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# Geochemical Studies of Detrital Zircon Grains from the River Banks and Beach Placers of Coastal Odisha, India

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**Abstract:** Zircon grains are reasonably ubiquitous in river banks and beach placers as detrital minerals, including along the ~1700 km long Indian east coast, from Odisha state to the state of Kerala. Zircons from beach placers and river banks located along the eastern part of Odisha, India, were studied using LA-ICP-MS in order to delineate their geochemical characteristics. Hf (mean = 11270 ppm) and Y (mean = 1064 ppm) were the two most abundant trace elements found within zircon grains as compared to other trace elements. The abundance of uranium was observed to be 2–4 times larger than that of thorium. Zircon overgrowths formed in equilibrium with a partial melt and were similar to magmatic zircon in terms of the high Y, Hf and P content, steep heavy-enriched REE pattern, positive Ce anomaly and negative Eu anomaly. The average low Th/U ratio of the studied zircon grains distinguished them from the magmatic ones. The REE present in zircon grains was restricted to high-grade metamorphic events. The result of the present study would be useful for delineating the source region and the efficacy of resource potential and indigenous export.

**Keywords:** detrital zircon; beach placer; river bank placer; rare earth element

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**Citation:** Mohanty, S.; Papadopoulos, A.; Petrelli, M.; Papadopoulou, L.; Sengupta, D. Geochemical Studies of Detrital Zircon Grains from the River Banks and Beach Placers of Coastal Odisha, India. *Minerals* **2023**, *13*, 192. https://doi.org/10.3390/min13020192

Academic Editor: Manuel Francisco Pereira

Received: 5 January 2023
Revised: 20 January 2023
Accepted: 23 January 2023
Published: 28 January 2023

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## 1. Introduction

Zircon is very stable during mechanical and chemical weathering [1]. Magmatic events as well as metamorphic events can be distinguished through trace element variation in zircons [2]. They are enriched in rare earths (REEs), Th and U, which are of potential economic significance, and are utilized in several modern day applications, viz., nuclear reactors, nuclear power generation, solar panels, mobiles and electric and hybrid vehicles [3,4], and are an essential part of 'Green Technology' [5].

The state of Odisha, in the eastern part of India, has a long coastline of ~670 km. It has been reasonably well studied in terms of its various economic resources, except for the REEs in beach placers. Few studies have been conducted in terms of rare earth resources [5–7] in specific locations along the southwest. However, the region extending from the Mahanadi basin to the catchment region of the Rushikulya river has not been explored yet. The present study, thus, focusses on the region from Paradeep to Podampata, crossing the Rushikulya river mouth. Rare earth resources comprise strategic minerals with an increasing and rapid demand for their futuristic applications. Rare earth oxides are used in mature markets (such as metallurgy, catalysts and glassmaking) and in newer, high-growth markets (such as permanent magnets, battery alloys and ceramics), which account for 59% and 41% of the total worldwide consumption of REEs, respectively [8]. This is more pertinent as China is the sole major contributor of rare earth resources worldwide. Apart from China, Australia, the USA and Europe have also started REE mining since

2000 [9]. Zirconium does not absorb neutrons, making it an ideal material for use in nuclear power reactors, in addition to its extensive use in abrasives. More than 90% of zirconium is used in similar applications [10]. India exports most of its zirconium to the United States, Germany and Australia [11]. This area on the eastern coast of India was studied via hand held radiometric counters for the presence of radioactive minerals, primarily monazite and zircon [5]. Selected samples were subsequently collected from the beaches of Paradeep and Jahania, as well as the Mahanadi river bank, the Rushikulya river bank and Podampata beach, in the southwestern part of Odisha state.

Zircon, being the oldest heavy mineral within the earth's crust, can sustain the imprint and geological record of numerous experienced metamorphic events due to its high stability. The primary aim of this study was to delineate the provenance in terms of the host rock. In this regard, the hinterland lithology is of prime importance as it could give an idea of the source rock and the nature of beneficiation due to fluvial and aeolian activity. In addition, the geochemical nature of zircon, especially the abundance/enrichment of REEs, U and Th in zircon, could help in elucidating its nature, LREE versus HREE and related aspects, as well as applications where it could be utilized. The present research work would also be useful for the resource evaluation and exploration of heavy minerals.

## 2. Geology of the Study Area

The study area extended from Paradeep in the northeast to Podampata on the southwest coast of Odisha, spanning two major perennial rivers, Mahanadi and Rushikulya (Figure 1a–c). The locations (Figure 1b,c) were studied using hand held radiometric counters, and selected samples of sand were collected from various parts of the beach subunits and river banks (samples RSR2 and J6) based on the observed count rates. Based on our research studies, using radiometric and geochemical methods for coastal subunits, such as beaches, dunes and berms, is important in terms of mineral placer formation. The coastal system is a dynamic region between the continental part and the sea, specifically close to the river mouth. The formation of mineral placers depends on grain size, mineral density, grain sorting and other relevant hydrodynamic parameters [12]. The natural radioactivity of these sediments can be used as an effective tracer for delineating and modelling the important processes involved [13].

The study area was located at the Eastern Ghats Mobile Belt composed of rocks such as khondalites, charnockitic gneisses, calc-granulites, banded iron formations and quarzites of Archean to upper Proterozoic age [14]. The granulite terrain underwent several metamorphic events during the course of time [15]. These high-grade metamorphic rocks were assembled into four zones, namely, the western basic charnockite zone, the western khondalite zone, the central migmatite and charnockite zone and the eastern khondalite zone [16]. The two study areas were between the Mahanadi rift and Godavari rift (Figure 1a).

## 3. Field Survey and Sample Preparation

Samples of river and beach sands of approximately 500 g were collected from seven different locations, namely, PR (Paradeep beach), S2 (Siali beach), J6 (Mahanadi river), J3 (Jahania beach) (Figure 1b), RSN10 (north of Rushikulya river), PM-3 (Podampata beach) and RSR2 (Rushikulya river) (Figure 1c), respectively. The field-based radioactive reconnaissance surveys were undertaken with a Micro R Survey Meter UR-709 manufactured by Nucleonix Systems Pvt. Ltd., Secunderabad, India (Figure 2). The data acquired were used to measure the gamma ray variation on the surface of the coastal region of eastern India. Each measurement was taken thrice at a specific location along a grid. The radiometric traverse and subsequent grids were taken both parallel to the coastline and at places along the perpendicular direction, as much as possible. This provided a two-dimensional picture of the in situ radionuclide abundance in parts of the coastal region studied. The minimum data recorded were approximately a few mR/h, where the sediments were enriched pri-

marily in quartz and feldspar. On the other hand, data as high as 250–300 mR/h were obtained close to the heavy minerals enriched in radioactivity.

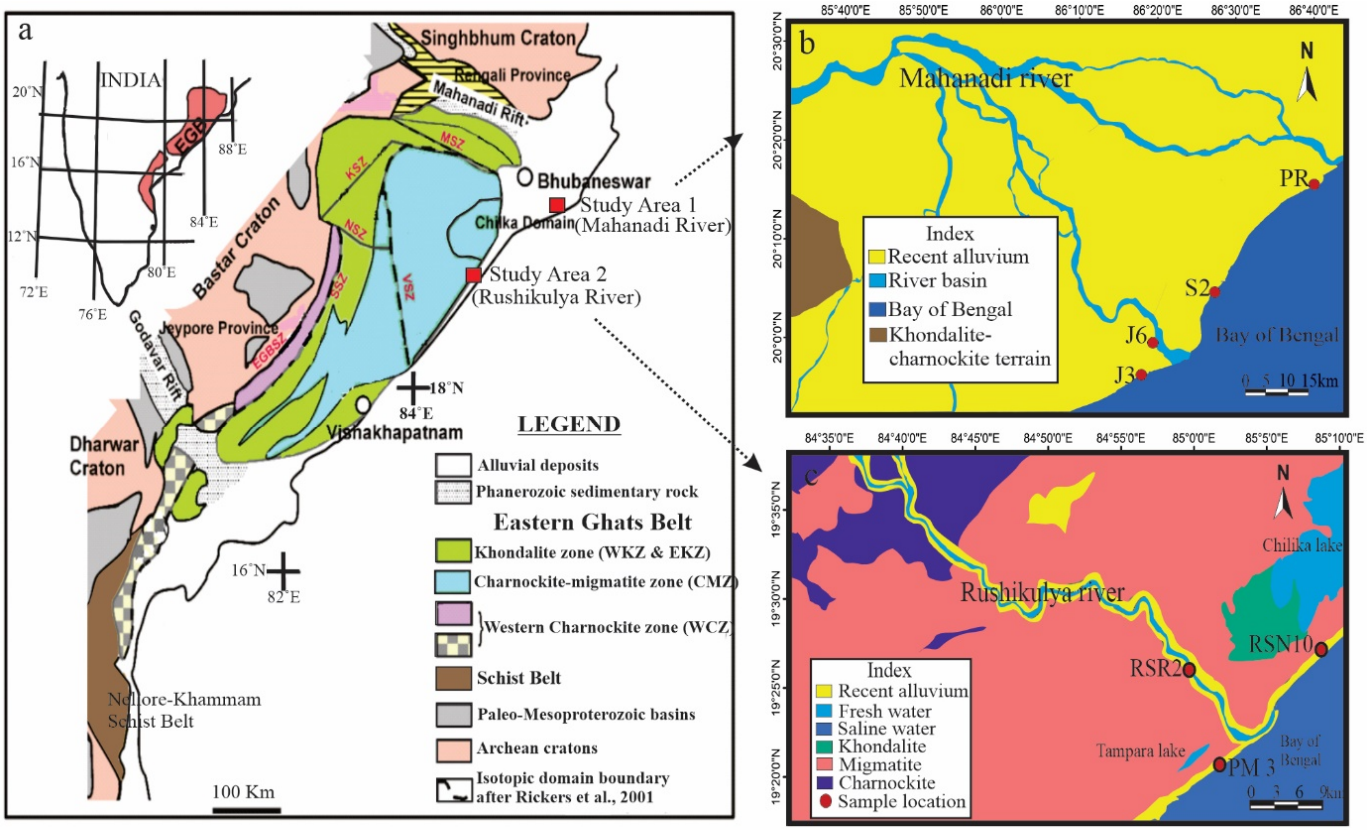



**Figure 1.** (**a**) Geological map of both study areas 1 and 2 (modified after [16]). (**b**) Location of sample collections from the Mahanadi river catchment area. (**c**) Location of sample collections from the Rushikulya river catchment area and adjacent beach.

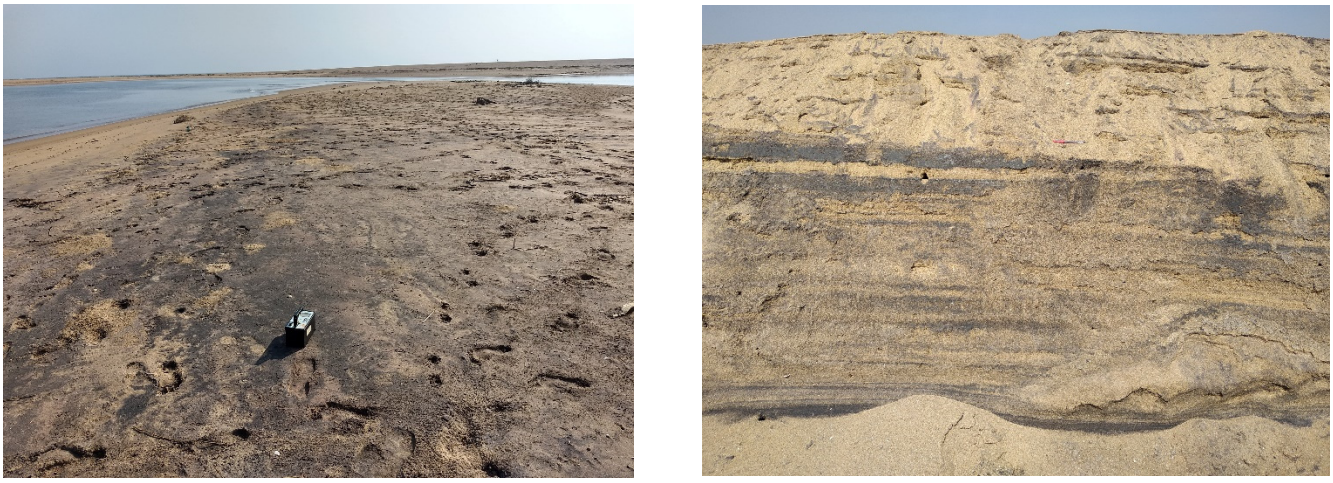


**Figure 2.** Field photograph with Micro R Survey Meter, which was used for radioactivity measurements during field work, and stratified deposits of heavy minerals from a sandy beach.

Seven samples of beach sand were collected in situ for the separation of heavy minerals, and were homogenised after coning and quartering. The samples were fine-grained to medium-grained and well to moderately well sorted [7]. The samples were abundant in heavy minerals such as ilmenite, zircons, monazite, garnet, rutile and sillimanite [5,7].

Heavy liquid separation techniques were used in order to retain the heavy minerals fraction containing zircons. Tetrabromoethane with a density of ~2.97 gm/cm$^3$ was poured into an upper (separatory) funnel to approximately half full. Then, the sample was poured into the tetrabromoethane and stirred thoroughly in order to wet all the particles. These were allowed to settle and were stirred periodically so that the particles would not adhere to the funnel wall. As the heavy minerals settled to the bottom of the separatory funnel, the pinchcock was opened and heavy mineral particles were collected on filter paper in the lower funnel. After being dried, the heavy mineral fraction and weight were recorded. Then, with the help of a reflected-light microscope, zircon grains were picked up with a wet brush and kept in clean glass vials, aiming to select the more euhedral zircon grains. Subsequently, these zircon grains were mounted in araldite and the mould was prepared for a trace element analysis.

## 4. Experimental Methodology

Sample locations selected for the present study were based on in situ radiometric data, obtained using a GM-based Micro R Survey Meter. These samples were subsequently homogenised through coning and quartering at the field site and used for the subsequent analysis. The SEM-EDS analysis of the bulk samples was performed at Aristotle University, where monazite and ilmenite were found along with zircon grains. The grains of monazite and ilmenite were too small, at <30 μm, to be further analysed with LA-ICP-MS. The LA-ICP-MS analyses were performed at the Department of Geosciences of the University of Perugia in Italy. The ICP-MS system was a Thermo-Electron X7 (Thermo Electron Corporation, Waltham, MA, USA) connected to a New Wave UP213 laser ablation unit. The latter converted the laser ablation base frequency of 1064 to 213 nm by using three harmonic generators. In the sample holder of the machine, the reference materials and the measured samples could be installed simultaneously. Helium was used as a carrier gas in the sample holder, instead of argon, in order to enhance the carrying capacity. Then, He was mixed with Ar before entering the ICP unit to ensure a stimulation with stable conditions. The repetition rate of the laser and its energy density were adjusted to 10 Hz and 10 J/cm$^3$, respectively. Data processing was performed using the Glitter software. The detection limits for U and Th, using a 40-micron laser diameter, were 0.002 and 0.002 mg/g, respectively. More details on the instrumental setup and the analytical protocols for the single-phase spatially resolved and bulk trace element analyses were presented by [17].

## 5. Results and Discussion

### *5.1. Radiometric Survey*

The radiometric surveys undertaken indicated that, generally, the beach regions exhibited higher count rates. Beach samples S2 and PM-3, collected from the adjacent beaches of the Mahanadi and Rushikulya rivers, showed highest radioactive count rates. S2 showed a radioactive count rate of 112 mR/h, whereas PM-3 showed 312 mR/h. Fluvial samples J6 and RSR2 showed almost similar count rates, 47 mR/h and 41 mR/h, respectively. Recent studies undertaken gave good results based on radioactive mapping and were also used in the present study (Figure 3) for the estimation of the ambient radioactivity.

### *5.2. Trace Elements and REE Geochemistry*

In general, zircons are unaffected by weathering and erosional cycles [2,18,19]. Detrital zircon grains are, in general, unaffected physically by weathering and erosion in high-energy marine environments, due to the geochemical immobility of Zr. The trace element contents of zircon were analysed using LA-ICP-MS. The most abundant trace elements were Hf (9554.13–12393.92 ppm), Y (750.29–1443.90 ppm), P (225.55–828.45 ppm), Th (124.72–248.41 ppm) and U (247.84–644.87 ppm) (Figure 4). Apart from this, there was also a higher enrichment of HREEs, mainly of Dy (80.89–146.04 ppm), Er (93.15–223.42 ppm) and Yb (183.00–395.01 ppm), than of LREEs (Figure 5). Other elements, such as Ti, were also present, but at less than 100 ppm. The lead content generally ranges from 2 to 30 ppm, as

reported by [18], but the sample from Jahania beach (J3) showed a Pb content of ~48 ppm, and also the highest Th/U ratio of 1.13 among the samples analysed in the present study. The U vs. U/Yb discrimination plot [20] provides a method for differentiating between zircon grains from the continental crust and those from the oceanic crust. The geochemical composition of zircon minerals in the present study laid within the continental field, as shown in Figure 6.

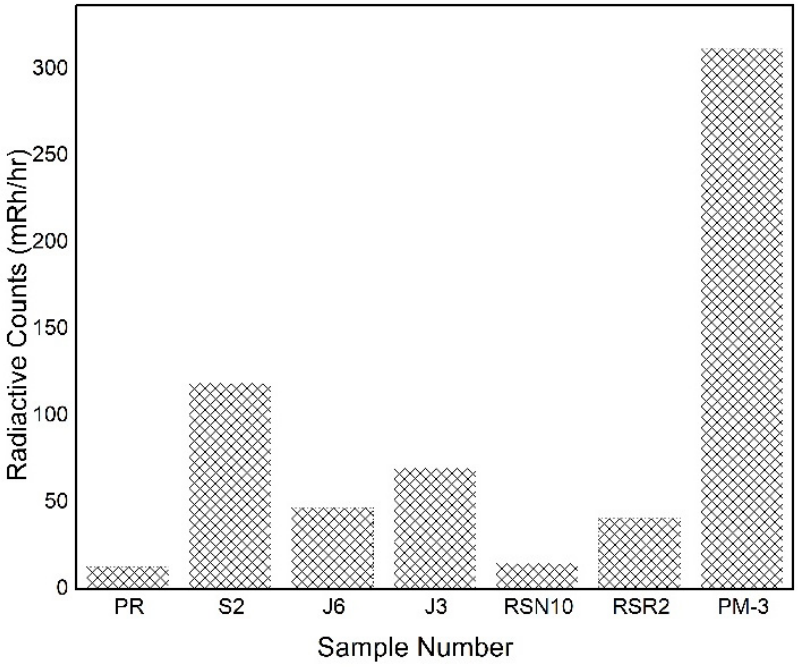



**Figure 3.** Histogram plot showing the radioactive count rates of samples collected from the study area.

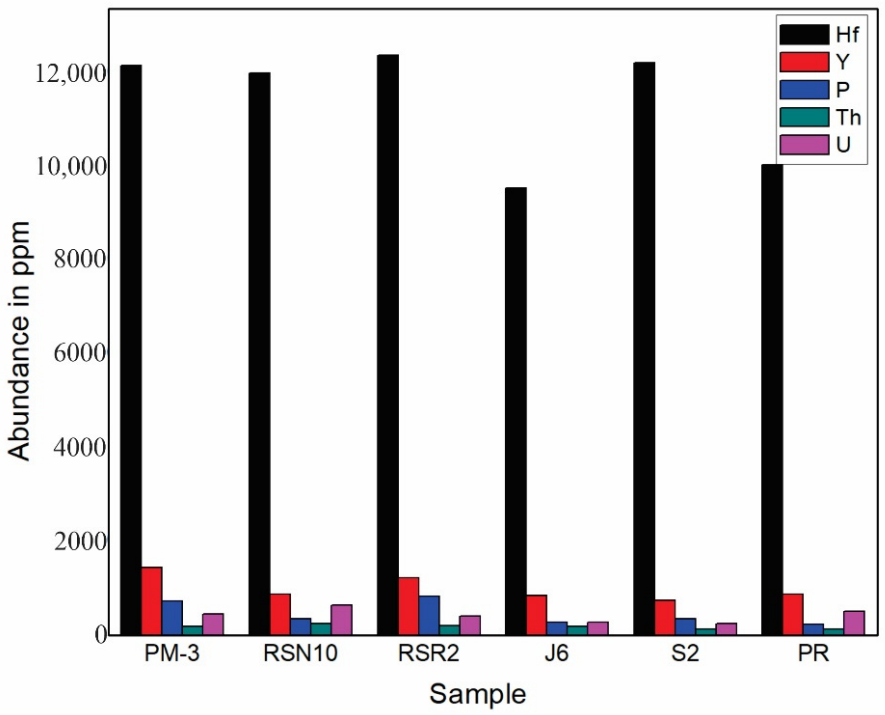



**Figure 4.** Abundance of trace elements and radioactive elements from different samples of sand.

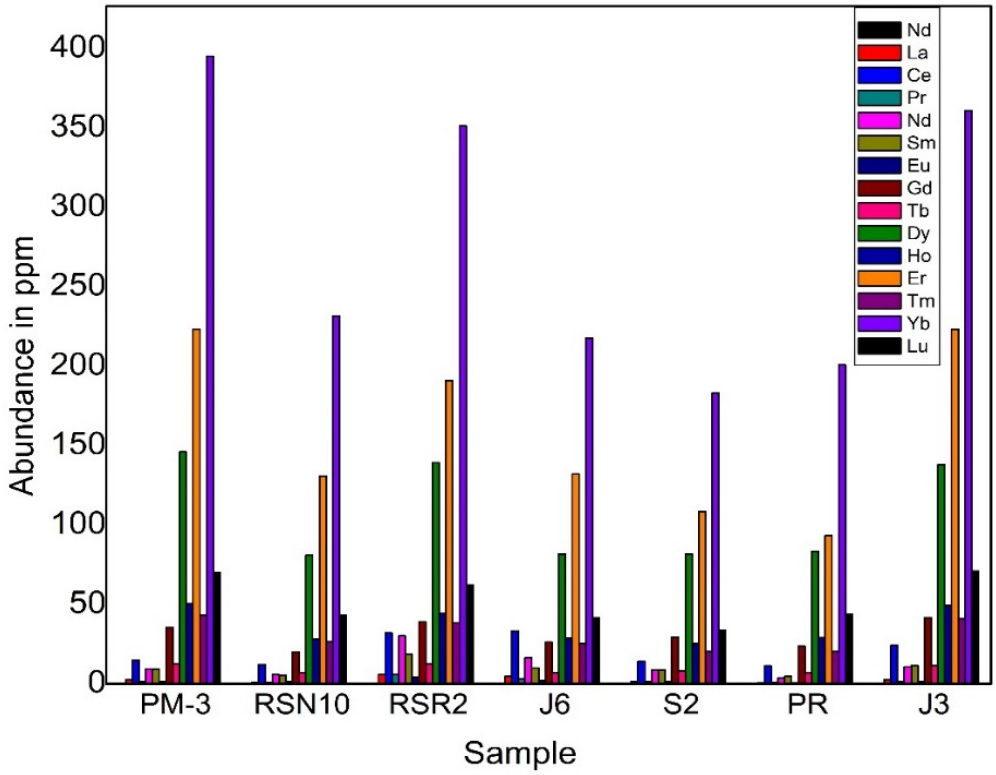



**Figure 5.** Abundance of REEs in zircon from different samples of sand.

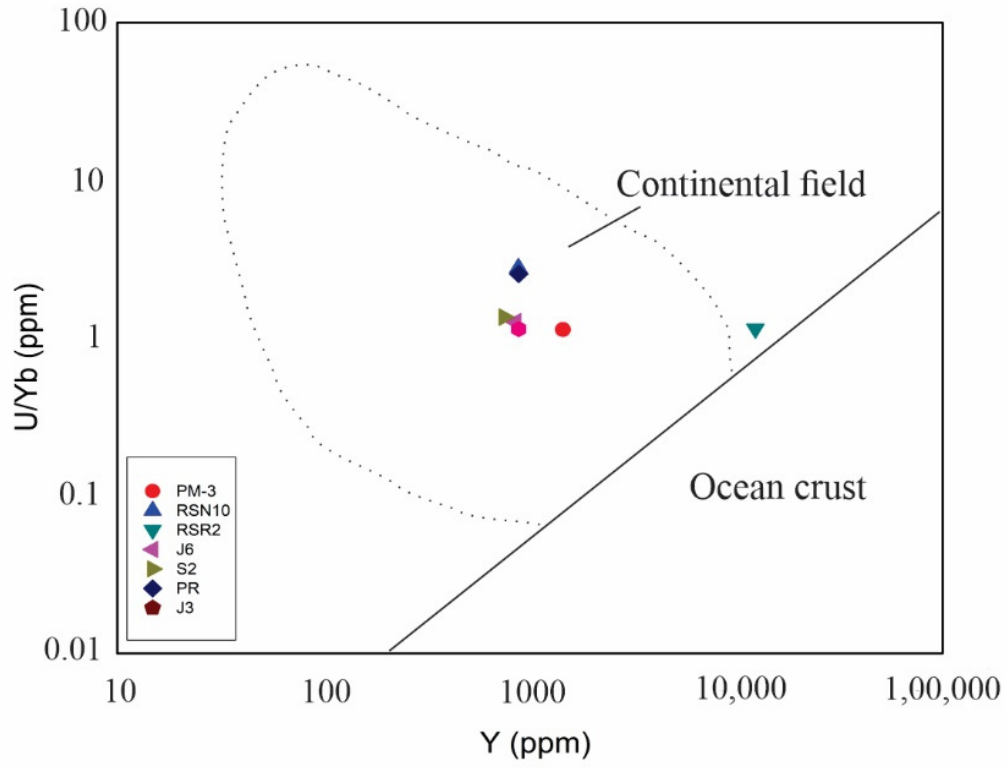



**Figure 6.** Discriminant diagram based on U/Yb vs. Y modified after [12] showing that all zircon grains from this study were derived from the continental crust.

The samples studied from seven selected locations were found to be enriched in P, especially the samples from the Rushikulya river (RSR2), Podampata (PM-3) and Jahania beach (J3), respectively (Table 1). The presence of P is not only confined to the present

area of study, but it is quite ubiquitous along other parts of the Indian coast, as well as the coastal part of South Africa [21,22]. The distribution of P in zircon could be formed through the fluctuation of P in the melt adjacent to the mineral–melt boundary, either because P diffuses more slowly than Zr in the melt or due to a surfacial interaction of the melt with crystals [23]. The presence of high hafnium (mean hafnium ~11,270 ppm) was observed in the zircon grains studied. Zr and Hf had closely similar ionic radii in both six- and eight-fold coordinations. The two elements behave nearly identically and always occur together; all Zr minerals contain some Hf [24,25]. It has been noted that the geochemical behaviours of Zr and Hf are similar during magma crystallisation [26]. Hafnium (Z = 72) substitutes for zirconium (Z = 40) in continuous solid solutions [25]. Zircon grains had higher U compared to Th, except in sample J3. The Th/U ratios in zircons varied from a minimum of 0.26 for Paradeep beach to a maximum of 1.31 for the Jahania beach sample, as summarised in Table 1. The average Th/U ratio was 30 [5] in the beach placers (including all heavy minerals) present on the eastern coast of Odisha. This was ten times higher than the UCC value of 3.8 [27]. It was observed in earlier studies [28] that the Th/U ratio varied in the grains of the same mineral, viz., zircon, due to different degrees of alteration caused by hydrothermal activity. The variation of the Th/U ratio in zircon grains also depends on the initial abundance of Th and U in the system and the breakdown and growth of monazite in equilibrium with zircon grains [29].

**Table 1.** Representative trace elements (in ppm) in zircons from various samples.

| | **PR (Paradeep Beach)** | **S2 (Siali Beach)** | **J3 (Jahanaia Beach)** | **J6 (Mahanadi River)** | **RSN10 (North of Rushikulya River)** | **PM-3 (Podampata)** | **RSR2 (Rushikulya River)** |
|---|---|---|---|---|---|---|---|
| P | 225.55 | 352.20 | 424.76 | 274.79 | 353.10 | 725.85 | 828.45 |
| Ca | <LOD | 390.49 | <LOD | 412.46 | <LOD | 405.64 | 453.08 |
| Ti | 11.24 | 12.22 | 18.48 | 15.59 | 10.44 | 11.94 | 17.49 |
| Mn | 2.62 | 19.39 | 10.93 | 101.10 | 3.73 | 15.52 | 11.27 |
| Fe | 208.26 | 291.80 | 693.59 | 1141.14 | 466.17 | 636.48 | 2336.75 |
| Ga | <LOD | <LOD | <LOD | <LOD | <LOD | <LOD | 2.65 |
| Rb | <LOD | 0.49 | 0.38 | <LOD | 0.27 | 0.67 | 0.47 |
| Sr | 0.35 | 0.71 | 0.62 | 2.96 | 0.58 | 0.89 | 0.75 |
| Y | 882 | 750 | 1413 | 852 | 879 | 1443 | 1230 |
| Nb | 4.50 | 2.60 | 6.07 | 4.74 | 2.65 | 5.71 | 8 |
| Ba | 0.62 | 0.97 | 0.8 | 1.30 | 0.57 | 0.90 | 2.64 |
| La | 0.55 | 1.51 | 2.60 | 4.49 | 0.93 | 2.28 | 5.74 |
| Ce | 11.13 | 14.01 | 24.06 | 33.05 | 12.16 | 14.80 | 32 |
| Pr | 0.67 | 1.39 | 1.47 | 3 | 0.92 | 1.40 | 5.84 |
| Nd | 3.54 | 8.57 | 10.55 | 16.47 | 5.79 | 9.44 | 30.2 |
| Sm | 4.76 | 8.57 | 11.34 | 10.02 | 5.51 | 9.03 | 18.47 |
| Eu | 0.55 | 1.38 | 1.67 | 1.85 | 1.27 | 1.45 | 4.27 |
| Gd | 23.60 | 29.39 | 41.63 | 26.23 | 19.98 | 35.34 | 39.03 |
| Tb | 6.78 | 8.09 | 11.57 | 7.02 | 6.80 | 12.34 | 12.54 |
| Dy | 83.28 | 81.75 | 138.02 | 81.74 | 80.89 | 146.04 | 139.24 |
| Ho | 29.02 | 25.24 | 49.49 | 29 | 28.30 | 50.36 | 44.52 |

**Table 1.** *Cont.*

| | PR (Paradeep Beach) | S2 (Siali Beach) | J3 (Jahanaia Beach) | J6 (Mahanadi River) | RSN10 (North of Rushikulya River) | PM-3 (Podampata) | RSR2 (Rushikulya River) |
|---|---|---|---|---|---|---|---|
| Er | 93.15 | 108.49 | 223.28 | 132.07 | 130.74 | 223.42 | 190.85 |
| Tm | 20.30 | 20.35 | 40.89 | 25.35 | 26.56 | 43.02 | 38.38 |
| Yb | 200.64 | 183.00 | 360.94 | 217.53 | 231.52 | 395.01 | 351.21 |
| Lu | 43.67 | 33.92 | 70.86 | 41.59 | 43.00 | 69.84 | 62.33 |
| Hf | 10,052 | 12,239 | 10,467 | 9554 | 12,013 | 12,171 | 12,393 |
| Ta | 2.23 | 1.15 | 2.29 | 1.81 | 1.72 | 3.43 | 5.87 |
| Pb | 23.38 | 20.66 | 47.83 | 28.63 | 27.02 | 29.69 | 20.68 |
| Th | 133.78 | 124.72 | 438.74 | 187.67 | 248.41 | 194.80 | 209.46 |
| U | 510.86 | 247.84 | 487.92 | 275.04 | 644.87 | 447.20 | 401.66 |
| U/Yb | 2.68 | 2.49 | 1.14 | 1.26 | 2.81 | 1.23 | 0.94 |
| Th/U | 0.26 | 0.50 | 1.13 | 0.68 | 0.38 | 0.43 | 0.52 |
| U/Ce | 45.89 | 17.69 | 16.12 | 8.32 | 53.03 | 30.21 | 12.55 |
| Y/Yb | 4.39 | 4.09 | 3.91 | 3.91 | 3.79 | 3.65 | 3.50 |
| Yb/Dy | 2.40 | 2.23 | 2.61 | 3.32 | 2.86 | 2.70 | 2.52 |
| Hf/Yb | 50.10 | 66.88 | 29.00 | 43.92 | 51.89 | 30.81 | 35.28 |

Chondrite-normalized REE plots (values obtained from [30]) are provided in Figure 7. The REE plots of the seven samples was almost similar in nature, exhibiting an enrichment of HREEs with lower LREEs. The geochemical trend indicated a negative Eu anomaly and a positive Sm anomaly. The normalized pattern was characterized by a steeply rising slope from the LREEs to HREEs, with a positive Ce anomaly and negative Eu anomaly (Figure 7). The observed geochemical trend was characteristic of unaltered igneous zircons [31,32]. This study showed a higher Hf, Y and P content, as compared to other regions, with the exception of zircon present on the west coast of South Africa (Table 2). This region was also enriched in U and Th, as compared to other coastal regions (Table 2). The U/Ce and Yb/Dy variation plots (Figure 8) show the metamorphic zircon growth in equilibrium with feldspar [33]. As both zircon and feldspar are silicate minerals, their protoliths are of felsic origin.

### *5.3. Textural Analysis of Zircons*

Selected zircon grains from the different locations of the study area were analysed using SEM-EDS at the Department of Geology and Geophysics, IIT Kharagpur, India. Most of the zircon grains exhibited cracks and fractures, due to abrasion and the collisional effect during transportation from the source to the depositional site. Some of the observed features could also be due to radiation damage experienced by the zircon grains (Figure 9c,d,g,h). The zircon sample (J6) obtained from the Mahanadi river showed more angularity than other zircons present in the beach sands. Due to a successive marine transgression and regression, the outer surface of the zircon grains became smoother with the passage of time (Figure 9 e,f). Reworked conchoidal fractures had developed in PM-3 (Figure 9i), which suggested a high-energy collisional nearshore subaqueous paleoenvironment [37].

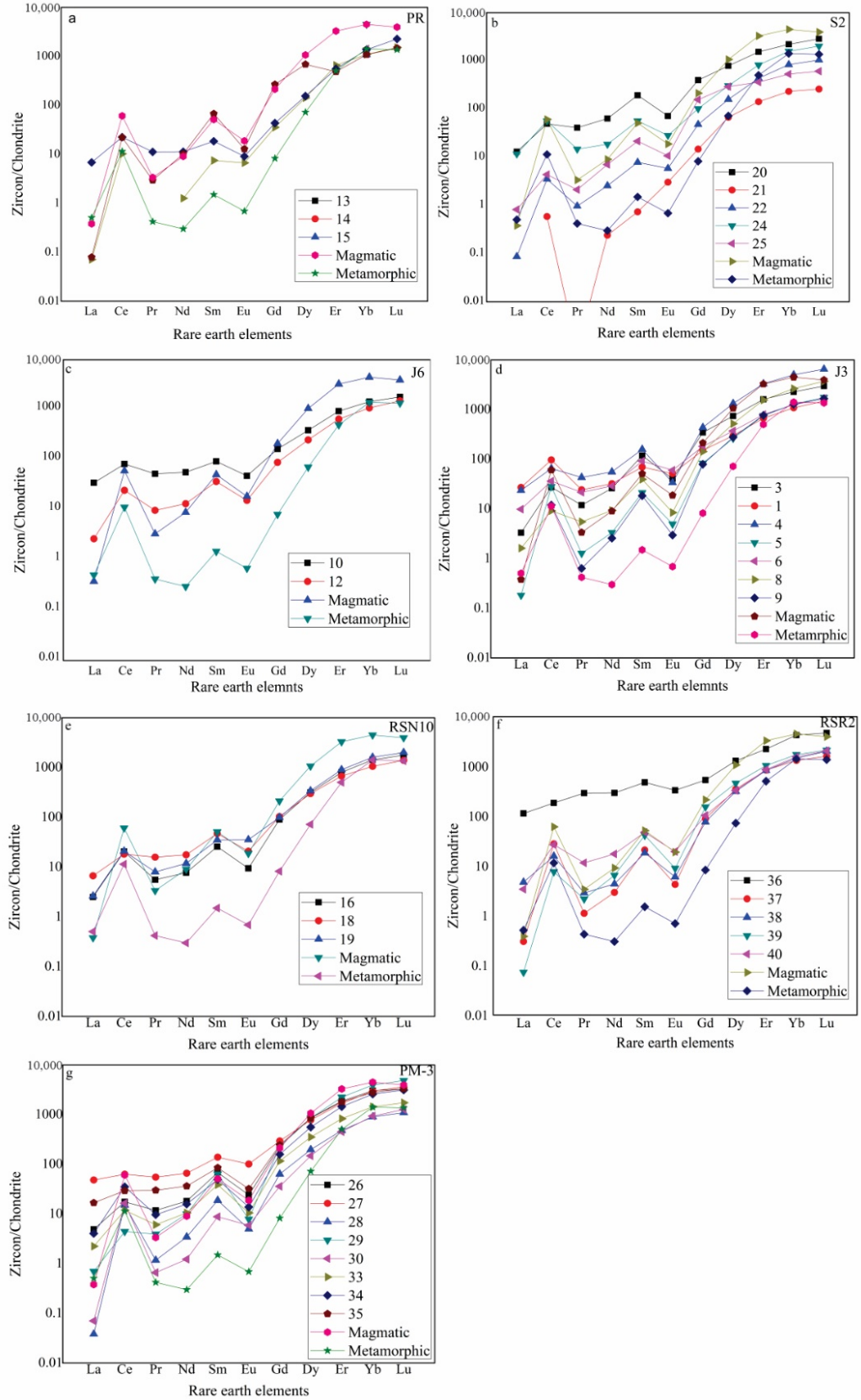



**Figure 7.** Chondrite-normalized diagram of REEs obtained from zircon samples. Chondrite values were obtained from [30]. Values of magmatic zircon and metamorphic zircon obtained from [34]. (**a**): sample PR; (**b**): sample S2; (**c**): sample J6; (**d**): sample J3; (**e**): sample RSN10; (**f**): sample RSR2, (**g**): sample PM-3

**Table 2.** Worldwide comparison of trace elements present in the zircon samples.

| | East Coast of Tamilnadu, India [21] (ppm) | West Coast of South Africa [22] (ppm) | Southeast Goergia [35] | Southwestern Gulf of Mexico [36] | Our Study (Eastern Coast of India, *n* = 7) |
|---|---|---|---|---|---|
| Hf | 3961 | 15,000 | 11,200 | 10,079.8 | 11,270.4 |
| Y | 32.5 | 1300 | 867 | - | 1064.5 |
| P | 3 | 1125 | - | - | 455 |
| Th | 6.5 | 150 | 112 | 74.10 | 219.6 |
| U | 1.82 | 50 | 261 | 125.58 | 416.5 |
| La | 81.06 | 52.5 | 8.8 | 1.82 | 2.6 |
| Ce | 54.38 | 87.25 | 38.4 | 24.49 | 19.5 |
| Pr | 11.5 | 4.25 | 3.05 | 0.28 | 2.2 |
| Nd | 51.81 | 26.25 | 12.7 | 1.99 | 12.3 |
| Sm | 9.78 | 13.75 | 6.2 | 2.06 | 9.4 |
| Eu | 1.08 | 4.25 | 1.13 | 0.52 | 1.8 |
| Gd | 8.21 | 60.75 | 19.9 | 10.17 | 28.9 |
| Dy | 7.1 | 192 | 70.7 | 44.30 | 102.2 |
| Er | 5.44 | 253.5 | 116 | 83.03 | 146.4 |
| Yb | 8.78 | 310 | 229 | 184.47 | 263.2 |
| Lu | 0.91 | - | 49.5 | 41.04 | 49.1 |

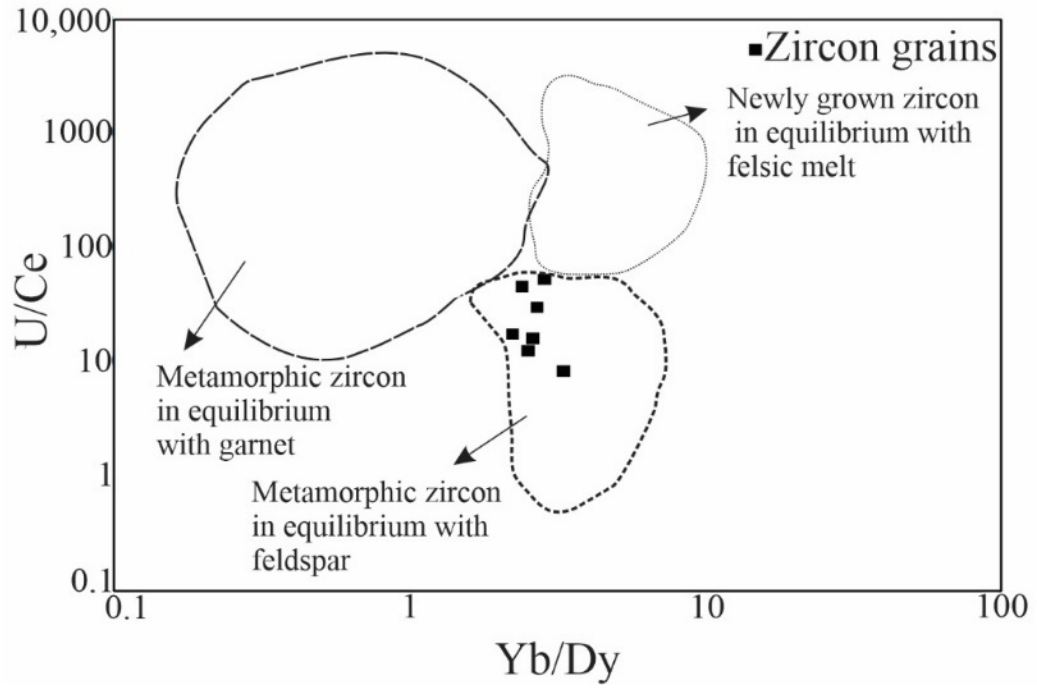



**Figure 8.** Yb/Dy vs. U/Ce variations in the zircons obtained from different samples of sand analysed in this study.

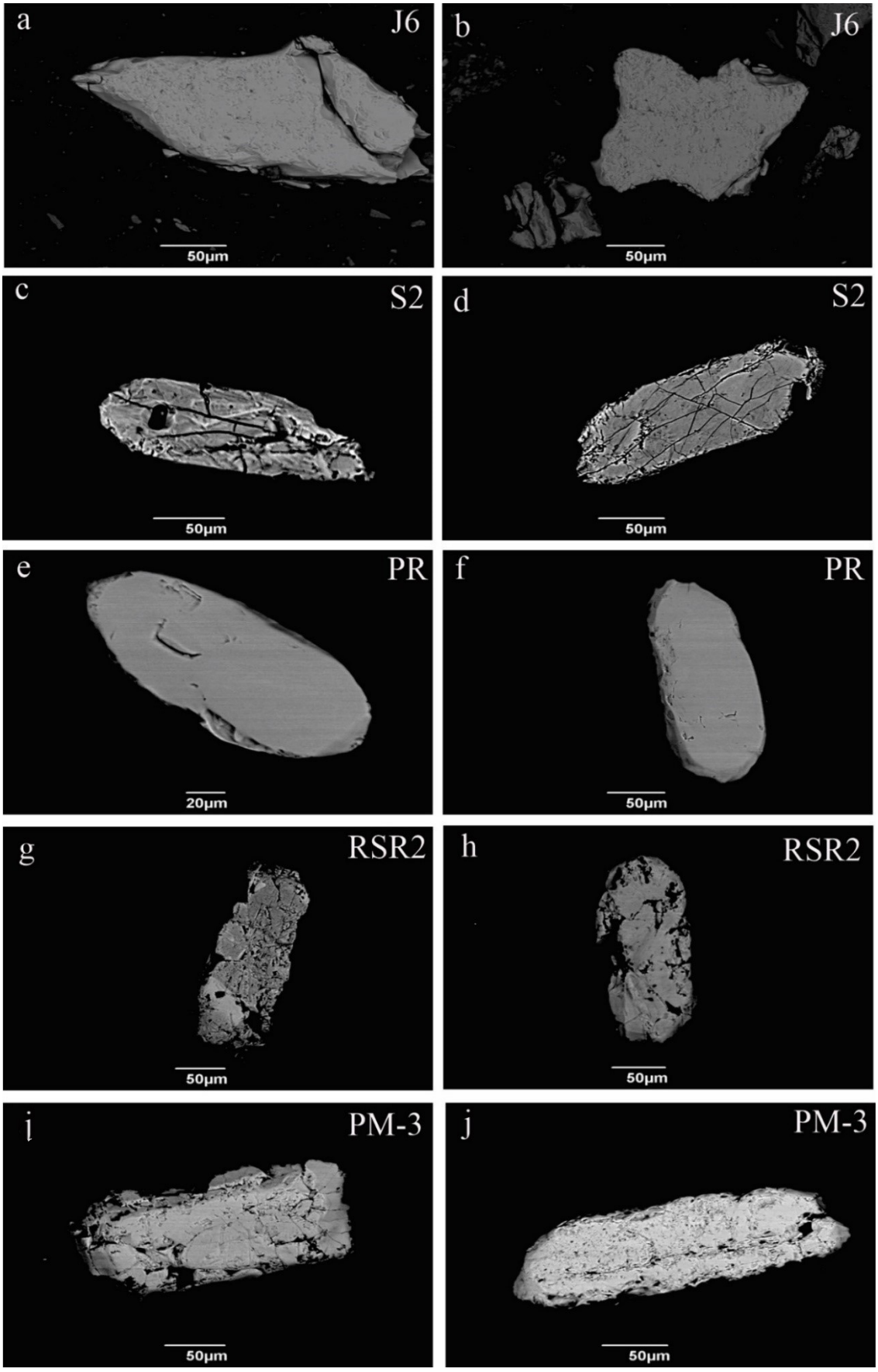



**Figure 9.** SEM-EDS images of zircon grains from different samples of sands analysed in the study. (**a**,**b**): sample J6; (**c**,**d**): sample S2; (**e**,**f**): sample PR; (**g**,**h**): sample RSR2; (**i**,**j**): sample PM-3.

## 6. Discussion

The charnockite–migmatite zone laid adjacent to study area two (Figure 1c) [16] and the majority of the Rushikulya catchment also laid within this zone. It was mostly charnockite, which exhibited an elevated activity concentration of the radioelements present [6]. This resulted in higher radioactive counts as observed in study area two, especially in the southern part of the Rushikulya river. This could be attributed to the presence of minerals such as monazites and zircons [5]. The meandering nature and subsequent erosion, primarily at the outer curvature of the river, were major contributors to the heavy mineral deposits [7]. The present study emphasized the contribution of perennial rivers such as Mahanadi and Rushikulya in the observed heavy mineral enrichment. The sediment dynamics and placer enrichment were controlled by the hinterland lithology, annual rainfall and the ambient elevation of the source region. Subsequently, the effect of waves, fluvial, tidal and marine currents played an important role during the deposition as mineral placers. The nature of the coastline, being nearly a straight line and a linear coast, led to extensive coastal erosion due to the longshore currents. This helped to transport water and sediments parallel to the shoreline. It, subsequently, deposited the sediments downward, mainly proximal to Podampata. The high P content and the presence of elements such as U, Th, Fe and Hf, respectively, in terms of potential economic resources, indicated the efficacy of such multielemental studies of detrital zircons for the estimation of the resource potential.

Subsequent studies on zircons indicated that, for closed-system scenarios, the low temperature of crystallisation at or near the wet solidus, would lead to Th/U ratios < 0.1, but, for open-system melting, due to melt loss at elevated temperatures, higher Th/U ratios > 0.1 were expected under higher temperature (UHT) conditions [29]. The high Y, Hf and P content, steep REE pattern, positive Ce anomaly and negative Eu anomaly suggested a magmatic origin of zircons [2]. Furthermore, the presence of a higher abundance of Ti and Fe resulted in the higher hardness of these zircon grains. Furthermore, it is known and has been reported on in Bangladesh that Zr- and Ti-rich minerals coexist in beach placers [38], which was true for the beach placers studied. The metamorphic zircons investigated from the high-grade granulite terrain were similar to magmatic zircons in terms of the high Hf and Y contents, positive Ce anomaly and the enrichment of HREEs with respect to LREEs. However, metamorphic zircons exhibit specific features that distinguish them from magmatic zircons, primarily their low Th/U ratios [2]. The zircons obtained from the Rushikulya river and adjacent beaches were more enriched with Hf, Y and P, but exhibited low Th/U ratios, suggesting a plausible metamorphic origin. In high-temperature and ultrahigh-temperature (UHT) metamorphic rocks, the Th/U ratio is frequently >0.1 [39–43]. In the study area (Eastern Ghats Mobile Belt), the UHT metamorphism of sediments was inferred to have occurred at ca. 1760 Ma, and a second high-grade metamorphism at ca. 1630–1600 Ma [44–46]. It was reported that the sediments from the Mahanadi river basin were derived from felsic metamorphic rocks [47]. However, the enrichment of the HREEs with LREEs was observed to be variable in nature, as was reported for magmatic zircons [1,2]. In terms of rare earths, high yttrium in zircons could mean crystallisation in a garnet-free rock or it could indicate different source regions, hence, the provenance of the detrital zircon grains.

The positive Ce anomaly in the REE chondrite-normalised plot was due to the preferential uptake of $Ce^{4+}$ from the melt, which was a typical feature of zircon [48–50]. $Ce^{4+}$ (0.97 Å) is smaller than $Ce^{3+}$ (1.14 Å), and should be a better substituent for $Zr^{4+}$ (0.84 Å). The whole rock showed a negative Eu anomaly due to the crystallisation of plagioclase, which traps all of the Eu during the crystallisation of magma [5], and zircon could have crystallised subsequent to the plagioclase crystallisation. The negative Eu anomaly observed in zircons could be either due to its coexistence with K-feldspar [48,51], a known sink for Eu, or due to the Eu depletion of the whole rock [5,50]. A positive Ce anomaly and a negative Pr anomaly were observed in the samples studied, which suggested a magmatic origin for most of the detrital zircon grains found in the analysed samples of sand [37]. The strong enrichment of the HREEs for zircons was consistent due to the absence of garnet [2,19]. The

detrital zircon grains underwent several marine transgressions and regressions, as observed from their textural analysis (Figure 9). The several cracks, fractures and pits developed in the detrital zircon grains were indicative of marine transgression and regression events.

## 7. Conclusions

1. The present study, undertaken for the first time, was useful in delineating the geochemical nature of zircon grains from beach placers and river banks of eastern India, in terms of their trace element variations. The abundance of specific trace elements and their radionuclide content is important for the evaluation of their resource potential for industrial-grade applications, both indigenously as well as in terms of their export potential. This would also be useful in terms of value addition, especially for zirconium, to meet the energy requirements of the country based on nuclear power.
2. The zircons studied exhibited a trace element variation in the following descending order: Hf (mean = 11,270 ppm) > Y (mean = 1064 ppm) > P (mean = 455 ppm) > U (mean = 430.77 ppm) > Th (mean = 220 ppm).
3. The low Th/U ratio in the zircons studied suggested a metamorphic origin due to high-grade metamorphism in the Eastern Ghats Mobile Belt.
4. The metamorphic zircons showed characteristics quite similar to magmatic zircons, as indicated by the high Y, Hf and P content, and a steep REE pattern, positive Ce anomaly and negative Eu anomaly. This could be attributed to the ultrahigh-temperature metamorphism experienced during the formation of zircons from the partial melt that occurred in the metamorphic neosome.

**Author Contributions:** S.M.: Conceptualization, Field Survey, writing—original manuscript; A.P.: Experimental analysis, Writing—editing and reviewing; M.P.: Experimental analysis, investigation, software; L.P.: Experimental analysis, writing—editing, software; D.S.: Conceptualisation, methodology, supervision, writing—reviewing-editing. All authors have read and agreed to the published version of the manuscript.

**Funding:** No funding information is available.

**Data Availability Statement:** Data could be used for academic purpose only with proper citation of the manuscript.

**Acknowledgments:** The authors would like to acknowledge the Department of Science and Technology (DST), India, for financial support in the form of a research fellowship during the current research work.

**Conflicts of Interest:** The authors declare no conflict of interest.

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