Geochemical constraints on the provenance and depositional setting of sedimentary rocks from the islands of Chios, Inousses and Psara, Aegean Sea, Greece: implications for the evolution of Palaeotethys

GUIDO MEINHOLD1, DIMITRIOS KOSTOPOULOS2 & THOMAS REISCHMANN3

1Institut für Geowissenschaften, Johannes Gutenberg-Universität, Becherweg 21, 55099 Mainz, Germany (e-mail: meinhold@uni-mainz.de)
2Department of Mineralogy and Petrology, National and Kapodistrian University of Athens, Panepistimioupoli Zographou, Athens 15784, Greece
3Max-Planck-Institut für Chemie, Abt. Geochemie, Postfach 3060, 55020 Mainz, Germany

Abstract: The provenance and depositional setting of Late Palaeozoic and Early Mesozoic clastic sediments from the eastern Aegean archipelago are examined here for the first time using whole-rock geochemistry and composition of detrital chrome spinel. Major- and trace-element data for Late Palaeozoic and Permo-Triassic clastic sediments from the Lower and Upper Units of Chios are compatible with an acidic to intermediate source, minor input of (ultra)mafic detritus and recycling of older sedimentary components. Chondrite-normalized REE profiles are uniform with light REE enrichments (LaN/YbN c. 7.7), negative Eu anomalies (Eu/Eu* c. 0.67) and flat heavy REE patterns (GdN/YbN c. 1.5), indicating an upper continental crustal source and/or young differentiated arc material. Detrital chrome spinel from the clastic sediments of Chios has Cr-number (Cr/(Cr + Al)) values between 0.29 and 0.89 and Mg-number (Mg/(Mg + Fe2+)) values between 0.24 and 0.70, suggesting a probably mixed (ultra)mafic source involving ridge peridotites (mid-ocean ridge type), fore-arc peridotites and island-arc basalts. The metasediments from the islands of Inousses and Psara have similar whole-rock chemical signatures to those of Chios, although no evidence was found for an (ultra)mafic source. We conclude that both the Late Palaeozoic sediments from the Lower and Upper Units of Chios and the metasediments from Inousses and Psara were deposited in a continental island-arc setting until at least Late Permian times, probably at a single Palaeotethyan margin. They are interpreted to be allochthonous, tectonically transported to their present position by Late Mesozoic to Cenozoic orogenic processes.

In the eastern Mediterranean, the Hellenides of Greece and the Pontides, Anatolides and Taurides of Turkey are an integral part of the Alpine–Himalayan orogenic system and have traditionally been subdivided into several geotectonic zones (Fig. 1). Late Palaeozoic and Mesozoic palaeogeographical reconstructions show the existence of two major oceanic realms in the eastern Mediterranean area: the Palaeotethys and the Neotethys (e.g. Stampfli 2000, and references therein). Following Stampfli & Borel (2002), the term Palaeotethys is used here to denote a seaway that separated Gondwana from fragments thereof in a time period from the Silurian to early Late Triassic, during which the same fragments drifted northward and accreted to Laurussia in a stepwise fashion. Palaeotethys was closed by the northward drift of the Cimmerian terranes in response to the opening of Neotethys in the south. Despite the accumulation of new data over recent decades, the Palaeozoic to early Mesozoic history of Palaeotethys is strongly debated (see Robertson et al. 1996; Stampfli 2000; Robertson et al. 2004) because evidence for subduction, in terms of accretionary complexes, blueschists and mafic arcs, is scarce. Moreover, the complex Mesozoic to Cenozoic structural and metamorphic overprint gave rise to equivocal palaeo-tectonic models and interpretations. Chios is a key area for understanding the closure of the Palaeotethys Ocean because it is one of the rare localities where very low-grade to virtually unmetamorphosed fossil-bearing Palaeozoic to Mesozoic sequences are preserved (see Besenecker et al. 1968). A similar succession of Late Palaeozoic age can be found in western Turkey east of Chios in the Karaburun peninsula (Kozur 1998; Robertson & Pickett 2000, and references therein), and in the Tavas nappe (Lycian nappes) further south (Kozur et al. 1998).

Identifying ancient source areas and depositional settings is of fundamental importance for palaeogeographical reconstructions in the Tethyan realm. As far as clastic sediments are concerned, several well-established discriminant diagrams exist based on their petrography, heavy-mineral assemblage and geochemistry (e.g. Dickinson & Suczek 1979; Bhatia 1985; Morton 1985; Bhatia & Crook 1986; McLennan 1989; McLennan et al. 1990, 1993). The Palaeozoic clastic sediments of Chios have already been studied using petrographical and heavy-mineral analyses (Neubauer & Stattegger 1995; Zanchi et al. 2003). These data indicate a recycled-ogen provenance, specifically of an alpine-type continent–continent collision zone, with minor influence from magmatic-arc sources. The presence of detrital chrome spinel also suggests an ultramafic source (Stattegger 1984; Neubauer & Stattegger 1995). Compared with Chios, little attention has been paid to the neighbouring islands of Inousses and Psara, where predominantly metasedimentary rocks of previously unknown stratigraphic age and uncertain affiliation occur.

This study focuses on the geochemistry of Late Palaeozoic and Early Mesozoic clastic sediments from the islands of Chios, Inousses and Psara. We present, for the first time, major- and trace-element whole-rock data, supplemented by detrital chrome spinel chemistry, to evaluate their source-rock lithologies and depositional settings. Elements useful for studying marine depos-
its are those with a short residence time in the ocean water, such as REE, Y, Sc, Th, Ti, Zr, Hf and Nb (Holland 1978; Taylor & McLennan 1985). These elements are transferred quantitatively into clastic sediments without significant interaction with seawater and can preserve the chemical record of their source (e.g. Bhatia & Crook 1986; McLennan 1989; McLennan et al. 1990, 1993). The geochemical data of this study can be used as a base for chronostratigraphic correlations with adjacent areas in Greece and Turkey. Based on previous publications and our own field and laboratory work we propose new tectonostratigraphic and facies concepts for the sedimentary units of Chios, Inousses and Psara, which can help to improve our understanding of the Palaeotethyan realm in the eastern Mediterranean region.

Regional geology

Chios

Late Palaeozoic rocks of the Lower Unit. The island of Chios is located in the eastern Aegean Sea, only a few kilometres west of the Karaburun peninsula on the Turkish mainland (Fig. 1). A detailed description of the geology of Chios was given by Besenecker et al. (1968) and Robertson & Pickett (2000). Simplified, Chios can be subdivided into two tectonostratigraphic units (Fig. 2): an ‘autochthonous’ Lower Unit and a tectonically overlying ‘allochthonous’ Upper Unit (Besenecker et al. 1968; Herget & Roth 1968). The nappe style of Chios is illustrated in Figure 3. The Lower Unit is commonly assumed to consist of clastic rocks of Late Palaeozoic age containing blocks of up to 100 m in diameter of massive and well-bedded limestones, cherty limestones, radiolarites and volcanic rocks. This succession was variably named ‘Chios mélange’, ‘Chios (wild)flysch’ or ‘Volissos turbidites’ (e.g. Robertson & Pickett 2000; Groves et al. 2003; Zanchi et al. 2003). Here we use the non-descriptive term Late Palaeozoic rocks of the Lower Unit. The major rock types of this unit are greywackes, minor sandstones and siltstones, as well as intercalated quartz-bearing conglomerates. The latter mainly contain clasts of quartz, black chert and quartzite embedded in a coarse-grained quartzose matrix. Limestone clasts are very rare. Erosional contacts at the base of greywacke and conglomerate beds and upward reduction in grain size can often be observed. In some outcrops, ripples and well-developed sole marks can be seen at the base of turbidite units. The facies of the turbidite–olistostrome succession resulted mainly from turbidity currents, debris flows and submarine slides. Layers rich in plant fragments can locally be found on bedding surfaces (e.g. at sample localities CH63, CH65 and CH66; see Fig. 2). A biostratigraphic age for these plant fragments has not been obtained as yet because of lack of characteristic features necessary for an accurate age determination (V. Wilde, pers. comm.). However, Broutin (cited by Groves et al. 2003) suggested a Middle–Late Viséan age for macrofloras from turbidites that occur along Papalia Beach, SW of Sidirounta village (see Fig. 2). Furthermore, Groves et al. (2003) reported in situ Mississippian microfossils from the terrigenous matrix sediments and suggested that the Late Palaeozoic rocks of the Lower Unit are most probably Late Viséan or Early Serpukhovian in age.

Fig. 1. Simplified map of Greece and western Turkey showing the main geotectonic zones (modified after Jacobshagen 1986; Okay et al. 1994, 2001).
The exotic limestone blocks that occur as olistoliths within the Late Palaeozoic rocks of the Lower Unit have been dated as Silurian to Carboniferous in age (Kauffmann 1965; Besenecker et al. 1968; Herget & Roth 1968). Recently, the chert olistoliths (ribbon radiolarites) were examined biostratigraphically by Larghi et al. (2005), who found age-diagnostic radiolarians and conodonts in two samples, which allowed them to establish Late Silurian (probably Pridolian) and Late Devonian (Famennian) ages, whereas only a more general age range from Devonian to Early (?) Carboniferous could be proposed for the remainder.

The olistoliths essentially define four olistostrome formations with a very clear predominance of younger blocks (Early Carboniferous) in the lower formation and of older blocks (Silurian) in the upper formation (Papanikolaou & Sideris 1983; Sideris 1989). The volcanic rocks (basic, intermediate and acid in composition) were studied in detail by Pe-Piper & Kotopouli (1994), who found clear evidence that at least some of the volcanic rocks intruded the deformed Palaeozoic clastic succession and therefore cannot be olistoliths. They suggested that these volcanic rocks probably formed in a back-arc setting above a subducting Palaeotethyan oceanic slab and correlated them with Early Permian granodiorites of the Karakaya Complex in Turkey.

Several tectonic models have been proposed for the origin of the Late Palaeozoic rocks of the Lower Unit. Papanikolaou & Sideris (1983) interpreted this unit as a post-Middle Carbonifer-
ous to pre-Scythian wildflysch bearing Silurian to Carboniferous olistoliths, and compared it with the Late Permian to Scythian rocks of Attica. Stampfli et al. (1991) proposed that the wildflysch represents a mainly Permian accretionary wedge that can be correlated with the Karakaya Complex of Turkey, which they considered to mark a Palaeotethyan suture. Robertson & Pickett (2000) maintained that the Late Palaeozoic rocks of the Lower Unit are a Late Carboniferous to ?Early Permian subduction–accretionary complex that developed near the southern margin of the Palaeotethys Ocean. Models invoking a rift setting or a long-lived, deep marine basin receiving olistoliths were also discussed by Robertson & Pickett (2000). Recently, Stampfli et al. (2003) and Zanchi et al. (2003) proposed a tectonic model of an arc–trench system that formed along the Palaeotethyan subduction zone in Carboniferous times.

### Permo-Triassic and younger rocks of the Lower Unit

The Late Palaeozoic rocks of the Lower Unit are overlain by non-fossiliferous conglomerates and sandstones (Besenecker et al. 1968) (Fig. 3). The conglomerates mainly contain clasts of quartz and black chert embedded in a coarse-grained quartzose matrix. Zanchi et al. (2003) described an angular unconformity at the base of this clastic succession, interpreted as a Variscan unconformity. However, the stratigraphic age of these possibly Early Triassic conglomerates and sandstones is uncertain because no biostratigraphic and only few geochronological ages exist so far. The youngest detrital zircon age is 326 Ma (Meinhold et al. 2006), thus giving a maximum age for deposition. Although the rounded shape of the youngest detrital zircon rather indicates a Permian sedimentation age for the conglomerates and sandstones, as has already been mentioned by Besenecker et al. (1968). Therefore, in the following discussion we use the term Permo-Triassic instead of Early Triassic. The conglomerates and sandstones pass upwards into well-bedded limestones of late Early Triassic age, followed by massive limestones that themselves interfinger with reddish ammonoid-bearing limestones of Hallstatt type in their upper parts (Besenecker et al. 1968). This sequence is overlain by a Middle Triassic (Anisian–?Carnian) volcano-sedimentary succession consisting of red to purple shales, radiolarites and tuffitic horizons (Besenecker et al. 1968; Gaetani et al. 1992), followed by well-bedded marly limestones of probably Late Anisian age and limestones of Ladinian to Rhaetian–Liassic age that are more than 1000 m thick (Besenecker et al. 1968). Few clastic intercalations (emergent horizons, Fig. 3) occur within the Ladinian–Liassic limestones. The latest Triassic–earliest Jurassic is marked by non-marine clastic deposits followed by well-bedded dolomites and limestones. Late Jurassic limestones (Cladocoropsis limestones) are known only from Venetiko near the southernmost cape of Chios (Besenecker et al. 1968). The youngest rocks on Chios are Cenozoic sediments and volcanic rocks cropping out mainly in the southeastern part of the island (Fig. 2).

### Permo-Carboniferous and younger rocks of the Upper Unit

The Upper Unit of Chios (Figs 2 and 3) belongs to the allochthonous nappe sensu Besenecker et al. (1968). Lithostratigraphically, its lowermost part consists of quartzose greywackes, sandstones and
minor siltstones of Late Carboniferous age occasionally containing lenses of black and greenish chert a few metres in size. One of these lenses, sampled near Mesta village in SW Chios (38°14′49″N, 25°54′48″E), yielded poorly preserved radiolarians (Entactinaria; A. Braun, pers. comm.), which are of only low stratigraphic significance. Layers rich in plant fossils can be found on the bedding surfaces of siltstones and fine-grained sandstones (e.g. near Langada village; see Fig. 2). Unfortunately, no biostratigraphic age could be obtained for these plant fragments because of the lack of characteristic features for an accurate determination (V. Wilde, pers. comm.). Fossil-bearing limestones of Late Carboniferous age are overlain by a clastic carbonaceous succession of Early Permian age (Kauffmann 1969). The Middle Permian is represented by fossiliferous carbonate sequences containing numerous Gymnocodiaceae algae and fusulinid foraminifera of the genus Verbeekina (e.g. Besenecker et al. 1968; Flajs et al. 1996; Angiolini et al. 2005). Rocks of Late Permian age are absent. Recently, Angiolini et al. (2005) carried out a palaeobiogeographical analysis of limestones from the Middle Permian succession. On the basis of the brachiopod fauna identified, Angiolini et al. (2005) suggested that the Middle Permian rocks of the Upper Unit have a Gondwanan affinity, in marked contrast to the interpretation of Zanchi et al. (2003), who proposed a Laurasian affinity for the Late Palaeozoic rocks of the Lower Unit. Nevertheless, a Middle Permian fossil assemblage similar to that found on Chios was described by Altiner et al. (2000) from the northern Taurides and ascribed to a distinct ‘Northern Biofacies Belt’.

Papanikolaou & Sideris (1983; cited by Sideris 1989) advocated that the Late Carboniferous to Early Permian flysch-type sequence changed to a shallow-water marine carbonate platform during Middle to Late Permian times. The Permian limestones are overlain by transgressive sediments of Early Jurassic age, starting with red conglomerates, sandstones and siltstones and passing upwards into thick-bedded limestones (Dachstein-type with bivalvia Megalodontidae) and minor dolomites (Besenecker et al. 1968). This sequence is locally overlain by transgressive sediments of Early Jurassic age, during Middle to Late Permian times. The Permian limestones of Late Carboniferous age, which are overlain by transgressive sediments of Early Jurassic age, are ascribed to a distinct ‘Northern Biofacies Belt’.

For example, in Chios, the Middle Permian rocks of the Upper Unit have a Gondwanan affinity, in marked contrast to the interpretation of Flajs et al. (1968), who proposed a Laurasian affinity for the Late Palaeozoic rocks of the Lower Unit. Nevertheless, a Middle Permian fossil assemblage similar to that found on Chios was described by Altiner et al. (2000) from the northern Taurides and ascribed to a distinct ‘Northern Biofacies Belt’.

The Middle Permian rocks of the Upper Unit are tectonostratigraphically affiliated to the Pelagonian Zone of mainland Greece (Besenecker et al. 1968; Flajs et al. 1996; Angiolini et al. 1999, fig. 1). However, the thick succession of Triassic rocks of the Lower Unit shows clear affinities to the Pelagonian Zone of mainland Greece (Besenecker et al. 1968; Gaetani et al. 1992), whereas the Upper Unit can be correlated with the autochthonous ‘basement’ of Lesbos to the north (e.g. Papanikolaou 1997; Robertson & Pickett 2000), which was assigned to the Paikon Unit of the Vardar Zone (Papanikolaou 1997). The Mesozoic platform of Chios and Karaburun was interpreted by Robertson & Pickett (2000) as part of a Mesozoic, northerly Neotethyan, oceanic basin bordering the Tauride–Anatolide Platform and the Menderes Metamorphic Massif to the south. All these equivocal interpretations illustrate the need to revisit Chios.

Inousses

Inousses (Figs 1 and 4) and its surrounding islets are located between Chios to the west and the Karaburun peninsula to the east. In NE Chios, metamorphic rocks crop out in a small area (c. 250 m × 280 m) that supposedly belongs to the metamorphic complex of Inousses (Kauffmann 1965; Besenecker et al. 1968, 1971). The contact between the metamorphic rocks and their...
overlying very low-grade to unmetamorphosed rocks is marked by a moderately steep, SW-dipping fault (Kaufmann 1965). Inousses itself consists of a flysch-like sequence comprising light grey quartzose metaconglomerates, fine-grained grey metapsammites, grey to dark grey pyrite-bearing metapelites (phyllites), pyrite-bearing greyish quartz-micaschists, and grey to dark grey platy marble layers or lenses (Kiliás 1987). Within the metasandstones and metagreywackes pyrite cubes with a crystal size ranging from a few millimetres to 1.5 cm can frequently be found. According to Besenecker et al. (1968, 1971) and our own field observations, the metasedimentary succession of Inousses can be lithostratigraphically subdivided into a lower and an upper part. The lower part is exposed in the centre and the south of the island, where medium- to coarse-grained metasediments including light grey metasandstones and metagreywackes with intercalations of light grey to greenish grey conglomerate layers predominantly occur; these pass upwards into medium- to very fine-grained metasediments including argillaceous metagreywackes and dark grey to black metapelites (phyllites). This lithostratigraphically upper part crops out mainly in the north and NW part of the island. The main structural feature on Inousses is multiple folding with two axial trends (Kiliás 1987; see Zanchi et al. 2003). The major foliation is folded with gently NNW-dipping fold axes.

In general, the monotonous character of the sedimentary succession, the lack of fossils and radiometric data and the greenschist-facies metamorphic overprint complicate its stratigraphic affiliation. Besenecker et al. (1968) assumed that the epimetamorphic flysch sequence of Inousses is older than the Pelaeozoic sequence of the autochthonous Lower Unit of Chios and thus forms its metamorphic basement. Mountrakis et al. (1983) correlated the Inousses metamorphic rocks with the Permian–Early Triassic metasediments of the western margin of the Pelagonian Zone of continental Greece and those of the Sporades. Kiliás (1987) also assumed an affiliation of the Inousses metamorphic rocks to the Pelagonian Zone. All this contradicts the interpretation of Kozur (1998), who compared the metasediments of Inousses with the monotonous siliciclastic Küçükbaçhe Formation of the Karaburun peninsula of probable Ordovician (or Cambro-Ordovician) age (Kozur 1998).

Psara
Psara is located c. 20 km west of Chios in the Aegean Sea (Fig. 1). Wallbrecher (cited by Dürr & Jacobshagen 1986) distinguished three units on Psara. In the southern and central part of the island very low-grade metamorphic slates, phyllites and greenschists interlayered with quartzites and metagreywackes occur. They are tectonically overlain by garnet-bearing micaschists and gneisses, in turn tectonically overlain by a marble unit c. 300 m thick. However, our field analysis showed only a Lower Unit and a tectonically overlying Upper Unit (Fig. 5a). The nappe style of Psara is illustrated in Figure 5b. The Lower Unit consists of dark grey metapelites (phyllites), metasandstones and metagreywackes that were intruded by mafic rocks (now greenschists). An intrusive contact with the country rocks could be observed along a fresh road cut north of Agios Ioannis (Fig. 5a). Some metasediments have minor carbonate content. The major foliation strikes approximately north–south and dips steeply either towards the east or the west (Fig. 5a). The Upper Unit of Psara mainly comprises mica schists (with garnets up to 0.8 cm in diameter) intercalated with calcischists and marble layers that pass up into pure marbles at the top. The predominant foliation dips mostly to the south and is folded with fold axes dipping gently to the east or west. Unfortunately, in both units neither fossils nor radiometric data are yet available, thus complicating their stratigraphic affiliation. Cenozoic volcanic rocks crop out in the northwestern and central part of Psara.

The tectonostratigraphic affiliation of Psara to units in Greece is undecided. Mountrakis et al. (1983) correlated both units of Psara with the Subpelagonian Zone of continental Greece, whereas Wallbrecher (cited by Dürr & Jacobshagen 1986) favoured an affiliation to successions from the southern Pelion peninsula and the northern Sporades of the Pelagonian Zone. Taken together with the findings from Chios and Inousses, all these equivocal interpretations suggested that a reinvestigation of the (meta)sedimentary successions in the eastern Aegean Sea would be worthwhile.

Sample description and methods
A total of 35 siliciclastic sediments including greywackes and sandstones, minor siltstones, phyllites and micaschists were collected from Chios, Inousses and Psara for whole-rock geochemical analyses (major and trace elements) and detrital chrome spinel microprobe analyses. The stratigraphic affiliation of the samples from Chios is based on work by Besenecker et al. (1968, 1971). Sample localities for Chios, Inousses and Psara are shown in Figures 2, 4 and 5a, respectively. Ages, lithologies, localities (including geographic coordinates), whole-rock chemical data and the mineral chemical data for the detrital chrome spinels referred to in this paper are available online at http://www.geolsoc.org.uk/SUP18270. A hard copy can be obtained from the Society Library.

Sample description
Chios. Petrographically, the clastic sediments of Late Palaeozoic age from the Lower and Upper Units of Chios have similar framework grains in varying amounts, consisting of monocrystalline and polycrystalline quartz, and sedimentary and volcanic lithoclasts. Feldspar grains are common and always present. Plagioclase (mainly albite) is by far the most abundant feldspar, whereas K-feldspar is rare. Plagioclase grains often display patchy sericitization and replacement by calcite. Single muscovite flakes and minor detrital biotite also occur. Interestingly, few grains showing myrmekitic texture were found in the Late Palaeozoic greywacke sample CH39. The polycrystalline quartz grains have irregular subgrain boundaries typical of their metamorphic origin. The sedimentary lithoclasts consist of phyllites, radiolarian chert and quartz-rich, low-grade metasedimentary rock fragments. Calcite clasts are rare in the Late Palaeozoic greywackes from the Lower Unit but common in the Permo Carboniferous from the Upper Unit. The volcanic lithoclasts are mainly acidic in composition. The few basic lithoclasts are often strongly altered (e.g. in sample CH26). All psammites are poorly sorted by size and dominated by angular to subangular clasts. This feature, together with the abundant unstable lithoclasts, indicates that the clasts were rapidly eroded and deposited without significant rounding or sorting, which is one of the characteristics of many greywackes transported by turbidity currents (see Pettijohn et al. 1972). The occurrence of iron hydroxides in some samples indicates secondary alteration processes. Accessory minerals include clay minerals, micas, chlorite and heavy minerals, mainly zircon, tourmaline, rutile and opaque minerals, minor chromite and epidote.

Inousses. The framework grains of the psammites from Inousses are mainly monocrystalline and polycrystalline quartz, sedimentary and altered volcanic lithoclasts, minor muscovite flakes, feldspar and detrital biotite. The latter is commonly strongly altered. In some samples the quartz grains are almost elongated and sigmoid-shaped, indicating that they were deformed at a temperature higher than c. 300 °C depending on strain rate, differential stress and the presence of water (Passchier & Trouw 2005). Feldspar grains often display patchy sericitization. All
Psammites are poorly sorted by size and dominated by angular to subangular clasts. A few grains are also subrounded to rounded. The psammites are clast-supported with a quartzose–sericitic matrix. Accessory minerals include clay minerals, but also heavy minerals, such as zircon, tourmaline, opaque minerals and epidote.

Psara. The framework grains of psammite sample CH25 from the Lower Unit of Psara are mainly monocrystalline and polycrystalline quartz, minor muscovite and twinned plagioclase grains. The psammite is poorly sorted by size and dominated by angular to subangular clasts. Iron hydroxides are common, indicating secondary alteration processes. The mica schists from the Upper Unit are mainly composed of quartz, muscovite, biotite, garnet and chlorite. Altered plagioclase grains (Ab70–86An13–30Or0–2) have also been found in small amounts. Aluminosilicates were not observed. Garnet (Alm63–65Gr53–58Pp6–11Sp5–6) forms porphyroblasts, up to 0.8 cm in diameter, which are strongly fractured. Biotite is often replaced by chlorite. Zircon, tourmaline and ilmenite are accessory minerals. The assemblage quartz–muscovite–chlorite–garnet–biotite suggests mid- to upper greenschist-facies metamorphic conditions (garnet-zone metapelites; c. 450 °C at low pressures).

Whole-rock geochemistry

The composition of clastic sediments is controlled by the lithology of their source area(s), weathering, transport and sorting, redox environment and diagenesis (Johnsson 1993). Commonly, the original composition and mineralogy of a rock is changed during metamorphism by metamorphic mineral reactions. Petrographical analysis for provenance studies of metamorphosed sediments is therefore not applicable. However, if the whole-rock geochemistry is not significantly modified by secondary processes it can be used to fingerprint the provenance and depositional setting of metasedimentary rocks. In general, the alkali and alkaline-earth elements can be strongly fractionated by weathering and diagenesis (e.g. Nesbitt et al. 1980), making them liable to movement and redistribution, and thus influencing the geochemical composition of the sediment. Therefore, discrimination diagrams using such elements must be treated with caution. Immobile trace elements are expected to be more useful in studying sedimentary provenance and depositional setting than major elements (e.g. Bhatia & Crook 1986; McLennan 1989; McLennan et al. 1990, 1993). The REE in particular are best suited for such studies, because of their relative immobility during weathering, transport, diagenesis and metamorphism (e.g. McLennan 1989). In some cases, however, fractionation and mobilization may occur as a result of source-rock weathering and diagenesis (e.g. Nesbitt 1979; Nesbitt et al. 1990; Milodowski & Zalasiewicz 1991).

The studied samples from Chios, Inousses and the Lower Unit of Psara are virtually unmetamorphosed or have undergone only a very low-grade metamorphic overprint. Significant element mobilization can be excluded (apart from volatile phases).
mica schists from the Upper Unit of Psara, however, show evidence of Barrovian-type, low-grade metamorphism, which might have influenced their primary geochemical signature. In this study, with the exception of a few major-element fingerprints, we have used only relatively immobile trace elements and REE for the characterization of sedimentary provenance and depositional setting.

**Analytical procedures**

For geochemical analyses, the samples were crushed into small pieces and then powdered using an agate mill. Sample powder was mixed with lithium tetraborate (1:7) and fused in platinum crucibles at 1200 °C to prepare fused discs. Major-element data were determined by X-ray fluorescence (XRF) on fused discs at the Institut für Geowissenschaften, Mainz, Germany, using a Philips MagiXPro X-ray spectrometer equipped with a Rh-anode tube. Selected trace elements were analysed using the same analytical equipment but measured on pressed powder pellets. Relative errors on major and trace elements are usually <2% and <5%, respectively. Loss on ignition (LOI) was determined gravimetrically by heating the samples to 1000 °C. Total iron is expressed as Fe₂O₃.

REE, Hf, Ta, Th, and U were analysed at the Department of Afdeling Fysisco-Chemische Geologie, Katholieke Universiteit Leuven, Belgium. The analytical procedures followed are those described by Mareels et al. (2004). Sample powder (0.2 g) was mixed with 1 g of lithium metaborate, and then powdered using an agate mill. Sample powder was mixed with lithium tetraborate (1:7) and fused in platinum crucibles at 1200 °C. The molten samples were dissolved in HNO₃ and homogenized and fused in a graphite crucible for 10 min at 1050 °C in a laboratory furnace. The molten samples were dissolved in HNO₃ and homogenized. After homogenization, quantitative REE hydroxide precipitation by Fe(III)-hydroxide scavenging was performed for each sample. After finishing the precipitation steps, 1 ml of each of In and Re mononuclear solutions were added to the sample solutions to serve as internal monitors during measurements. Samples, blanks and standards (USGS rocks) were analysed by inductively coupled plasma mass spectrometry (ICP-MS) using a Hewlett-Packard 4500 quadrupole system coupled to a Cetac 500SX sample changer. All measurements were corrected for instrumental drift using the peak intensities of the 115In and 185Re internal monitors. Accuracy was better than 10% for all analysed elements.

The REE data were normalized against both PAAS (Post-Archaean Australian Shale; values from McLennan 1989) and C1-chondrite (values from Taylor & McLennan 1985). In addition to the PAAS- and chondrite-normalized REE patterns, the normalized Eu anomaly (Eu/Eu*) also serves as a useful discriminant between samples and between plate-tectonic settings (e.g. Bhatia 1985; McLennan 1989; McLennan et al. 1990), where Eu* is a theoretical Eu concentration calculated by interpolation between Sm and Gd. The Eu anomaly was calculated according to McLennan (1989): Eu/Eu* = Eu/N / (Sm/N × Gd/N)², where the subscript N denotes chondrite-normalized values. Values of Eu/Eu* > 1 are considered to be positive, whereas values <1 are considered to be negative (McLennan et al. 1990).

**Mineral chemistry**

Detrital chrome spinel compositions were determined on polished thin sections and on polished heavy mineral separates. To prepare the latter, samples were crushed using a hydraulic press and a rotary mill, then processed using a Wilfley table, a Frantz isodynamic magnetic separator and heavy liquids (diiodomethane). The heavy mineral fractions thus obtained were mounted in epoxy resin, sectioned and polished. Mineral analyses were carried out using a Jeol JXA 8900 RL electron microprobe at the University of Mainz, Germany, operated at an accelerating voltage of 20 kV and a beam current of 12 nA, with a beam diameter of 2 µm. Following common practice for chrome spinel interpretation, the Cr-number (Cr – number = Cr/(Cr + Al)) and Mg-number (Mg – number = Mg/(Mg + Fe⁺)) for each analysis were calculated assuming stoichiometry (e.g. Dick & Bullen 1984; Cookenboo et al. 1997; Barnes & Roeder 2001; Kamenetsky et al. 2001).

**Geochemical results**

**Chemical classification**

Because many discrimination diagrams for identifying source-areal lithologies and tectonic settings of sedimentary rocks yield different results for psammitic and pelitic protoliths (as a result of, e.g. sorting effects), a differentiation between psammitic and pelitic sediments was deemed necessary. In this study, pelites include very fine-grained sediments such as shales and siltstones, whereas psammites include medium- to coarse-grained clastic sediments such as litharenites, sublitharenites and sandstones. Various classification schemes for clastic sediments based on whole-rock chemical data have been established (e.g. Pettijohn et al. 1972; Herron 1988, and references therein). Figure 6 shows the classification diagram of Herron (1988), which distinguishes between lithologies according to their logarithmic ratios of SiO₂/Al₂O₃ v. Fe₂O₃/K₂O. The SiO₂/Al₂O₃ ratio distinguishes between quartz-rich (high ratios) and clay-rich (low ratios) sediments. SiO₂ reflects the content of quartz and Al₂O₃ that of clay minerals. With an increasing SiO₂/Al₂O₃ ratio the grain size also increases, as do the grade of recycling and the maturity of the sediment. The Fe₂O₃/K₂O ratio is used as an indicator of mineralogical stability and distinguishes lithic fragments from feldspar (Herron 1988). Most of the analysed sediments are classified as unstable immature wackes (i.e. greywackes) and litharenites because of their quartz and lithic contents; two samples are classified as sublitharenites and nine as shales (Fig. 6). The geochemical classification is broadly coincident with the petrographical observations.

**Mineral controls on whole-rock geochemistry**

Figure 7 shows some bivariate diagrams to identify mineral controls on whole-rock geochemistry. The strong positive linear
correlations between K₂O and Rb with Al₂O₃ (Fig. 7a and b) suggest that both K and Rb reside in phyllosilicates. Inasmuch as pelites are more enriched in clay minerals and/or micas than psammites, they occupy distinct fields in Figure 7a and b, except for two pelite samples with a high carbonate content that plot in the field of psammites. The clastic sediments from the Late Palaeozoic rocks of the Lower Unit of Chios and from Inousses are characterized by very low CaO contents (<1.7 wt%), whereas samples from the Upper Unit and the Permo-Triassic of Chios, as well as the garnet–mica schists of Psara, generally have much higher CaO contents (Fig. 7c). CaO is mainly bound in carbonates as indicated by the positive correlation between CaO and LOI (Fig. 7d). Most samples show a positive linear correlation between Cr and Al₂O₃ (Fig. 7e), suggesting that the Cr content is controlled by Cr-bearing aluminous phases such as clay minerals. A lack of correlation might be indicative of the presence of Cr-bearing accessory oxide minerals such as chromite. Total REE contents correlate negatively with SiO₂ and positively with Al₂O₃, K₂O, TiO₂, and Nb (diagrams not shown), indicating that the REE are controlled by various amounts of phyllosilicate minerals and rutile (as carrier of Ti and Nb). The less pronounced positive correlation between total REE and Zr suggests that the heavy mineral zircon has a minor influence on total REE contents, probably because it is largely controlled by irregular distribution during sedimentation.

Fig. 7. Correlation diagrams of K, Rb, Ca and Cr v. Al₂O₃ and Ca v. LOI for clastic sediments of Chios, Inousses and Psara.
Weathering and sediment recycling

Figure 8a shows the Th/U v. Th plot of McLennan et al. (1993). In contrast to Th, U is easily mobilized during weathering and sedimentary recycling, resulting in an increase of the Th/U ratio. Although highly reduced sedimentary environments can be enriched in U leading to low Th/U ratios, weathering favours the oxidation of insoluble $U^{4+}$ to soluble $U^{6+}$ with subsequent loss of U to solution and elevation of Th/U ratios (McLennan & Taylor 1980, 1991; McLennan et al. 1990). Upper crustal rocks have a Th/U ratio averaging around 3.8 (Taylor & McLennan 1985). The Th/U ratios of all studied sediments are c. 2–6, with the exception of one garnet–mica schist from the Upper Unit of Psara (Fig. 8a). Considering that, on average, the Th/U ratio of most psammites here lies below the value for the upper continental crust (UCC), it is likely that these sediments were derived from source rocks with the least weathering and/or from material with the least recycling. In contrast, the pelites (and very few psammites) follow the normal weathering trend. One psammite from the Late Palaeozoic rocks of the Lower Unit, two Permo-Triassic psammites and one psammite from the Upper Unit of Chios lie in the field of depleted mantle sources. Their source rocks were probably non-recycled arc magmatic rocks that have undergone a minimal degree of weathering.

The compositional variation and the degree of sediment reworking and heavy mineral sorting can be illustrated in a plot of Th/Sc v. Zr/Sc (McLennan et al. 1993). A positive linear correlation between the two ratios expresses the igneous differentiation trend. The Th/Sc ratio of sedimentary rocks characterizes the average provenance, whereas an increase in the Zr/Sc ratio alone indicates significant sediment reworking, consistent with zircon enrichment (McLennan et al. 1993). The Zr/Sc ratios are smaller for pelites than for psammites (Fig. 8b), suggesting concentration of zircon in the coarser fraction. All sediments have undergone minor degree of weathering and no significant sediment recycling.

Provenance

Figure 9 summarizes various diagrams for sedimentary provenance. Roser & Korsch (1988) reported discriminant functions (DFs) for sedimentary provenance using major-element ratios (Fig. 9a). In one sample (CH34), the $Al_2O_3$ content is very low, resulting in a DF2 value of about 19. For illustration purposes, this sample has been plotted at 10 on the y-axis of Figure 9a. All data lie mainly in the field of quartzose sedimentary provenance and close to or in the field of intermediate igneous provenance. Only one sample from the Upper Unit of Chios lies in the field of mafic igneous provenance.

Floyd & Leveridge (1987) established a discrimination diagram using the La/Th ratio v. Hf to determine different arc compositions and sources (Fig. 9b). Apart from one metapsammite from Inousses that plots near the andesitic arc source field, uniform low La/Th ratios (<5) and Hf contents of about 3.2–7.8 ppm for all the sediments studied here suggest derivation predominantly from an acidic arc source and the minor influence of an old sediment component.

Figure 9c is a plot of Cr/V v. Y/Ni that illustrates the importance of ophiolitic provenance (McLennan et al. 1993). The Cr/V ratio monitors the enrichment of Cr over other ferromagnesian trace elements, whereas the Y/Ni ratio shows the general level of ferromagnesian trace elements (Ni) compared with Y, which is used as a proxy for the heavy REE (McLennan et al. 1993). Mafic–ultramafic sources tend to have higher Cr/V and lower Y/Ni ratios. Only one Permo-Triassic psammite from the Lower Unit and one Permo-Carboniferous psammite from the Upper Unit of Chios tend towards an ophiolitic source (Fig. 9c).

Garver et al. (1996) used Cr and Ni whole-rock geochemistry to identify ophiolitic rock sources. They suggested that values of $Cr >150$ ppm, $Ni >100$ ppm, $Cr/Ni$ c. 1.3–1.5 and a high correlation coefficient between Cr and Ni are diagnostic of ultramafic rocks in the source area, whereas higher Cr/Ni ratios (around 2.0 and higher) indicate mafic volcanic detritus. Cr/Ni ratios of >3.0 for sandstones suggest significant sedimentary fractionation (Garver et al. 1996). The siliciclastic sediments from Chios have Cr/Ni ratios of 2.2–4.4 (Cr 59–154 ppm, Ni 12–61 ppm), those from Inousses 2.5–3.7 (Cr 34–128 ppm, Ni 11–48 ppm) and those from Psara 2.0–2.8 (Cr 68–135 ppm, Ni 27–45 ppm). The Cr–Ni signatures typify an input of mafic volcanic rocks rather than ultramafic rocks from the source area.
Some psammites (e.g. samples CH11, CH34, CH39 and CH70) have been affected by sedimentary fractionation. To identify the input of mafic and/or ultramafic rocks, the chemical compositions of detrital chrome spinel grains were analysed. Detrital chromites are known as provenance indicators of mafic and ultramafic rocks and their chemistry reflects the tectonic setting of source rocks from which they were derived (e.g. Dick & Bullen 1984; Pober & Faupl 1988; Cookenboo et al. 1997; Barnes & Roeder 2001; Kamenetsky et al. 2001, and references therein). The detrital chromite grains analysed here are light brown to dark reddish brown and black with variable major-element concentrations. The observed spread in Cr-number (0.29 and 0.89) and Mg-number (0.24 and 0.70) typifies a mixed (ultra)mafic source of highly depleted peridotites of mainly harzburgite and minor lherzolite composition (Fig. 10a). Except for two grains, all spinels are characterized by low contents of TiO$_2$ (<1.0 wt%) and Al$_2$O$_3$ values between 4.9 and 40.7 wt%, indicating an origin from mid-ocean ridge (MOR)-type peridotites, supra-subduction zone (SSZ) peridotites and island-arc basalts (Fig. 10b). For illustration purposes, five samples with a TiO$_2$ value below the detection limit have been plotted at 0.01 on the $y$-axis of Figure 10b. Few detrital chromite grains have Cr-number $>$0.8, which might be taken to indicate an input of boninitic material (see Dick & Bullen 1984; Barnes & Roeder 2001). Boninites are typical second-stage melts formed in fore-arc regions during the earliest stages of intraoceanic subduction (Bloomer & Hawkins 1987; Duncan & Green 1987; Kostopoulos & Murton 1992) and their presence is indicative of this special tectonic setting.

Figure 11 illustrates the fractionation within the REE in relation to the Eu anomaly. For comparison, the average value for the UCC (data from Taylor & McLennan 1985) is also included. The Eu anomaly in clastic sediments is a good fingerprint for source rock characterization. This parameter reflects changes in a mixture between juvenile crustal influx, without Eu anomaly, characterizing active continental-margin settings, and recycled crustal material, with significant Eu anomaly, characterizing evolved stable cratons (Gao & Wedepohl 1995). The sediments studied here display variable negative Eu anomalies with values in the range of 0.60–0.78 (mean 0.67) for Chios, 0.60–0.65 (mean 0.62) for Inousses and 0.55–0.64 (mean 0.60) for Psara. These values suggest that intracrustal differentiation processes such as partial melting or fractional crystallization had affected the source rocks (see McLennan 1989, for discussion).

The degree of light REE (LREE: La–Sm) v. heavy REE (HREE: Gd–Lu) enrichment is assessed in Figure 11b through the ratio of chondrite-normalized La and Yb values ($La_{N}/Yb_{N}$). Fractionation within the LREE and the HREE is illustrated in Figure 11c and d, respectively. All samples reveal significant LREE enrichment with $La_{N}/Yb_{N}$ c. 7.7 for sediments from Chios, c. 8.2 for sediments from Inousses and c. 9.5 for sediments from Psara. With regard to $La_{N}/Sm_{N}$ ratios, they all fall within a narrow range from 3.1 to 3.8, with the exception of one psammite from Inousses. As for the $Gd_{N}/Yb_{N}$ ratios, all but two samples from Psara range from 1.3 to 1.7, indicating nearly flat chondrite-normalized HREE patterns. Both $Gd_{N}/Yb_{N}$ ratios and Eu/Eu* ratios are similar to the mean values for the UCC. Two pelites from Psara show HREE-depleted patterns ($Gd_{N}/Yb_{N}$ c. 2.1), reflecting fractionation of garnet from the source rocks (e.g. McLennan et al. 1993, for discussion).

Figure 12 shows REE patterns for the analysed sediments normalized both to PAAS (Fig. 12a–e) and chondrite (Fig. 12f–j). The PAAS-normalized patterns are similar for all psammites,
with depleted (<1) LREE and relatively flat HREE. The Early Carboniferous greywackes from the Lower Unit of Chios have HREE concentrations closely matching those of PAAS (Fig. 12c) because of their higher content of phyllosilicate minerals in the matrix. Pelites from Inousses have similar PAAS-normalized patterns to the psammites from the island, and they are enriched in absolute REE abundances relative to PAAS. The patterns of pelites from Psara are more variable, but on the whole similar to PAAS. The depletion of total REE in some psammites (samples CH11, CH27, CH31, IN5, IN6) can be attributed to quartz dilution (Taylor & McLennan 1985), consistent with their high SiO2 contents (71–85 wt%). The chondrite-normalized patterns in all samples show strong LREE enrichment, negative Eu anomalies and flat HREE, the exception being one psammite from the Late Palaeozoic rocks of the Lower Unit (sample CH31) with an indistinct Eu anomaly (Fig. 12h). This sample also has higher contents of Na2O and Sr. A higher Na2O content suggests plagioclase enrichment. Given the fact that Eu2+ and Sr2+ have comparable ionic sizes and that both partly substitute for Ca2+ in plagioclase, a higher Sr content with no concomitant Eu anomaly may reflect input of juvenile crustal material (McLennan 1989; Gao & Wedepohl 1995). The lack of a Eu anomaly probably resulted from concentration of plagioclase in the sand-size fraction during sorting (e.g. McLennan et al. 1990).

In general, according to Bhatia (1985), McLennan et al. (1990, 1993) and McLennan & Taylor (1991), the PAAS- and chondrite-normalized patterns in Figure 12 suggest a derivation from predominantly upper continental crust and/or young differentiated arc material.

**Tectonic setting**

Trace elements with relatively low mobility and low residence time in ocean water, such as La, Th, Zr and Sc, are transferred

---

**Fig. 10.** Compositional data for detrital chrome spinel from Late Palaeozoic and Early Mesozoic clastic sediments of Chios. (a) Cr/(Cr + Al) v. Mg/(Mg + Fe2+) diagram showing the discrimination fields of chrome spinel derived from the two major peridotite subtypes after Pober & Faupl (1988). (b) TiO2 v. Al2O3 diagram showing the discrimination fields of chrome spinel derived from various types of mafic and ultramafic rocks after Kamenetsky et al. (2001). MORB, mid-ocean ridge basalt; OIB, ocean-island basalt; LIP, large igneous province; ARC, island-arc magmas; SSZ, supra-subduction zone.

**Fig. 11.** (a) Total REE content in relation to the Eu anomaly (Eu/Eu*). (b) Fractionation of LREE and HREE in relation to Eu/Eu*. (c) Fractionation within the LREE in relation to Eu/Eu*. (d) Fractionation within the HREE in relation to Eu/Eu*. Fields are after McLennan (1989). The average upper continental crust (UCC; values from Taylor & McLennan 1985) is also included. Symbols are the same as in Figure 7.
quantitatively into clastic sediments during primary weathering and transportation, and are thus useful fingerprints for chemical discrimination of plate-tectonic settings (e.g. Bhatia & Crook 1986). The following settings are generally distinguished: oceanic island arc (OIA), continental island arc (CIA), active continental margin (ACM), and passive margin (PM). In the ternary diagrams of Bhatia & Crook (1986) all psammites plot in the continental island-arc field (Fig. 13a and b), except for one psammite from the Lower Unit of Psara that lies in the active continental-margin field (Fig. 13a) and one psammite from Inousses that plots outside the discriminant fields but close to the continental island-arc field (Fig. 13b). Whereas a continental island arc is by definition an ‘island arc formed on well-developed continental crust or on thin continental margin’ with a provenance of a ‘dissected magmatic arc-recycled orogen’, an active continental margin is formed on a ‘thick continental margin’ and on ‘crystalline basement’ with a provenance of ‘uplifted basement’ and comprises both Andean-type margin and strike-slip type settings (for further details, see Bhatia 1983; Bhatia & Crook 1986). The overall geochemical fingerprints for all analysed psammites suggest a continental island arc as the depositional setting. Thus, based on trace-element signatures, a passive-margin setting and an oceanic island-arc setting can be excluded.

However, sediment geochemistry does not indicate the age of the continental island arc. Remains of an older continental island-arc basement exposed to erosion at a passive margin environment could impart its signature to the whole-rock chemistry of the deposited sediments. Nevertheless, a continental island-arc setting seems the most plausible alternative for the Late Palaeozoic, as geochronological studies of orthogneisses from the Aegean and the surrounding area document a major igneous event between c. 290 and 325 Ma (e.g. Engel & Reischmann 1998, 1999; Reischmann 1998; Özmen & Reischmann 1999; Vavassiss et al. 2000; Reischmann et al. 2001; Anders et al. 2006a, b; Xypolias et al. 2006). Geochemical analyses indicate a volcanic-arc or active continental-margin setting at this time (e.g. Pe-Piper & Piper 2002, and references

Discussions

The sedimentary record of the Late Palaeozoic rocks of the Lower Unit from Chios is the key to understanding the closure of the Palaeotethys Ocean in space and time. These consist of greywackes, minor sandstones and siltstones as well as intercalated quartz-bearing conglomerates containing blocks of massive and well-bedded limestones, cherty limestones, radioliters and volcanic rocks. Petrographical and geochemical analyses reveal no clear differences between Late Palaeozoic clastic sediments from the Lower and the Upper Units of Chios. The Permo-Triassic clastic sediments from the Lower Unit are similar to the Late Palaeozoic clastic sediments. Only the carbonate content of the clastic sediments can provide some means of discrimination. Permo-Triassic clastic sediments from the Lower Unit and Permo-Carboniferous clastic sediments from the Upper Unit commonly have a higher carbonate content than Late Palaeozoic clastic sediments from the Lower Unit, probably because of deposition above the calcite compensation depth (CCD).

For most psammites, high SiO₂ contents (>70 wt%) and low trace-element concentrations indicate typical quartz-rich sources. The significant enrichment in LREE, the negative Eu anomalies and the flat HREE patterns suggest derivation chiefly from old upper continental crust and/or young differentiated arc material. The negative Eu anomalies also indicate that intracrustal differentiation processes such as partial melting or fractional crystallization, involving separation of plagioclase, had affected the source rocks (e.g. McLennan 1989; McLennan et al. 1990). The nature of a mainly acidic (magmatic and sedimentary) source is consistent with petrographical and heavy mineral analyses presented by Neubauer & Stattegger (1995) and Zanchi et al. (2003). Petrography indicates that the source was composed of three main constituents: volcanic and plutonic acidic rocks, low-grade metamorphosed sedimentary rocks and minor (ultra)mafic rocks. According to the discriminant diagrams of Bhatia & Crook (1986), all psammites appear to have been deposited predominantly in a continental island-arc setting. The source rocks were slightly affected by weathering and sediment recyling, indicated by low to moderate Th/U and Zr/Sc ratios and also by high proportions of angular to subangular framework clasts. These observations indicate that (1) the depositional environment was relatively close to the source rocks and (2) the source rocks may be of two types, a continental source (responsible for the quartz and low-grade metamorphic fragments) and a volcanic-arc source (responsible for the amounts of plagioclase and volcanic fragments).

Our new field observations suggest that it might be possible to divide the Late Palaeozoic rocks of the Lower Unit into at least two formations: a lower formation equivalent to the ‘Chios mélange’, consisting of siliciclastic matrix sediments including the olistoliths, and a conformably overlying upper formation consisting mainly of quartzose greywackes and sandstones. Both formations together with the Late Palaeozoic of the Upper Unit may be correlated to the Late Palaeozoic formations on the Turkish Karaburun peninsula described by Stampfl et al. (2003). It appears that remapping of the Late Palaeozoic of Chios is necessary to clarify the tectonostratigraphy of the island.

Inousses

The metasedimentary sequence of Inousses consists of light grey quartzose metaconglomerates, fine-grained grey metapsammites, pyrite-bearing metapelites and platy marble layers or lenses (e.g. Kilias 1987). The metapsammites have high SiO₂ contents (>75 wt%), and low trace-element concentrations typical of quartz-rich sources. The significant enrichment in LREE, the negative Eu anomalies and the flat HREE patterns suggest chief derivation from an old upper continental crust and/or young differentiated arc material. The negative Eu anomalies also indicate that intracrustal differentiation processes, such as partial melting leaving residual plagioclase or fractional crystallization involving removal of plagioclase, had affected the source rocks (e.g. McLennan 1989; McLennan et al. 1990). Generally, the geochemical signature of the metasedimentary succession of Inousses is similar to that of Late Palaeozoic sediments of Chios. The protoliths of this succession derived from acidic magmatic and sedimentary source rocks and were deposited in a continental island-arc setting. The conglomerates probably represent prox-
imal-facies deposits, presumably in a submarine canyon or feeder channel. The crystalline dark limestones (Kilias 1987) may have been primarily transported into a deeper marine environment, probably from the edge of a carbonate platform.

Rock successions similar to those of Inousses crop out on the northern Sporades and Pelion peninsula in central Greece (e.g. Jacobshagen & Wallbrecher 1984). At the present state of knowledge, we agree with the interpretation of Kilias (1987) and correlate the metasedimentary rocks of Inousses with Late Palaeozoic rocks of the Pelagonian nappes in mainland Greece.

**Psara**

Psara can be divided into two metasedimentary units. The Lower Unit consists of turbidite-type dark grey metapelites and phyllites, metasandstones and metagreywackes that were locally intruded by mafic rocks. Some metasediments are slightly carbonate-bearing. The geochemical signature of this unit is similar to that of clastic sediments from Chios and Inousses, indicating a quartzose sedimentary to intermediate igneous provenance. The significant enrichment in LREE, the negative Eu anomalies and the flat HREE patterns suggest derivation predominantly from an old upper continental crust and/or young differentiated arc material. The tectonic setting varies between that of an active continental margin and a continental island arc.

The tectonically overlying Upper Unit consists of garnet-bearing mica schists, calcschists and marbles. The geochemical signature of the mica schists is similar to that of clastic sediments from Chios and Inousses, indicating a quartzose sedimentary to intermediate igneous provenance. The significant enrichment in LREE, the negative Eu anomalies and the flat HREE patterns suggest chief derivation from an old upper continental crust and/or young differentiated arc material. The protoliths of the calcschists and marbles have been chalky sand- and siltstones and limestones, respectively, probably deposited under shallow-water conditions above the CCD.

The metasedimentary units of Psara are most probably an eastern extension of the Pelagian nappes sensu Jacobshagen et al. (1978). We follow the assumption of Wallbrecher (cited by Dür & Jacobshagen 1986) and correlate the clastic sequences of the Lower Unit with the Skihatos Unit of the northern Sporades and Pelion peninsula, whereas the tectonically overlying Upper Unit probably represents a fragment of the Pelagonian marbles.

**Implications for Palaeotethyan evolution**

Our petrographical and geochemical analysis presented here reveals no significant differences in provenance and tectonic setting between Late Palaeozoic and Early Mesozoic clastic sediments from the Lower and the Upper Units of Chios. Furthermore, the metasedimentary rocks of Inousses and Psara have similar petrographical and geochemical characteristics, although lacking evidence for an (ultra)mafic source. It seems that the source area of all sediments remained unchanged from Late Palaeozoic to Early Mesozoic times. We interpret the Late Palaeozoic sediments from both the Lower and Upper Units of Chios as having been deposited along the same Palaeotethyan margin but at some distance from each other, which gave rise to the observed facies variations. The Late Palaeozoic turbidite–olistostrome sedimentation is proposed to have taken place in a continental island-arc environment as a result of subduction of a branch of the Palaeotethys Ocean beneath either Pelagonia (e.g. Stampfli et al. 2003) or Sakarya; detrital zircon ages indicate that basement rocks from the latter supplied detritus to the clastic sediments of Chios (Meinhold et al. 2006). Pelagonia itself is regarded as a Carboniferous magmatic arc formed in an active continental-margin environment (e.g. Vavassis et al. 2000; Reischmann et al. 2001) with the Palaeotethyan suture located at its southern margin (e.g. Vavassis et al. 2000; Stampfli et al. 2003). Sakarya consists of several tectonosтратigraphic units of pre-Jurassic age (e.g. Okay et al. 1996; Ozmen & Reischmann 1999) forming the Sakarya Composite Terrane (Gönçüoğlu et al. 1997) with the Palaeotethys suture also located at its southern margin (e.g. Vavassis et al. 2000; Stampfli et al. 2003).

The source rocks of the detrital chrome spinels in the Palaeozoic sediments of Chios must be sought in the Late Neoproterozoic ophiolitic successions of both MORB and SSZ affinities that occur in NW Turkey (Cele ophiolite; Yıtıbaş et al. 2004) and western Bulgaria–eastern Serbia (Balkan–Carpathian ophiolite; Savos et al. 2001) or equivalents to those that are not preserved. They represent Prototethyan oceanic crust that was accreted to the northern Gondwana margin during the late stages of the Pan-African collisional event. Prototethys represents a peri-Gondwana ocean, the southward subduction of which under the northern Gondwana margin resulted in the diachronous fragmentation of this margin and the opening of back-arc basins from Late Neoproterozoic to Silurian times (Stampfli & Borel 2002). The rifted fragments (Avalonian terranes, Hun superterrane) were eventually transported northward to be accreted to the southern margin of Laurussia. In the case of the Palaeotethys Ocean, ocean-floor spreading resulted in northward drifting of the Hun superterrane and its final amalgamation with the southern Laurussian margin by the Late Carboniferous (Stampfli & Borel 2002; Von Raumer et al. 2003). It should be noted that northward subduction of Palaeotethys under the Hun superterrane had already started by the Early Carboniferous (Stampfli & Borel 2002). Clearly then, we favour a scenario of northward-directed subduction of a branch of the Palaeotethys Ocean beneath the Sakarya microcontinent (terrace) in close proximity to the southern active margin of Eurasia in Late Palaeozoic times. This is in contradiction to Robertson & Pickett (2000), who placed the Chios–Karaburun units at the southern margin of the Palaeotethys Ocean; that is, at the northern margin of Gondwana. However, the Carboniferous foraminiferal fauna of the Chios–Karaburun units shows rather distinct biogeographical affinities to those of the southern Laurussian shelf (Kalvoda 2003). In general, the accretion of Gondwana-derived terranes to the southeastern margin of Eurasia was probably a common feature throughout Tethys history, consolidating, for example, the pre-Alpine basement of the Internal Hellenides (e.g. Anders et al. 2006a; Himmerkus et al. 2006, 2007).

The sedimentological record indicates an upward transition of the Carboniferous turbiditic fan system to more proximal quartz-rich greywackes and sandstones, followed by carbonate-bearing sandstones with increasing intercalations of limestone beds through to thick limestones; it marks a shallowing-upward trend above the CCD and the initiation of a carbonate platform in Permian times (Fig. 14). The sedimentary input of plant fragments indicates proximity to a hinterland with vegetation. The fossil assemblage of the Permian limestones (e.g. Besenek er et al. 1968; Flajs et al. 1996) can be assigned to the ‘Northern Biofacies Belt’ of Altiner et al. (2000), which would indicate an affinity of Chios to the Late Palaeozoic cover sequences of the northern Taurides (Altiner et al. 2000). Benthic Foraminifera and calcareous algae associations suggest that Chios must have been situated at the southern margin of the Sakarya microcontinent in the late Early Permian (Jenny & Stampfli 2000).
illustrates the location of Chios in close proximity to the Sakarya microcontinent in a Late Palaeozoic palaeogeographical reconstruction. During the Late Permian parts of the northern Anatolide–Tauride Block and the basement of the Sakarya microcontinent were covered by the same extensive carbonate platform and the two units were possibly attached to each other prior to the opening of the Izmir–Ankara branch of the Neotethys (Turhan et al. 2004). Furthermore, bearing in mind that the Permian succession of Chios can be correlated with Permian sediments from Pelagonia (e.g. Hydra; see Baud et al. 1991), a novel terrane assemblage emerges at the northern margin of Palaeotethys during the Late Palaeozoic including parts of the northern Anatolide–Tauride Block, the Sakarya microcontinent and Pelagonia (or parts of them) (see Kalvoda 2003, fig. 3; Stampfli et al. 2003, fig. 9a and b). This is in contradiction to palaeogeographical models that suggest a southward subduction of Palaeotethys beneath the northern margin of Gondwana during the Late Palaeozoic (e.g. Şengör et al. 1984; Okay et al. 1996; Xypolias et al. 2006). However, an in-depth analysis of the palaeotectonic and palaeogeographical reconstructions of the eastern Mediterranean region is beyond the scope of the present paper.

In the late Permian (Fig. 15), rifting and extension became dominant, forming, for example, the Karakaya basin (e.g. Turhan et al. 2004, and references therein). This extensional setting was probably accompanied by the development of horst and graben structures. The Late Palaeozoic sedimentary succession of the Lower Unit of Chios was probably situated on a horst structure and therefore partly eroded and redeposited as olistoliths (blocks) in the Karakaya basin. This could explain the absence of Permian rocks in this unit. The Permian of the Upper Unit, however, probably survived in a graben structure. After uplift and erosion, the Palaeozoic successions were unconformably overlain by transgressive Permo-Triassic clastic and late Early Triassic carbonaceous sequences followed by increasing subsidence and volcanism. The Permo-Triassic clastic sediments originated from input of in situ reworked Late Palaeozoic detritus. Detrital zircon ages clearly show an input from the Sakarya basement (Meinhold et al. 2006). Crustal extension continued to the Middle Triassic (see Gaetani et al. 1992) and initiated the formation of new Tethyan back-arc oceans (see Stampfli et al. 2003). The Hallstatt facies of the Early Triassic limestones indicates this rapid deepening (e.g. Baud et al. 1991; Stampfli et al. 1991; Gaetani et al. 1992). However, Chios must always have occupied an external (distal) position to these new oceans because very few tuffitic
horizons occur on the island. The Triassic cover sequence of Chios clearly has a Pelagonian affinity (e.g. Besenecker et al. 1968; Gaetani et al. 1992), whereas the Late Triassic–Early Jurassic succession shows strong affinities to the western Taurides (Rosselet & Stampfli 2003). The latest Triassic–earliest Jurassic emergent horizon of both the Lower and Upper Units of Chios can also be found in the Karaburun peninsula succession (e.g. Robertson & Pickett 2000), in the cover sequences of the Sakarya microcontinent (e.g. Okay et al. 1996; Göncüoğlu et al. 1997) and in the Tauride autochthon (e.g. Robertson et al. 2004); it could either be related to a Cimmerian collision (Robertson & Pickett 2000) or document the opening of a new Neotethyan branch.

We conclude that in Triassic times Chios was probably situated at the passive margin of a microcontinent consisting of Pelagonia and an attached fragment of Sakarya. The latter can be considered as the southernmost or southwesternmost margin of the present-day Karakaya basin. In the Early Jurassic this microcontinent was located close to or became attached to the western Taurides. The metasedimentary sequences of Inousses and of the Lower Unit of Psara are lithologically comparable with the Taurides. The metasedimentary rocks of the Lower Unit are correlated with the formation of the Neotethyan ocean(s). Chios and its surrounding islands of Inousses and Psara most probably represent a link between Pelagonian units in Greece and Sakarya–Anatolide–Tauride units in Turkey.

Conclusions

The new field-work and geochemical data presented in this study have led us to the following conclusions about the provenance, depositional setting and stratigraphic affiliation of sedimentary units from the East Aegean region of Greece.

(1) Geochemical fingerprints of Late Palaeozoic and Permotriassic clastic sediments of Chios are similar and consistent with sediment petrography suggesting a derivation predominantly from acidic magmatic and sedimentary rocks and minor (ultra)mafic input. Detrital chromite chemistry suggests a probably mixed (ultra)mafic source of MOR-type peridotites, fore-arc peridotites, island-arc basalts and possibly boninites. Generally, the sedimentary geochemistry indicates a continental island arc as the depositional setting, probably formed as a result of subduction of a branch of PalaeoTethys beneath the Sakarya microcontinent in Late Palaeozoic time.

(2) The protoliths of the metasedimentary succession of Inousses were deposited in a continental island-arc setting probably in Late Palaeozoic or Triassic times and originated from acidic magmatic and sedimentary sources. This succession is assigned to the Pelagonian nappes of mainland Greece.

(3) The protoliths of the metasediments from the Lower and Upper Units of Psara were deposited in a continental island-arc setting and mainly originated from acidic magmatic and sedimentary sources. The high amount of carbonate in the Upper Unit indicates a shallow marine environment. The very low-grade metasediments of the Lower Unit are correlated with the Skaithos Unit, whereas the more carbonate-dominated Upper Unit is assigned to the Pelagonian marble nappes of the northern Sporades and the nearby Pelion peninsula.

To summarize, the combined analysis of provenance, depositional setting and stratigraphic affiliation of (meta)sedimentary units in the Aegean region indicates turbidite–olistostrome sedimentation in a continental island-arc setting as a result of subduction of a branch of PalaeoTethys beneath Pelagonia and/or Sakarya in Carboniferous times. The final closure of this branch is marked by a shallowing-upward trend in sedimentation in Late Carboniferous and Permian times. Early Triassic rifting marks the formation of the Neotethyan ocean(s). Chios and its surrounding islands of Inousses and Psara most probably represent a link between Pelagonian units in Greece and Sakarya–Anatolide–Tauride units in Turkey.

Funding by the Deutsche Forschungsgemeinschaft and the Land Rheinland-Pfalz through the Graduiertenkolleg 392 ‘Stoffbestand und Entwicklung von Kruste und Mantel’ is gratefully acknowledged. Laboratory facilities at the Max-Planck-Institut für Chemie, Mainz, Germany, as well as at the Department of Afdeling Fysico-Chemische Geologie, K. U. Leuven, Belgium, are gratefully appreciated. G.M. thanks J. Hertogen and R. Meyer for the support and helpful assistance during the REE analyses, and A. Braun and V. Wilde for biostratigraphical investigations. G. Hampson and two anonymous referees are thanked for their helpful reviews and comments.

References


ANGIOLINI, L., CARABELL, L. & GAETANI, M. 2005. Middle Permian brachiopods from Greece and their palaeobiogeographical significance: new evidence for a