

Article

Trace Element Content and U-Pb Geochronology of Detrital Rutile in the Cretaceous-to-Eocene Julian and Brkini Flysch Basins (SE Alps and NW Dinarides, Italy and Slovenia)

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Abstract

The Cretaceous-to-Eocene Julian (JB) and Brkini (BK) flysch basins have recently been studied for their heavy mineral assemblages; however, the rutile component has so far been neglected. To fill this gap, this study explores their detrital rutile trace element contents and U-Pb ages to define their possible provenance(s). In JB, there are very few rutile grains, mainly related to amphibolite–eclogite facies metamorphic units, with about 80% metapelitic grains. Among the few rutile grains from JB, only eight gave robust U-Pb ages. These ages are all Palaeozoic, resembling those of the closure/opening of the Rheic Ocean and the Variscan orogeny. In BK, the number of rutile grains is much higher than in JB, testifying to differences in the supply areas. The rutile grains are mainly in the amphibolite–eclogite facies, but they decrease, moving upward, accompanied by an increase in UHT. The metapelitic rutile component is higher than 74%. When considering the BK rutile grains, there are no Palaeozoic ages at the bottom of the sequence, while they are newly visible upward. In BK, the most abundant rutile grains show Mesozoic ages that can be considered as representatives of the opening/closure of the Vardar Ocean and the ophiolite emplacement in the Dinarides area.

Keywords: detrital rutile; geochronology; trace elements; flysch



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1. Introduction

Rutile (TiO₂) is an important accessory mineral occurring in a large range of medium- to high-grade metamorphic rocks. It shows high mechanical and chemical stability during weathering, transport and diagenesis [1] making it a prime candidate in provenance studies. Specifically, it is part of the informally named ZTR (zircon–tourmaline–rutile) association of stable heavy minerals. Rutile can incorporate significant amounts of trace elements. The most representative trace elements are Fe, Nb, Cr, V, Zr and Ta [2–7], offering valuable information on the presence of diverse lithologies in the source area as they might be controlled by the protolith composition or by metamorphic conditions [8–12].

Specifically, as there is a strong correlation between whole-rock Nb/TiO₂ and Cr/TiO₂ ratios and the Nb and Cr content in associated rutiles [2], a classification of rutiles into mafic and pelitic host rock protoliths according to their Cr and Nb concentrations was introduced. Also, according to [13], Mg and Al contents can distinguish rutile derived from crustal and mantle sources, and Al, Cr and Nb contents further allow distinction between various mantle-derived rocks such as eclogite, metasomatic rutile-dominated nodules and mica–amphibole–rutile–ilmenite–diopside [14] xenoliths. When elements such as V, Ni, Cu, Sn, Sb and W are detected in high concentrations in detrital rutile, they indicate a source that includes metal ores [8,15]. Moreover, ref. [10] demonstrated that the Zr concentration in rutile is strongly temperature-dependent, so the authors presented an empirically calibrated Zr-in-rutile thermometer later revised by [16]. Finally, in the last few years, U–Pb dating of detrital rutiles has received increased attention [17–25]. For further information on the important role of rutile in provenance studies, the reader is referred to reviews by [10,26,27].

The Julian and Brkini sedimentary basins in the SE Alps and NW Dinarides are two basins spanning in age from Cretaceous to Eocene, characterized by turbidite sedimentation. Several studies dealt with their mineralogy in terms of their main constituents, as well as clay or heavy minerals fractions. Among the heavy minerals, detailed studies have been dedicated to Cr-spinels [28–31], garnets [32], HP-LT minerals such as amphibole and omphacitic pyroxene [33], tourmaline [34], and pyroxene [35]. In 1972, ref. [36] recognized pyrite, opaque minerals, rutile, zircon, tourmaline and garnet in the heavy mineral assemblage of Brkini flysch.

Regardless of the reported presence of rutile in heavy mineral separates, no additional studies have been performed on this mineral in the two basins. This contribution is aimed at filling this knowledge gap by detailed characterization of the amount, trace element content and U–Pb age of detrital rutile in JB and BK basins in order to verify changes in space and time across the two basins, with the ultimate goal of better defining the provenance area(s) of the siliciclastic fraction of the sediment and helping to frame the direction of the turbiditic currents.

2. Geological Setting

The geodynamic evolution of the Peri-Mediterranean area in Mesozoic–Cenozoic times is still debated. Several authors suggest that during the Permian [37,38], the northward subduction of the Palaeotethys under the southern part of the Laurussia formed a mechanism that detached a ribbon-like terrane from northern Gondwana, resulting in the opening of the Neotethys. The subduction rollback created several spreading centres (i.e., oceanic ridges), generally considered to be NW–SE–elongated, i.e., Meliata, Maliac, and Pindos [39] or Vardar and Pindos [40]. In particular, the Meliata rift might have affected the continental plate from the Balkans to northern Italy (Ivrea), where Permian basic magmatism is widespread [41]. On the contrary, refs. [42–45] suggested that the Triassic Eastern Tethys was formed by a single branch. These authors use the term “Neotethys” to describe all oceanic realms located in an area southeast of the Alpine Tethys and the future Western Alps that opened during and after the Permian-to-Triassic closure of the Palaeotethys. The breakup of Pangea started in the Late Triassic and could be due to the restart of the extension in the Ionian basin, which linked the Atlantic and Atlas extensional system with the rifting of the Anatolide–Tauride platform ([46] and references therein). The opening of the Atlantic Ocean during the Toarcian [47] led to a rotation of the Adria Plate with respect to the Eurasian terranes, determining spreading in a northwest–southeast direction between the two, while the Vardar zone ridge segments were constrained by the Cimmeria alone. The difference in movement between the Adria and Vardar plates suggests that a

new extension formed along Gondwana that led to the formation of several basins (the Hallstatt, Belluno and Bosnian Troughs and the Inner Tauride Ocean; [48–51]). The opening of the Atlantic Ocean was also the driver for a new pulse of subductions in the Neotethyan basins in the Early–Middle Jurassic; the remnants of these subductions are now found in the Alpine mountain belts of the Mediterranean region (Dinarides, Hellenides and Rhodopes). At the end of the Cretaceous–Early Palaeocene, the Peri-Mediterranean and Central European realms were formed by several microplates separated by small oceanic domains [52]. The Palaeocene movement of the Adria Plate toward the north generated a build-up of compression in the Alpine, Western Carpathian and Dinaridic orogenic systems [53–57], triggering the westward to southwestward propagation of the Dinaridic orogenic wedge. The evolution of the orogenic system occurred simultaneously with a NW–SE-oriented dextral shear along the easternmost segment of the Periadriatic Fault, which separates the Central Western Carpathians and units of the Northern Pannonian [52]. The Early and Middle Eocene were also characterized by reactivation of the left lateral strike-slip fault between Adria and Apula s.s. and the right lateral fault zone within the Dinaric domain [46], which was responsible for the northwestern drift of the Adria Plate and its subduction beneath the Pannonian block. During the Late Eocene, the lateral movement among Adria, Apula and Dinarides areas stopped, and the first two reached their present position with respect to each other. Coevally, a compressional deformation occurred within the Dinarides zone, registering the main deformation of the orogeny. During this phase, the outlying basins were continuously filled by turbidite sediments.

According to [58,59], in the Julian basin (JB; sometimes described as the Slovenian Trough) the deposition of the turbiditic sequence started during the Late Cretaceous and continued until the Early Eocene (Figure 1) as a mixed siliciclastic–carbonate turbiditic sequence with a total thickness of about 4000 m. Miklavič and Rožič (2008) [60] suggested the siliciclastic turbidites alternated with carbonate strata from the Dinaric carbonate platform during regression so that several carbonate megabeds are present [61–63]. References [34,64] classified them as lithic greywacke, recognizing quartz and calcite as the main constituents, followed by plagioclases, clay minerals and dolomites. Microcline and micas are very rare. Among the lithic fragments, dolostones, limestones, radiolarites, cherts, diabase, sandstones, quartzites, gneisses and low-grade schist have been recognized.

The Brkini basin (BK) (Figure 1) was formerly a synform basin located in southwestern Slovenia, where sedimentation was active from the Late Palaeocene, but flysch and molasse material filled the basin during the Early–Middle Eocene to a thickness of about 1000 m [65]. In the literature, the Brkini succession has never been described in its entirety due to the presence of several faults dissecting the sequence. Orehek (1972) [36] studied the basal part, while [65] focused on its upward continuation that is composed mainly of siliciclastic turbiditic strata. Specifically, ref. [65] described the stratigraphy of BK in several segments comprising basement strata composed by an underwater landslide, which could be related to a large calcirudite–calcareenite block, representing the only re-sedimentation episode of the coeval part of the JB flysch; terrigenous turbiditic deposits (with the presence of large calcareous blocks) embedded with calcarenite strata showing a fining-upwards granulometry, becoming marls with a strata thickness of over 10 m; an alternation of fine sandstones and marls; a marl–arenaceous flysch rich in bioturbation with the insertion of frequent hybrid turbiditic strata and bio-calcareenites; conglomerates related mainly to distal terrigenous turbidites and hybrid turbiditic strata; a series of distal terrigenous turbidites rarely interrupted by thin calcarenite strata; and a thickening of the arenaceous fraction with the presence of the first thick conglomeratic sandstone strata. The basin ends with grey-yellowish silt strata and silty marls, which are overlain by thin poorly cemented sandstones with a thickness of ~100 m.

The studies of [36,66] indicate signals of palaeocurrents with mainly northwesterly and partially westerly flow direction, suggesting the basement rocks buried in the Adriatic and Gorski Kotar areas as possible sediment sources. On the contrary, ref. [65] observed several flute casts suggesting opposite directions, similar to those measured in the Cormons area (Italy), Dornberk and Ajdovščina (Slovenia). These authors also agree with the possibility of a palaeogeographic link between the Brkini basin and those located in the nearby western area.

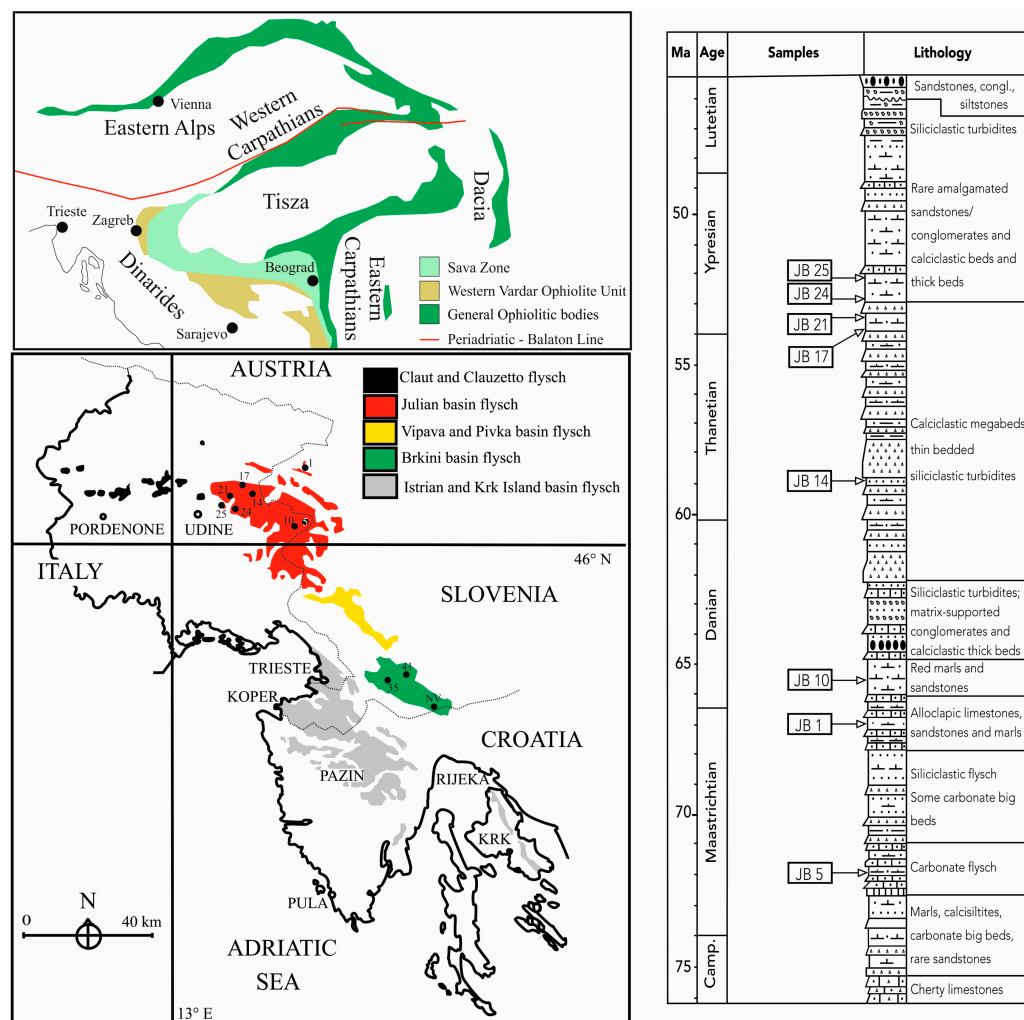


Figure 1. (left above) Main geological units and the main ophiolitic bodies in the area according to [67]. (left below) Flysch basins of the SE Alps and (right) stratigraphic column of the Julian basin with sample positions [68]. No continuous stratigraphic column is available for the Brkini basin (see text for details).

3. Materials and Methods

Seven samples from the Julian basin were selected according to their inferred stratigraphic age: JB5 is Maastrichtian; JB10 is Danian; JB14 is Thanetian; and JB17, JB21, JB24 and JB25 are Ypresian (Figure 1). Three samples from the Brkini basin were selected, considering that their Cr-spinel and garnet content has been already studied. BK41 is from the base of the sedimentation cycle in Brkini, BK35 is from the top and BKNV represents the molasse facies closing the sedimentation in the basin.

As described in [34], the rocks were crushed in a mortar; then, the heavy minerals were concentrated using sieving and heavy liquids (sodium polytungstate Na₆(H₂W₁₂O₄₀)) at

the Department of Earth and Environmental Sciences of Bicocca University in Milan. Rutile crystals were identified via optical microscopy and hand-picked for further analyses.

3.1. Raman Spectroscopy

Triebold et al. (2011) [69] demonstrated that trace element contents in rutile, anatase, and brookite differ systematically, so that the Zr-in-rutile thermometry and lithology discrimination based on trace elements would lead to serious mistakes in provenance interpretation. In this context, Raman spectroscopy allows clear and fast identification of the individual TiO₂ polymorphs.

The Raman spectra were collected at the University of Trieste using Oxford Instruments devices—a WITec alpha300 apyron R Raman microscope, equipped with an ultra-high-throughput monochromator (UHTS 300S VIS) with a focal length of 300 mm, and an Andor DV401_BVF CCD detector, cooled to −60 °C.

For the large-area scan (2D map), the 532 nm laser had 11 mW at the sample, the grating used was 1800 g/mm (blazing at 500 nm), and the objective used was a Zeiss EC Epiplan-Neofluar (20×, NA 0.5). An area of 240 × 210 (x × y) micrometres was mapped as a 42 × 48 point xy map (one grid point, i.e., spectrum, every 5 microns), for a total of 2016 spectra. The integration time was 0.5 s per each spectrum (i.e., grid point).

For the analysis of the 2D Raman maps, data were first processed and analysed with the WITec Project SIX 6.1 software, using the True Component Analysis menu, with 5 components (1 of which was the spectrum embedding resin).

3.2. U-Pb Dating and Trace Element Analysis

The trace element contents and U-Pb isotopic composition of rutile were analysed in tandem at ETH Zürich, Switzerland, by laser ablation–inductively coupled plasma–sector field–mass spectrometry (LA-ICP-SF-MS) using a RESolution S-155 (ASI/Applied Spectra) 193 nm ArF excimer laser system attached to an Element XR (Thermo) sector field ICP-MS. Ablation was executed in a dual-volume, fast-washout S-155 ablation cell (Laurin Technic) and fluxed with a carrier gas (ca. 0.25 L/min He) followed by a make-up gas (ca. 1 L/min Ar and 2 mL/min N₂). Before introduction into the ICP-MS, the ablated aerosol was homogenized by flushing through an in-house squid device. The instrument was optimized for high sensitivity on Pb, Th and U masses whilst keeping production of oxides ($^{248}\text{ThO}^+ / ^{232}\text{ThO}^+ \leq 0.25\%$) low and the U/Th ratio at ca. 1 (on NIST SRM612 glass; [70]). We used a spot size of 29 µm with a laser repetition rate of 3 Hz and a laser energy density on the surface of ca. 3 J/cm². Before each analysis, the sample surface was cleansed by three pre-ablation pulses; measurements for U-Pb dating and trace elements typically consisted of 28 s background acquisition followed by 30 s of sample ablation. Detailed information on the equipment, instrumental conditions and set of isotopes used during analyses is given in Table S1 in the Supplementary Material File.

Trace element abundances were quantified in Iolite (version 4.10; [71,72]) via conventional standard-sample bracketing (Trace Elements Data Reduction Scheme) using the synthetic glass standard GSD-1G as primary reference material [73]. As an internal standard, we used isotope ⁴⁹Ti and assumed a concentration of 59.94 wt.% based on rutile stoichiometry. To validate the accuracy and reproducibility of the trace element analyses, we used NIST610 glass [70] and the rutile R10 [74]. Calculated mass fractions for selected elements from R10 (including, Cr, Nb, and Zr) are within the range of mass fractions presented in [74] and overlap with 2SD with the provisional values of [74]. The complete set of trace element data, including uncertainty and limits of detection for unknowns and reference materials, are provided in Tables S2 and S3 of the Supplementary Material File.

The resulting intensities on isotopes ^{202}Hg , ^{204}Pb , ^{206}Pb , ^{207}Pb , ^{208}Pb , ^{232}Th , ^{235}U and ^{238}U were processed offline in Iolite (ver 4.10; [71,72]), using the VizualAge Ucompbine data reduction scheme for U-Pb dating [75]. The rutile reference material R10 (1090 ± 5 Ma; [74]) was used for calibration of the U-Pb isotope ratios, whilst R13 (504 ± 4 Ma, [76]) and WOD-B (in-house) were used as quality control materials. As the resulting isotopic intensities revealed a significant component of non-radiogenic (i.e., common) Pb, a correction was applied to both the reference materials and detrital rutile grains using the ^{208}Pb (no Th) approach, using the common Pb model of [77]. The same correction was applied to all analyses, and it was assumed that no thorium was present in the analysed rutile [78]. However, several analyses were characterized by thorium counts above the background, which might have led to an overestimation of the common Pb correction and thus resulted in negative $^{207}\text{Pb}/^{235}\text{U}$ ratios, especially in low-U grains (see also [19]). Another characteristic of our dataset is the substantial variability of the common Pb component (tracked by the $^{206}\text{Pb}/^{208}\text{Pb}$ ratio; [78]), which can be predominant in a given analysis, thus leading to inaccurate and imprecise corrected ratios. Given these shortcomings, and to ensure that only U-Pb dates that are accurate and precise were considered, we established a set of screening criteria which included U content (>1 ppm), Th content ($^{232}\text{Th}/^{238}\text{U} < 0.5$) and common Pb component ($^{206}\text{Pb}/^{208}\text{Pb} > 0.5$). Only ^{208}Pb -corrected ratios of analyses that fulfilled this set of criteria were considered robust and used to calculate $^{207}\text{Pb}/^{235}\text{U}$ and $^{206}\text{Pb}/^{238}\text{U}$ single grain dates. The final quoted 2s uncertainties for these dates include: (i) the uncertainty of the common Pb ratios for the common Pb correction, (ii) the uncertainty for the decay constant, (iii) the uncertainty of the ratios for primary and secondary reference materials, and (iv) the long-term excess variance (sensu [79]). The full dataset, including uncorrected and ^{208}Pb -corrected U-Pb ratios for unknowns and rutile reference materials and calculated $^{207}\text{Pb}/^{235}\text{U}$ and $^{206}\text{Pb}/^{238}\text{U}$ dates using IsoplotR [80], is provided in Tables S2 and S3 of the Supplementary Material File.

3.3. Statistical Elaboration

Several multivariate statistical methods were used to explore the combined U-Pb and trace elements dataset in order to find homogenous groups. Clustering is a common technique used for grouping samples that are most similar to each other and less similar to samples belonging to other clusters. The similarity criterion can be based on distance (e.g., Euclidean distance) between samples in a given space or it can be based on similarity/dissimilarity coefficients (e.g., correlation coefficients). The relationships between the variables or observations can be graphically expressed using a dendrogram [81]. Principal component analysis (PCA) is a multivariate statistical method used to simplify complex datasets by using fewer variables to represent significant information. This is accomplished by creating new variables, called principal components, which are linear combinations of the original variables, and summarising the main features of the data [81]. The first principal component (PC1) is determined by fitting a regression line that best represents the direction of maximum variance, minimizing the residuals. The second principal component (PC2) is constructed so that it is perpendicular to, and statistically independent from, PC1 and denotes the next greatest direction of variance. Each additional component explains progressively less variation in the data [82]. The resulting plot combines loadings and scores, with PC1 on the x-axis and PC2 on the y-axis. The term loading describes how variables are represented or distributed along the two principal components (PC1 and PC2), whereas the score refers to how the samples are arranged or positioned within this component space.

In this study, the main variables used in the cluster analysis and PCA were the concentrations of trace elements (Mg, Al, Sc, V, Cr, Fe, Zr, Nb, Sn, Sb, Hf, Ta, W, and U) and rutile crystallization temperature as determined by a Zr-in-rutile geothermometer [10,16].

To prevent significant distortion, element concentrations below the detection limit were excluded, with a total of 121 individual analyses included out of a total of 129. Cluster analysis was performed using Ward's hierarchical agglomerative method and Euclidean distance as the similarity criterion.

Before performing the statistical analysis, the original geochemical data were subjected to pre-processing: a logratio transformation (Log_{10}) and standardization by means of the z-score method were applied. Logarithmic transformation reduces the impact of outliers and standardization brings all variables to a common scale (mean 0 and standard deviation 1) to ensure that all trace element concentrations were equally weighted. The Kaiser–Meyer–Olkin test was applied combined with Bartlett's Test of Sphericity to verify the suitability of the data for principal component analysis (PCA) and to ensure that the results are meaningful and reliable. All statistical calculations were carried out using the "R" software ver. 4.4.1 [82].

4. Results

4.1. Trace Element Variations

Following Raman analyses, all the mounted crystals were found to be rutile, except one which was a mixture of rutile, anatase and sphene (Figure 2). A total of 170 rutile crystals were analysed for age determination and trace element composition from JB and BK. Among the heavy mineral assemblage, 21 rutile grains were found across the eight JB samples. For this reason, we decided to group all JB rutile grains, considering them as one group (i.e., JB). On the contrary, rutile is very abundant in BK samples, so that 149 crystals out of 3 samples were analysed. The difference in abundance is comparable to that identified by [34] for tourmalines from the same samples (56 tourmaline crystals in JB vs. 184 crystals in BK).

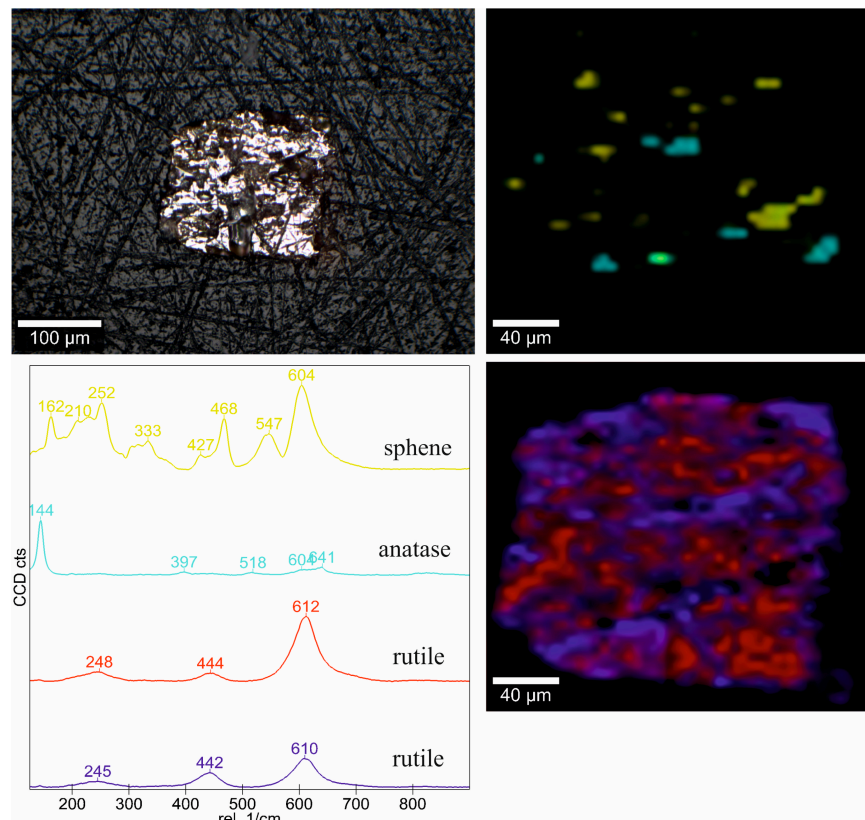


Figure 2. (Left top) image of the grain; (right top) Raman map of the anatase and sphene parts; (left bottom) Raman spectra of the different parts constituting the grain (colours as in the maps); (right bottom) Raman map of rutile.

In our samples, when considering abundances of trace elements commonly used for provenance studies (i.e., Mg, Al, Cr, Nb, Fe, V, Ta, W and Zr), no major differences were detected (Figure 3).

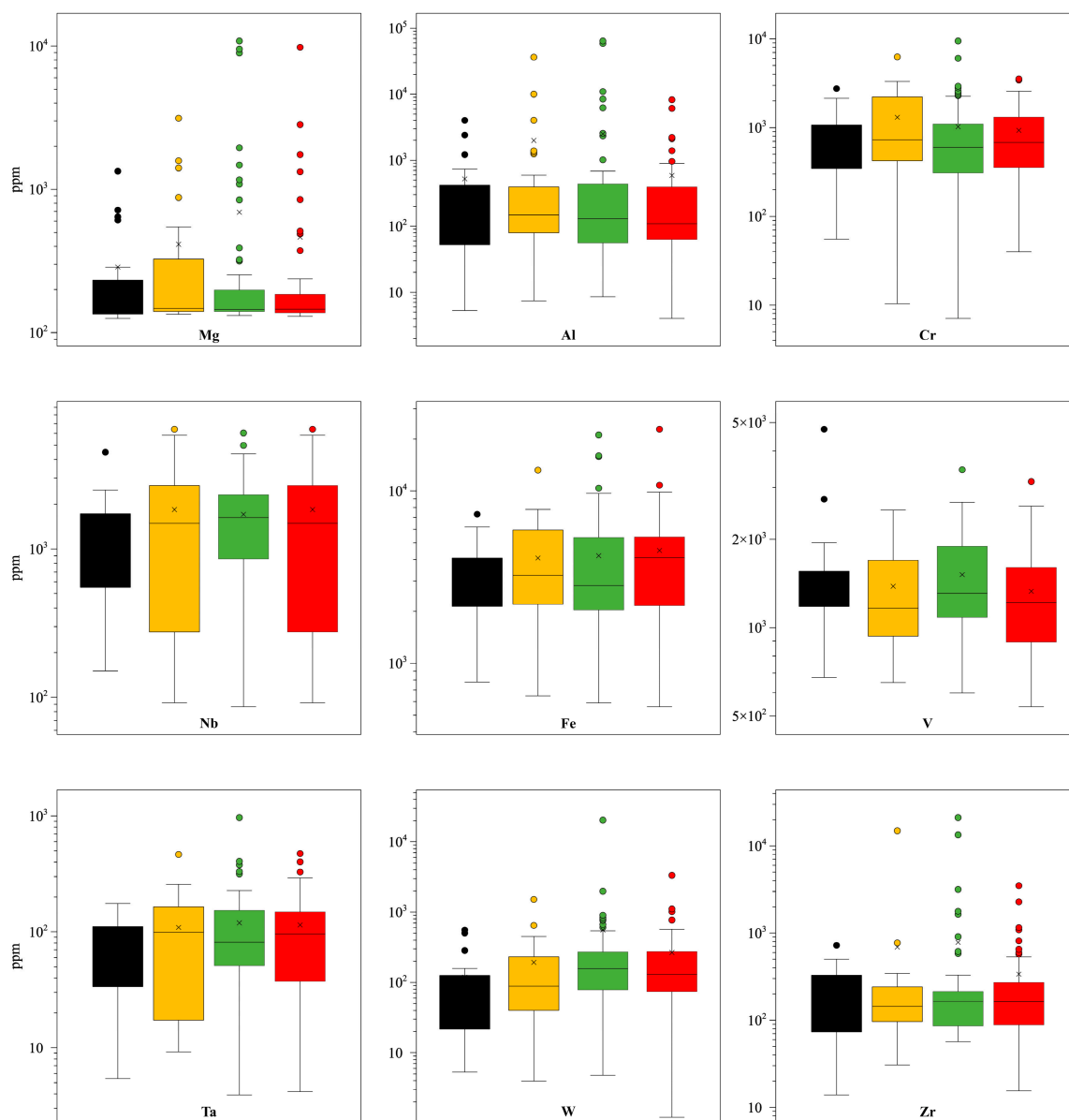


Figure 3. Comparison of rutile trace element compositions (Mg, Al, Cr, Nb, V, Fe, Ta, W and Zr) in JB (black box), BK41 (orange), BK35 (green), and BKNV (red) samples.

4.2. U-Pb Geochronology

Out of the 21 analysed JB grains, only eight provided robust $^{206}\text{Pb}/^{238}\text{U}$ ages after ^{208}Pb correction, ranging from the Ordovician to Permian (476 to 264 Ma, only one being Mesozoic; Figure 3). In BK, 57 robust ages were obtained, covering a temporal interval between about 675 and 79 Ma; the largest amount of rutile grains in BK is Mesozoic (67%–93%), followed by Palaeozoic (0–29%) and Precambrian (0–7%) ones. Two Precambrian rutile grains were found in BK41 and BK35 samples (one each). No Palaeozoic rutile grains are present in BK41. It is important to notice the difference between JB rutile grains (almost all Palaeozoic) and those from BK41 (almost all Mesozoic and not one from the Palaeozoic) (Figure 4).

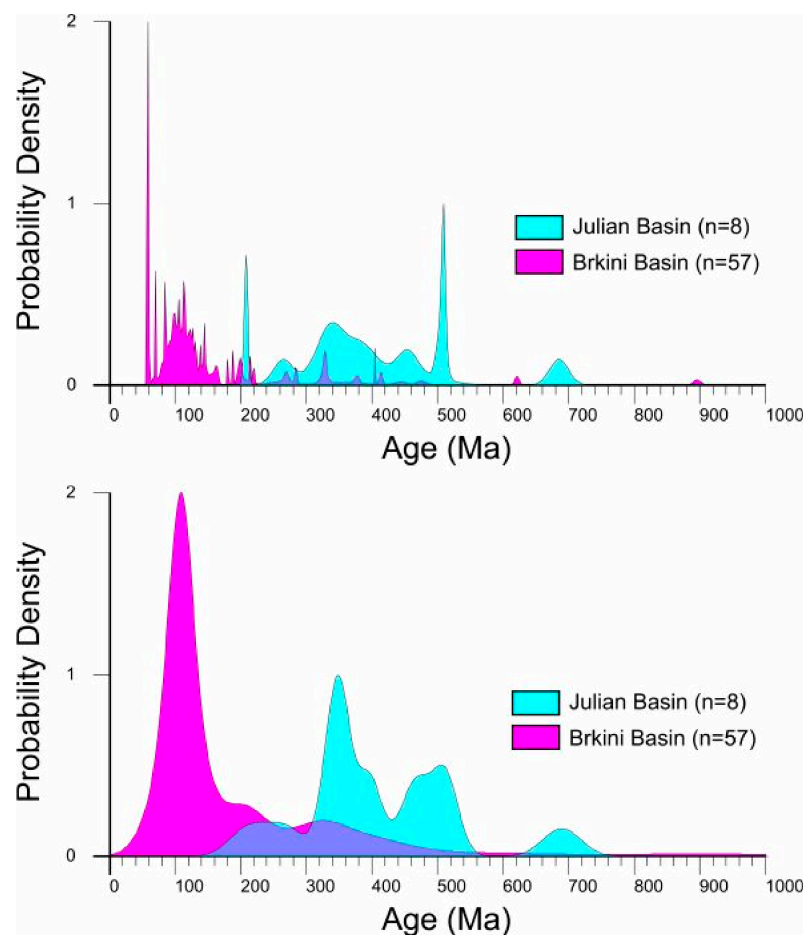


Figure 4. Probability density plot (**above**) and Kernell diagram (**below**) with age distribution for JB and BK basins.

5. Discussion

5.1. Provenance—Trace Element Considerations

According to [9,16] the Zr-in-rutile geothermometers suggested temperatures of crystallization varying between 326 and 1263 °C and 446 and 1200 °C, respectively (Figure 5). Considering the two basins, JB crystals yield temperatures between 326 and 1099 °C and 445 and 972 °C according to different thermometers ([9,16], respectively), while those from BK are in the ranges of 340–1263 °C [9] and 451–1200 °C [16]. Generally, the two methods show good agreement for intermediate temperatures, while major differences appear at the highest temperatures. A simple comparison between the [9] and [16] geothermometers shows that the percentages of rutile crystals assigned to the different metamorphic facies slightly differ with an increase in rutile from granulite/HT eclogite using the Zack thermometer (Figure 5). Considering that several authors [28–30] suggested the Dinarides as a possible source area for these sandstones on the basis of Cr-spinels chemistry, we focused on possible rutile sources in that area to decide which geothermometer should be used. References [83–85] recorded temperatures up to 1000 °C in the metamorphic soles of the ophiolitic zones, so we decided to use the [9] thermometer for higher temperatures.

According to [22], facies boundaries are taken from the lower pressure end of the facies diagram in [86]. Figure 5 shows that, in both basins (JB and BK), the major supplies are from amphibolite–eclogite facies rocks, whereas only sporadic supplies came from other facies. Only in the youngest sample (BKNV) is there a noticeable supply from granulite–HT eclogite occurrences.

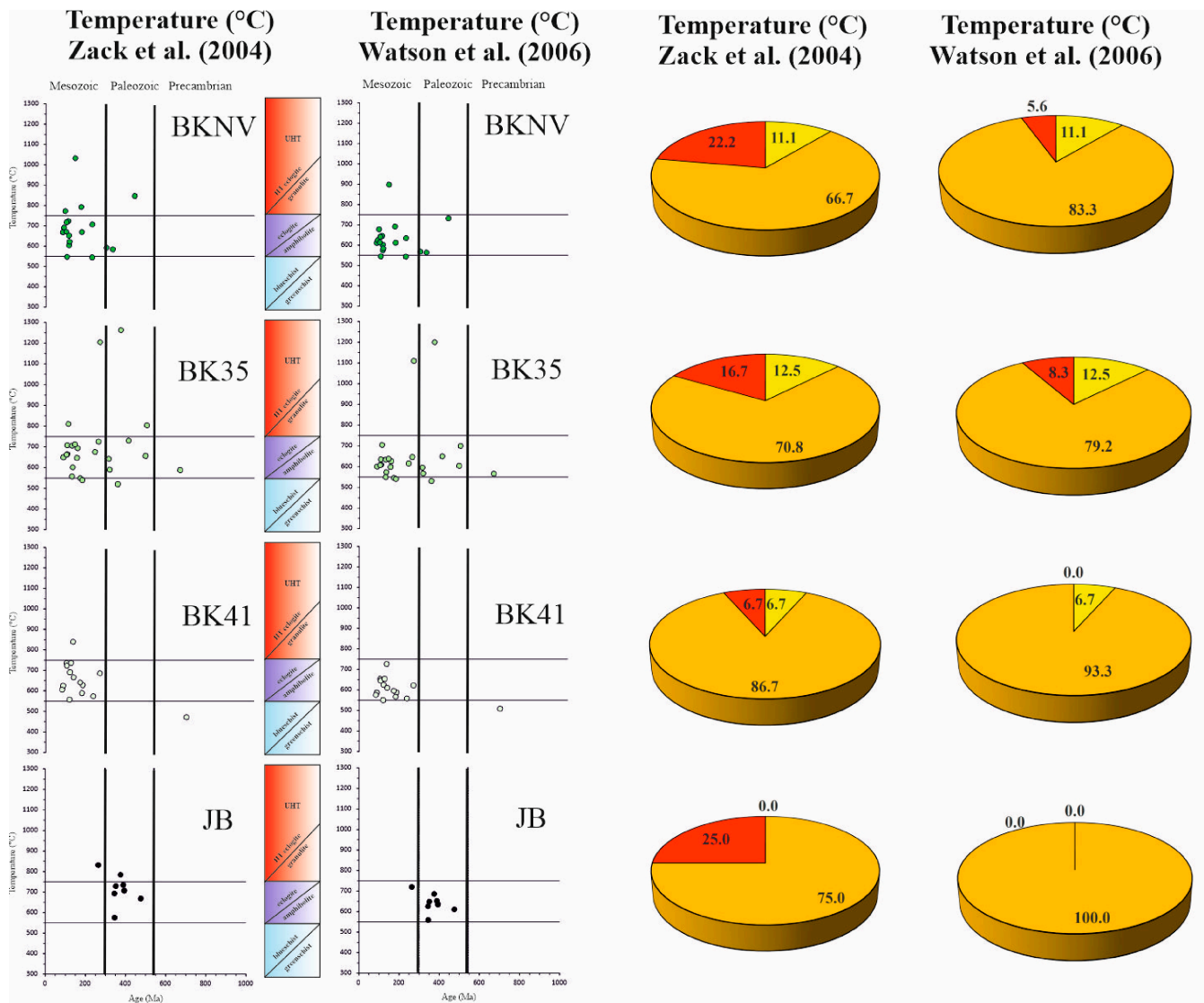


Figure 5. On the left, age-versus-temperature diagram. Temperature calculated using the thermometers in [9,16]. On the right, pie chart diagrams showing the different proportions of rutile falling in the blue-greenschist (<550 °C), amphibolite–eclogite (550–750 °C), and granulite–HT eclogite (>750 °C) facies according to their temperature calculated with [9,16] thermometers. Facies boundaries are taken from [86].

The Cr vs. Nb discrimination diagram has been introduced by [2,10], which proposed the definition “metapelitic” for SiO₂-rich rocks that commonly form Nb-rich rutile and “metamafic” to indicate metamorphic rocks with a mafic protolith that are responsible for Nb-poor rutile crystallization. Although recently [22] has advanced the term “metafelsic” instead of “metapelitic”, as Nb-rich rutile could be derived from both granites and metapelites, in this study we use the classic metapelitic terminology. Zack et al. (2002) [2] and [10], considering a compilation of whole-rock Nb/TiO₂ values for pelites, established an average Nb content in metapelites in the range of 900–2700 ppm. Later on, ref. [87] proposed to set the lower limit of Nb at 800 ppm. Therefore, rutile grains with an overall Cr content less than Nb accompanied by Nb > 800 ppm are interpreted to be derived from metapelitic rocks (e.g., mica-schists, paragneisses, and felsic granulites). Rutiles with Cr > Nb and those with Cr < Nb paired to Nb < 800 ppm are interpreted to be derived from metamafic rocks such as eclogites and mafic granulites. As the protoliths of amphibolites

can be either sedimentary or mafic igneous in origin, rutiles from amphibolites plot in both fields using this classification scheme.

Examining the data using a $\log(\text{Cr}/\text{Nb})$ vs. Nb diagram (Figure 6) highlights the prevalence of metamafic affinities (62% vs. 38%) for JB rutile, not previously observed by [88], which reported a smaller metamafic prevalence (52% vs. 48%). This discrepancy between the two datasets might be due to the smaller sample size of the JB dataset in this study. Regardless of this observation, the source-rock proportions change in BK with (i) BK41 rutile crystals showing an almost 1:1 ratio (48% vs. 52%) and (ii) samples BK35 and BKNV both displaying an increase in the metapelitic compared to metamafic compositions (60% vs. 40%).

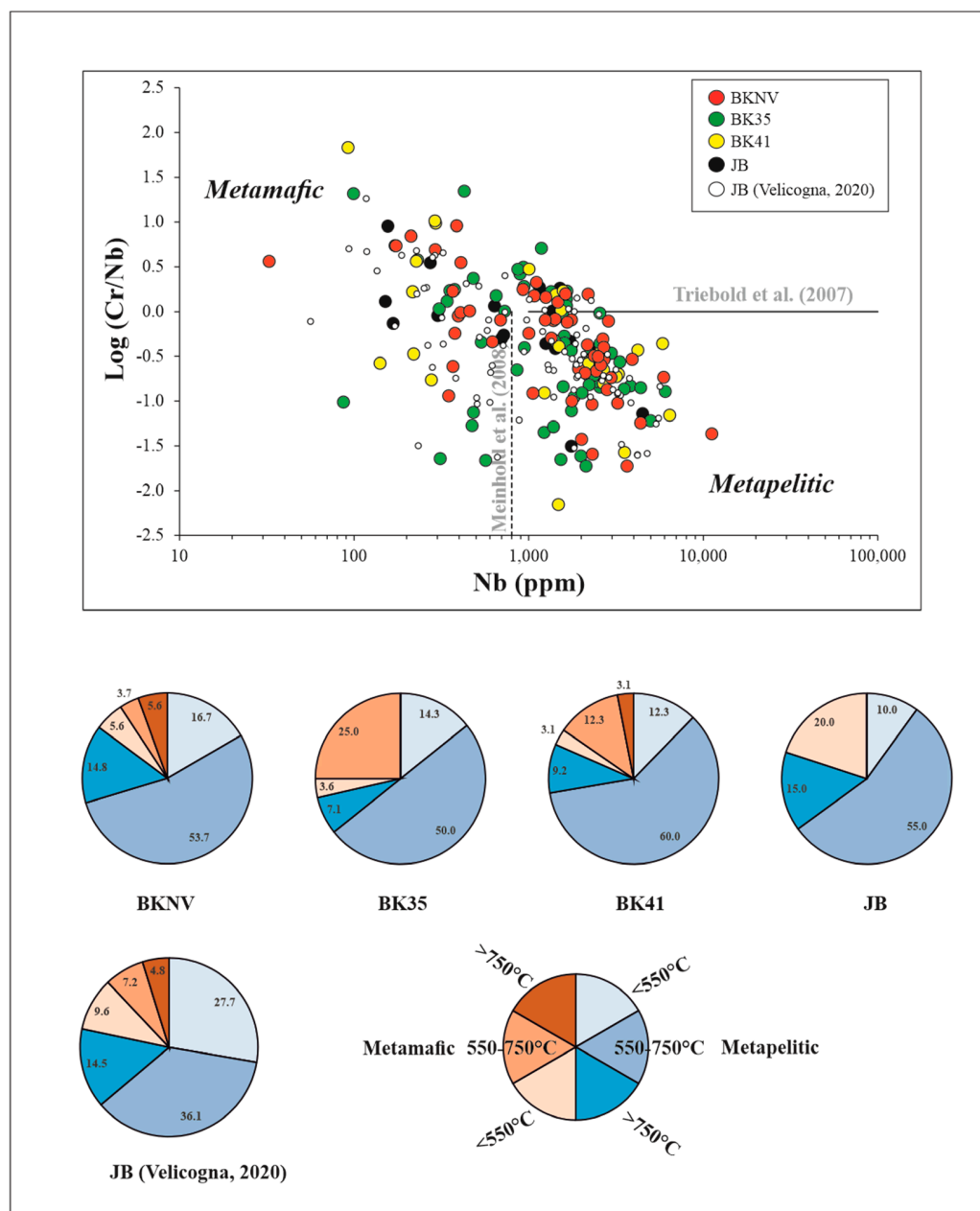


Figure 6. (Above) $\log(\text{Cr}/\text{Nb})$ vs. Nb diagram. Metamafic and metapelitic fields are identified according to [2], later modified by [86,88]. Open circle: rutile from JB [87]; black circle: JB (this study); yellow circle: BK41 (this study); green circle: BK35 (this study); red circle: BKNV (this study). (Below) pie chart diagrams showing the different proportions of rutile falling in the metamafic and metapelitic fields according to their temperatures calculated with [9,10].

As Mg is one of the least compatible elements in rutile [26], Mg-rich rutile can be ascribed to mantle rocks crystallized under HP and UHP conditions. In the same rutile crystals, Al can be elevated, so ref. [13] proposed an Al vs. Mg diagram to discriminate crustal or mantle sources (Figure 7). It is interesting to notice that, while in the JB samples the rutile crystals of possible mantle sources are characterized by low temperatures (<550 °C), in the BK42 and BK35 samples they are of intermediate temperature (550–750 °C) and in BKNV they are of intermediate and high temperature.

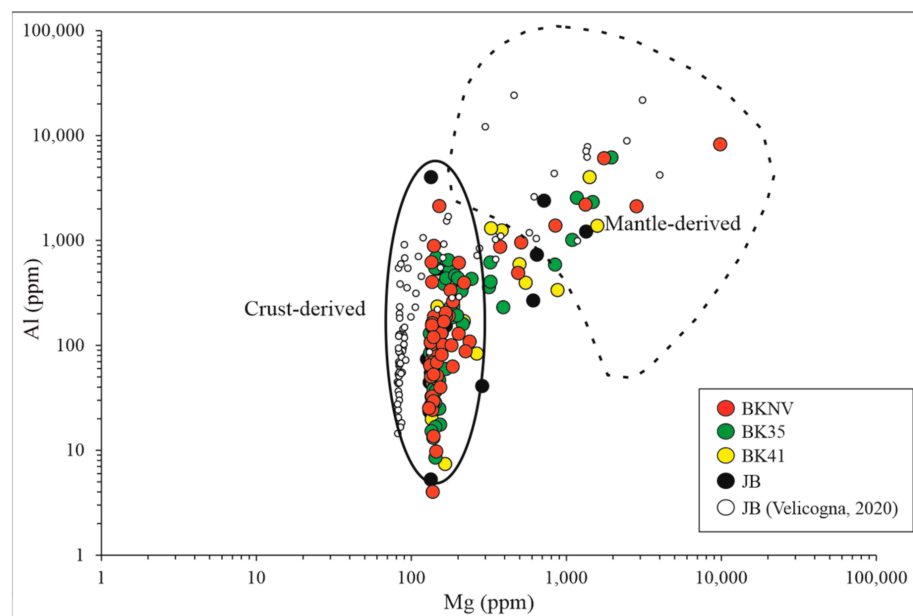


Figure 7. Al vs. Mg diagram according to [13]. Symbols as in Figure 6 [87].

Studies by several authors ([2,89–92], among others) showed that rutile dominates the budgets of Nb and Ta in cratonic eclogites at 91%–100% and 68%–100% of the budget, respectively, while other high-field-strength elements such as Zr and Hf are distributed between minerals, with rutile generally only hosting <30% of the budget of these elements. So, Nb and Ta are often used to obtain constraints on the rock sources and their geodynamical implications, in particular their ratios (Nb/Ta; [93–97]). Due to their strong affinity with Ti, both Nb and Ta (Ti vicarious) are particularly abundant in rutile; in its polymorphs; and, more generally, in all Ti-rich phases (e.g., sphene or ilmenite). However, Ti-bearing magmatic silicates like high-Ti clinopyroxenes, hornblende and biotite–phlogopite series show a general depletion in Ti–Nb–Ta during metamorphic or subsolidus recrystallization. The difference in Nb/Ta ratio in rutile could be due to the growth of the rutile together with sphene and ilmenite during prograde metamorphism in amphibolite–eclogite and granulite facies conditions [3,74,95,98,99]. In particular, subchondritic values are related to mineral dehydration during eclogitization. Otherwise, the trigger for such differences is the breakdown during HP metamorphism of Ti-rich minerals, such as biotite, that are responsible for the diffusion of elements such as Zr, Nb, Ta and Ti during crystal re-equilibration. Between the two elements, Nb is more compatible in rutile than in the other phases, while Ta prefers ilmenite/sphene/biotite, suggesting that the first rutile grains crystallizing should have a higher Nb/Ta ratio than the last ones. Furthermore, the ratio could also depend on the amount of reacting Ti-rich minerals hosted by the source rock. Finally, an aqueous solution with a high Nb/Ta ratio could derive from the breakdown of hydrous minerals, such as phengite, in which Nb is more compatible than Ta during HP metamorphism [100,101].

For these reasons, the Nb/Ta ratio of rutiles can be interpreted as the ratio of the bulk rock and equal to or slightly lower than that of the protolith and coexisting partial

melts, with a low Nb content and a high Nb/Ta ratio [74,98,101]. Continental crust and depleted mantle show sub-chondritic values, while mantle xenolith eclogites and migmatites obtained by intracrustal differentiation of TTG show supra-chondritic ones [98,102].

The studied rutile grains show high variable Nb/Ta ratios (Figure 8) between 3.6 and 55.6.

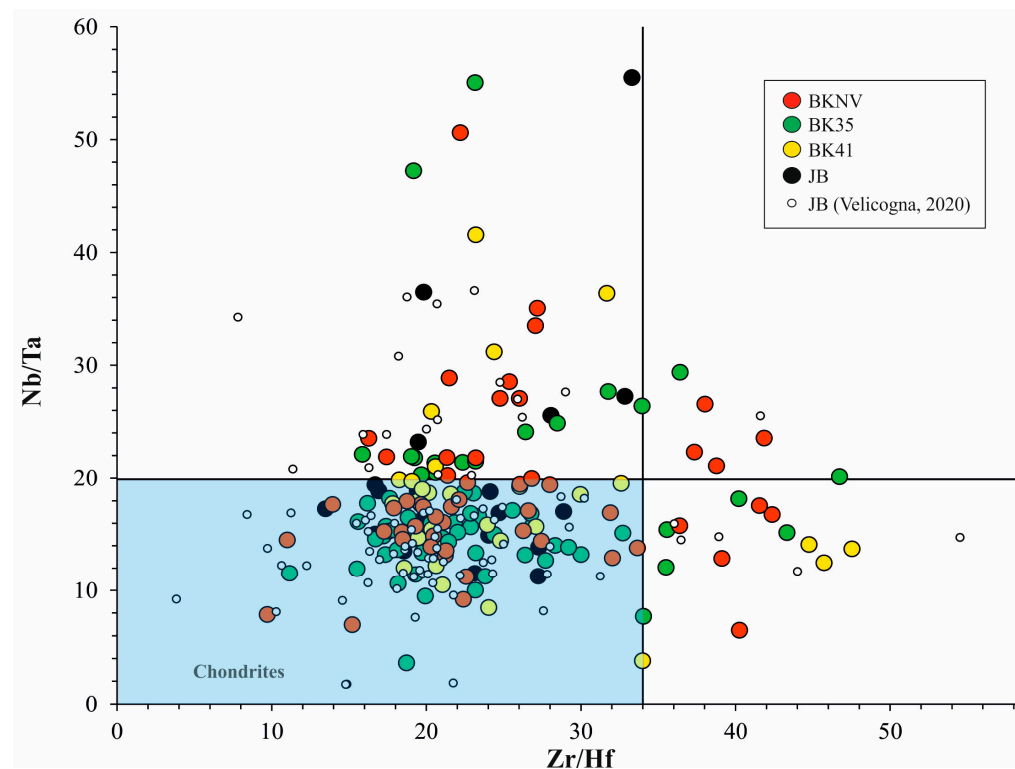


Figure 8. Nb/Ta vs. Zr/Hf diagram showing chondritic and non-chondritic composition for the studied rutile crystals. Chondrite value equal to 19.9 according to [92]. Symbols as in Figure 6 [87].

Ref. [103] suggested that 4^+ is the most compatible valence state for vanadium in rutile, whereas the presence of significant V^{3+} at low f_{O_2} would facilitate incorporation of Nb^{5+} in the rutile lattice via coupled substitution. According to this mechanism, an increase in Nb/Ta in rutile would be explained by increasing V abundance in rutile under appropriate f_{O_2} conditions; however, no correlation can be seen in our rutile grains (Figure 9).

Tang et al. (2019) [96], using the global arc magmas database, observed that arc basalts have average Nb/Ta ratios similar to those of mid-ocean ridge basalts. This fact suggested that the influence of the slab or mantle on Nb/Ta systematics in arc magmas is small. The Nb/Ta ratio decreases only with intracrustal differentiation, so that in mature continental arcs (i.e., a crustal thickness greater than 50 km) it decreases to ~ 9 when SiO_2 exceeds 60 wt.%, while in island arcs, the ratio decreases only after SiO_2 higher than 70%. These observations suggest that the low Nb/Ta ratio is not inherited from the source but is instead a feature of intracrustal differentiation. Tang et al. (2019) [96] also suggested a Nb/Ta value for continental crust in the range of 11–13 and a value in the range of 15–16 for basalts, while it must be 16 or higher in subduction-related fluids [104]. During the arc magma differentiation, ref. [97] suggested that the extent of Nb/Ta fractionation varies with crustal thickness, with the lowest Nb/Ta seen in continental arc magmas, and that there is a crustal thickness control of Nb/Ta explained by rutile saturation being favoured at higher pressure.

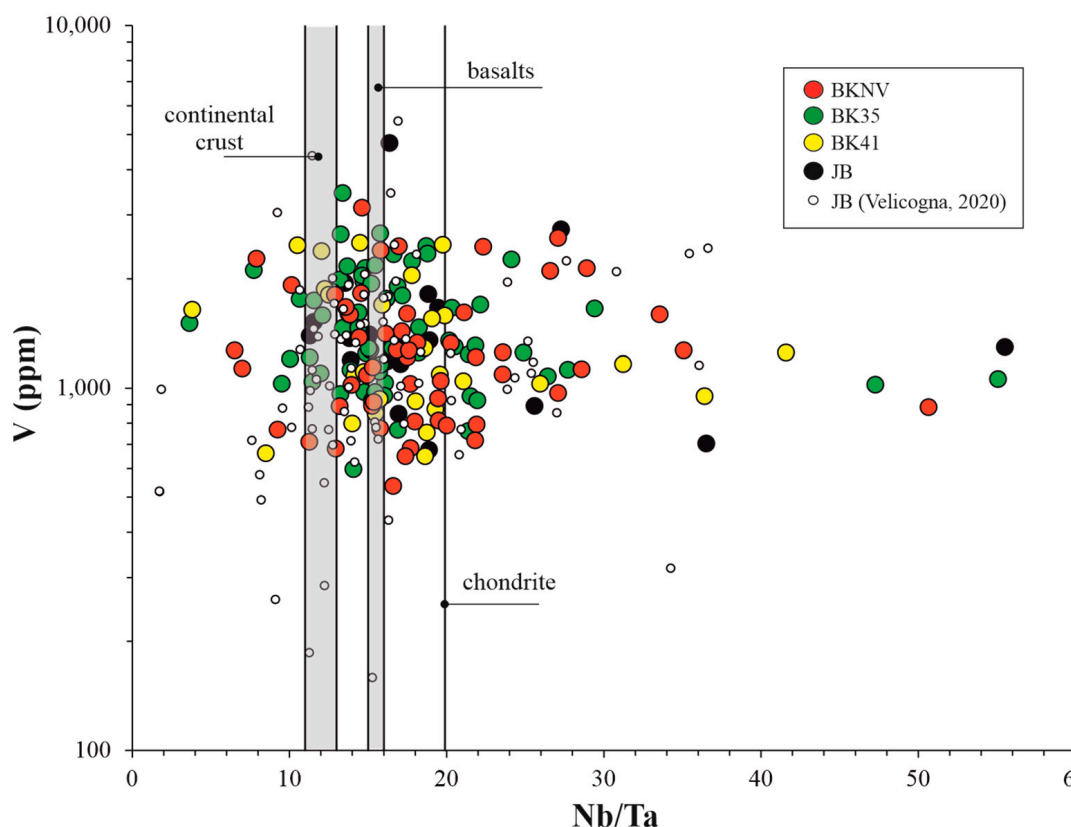


Figure 9. V vs. Nb/Ta diagram. Chondritic ratio of 19.9 from [93], the continental crust value of 11–13 and the one of basalt of 15–16 from [97]. Symbols as in Figure 6 [87].

Hafnium is also often considered because of its high partition coefficient between melt and rutile and because it generally shows a positive correlation with its vicarious Zr [93,94,105,106]. However, the two elements are not characteristic of the protolith, since they show also quite high partition coefficients with clinopyroxenes. In the rutile crystals analysed, Nb/Ta and Zr/Hf ratios seem to be mainly controlled by the decrease in Ta and the increase in Zr. The first is generally in agreement with the literature [89,107,108], which suggests the metamorphic dehydration in subduction zones as the main trigger for the ratio increase as well as for rutile formation. On the other hand, Zr/Hf seems to be controlled mainly by the Zr content, rather than the Hf. However, the bilogarithmic Zr vs. Hf diagram shows a quite good linear correlation between the two (Figure 10). All the basins' trendlines show a good R^2 (JB = 0.997, BK41 = 0.998, BK35 = 0.983 and BKNV = 0.963), with JB and samples of JB studied by [88] showing similar slopes (angular coefficient: 0.0515–0.0529) and BK samples showing angular coefficients in the range of 0.0208–0.0245. Notably, it seems from Figure 10 that JB rutile grains fall on one line, testifying to a possible common source, while BK rutile grains fall on Zr/Hf ratios equal to 20 and 40, signifying multiple sources. Only some of the rutile grains show a Zr/Hf ratio close to 40, while the majority of the grains fall on the Zr/Hf-equal-to-20 trendline (Figure 10). Münker et al. (2004) [104] showed that the Zr/Hf ratios in the slab melts are in the range of 35–38, similar to the average MORB value (32–38; [93,109]). However, while the Nb/Ta ratio is mainly controlled by rutile, the Zr/Hf one can be related to many other different concurrent phases.

Rutile crystals from JB fall along the Zr/Hf ratio equal to 20 as well as many crystals from BK (Figure 10). However, there is a certain amount of BK rutile crystals along the line with the higher ratio (40). These data suggest a different provenance for such crystals.

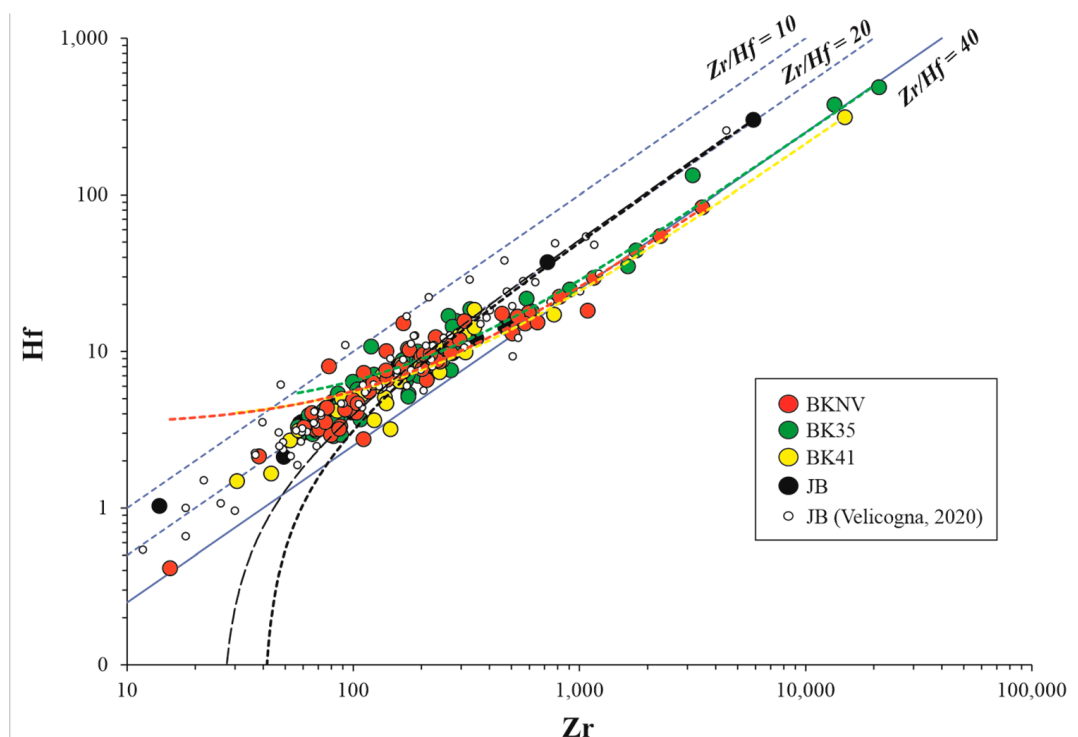


Figure 10. Hf vs. Zr diagram. Trendline and lines with Zr/Hf ratios equal to 10, 20 and 40 are also represented. Symbols as in Figure 6 [87].

The Zr and Hf pair is also important because it can help us in defining the possible deviation of these elements from the equilibrium magmatic condition and, in our cases, if there can be a possible alteration or modification due to diagenetic effects. The twin pairs Y-Ho and Zr-Hf show elements of similar charge and radius that can be considered as CHARGE-and-RADIUS-Controlled (CHARAC) trace elements [110]. They display extremely coherent behaviour, retaining their respective chondritic ratios so that basic-to-intermediate igneous rocks show Y/Ho and Zr/Hf ratios close to the chondritic one. Aqueous solutions and their precipitates, like those shown in Figure 11, show non-chondritic ratios for these pairs. At the same time, highly evolved magmas, metamorphics and authigenic minerals will show non-chondritic ratios [110]. Only some of our rutile grains retain the CHARAC behaviour, while the others are displaced (Figure 11), even if they are not as distantly removed from the CHARAC field and far from the hydrothermal vein fluorite, seawater and hydrogenetic Fe-Mn crust fields determined by [110]. Consequently, we could consider that the rutile grains studied here are all detrital and that the effects of metamorphism were possibly limited and possibly suffered a dissolution–reprecipitation process like that shown in [111] for some rutile grains present in some Brazilian metasandstones (type-1 rutile grains in Figure 11). The so-called type-2 rutile grains in [111] are mostly authigenic and formed after dissolution of pre-existing detrital rutile grains and subsequent transport and homogenization of trace elements.

Due to their geochemical importance in rutile, the ternary diagram in Figure 12 correlates Ta, Nb, and Zr. The blue field represents micaschist–quartzite protoliths [112], the lilac and yellow ones represent mafic protoliths that underwent amphibolitic facies metamorphism [6,99,101,107,112–114], and the pinkish area shows the gabbroic rutile data of [114]. Most of the rutile grains fall in the upper fields, while only a few grains from the youngest BK samples are enriched in Zr with respect to Nb and Ta (Figure 12).

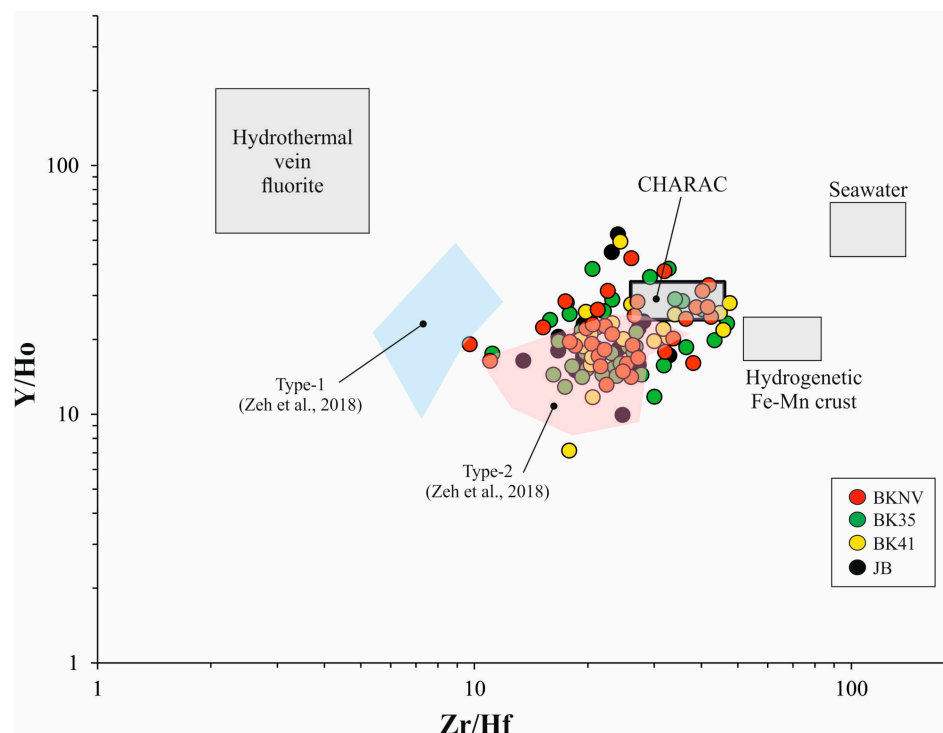


Figure 11. Y/Ho vs. Zr/Hf ratio diagrams of rutile grains. CHARAC (CHArge-and-RAdius-Controlled) trace elements, hydrothermal vein fluorite, seawater and hydrogenetic Fe-Mn crust fields are from [110]. Type-1 and type-2 fields are from [111]; see text for details. Symbols as in Figure 6.

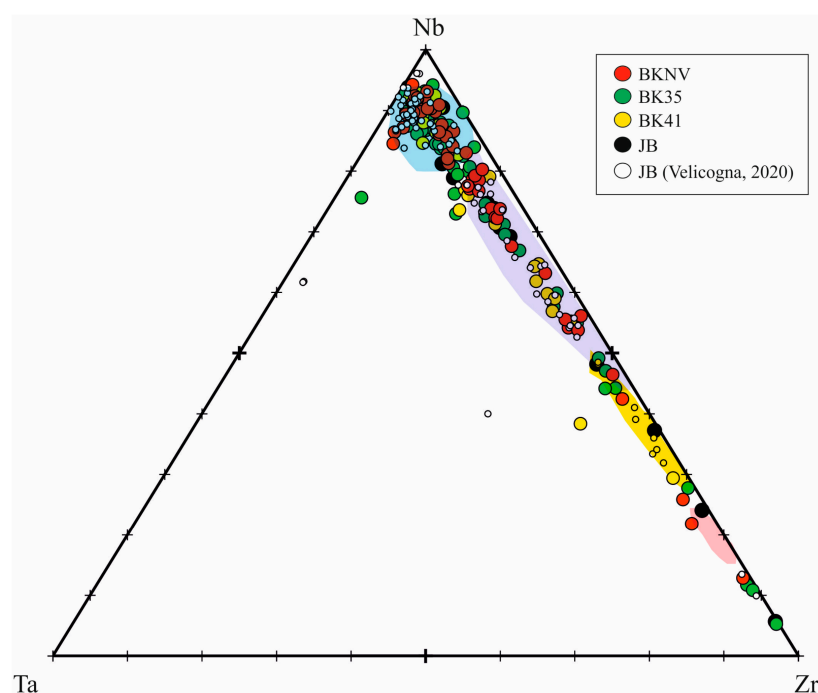


Figure 12. Nb-Ta-Zr rutile ternary diagram. Blue field: micaschist–quartzite protoliths [112]; lilac and yellow fields: mafic protoliths that underwent amphibolitic facies metamorphism [6,99,101,107,112–114]; pink field: gabbro [114]. Symbols as in Figure 6 [87].

The factor matrix shows the correlation between each original variable and the principal components (PCs) derived from the principal component analysis (PCA). The values in the matrix, referred to as factor loadings, represent the relative contribution of each variable

to the formation of each component. The two main principal components explain 48% of the total variability of the dataset. PC1 is the component that explains the majority of the variability (28.8%). The analysis of factor loadings reveals that Hf, Zr, U and temperature exhibit comparable values (0.404, 0.387, 0.346 and 0.391 respectively; Table 1). It can be assumed that PC1 is primarily related to the group of variables Hf, Zr and temperature. PC2, which explains 19.4% of the variability, is defined by a strong positive correlation between elements with positive loadings. The highest values are represented by Fe (0.360), Nb (0.493), Ta (0.462), and W (0.345).

Table 1. Summary table of median concentrations of the elements under examination (in ppm), temperature and age divided by cluster.

	Mg	Al	Sc	V	Cr	Fe	Zr	Nb	Sn	Sb	Hf	Ta	W	U	Temp (°C)
1 (n = 44)	142	55.8	5.9	1630	999	1897	224	935	45.6	5.7	9.8	48.6	122	2.4	682
2 (n = 13)	138	73.9	2.7	1354	124	2326	99.5	377	8.3	10.5	3.5	24.1	9.4	0.1	578
3 (n = 64)	142	105	11.1	1153	547	4079	123	2283	83.4	10.9	6.6	130	184	2.2	605

The bivariate plot in Figure 13 provides a visual representation of the PCA results, combining both the scores of the observations (points) and the factor loadings of the variables (arrows). Hafnium, Zr and temperature are clearly distinguished by the other elements. PC2 is dominated by a positive correlation between a distinct group of elements, as suggested by their high loadings and angular closeness in the biplot. The independence between PC1 and PC2 is highlighted by the orthogonality of the vectors that define their respective axes; for example, the angle between the temperature (PC1) and Fe (PC2) suggests that the processes controlling the variation in the first component are distinct from those regulating the abundance in the second component. It is important to notice the relative position of Cr and Nb suggesting more metamafic or metapelitic affinities.

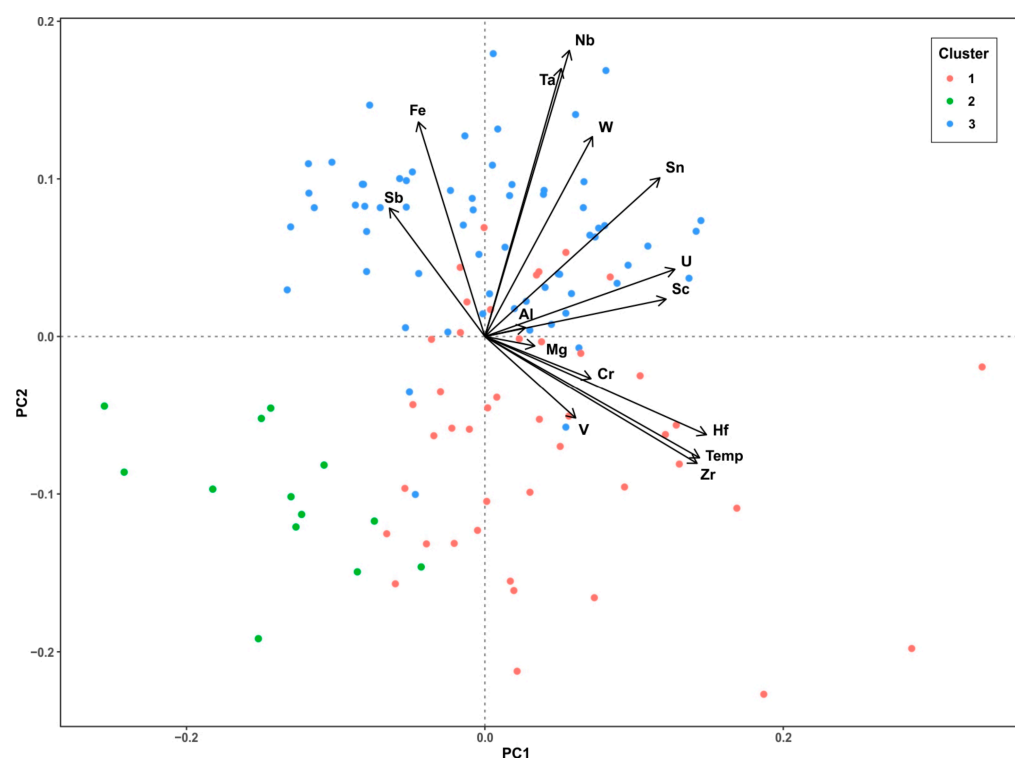


Figure 13. Biplot of PC1 and PC2 loadings and sample scores for trace elements and temperature.

The dendrogram in Figure 14 shows the samples grouped into three main clusters (1, 2 and 3) based on their similarity, in accordance with the PCA results. Due to the high degree of dispersion observed in the concentration data, the characteristics of the clusters are described using the median value, thus minimizing the influence of any present outlier (Table 1).

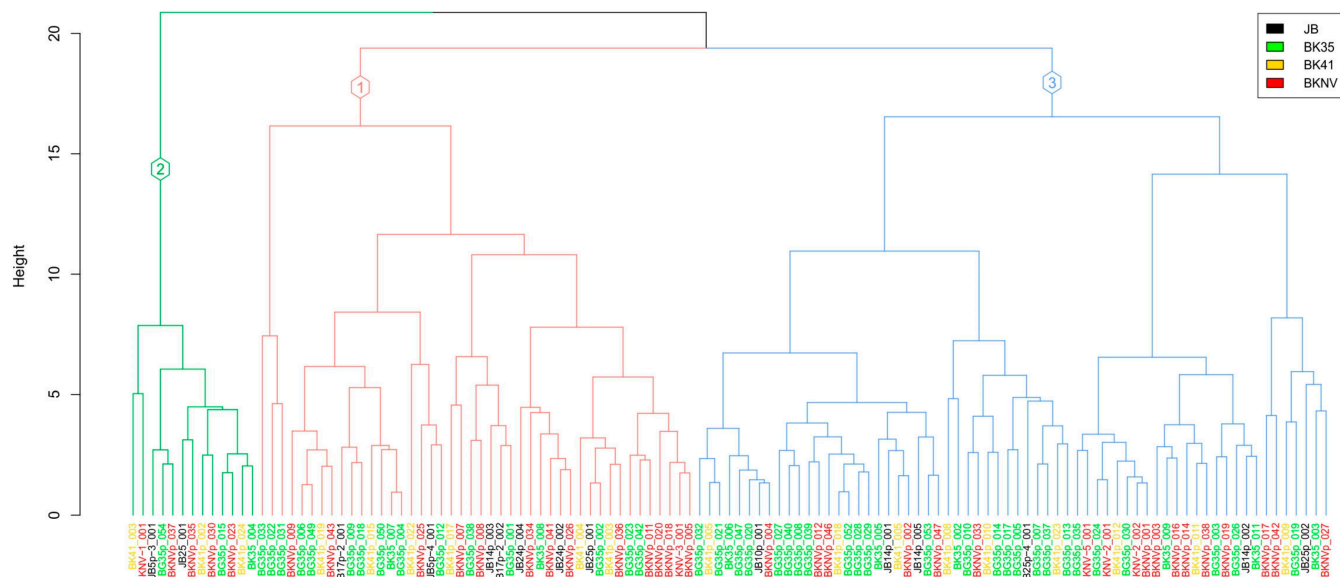


Figure 14. Dendrogram obtained by cluster analysis (Euclidean distance and Ward linkage).

The associations between variables as identified by PCA are consistently reflected in the results obtained from cluster analysis, thus confirming the directions of maximum variance (PC1 and PC2) as highlighted by PCA.

5.2. Provenance—Age Considerations

In the nearby areas, the occurrence of other flysch basins allows direct comparison with rutile occurrence in the Julian and Brkini basins. The Bosnian flysch is a folded deposit of Jurassic-to-Cretaceous age. In the Bosnian basin, according to [115], the rutile grains that originated from a metapelitic source are between 60% and 80%. These authors found only metapelitic rutile grains obtaining two populations (650–860 and 500–650 °C) for the Dinarides Ophiolitic Zone mélange and a 550–700 °C cluster for the Vranduk and Ugar flysch formations. Temperatures in the range of 550–630 °C, according to [67], seem to be related to the metamorphic event occurred in the Late Cretaceous during the Sava-Adria collision. To the north, the Maastrichtian Glog formation is the youngest part of an Upper Cretaceous alluvial-to-deep-water succession where ZTR minerals are present [116]. No trace elements or ages of rutile grains are present in this study. ZTR association dominates the deep-water turbiditic deposits of the Albian–Cenomanian Kravljak formation, but rutile has not been studied in detail in this area either [117]. The Belluno, Bovec, Bled and Tolmin basins are present in the Alpine domains [49,50,118,119], but for none of them has a detailed study of rutile been carried out.

As can be seen in Figure 4, in JB samples, the largest proportion of rutile grains are Palaeozoic (~88%), while Mesozoic grains are less prominent (~12). In Europe, Palaeozoic age is strictly related to the Variscan orogeny that heavily influenced the European geology of that time. Conversely, in the Brkini samples, the Mesozoic rutile grains are the main fraction (about 80%). This cluster of ages can be related to the Triassic rifting events that occurred along the border of the Adria Plate [120,121], the Jurassic subduction of the Vardar Ocean and the Cretaceous Pelagonian–Macedonian collision.

The presence of detrital rutile of Variscan age is widespread in Central Europe. Rösel et al. (2025) [19] identified 320–330 Ma rutile crystals with mainly metapelitic affinities and upper-amphibolite-to-lower-granulite-facies metamorphic conditions in the Saxonian Cretaceous basin of the Elbtal Group, assuming the Erzgebirge metamorphic lithologies as likely proto-sources. Similar ages (320–330 Ma) for detrital rutile grains have been found by [122] in a Cenomanian–Middle Coniacian succession of quartz arenites in the Kreibitz–Zittau area in the northern margin of the Bohemian Massif (Czech–German border region). This rutile supply has been considered as a second sedimentary cycle deriving from a Permo–Carboniferous Variscan molasse derived from the uplift of the gneissic–migmatitic Góry Sowie Massif. Previously, ref. [18], studying the detrital rutile in the Late Ordovician Saxo-Thuringian zone of the Bohemian Massif, found a cluster of Late Neoproterozoic-to-Early Palaeozoic ages (700–500 Ma) typical of magmatic and high-grade metamorphism along the Pan-African orogenic belts throughout Gondwana, but also some younger ages in the range of 440–490 Ma, which could be related to the opening of the Rheic Ocean. At the same time, magmatism and HT metamorphism along the northern margin of Gondwana was widespread [123], suggesting that this material may also represent the source of the 440–490 Ma rutile population. Szczuka et al. (2022) [124] found 344.7 Ma old rutile grains in the Palaeocene Istebna Formation of the Outer Western Carpathians, Poland. They suggested that the sources of the eroded material were granitoid rocks and their metamorphic host in the Silesian ridge.

Similarly, our oldest rutile grains in JB could be related to the closing and opening of the Rheic Ocean (390–460 Ma; [25,125–127]) and to the Variscan orogeny (300–420 Ma). It is, however, unclear whether such supplies are from the north or from the east of the study area (e.g., the Serbo-Macedonian Massif). This is an almost entirely metamorphic belt outcropping from the Pannonian basin in the north to the Aegean Sea in the south, constituted by amphibolite facies schist and gneisses, amphibolites and marbles [128]. There, several stages of igneous activity have been recognized, from the Late Cadomian magmatic arc (562–522 Ma) throughout the Palaeozoic (reactivation of subduction: 490–478 Ma, emplacement of mafic dykes: 472–456 Ma, felsic within-plate magmatism: 439 Ma, late to post-collisional granite emplacement: 328–304 Ma) and the Permian–Triassic (255–253 Ma), related to the opening of the Mesozoic Tethys with late- to post-collisional and within-plate felsic magmatism [129].

Following a Hercynian deformation and a granite intrusion, the Vardar Zone rifted in Permian–Triassic time, creating the so-called Vardar Ocean during the Late Triassic–Early Jurassic [130,131], which subducted eastwards underneath the Serbo-Macedonian Massif [132]. Another small ocean (i.e., Pindos) opened to the west of a Pelagonian microcontinent at the same time. Ophiolites were emplaced northeastwards from the Pindos Ocean onto the Pelagonian microcontinent during the Mid–Late Jurassic–pre–Late Oxfordian–Early Kimmeridgian) causing greenschist or amphibolite facies metamorphism [130,131]. These lithologies could represent the source of the Jurassic rutile in the present study. The metamorphic soles of the Dinarides, Albanides and Hellenides, mainly composed of amphibolite, have been dated at 174–162 Ma by Ar–Ar and at 174–147 Ma by K–Ar ([133] and references therein). Younger ages of 136 ± 15 Ma and 146.8 ± 4.9 Ma have also been obtained by [134] for ilmenites and [135] for garnet pyroxenite, respectively, via Sm–Nd. It is important to note that high-pressure conditions (~ 10 kb at up to 1000 °C for garnet–clinopyroxene amphibolites [85,135]) have been found locally. Exhumation of these areas happened during Late Jurassic–Early Cretaceous time [45,130,136]. According to [131], a small remnant of the Vardar Ocean survived into the Late Cretaceous until its closure during the Latest Cretaceous–Early Cenozoic, triggering continental collision and thick-skinned folding/thrusting of the Pelagonian, Vardar and Serbo-Macedonian zones

towards the W/SW. The youngest rutile grains found in the BK basins are probably related to these last events.

Several other heavy minerals are present in the studied rocks, and some of them have been studied in detail. As regards Cr-spinels, there are different supplies from MORB or MORB-type back-arc rocks, subduction-related back-arc and continental rifting, plume-related intraplate basalts, and island arc tholeiites or boninites, with some differences in supplies of Cr-spinels in JB and BK basins suggesting that they were derived from both the Internal and External Dinarides [30,31].

Recently, ref. [32] studied the garnets of JB and BK. The authors suggested that there are supplies from the suprasubduction zone (SSZ) of the Vardar ophiolites and their metamorphic soles. A possible involvement of different ophiolitic sources, but also sources from the Drina–Ivanica terrane, is suggested by garnets related to amphibolite facies metasediments.

Lenaz and Princivalle (2002) [33] found amphiboles (actinolite, Mg-hornblende, barroisite, and glaucophane) associated with pyroxenes in Lower Eocene turbidites of the JB. While actinolite and Mg-hornblende are derived from low-to-medium-grade metamorphic rocks (metavolcanics in greenschist facies), barroisite is the ultra-high-pressure type of calcic amphibole, and it is considered a marker of retrogressive metamorphism. Glaucophane and omphacites represent supplies of high-pressure blueschist and eclogite facies metamorphic rocks.

A study on the detrital tourmalines from the same samples was not useful in determining a precise provenance; however, it suggested an important change in the provenance detritus based on the relative amount of tourmaline in JB and BK samples [34]. It is, however, worth pointing out that their chemistry is similar, so the provenance could be the same [34].

All these findings suggest a main supply from the Dinarides area, even if some minor contribution could be ascribed to other sources mainly based on some sedimentological feature as palaeocurrent [65,66]. This study shows how rutiles from JB could be best considered for an Alpine supply, while those in BK accompany the other minerals from a Dinaric provenance.

6. Conclusions

The present study on rutile grains from the JB and BK flysch basins shows some important results. First of all, the abundance of rutile crystals in BK is higher than in JB, similarly to the tourmaline behaviour [34], testifying to an increase in metamorphic material in the latter basin, as also evidenced by the increase in non-igneous quartz recorded by [137].

As far as the ages of the rutile are concerned, these clearly differ in the two basins. Almost all the rutile grains from JB show Palaeozoic ages resembling those of the closure/opening of the Rheic Ocean and the Variscan orogeny. Such ages could be present, even if in limited areas, in the Serbo-Macedonian massif or in the Tisza unit present in Croatia. It is unclear, as there are no rutile ages for the Balkan areas, if this could be a true provenance. Other minerals are surely connected to Dinaridic supplies (Cr-spinels and garnets); however, ref. [59] suggested that silicoclastic supplies in the JB could be from the north. Consequently, we suggest a possible supply from the Alpine realm but do not exclude a western–southwestern one (Figure 15).

When considering the BK rutile grains, in BK41 there are no Palaeozoic ages that are newly visible at the top of the BK sequence (BK35 and BKNV). However, in BK, the most abundant rutile grains show Mesozoic ages that can be considered as representa-

tives of the opening/closure of the Vardar Ocean and the ophiolite emplacement in the Dinarides area.

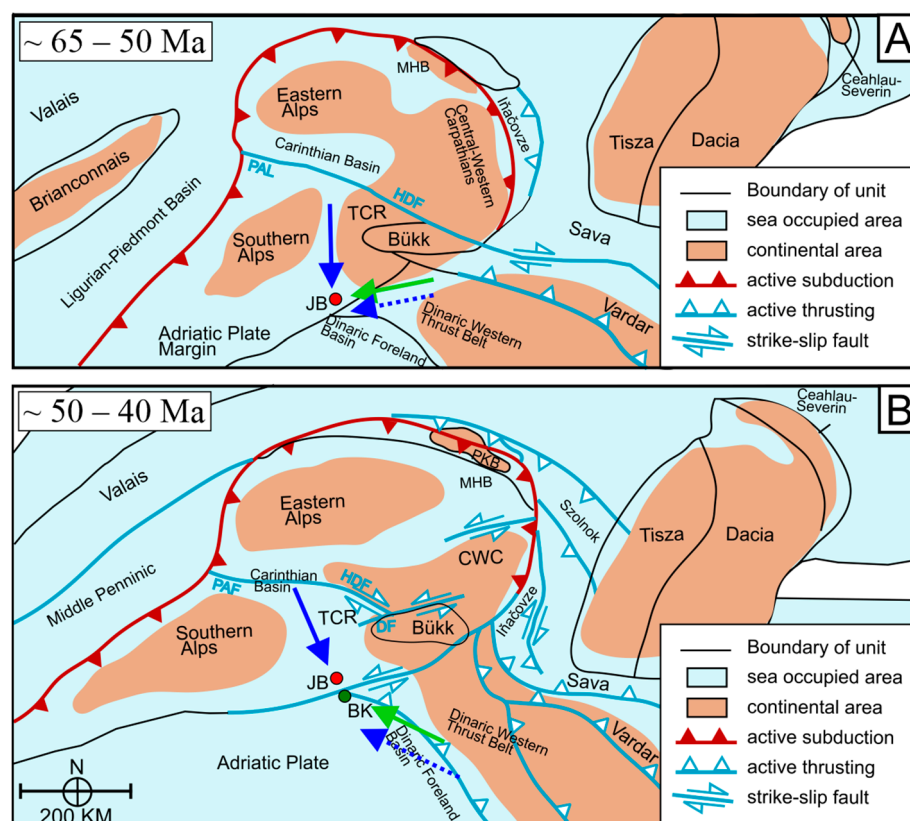


Figure 15. Palaeogeographic reconstruction for the Western Carpathians, Northern Pannonian domain and adjoining areas during the Cretaceous–Early Palaeogene (A) and the Early–Middle Eocene (B), modified from [52]. Abbreviations: CWC—Central Western Carpathians, PKB—Pieniny Klippen Belt, CR—Czorsztyn Ridge, TCR—Transdanubian Central Range, MHB—Myjava–Hričov Basin, PAF—Periadriatic Fault, HDF—Hurbanovo–Diósjenő Fault, DF—Darnó Fault, JB—Julian Basin, BK—Brkini Basin. Blue arrow: most probable rutile provenance; dotted blue arrow: possible rutile provenance; green arrow: Cr-spinel and garnet provenance according to [30–32].

According to the thermometer used in [9,10], rutile grains within amphibolite–eclogite facies are the most abundant. Among the BK samples, there was a decrease in such rutile grains from BK41 to BKNV accompanied by an increase in UHT rutile grains, testifying to new inputs from a UHT source, which, however, seem to be limited.

Metapelitic rutile grains are more abundant than metamafic grains, and crust-derived rutile grains are more abundant than mantle-derived grains. Recently, ref. [138] proposed a chemical discrimination of rutile from different metamorphic source rocks, introducing a hierarchical data structure in a random forest classification, where 16 different elements are considered. According to the web application provided by the authors, it is possible to discriminate felsic (metapelitic) and mafic metamorphic rutile in about 89% of the cases and low T/P (≤ 350 °C/GPa) and high T/P ratios (> 350 °C/GPa) in about 84%, and it is correct in both predictions in 72% of cases. By using this application, the discrimination of the rutile grains examined in this study is different, with a prevalence of mafic over felsic rutile (JB: mafic: 70%, felsic: 30%; BK41: mafic: 62, felsic: 38; BK35: mafic: 51, felsic: 49; BKNV: mafic: 71, felsic: 29). These changes, in our opinion, could be related to the use of multiple elements instead of solely Cr and Nb.

Supplementary Materials: The following supporting information can be downloaded at <https://www.mdpi.com/article/10.3390/min16080856/s1>: Table S1: Laser and ICP-MS parameters (including data processing); Table S2: Laser ablation ICP-MS U-Pb and trace elements data (samples); Table S3: Laser ablation ICP-MS U-Pb and trace elements data (reference materials). References [3,70–72,75,139] are cited in the supplementary materials.

Author Contributions: Conceptualization D.L., M.V. and M.G.; methodology, D.L., L.T. and A.B.; formal analysis, D.L., M.V., M.G., L.T., A.B., S.A. and C.P.; resources, D.L. and F.P.; data curation, L.T. and D.L.; writing—original draft preparation, D.L., M.V., M.G., A.B., L.T. and C.P.; writing—review and editing, D.L., S.A. and F.P.; supervision, D.L. All authors have read and agreed to the published version of the manuscript.

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References

1. Morton, A.C.; Hallsworth, C.R. Processes controlling the composition of detrital heavy mineral assemblages in sandstones. *Sediment. Geol.* **1999**, *124*, 3–29. [\[CrossRef\]](#)
2. Zack, T.; Kronz, A.; Foley, S.F.; Rivers, T. Trace element abundances in rutiles from eclogites and associated garnet mica schists. *Chem. Geol.* **2002**, *184*, 97–122. [\[CrossRef\]](#)
3. Luvizotto, G.L.; Zack, T. Nb and Zr behavior in rutile during high-grade metamorphism and retrogression: An example from the Ivrea-Verbano Zone. *Chem. Geol.* **2009**, *261*, 303–317. [\[CrossRef\]](#)
4. Kooijman, E.; Smit, M.A.; Mezger, K.; Berndt, J. Trace element systematics in granulite facies rutile: Implications for Zr geothermometry and provenance studies. *J. Metamorph. Geol.* **2012**, *30*, 397–412. [\[CrossRef\]](#)
5. Hart, E.; Storey, C.; Harley, S.L.; Fowler, M. A window into the lower crust: Trace element systematics and the occurrence of inclusions/intergrowths in granulite-facies rutile. *Gondwana Res.* **2018**, *59*, 76–86. [\[CrossRef\]](#)
6. Pereira, I.; Storey, C.; Darling, J.; Lana, C.; Alkmim, A.R. Two billion years of evolution enclosed in hydrothermal rutile: Recycling of the Sao Francisco Craton Crust and constraints on gold remobilisation processes. *Gondwana Res.* **2019**, *68*, 69–92. [\[CrossRef\]](#)
7. Pereira, I.; Storey, C.D.; Darling, J.R.; Moreira, H.; Strachan, R.A.; Cawood, P.A. Detrital rutile tracks the first appearance of subduction zone low T/P paired metamorphism in the Palaeoproterozoic. *Earth Planet. Sci. Lett.* **2021**, *570*, 117069. [\[CrossRef\]](#)
8. Clark, J.R.; Williams-Jones, A.E. *Rutile as a Potential Indicator Mineral for Metamorphosed Metallic Ore Deposits*; Rapport Final de DIVEX, Sous-Projet SC2; Divex: Montréal, QC, Canada, 2004; 17p.
9. Zack, T.; von Eynatten, H.; Kronz, A. Rutile geochemistry and its potential use in quantitative provenance studies. *Sediment. Geol.* **2004**, *171*, 37–58. [\[CrossRef\]](#)
10. Zack, T.; Moraes, R.; Kronz, A. Temperature dependence of Zr in rutile Empirical calibration of a rutile thermometer. *Contrib. Mineral. Petrol.* **2004**, *148*, 471–488. [\[CrossRef\]](#)
11. Tomkins, H.S.; Powell, R.; Ellis, D.J. The pressure dependence of the zirconium-in-rutile thermometer. *J. Metamorph. Geol.* **2007**, *25*, 703–713. [\[CrossRef\]](#)
12. Agangi, A.; Reddy, S.M.; Plavsa, D.; Fougereuse, D.; Clark, C.; Roberts, M.; Johnson, T.E. Antimony in rutile as a pathfinder for orogenic gold deposits. *Ore Geol. Rev.* **2019**, *106*, 1–11. [\[CrossRef\]](#)
13. Smythe, D.J.; Schulze, D.J.; Brenan, J.M. Rutile as a kimberlite indicator mineral: Minor and trace element geochemistry. In *9th International Kimberlite Conference: Extended Abstracts*; No. 9IKC-A-00193; University of Alberta: Edmonton, AB, Canada, 2008.
14. Dawson, J.B.; Smith, J.V. The MARID (mica–amphibole–rutile–ilmenite–diopside) suite of xenoliths in kimberlite. *Geochim. Cosmochim. Acta* **1977**, *41*, 309–323. [\[CrossRef\]](#)
15. Scott, K.M. Rutile geochemistry as a guide to porphyry Cu–Au mineralization, Northparkes, New South Wales, Australia. *Geochem. Explor. Environ. Anal.* **2005**, *5*, 247–253. [\[CrossRef\]](#)

16. Watson, E.B.; Wark, D.A.; Thomas, J.B. Crystallization thermometers for zircon and rutile. *Contrib. Mineral. Petrol.* **2006**, *151*, 413–433. [\[CrossRef\]](#)
17. Barber, D.E.; Stockli, D.F.; Galster, F. The Proto-Zagros foreland basin in Lorestan, western Iran: Insights from multiminerall detrital geothermochronometric and trace elemental provenance analysis. *Geochem. Geophys. Geosyst.* **2019**, *20*, 2657–2680. [\[CrossRef\]](#)
18. Rösel, D.; Zack, T.; Möller, A. Interpretation and significance of combined trace element and U-Pb isotopic data of detrital rutile: A case study from late Ordovician sedimentary rocks of Saxo-Thuringia, Germany. *Int. J. Earth Sci.* **2019**, *108*, 1–25. [\[CrossRef\]](#)
19. Rösel, D.; Schulze, M.C.; Wilmsen, M.; Zieger-Hofmann, M.; Linnemann, U.; Mertz-Kraus, R. LA-ICP-MS U-Pb dating and trace element analyses of detrital rutile from the Elbtal Group (Saxony, Germany): Provenance constraints of the Saxonian Cretaceous Basin. *Int. J. Earth Sci.* **2025**, *114*, 1–21. [\[CrossRef\]](#)
20. Pereira, I.; Storey, C.D.; Strachan, R.A.; Bento dos Santos, T.; Darling, J.R. Detrital rutile ages can deduce the tectonic setting of sedimentary basins. *Earth Planet. Sci. Lett.* **2020**, *537*, 116193. [\[CrossRef\]](#)
21. Belinga Belinga, C.; Ekomane, E.; Bineli Betsi, T.; Ngo Bandong, P.M.C.; Ashukem, E.N.; Bokanda, E.E.; Ingom, M.F.; Tonye, M.D.; Onana, E.L.; Bisse, S.B. Trace element geochemistry and U-Pb ages of alluvial rutiles from a Neoproterozoic coastal area, southwestern Cameroon: Implication for source rocks. *J. Afr. Earth Sci.* **2022**, *185*, 104399. [\[CrossRef\]](#)
22. Pereira, I.; Storey, C.D. Detrital rutile: Records of the deep crust, ores and fluids. *Lithos* **2023**, *438*, 107010. [\[CrossRef\]](#)
23. Moazzen, M.; Mohammadi, A.; Topuz, G.; Mojdeh, P.; Zack, T. Detrital zircon and rutile geochronology, geochemistry and provenance of Cambrian sandstones of Iranian Azerbaijan: Implications for the Neoproterozoic-Cambrian evolution of the northern Gondwana margin. *Int. J. Earth Sci.* **2024**, *113*, 303–318. [\[CrossRef\]](#)
24. Mueller, M.A.; Licht, A.; Möller, A.; Condit, C.B.; Fosdick, J.C.; Ocakoğlu, F.; Campbell, C. Navigating the complexity of detrital rutile provenance: Methodological insights from the Neotethys orogen in Anatolia. *Geochronology* **2024**, *6*, 265–290. [\[CrossRef\]](#)
25. Odlum, M.L.; Capaldi, T.N.; Thomson, K.D.; Stockli, D.F. Tracking cycles of Phanerozoic opening and closing of ocean basins using detrital rutile and zircon geochronology and geochemistry. *Geology* **2024**, *52*, 357–361. [\[CrossRef\]](#)
26. Meinhold, G. Rutile and its applications in earth sciences. *Earth Sci. Rev.* **2010**, *102*, 1–28. [\[CrossRef\]](#)
27. Triebold, S.; von Eynatten, H.; Zack, T. A recipe for the use of rutile in sedimentary provenance analysis. *Sediment. Geol.* **2012**, *282*, 268–275. [\[CrossRef\]](#)
28. Lenaz, D.; Princivalle, F. Crystal-chemistry of detrital chromites in sandstones from Trieste (NE Italy). *Neues Jahrb. Mineral. Monatshefte* **1996**, *9*, 429–434.
29. Lenaz, D.; Princivalle, F. The crystal chemistry of detrital chromian spinel from the Southeastern Alps and Outer Dinarides: The discrimination of supplies from areas of similar tectonic setting? *Can. Mineral.* **2005**, *43*, 1305–1314. [\[CrossRef\]](#)
30. Lenaz, D.; Kamenetsky, V.S.; Crawford, A.J.; Princivalle, F. Melt inclusions in detrital spinels from the SE Alps (Italy-Slovenia): A new approach to provenance studies of sedimentary basins. *Contrib. Mineral. Petrol.* **2000**, *139*, 748–758. [\[CrossRef\]](#)
31. Lenaz, D.; Kamenetsky, V.; Princivalle, F. Cr-spinel supply in the Brkini, Istrian and Krk Island flysch basins (Slovenia, Italy and Croatia). *Geol. Mag.* **2003**, *140*, 335–372. [\[CrossRef\]](#)
32. Lenaz, D.; Mazzoli, C.; Velicogna, M.; Princivalle, F. Trace and Rare Earth Elements chemistry of detrital garnets from SE Alps and Outer Dinarides flysch basins: An important tool to better define the source areas of sandstones. *Mar. Pet. Geol.* **2018**, *98*, 653–661. [\[CrossRef\]](#)
33. Lenaz, D.; Princivalle, F. Detrital high pressure—Low temperature minerals in Lower Eocene deep-sea turbidites of the Julian Alps (NE Italy). *Period. Mineral.* **2002**, *71*, 127–135.
34. Lenaz, D.; Garlatti, G.; Bernardi, F.; Andò, S. Detrital tourmalines in the Cretaceous-Eocene Julian and Brkini flysch basins (SE Alps, Italy and Slovenia). *Minerals* **2024**, *14*, 598. [\[CrossRef\]](#)
35. Lenaz, D. Detrital pyroxenes in the Eocene flysch of the Istrian basin (Slovenia, Croatia). *Geol. Acta* **2008**, *6*, 259–266. [\[CrossRef\]](#)
36. Orehek, S. Eocensli fliš Pivške Kotline in Brkinov. In *7th Kongres Geologov SFRJ, Predavanja*; University of Zagreb: Zagreb, Croatia, 1972; pp. 252–270.
37. Golonka, J. Plate tectonic evolution of the southern margin of Eurasia in the Mesozoic and Cenozoic. *Tectonophysics* **2004**, *381*, 235–273. [\[CrossRef\]](#)
38. Stampfli, G.M.; Kozur, H.W. Europe from the Variscan to the Alpine Cycles. In *Geological Society, London, Memoirs*; Geological Society of London: London, UK, 2006.
39. Stampfli, G.M.; von Raumer, J.F.; Borel, G. The Paleozoic evolution of pre-Variscan terranes: From Gondwana to the Variscan collision. In *Variscan-Appalachian Dynamics: The building of the Late Paleozoic Basement*; Martínez Catalán, J.R., Hatcher, R.D., Jr., Arenas, R., Díaz Garcia, F., Eds.; Geological Society of America Special Papers: Boulder, CO, USA; Geological Society of America: Boulder, CO, USA, 2002; Volume 364, pp. 263–280.
40. Csontos, L.; Vörös, A. Mesozoic plate tectonic reconstruction of the Carpathian region. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* **2004**, *210*, 1–56. [\[CrossRef\]](#)

41. Zanetti, A.; Mazzucchelli, M.; Sinigoi, S.; Giovanardi, T.; Peressini, G.; Fanning, M. SHRIMP U-Pb Zircon Triassic Intrusion Age of the Finero Mafic Complex (Ivrea-Verbanò Zone, Western Alps) and its Geodynamic Implications. *J. Petrol.* **2013**, *54*, 2235–2265. [\[CrossRef\]](#)
42. Bortolotti, V.; Principi, G. Tethyan ophiolites and Pangea break-up. *Isl. Arc* **2005**, *14*, 442–470. [\[CrossRef\]](#)
43. Schmid, S.M.; Bernoulli, D.; Fügenschuh, B.; Matenco, L.; Schefer, S.; Schuster, R.; Tischler, M.; Ustaszewski, K. The Alpine-Carpathian-Dinaridic orogenic system: Correlation and evolution of tectonic units. *Swiss J. Geosci.* **2008**, *101*, 139–183. [\[CrossRef\]](#)
44. Muttoni, G.; Gaetani, M.; Kent, D.V.; Sciunnach, D.; Angiolini, L.; Berra, F.; Garzanti, E.; Mattei, M.; Zanchi, A. Opening of the Neo-Tethys Ocean and the Pangea B to Pangea A transformation during the Permian. *GeoArabia* **2009**, *14*, 17–48. [\[CrossRef\]](#)
45. Maffione, M.; van Hinsbergen, D.J.J. Reconstructing plate boundaries in the Jurassic Neo-Tethys from the East and West Vardar Ophiolites (Greece and Serbia). *Tectonics* **2018**, *37*, 858–887. [\[CrossRef\]](#)
46. Schettino, A.; Turco, E. Tectonic history of the western Tethys since the Late Triassic. *Geol. Soc. Am. Bull.* **2011**, *123*, 89–105. [\[CrossRef\]](#)
47. Stampfli, G.M.; Hochard, C. *Plate Tectonics of the Alpine Realm*; Geological Society, London, Special Publications: London, UK; Geological Society of London: London, UK, 2009; pp. 89–111.
48. Channell, J.E.T. Paleomagnetic data from Umbria (Italy): Implications for the rotation of Adria and Mesozoic apparent polar wander paths. *Tectonophysics* **1992**, *216*, 365–378. [\[CrossRef\]](#)
49. Stefani, C.; Zattin, M.; Grandesso, P. Petrography of Paleogene turbiditic sedimentation in northeastern Italy. In *Sedimentary Provenance and Petrogenesis: Perspectives from Petrography and Geochemistry*; Arribas, J., Critelli, S., Johnsson, M.J., Eds.; Geological Society of America Special Papers: Boulder, CO, USA; Geological Society of America: Boulder, CO, USA, 2007; Volume 420, pp. 37–55. [\[CrossRef\]](#)
50. Stefani, C.; Fellin, M.G.; Zattin, M.; Zuffa, G.G.; Dalmonte, C.; Mancin, N.; Zanferrari, A. Provenance and Paleogeographic Evolution in a Multi-Source Foreland: The Cenozoic Venetian–Friulian Basin (NE Italy). *J. Sediment. Res.* **2007**, *77*, 867–887. [\[CrossRef\]](#)
51. Sölva, H.; Grasemann, B.; Thöni, M.; Thiede, R.; Habler, G. The Schneeberg Normal Fault Zone: Normal faulting associated with Cretaceous SE-directed extrusion in the Eastern Alps (Italy/Austria). *Tectonophysics* **2015**, *401*, 143–166.
52. Kováč, M.; Plašienka, D.; Soták, J.; Vojtko, R.; Oszczypko, N.; Less, G.; Čosović, V.; Fügenschuh, B.; Králiková, S. Paleogene palaeogeography and basin evolution of the Western Carpathians, Northern Pannonian domain and adjoining areas. *Glob. Planet. Change* **2016**, *140*, 9–27. [\[CrossRef\]](#)
53. Dercourt, J.; Zonenshain, L.P.; Ricou, L.E.; Kazmin, V.G.; Le Pichon, X.; Knipper, A.L.; Grandjacquet, C.; Sbortshikov, I.M.; Geyssant, J.; Lepvrier, C.; et al. Geological evolution of the Tethys belt from the Atlantic to the Pamirs since the Lias. *Tectonophysics* **1986**, *123*, 241–315. [\[CrossRef\]](#)
54. Albarello, D.; Mantovani, E.; Babbucci, D.; Tamburelli, C. Africa-Eurasia kinematics: Main constraints and uncertainties. *Tectonophysics* **1995**, *243*, 25–36. [\[CrossRef\]](#)
55. Rosenbaum, G.; Lister, G.S.; Duboz, C. Relative motions of Africa, Iberia and Europe during Alpine orogeny. *Tectonophysics* **2002**, *359*, 117–129. [\[CrossRef\]](#)
56. Rosenbaum, G.; Lister, G.S.; Duboz, C. The Mesozoic and Cenozoic motion of Adria (central Mediterranean): A review of constraints and limitations. *Geodinam. Acta* **2004**, *17*, 125–139. [\[CrossRef\]](#)
57. Rosenbaum, G.; Lister, G.S. The Western Alps from the Jurassic to Oligocene: Spatio-temporal constraints and evolutionary reconstructions. *Earth-Sci. Rev.* **2005**, *69*, 281–306. [\[CrossRef\]](#)
58. Ogorelec, B.; Šribar, L.; Buser, S. O litologiji in biostratigrafiji volcanskega apnenca. *Geologija* **1976**, *19*, 126–151.
59. Tunis, G.; Pirini Radizzani, C. Flyschoid deposits of Goriška Brda (Collio) between Soca (Isonzo) river and Idrija (Iudrio) river—Facies and paleoenvironments. *Geologija* **1987**, *30*, 123–148.
60. Miklavič, B.; Rožič, B. The onset of Maastrichtian basinal sedimentation on Mt. Matajur, NW Slovenia Začetek maastrichtijske bazenske sedimentacije na Matajurju, SZ Slovenija. *Mater. Geoenviron.* **2008**, *55*, 199–214.
61. Tunis, G.; Venturini, S. Nuove osservazioni stratigrafiche sul Mesozoico delle Valli del Natisone (Friuli orientale). *Gortania* **1987**, *8*, 17–68.
62. Ogata, K.; Pogačnik, Ž.; Pini, G.A.; Festa, A.; Camerlenghi, A.; Rebesco, M. The carbonate mass transport deposits of the Paleogene Friuli Basin (Italy/Slovenia): Internal anatomy and inferred genetic processes. *Mar. Geol.* **2014**, *356*, 88–110. [\[CrossRef\]](#)
63. Ogata, K.; Festa, A.; Pini, G.A.; Pogačnik, Z.; Lucente, C.C. Substrate deformation and incorporation in sedimentary mélanges (olistostromes): Examples from the northern Apennines (Italy) and northwestern Dinarides (Slovenia). *Gondwana Res.* **2019**, *74*, 101–125. [\[CrossRef\]](#)
64. Venturini, S.; Tunis, G. La composizione dei conglomerati cenozoici del Friuli: Dati preliminary. *Studi Geol. Camerti* **1992**, *CROP 1-1A*, 285–295. (In Italian)

65. Tunis, G.; Venturini, S. L'Eocene delle Prealpi Carniche, dell'Altipiano di Brkini e dell'Istria: Precisazioni biostratigrafiche e paleoambientali. *Nat. Nascosta* **1996**, *13*, 40–49.
66. Orehek, S. Palaeotransport of SW Slovenian Flysch. In *Field Trip Guidebook. IGCP Project 286—Early Paleogene Benthos, 2nd Meeting Postojna*; University of Ljubljana: Ljubljana, Slovenia, 1991; pp. 27–31.
67. Ustaszewski, K.; Kounov, A.; Schmid, S.M.; Schaltegger, U.; Krenn, E.; Frank, W.; Fügenschuh, B. Evolution of the Adria-Europe plate boundary in the northern Dinarides: From continent-continent collision to back-arc extension. *Tectonics* **2010**, *29*, TC6017. [\[CrossRef\]](#)
68. Tunis, G.; Venturini, S. Evolution of the Southern Margin of the Julian Basin with Emphasis on the Megabeds and Turbidites Sequence of the Southern Julian Prealps (NE Italy). *Geol. Croat.* **1992**, *45*, 127–150.
69. Triebold, S.; Luvizotto, G.L.; Tolosana-Delgado, R.; Zack, T.; von Eynatten, H. Discrimination of TiO₂ polymorphs in sedimentary and metamorphic rocks. *Contrib. Mineral. Petrol.* **2011**, *161*, 581–596. [\[CrossRef\]](#)
70. Jochum, K.P.; Weis, U.; Stoll, B.; Kuzmin, D.; Yang, Q.; Raczek, I.; Jacob, D.E.; Stracke, A.; Birbaum, K.; Frick, D.A.; et al. Determination of reference values for NIST SRM 610-617 glasses following ISO guidelines. *Geostand. Geoanal. Res.* **2011**, *35*, 397–429. [\[CrossRef\]](#)
71. Paton, C.; Woodhead, J.D.; Hellstrom, J.C.; Hergt, J.M.; Greig, A.; Maas, R. Improved laser ablation U-Pb zircon geochronology through robust downhole fractionation correction: Improved laser ablation U-Pb geochronology. *Geochim. Geophys. Geosyst.* **2010**, *11*, Q0AA06. [\[CrossRef\]](#)
72. Paton, C.; Hellstrom, J.; Paul, B.; Woodhead, J.; Hergt, J. Iolite: Freeware for the visualisation and processing of mass spectrometric data. *J. Anal. At. Spectrom.* **2011**, *26*, 2508–2518. [\[CrossRef\]](#)
73. Guillong, M.; Meier, D.; Allan, M.; Heinrich, C.; Yardley, B. SILLS: A MATLAB-based program for the reduction of laser ablation ICP-MS data of homogeneous materials and inclusions. In *Laser Ablation ICP-MS in the Earth Sciences: Current Practices and Outstanding Issues: Mineralogical Association of Canada Short Course*; Sylvester, P., Ed.; Mineralogical Association of Canada: Vancouver, BC, Canada, 2008; Volume 40, pp. 328–333.
74. Chew, D.M.; Petrus, J.A.; Kamber, B.S. U–Pb LA–ICPMS dating using accessory mineral standards with variable common Pb. *Chem. Geol.* **2014**, *363*, 185–199. [\[CrossRef\]](#)
75. Schmitt, A.K.; Zack, T. High-sensitivity U–Pb rutile dating by secondary ion mass spectrometry (SIMS) with an O²⁺ primary beam. *Chem. Geol.* **2012**, *332*, 65–73. [\[CrossRef\]](#)
76. Stacey, J.S.; Kramers, J.D. Approximation of terrestrial lead isotope evolution by a two-stage model. *Earth Planet. Sci. Lett.* **1975**, *26*, 207–221. [\[CrossRef\]](#)
77. Zack, T.; Stockli, D.F.; Luvizotto, G.L.; Barth, M.G.; Belousova, E.; Wolfe, M.R.; Hinton, R.W. In situ U–Pb rutile dating by LA-ICP-MS: 208Pb correction and prospects for geological applications. *Contrib. Mineral. Petrol.* **2011**, *162*, 515–530. [\[CrossRef\]](#)
78. Sliwinski, J.T.; Guillong, M.; Horstwood, M.S.A.; Bachmann, O. Quantifying Long-Term Reproducibility of Zircon Reference Materials by U–Pb LA-ICP-MS Dating. *Geostand. Geoanal. Res.* **2022**, *46*, 401–409. [\[CrossRef\]](#)
79. Vermeesch, P. IsoplotR: A free and open toolbox for geochronology. *Geosci. Front.* **2018**, *9*, 1479–1493. [\[CrossRef\]](#)
80. Grunsky, E.C. The interpretation of geochemical survey data. *Geochem. Explor. Environ. Anal.* **2010**, *10*, 27–74. [\[CrossRef\]](#) [\[PubMed\]](#)
81. Porter, J.K.; McNaughton, N.J.; Evans, N.J.; McDonald, B.J. Rutile as a pathfinder for metals exploration. *Ore Geol. Rev.* **2020**, *120*, 103406. [\[CrossRef\]](#)
82. R Core Team. *R: A Language and Environment for Statistical Computing*; R Foundation for Statistical Computing: Vienna, Austria, 2024. Available online: <https://www.R-project.org/> (accessed on 13 August 2026).
83. Bazylev, B.; Zakariadze, G.; Popević, A.; Kononkova, N.; Karpenko, S.; Milovanović, D.; Simakin, S. Spinel peridotites and garnet pyroxenites from Bistrica massif (Dinaridic ophiolite belt): The possible fragment of a sub-continental mantle. In *International Symposium on the Mesozoic Ophiolite Belts of the Northern Part of the Balkan Peninsula, Proceedings of the International Symposium*; Faculty of Mining and Geology, University of Belgrade: Belgrade, Serbia, 2006; pp. 12–14.
84. Balen, D.; Massonne, H.-J. Two contrasting P–T paths for metamorphic sole amphibolites of the Dinaride Ophiolite Zone (Krivaja-Konjuh ultramafic massif, Central Bosnia and Herzegovina) and their geodynamic implications. *Lithos* **2021**, *394–395*, 106184. [\[CrossRef\]](#)
85. Bucher, K.; Grapes, R. *Petrogenesis of Metamorphic Rocks*, 8th ed.; Springer Science & Business Media: Berlin, Germany, 2011.
86. Meinhold, G.; Anders, B.; Kostopoulos, D.; Reischmann, T. Rutile chemistry and thermometry as provenance indicator: An example from Chios Island, Greece. *Sediment. Geol.* **2008**, *203*, 98–111. [\[CrossRef\]](#)
87. Velicogna, M. Zircon Dating and Trace Element Content of Transparent Heavy Minerals in Sandstones from the SE Alps and Outer Dinarides Flysch Basins. Ph.D. Thesis, University of Trieste, Trieste, Italy, 2020; 194p.
88. Triebold, S.; von Eynatten, H.; Luvizotto, G.L.; Zack, T. Deducing source rock lithology from detrital rutile geochemistry: An example from the Erzgebirge, Germany. *Chem. Geol.* **2007**, *244*, 421–436. [\[CrossRef\]](#)

89. Schmidt, A.; Weyer, S.; John, T.; Brey, G.P. HFSE systematics of rutile-bearing eclogites: New insights into subduction zone processes and implications for the Earth's HFSE budget. *Geochim. Cosmochim. Acta* **2009**, *73*, 455–468. [\[CrossRef\]](#)
90. Aulbach, S.; O'Reilly, S.Y.; Pearson, N.J. Constraints from eclogite and MARID xenoliths on origin of mantle Zr/Hf-Nb-Ta variability. *Contrib. Mineral. Petrol.* **2011**, *162*, 1047–1062. [\[CrossRef\]](#)
91. Nicklas, R.W.; Aulbach, S.; Baxter, E.F. High field strength element systematics of rutile in cratonic eclogites: Evidence for Nb-Ta disequilibrium. *Lithos* **2025**, *508–509*, 108080. [\[CrossRef\]](#)
92. Münker, C.; Pfänder, J.A.; Weyer, S.; Buchl, A.; Kleine, T.; Mezger, K. Evolution of planetary cores and the Earth-Moon system from Nb-Ta systematics. *Science* **2003**, *301*, 84–87. [\[CrossRef\]](#) [\[PubMed\]](#)
93. John, T.; Klemm, R.; Klemme, S.; Pfänder, J.A.; Hoffmann, J.E.; Gao, J. Nb-Ta fractionation by partial melting at the titanite-rutile transition. *Contrib. Mineral. Petrol.* **2011**, *161*, 35–45. [\[CrossRef\]](#)
94. Meyer, M.; John, T.; Brandt, S.; Klemm, R. Trace element composition of rutile and the application of Zr-in-rutile thermometry to UHT metamorphism (Epupa Complex, NW Namibia). *Lithos* **2011**, *126*, 388–401. [\[CrossRef\]](#)
95. Cave, B.J.; Stepanov, A.S.; Craw, D.; Large, R.R.; Halpin, J.A.; Thompson, J. Release of trace elements through the sub-greenschist facies breakdown of detrital rutile to metamorphic titanite in the Otago schist, New Zealand. *Can. Mineral.* **2015**, *53*, 379–400. [\[CrossRef\]](#)
96. Tang, M.; Lee, C.-T.A.; Chen, K.; Erdman, M.; Costin, G.; Jiang, H. Nb-Ta systematics in arc magma differentiation and the role of arclogites in continent formation. *Nat. Commun.* **2019**, *10*, 235. [\[CrossRef\]](#) [\[PubMed\]](#)
97. Luvizotto, G.L.; Zack, T.; Triebold, S.; von Eynatten, H. Rutile occurrence and trace element behavior in medium-grade metasedimentary rocks: Example from the Erzgebirge, Germany. *Mineral. Petrol.* **2009**, *97*, 233–249. [\[CrossRef\]](#)
98. Stepanov, A.S.; Hermann, J. Fractionation of Nb and Ta by biotite and phengite: Implications for the “missing Nb paradox”. *Geology* **2013**, *41*, 303–306. [\[CrossRef\]](#)
99. Şengün, F.; Zack, T.; Topuz, G. Rutile geochemistry and thermometry of eclogites and associated garnet-mica schists in the Biga Peninsula, NW Turkey. *Geochemistry* **2017**, *77*, 503–515. [\[CrossRef\]](#)
100. Zheng, Y.F.; Gao, X.Y.; Chen, R.X.; Gao, T. Zr-in-rutile thermometry of eclogite in the Dabie orogen: Constraints on rutile growth during continental subduction-zone metamorphism. *J. Asian Earth Sci.* **2011**, *40*, 427–451. [\[CrossRef\]](#)
101. Şengün, F.; Zack, T. Trace element composition of rutile and Zr-in-rutile thermometry in meta-ophiolitic rocks from the Kazdağ Massif, NW Turkey. *Mineral. Petrol.* **2016**, *110*, 547–560. [\[CrossRef\]](#)
102. Rudnick, R.L.; Barth, M.; Horn, I.; McDonough, W.F. Rutile-Bearing Refractory Eclogites: Missing Link Between Continents and Depleted Mantle. *Science* **2000**, *287*, 278–281. [\[CrossRef\]](#) [\[PubMed\]](#)
103. Liu, L.; Xiao, Y.; Aulbach, S.; Li, D.; Hou, Z. Vanadium and niobium behavior in rutile as a function of oxygen fugacity: Evidence from natural samples. *Contrib. Mineral. Petrol.* **2014**, *167*, 1026. [\[CrossRef\]](#)
104. Münker, C.; Wörner, G.; Yogodzinski, G.; Churikova, T. Behavior of high field strength elements in subduction zones: Constraints from Kamchatka-Aleutian arc lavas. *Earth Planet. Sci. Lett.* **2004**, *224*, 275–293. [\[CrossRef\]](#)
105. Kalfoun, F.; Ionov, D.; Merleta, C. HFSE residence and Nb-Ta ratios in metasomatised, rutile-bearing mantle peridotites. *Earth Planet. Sci. Lett.* **2002**, *199*, 49–65. [\[CrossRef\]](#)
106. Xiong, X.L.; Adam, J.; Green, T.H. Rutile stability and rutile/melt HFSE partitioning during partial melting of hydrous basalt: Implications for TTG genesis. *Chem. Geol.* **2005**, *218*, 339–359. [\[CrossRef\]](#)
107. Şengün, F. Zr-in-rutile thermometry of eclogites from the Karakaya Complex in NW Turkey: Implications for rutile growth during subduction zone metamorphism. *Geochemistry* **2017**, *77*, 95–104. [\[CrossRef\]](#)
108. Gao, X.Y.; Zheng, Y.F.; Xia, X.P.; Chen, Y.X. U-Pb ages and trace elements of metamorphic rutile from ultrahigh-pressure quartzite in the Sulu orogen. *Geochim. Cosmochim. Acta* **2014**, *143*, 87–114. [\[CrossRef\]](#)
109. Green, T.H. Significance of Nb-Ta as an indicator of geochemical processes in the crust mantle system. *Chem. Geol.* **1995**, *120*, 347–359. [\[CrossRef\]](#)
110. Bau, M. Controls on the fractionation of isovalent trace elements in magmatic and aqueous systems: Evidence from Y/Ho, Zr/Hf, and lanthanide tetrad effect. *Contrib. Mineral. Petrol.* **1996**, *123*, 323–333. [\[CrossRef\]](#)
111. Zeh, A.; Cabral, A.R.; Koglin, N.; Decker, M. Rutile alteration and authigenic growth in metasandstones of the Moeda Formation, Minas Gerais, Brazil—A result of Transamazonian fluid-rock interaction. *Chem. Geol.* **2018**, *483*, 397–409. [\[CrossRef\]](#)
112. Hart, E.; Storey, C.; Bruand, E.; Schertl, H.P.; Alexander, B.D. Mineral inclusions in rutile: A novel recorder of HP-UHP metamorphism. *Earth Planet. Sci. Lett.* **2016**, *446*, 137–148. [\[CrossRef\]](#)
113. Bracciali, L.; Parrish, R.R.; Horstwood, M.S.A.; Condon, D.J.; Najman, Y. U-Pb LA-(MC)-ICP-MS dating of rutile: New reference materials and applications to sedimentary provenance. *Chem. Geol.* **2013**, *347*, 82–101. [\[CrossRef\]](#)
114. Triantafyllou, A.; Berger, J.; Baele, J.-M.; Bruguier, O.; Diot, H.; Ennih, N.; Monnier, C.; Plissart, G.; Vandycke, S.; Watlet, A. Intra-oceanic arc growth driven by magmatic and tectonic processes recorded in the Neoproterozoic Bougmane arc complex (Anti-Atlas, Morocco). *Precambrian Res.* **2018**, *304*, 39–63. [\[CrossRef\]](#)

115. Mikes, T.; Christ, D.; Petri, R.; Dunkl, I.; Frei, D.; Baldi-Beke, M.; Reitner, J.; Wemmer, K.; Hrvatović, H.; von Eynatten, H. Provenance of the Bosnian Flysch. *Swiss J. Geosci.* **2008**, *101*, S31–S54. [\[CrossRef\]](#)
116. Crnjaković, M. Maastrichtian flysch sediments in the south–west part of Mt. Medvednica. *Geol. Vjesn. Zagreb* **1981**, *34*, 47–61.
117. Zupanič, J. Non-carbonate detritus from arenite sediments of Maastrichtian Vivodina Flysch (Žumberak, Western Dinarides). *Geol. Vjesn.* **1981**, *34*, 109–120.
118. Goričan, Š.; Košir, A.; Rožič, B.; Šmuc, A.; Gale, L.; Kukoč, D.; Celarc, B.; Črne, A.E.; Kolar-Jurkovšek, T.; Placer, L. Mesozoic deep-water basins of the eastern Southern Alps (NW Slovenia). *J. Alp. Geol.* **2012**, *54*, 101–143.
119. Goričan, Š.; Žibret, L.; Košir, A.; Kukoč, D.; Horvat, A. Stratigraphic correlation and structural position of Lower Cretaceous flysch-type deposits in the eastern Southern Alps (NW Slovenia). *Int. J. Earth Sci.* **2018**, *107*, 2933–2953. [\[CrossRef\]](#)
120. De Min, A.; Velicogna, M.; Ziberna, L.; Chiaradia, M.; Alberti, A.; Marzoli, A. Triassic magmatism in the European Southern Alps as an early phase of Pangea break-up. *Geol. Mag.* **2020**, *157*, 1800–1822. [\[CrossRef\]](#)
121. Velicogna, M.; De Min, A.; Prašek, M.K.; Ziberna, L.; Brombin, V.; Jourdan, F.; Renne, P.R.; Balen, D.; Grégoire, M.; Marzoli, A. The Norian magmatic rocks of Jabuka, Brusnik and Vis Islands (Croatia) and their bearing on the evolution of Triassic magmatism in the Northern Mediterranean. *Int. Geol. Rev.* **2024**, *65*, 2558–2579. [\[CrossRef\]](#)
122. Gärtner, A.; Niebuhr, B.; Breitfeld, H.T.; Rösel, D.; Schulze, M.C.; Wilmsen, M. Multi-proxy provenance study of sandstones from the northern Bohemian Cretaceous Basin (Germany, Czechia) focused on tourmaline, rutile and garnet. *Cretac. Res.* **2026**, *177*, 106203. [\[CrossRef\]](#)
123. von Raumer, J.F.; Bussy, F.; Schaltegger, U.; Schulz, B.; Stampfli, G.M. Pre-Mesozoic Alpine basements—Their place in the European Paleozoic framework. *Geol. Soc. Am. Bull.* **2013**, *125*, 89–108. [\[CrossRef\]](#)
124. Szczuka, M.; Gawęda, A.; Waśkowska, A.; Golonka, J.; Szopa, K.; Chew, D.; Drakou, F. The Silesian Ridge in the light of petrological and LA-ICP-MS U-Pb analyses of cohesive debrites from the Istebna Formation (Silesian Nappe, Outer Western Carpathians, Poland). *Geol. Q.* **2022**, *66*, 20. [\[CrossRef\]](#)
125. Bahlburg, H.; Vervoort, J.D.; Du Frane, S.A. Plate tectonic significance of Middle Cambrian and Ordovician siliciclastic rocks of the Bavarian Facies, Armorican Terrane Assemblage, Germany—U-Pb and Hf isotope evidence from detrital zircons. *Gondwana Res.* **2010**, *17*, 223–235. [\[CrossRef\]](#)
126. Nance, R.D.; Gutiérrez-Alonso, G.; Keppie, J.D.; Linnemann, U.; Murphy, J.B.; Quesada, C.; Strachan, R.A.; Woodcock, N.H. Evolution of the Rheic Ocean. *Gondwana Res.* **2010**, *17*, 194–222. [\[CrossRef\]](#)
127. Nance, R.D.; Gutiérrez-Alonso, G.; Keppie, J.D.; Linnemann, U.; Murphy, J.B.; Quesada, C.; Strachan, R.A.; Woodcock, N.H. A brief history of the Rheic Ocean. *Geosci. Front.* **2012**, *3*, 125–135. [\[CrossRef\]](#)
128. Abbo, A.; Avigad, D.; Gerdes, A. Crustal evolution of peri-Gondwana crust into present day Europe: The Serbo-Macedonian and Rhodope massifs as a case study. *Lithos* **2020**, *356–357*, 105295. [\[CrossRef\]](#)
129. Antić, M.; Peytcheva, I.; von Quadt, A.; Kounov, A.; Trivić, B.; Serafimovski, T.; Tasev, G.; Gerdjikov, I.; Wetzel, A. Pre-Alpine evolution of a segment of the North-Gondwana margin: Geochronological and geochemical evidence from the central Serbo-Macedonian Massif. *Gondwana Res.* **2016**, *36*, 523–544. [\[CrossRef\]](#)
130. Sharp, I.R.; Robertson, A.H.F. Tectonic-sedimentary evolution of the western margin of the Mesozoic Vardar Ocean: Evidence from the Pelagonian and Almopias zones, Northern Greece. *Geol. Soc. Lond. Spec. Publ.* **2006**, *20*, 373–412. [\[CrossRef\]](#)
131. Robertson, A.H.F.; Trivić, B.; Đerić, N.; Bocur, I.I. Tectonic development of the Vardar Ocean and its margins: Evidence from the Republic of Macedonia and Greek Macedonia. *Tectonophysics* **2013**, *595–596*, 25–54. [\[CrossRef\]](#)
132. Saccani, E.; Photiades, A.; Santato, A.; Zeda, O. New evidence for supra-subduction zone ophiolites in the Vardar Zone of Northern Greece: Implications for the tectono-magmatic evolution of the Vardar oceanic basin. *Ophioliti* **2008**, *33*, 65–85.
133. Robertson, A.H.F.; Karamata, S.; Šarić, K. Overview of ophiolites and related units in the Late Palaeozoic–Early Cenozoic magmatic and tectonic development of Tethys in the northern part of the Balkan region. *Lithos* **2009**, *108*, 1–36. [\[CrossRef\]](#)
134. Lugović, B.; Altherr, R.; Raczek, I.; Hofmann, A.; Majer, V. Geochemistry of peridotites and mafic igneous rocks from the Central Dinaridic Ophiolite Belt, Yugoslavia. *Contrib. Mineral. Petrol.* **1991**, *106*, 201–216. [\[CrossRef\]](#)
135. Bazylev, B.A.; Popević, A.; Karamata, S.; Kononkova, N.N.; Simakin, S.G.; Olujić, J.; Vujnović, L.; Memović, E. Mantle peridotites from the Dinaridic ophiolite belt and the Vardar zone western belt, central Balkan: A petrological comparison. *Lithos* **2009**, *108*, 37–71. [\[CrossRef\]](#)
136. Scherreiks, R.; BouDagher-Fadel, M. The closure of the Vardar Ocean (the western domain of the northern Neotethys) from the early Middle Jurassic to the Paleocene time, based on the surface geology of eastern Pelagonia and the Vardar zone, biostratigraphy, and seismic-tomographic images of the mantle below the Central Hellenides. *UCL Open Environ.* **2021**, *3*, e024. [\[CrossRef\]](#) [\[PubMed\]](#)
137. Bernardi, F.; Skogby, H.; Lenaz, D. OH-defects in detrital quartz grains from the Julian Basin (NE Italy and Slovenia): A Fourier-Transform Infrared study. *Geosciences* **2022**, *12*, 90, Correction in *Geosciences* **2023**, *13*, 127. [\[CrossRef\]](#)

138. Schönig, J.; Zack, T.; Rösel, D.; Tolosana-Delgado, R.; Marschall, H.; von Eynatten, H.; Lünsdorf, N.K.; Lueder, M.; Konrad-Schmolke, M.; Walters, J.B. Chemical discrimination of rutile from different metamorphic source rocks: Dealing with hierarchical data structures in random forest classification. *J. Metamorph. Geol.* **2026**, *44*, 112–137. [[CrossRef](#)]
139. Guillong, M.; Hametner, K.; Reusser, E.; Wilson, S.A.; Gunther, D. Preliminary characterisation of new glass reference materials (gsa-1g, gsc-1g, gsd-1g and gse-1g) by laser ablation-inductively coupled plasma-mass spectrometry using 193 nm, 213 nm and 266 nm wavelengths. *Geostand. Geoanalytical Res.* **2005**, *29*, 315–331. [[CrossRef](#)]

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