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Diagenetic and very low-grade metamorphic characteristics of the Paleozoic series of the Istanbul Terrane (NW Turkey)

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Abstract The Istanbul Terrane along the Black Sea coast in NW Anatolia, is a Gondwana-derived continental microplate, comprising a well-developed Paleozoic succession. Petrographic and X-ray diffraction studies were performed on rock samples from measured sections throughout Ordovician–Carboniferous sedimentary units. Diagenetic-very low-grade metamorphic clastic (shale/mudstone, siltstone, sandstone) and calcareous rocks (limestone, dolomite) mainly contain phyllosilicates, quartz, feldspar, calcite, dolomite, hematite and goethite minerals. Phyllosilicates are primarily represented by illite, chlorite, mixed-layered chlorite–vermiculite (C–V), chlorite–smectite (C–S) and illite–chlorite (I–C). Feldspar is commonly present in the Ordovician and Carboniferous units, whereas calcite and dolomite are abundant in the Silurian and Devonian sediments. The most important phyllosilicate assemblage is illite + chlorite + I–C + C–V + C–S. Illite and chlorite-bearing mixed layer clays are found in all units. The amounts of illites increase in the upper parts of the Silurian series and the lower parts of the Devonian series, whereas chlorite and chlorite-bearing mixed-layers are dominant in the Ordovician and Carboniferous units. Kübler index values of illites reflect high-grade anchimetamorphism for the Early Ordovician rocks, low-grade metamorphism to high-grade diagenesis for the Middle Ordovician–Early Silurian rocks and high-grade diagenesis for the Late Silurian–Devonian units. The K-white micas *b* cell dimensions indicate intermediate pressure conditions in the Early Ordovician–Early Silurian units, but lower pressure conditions in the Middle Silurian–Devonian units. Illites are composed of $2M_1 \pm 1M_d$ polytypes in all units, except for Upper Ordovician–Lower Silurian units which involve $1M$ polytype in addition to $2M_1$ and $1M_d$ polytypes. The $2M_1/(2M_1 + 1M\mathrm{d})$ ratios rise from Devonian to Ordovician together with the increasing diagenetic-metamorphic grade. Chlorites have IIb polytype. In general, crystal-chemical data of clay minerals in the Istanbul Terrane show a gradual increase in the diagenetic/metamorphic grade together with increasing depth. The new data presented in this work indicate that the diagenetic/metamorphic grade of the Paleozoic of the Istanbul Terrane is higher than that of the neighboring Zonguldak Terrane and generated by a single metamorphic phase developed at the end of Carboniferous. This finding contrasts with the metamorphic history of the neighboring Zonguldak Terrane that displays a distinct Early Devonian unconformity and a thermal event.

Keywords Very low-grade metamorphism · Paleozoic · Istanbul Terrane · Phyllosilicates · Illite kübler index · K-white micas *b* cell dimensions · Polytype

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1 Introduction

The Istanbul–Zonguldak Terrane comprising the classical successions of the "Paleozoic of Istanbul" (e.g., de Verneuil 1837) is a Variscan Terrane assemblage (Fig. 1) (Göncüoğlu et al. 1997) in the sense of Howell (1989). Its original position and correlation with the Western and Central European Domains (e.g., Baltica, Avalonia,

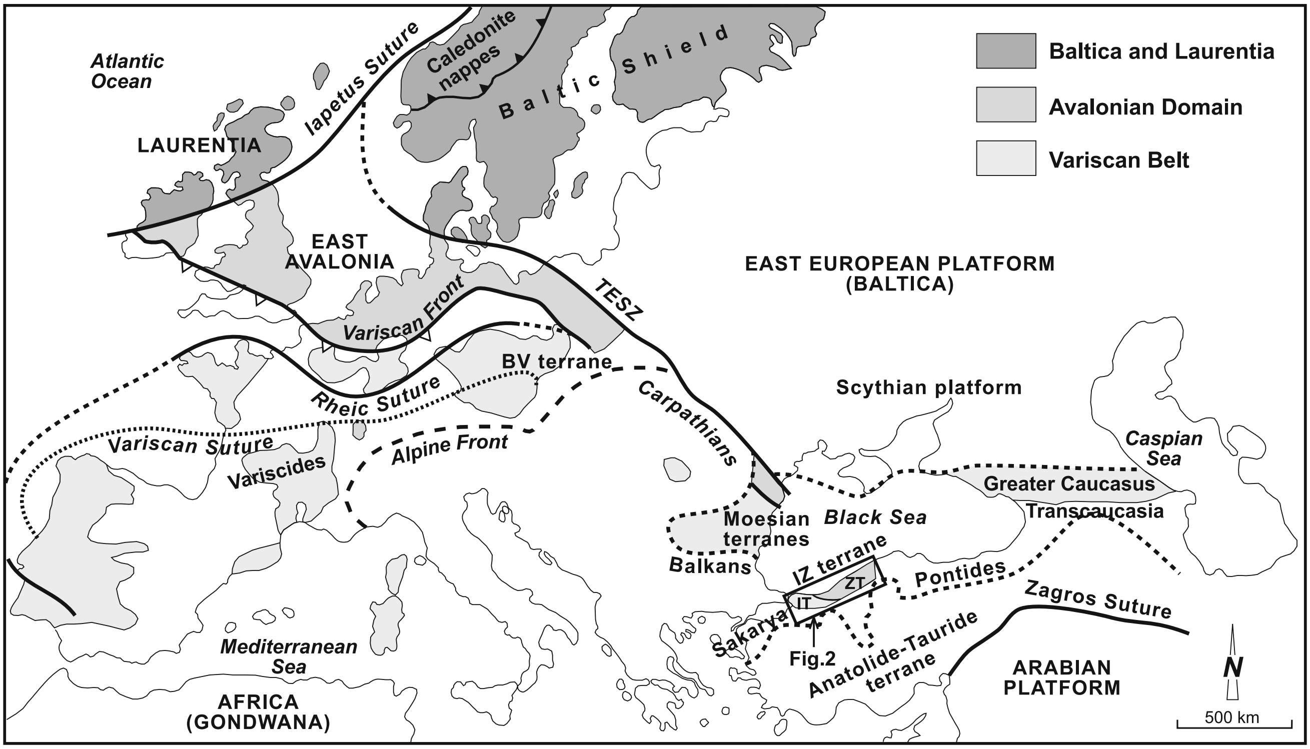

Fig. 1 Location of the Istanbul-Zonguldak terrane within the Western and Central European Variscan Belt (*IT* Istanbul terrane, *ZT* Zonguldak terrane)

Armorica) during the Paleozoic is a matter of debate (e.g., Kalvoda et al. 2003; Kalvoda and Babek 2010). Some authors suggested that the Istanbul–Zonguldak Terrane 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 it reached its present location due to the southward drift related to the opening of the western Black Sea basin (e.g., Okay and Tüysüz 1999). Another idea is that this unit was formed by the assemblage of two different elements of Gondwana origin (Göncüoğlu 1997, 2010); the Istanbul Terrane (IT) in the W covering Istanbul, Gebze and South Çamdag areas, and the Zonguldak Terrane (ZT) located in Çamdag, Zonguldak and Safranbolu areas in the E and NE (Göncüoğlu and Kozur 1998, 1999; Göncüoğlu and Kozlu 2000; Kozur and Göncüoğlu 2000; Yanev et al. 2006; Sachanski et al. 2012; Fig. 2a). The main differences between the Zonguldak and Istanbul Terranes were elucidated on the basis of stratigraphic variations, and the presence of a post Wenlock-pre Emsian unconformity as well as a thermal event in ZT (Göncüoğlu 1997; Yanev et al. 2006). The presence of this thermal event was also confirmed by clay mineralogical data (Bozkaya et al. 2011, 2012). On the contrary, the IT is characterized by a well-developed sedimentary sequence without any major break from Early Ordovician to Late Carboniferous.

In copious detailed studies on the Paleozoic successions in different orogenic belts, textural and mineralogical parameters were used to interpret the variations in thermal maturity of them (e.g., Merriman and Frey 1999; Merriman and Peacor 1999; Bozkaya et al. 2002; Bozkaya et al. 2006). In this study, it is aimed to establish diagenetic/metamorphic characteristics of the Ordovician–Carboniferous sequence of IT by means of detailed petrographic and X-ray diffraction methods (bulk and clay mineralogy, Kübler index values (KI), polytypes and *b* cell dimensions of K-white micas), to correlate them with the mineralogical fingerprints of ZT (Bozkaya et al. 2012). Finally we aim to evaluate the differences and similarities of these units in regard to their tectonothermal history. By this, it is intended to understand their geological evolution whether they behaved as parts of a single terrane or as separate terranes in the Paleozoic Rheic Ocean that closed by successive collision of these Peri Gondwanan Terranes with Laurussia.

2 Geological framework

In the NW Anatolia, IT and ZT involve lithologically similar basement rocks consisting of a crystalline series with ortho- and paragneisses of continental crust origin, and an oceanic assemblage (metagabbros and metabasalts)

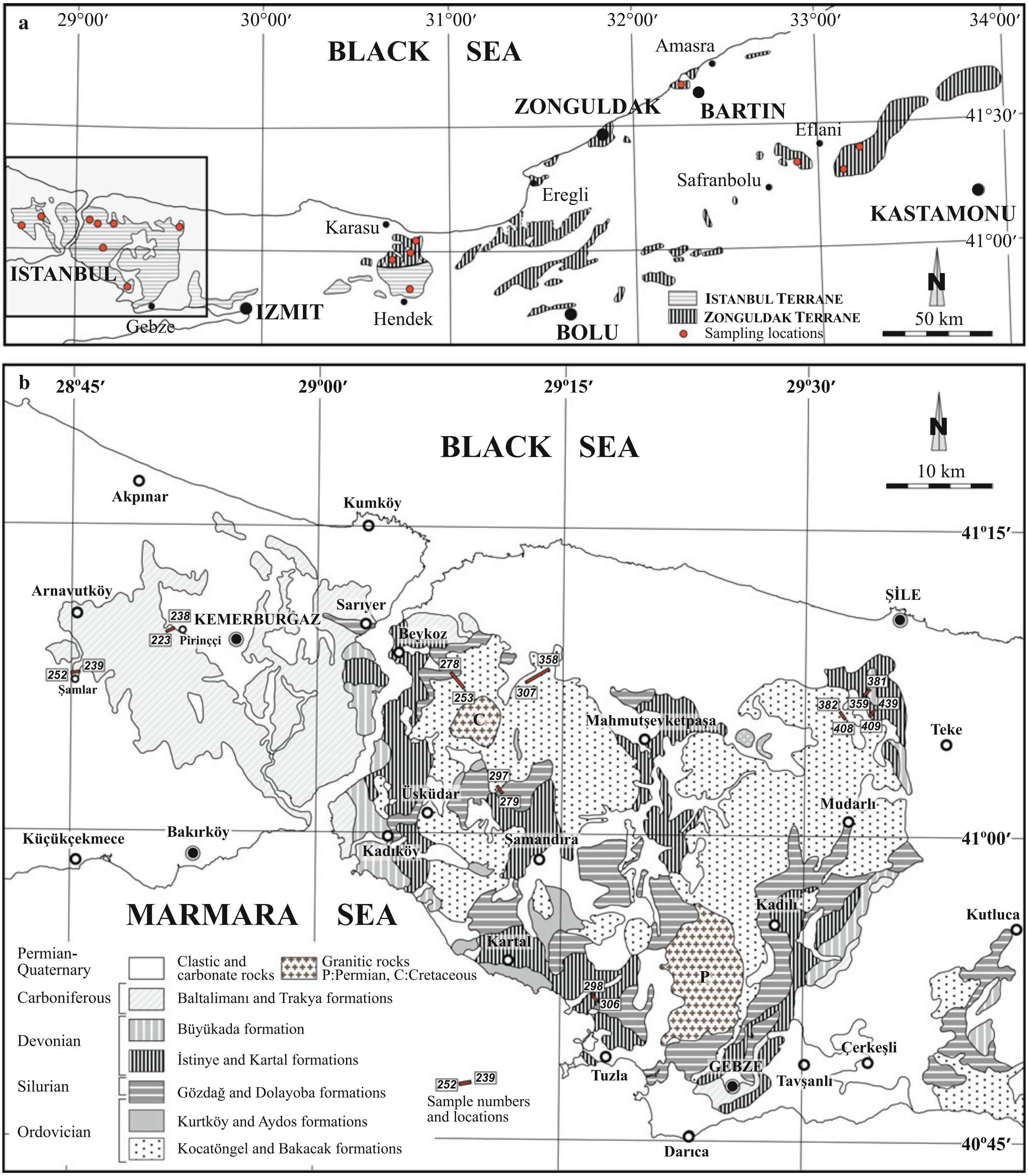

Fig. 2 **a** Distribution of the Paleozoic rock-units in the Istanbul and Zonguldak Terranes, **b** Geological map (MTA 2002) and sampling locations of the studied units

intruded by Cadomian granitoids (Ustaömer and Rogers 1999). In the IT, the crystalline basement is unconformably covered by Early Ordovician–Late Carboniferous sedimentary sequences. The Early Ordovician–Early Devonian succession represents a passive continental marginal deposit that is conformably overlain by Middle Devonian–Early Carboniferous slope- and flysch-type sediments. This Paleozoic succession was affected by a Variscan

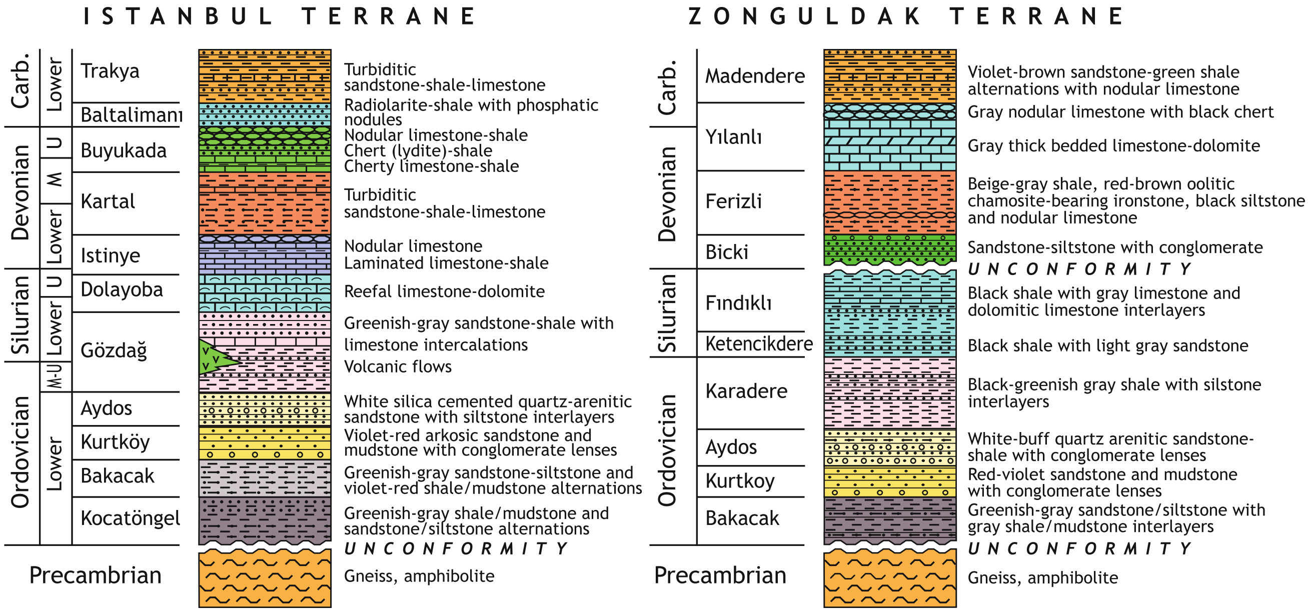

Fig. 3 Correlation of generalized lithostratigraphic sections of the Istanbul and Zonguldak Terranes

deformation during the Early Carboniferous, intruded by granitoids and unconformably overlain by Early Triassic clastics.

The Early Ordovician rocks include greenish-grey siltstones and mudstones (Kocatöngel and Bakacak formations) and violet-red sandstones and conglomerates with mudstone and shale intercalations (Kurtköy and Aydos formations). The lower Paleozoic parts of the IT and ZT are similar on the basis of lithology and depositional features (Fig. 3). Kocatöngel formation is characterized by very low-grade metaclastic rocks with distinct lamination and sandstone layers increase toward upper parts. The presence of violet-red colored arenites in Bakacak formation is the distinguishing feature from the Kocatöngel formation (Gedik et al. 2005). The fluvial conglomerates of Kurtköy formation contain medium to well rounded pebbles of quartz, quartzite, metagranite, rhyolite and micaschist indicating a crystalline basement source. Siliciclastic rocks as mainly white quartz-arenites with bands and lenses of conglomerates of Aydos formation are transgressive on the Kurtköy formation. The Early Silurian period is mainly characterized by brachiopod- and partly oolitic ironstone-bearing green sandstones/siltstones, gray mudstone/shales (Gözdağ formation). Andesitic, trachytic volcanic rocks are also found as dikes and sills within the clastic rocks of both lower parts of Gözdağ formation and upper parts of Aydos formation in some locations, in which local hydrothermal alteration zones were developed. Silurian and Devonian parts of IT are different from ZT and they consist mainly of Early Silurian light-gray pinkish reefal limestones (Dolayoba formation) and laminated and nodular limestones with shale interbeds (İstinye formation). Of these, İstinye formation was divided into three members (Gedik et al. 2005) made of thin laminated limestone-shale alternations (Sedefadası member), thin-medium bedded limestones (Gebze member) and nodular limestone-shale alternations (Kaynarca member). This unit is conformably overlain by Middle–Late Devonian turbiditic green-gray sandstone-shale alternations with partly nodular limestone intercalations (Kartal formation). Late Devonian units are represented by lydites, cherty and nodular limestones with shale alternations (Büyükada formation). It has three members, named as Bostancı (cherty limestone-shale), Yörükali (lydites) and Ayineburnu (thin nodular limestone-shale) members (Gedik et al. 2005). The Devonian–Carboniferous boundary is located within the upper part of the Ayineburnu member (Göncüoğlu et al. 2004). The Baltalimanı formation represents the lowest parts of the Early Carboniferous and is constituted by radiolarian cherts and shales with phosphatic nodules. These siliceous rocks are followed by a thick succession of turbiditic sandstone-shale-limestone alternations (Trakya formation) of Early Carboniferous (Tournasian-Visean) age (Gedik et al. 2005; Okay et al. 2008). The Paleozoic succession of the IT is intruded by Late Permian (255 Ma; Yılmaz-Şahin et al. 2010) and unconformably overlain by Permo-Triassic continental clastics (e.g., Özgül 2012).

The contact of the IT towards W with the Rhodopian Strandja Unit is a strike-slip fault. The contact towards E with the ZT is generally obscured by the Tertiary cover units. The only exception is the area to the N of Hendek (Fig. 2a), where Ordovician basement rocks of the ZT are thrust over the Devonian clastics (Kartal formation) of the IT (Gedik and Önalan 2001; Boncheva et al. 2009) from N to S. This S-verging thrusting is also observed in the eastern Çamdağ and Istanbul areas (e.g., Özgül 2012) and is post-Eocene in age.

In this study, the Early Ordovician–Late Carboniferous units from well exposed outcrops were measured and sampled at localities showed in Fig. 2a and b.

3 Material and method

A total of 452 rock samples (230 from IT, 222 from ZT) were collected and analyzed by optical and X-ray diffraction (XRD) methods.

Textural and mineralogical features of metaclastic-rock samples were conducted by transmitted light microscopy. In addition, gold- and carbon-coated fragments were examined by scanning electron microscopy (SEM) with a JEOL JSM-6490 instrument equipped with IXRF energy-dispersive spectrometry (EDS) system at the Turkish Petroleum Corporation in Ankara, Turkey. Operating conditions were 32 s counting time and 20 kV accelerating voltage. These investigations were focused on diagenetic to very low-grade metamorphic samples to describe both authigenetic/neoformed and transformed phyllosilicate minerals. EDS spot analyses (spot size of 50 µm for focused electron beam) were also used during SEM investigations to differentiate some minerals from each others.

The XRD studies were performed by the X-ray diffractometer (Rigaku DMAX IIIC) at the Geological Engineering Department of Cumhuriyet University in Sivas, Turkey. The analysis were made by using Cu$K\alpha$ ($\lambda = 1.541871$ Å) irradiation, Ni filter or monochromator, 35 kV and 20 mA voltage and current, slits (divergence = 1°, scatter = 1°, receiving = 0.3 mm, receiving monochromator = 0.8 mm). Scan speed was set as 2°2θ/min in the range from 5 to 35°2θ for whole-rock, and 1°2θ/min in the range from 2 to 30°2θ for oriented clay fractions. The clay particles (<2 µm) were separated by centrifuge after dispersion by sedimentation. Calcite, dolomite and organic matter were eliminated by CH_3COOH (10 %), HCl (5 %) and H_2O_2 (10 %) acid treatments, respectively. In addition to air-dried, clay specimens are also saturated with ethylene glycol at 60 °C for 16 h, and heated to 490 °C for 4 h. After sample preparation and clay separation processes, the semi-quantitative percentages of the rock-forming minerals and clay-size fractions were calculated by 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 the methods of Moore and Reynolds (1997). NEWMOD© (Reynolds 1985) and WINFIT (Krumm 1996) programs were also applied for precise interpretation of mixed-layer clay minerals.

The widths of the 10-Å illite peaks at half-height (Kübler index-KI °$\Delta 2\theta$; 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, although the compatibility of calibration of CIS is controversial as discussed in detail in two papers of this volume (Ferreiro Mählmann et al. 2012; Ferreiro Mählmann and Frey 2012). 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 obtained from fitted peaks by WINFIT program in order to minimize measuring errors.

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

In order to determine illite and chlorite polytypes, random powder mounts were respectively, scanned in the ranges 16°–36° and 31°–52° 2θ. WINFIT decomposition by profile fitting was used for determination of areas and intensities of the specific peaks of $1M$ and $2M_1$ polytypes for quantification of individual ones with the equations of Grathoff and Moore (1996).

4 Petrography

4.1 Optical microscopy

Paleozoic units are represented mainly by shale, siltstone, sandstone (quartz–arenite, arkose and litharenite or greywacke) and limestone/dolomite and their very low-grade metamorphic equivalents. Siliciclastic rocks contain mono- and poly-crystalline quartz, polysynthetic and zoned plagioclase, calcite, biotite, muscovite, chlorite, orthoclase, dolomite, hematite, zircon, tourmaline, apatite, goethite, opaque minerals and lithic fragments such as metamorphic, magmatic and sedimentary rocks as the main components.

The amount of feldspar, biotite, chlorite and rock fragments are relatively high in Early Ordovician and Carboniferous formations, whereas quartz, muscovite and fine-grained white K-mica content increases in the Silurian-Devonian formations. Sandstones and siltstones of Early Ordovician (Kocatöngel, Bakacak and Kurtköy formations) and Carboniferous (Trakya formation) have essentially arkose and partly greywacke or litharenite compositions. Litharenites contain mostly metamorphic (phyllite, schist, quartzite) and volcanic rock fragments and curved muscovite, biotite and chlorite plates which were derived from a crystalline basement.

Detrital biotites are significantly chloritized; only a small amount of biotite has escaped alteration. White K-micas are fine-grained occurrences in the matrix as a result of recrystallization of clays and coarse-grained muscovite sheets or flakes of detrital origin. Similar to white K-micas, chlorites were observed as both authigenic products within the micro pores and/or fissures, and as alteration products of detrital biotites in the siltstones and sandstones. Chlorite-like minerals mostly reflect in reality chlorite-bearing mixed-layer phases (C–S, C–V and I–C). In general C–V and C–S occur in chlorite-rich samples, whereas I–C is found in chloritized biotite-bearing samples.

The groundmass or matrix consists mainly of fine-grained mica and chlorite, and subordinate silica and carbonate minerals. Besides, Middle Ordovician–Early Silurian sandstones comprise relatively high amount of iron oxide (hematite, goethite) cement.

Fine-grained clastic rocks from Early Ordovician units show moderate- to well-developed cleavage planes (S_1) nearly perpendicular to bedding planes (S_0) (Fig. 4a). Whereas siltstones display relatively poor developed cleavages, in which chlorite-mica stacks (CMS) are cut by cleavage planes (Fig. 4b). CMS display stubby forms displaying that they are formed prior to the slaty cleavage. For this reason it is believed that CMS were developed from clastic micas (e.g., Piqué and Wybrecht 1987; Milodowski and Zalasiewicz 1991; Bozkaya et al. 2002). The (001) planes of chlorite and micas in most CMS are nearly parallel to the bedding but are in high angles or nearly perpendicular to cleavage planes. These facts, as well as the occurrence of chloritized biotite relicts and iron-rich chlorite in some CMS may indicate that they were formed by the alteration of detrital biotites, prior to cleavage development (e.g., Bevins and Robinson 1988). The decreasing amount of detrital biotite is linked up with the increase of relative abundance of chlorite in clastic rocks toward the base of the stratigraphic sequence.

In weakly cleaved quartz-arenites from the Ordovician Aydos formation, sub-rounded and sub-angular quartz grains display sutured margins with fine-grained groundmass, white K-micas and chlorites (Fig. 4c), due to reactions between grain and matrix caused by pressure solution mechanism. Late Silurian–Carboniferous units mostly preserve their primary sedimentary textures without any metamorphic overprint. Siltstones of Devonian Kartal formation have isotropic fabric relations (Fig. 4d) indicating lower diagenetic/metamorphic grades than underlying formations. Fossil remains in micritic limestones of Kartal formation show an orientation parallel to bedding and are cut by thick carbonate filled fissures with high angle or perpendicular to bedding planes (Fig. 4e). In the Carboniferous biogenic siliceous rocks, radiolarian fossils within the groundmass are filled by cryptocrystalline silica (chalcedony) and illustrate vaguely orientation parallel to bedding (Fig. 4f).

4.2 Scanning electron microscopy

Illites are generally observed as bended coarse flakes in anchizonal samples of Ordovician-Lower Silurian units. In slate samples of Gözdag formation, acicular illites occur in addition to coarse flakes with higher amounts of K_2O and Fe_2O (Fig. 5a). Acicular illites were observed in altered zones near the Tertiary volcanic intrusions. Therefore they are considered as neoformations during late stage hydrothermal alteration. C–S is developed as both authigenic thread-like filaments within the pores and honeycombs-like flakes on groundmass or matrix as a replacement of original minerals in the volcanogenic sediments of Gözdag formation (Fig. 5b). According to our observations, C–S occurrences are principally related to chlorite-rich groundmass rather than detrital coarse-grained biotite stacks. Kaolinites in Devonian Kartal formation show anhedral to subhedral rose-like plates within the pores indicating typical authigenic origin (Fig. 5c). The loose packets of kaolinite plates specify relatively lower diagenetic grades than the underlying formations. Mixed-layered I–C minerals were developed as short rod-shaped radial assemblages on subhedral and anhedral quartz grains into the pores of the rock, whereas illite crystals were visible as coarse grained flakes in the anchizonal sample of Early Ordovician Kocatöngel formation (Fig. 5d). Siltstone sample of Carboniferous Trakya formation contains pores filled with an assemblage of small framboidal pyrite of diagenetic origin and chloritized biotite (biotite–chlorite) plates (Fig. 5e). This sample also contains high amounts of mixed-layered C–V with anomalously high iron contents and flower-like morphology on the large chloritized biotite flakes (Fig. 5f). SEM investigations point out that the chlorite-bearing mixed layered minerals were not only developed from detrital biotite flakes, they are also of authigenic origin.

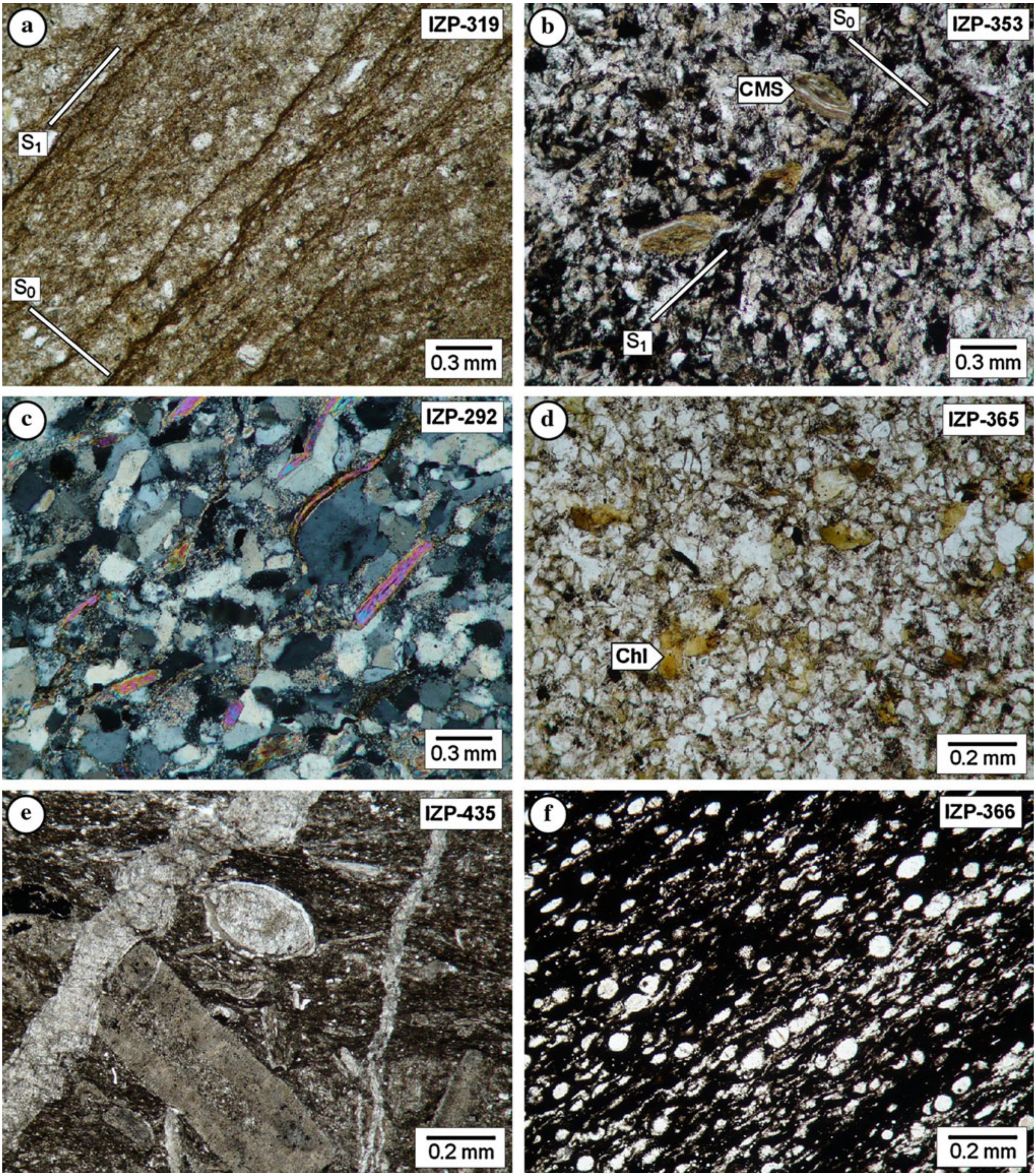

Fig. 4 Characteristic textural features of the Ordovician–Carboniferous units in the IT. **a** Bedding (S_0) and cleavage planes (S_1) perpendicular to each other in a slate of Kocatöngel formation (*ppl* plane polarized light), **b** CMS cut by cleavage planes in metasiltstone of Kurtköy formation (ppl), **c** sutured margin relationships of quartz grains and a matrix composed by fine-grained white mica and chlorite, and oriented mica flakes in metasandstone of Aydos formation (*cn* crossed nicols), **d** authigenetic chlorite (Chl) without preferred orientation within the pores of a siltstone of Kartal formation (ppl), **e** groundmass depicting a weakly developed orientations, cut by post-sedimentary carbonate filling fissures in a biomicritic limestone of Dolayoba formation (ppl), **f** oriented radiolarian fossils within the iron-oxide and clay matrix in a radiolarite of Baltalimanı formation (ppl)

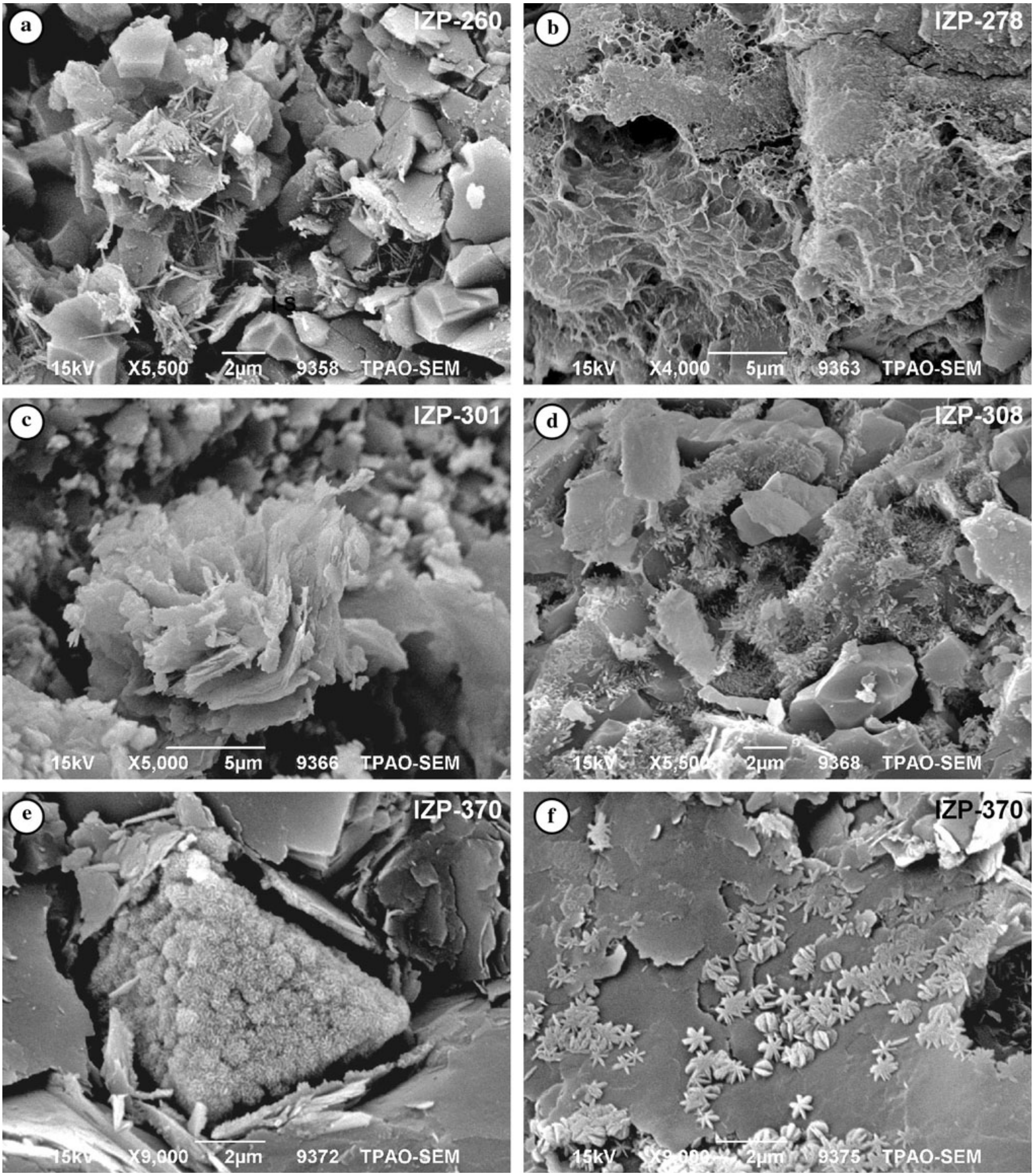

Fig. 5 SEM microphotographs of the phyllosilicates in the IT units. **a** Acicular illites and coarse-grained micaceous flakes in a slate sample of Gözdag formation, **b** thread-like authigenic C–S flakes within the pores and honeycomb-like replacements to groundmass of volcanic sample in Gözdag formation, **c** Anhedral to subhedral rose-like authigenic kaolinite in shale of Kartal formation, **d** shorty rod-like aggregates of authigenic I–C within the pores of quartz grains in metasiltstone samples of Kocatöngel formation, **e** framboidal pyrite assemblages among the mica plates in a siltstone of Trakya formation, **f** authigenic flower petals-like C–V occurrences on the biotite plates in siltstone of Trakya formation

5 X-ray mineralogy

5.1 Bulk and clay mineralogy

Early Ordovician–Carboniferous rocks of the IT are composed mainly of phyllosilicates, quartz, feldspar, calcite, dolomite, hematite, and goethite. Phyllosilicate minerals are represented by illite, chlorite, kaolinite, C–V, C–S and I–C mixed-layers (Figs. 6, 7).

Quartz, feldspar and phyllosilicates prevail in all formations, whereas the abundances of calcite, dolomite and hematite increase in Silurian–Devonian units. The types and associations of phyllosilicates show generally similarities through the succession except for the presence of kaolinite in Aydos, Gözdağ and Kartal formations, and some differences in abundances are also recorded with respect to the formations (Fig. 7).

In the Early Ordovician parts of the succession, the amounts of chlorite, I–C, C–V and C–S mixed-layers increase together with the increase in feldspar amount. C–S appears in Bakacak and Kurtköy formations, but it was not observed in Kocatöngel and Aydos formations (Fig. 7). The siliciclastic rocks of the Aydos formation comprise more quartz and illite, but less feldspar than those in the underlying formations. Clay fractions of Silurian–Lower Devonian parts are predominantly composed of illites and minor chlorites. Devonian–Carboniferous flysch-type sediments have high amounts of chlorite-bearing mixed-layers.

5.2 Illite Kübler index (KI)

KI values were determined on 190 samples taken from Ordovician to Carboniferous units and provide a wide

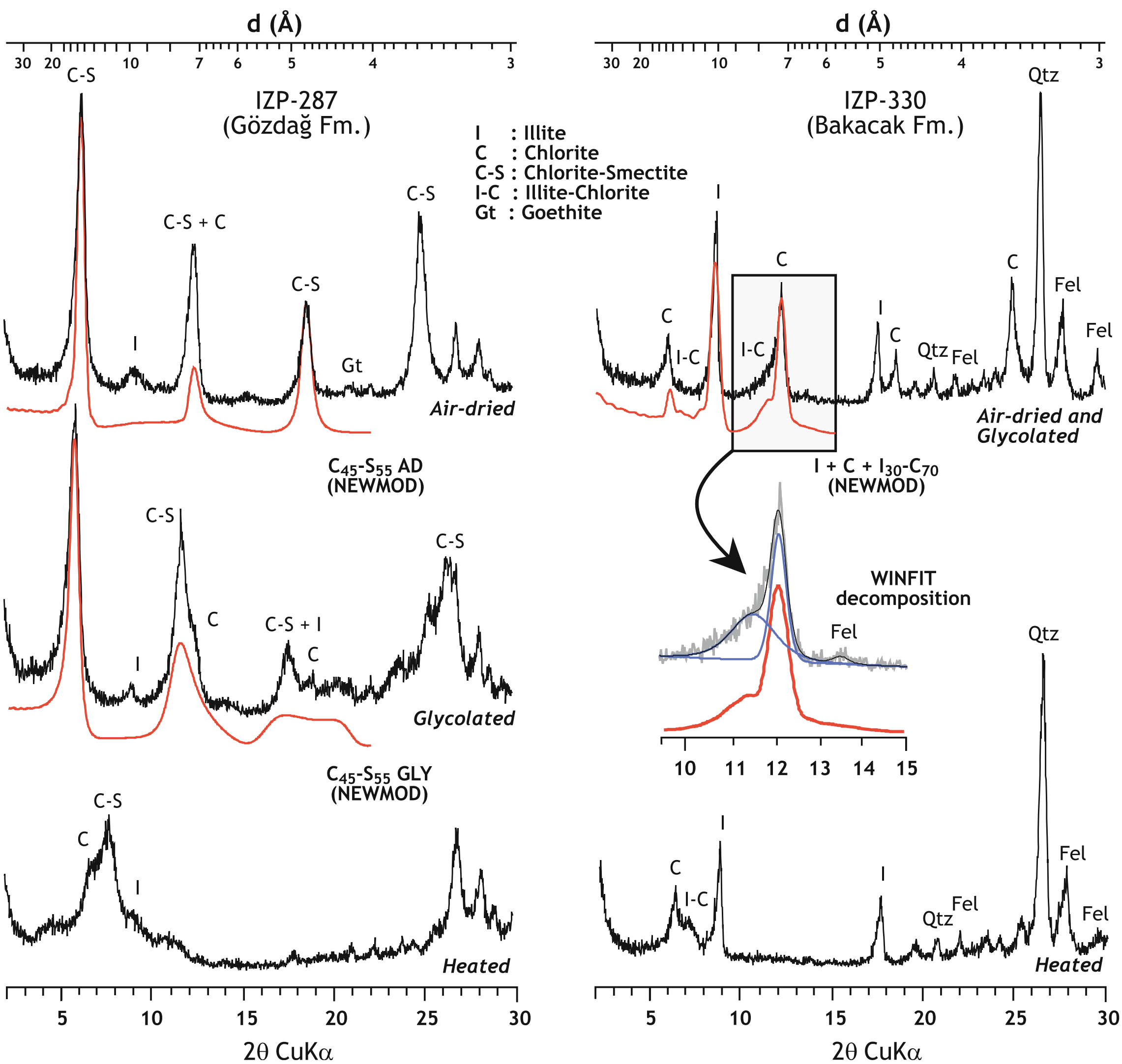

Fig. 6 XRD patterns of main clay types and correlation with calculated and decomposed peaks obtained from NEWMOD© and WINFIT programs

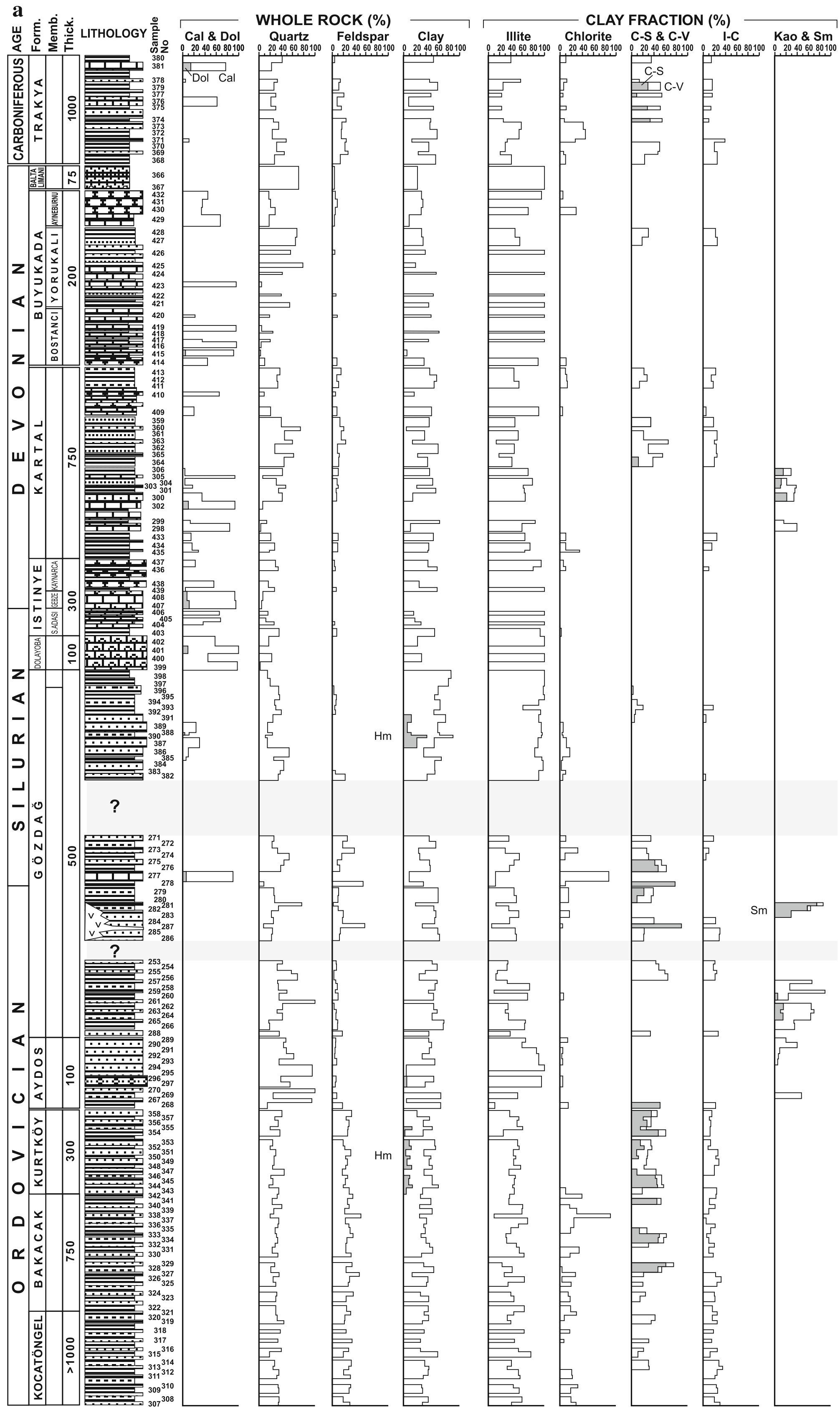

Fig. 7 Vertical distributions of main minerals in samples and some crystal-chemical parameters of Ordovician–Carboniferous sequence of IT

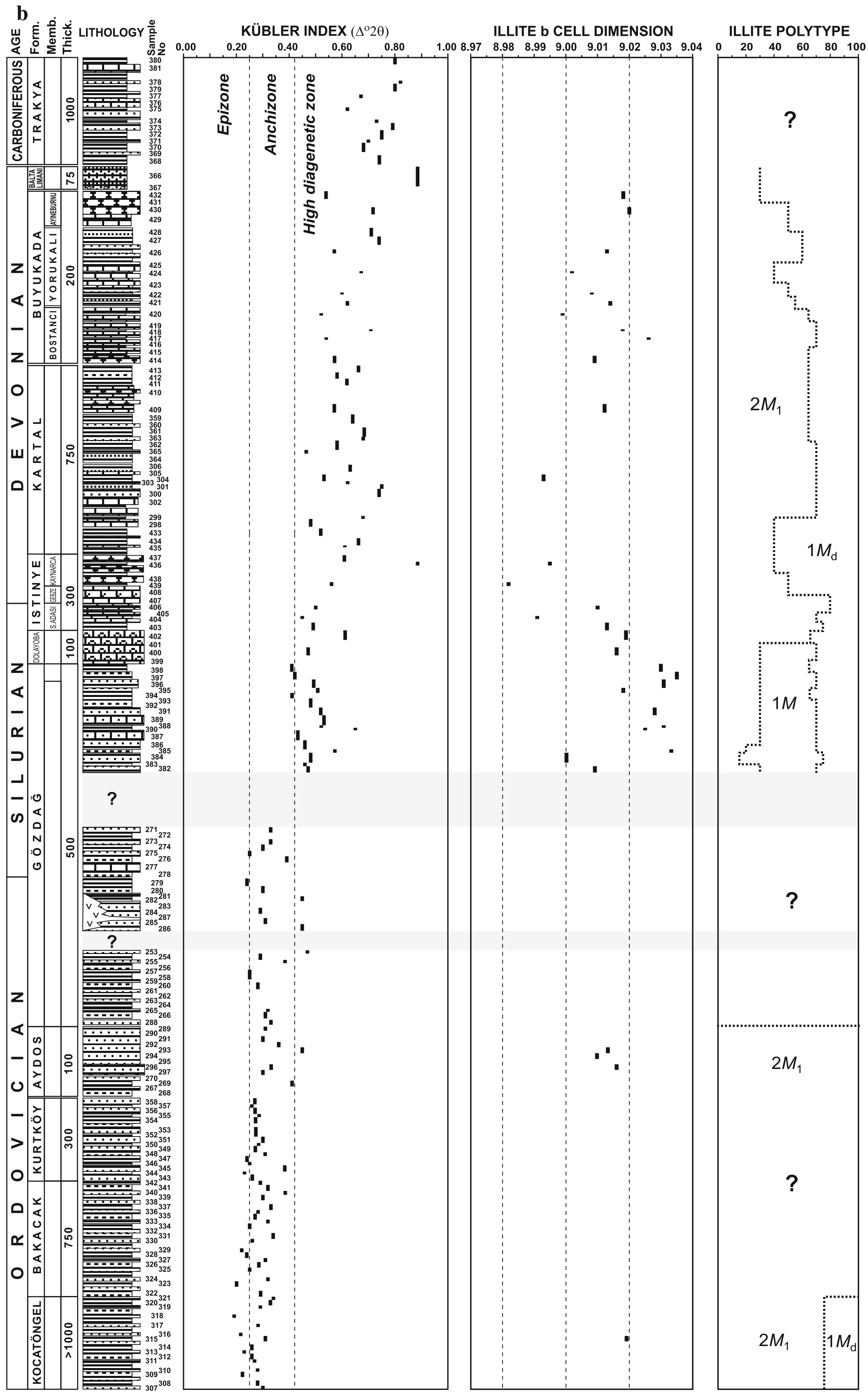

Fig. 7 continued

range as 0.19–0.88 Δ°2θ, indicating different degrees of diagenetic/metamorphic grades through vertical distribution of the Ordovician–Carboniferous section (Figs. 7, 8). Early Ordovician–Lower Silurian part of the section are characterized by the KI values which vary within a narrow range of epizone to low anchizone (0.19–0.39 Δ°2θ). On the other hand, Silurian–Carboniferous units exhibit a wider range of KI values from low anchizone to high-grade diagenesis (0.41–0.88 Δ°2θ). In general, diagenetic/metamorphic grades of Paleozoic units of the IT reveal a gradual increase from Carboniferous to Ordovician without any distinct break along the transition of Late Silurian and Early Devonian (Fig. 7). However, at the bottom of the section, KI values suddenly change from high diagenesis to middle anchizone at the middle of the Gözdag formation. This break probably depends on sampling gap, as the generalized section was constructed by partial sections from different locations (see sample locations in Fig. 2).

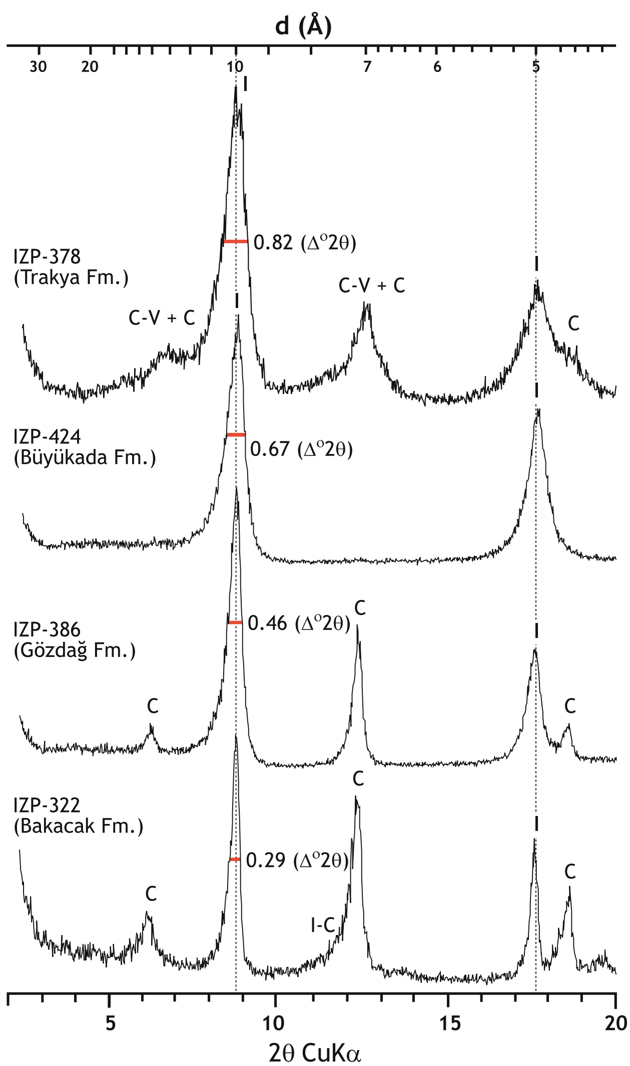

Fig. 8 Representative peak width variations of illite 10 Å peaks from Ordovician–Carboniferous together with the increasing diagenetic/metamorphic grade

5.3 K-white micas *b* cell dimensions

The K-white mica *b* cell dimension values of anchi-epimetamorphic illites from Ordovician–Lower Silurian units (Kocatöngel and Aydos formations) range from 9.010 to 9.025 Å (average 9.017 ± 0.006), whereas late diagenetic illites from Silurian units (Gözdağ formation) exhibit higher values (9.018–9.035 Å, average 9.029 ± 0.005) except for two samples with anomalously low values (9.000 and 9.009 Å; Fig. 7). Fe + Mg contents calculated from d_{060} values of illites indicate compositions varying from muscovite to phengite. Upper part of the Gözdag formation have higher *b* values than the underlying and overlying levels (Fig. 7b), that may have been affected by the presence of 1*M* illites of celadonitic and/or phengitic nature (e.g., Bailey 1984). High diagenetic samples of Late Silurian–Carboniferous units show a rough decreasing trend of *b* values from Late Devonian (Büyükada formation) to Late Silurian (Dolayoba formation), whereas anchimetamorphic samples of Ordovician units display no distinct trend. By this, the vertical distribution of *b* values is not only related to diagenetic-metamorphic grade, but also to the detrital nature in diagenetic samples (e.g., Abad et al. 2003). On point of monitoring the pressure condition (Sassi and Scolari 1974; Guidotti and Sassi 1986); compiled data of *b* values from all samples seem to be reflecting relatively higher pressure conditions for Ordovician–Lower Silurian units than the younger rocks (Fig. 9a), although most of data belong to the late diagenetic grades and 1*M* illite polytype (Fig. 9b). It can be specified that there are more or less positive relationships between diagenetic/metamorphic grades and *b* values of illites, in spite of the complexity in the vertical distribution of mineralogical data (Fig. 7b). The Ordovician–Lower Silurian succession reflects intermediate pressure facies condition when only the *b* cell dimension values of anchi-epimetamorphic K-white micas are taken into consideration.

5.4 Polytypes

Dioctahedral micas consist of three or two polytypes ($2M_1 + 1M + 1M_d$ or $2M_1 + 1M_d$) in most of the levels, except for the samples from Ordovician Aydos formation, which only contain $2M_1$ polytype (Fig. 10). The $2M_1$ polytype is more abundant in dioctahedral micas from Ordovician formations than those of Silurian-Devonian formations. The presence of high proportion of 1*M* polytype in dioctahedral micas in Upper Silurian formations could be used as parameter to distinguish the Gözdağ formation from the Aydos and Dolayoba formations.

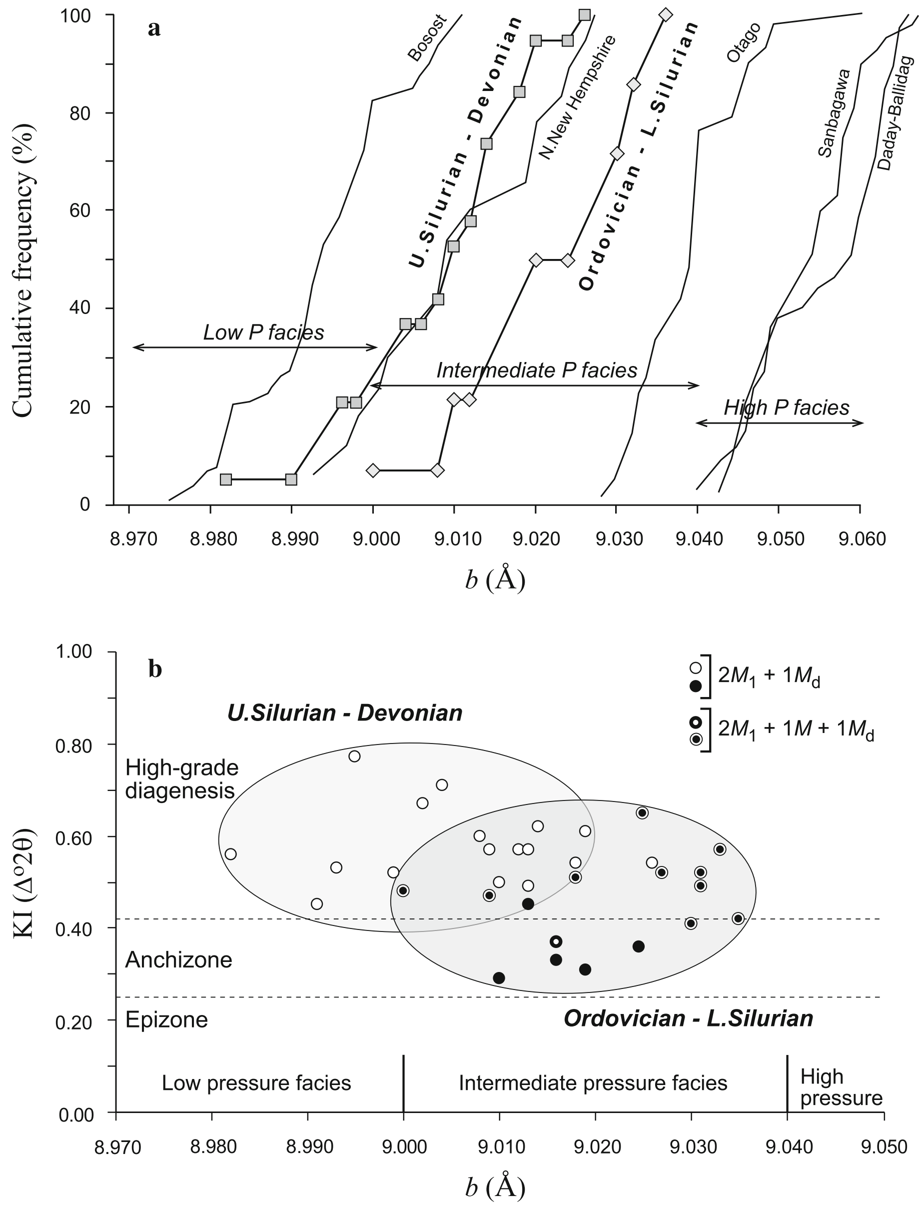

Fig. 9 **a** Different distribution of K-white micas *b* cell dimensions in terms of pressure series (b_0 curves of different areas from Sassi and Scolari 1974), **b** distribution of K-white micas *b* cell dimensions and illite KI values

Increasing ratios of $2M_1/(2M_1 + 1M + 1M_d)$ illite polytypes toward Ordovician, except for upper parts of Gözdag formation with $1M$ illites (Figs. 7b and 10), are related to increasing diagenetic/metamorphic grade (e.g., Frey 1987; Merriman and Peacor 1999).

6 Discussion

The Early Ordovician units (Kocatöngel and Bakacak formations) unconformably overlaying the Cadomian basement in IT are characterized by very low-grade metamorphic arkosic sandstones and siltstones with mudstone and shale alternations. The feldspar was originated from metagranites, metavolcanites and gneisses. The sequence is followed by fluvial conglomerates with mudstones (Kurtköy formation), and beach-type quartz-arenites (Aydos formation). Mineralogic compositions of the Paleozoic sequences are generally similar to each other, but there are some differences that could be related either to the lithology of the source area or to post depositional evolution. The abundances of polysynthetic and zoned plagioclase, biotite, chlorite and CMS in Early Ordovician, Middle Devonian and Early Carboniferous units seem to be related to volcanogenic contribution in addition to metamorphic input. Kocatöngel and Bakacak formations have comparable compositions except for the presence of C–S in Bakacak formation (Fig. 7). Early Ordovician units are followed by the siliciclastic lithologies with high quartz percentage but low amount of illite-rich clay matrix. These relatively well

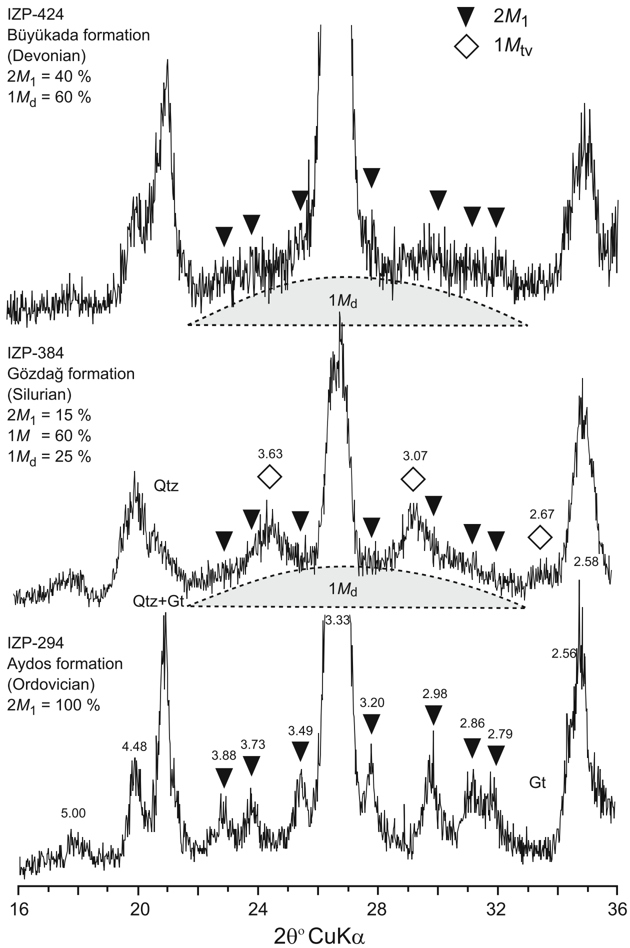

Fig. 10 Representative non-oriented XRD patterns and peak characteristics of different illite polytypes from Ordovican–Devonian units

sorted sandstones of Aydos formation indicate high energy depositional conditions. Early Silurian units cover continental clastics and carbonates with late diagenetic/anchimetamorphic grades (Gözdağ, Dolayoba and İstinye formations) were deposited on a platform margin as the underlying Early Ordovician sediments. Middle Devonian–Carboniferous part of the Paleozoic section are represented by slope- and flysch-type sediments (Kartal and Trakya formations) together with calcareous and siliceous deposits (Büyükada and Baltalimanı formations) depicting diagenetic grades. The presence of radiolarites with phosphate nodules within the iron-oxide and illite-rich clay matrix in Baltalimanı formation anticipates deeper conditions, below the limit of carbonate compensation depth.

Clay mineral assemblages in Paleozoic sequences of IT point out both pre-burial and post-burial conditions. The occurrence of chlorite and chlorite-bearing mixed layers in Ordovician–Carboniferous sequence in high amounts are mainly related to the source area. Chlorites are thought to be associated with metamorphic and/or igneous provenances with basic composition. But according to the optical and SEM observations, chlorite and chlorite-bearing mixed-layer clays are in part detrital, but also authigenic in origin. Kaolinite is generally present in feldspar-poor levels, it occurs in low amounts in Gözdag and Kartal formations. According to SEM observations it was precipitated within the micro-pores during diagenesis.

Mixed-layers C–S, C–V and I–C occur in both late diagenetic and anchi-epimetamorpic units, and their amount and types are independent from diagenetic/metamorphic grades. These minerals seem to be formed by transformation of detrital biotite to vermiculite as a result of retrograde reactions, rather than authigenetic formation from smectite with prograde reactions during burial diagenesis (Hoffman and Hower 1979; Chang et al. 1986; Nieto et al. 1996). The increasing of C–V and C–S in chloritized biotite-rich rocks is indicative of alteration from biotite (e.g., Inoue et al. 1984; Inoue and Utada 1991). The occurrence of mixed layers C–V and C–S in the anchi-epizonal rocks are inconsistent with the metamorphic grade as indicated by KI values; therefore these phases should represent retrograde alteration products (e.g. Nieto et al. 1994, 2005; Bozkaya and Yalçın 2004). Additionally, the prevalence of I–C in the lowest parts of the sequence implicates that they derive from metamorphic basement rocks, such as mica-schist and mica-gneiss, by the retrograde reaction of biotite to chlorite (e.g. Veblen and Ferry 1983; Eggleton and Banfield 1985) during the burial diagenetic/metamorphic processes. In fact, the occurrence of the chlorite-bearing mixed layers is not totally associated with retrograde processes, because authigenetic types were also determined on the optic microscope and SEM investigations.

The vertical distributions of the crystal-chemical data of illites from the Paleozoic units of IT pointed out almost regular changes with diagenetic/metamorphic grade. The progressive changes of KI data from Carboniferous to Ordovician were developed gradually and reflect increasing diagenetic/metamorphic grades together with the increasing depth and age. K-white mica *b* cell dimension values raise toward lower parts, except for anomalously rising in $1M$ illite levels (Fig. 7b), which were caused from the Fe + Mg rich nature of $1M$ illite polytype. The presence of $1M$ illites in upper part of the Gözdağ formation may be related to the changes in source and depositional environment. According to general assumptions, $1M$ and $1M_d$ illites are diagenetic, but $2M_1$ illite has also detrital origin (e.g., Merriman and Peacor 1999; Grathoff et al. 2001). $1M$ and $1M_d$ illites transform to $2M_1$ illites together with the increasing metamorphic grade, for this reason the proportion of $2M_1$ polytype gradually increases with burial. In the study area, $1M$ illites are associated with the late diagenetic grade thus this type of polytype is preserved

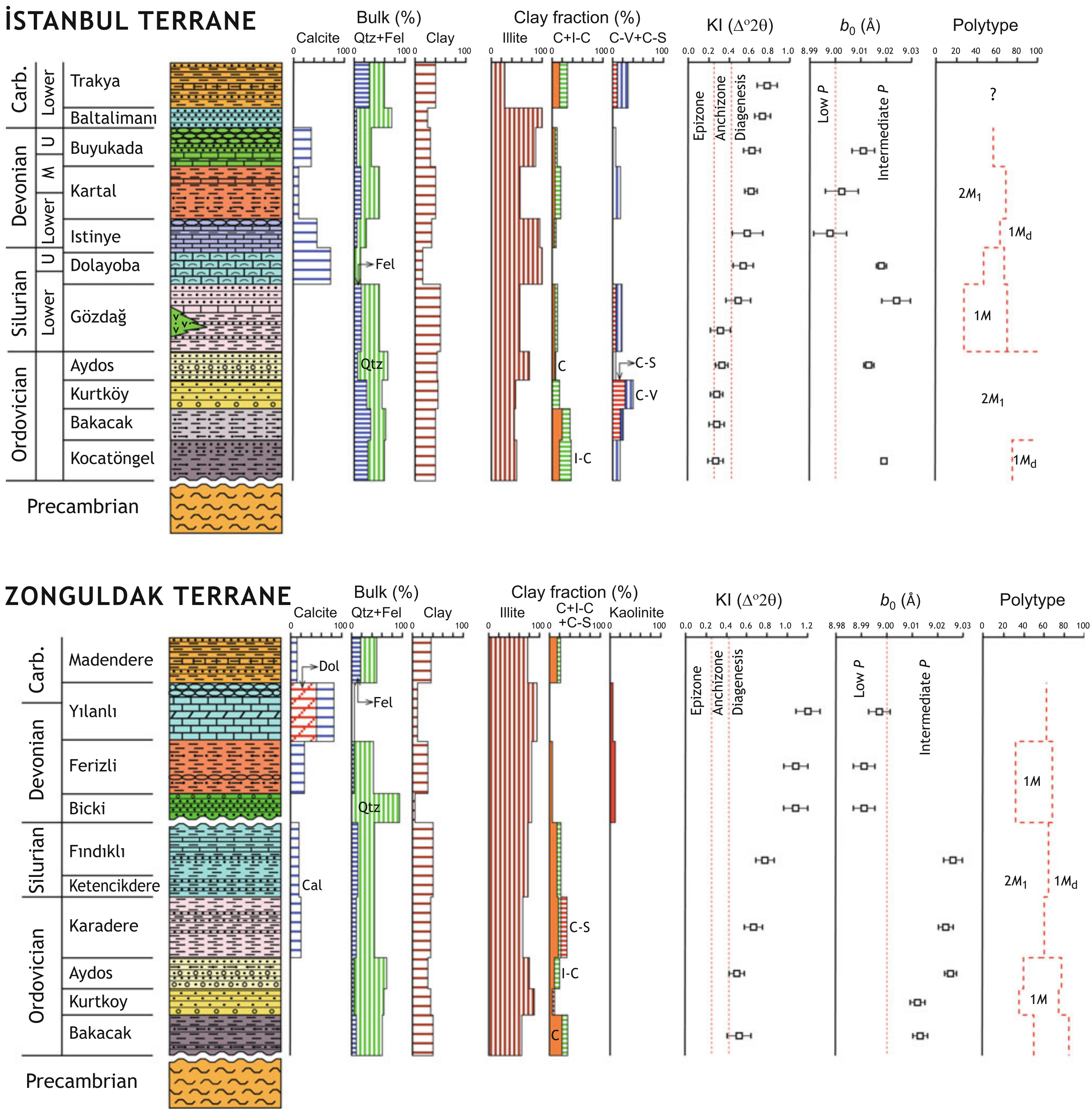

Fig. 11 Vertical distributions of mineralogical data of the IT and ZT

without transformation to $2M_1$, although several authors consider that $1M$ polytype does not represent an intermediate stage between $2M_1$ and $1M_d$ polytypes in dioctahedral micas (i.e., Dong and Peacor 1996). Gradually increasing $2M_1$ polytype proportion of illites from diagenesis to epizone suggests diagenetic/metamorphic origin for both $2M_1$ and $1M_d$ illite polytypes. While the $2M_1$ polytype is more abundant at higher grades, the coexistence of $2M_1$ and $1M_d$ polytypes over a wide range of temperatures is evaluated as a consequence of lack of equilibrium (López-Munguira and Nieto 2000).

The vertical and lateral distributions of the average mineralogical data of IT and ZT (for details see Bozkaya et al. 2012) are given in Figs. 11 and 12. Vertical distributions of clay mineral assemblages of IT and ZT show some differences such as illite contents and first appearance of kaolinite in Devonian parts. However chlorite and chlorite-bearing mixed layered minerals exhibit similar

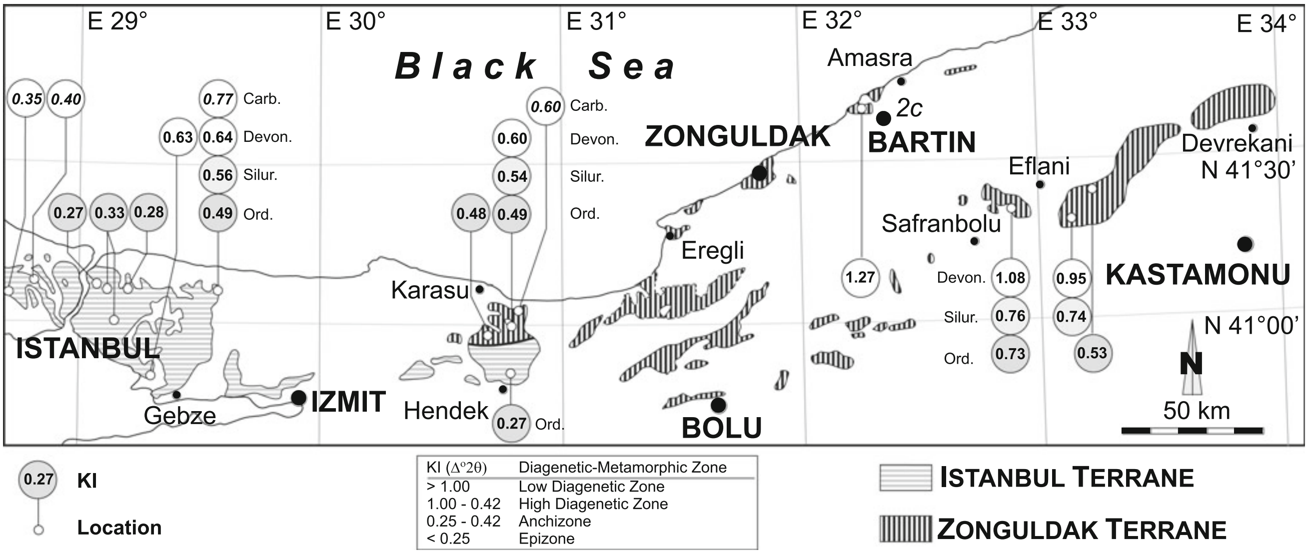

Fig. 12 Lateral distribution of KI values of illites in the Ordovician–Carboniferous units of the IT and ZT

distribution. The existence of kaolinite together with smectite in upper parts of the Ordovician rocks (Fig. 7b) is related to local hydrothermal activity rather than a sedimentary origin. Therefore these minerals were not shown in Fig. 11. KI values indicate higher diagenetic/metamorphic grades for IT than those of ZT, and accordingly higher K-white micas *b* cell dimensions and $2M_1$ ratios. On the basis of the lateral distributions of KI values of white K-micas in clastic/metaclastic rocks, the sedimentary units of the IT show higher diagenetic/metamorphic grades than those of the ZT, which may indicate some differences about their tectonothermal evolutions. On the other hand, KI values decrease or diagenetic/metamorphic grades increase from east to west in both terranes (Fig. 12).

Relatively higher degrees in diagenesis-metamorphism in coeval formations could be linked to post-Eocene (Alpine) imbrications in NW Anatolia. Therefore, these values were excluded from general evaluation on the evolution of the terrains.

In addition to general differences in both terranes (e.g., Göncüoğlu and Kozur 1998), mineralogical data in the ZT is characterized by a sudden change between the Silurian and Devonian rocks, indicating that the Ordovician–Silurian rocks were subjected to a tectonothermal event prior to the Middle Devonian transgression and the development of the angular unconformity between these two series (Bozkaya et al. 2012). On the contrary, no drastic changes in mineralogical characteristics of clay minerals were observed through the Paleozoic sequence in IT. This is indicative for a progressive and gradual change in diagenetic/metamorphic features without an episodic tectonothermal event. On the other hand, this tectonothermal event during the Early Devonian was ascribed to a deformation of the ZT by collision with Laurussia (Göncüoğlu 1997), prior to the final closure of the southeast European Rheic ocean (e.g. Nance and Linnemann 2009). The absence of the same in IT has therefore important tectonic constraints in regard to the paleogeographic distribution of the Paleozoic Terranes.

These paleogeographic constraints are not only based on differences in metamorphism but also supported by differences in the stratigraphic features. The IT shares the same Cadomian basement and its Ordovician cover with the Zonguldak and Balkan Terranes. From Silurian onwards, the depositional features of the IT and ZT start to differ (Sachanski et al. 2010). In Devonian, there are two completely different lithostratigraphic developments in these terranes. In contrast to the Early Devonian regional unconformity in the ZT, the Wenlock-early Emsian interval in IT is characterized, by a continuous 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 environments at the end of Devonian. In ZT, following the Emsian transgression onto the low-grade metamorphic Mid-Silurian siliciclastics the Mid-Devonian–Mississippian deposition is characterized by platform-type carbonates that are followed by coal-bearing fluvial clastics of Lower Pennsylvanian. Overall this stratigraphy is very similar to Dobrugea (Seghedi et al. 2005; Seghedi 2012). By this, obviously, the IT and ZT were not in the same geodynamic position in respect to the Variscan orogenic front, as initially proposed by Göncüoğlu (1997). Towards W and NW the succession of events described in IT can be followed along the W Moesia/Balkan-Kreishte regions and may be linked with the Central European Terranes and Montagne Noire and Pyrenees in South France (e.g., Faure et al. 2005). The ZT, on the other hand has its correlatives in W Moesia and further W in the terranes with Avalonia-type geological characteristics. The juxtaposition of the Zonguldak-E Moesian and the Istanbul-Balkan Terranes is attributed to strike-slip faults (Göncüoğlu 1997; Okay et al. 2008) and must have been realized prior to Late Permian considering their earliest common cover in NW Anatolia (Göncüoğlu et al. 2011).

7 Conclusions

In NW Anatolia Paleozoic rocks outcrop along a narrow strip along the Black Sea and consist of the Istanbul and Zonguldak Terranes. The Istanbul Terrane comprises a well-developed and continuous Paleozoic succession characterizing a complete Variscan cycle. It starts with a fluvial Lower Ordovician series on a Cadomian basement and grades into shallow-marine siliciclastics of Late Ordovician. The Silurian–Early Devonian period is represented by platformal deposition, followed by slope and basin-type sediments of Late Devonian and Early Carboniferous age. The late Early Carboniferous consists of a thick flysch-like succession of turbiditic sandstone-shale alternations.

Mineralogical data based on the optical and electron microscopy and X-ray diffraction suggests that Paleozoic rocks of IT show very low-grade metamorphic character, that Ordovician–Early Silurian units have mostly epizonal/anchizonal grades and intermediate pressure facies conditions, whereas Middle Silurian–Devonian parts have high-grade diagenetic character and low pressure facies conditions. The evaluation of the crystal-chemical data of clay minerals in the Istanbul Terrane shows a gradual increase in the diagenetic/metamorphic grade together with increasing depth (Figs. 7b, 11). Moreover, the textural as well as the mineralogical data indicates only a single act of metamorphism at the end of Carboniferous in high diagenetic to low epizonal conditions.

This feature is not in accordance with the overall characteristics of the neighboring Zonguldak Terrane where a tectonothermal event and an angular unconformity are recorded in the Early Devonian (Bozkaya et al. 2012). The regional geological implication of this disparity between the Istanbul and Zonguldak Terranes is that they were variably affected from the end Paleozoic orogeny. In other words, they were in completely different paleogeographic and tectonic position during the Variscan closure of the Rheic Ocean and assembled prior to Late Permian.

A correlation with the surrounding terranes in NW Anatolia, Dobrugea, Moesia and Balkan Terranes suggests that the geological characteristics of the Istanbul Terrane are more akin to the Balkans and the Central European Terranes whereas the Zonguldak Terrane resembles the Dobrugea Terrane.

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