Periodico di Mineralogia (2014), 83, 2, 141-158 DOI: 10.2451/2014PM0008

**PERIODICO di MINERALOGIA**
*established in 1930*

***An International Journal of***
*MINERALOGY, CRYSTALLOGRAPHY, GEOCHEMISTRY,*
*ORE DEPOSITS, PETROLOGY, VOLCANOLOGY*
*and applied topics on Environment, Archaeometry and Cultural Heritage*

# Geochemistry of the Late Mesozoic - Early Cenozoic turbidites from the NE part of the Adria microplate

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## Abstract

Cretaceous to Eocene sandstones from the Southeastern Alps and Outer Dinarides (Italy, Slovenia and Croatia) have been geochemically determined to detect their provenance. The first arenaceous strata of the Julian Basin are strongly chemically influenced by the disgregation of metamorphic and not-metamorphic rock types related to the ancient Vardar sea closure where Island Arc and MORB-like related rock types were generated. At about 56 Ma, one level testifies the strong involvement of continental upper crustal source rocks as a consequence of the rapid arising of the Dinarides. Such contribution is well evidenced also in the Claut basin strata. After this first stage, a new moment of upwelling involved the Julian sediments which contributed, with recycled materials, to the creation of Brkini (and Vipava) basins. Moreover, other protolith rock types, which will represent the main source of the Istrian Basin, begin to be significant.

*Key words*: geochemistry; flysch; SE Alps; Outer Dinarides; Late Cretaceous; Eocene.

## Introduction

Geochemical composition of sedimentary terrigenous rocks is a function of many factors such as (1) source rock composition, (2) weathering, (3) transport (in which several parameters as distance of provenance, flux energy and so on are included) and (4) diagenesis (e.g. Fralick and Kronberg, 1997; Zaghloul et al., 2010; Perri et al., 2008a, 2008b, 2011, 2013). Moreover, metamorphism or hydrotermal alteration can be important in particular geodynamic settings.

Among the terrigenous rock types, turbidites are an important component of sediment that accumulates at the edges of continents and are common in the geological record. For this reason a geochemical study can provide information about the differentiation of supplies from different rocks such as rocks of the upper of the lower continental crust or oceanic crust rocks.

Certain elements (notably REEs, Th and Sc) in terrigenous sediments provide an index of the average composition of the provenance, and it could be possible to trace the composition of the exposed crust through time by studying the geochemistry of terrigenous sediments themselves (see review in Taylor and McLennan, 1985). Among the previous studies on trace element and REE of sedimentary terrigenous rocks there are those of Bhatia and Crook (1986), Nelson and DePaolo (1988), McLennan et al. (1990), McLennan and Hemming (1992), Zhao et al. (1992), Fralick and Kronberg (1997), Henry et al. (1997), Cullers and Berendsen (1998), Schneider et al. (1998), Toulkeridis et al. (1999), Mongelli et al. (2006) and Critelli et al. (2008).

Even if there are important outcrops of Late Cretaceous - Eocene sandstones in the area of the SE Alps and Outer Dinarides the only geochemical study have been performed by Mikes et al. (2006) on sandstones from the NW External Dinarides (Brkini, Vipava and Istrian flysch). They showed that framework constituents of the lithic arenites reveal low-grade metamorphics, acidic plutonic, and to a lesser extent, mafic volcanic and ultrabasic sediment sources, with evidence for a small degree of sediment recycling as well. From the Early Paleogene, extensive sediment mixing occurred in front of the Dinaride orogenic thrust wedge. In the Eocene, a likely source of the mafic-ultramafic detritus was the Jurassic ophiolitic mélange in the NE Dinarides. As far as concern the SE Alps sector no geochemical analyses exists, the most recent studies focusing mainly on the detrital mineral such as Cr-spinels (Lenaz et al., 2000; 2003; Lenaz and Princivalle, 1996; 2005), pyroxene and amphiboles (Lenaz and Princivalle, 2002; Lenaz, 2008) and the petrology of the igneous rock clasts from the Maastrichtrian Bovec flysch (Julian Basin) (De Min et al., 2007). These results, combined with the data on regional ophiolitic complexes and tectonic reconstructions favour the Internal Dinarides as a possible source area for the SE Alps (Claut and Julian Basins) sediments and the External Dinarides for the Istrian Basin where recycling is also possible (Lenaz et al., 2003).

The aim of the present study is to contribute to the evolution of the sedimentary record from the Maastrichtian to Middle Eocene deposition (from turbidites to molasse deposition) in the sandstones of the SE Alps by using trace and REE elements. This data will be compared with those from some turbiditic samples from the Middle - Late Eocene deposits of the Outer Dinarides.

## Geological setting

In NE-Italy, W-Slovenia and NW-Croazia, Late Cretaceous-Eocene times are characterized by the presence of turbiditic deposits indicating the formation and the evolution of several distinct sedimentary basins divided by minor sedimentary units (Figure 1).

The first turbiditic deposits occurred in the

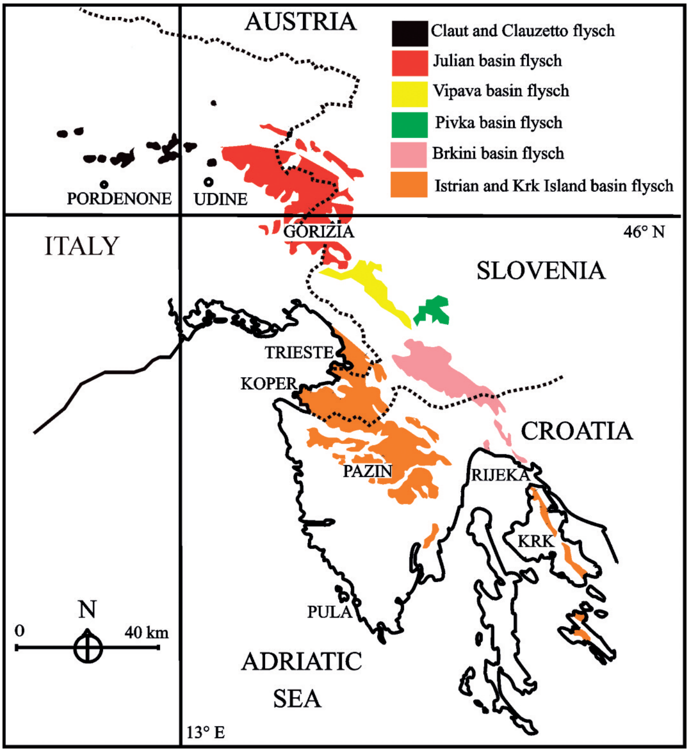

Figure 1. Flysch deposits of the Southeastern Alps and Outer Dinarides (Lenaz et al., 2003).

northern part of the studied region (Table 1) while in the southern part lagoonal deposits, sometimes alternated by bauxites testifying emersion moments, were present (Gregorič et al., 1998; Lenaz et al., 2002). This indicates a progressive northward movement of the continental platform as evidenced by Csontos and Voros (2004) for the evolution of the Pindos Sea.

In the Julian Basin, at first, siliciclastic and calciclastic turbidites associated with megabeds appeared, while deposits related to shallow marine condition (prodelta, front and delta plain; Tunis and Venturini, 1989; Venturini and Tunis, 1991) occurred at the top of the sequence. It is to notice that there is a progressive southernward shifting of the basins so that Vipava and Brkini Basins began their activity when Julian Basin is going to its closure and, similarly the Istrian Basin began after the closure of the Brkini one.

The sources of the siliciclastic sediments of Claut / Clauzetto and Julian Basins are supposed to belong to an alpine domain (Venturini and Tunis, 1992; Kuscer et al., 1974), while Brkini and Istrian Basins paleocurrent data are controversial. For Brkini, Orehek (1972, 1991) suggested supplies from southeastern area while Tunis and Venturini (1996) suggested supplies from the Alps domains also for this basin.

Table 1. Stratigraphic position of the selected samples.

| Stratigraphic Position | Basin | Informal units | Sample |
|---|---|---|---|
| Lower Maastrichtian p.p. | Julian | Drenchia Unit | - |
| “ | “ | Clodig Flysch | JB 5 |
| “ | “ | Iudrio Flysch | - |
| Upper Maastrichtian | “ | Mt. Brieka Flysch | JB 1 |
| Lower Paleocene (Danian) | “ | Calla Flysch | JB 10 |
| Middle - Upper Paleocene | “ | Masarolis Flysch | - |
| Lower Paleocene (Danian) | “ | Grivò Flysch | JB 13 |
| Lower Paleocene (Thanetian) | “ | “ | JB 16 |
| “ | “ | “ | JB 21 |
| Middle Paleocene (Ypresian) | “ | Cormons Flysch | JB 26 |
| | | | |
| Upper Paleocene - Lower Eocene | Claut-Clauzetto | Claut Flysch | CL 1 |
| Lower - Middle Eocene | Brkini | Brkini B. | BK 22 |
| “ | “ | | BK 34 |
| “ | “ | | BK 35 |
| Lower Eocene | Istrian | Istrian B. | K 1 |
| Upper Eocene | “ | Istrian B. | Koslo |
| Eocene - Oligocene (?) | “ | Krk Flysch | KRK 3 |

Data from Ogorelec et al., 1976; Pirini et al., 1986; Tunis and Venturini, 1987, 1989, 1992, 1996; Venturini and Tunis, 1991, 1992; Bonazzi et al., 1996; Grandesso and Stefani, 1996; Marincic et al., 1996.

According to the heavy mineral association, Lenaz et al. (2001) suggested that both the sources could be considered. With regard to the Istrian Basin, Marincic et al. (1996) suggested a north-eastern source, while other authors indicate opposite directions of paleotransport (Magdalenic, 1972; Orehek, 1972) or even a 360° distribution of paleocurrent directions (Marjanac, 1988). In summary, the turbiditic rocks of the studied area testify an approximately 30 Ma long compressive moment that, to the East, can be brought back to the Dinaric orogenesis.

## Stratigraphy

The stratigraphical position of the collected samples and a summary of the ages of the respective flysch units are presented in Table 1. All the samples presented in this work have been previously studied for some aspects concerning the heavy mineral assemblage in Lenaz et al. (2000) (spinels from Julian and Claut basins), Lenaz et al. (2003) (spinels from Istrian and Brkini basins) and Lenaz et al. (2002) (HP-LT minerals).

### *Julian Basin*

Most of the studied samples are from the Julian Basin where the longest period of sedimentation occurred and the stratigraphic sequence is well known. In this area the turbidite deposition began in Maastrichtian p.p. (Ogorelec et al., 1976; Tunis and Venturini, 1984) and closed in the Lower Eocene (Tunis and Venturini, 1987) with delta facies. Several informal units have been instituted in this deposition cycle.

In the Cretaceous there are:

a) Drenchia Unit (Lower Maastrichtian p.p.) beginning with an erosion breccia followed by siltites and calcarenites;

b) Clodig Flysch (Lower Maastrichtian p.p.) characterised by calcarenites and calcilutites with carbonate interbedded. JB5 sample is from this unit;

c) Iudrio Flysch (Lower Maastrichtiano p.p. - Upper Maastrichtian);

d) Mt. Brieka Flysch (Middle Maastrichtian - Upper Maastrichtian) constituted by sandstones, marls, calcarenites and calcilutites. JB1 sample is from the Upper Maastrichtian flysch of this unit where siliciclastic flysch are more abundant.

Paleocene sediments of Julian basin are subdivided in the following units (Pirini Radrizzani et al., 1986):

e) Calla Flysch (Lower Paleocene - Middle Paleocene p.p.) characterised by reddish and greenish marls, carbonate level marls and thin sandstones level. JB10 sample is from this unit;

f) Masarolis Flysch (Middle Paleocene p.p. - Upper Paleocene p.p.) characterised by predominant medium-thick siliciclastic turbidites. Carbonate proximal turbidites and paraconglomerates rich in chert pebbles are interbedded within the siliciclastic turbidites (Tunis and Venturini, 1992).

At the end of the deposition two more unit have been recognised:

g) Grivò Flysch (Upper Paleocene - Lower Eocene; Tunis and Venturini, 1989) constituted by siliciclastic distal turbidites and several carbonate megabeds (Mt. Ioanaz, Mt. Staipa - Topli Uorch, Vernasso e Porzus; Tunis and Venturini, 1987; 1992) attributed to tectonic distensive-transtensive processes supposed to be related to earthquakes for an estimated period of 3 My (Tunis and Venturini, 1992). In the lower (JB13 sample) and middle part (JB16) of the unit distal siliciclastic turbidites prevail while in the upper part (JB21) proximal turbidites appear.

h) Cormons Flysch (Lower-Middle Eocene) where a progressive decrease in paleobathimetry is recognised in good agreement with the vertical changes of the sedimentary structures (Tunis and Venturini, 1989; Venturini and Tunis, 1991). Siliciclastic sediments of this unit are represented by the sample JB26.

### *Claut and Clauzetto Flysch*

In the western part of the studied area (Figure 1) at the same latitude of Julian basin there are small and incomplete sedimentary sequences known as Claut Flysch (Upper Paleocene-Lower Eocene, Venturini and Tunis, 1992; Upper Paleocene, Grandesso and Stefani, 1996), and Clauzetto Flysch (Lower Eocene-Lutetian, Cousin, 1981; Lower Eocene, Grandesso and Stefani, 1996; Tunis and Venturini, 1996). The first one is constituted by proximal siliciclastic turbidites interbedded with calcirudites and megabeds. Sample CL1 is from this formation and according to its stratigraphic position aged about 54 Ma. According to Venturini and Tunis (1991) these deposits could be coeval of the Grivò Flysch in the Julian Basin. The Flysch of Clauzetto lacks of carbonate megabeds and could be related to the Cormons Flysch in the Julian Basin (Venturini and Tunis, 1991).

### *Vipava*

Vipava Basin is located to the SE of the Julian Basin. Pavlovec (1963) and Krasheninnikov et al. (1968) suggested a Lower Cuisian deposition age. Engel (1974) reported for the beginning of deposition an Upper Paleocene age. The sediments are represented by calcarenite and shales intercalated by clastic breccias (Potok and Planina breccia). Tunis and Venturini (1992) argued that these deposits could be attributed partly to the upper section of the Grivò Flysch and partly to the lower-middle section of the Cormons Flysch. For the presence of a very high concentration (about 90 modal %) of carbonates in all the sampled rocks, no sample was selected for geochemical analyses.

### *Brkini*

The Brkini Basin flysch spans from Early to Middle Eocene (Tunis and Venturini, 1996). It is constituted by conglomerate, microconglomerate, biocalcirudite, biocalcarenite, sandstone, claystone and marls (Orehek, 1972). Numerous folds and dissected flysch sections are observed, so, due to strong folding, several small synclines were formed. For this reason the stratigraphic sequence of the flysch of Brkini has never been described as a whole (Pavlovec et al., 1991). Pavlovec et al. (1991) described its basal part while Tunis and Venturini (1996) noticed that the succession continues with siliciclastic turbiditic strata interbedded with calcarenite, sandy carbonate and marl followed by thin interbedded sandstoned and marlstones intercalations. The succession is closed by less than one hundred meters of siltites and fine sandstones presumably representing a molassic sedimentation (Lutetian and/or post-Lutetian; Tunis and Venturini, 1996). Samples BK22 and BK34 are from the lower and middle part of the sequence, respectively. The end of sedimentation in this basin is represented by molasse sediment (BK35) that, according to Tunis and Venturini (1996) could be related in age to the Cormons Flysch.

### *Istrian*

The southern part of the studied area is interested by the Istrian Basin (Middle to Late Eocene; Marincic et al., 1996). It is constituted by two small basins: the Trieste-Koper and the Pazin one (Bonazzi et al., 1996). The flysch deposits of the Trieste-Koper basin accumulated in a narrow short-living deep-sea trough from the Lutetian in the north-western area and from the Late Eocene in the south-eastern one. The flysch deposits are about 300-350 meters thick and are dominated by thin- and medium-bedded turbidites in the lower and middle parts, and by medium- to thick-bedded turbidites in the upper part (Marincic et al., 1996). The flysch deposits of the Pazin basin are mainly represented by calcareous turbidites and, to a lesser extent, by megabeds. According to the faunal association, the flysch sequence is assigned to the Middle Eocene age (Magdalenic, 1972).

The relationship of the Krk Island flysch to the Brkini or to the Istrian flysch is not clear. The age is Upper Lutetian - Bartonian -Priabonian (Bonazzi et al., 1996).

Koslo sample represents the middle part, while K1 and KRK3 represent the upper part of the western and eastern sequence, respectively.

## Methods

The description of primary mineralogy of the sandstones is based on the study of thin sections and X-ray diffraction (XRD) analyses. XRD patterns were obtained on powdered samples spread out on aluminum plates using a STOE D 500 X-ray diffractometer at room temperature at the Department of Mathematics and Geosciences of Trieste University. CuKα radiation was used through a flat graphite crystal monochromator. The current used was 20 mA and the voltage was set at 40 kV. The scanning angle ranged from 2 to 40° of 2θ, steps were of 0.01° of 2θ, and the counting time was of 2 s/step.

The sandstone samples were disintegrated by mortar and ultrasonic treatment. For the chemical analyses, unweathered rocks were crushed in an agate mortar. Major, trace elements and REE composition were analysed by ICP-MS emission at CNRS-CRPG (Nancy, France) (Tables 2 and 3). The analytical uncertainties are estimated to be between 5 and 10% (Govindaraju and Mevelle, 1987).

## Results and discussion

The grain size range from 0.11 to 0.55 mm and the grains do not appear rounded indicating low maturity. Moreover, all the studied sediments optically appear to be quartzolithic sandstones. The modal allumosilicatic/carbonate ratio, calculated for the lithic fragments spans from 0.7 to 1.4. Petrographic observations testified that carbonates are present as the most common matrix and as variable amount of clasts. Quartz is always present while the recognizable feldspars are generally plagioclase with extinction angles of albite twins (Deer et al., 1992) ranging from 0° to 40° to suggest a composition which span from 10 to 70% of anorthite. Phaneritic rock fragments are “granitic” (quartz, plagioclase with low extinction angle ± K-feldspar ± rare chloritized biotite) or “gabbroic” (plagioclase with 15-35° extinction angle ± rare oxide) fabric. Micas (muscovite and biotite) and chlorite are scattered within the sections. In thin section several extraclasts, sedimentary, igneous and metamorphic as dolostones, limestones, radiolarites, chert, vulcanites (diabases), sandstones, quartzites, gneiss, phillytes, low grade schists are present (Venturini and Tunis, 1992).

In the different areas several heavy minerals are present such as apatite, sphene, tourmaline, pyrite, rutile, zircon, garnet, Cr-spinel, epidote, brookite, chloritoide, glaucophane, omphacite, augite and pigeonite (Magdalenic, 1972; Orehek, 1972; Kuscer et al., 1974; Lenaz et al., 2000, 2001, 2003; Lenaz and Princivalle, 1996, 2002, 2005; Lenaz, 2008).

X-ray powder diffraction analyses indicate that all the samples could be represented by five

Table 2. ICP-emission analyses (wt.%).

| | $SiO_2$ | $TiO_2$ | $Al_2O_3$ | FeO | MnO | MgO | CaO | $Na_2O$ | $K_2O$ | $P_2O_5$ | LOI | Σ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| JB1 | 51.90 | 0.77 | 7.02 | 5.25 | 0.21 | 2.46 | 16.21 | 1.30 | 0.88 | 0.25 | 13.69 | 99.94 |
| JB5 | 52.10 | 0.73 | 8.54 | 5.47 | 0.04 | 2.38 | 14.16 | 1.30 | 0.99 | 0.25 | 13.98 | 99.94 |
| JB10 | 51.73 | 0.17 | 2.02 | 2.06 | 0.23 | 2.21 | 22.33 | 0.31 | 0.26 | u.d.l. | 18.89 | 100.38 |
| JB13 | 48.35 | 0.31 | 3.75 | 2.43 | 0.16 | 1.22 | 23.81 | 0.78 | 0.47 | u.d.l. | 19.00 | 100.45 |
| JB16 | 58.79 | 0.21 | 2.11 | 1.22 | 0.05 | 0.51 | 20.67 | 0.40 | 0.31 | u.d.l. | 16.06 | 100.47 |
| JB21 | 53.73 | 0.19 | 2.39 | 2.16 | 0.21 | 2.11 | 20.94 | 0.39 | 0.29 | u.d.l. | 17.51 | 100.11 |
| JB26 | 47.34 | 0.25 | 3.65 | 2.61 | 0.11 | 0.88 | 24.35 | 0.52 | 0.52 | u.d.l. | 18.07 | 98.49 |
| CL1 | 44.32 | 0.33 | 3.93 | 2.52 | 0.05 | 2.20 | 24.19 | 0.45 | 0.74 | u.d.l. | 21.19 | 100.11 |
| BK22 | 68.19 | 0.63 | 9.22 | 3.80 | 0.13 | 1.05 | 6.62 | 1.80 | 1.17 | 0.21 | 7.13 | 99.95 |
| BK34 | 41.63 | 0.40 | 6.65 | 3.26 | 0.10 | 1.36 | 24.89 | 1.00 | 0.97 | 0.22 | 19.95 | 100.43 |
| BK35 | 68.14 | 0.93 | 13.54 | 5.40 | 0.08 | 2.34 | 0.42 | 2.61 | 1.71 | u.d.l. | 4.59 | 99.95 |
| K1 | 62.64 | 0.56 | 9.41 | 3.96 | 0.20 | 1.57 | 8.42 | 1.61 | 1.54 | u.d.l. | 8.66 | 98.68 |
| Koslo | 46.78 | 0.43 | 6.33 | 2.63 | 0.12 | 1.26 | 21.66 | 1.21 | 0.94 | u.d.l. | 18.24 | 99.67 |
| KRK3 | 38.06 | 0.39 | 4.25 | 1.94 | 0.10 | 1.53 | 28.76 | 0.87 | 0.80 | u.d.l. | 22.99 | 99.72 |

u.d.l.: under detection limit.

predominant mineral phases: calcite, quartz, clay minerals, feldspar and rare dolomite. For the Julian Basin it is possible to note a prevalence of silicatic minerals (mainly quartz) in the first deposition events (Maastrichtian) followed by an increase of the carbonatic component during Paleocene time and by a new increase in allumosilicic minerals (mainly feldspar and clay minerals) particularly concentrated in the Grivò and Cormons basins.

For the other basins, the carbonate component decrease moving from the hinterland toward the Adriatic coast.

Notably, mass balance suggests the presence of part of $Al_2O_3$ and $Fe_2O_3$ as colloidal phases.

In general the studied rocks show, for comparable $Fe_2O_3/K_2O$ ratios, an important spread in term of $SiO_2/Al_2O_3$ value and this is particularly evident for the Julian samples which plot as Fe-rich sandstones in Figure 2. Brkini and two out of three Istrian samples plot in the wacke field. The third Istrian sample and Claut sample fall in the litharenite sample. In the inset of Figure 2 the composition of some sandstones from the Vipava, Brkini and Istrian Basins are plotted by comparison (Mikes et al., 2006). Almost all the samples fall in the wacke and litharenite fields. Notably, as already evidenced by Mikes et al. (2006), the studied samples do not show evidence of maturity trends.

As also evidenced by Mikes et al. (2006), the chemical analyses testifies of an allumosilicatic

Table 3. Trace elements and REE chemical analyses by ICP-MS (ppm).

| | JB1 | JB5 | JB10 | JB13 | JB16 | JB21 | JB26 | CL1 | BK22 | BK34 | BK35 | K1 | Koslo | KRK |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| LILE | | | | | | | | | | | | | | |
| Rb | 30.20 | 40.80 | 12.00 | 19.90 | 12.90 | 15.10 | 23.30 | 33.70 | 47.80 | 41.10 | 66.50 | 60.5 | 36.5 | 22.8 |
| Sr | 191 | 222 | 493 | 711 | 373 | 479 | 349 | 508 | 146 | 355 | 61.20 | 161 | 311 | 563 |
| Ba | 120 | 236 | 68.10 | 129 | 152 | 80.20 | 204 | 223 | 165 | 97.30 | 251 | 194 | 139 | 135 |
| Pb | 9.24 | 10.30 | 7.64 | 8.28 | 4.76 | 9.03 | 8.60 | 7.58 | 8.53 | 8.48 | 14.80 | 13.4 | 8.63 | 8.46 |
| HFSE | | | | | | | | | | | | | | |
| Y | 18.40 | 17.60 | 9.97 | 13.50 | 9.80 | 11.10 | 15.00 | 15.50 | 20.60 | 14.20 | 28.00 | 21.2 | 16.6 | 12.0 |
| Zr | 97.30 | 117 | 68.60 | 92.30 | 139 | 107 | 135 | 192 | 352 | 210 | 425 | 138 | 131 | 148 |
| Nb | 4.50 | 6.67 | 2.51 | 3.91 | 3.08 | 2.78 | 3.13 | 5.36 | 8.79 | 5.86 | 13.20 | 8.77 | 6.49 | 6.33 |
| Th | 3.03 | 4.58 | 1.81 | 2.66 | 2.43 | 1.96 | 2.36 | 5.65 | 6.46 | 5.12 | 11.70 | 6.57 | 4.93 | 3.30 |
| Hf | 2.57 | 2.78 | 1.59 | 2.02 | 3.06 | 2.54 | 3.01 | 4.96 | 8.33 | 5.53 | 11.10 | 3.33 | 3.16 | 3.45 |
| Ta | 0.38 | 0.97 | 0.66 | 0.68 | 0.71 | 0.23 | 0.26 | 0.48 | 0.76 | 0.57 | 1.27 | 1.08 | 0.60 | 0.53 |
| Trans. El. | | | | | | | | | | | | | | |
| Sc | 13.60 | 12.15 | 7.28 | 7.91 | 6.85 | 7.23 | 9.44 | 7.95 | 9.12 | 7.31 | 7.77 | 7.12 | - | - |
| V | 122 | 96.80 | 19.40 | 37 | 21.40 | 23.90 | 38.90 | 37.20 | 59.30 | 56.00 | 84.90 | 66.4 | 45.8 | 36.5 |
| Cr | 332 | 165 | 258 | 380 | 710 | 410 | 496 | 331 | 363 | 275 | 758 | 190 | 218 | 418 |
| Ni | 69.40 | 79.90 | 39.60 | 69.90 | 41.20 | 45.20 | 65.50 | 53.70 | 64.70 | 73.30 | 173 | 88.4 | 81.7 | 80.6 |
| Cu | 32.6 | 31.50 | 9.40 | 11.90 | 8.20 | 15.90 | 28.00 | 23.50 | 21.70 | 24.80 | 24.50 | 20.7 | 14.3 | 18.7 |
| Zn | 59 | 79.80 | 19.20 | 46.50 | 22.50 | 19.10 | 27.50 | 32.60 | 47.70 | 39.80 | 64.00 | 63.7 | 49.8 | 31.9 |
| REE | | | | | | | | | | | | | | |
| La | 12.70 | 16.10 | 8.25 | 11.90 | 11.20 | 8.25 | 10.20 | 21.20 | 19.50 | 15.40 | 35.90 | 19.4 | 16.3 | 13.2 |
| Ce | 29.80 | 35.60 | 16.10 | 23.40 | 20.90 | 16.00 | 20.20 | 34.90 | 40.20 | 31.30 | 73.50 | 41.2 | 34.5 | 25.8 |
| Pr | 3.39 | 4.20 | 2.03 | 2.71 | 2.50 | 1.88 | 2.50 | 4.33 | 4.51 | 3.56 | 8.29 | 4.61 | 3.96 | 2.93 |
| Nd | 13.50 | 16.70 | 8.18 | 11.00 | 10.10 | 8.02 | 10.70 | 15.50 | 17.60 | 14.20 | 31.70 | 18.4 | 15.2 | 11.3 |
| Sm | 2.79 | 3.53 | 1.72 | 2.20 | 1.73 | 1.72 | 2.44 | 3.37 | 3.77 | 2.56 | 6.04 | 3.84 | 3.29 | 2.17 |
| Eu | 0.982 | 0.849 | 0.471 | 0.517 | 0.388 | 0.521 | 0.580 | 0.664 | 0.881 | 0.605 | 1.260 | 0.920 | 0.724 | 0.533 |
| Gd | 3.22 | 3.03 | 1.55 | 1.84 | 1.58 | 1.62 | 2.16 | 2.53 | 3.44 | 2.56 | 5.40 | 3.57 | 2.79 | 2.00 |
| Tb | 0.525 | 0.536 | 0.253 | 0.323 | 0.256 | 0.266 | 0.335 | 0.396 | 0.535 | 0.418 | 0.861 | 0.533 | 0.435 | 0.350 |
| Dy | 2.92 | 2.87 | 1.27 | 1.92 | 1.43 | 1.44 | 2.06 | 2.16 | 3.33 | 2.15 | 4.51 | 3.27 | 2.61 | 1.94 |
| Ho | 0.668 | 0.613 | 0.311 | 0.387 | 0.307 | 0.331 | 0.407 | 0.504 | 0.639 | 0.489 | 1.01 | 0.685 | 0.576 | 0.397 |
| Er | 1.60 | 1.60 | 0.799 | 0.997 | 0.826 | 0.799 | 1.16 | 1.32 | 1.77 | 1.46 | 2.77 | 1.75 | 1.43 | 1.05 |
| Yb | 1.61 | 1.83 | 0.657 | 1.06 | 0.797 | 0.836 | 1.12 | 1.30 | 1.95 | 1.46 | 3.10 | 1.63 | 1.39 | 1.02 |

component variably diluted by carbonates (Figure 3). In fact, chemical analyses show that $SiO_2$ and CaO are the most abundant oxides and the percentages are in the range 40-70% and 0-25% respectively, the molasse sample from the Brkini Basin showing the lower value of CaO (0.42 %) due to the lacking of calcite. $Al_2O_3$ is in the range between 2 and 14%. In Figure 3, it is possible to see very good correlations between CaO and $SiO_2$ + $Al_2O_3$ vs. L.O.I., respectively ($Res^2$ = 0.99). Other oxides are in the range between 0 and 6 % (Table 1).

Despite the $CaCO_3$ dilution, it is possible to see as $K_2O$, for comparable $Al_2O_3$ contents, generally increase from the Julian (mean $K_2O/Al_2O_3$ = 0.129) to the Istrian (mean $K_2O/Al_2O_3$ = 0.173). Moreover the samples of the two basins show two distinctive and rather good $K_2O/Al_2O_3$ trend ($Res^2$ = 0.91 and 0.98) suggesting systematic differences in the protolithic sources (Figure 4).

On the contrary, Brkini sedimentary basins, which is temporary and geographically located between the Julian and Istrian ones, mainly show intermediate behaviours, as well as very bad $K_2O/Al_2O_3$ trends (Brkini $Res^2$ = 0.47). This might be related to a partial redeposition of the Julian Basin sediments.

Strong differences between Julian and Istrian basins are also evidenced by trace element

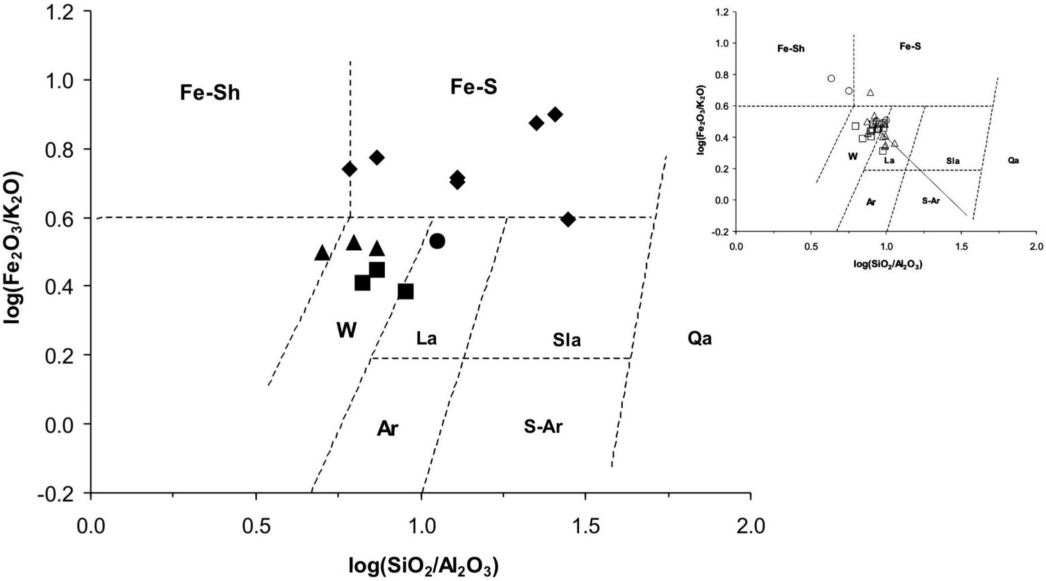

Figure 2. log ($Fe_2O_3/K_2O$) vs log ($SiO_2/Al_2O_3$) classification diagram (Herron, 1988) for the turbiditic sandstones. Full circle: Claut Basin (this study); full diamond: Julian basin (this study); full square: Istrian Basin (this study); full triangle: Brkini Basin (this study). In the inset: open circle: Vipava Basin (Mikes et al., 2006); open triangle: Brkini Basin (Mikes et al., 2006); open square: Istrian Basin (Mikes et al., 2006). Fe-Sh: Iron-rich shales; Fe-S: Iron-rich sandstones; W: wacke; La: litharenites; Sla: sub lithoarenites; Ar: arkose; S-Ar: sub arkose; Qa: quartzarenite. The line represents a trend of maturity as proposed by Mikes et al. (2006).

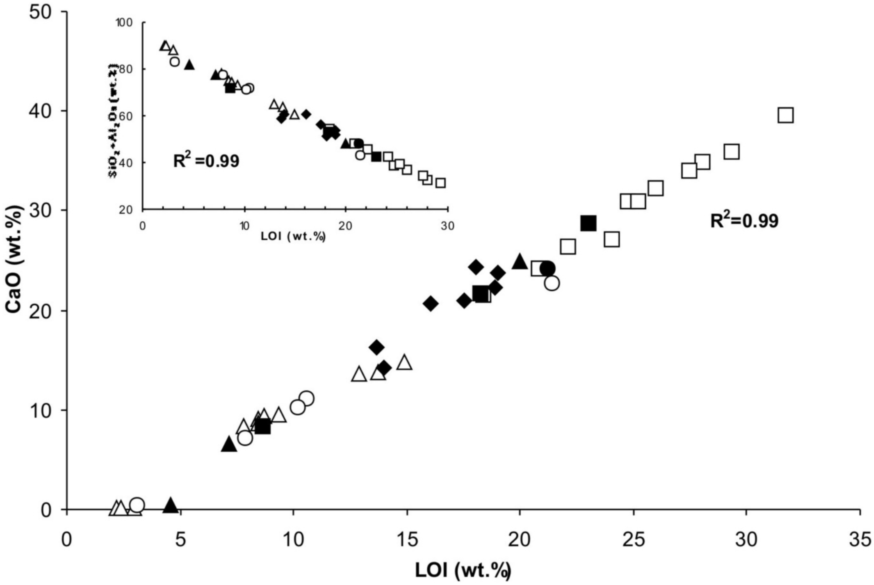

Figure 3. CaO vs. LOI. In the inset $SiO_2 + Al_2O_3$ vs. LOI. Evidence of chemical dilution of Al and Si by the presence of carbonates. Full square: Istrian Basin (this study); open square: Istrian Basin (Mikes et al., 2006); full triangle: Brkini Basin (this study); open triangle: Brkini Basin (Mikes et al., 2006); full circle: Claut Basin (this study); full diamond: Julian basin (this study).

behaviour. The differences between the two basins appear extreme in the Cr/V vs. Y/Ni plot of Figure 5. The increase of the Y/Ni ratio among the Istrian samples could be interpreted as an increase in a granitic component as suggested by Mikes et al. (2006) and by the $K_2O$ vs. $Al_2O_3$ plot, but more probably this ratio indicate a decrease of ultrabasic contribution after the closure of the Julian Basin. In fact, in the Zr vs. Cr diagram (inset of Figure 5) the JB samples show higher Cr content (average Cr/Zr = 3.61 vs. 1.64-1.70) with respect to all the other basins and in particular in comparison with the IB, but show comparable Zr contents.

The variation in the Cr/V value, which is evident only in the JB samples, and reaches in the sample JB16 the value of 33.22 (peridotitic rock types generally span from 2 to 20), probably refer to a concentration of Cr-bearing material.

Important differences in terms of source rocks is suggested by the logNb/logTa plot of Figure 6 (Pfänder et al., 2007). Such strongly substituting elements can not be easily modified by dynamic fractionation (due to variation in the flux energy and/or differences in term of specific weight among the mineral phases), so that their behaviour only reflects the differences of the proto-magmatic sources related to different geodynamic contexts. In the plot, as representative of the protolithic sources, four end -members have been considered:

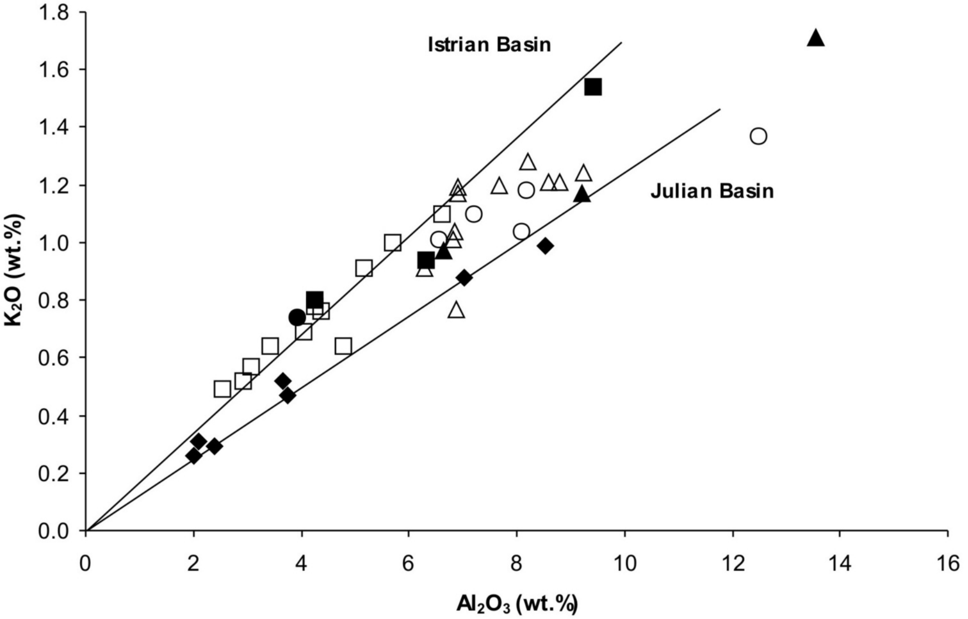

Figure 4. $K_2O$ vs $Al_2O_3$. Symbols as in Figure 3.

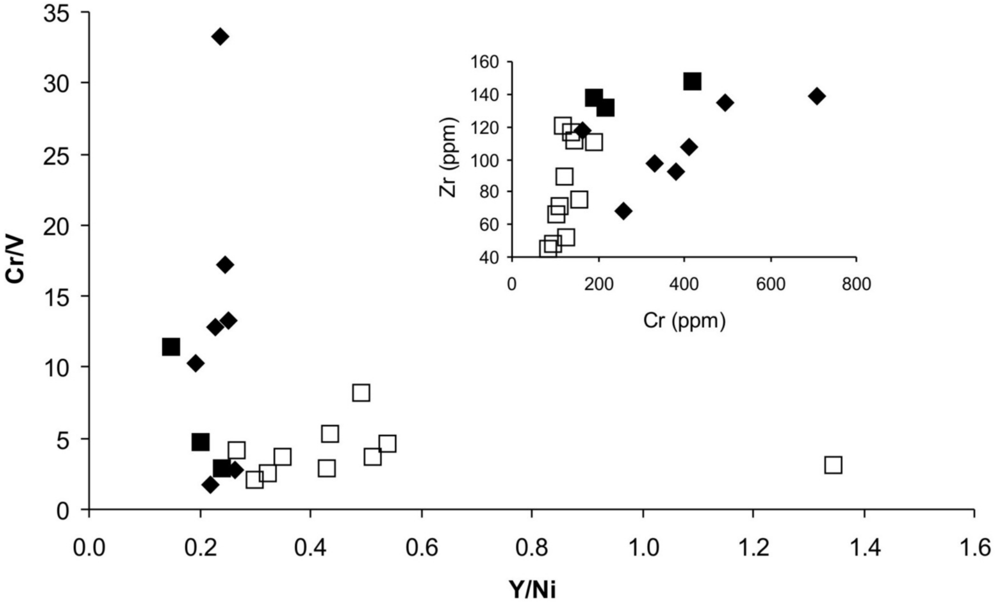

Figure 5. Cr/V ratio vs. Y/Ni ratio. In the inset Zr vs. Cr. Symbols as in Figure 3.

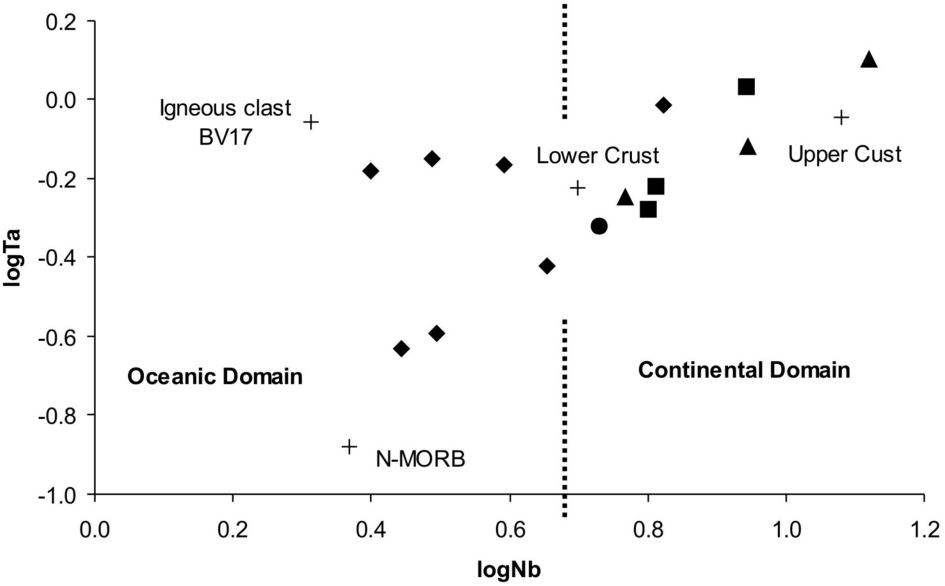

Figure 6. log Nb vs log Ta. Crosses represent the selected end-member of possible protolithic sources: N-MORB (Mc Donough and Sun, 1995); Upper and Lower Crust (Rudnick and Gao, 2004); sample BV17 from De Min et al., 2007. Other symbols as in Figure 3.

the Upper and Lower Crust (Rudnick and Gao, 2004) as indicative of a "continental" domain, the N-MORB (McDonough and Sun, 1995) as indicative of "oceanic floor" and finally a non - metamorphosed basaltic clast found in the Cretaceous flysch of Bovec in the JB as indicative of the Vardar island arc-system (De Min et al., 2007). These last end-members both refer to a generalized "oceanic domain". The selected samples from JB move from both the end-members of oceanic domain and stop with one sample (JB16) in the "continental" domain. In comparison, all the other samples (IB and BK) plot only in the "continental" domain.

Moreover, Nb and Ta behaviour can give good information to discriminate different contribution in term of MORB or ARC rock types from oceanic domains, such elements cannot be easily used to indicate a possible increasing of a granitic component (or better a major involvement of the Upper Crust End-Member) being Nb and Ta mainly hosted inside Mg-Fe silicate and primary oxides. To resolve this fact, more information could be obtained by REE behaviours. In the Eu/Eu* vs La/Sm (normalized to the Upper Crust by Rudnick and Gao, 2004) plot of Figure 7, JB samples generally show high Eu/Eu* values (to indicate the original great involvement of plagioclase) and low La/Sm values as suggested by their "oceanic" nature. Make exception the sample JB16 which well plot (Figure 6), as the quite coeval CL sample, close to the Upper Crust composition. BK and IB samples show intermediate behaviour.

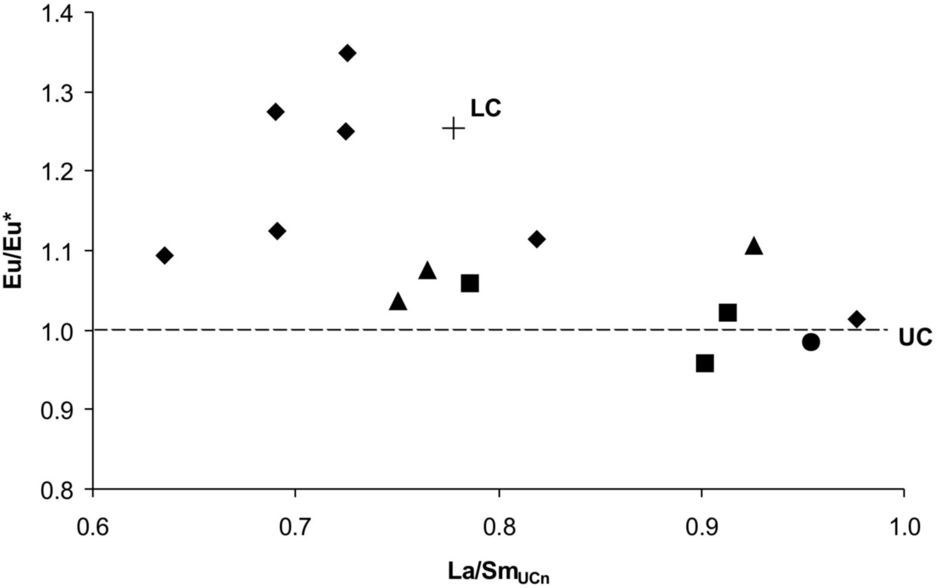

Figure 7. Eu/Eu* vs. La/Sm$_{UCn}$. UC = upper crust (Rudnick and Gao, 2004); Symbols as in Figure 3.

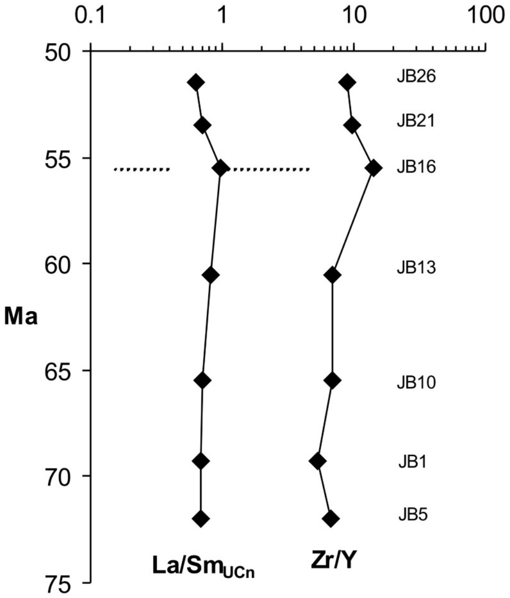

Figure 8. Stratigraphic age vs. La/Sm$_{UCn}$ and Zr/Y ratios for the Julian Basin.

Stratigraphic variations in the sediment chemistry are best considered using the sequence of the JB, where the whole sequence, from the Maastrichtian to the Middle Eocene, is well exposed. The small number of samples does not allowed a detailed reconstruction of the chemical evolution of the basin deposition although several features can be noticed using some elements. In fact, when considering the Zr/Y (Figure 8) ratio it can be seen that it is comprised between 5.3 and 6.9 for the older samples. It corresponds to 14.2 in sample JB16 and it is between 9 and 9.6 for younger samples. The (La/Sm)$_{UCn}$ ratio is below 0.81 for older samples, it is 0.97 for JB16 and lower than 0.72 for younger samples. It is interesting to see that the greater variation corresponds to the sample JB16. Such chemical variation seems to slightly anticipate the paroxistic moment of the Dinaridic orogenesis, supposed at about 56 Ma (Lawrence et al., 1995), as also stated by Lenaz and Princivalle (2002) considering the presence of detrital omphacite and glaucophane in a limited occurrence in a sandstone of the JB. Lenaz et al. (2003) showed that this age corresponds to a change in the chemistry of detrital spinels from suprasubduction-, BABB-type -, island arc- related spinels to MORB-type related spinels.

## Conclusions

The first arenaceous strata of the JB are strongly chemically influenced by the disgregation of metamorphic and not-metamorphic rock types related to the ancient Vardar sea closure where Island Arc and BABB-like related rock types were generated.

At about 56 Ma, the sample JB16 testifies the strong involvement of continental upper crustal lithotypes (possibly the Driva-Ivanjica microcontinent according to the reconstruction by Lenaz et al. 2003) as a consequence of the rapid arising of the Dinarides. A continental upper crustal contribution is well evidenced also in the CL sample, but its source could be different from that supposed for the JB samples due to the presence of staurolite not present elsewhere.

After this first stage, a new moment of upwelling involved the Julian sediments which contributed, with recycled materials, to the Brkini (and Vipava) basin sediments. Moreover, other protolith rock types, which will represent the main source of the Istrian Basin, begin to be significant (Lenaz et al., 2001).

## Acknowledgements

G. Tunis is kindly acknowledged for assistance in sampling and stratigraphy. S. Critelli and one anonymous referee are thanked for their helpful suggestions.

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*Submitted, February 2014 - Accepted, May 2014*