For the first time, few detrital augite and pigeonite crystals have been found in the Eocene flysch basins of Istria (Trieste-Koper basin; Italy, Slovenia, Croatia) and Krk Island (Croatia). Their chemistry suggests that they are related to subalkaline rocks (within-plate tholeiites) crystallized at a pressure between 0 and 5 kbar. As a possible source, the nearby basaltic andesites of Ljubač have been taken into consideration. The argument for a Late Tertiary age of the Ljubač volcanics is that no detrital pyroxenes have been found in the Eocene flysch and Oligo-Miocene molasse deposits of the area (Lugović et al., 1998). Radiometric data are not available until now. The detection of detrital pyroxene could be an indication of an older age of the Ljubač volcanics. The presence of similar pyroxenes in the Trieste-Koper and the Krk Island flysch and their absence in Brkini flysch suggest that the basin of Krk was linked with the Istrian basin rather than the Brkini basin.
assemblage comprises pyrite, ilmenite, zircon, tourmaline, garnet, rutile (Malaroda, 1947; Wiesender, 1960; Magdalenič, 1972), anatase, monazite (Wiesender, 1960), staurolite, brookite, chloritoid, glaucophane (Magdalenič, 1972), and Cr-spinel (Wiesender, 1960; Magdalenič, 1972; Lenaz and Princivalle, 1996; Lenaz et al., 2003). This paper reports on the first discovery of detrital clinopyroxene from three outcrops located in the Trieste – Koper (Koštabona, Slovenia, and Koslovici, Croatia) and Krk Island (Croatia) flysch with the goal to find out their possible source. Microprobe analyses of clinopyroxenes have been used to determine the magmatic affinities of the source rock and progressive evolution of the volcanic source as well as to contribute to the unravelling of the tectonic history of this part of the Adria plate.

GEOLOGICAL SETTING

In Early Mesozoic times the Apulian plate was formed as a minor entity between the Proto-Mediterranean and the Western Tethys. The continental rifting caused a Triassic volcanism in the Periadriatic region. Along the Northeastern margin of the Apulian platform, the rifting cycle came to an end during the later part of the Late Triassic (Pamić et al., 1998). The Jurassic period was characterized by seafloor spreading to the west and north of the Adria plate, causing the subduction of Tethys along the eastern border of the Adriatic promontory (Robertson and Karamata, 1994). In Early and Middle Cretaceous times further seafloor spreading occurred so that island arcs and parts of the eastern microplate collided, resulting in two suture zones from which Dinarides originated. In Late Cretaceous, subduction of oceanic crust occurred in the north of the Adria plate followed by collision and formation of ophiolitic complexes. Closure culminated in Late Cretaceous to Early Eocene times (Lawrence et al., 1995; Channell and Kozur, 1997). As a consequence, a nearly continuous belt of Upper Cretaceous to Miocene flysch successions extends from the Southern Alps along the entire outer margin of the External Dinarides.

The Istrian flysch is spread over Italy, Slovenia and Croatia (Fig. 1). It seems that this flysch is divided into two sub-basins: the Trieste-Koper and the Pazin basins are partially separated by the E-W trending Savudrija-Buzet anticline (Bonazzi et al., 1996). The flysch deposits of the Trieste-Koper basin accumulated in a narrow short-living deep-sea trough. Sedimentation started during Lutetian time in the north-western area whereas in the south-east it started in the Late Eocene. A mixed calcareous-terrigenous detritus is more abundant than a pure siliciclastic one. The flysch successions are about 300-350 m thick and are dominated by thin to medium-bedded turbidites in the lower and middle parts, and by medium- to thick-bedded turbidites in the upper part (Marinčič et al., 1996). Marinčič et al. (1996) suggest that feeding of the trough was from the NW.

The flysch deposits of the Pazin basin are mainly represented by calcareous-terrigenous turbidites and, to a lesser extent, by carbonatic megabeds. According to the faunal association, the flysch sequence is assigned to the Middle Eocene (Magdalenič, 1972). A supply from the SE has been established by measurements of linear directional structures; but a lateral sediment input can also be assumed from the lands situated north and northeast of the flysch trough (Magdalenič, 1972).

The relationship of the Krk Island flysch to the Istrian and / or Brkini flysch is not clear. The age of the Krk Island flysch is Upper Lutetian to Priabonian (Bonazzi et al., 1996). According to detrital Cr-spinel chemistry it seems that it could be preferably linked with the Istrian flysch (Lenaz et al., 2003; Lenaz and Princivalle, 2005).

The Brkini flysch basin (Lower – Middle Eocene; Slovenia, Croatia) covers an area between the Julian basin (Maastrichtian – Middle Eocene; Italy and Slovenia) and the Istrian basin (Middle – Upper Eocene; Italy, Slovenia and Croatia). The ratio of marlstone to sandstone bed thickness changes as does the average thickness of the beds and also lithology and sedimentary structures change, sometimes significantly, throughout the stratigraphic column. The sandstone beds are siliciclastic turbidites, the matrix of the usually well sorted sandstones is carbonate (Lenaz et al., 2001 and reference therein).

FIGURE 1 | Sketch map of the Istrian, Krk Island and Brkini flysch basins. Open circles: sampling localities, 1: Koštabona; 2: Koslovici; 3: Krk Island; In the inset: A: Ljubuč late Tertiary volcanics; B: Bovec conglomerate; C: Dinarides; D: Medvenica Mts; E: Požega gora Mt.
Based on the heavy mineral associations of Istrian flysch, Magdalenić (1972) concluded that a large part of the detrital material was derived from the Alps, with only minor contributions from the Dinarides. However, Marinčič et al. (1996) proposed that the entire clastic material was derived from the Dinarides and explained axial flow directions by flow deflection. Lenaz et al. (2003) and Lenaz and Princivalle (2005), according to chemistry and structural parameters of Cr-spinels, suggested that Cr-spinels derived from the Dinarides. However, clinopyroxene was never recognized. This is the first description of detrital clinopyroxenes in flysch sediments from the Trieste-Koper basin and the Krk Island.

METHODS

Several samples were selected from medium-grained sandstones from the flysch sequences cropping out. Pyroxenes have been found only in three samples from Koštabona, Koslovici and in the Krk Island. The most unweathered material was crushed and the 63-200 μm fraction was obtained by sieving. The heavy minerals were examined under the microscope. Only very few pyroxene crystals could be detected. All of them (about 50) were handpicked, mounted in epoxy resin and analysed by electron microprobe using the Cameca/ Camebax electron microprobe (15kV accelerating voltage, 10 nA beam current) at the University of Padova (Italy). Synthetic oxide standards (SiO₂, Al₂O₃, TiO₂, MgO, FeO, MnO, CaO, Na₂O, Cr₂O₃,) were used. Results are considered accurate to within 1-2% for major and less than 5% for minor elements. Raw data were reduced by PAP-type correction software provided by CAMECA. Some selected analyses are presented in Table 1.

RESULTS

All the rocks sampled for this study are classified as lithic graywackes. The main constituents are quartz and calcite; plagioclases, clay minerals and dolomites are of minor content. K-feldspars (microcline), muscovite, chlorite, and biotite are very rare.

The analysed clinopyroxenes from the Istrian and Krk Island basins, detected in the heavy mineral associations, fall in the augite and pigeonite field (Fig. 2). Few variations in the chemistry of augites can be evidenced, even if they show a weak zonation. By comparison, the fields of pyroxenes from Ljubac (Lugović et al., 1998) and from volcanic clasts in the Cretaceous conglomerates of Bovec Detrital pyroxenes in the Istrian Basin Eocene flysch

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Selected chemical analyses of the studied detrital pyroxenes. Analyses No. 1 – 5 from Krk Island; 6 – 8 from Koštabona (Istrian basin); 9 – 13 from Koslovici (Istrian basin). For locations see Figure 1.
are also plotted. The latter differ from the here analysed detrital pyroxenes so that they will not be plotted in the further figures. According to Le Bas (1962), using a SiO₂-Al₂O₃ covariation diagram with the position of boundaries between subalkaline, alkaline and peralkaline magma types, all the pyroxenes plot into the subalkaline field (Fig. 3). This implies that the studied clinopyroxenes were derived from an evolved basaltic magma such as within plate tholeiites (WPT), ocean floor basalts (OFB) or volcanic arc basalts (VAB). In the simplified eigenvector-based discrimination diagram of Nisbet and Pearce (1977) these samples plot in the WPT field (Fig. 4). In Figs. 3 and 4 fields of pyroxenes from the Ljubač volcanics are also reported (see discussion below). According to Leterrier et al. (1982), using a Ti-Al and a Ti-(Ca+Na) covariation diagram the studied pyroxenes fall in the calcalkaline basalts field (Fig. 5A and B).

Nimis (1995, 1999) modeled the crystal structure of more than 200 experimentally synthetized and igneous clinopyroxenes from electron microprobe data. Then, the crystal chemical response of basalt clinopyroxene to increasing pressure was investigated under experimental conditions pertaining to Earth’s crust and uppermost mantle and a variety of fO₂ values and mineral assemblages. The general internal consistency of the simulation data permitted the construction of an empirical geobarometer based on the relationship of cell volume vs. M1-site volume. According to the geobarometric formulation of Nimis (1995), the pressure of formation of the studied clinopyroxenes ranges between 0 and 5 kbar.

**ON THE SOURCE ROCKS OF THE DETRITAL CLINOPYROXENES**

Previous works on detrital Cr-spinels revealed that the flysch sediments of the Istrian basin bear lherzolite and backarc-related spinels as well as reworked spinels (from the Julian and Brkini basins; both located to the north of the Istria peninsula) from the suprasubduction zone of the Vardar Ocean (peridotite spinels with harzburgite affinity, volcanic spinels from back-arc,
island arc and intraplate extrusive rocks) (Lenaz et al., 2003; Lenaz and Princivalle, 2005).

In this paper, a terrigenous supply into the Trieste-Koper and Krk Island flysch basins from the N-NE areas will not be considered because in the heavy mineral assemblages of the Julian and Brkini basins such kind of clinopyroxenes have not been recognised. Only omphacite has been found in the Julian basin (Lenaz and Princivalle, 2002). Therefore, as a possible source for the detrital clinopyroxenes, the ultramafic rocks with their associated amphibolites, and/or some volcanic rocks in south-eastern regions of the Dinarides could be considered.

In the ultramafic rocks of the Dinarides diopside or Cr-diopside have been recognised by Pamić and Mayer (1977). In the associated amphibolites the clinopyroxenes are diopside and diopside with jadeite-acmite content (Pamić et al., 1973).

Volcanic activity has been assumed to be restricted to a few isolated occurrences in the Internal Dinarides near to the Pannonian Basin (Pamić, 1993) and in two unique occurrences of the External Dinarides, in Ljubač and Donje Pazarište (Lugović et al., 1998). As a consequence of subduction of Tethyan oceanic crust, clastic sediments and volcanic rocks were affected by metamorphic conditions of the upper pumpellyite-actinolite to lower greenschist facies during the Eo-Hellenic orogenic phase (160–120 Ma), as well as by a very low to low-grade metamorphism during the late Early Cretaceous (120–100 Ma, Austrian orogenic phase). An island-arc source has been suggested for magmatic rocks in Medvenica Mts. (Croatia). Greenschists from the same areas revealed that an intra-oceanic island arc of possible Jurassic age might have been involved in these tectonics (Lugović et al., 2006). Recently, De Min et al. (2007) described the occurrences of volcanic clasts in the Upper Cretaceous conglomerate of Bovec (Slovenia). These clasts are tholeiites with a strong arc-type signature showing a chemical affinity to the tholeiites from the Internal Dinarides, as well as to all the Jurassic arc magmatism of the Dinaridic-Carpathian region. The pyroxenes of those clasts are mainly represented by micro-phenocrysts of augite (Wo 39-42 En 41-48 Fs 11-20), quite homogeneous in composition, and rare unaltered pigeonites (Wo 13 En 48-49 Fs 37-38) (Fig. 2).

Upper Cretaceous-Paleogene within-plate tholeiites crop out on the southern margin of the Pannonian Basin (Požeska Gora Mt; Fig. 1). These basalts were affected by hydrothermal metamorphism (Belak et al., 1998). Augite is one of the major constituents of these basalts (Belak et al., 1998).

In the volcanic rocks of Ljubač the clinopyroxene are Al-augite with Al-diopside rims. In these rocks pigeonites were also recognised (Lugović et al., 1998). According to the geobarometric formulation of Nimis (1995), the pressure of formation of these clinopyroxenes ranges between 0 and 5 kbar. In the location of Donje Pazarište, pyroxenes show diopsidic compositions.

Chemical analyses (Table 1) show that the studied pyroxenes are pigeonites and weakly zoned augites. By comparison with literature data the detrital clinopyroxenes found in the Istrian Basin are similar to the pyroxenes of the so-called post-collisional volcanic rock of Ljubač (Lugović et al., 1998). Moreover, the location of Ljubač in northern Dalmatia is very close to the studied area of the Krk Island (Fig. 1).

Under these circumstances, ultramafic rocks and associated amphibolites can be excluded as possible sources for the detrital pyroxenes.

The remaining possibilities are as follows:
1. The clinopyroxenes are supplied from volcanic rocks of the Internal Dinarides; these rocks, as seen above, were sometimes affected by Cretaceous low-grade metamorphism; unaltered clasts, probably derived from these rocks, show a pyroxene chemistry different from that observed in the studied pyroxenes.

2. The clinopyroxenes were supplied from small occurrences of rocks similar to those cropping out in Požeška gora Mt. and are now completely eroded and/or lately metamorphosed (Fig. 6).

3. The clinopyroxenes are supplied from volcanic rocks of the External Dinarides, such as Ljubač volcanic. Unfortunately, Lugović et al. (1998) have not performed a radiometric age of these volcanic rocks. The assumed Late Tertiary age has only been determined following the consideration that neither the Eocene flysch nor the Oligocene-Miocene molasse of the region contain clasts of volcanic rocks (Tari-Kovačić and Mrinjek, 1994). Therefore, if the Ljubač volcanics are assumed as a possible source for the detrital pyroxenes in the Istrian and Krk Island flysch, as it is strongly indicated by their chemistry and pressure estimation, then, the age of the volcanics has to be definitely older than Late Tertiary as has been previously supposed by Lugović et al. (1998).

CONCLUSIONS

1. For the first time, detrital augite and pigeonite crystals are recognised in the Trieste-Koper and in Krk Island Eocene flysch basins.

2. These pyroxenes are related to subalkaline parent rocks (within-plate tholeiites; calcalkaline basalts) crystallized at a pressure between 0 and 5 kbar.

3. According to their chemistry it seems possible that their source could be the basaltic andesites of Ljubač in northern Dalmatia. In this case, the assumed Late Tertiary age of these volcanics have to be re-evaluated as probably ?Upper Cretaceous-Paleocene (Fig. 6).

4. An alternative hypothesis is that these pyroxenes are related to within-plate tholeiites similar to those, actually altered, cropping out in Požeška gora Mt. In this case, these pyroxenes are the only unaltered representatives of this volcanism (Fig. 6).

5. The presence of similar pyroxenes detritus in Trieste-Koper and Krk Island flysch and their absence in Brkini flysch suggest, as has already been stated in the case of detrital Cr-spinels, that the basin of Krk was linked with the Trieste-Koper basin rather than with Brkini basin.
6. Due to the scarcity of detrital pyroxenes it could be suggested that the source rocks had a very limited areal distribution.

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