzoli, C., Sassi, F.P., and Blencoe, J.G. 1992. Compositional controls on the cell dimensions of 2M1 muscovite and paragonite. European Journal of Mineralogy, **4**: 283–297.

Haas, W. 1968. Das Alt-Paleozoikum von Bithynian (Nordwest Türkei). Neues Jahrbuch für Geologie und Palaontologie. Abhandlungen, **131**: 178–242.

Hoffman, J., and Hower, J. 1979. Clay mineral assemblages as low grade metamorphic geothermometers: application to the thrust faulted disturbed belt of Montana, USA. *In* Aspects of Diagenesis, Society of Economic Paleontologists and Mineralogists. *Edited by* P.A. Scholle and P.R. Schluger. Special Publication, 26, New York. pp. 55–79.

Howell, D.G. 1989. Tectonics of Suspect Terranes. Chapman & Hall, London. 232 pp.

Inglès, M., and Anadón, P. 1991. Relationship of clay minerals to depositional environment in the non-marine Eocene Pontils Group, SE Ebro Basin (Spain). Journal of Sedimentary Petrology, **61**: 926–939.

Inglès, M., and Ramos-Guerrero, E. 1995. Sedimentological control on the clay mineral distribution in the marine and non-marine Palaeogene deposits of Mallorca (Western Mediterranean). Sedimentary Geology, **94**(3–4): 229–243. doi:10.1016/0037-0738(94)00089-D.

Inoue, A., and Utada, M. 1991. Smectite-to-chlorite transformation in thermally metamorphosed volcanoclastic rocks in the Kamikita area, Northern Honshu, Japan. The American Mineralogist, **76**: 628–640.

Inoue, A., Utada, M., Nagata, H., and Watanabe, T. 1984. Conversion of triochahedral smectite to interstratified chlorite-smectite in Pliocene acidic pyroclastic sediments of the Ohyu District, Akita Prefecture, Japan. Clay Science, **6**: 103–116.

Kalvoda, J., and Babek, O. 2010. The margins of Laurussia in Central and Southeast Europe and Southwest Asia. Gondwana Research, **17**(2–3): 526–545. doi:10.1016/j.gr.2009.09.012.

Kalvoda, J., Leichmann, J., Babek, O., and Melichar, R. 2003. Brunovistulian Terrane (Central Europe) and Istanbul Zone (NW Turkey): Late Proterozoic and Paleozoic tectonostratigraphic development and Paleogeography. Geologica Carpathica, **54**: 139–152.

Kerey, I.E. 1984. Facies and tectonic setting of the Upper Carboniferous rocks of NW Turkey. *In* The Geological evolution of the Eastern Meditteranean. *Edited by* J.E. Dixon and A.H.F. Robertson. Geological Society, London, Special Publication, 17: 123–128.

Kisch, H.J. 1980. Illite crystallinity and coal rank associated with lowest-grade metamorphism of the Taveyanne greywacke in the Helvetic zone of the Swiss Alps. Eclogae Geologicae Helvetiae, **73**: 753–777.

Kozur, H.W., and Göncüoglu, M.C. 2000. Mean features of the pre-Variscan development in turkey. Acta Universitatis Carolinae-Geologica, **42**: 459–464.

Krumm, S. 1996. WINFIT 1.2: version of November 1996 (The Erlangen geological and mineralogical software collection) of WINFIT 1.0: a public domain program for interactive profile-analysis under WINDOWS. XIII Conference on Clay Mineralogy and Petrology, Praha, 1994. Acta Universitatis Carolinae Geologica, **38**: 253–261.

Kübler, B. 1968. Evaluation quantitative du métamorphisme par la cristallinité de l'illite. Bulletin-Centre de Recherches Pau-SNPA, **2**: 385–397.

Kübler, B. 1969. Crystallinity of illite. Detection of metamorphism in some frontal parts of the Alpine. Fortschritte der Mineralogie, **47**: 39–40.

Lakova, I., Sachanski, V., and Göncüoglu, M.C. 2006. Earliest cryptospore record in NW Anatolia dated by graptolites and acritarchs, Lower Ordovician Bakacak Formation, Zonguldak Terrane, NW Anatolia. GCP 503 Ordovician Paleogeography Ann. Meeting, 30 Aug–1 Sept., Glasgow-UK, Abstracts and Field Excursion Guide, 30–31.

Merriman, R.J., and Frey, M. 1999. Patterns of very low-grade metamorphism in metapelitic rocks. *In* Low Grade Metamorphism. *Edited by* M. Frey and D. Robinson. Blackwell Sciences Ltd., Oxford. pp. 61–107

Merriman, R.J., and Peacor, D.R. 1999. Very low-grade metapelites: mineralogy, microfabrics and measuring reaction progress. *In* Low Grade Metamorphism. *Edited by* M. Frey and D. Robinson. Blackwell Sciences Ltd., Oxford. pp. 10–60.

Moore, D.M., and Reynolds, R.C. 1997. X-ray Diffraction and the Identification and Analysis of Clay Minerals. Oxford University Press, Oxford. 378 p.

Nance, D.R., and Linnemann, U. 2009. The Rheic Ocean: Origin, evolution, and significance. GSA Today, **18**(12): 4–12. doi:10.1130/GSATG24A.1.

Nieto, F., Velilla, N., Peacor, D.R., and Ortega-Huertas, M. 1994. Regional retrograde alteration of sub-greenschist facies chlorite to smectite. Contributions to Mineralogy and Petrology, **115**(3): 243–252. doi:10.1007/BF00310765.

Nieto, F., Ortega-Huertas, M., Peacor, D., and Arostegui, J. 1996. Evolution of illite/smectite from early diagenesis through incipient metamorphism in sediments of the Basque-Cantabrian basin. Clays and Clay Minerals, **44**(3): 304–323. doi:10.1346/CCMN.1996.0440302.

Nieto, F., Mata, M.P., Bauluz, B., Giorgetti, G., Arkai, P., and Peacor, D.R. 2005. Retrograde diagenesis, a widespread process on a regional scale. Clay Minerals, **40**(1): 93–104. doi:10.1180/0009855054010158.

Nzegge, O.M., Satır, M.A., Siebel, W.A., and Taubald, H.A. 2006. Geochemical and isotopic constraints on the genesis of the Late Palaeozoic Deliktaş and Sivrikaya granites from the Kastamonu granitoid belt (Central Pontides, Turkey). Neues Jahrbuch fur Mineralogie-Abhandlungen, **183**(1): 27–40. doi:10.1127/0077-7757/2006/0057.

Okay, A.I., and Tüysüz, O. 1999. Tethyan sutures of northern Turkey. *In* The Mediterranean Basin: Tertiary Extension within the Alpine Orogen. *Edited by* B. Durand, L. Jolivet, F. Horváth, and M. Seranne. Geological Society, London, Special Publication, **156:** 475–515.

Okay, A.I., Bozkurt, E., Satır, M., Yiğitbaş, E., Crowley, Q.G., and Shang, C.K. 2008. Defining the southern margin of Avalonia in the Pontides: Geochronological data from the Late Proterozoic and Ordovician granitoids from NW Turkey. Tectonophysics, **461**(1–4): 252–264. doi:10.1016/j.tecto.2008.02.004.

Okay, N., Zack, T., and Okay, A.I. 2010. A missing provenance: sandstone petrography and detrital zircon-rutile geochronology of the Carboniferous flysch of the Istanbul zone. Tectonic Crossroads: Evolving Orogens of Eurasia-Africa-Arabia, Geological Society of America, Ankara, Abstract No 35–2, p. 67.

Pană, C. 1997. Studiul biostratigrafic al formaţiunilor paleozoic superioare din Platforma Moesică. Unpublished Ph.D. thesis, University of Bucureşti. 133 p.

Reynolds, R.C., Jr. 1985. NEWMOD©. A Computer Program for the calculation of One-Dimensional Diffraction Patterns of Mixed-Layered Clays. R.C. Reynolds, Jr., 8 Brook Rd., Hanover, NH.

Sachanski, V., Göncüoglu, M.C., and Gedik, I. 2010. Late Telychian (early Silurian) graptolitic shales and the maximum Silurian highstand in the NW Anatolian Palaeozoic terranes. Palaeogeography, Palaeoclimatology, Palaeoecology, **291**(3–4): 419–428. doi:10.1016/j.palaeo.2010.03.011.

Sassi, F.P., and Scolari, A. 1974. The b0 value of the potassic white micas as a barometric indicator in low-grade metamorphism of pelitic schists. Contributions to Mineralogy and Petrology, **45**(2): 143–152. doi:10.1007/BF00371166.

Seghedi, A., Vaida, M., Iordan, M., and Verniers, J. 2005. Paleozoic evolution of the Romanian part of the Moesian Platform: an overview. Geologica Belgica, **8**: 99–120.

Środoń, J. 1984. X-ray powder diffraction identification of illitic materials. Clays and Clay Minerals, **32**(5): 337–349. doi:10.1346/CCMN.1984.0320501.

Stampfli, G.M. 2000. Tethyan oceans. *In* Tectonics and magmatism in Turkey and surrounding area. *Edited by* E. Bozkurt, J.A. Winchester and J.D.A. Piper. Geological Society of London, Special Publication, **173:** 1–23.

Ustaömer, P.A., and Rogers, G. 1999. The Bolu Massif: remnant of a pre-Early Ordovician active margin in the west Pontides, northern Turkey. Geological Magazine, **136**(5): 579–592. doi:10.1017/S0016756899003015.

Veblen, D.R., and Ferry, J.M. 1983. A TEM study of the biotite-chlorite reaction and comparison with petrologic observations. The American Mineralogist, **68**: 1160–1168.

von Raumer, J.V., Stampfli, G.M., and Bussy, F. 2003. Gondwana-derived microcontinents — the constituents of the Varsican and Alpine collisional orogens. Tectonophysics, **365**(1–4): 7–22. doi:10.1016/S0040-1951(03)00015-5.

Warr, L.N., and Rice, A.H.N. 1994. Interlaboratory standartization and calibration of clay mineral crystallinity and crystallite size data. Journal of Metamorphic Geology, **12**(2): 141–152. doi:10.1111/j.1525-1314.1994.tb00010.x.

Winchester, J.A.PACE TMR Network Team. 2002. Palaeozoic amalgamation of Central Europe: new results from recent geological and geophysical investigations. Tectonophysics, **360**(1–4): 5–21. doi:10.1016/S0040-1951(02)00344-X.

Yanev, S. 1993. Gondwana Palaeozoic terranes in the Alpine collage system of the Balkans. Hymalaian Geology, **4**: 257–270.

Yanev, S., Tzankov, T., and Boncheva, I. 1995. Lithostratigraphy and Late Alpine structure of the Palaeozoic Terrains in the Shipka Part of Stara Planina Mountains. Geologica Balcanica, **25**: 3–26.

Yanev, S., Göncüoglu, M.C., Gedik, İ., Lakova, I., Boncheva, I., Sachanski, V., et al. 2006. Stratigraphy, correlations and palaeogeography of Palaeozoic terranes in Bulgaria and NW Turkey: A review of recent data. *In* Tectonic development of the Eastern Mediterranean Region. *Edited by* A.H.F. Robertson, D. Mountrakis. Geological Society, London, Special Publications 260, pp. 51–67.