Abstract: The geochemical investigation of shales from the Early to Middle Cretaceous Chichali Formation in the Hazara Basin was conducted to determine the origin, tectonic setting and evolution, paleo-weathering conditions, and paleo-oceanographic reconstruction. The research included a comprehensive field survey, sample collection, and analysis of a variety of main, trace, and rare-earth elements using an X-ray fluorescence spectrometer (XRF). Bivariate plots and ternary diagrams were used to determine the provenance, tectonic setting, and paleo-weathering conditions that existed during the development of the Chichali Formation in the Hazara Basin. The values of Ba/Sc, Ba/Co, Th/Sc, Cr/Th, Cr/Zr, Th/Co, Th/Cr, Sc/Th, bivariate plots of Al2O3 vs. TiO2, TiO2 vs. Zr, TiO2 vs. Ni, Df1–Df2, Zr vs. Nb, and La/Sc vs. Th/Co, and ternary diagram of K2O–Fe2O3–Al2O3 were used to illustrate the passive continental margin setting of Chichali Formation shales. The detailed chemical analysis also provides an understanding of the marine geochemical cycle, which reflects the origin of these sediments. The average K2O/Al2O3 value is less than 0.4, indicating that the shale contains clay minerals. The Chichali Formation’s Chemical Index of Alteration (mean = 71) and Index of Compositional Variation (mean = 1.12) values show a modest degree of chemical weathering in the source locations. From an environmental standpoint, the Chichali Formation is richer in toxic elements such as Ba, Zn, Ni, Cr, and Cu, which may be damaging to agricultural soils and drinking water when present in excess. These metals are incorporated into the formation during the weathering process.

Keywords: provenance; paleo-weathering; paleo-oceanographic reconstruction; tectonic evolution; marine geochemical cycle; passive continental margin; Chichali Formation; Pakistan

1. Introduction

The Hazara Basin is located in northern Pakistan’s Lesser Himalaya and provides exceptional exposure to sedimentary strata ranging from the Late Proterozoic to the Holocene. It is a significant geological province due to its stratigraphic, sedimentological, and structural connections to the Himalayan orogeny [1]. The Chichali Formation is located in the Western Salt Range, Northern Kohat ranges, Trans Indus ranges, Kala-Chitta, Nizampur, and Southern Hazara. The Chichali Formation is mainly exposed in the Hazara area in...
Riyala, Abbottabad Township, Hernoi, Galyat, and Balolia [2]. The formation is composed of yellowish-brown to dark grey to black shale with a few interbeds of marl and sandstone in the research region [3,4]. The Chichali Formation is thought to have been deposited in mid-to-upper-outer-shelf settings [1]. Its lower contact with the Samana Suk Formation is unconformable, whereas the upper contact with the Lumshiwal Formation is transitional [5]. The formation is highly fossiliferous and ranges in age from the Late Jurassic to the Early Cretaceous [6].

There is relatively limited published work on geochemical analysis of the Chichali Formation in Pakistan’s Hazara Basin, and no major study on the geochemical investigation of these shales has been conducted so far. Shale is a common form of sedimentary rock that is exposed to the Earth’s surface [7]. The concentration of elements in shale is influenced by a variety of processes, including weathering, transport, and sedimentation into the marine environment. The chemical composition of siliciclastic sediments has been extensively used to identify the features of the source rocks [8–10]. The relative variation of major components within shale determines the tectonic setting of sedimentary basins [11]. Major element analysis may be used to interpret both paleo-weathering and paleo-tectonic settings [12].

Water and soil are of prime concern to mankind as both are directly linked to human health. The incorporation of increased levels of trace elements in marine sedimentary deposits above their acceptable limits produces toxic effects on soils and marine fauna. Weathered agricultural soil may be toxic to crops, and when these crops are consumed by live organisms, they can have negative effects. It can be hazardous to aquatic life as well if it mixes with the surface streams. Surface runoff and erosion of sediments will ultimately have adverse effects if they reach the underground water by percolating through the soil deep into the ground, thus contaminating the groundwater and causing adverse effects on the environment. Overall, this research will explore the geochemical characterization of shales to obtain a better understanding of the study area’s source rock potential, origin, tectonic context, and paleo-weathering environmental conditions.

2. Geological Setting and Stratigraphy

During the Cenozoic, the collision of India and Asia resulted in the formation of the Himalayas, a huge mountain chain [2,13]. The southern Hazara was formed as a result of the collision of the Indian and Eurasian plates. It is a part of the Himalayan fold and thrust belt [14,15]. The study area is in Hazara, which is situated within the Hazara Kashmir Syntaxis (Figure 1).
Figure 1. Tectonic map showing a segment of the Northwestern Himalayas’ fold and thrust belt. The rectangle indicates the location of the research area.

The exposed rocks in the Hazara area vary in age from Precambrian to Holocene [1,16], except the middle and upper Paleozoic (Figure 2) [17,18].

The Chichali Formation is well exposed in the Hazara region, particularly at Riyala (Section 1), Township Abbottabad (Section 2), and Hernoi (Section 3). The formation’s major composition is shale with intercalations of marl and sandstone. The thickness of the formation varies from 33 m in Section 1 to about 55 m in Sections 2 and 3. Shale is yellowish-brown, greenish to dark grey, and black. Due to the prevalence of glauconite, the weathered surface is yellowish-brown, but the fresh unweathered surface is greenish-grey to black. The base of Chichali, near Section 3, has coal seams, and some of those seams have been mined (Figure 3) [19,20].
| ERA   | PERIOD     | EPOCH     | FORMATION               | LITHOLOGY                                                   | DESCRIPTION                                                                 |
|-------|------------|-----------|-------------------------|-------------------------------------------------------------|-----------------------------------------------------------------------------|
| Cenozoic | Tertiary   | Eocene    | Margala Hill Limestone  | Grey fossiliferous nodular limestone with shale and marl interbedded. |
|       |            | Paleocene | Patala Shale            | Greenish grey shale and siltstone.                          |
|       |            |           | Lockhart Limestone      | Grey nodular limestone, shale and marl interbedded.         |
| Mesozoic | Cretaceous |           | Kawagarh Formation      | Yellowish grey and creamish limestone.                      |
|       |            |           | Lumshiwal Formation     | Yellowish brown massive sandstone.                         |
|       |            |           | Chichali Formation      | Yellowish brown to grey organic rich shales. At places the color of the shales is light to dark brown with interbedded marl and sandstone. |
| Jurassic |          |           | Samana Suk Formation    | Grey oolitic limestone with subordinate marl and shale.    |
| Ordovician |            |           | Galdanian Formation     | Sandstone, quartzite, shale and siltstone and some calcareous sandstone. |
| Paleozoic | Cambrian   |           | Hazira Formation        | Parallel laminated sandstone, shale and siltstone.          |
|         |            |           | Abbottabad Formation    | Shale, sandstone, dolomite and limestone.                   |
|         |            |           | Kakul Formation         | Sandstone with minor shale..                               |
|         |            |           | Tanawal Formation       | Sandstone, quartzite, quartzose schist and shale.          |
|         |            |           | Hazara Formation        | Greenish grey and light brown shale, sandstone, siltstone, and slate/phyllite. |

**Figure 2.** Representation of the generalized stratigraphic succession of the Hazara Basin.
The Chichali Formation is well exposed in the Hazara region, particularly at Riyala (Section 1), Township Abbottabad (Section 2), and Hernoi (Section 3). The formation’s major composition is shale with intercalations of marl and sandstone. The thickness of the formation varies from 33 m in Section 1 to about 55 m in Sections 2 and 3. Shale is yellowish-brown, greenish to dark grey, and black. Due to the prevalence of glauconite, the weathered surface is yellowish-brown, but the fresh unweathered surface is greenish-grey to black. The base of Chichali, near Section 3, has coal seams, and some of those seams have been mined (Figure 3) [19,20].

Figure 3. Field photographs of the Chichali Formation: (A,B) Yellowish brown to grey shales (Section 1), (C–E) organic-rich shales (Section 2), (F–H) light to dark brown shales with interbedded marl and sandstone (Section 3).

3. Material and Methods

Fieldwork was conducted in detail, and three stratigraphic sections were selected for measurement and sampling. Three stratigraphic sections were measured, described, and sampled in the field (Riyala, Township Abbottabad, and Hernoi). In the field, a total of 40 shale samples were collected. The concentration of major and trace elements was determined for seventeen shale samples. An X-ray fluorescence spectrometer was used.
to determine the percentages of main and trace elements at Bestway Cements Limited in Hattar (PANalytical Cubix 2300 XRF), Almelo, The Netherlands.

Chemical Index of Alteration (CIA) values and the A–CN–K ternary plot reveal the paleo-weathering and tectonic history of sedimentary rocks [21]. This equation was used to calculate the Chemical Index of Alteration (CIA) for paleo-weathering analysis.

The Chemical Index of Alteration (CIA) was derived for paleo-weathering analysis using the following equation:

$$\text{CIA} = \frac{\text{Al}_2\text{O}_3}{(\text{Al}_2\text{O}_3 + \text{CaO} + \text{Na}_2\text{O} + \text{K}_2\text{O})} \times 100$$

(1)

The index of compositional variability (ICV) quantifies the maturity of the aluminosilicates transported to the depositional location, i.e., basin [22]. The following formula was used to calculate ICV [22]:

$$\text{ICV} = \frac{(\text{Fe}_2\text{O}_3 + \text{K}_2\text{O} + \text{Na}_2\text{O} + \text{CaO} + \text{MgO} + \text{TiO}_2)}{\text{Al}_2\text{O}_3}$$

(2)

4. Results

4.1. Major and Trace Elements

The major and trace element studies of the Chichali Formation shales are summarized in Table 1. Among the principal elements analyzed, SiO$_2$ ranges from 17.89 to 60.14 wt%; Al$_2$O$_3$ ranges from 4.89 to 21.19 wt%; TiO$_2$ ranges from 0.5 to 1.48 wt%; Fe$_2$O$_3$ ranges from 1.26 to 9.27 wt%; K$_2$O ranges from 0.61 to 5.75 wt%; and Na$_2$O ranges from 0.01 to 0.17 wt%.

Table 1. Major and trace element data for whole-rock samples of the Chichali Formation. The concentration of major components is expressed as wt%, while trace element concentration is in ppm. CIA is an abbreviation for Chemical Index of Alteration, while ICV is an abbreviation for Index of Compositional Variability.

| Section 1 | Section 2 | Section 3 |
|-----------|-----------|-----------|
| Major Oxides/Trace Elements | RC-1 | RC-2 | RC-3 | TC-1 | TC-2 | TC-3 | TC-4 | TC-5 | TC-6 | TC-7 | TC-8 | HC-1 | HC-2 | HC-3 | HC-4 | HC-5 | HC-6 |
| SiO$_2$ | 55.1 | 47.4 | 49.0 | 29.3 | 27.2 | 44.6 | 43.7 | 44.6 | 41.8 | 40.7 | 17.8 | 54.1 | 56.4 | 53.0 | 60.1 | 52.8 | 51.0 |
| Al$_2$O$_3$ | 9.49 | 7.93 | 8.02 | 7.03 | 6.91 | 11.2 | 11.6 | 11.3 | 10.8 | 9.56 | 4.89 | 21.1 | 20.6 | 21.2 | 19.1 | 19.0 | 19.2 |
| Fe$_2$O$_3$ | 3.51 | 3.74 | 3.61 | 3.74 | 3.17 | 4.75 | 4.77 | 4.77 | 4.82 | 4.58 | 1.36 | 5.9 | 6.7 | 5.7 | 5.34 | 4.57 | 9.27 |
| CaO | 2.04 | 0.99 | 1.77 | 1.24 | 2.06 | 1 | 1.83 | 1.9 | 1.66 | 1.52 | 2.88 | 1.02 | 1.77 | 1.47 | 1.73 | 1.48 | 1.79 |
| MgO | 5.85 | 7.27 | 7.1 | 1.4 | 1.26 | 1.52 | 1.82 | 1 | 1.46 | 1.54 | 1.34 | 1.4 | 1.39 | 1.42 | 1.09 | 1.14 | 1.22 |
| SO$_3$ | 0.03 | 0.05 | 0.04 | 0.01 | 0.03 | 0.02 | 0.02 | 0.02 | 0.01 | 0.01 | 0.01 | 0 | 0.05 | 0.03 | 0.07 | 0.01 | 0.06 |
| Na$_2$O | 0.04 | 0.05 | 0.05 | 0.01 | 0.01 | 0.03 | 0.02 | 0.02 | 0.02 | 0.02 | 0.12 | 0.01 | 0.13 | 0.13 | 0.17 | 0.13 | 0.11 |
| K$_2$O | 3.54 | 3.36 | 3.28 | 1.74 | 1.7 | 2.01 | 1.74 | 1.48 | 1.86 | 1.97 | 0.61 | 5.5 | 5.23 | 5.75 | 4.6 | 5.55 | 5.19 |
| TiO$_2$ | 0.67 | 0.53 | 0.5 | 0.5 | 0.5 | 1 | 0.97 | 1.05 | 1.07 | 1.05 | 0.53 | 1.27 | 1.17 | 1.38 | 1.48 | 1.42 | 1.4 |
| CIA | 62.8 | 64.3 | 61.1 | 70.1 | 66.7 | 78.6 | 76.3 | 76.9 | 74.8 | 73.2 | 58.2 | 76.1 | 74.3 | 74.4 | 74.6 | 75.5 | 73.0 |
| ICV | 2.03 | 2.01 | 2.03 | 1.24 | 1.21 | 0.92 | 0.83 | 0.9 | 1.01 | 1.12 | 1.38 | 0.72 | 0.76 | 0.74 | 0.75 | 0.7 | 0.99 |
| Sc | 5.36 | 7 | 9.64 | 11.8 | 16 | 14.9 | 11 | 15.3 | 11.7 | 12.2 | 13.4 | 14.1 | 7.75 | 6.37 | 8.73 | 11.9 | 4.1 |
| Cr | 149 | 120 | 125 | 95.7 | 127 | 122 | 122 | 125 | 135 | 129 | 94 | 94 | 122 | 142 | 91 | 85 | 112 |
| V | 64 | 65 | 97 | 138 | 28 | 150 | 130 | 70 | 112 | 119 | 97 | 110 | 82 | 67 | 83 | 270 | 70 |
| Co | 6.41 | 4.21 | 3.71 | 5.99 | 5.03 | 6.05 | 4.46 | 5.54 | 3.9 | 4.17 | 5.01 | 11.4 | 7.96 | 6.16 | 9.01 | 5.29 | 8.39 |
| Ni | 9 | 9 | 10 | 15 | 19 | 11 | 18 | 22 | 20 | 19 | 21 | 28 | 14 | 13 | 17 | 12 | 21 |
| Cu | 65 | 65 | 67 | 57 | 42 | 45 | 24 | 44 | 18 | 36 | 29 | 46 | 33 | 32 | 56 | 79 | 66 |
| Zn | 112 | 169 | 89 | 86 | 41 | 78 | 47 | 42 | 57 | 46 | 51 | 81 | 89 | 121 | 114 | 154 | 139 |
| Rb | 190 | 119 | 193 | 198 | 169 | 248 | 184 | 199 | 131 | 175 | 183 | 151 | 194 | 159 | 213 | 211 | 227 |
| Sr | 130 | 211 | 148 | 232 | 261 | 103 | 200 | 142 | 350 | 212 | 222 | 144 | 234 | 124 | 135 | 136 | 139 |
| Zr | 31 | 347 | 321 | 331 | 259 | 100 | 300 | 200 | 190 | 241 | 210 | 388 | 485 | 476 | 438 | 454 | 327 |
| Nb | 74 | 64 | 54 | 45 | 47 | 85 | 39 | 55 | 70 | 57 | 48 | 68 | 50 | 61 | 73 | 44 | 54 |
| Sb | 0.6 | 0.38 | 0.25 | 0.23 | 0.65 | 0.15 | 0.46 | 0.32 | 0.39 | 0.36 | 0.41 | 0.59 | 0.37 | 0.29 | 0.39 | 0.3 | 0.37 |
Table 1. Cont.

| Major Oxides/Trace Elements | Section 1 | Section 2 | Section 3 |
|-----------------------------|-----------|-----------|-----------|
|                             | RC-1      | RC-2      | RC-3      |
| Cs                           | 2.02      | 2.99      | 2.59      |
| Ba                           | 299       | 153       | 194       |
| La                           | 21.1      | 29.3      | 19.8      |
| Ce                           | 306       | 157       | 77.9      |
| Nd                           | 125       | 51.9      | 37.2      |
| Sm                           | 19        | 7.98      | 5.06      |
| Eu                           | 3.17      | 1.38      | 1.41      |
| Gd                           | 9.7       | 5.13      | 5.31      |
| Tb                            | 1.65      | 0.92      | 0.96      |
| Tm                           | 0.89      | 0.6       | 0.61      |
| Yb                           | 6.57      | 4.16      | 3.99      |
| Lu                           | 1.03      | 0.64      | 0.61      |
| Hf                           | 3.46      | 5.29      | 3.33      |
| Th                            | 38.2      | 28.4      | 29        |
| U                             | 5.3       | 4.76      | 4.53      |

Sc ranges from 4.1–15.3 parts per million; V ranges from 64–270 ppm; Cr ranges from 85–135 ppm; Co ranges from 3.71–11.4 ppm; Ni ranges from 9–28 ppm; Cu ranges from 29–79 ppm; Zn ranges from 41–169 ppm; Rb ranges from 119–248 ppm; Sr ranges from 103–350 ppm; La ranges from 100–485 ppm; Ca ranges from 15.6–39.9 ppm; Th ranges from 15.1–38.2 ppm; and U ranges from 2.4–5.3 ppm. CaO is present in small amounts in the sediments owing to the lack of carbonate cement. MgO and CaO are often found in association with dolomite, ferrous carbonates, and calcite [23]. Increased MgO and CaO concentrations indicate the presence of carbonate minerals, while a low concentration indicates the presence of clay minerals [24]. The reduced Na₂O demonstrates the source rock’s recycling, moderate to severe weathering, and its removal during transportation [25]. The K₂O/Al₂O₃ ratio is used to determine the original composition of ancient mud rocks. The K₂O/Al₂O₃ ratios in the Hazara area’s Chichali Formation shales are less than 0.4, indicating the presence of clay minerals.

The trace element ratio is frequently used to estimate the felsic and mafic composition of rocks. This research makes use of the Th/Sc, Th/Cr, Th/Co, and La/Sc ratios [26]. The results of the present study’s elemental ratio analysis were compared to the conventional values for felsic and mafic rocks (Table 2). The findings indicate that all trace element ratios are in favor of a felsic composition (Table 2).

Table 2. The elemental ratios of shales from the Chichali Formation were compared to those of equivalent fractions obtained from felsic and mafic rocks in this research.

| Elemental Ratio | Range of Shales from the Chichali Formation | Range of Sediments (Based on Cullers [27]). |
|-----------------|---------------------------------------------|---------------------------------------------|
|                 | Felsic Rocks                                | Mafic Rocks                                 |
| Th/Sc           | 1.26–7.12                                   | 0.84–20.5                                   |
| Th/Co           | 2.52–7.81                                   | 0.67–19.4                                   |
| Th/Cr           | 0.17–0.31                                   | 0.13–2.7                                    |
| La/Sc           | 1.24–7.39                                   | 2.5–16.3                                    |

7 of 23
4.2. Provenance and Source Rock Potential

The relationship between TiO$_2$ and Al$_2$O$_3$ was employed to determine the provenance [28]. The bivariate Al$_2$O$_3$ and TiO$_2$ graph shows a concentration of data in the granodiorite area and some in the granite and basalt region (Figure 4). The plot of TiO$_2$ vs. Ni is often used to classify rocks into acidic and basic igneous regions [29]. According to the TiO$_2$ vs. Ni plot in our model, the Chichali Formation is derived from intermediate igneous rocks (Figure 5).

**Figure 4.** Plot of Al$_2$O$_3$ versus TiO$_2$ plot for Chichali Formation shales.

**Figure 5.** Diagram illustrating provenance, bivariate diagram of TiO$_2$ wt% vs. Ni (ppm).
The ternary diagram of $\text{K}_2\text{O}-\text{Fe}_2\text{O}_3-\text{Al}_2\text{O}_3$ [30] demonstrates that all shales of the Chichali Formation plotted around the $\text{Al}_2\text{O}_3$ apex, indicating $\text{Al}_2\text{O}_3$ enrichment. This finding implies that clay minerals controlled the element abundances in this shale (Figure 6) [29,31]. The plot of La/Sc vs. Th/Co may be used to identify the composition of the source rock [32]. The plotted data for La/Sc and Th/Co [32] indicate the presence of a silicic rock composition zone (Figure 7). The quantity of a trace element may be a reliable predictor of its origin [33]. The concentrations of Ni and Cr are used to indicate the presence of ultramafic rocks in the source location ($\text{Cr} > 150$ ppm and $\text{Ni} > 100$ ppm). The Chichali Formation samples show an average Cr value of 117.62 ppm and a Ni concentration of 16.35 ppm, indicating the lack of ultramafic rocks in the source region. The relationship between $\text{SiO}_2/\text{Al}_2\text{O}_3$ and $\text{K}_2\text{O}/\text{Na}_2\text{O}$ [10,28] suggests that the majority of the Chichali shale data plotted in the field reflect Proterozoic–Phanerozoic shale composition, demonstrating that clay minerals regulate the main element composition (Figure 8) [10,28].

Figure 6. Ternary $\text{K}_2\text{O}-\text{Fe}_2\text{O}_3-\text{Al}_2\text{O}_3$ diagram for Chichali Formation shale.
Numerous authors, such as Adriano [33], Eqani, et al. [34], Qasim, et al. [35], and Martini, Walter, Ku, Budai, McIntosh and Schoell [11], have presented a variety of diagrams for discriminating between major and trace elements. To establish the provenance, the discrimination diagram makes use of variably mobile major elements and static minor elements [36]. In the discriminating diagram, Sections 2 and 3 are mostly plotted in the field of intermediate igneous rock, while Section 1 is primarily plotted in the field of quartzose sedimentary provenance (Figure 9). Additionally, the ternary diagram of K₂O–Fe₂O₃–Al₂O₃ reveals important information concerning its origin [30].
Numerous authors, such as Adriano [33], Eqani et al. [34], Qasim et al. [35], and Martini, Walter, Ku, Budai, McIntosh and Schoell [11], have presented a variety of diagrams for discriminating between major and trace elements. To establish the provenance, the discrimination diagram makes use of variably mobile major elements and static minor elements [36]. In the discriminating diagram, Sections 2 and 3 are mostly plotted in the field of intermediate igneous rock, while Section 1 is primarily plotted in the field of quartzose sedimentary provenance (Figure 9). Additionally, the ternary diagram of K$_2$O–Fe$_2$O$_3$–Al$_2$O$_3$ reveals important information concerning its origin [30].

**Figure 9.** Provenance discrimination diagram for shales. Discriminant function 1 = (−1.773 × TiO$_2$%) + (0.607 × Al$_2$O$_3$%) + (0.76 × Fe$_2$O$_3$%) + (−1.5 × MgO%) + (0.616 × CaO%) + (0.509 × Na$_2$O%) + (−1.22 × K$_2$O%) + (−9.09). Discriminant function 2 = (0.445 × TiO$_2$%) + (0.07 × Al$_2$O$_3$%) + (−0.25 × Fe$_2$O$_3$T%) + (−1.142 × MgO%) + (0.438 × CaO%) + (0.432 × Na$_2$O%) + (1.426 × K$_2$O%) + (−6.861).

### 4.3. Tectonic Setting

The binary diagram shows that all samples are plotted within the passive margin field, indicating that the Chichali Formation was deposited within a passive margin environment (Figure 10). The plot of SiO$_2$ vs. K$_2$O/Na$_2$O is used to determine whether the shale was deposited on passive continental edges, active continental margins, or oceanic island arc margins [37]. Additionally, by incorporating major and trace element data, the discrimination diagrams can be used to infer the tectonic settings of previous terrains [38–40], distinguishing oceanic island arc, active continental margin, passive continental margin, and continental island arc (Figure 11).

### 4.4. Paleo-Weathering in the Source Area

The findings indicate that the average CIA values for all three examined sections ranged from 58 to 78, with an average of 71, indicating that the weathering conditions for these shales were mild (Table 1). Al$_2$O$_3$ represents the immobile component in the CIA index, while CaO, Na$_2$O, and K$_2$O represent the mobile components. CaO, K$_2$O, and Na$_2$O are employed as mobile components due to their susceptibility to weathering and their propensity for leaching during weathering. The rise in CIA values indicates that CaO, K$_2$O, and Na$_2$O are being removed at a faster rate than the more stable Al$_2$O$_3$ (Figure 12).

For kaolinite and chlorite, the CIA value is close to 100; for shale, the average value is between 70 and 75 [41]; and for fresh granite, the average value is about 50 [42].

The ICV values of the shale studied in this research are modest, with an average of 1.12. ICV values greater than one indicate immature shale, which includes rock-forming minerals such as plagioclase, K-feldspar, amphiboles, and pyroxene. The present study’s average ICV results indicate the existence of K-feldspar (0.8–1) [43]. A cross plot of the CIA and ICV values reveals an interesting picture of the chemistry of the key elements. According
to Figure 13, the source rock is felsic to intermediate in composition. The classification of siliciclastic rocks is based on the plot between SiO$_2$/Al$_2$O$_3$ and Fe$_2$O$_3$/K$_2$O [44]. Due to the samples' low SiO$_2$/Al$_2$O$_3$ and Fe$_2$O$_3$/K$_2$O contents, they all fall into the shale field when plotted in the SiO$_2$/Al$_2$O$_3$ and Fe$_2$O$_3$/K$_2$O binary plots (Figure 14).

Figure 10. Plot of SiO$_2$ versus K2O/Na2O for shales of the Chichali Formation.

Figure 11. Discrimination function plot of the Chichali shales. Discrimination function 1 = 0.303 – 0.0447SiO$_2$ 0.972TiO$_2$ + 0.008Al$_2$O$_3$ 0.267Fe$_2$O$_3$ + 0.14MgO + 0.195CaO + 0.719Na$_2$O – 0.032K$_2$O. Discrimination function 2 = 43.57 – 0.421SiO$_2$ + 1.988TiO$_2$ – 0.526Al$_2$O$_3$ – 0.551Fe$_2$O$_3$ + 0.881MgO – 0.907CaO 0.177Na$_2$O – 1.84K$_2$O.
The ICV values of the shale studied in this research are modest, with an average of 1.12. ICV values greater than one indicate immature shale, which includes rock-forming minerals such as plagioclase, K-feldspar, amphiboles, and pyroxene. The present study’s average ICV results indicate the existence of K-feldspar (0.8–1) [43]. A cross plot of the CIA and ICV values reveals an interesting picture of the chemistry of the key elements. According to Figure 13, the source rock is felsic to intermediate in composition. The classification of siliciclastic rocks is based on the plot between SiO$_2$/Al$_2$O$_3$ and Fe$_2$O$_3$/K$_2$O [44]. Due to the samples’ low SiO$_2$/Al$_2$O$_3$ and Fe$_2$O$_3$/K$_2$O contents, they all fall into the shale field when plotted in the SiO$_2$/Al$_2$O$_3$ and Fe$_2$O$_3$/K$_2$O binary plots (Figure 14).

Figure 12. Al$_2$O$_3$–CaO+Na$_2$O–K$_2$O ternary diagram.

Figure 13. Weathering indicators, the Chemical Index of Alteration (CIA), and the Index of Chemical Variation (ICV) in Chichali Formation shales.

Th/Sc vs. Zr/Sc plots may be used to monitor sedimentary recycling and sorting. While first-order sediments exhibit a straightforward association between Th/Sc and Zr/Sc ratios, recycled sediments exhibit a significant rise in Zr/Sc relative to Th/Sc. The Th/Sc ratio is utilized to indicate chemical differentiation in the plot [40], while the Zr/Sc ratio indicates sediment recycling in the source area [45]. Zr is an abbreviation for zircon, a physically and chemically very stable mineral that may be used to determine the influence...
of recycling in the source location. All samples examined in the Th/Sc vs. Zr/Sc binary plot [45] exhibit a linearly rising compositional tendency toward a higher Zr/Sc ratio, and all samples plotted in the sediment recycling field (zircon added) exhibit a linearly increasing compositional trend toward a higher Zr/Sc ratio (Figure 15). These findings indicate that the rise in zircon content in the source region occurred before sediment transfer to the Hazara basin. Thus, a binary plot of Th/Sc vs. Zr/Sc is used to figure out the effect of recycling.

![Figure 14. Classification of siliciclastic rocks.](image)

![Figure 15. Plot of the Th/Sc ratio against the ratio of Zr to Sc for the Chichali Formation.](image)

The findings indicate that the average Zr/Hf ratios in the examined samples are much higher (26.73–182.37, with an average of 81.24) than in UCC and PAAS (31.6 and 42,
respectively) [46]. These increased ratios may be the outcome of recycling in the source location. The $\text{Al}_2\text{O}_3/\text{K}_2\text{O}$ ratio exceeds 0.3, indicating the existence of K-feldspar [47].

Zr has a positive correlation value with Hf, $r = 0.36$. The Zr/Hf ratio of the Chichali Formation samples analyzed in the Hazara basin ranges from 26 to 182, with an average of 81. If the Zr/Hf ratio is greater than 40, zircon controls these elements. The favorable correlations between $\text{K}_2\text{O}$ and Sc, $\text{K}_2\text{O}$ and Co, Sc–$\text{Al}_2\text{O}_3$, and Co–$\text{Al}_2\text{O}_3$ indicate that these elements are concentrated in phyllosilicates after they have been broken down by the weather.

$\text{Al}_2\text{O}_3$ has a declining trend when plotted against $\text{SiO}_2/\text{Al}_2\text{O}_3$, $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$, and $\text{K}_2\text{O}/\text{Al}_2\text{O}_3$ ratios for samples obtained from the Chichali Formation (Figure 16A–C). As a result of these plots, it can be deduced that as weathering proceeds, $\text{Al}_2\text{O}_3$ stays as a residue while $\text{Fe}_2\text{O}_3$, $\text{K}_2\text{O}$, and $\text{Na}_2\text{O}$ weather away. As a result, it is indicative of the existence of clay minerals.

Figure 16. Cont.
4.5. Geochemical Analysis of Chichali Formation

The quantities of various components in the samples investigated are summarized in Table 1. Soils are formed as a result of the weathering of rocks. In Figure 17, V, Cu, Ba, Zn, and U histograms are compared to the normal elemental concentrations of Cu, Ba, Zn, and U in soils (Figure 17) [48]. Cu levels greater than usual are seen in Sections 1 (65.67 ppm), 2 (36.88 ppm), and 3 (52 ppm) (Figure 17). Cu enrichment beyond the recommended level may result in stunting, discoloration of the root system, decreased growth, and chlorosis [49].

![Figure 16. Plots of Al₂O₃ against (A): Fe₂O₃ / Al₂O₃ ratio, (B): SiO₂ / Al₂O₃ ratio, and (C): K₂O / Al₂O₃.](image)

![Figure 17. Histogram comparing the averages of the main oxides.](image)

At 90 ppm, Zinc is recommended to be in typical soils around the globe [50]. Zn readings are greater than usual in Sections 1 (123.33 ppm) and 3 (116.33 ppm) but are within allowed limits in Section 2 (56 ppm) (Figure 17). These elevated levels cause toxicity in plants and crops. Ni levels are lower than usual in all three parts investigated, namely,
Section 1 (9.33 ppm), Section 2 (18.125 ppm), and Section 3 (17.5 ppm). The examined sections show that Cr levels are much higher than usual in all of them, including Section 1 (131 ppm), Section 2 (115 ppm), and Section 3 (114 ppm).

Comparison of the average values of main oxides in the analyzed portions is displayed in the histogram (Figure 18). Section-wise comparison of SiO_2 indicates that SiO_2 is practically similar in Sections 1 and 3 and less in Section 2. Fe_2O_3 concentration is greater in Section 3 compared to Sections 1 and 2. The peaks of CaO are extremely lower, suggesting the lack of carbonates in these sediments. MgO content in Section 1 is greater than Sections 2 and 3. The presence of mafic minerals suggests a high concentration of MgO, yet the concentration of MgO here is considerably smaller compared to the mafic minerals. Sections 2 and 3 contain about the same quantity of MgO. Na_2O concentration may also be observed in the histogram (Figure 18), which reveals extremely low concentration of Na_2O in all the sections. This may be rationalized by the weathering events which dissolved Na_2O to generate clay minerals in the examined portions.

![Figure 18. Concentrations of elements in soils generated from shales.](image)

4.6. Statistical Analysis

Other intriguing aspects of the shale are shown by the ratios of key oxides and correlation coefficient data for major and trace elements. The Pearson coefficients of correlation are listed in Supplementary Table S1. Microsoft Excel was used to compute the correlation coefficients for the major and selected trace elements in the studied shale. Correlation coefficient data aided in the comprehension of the geochemical characteristics of the Chichali Formation.

Correlations between Al_2O_3 and TiO_2 (r = 0.90) and K_2O (r = 0.88) are statistically significant. Al_2O_3 has a negative Pearson correlation value of −0.30 and −0.39 with CaO and MgO, respectively. Al_2O_3 has a highly positive and significant association with Na_2O and Fe_2O_3 at 0.83 and 0.76, respectively. All of these correlations indicate that sediments arrange themselves during transportation. Al_2O_3 has a substantial positive correlation with K_2O (r = 0.88) and SiO_2 (r = 0.75), suggesting the existence of kaolinite and K-feldspar.

TiO_2 has a significant positive correlation (r = 0.90) with Al_2O_3 and a negative association (r = −0.25) and MgO (r = −0.56) with CaO and MgO. TiO_2 correlates positively with both Na_2O and K_2O (r = 0.75 and 0.65, respectively). This indicates that TiO_2 is a key chemical element of clays, rather than mafic minerals. SiO_2 has a negative correlation with a number of key elements, suggesting that quartz has been dissolved. The strong
relationship between TiO$_2$ and Al$_2$O$_3$ and the negative correlation between TiO$_2$ and other significant elements (CaO and MgO) indicate that TiO$_2$ is a key chemical ingredient of clays (kaolinite) rather than mafic minerals. Al$_2$O$_3$ correlates positively with K$_2$O ($r = 0.88$) and strongly positively with SiO$_2$ ($r = 0.75$). These linear lines indicate the traces of kaolinite. CaO has a negative correlation with SiO$_2$ ($r = -0.44$), indicating that calcite is somewhat dominant over other minerals.

Na$_2$O has a positive correlation with SiO$_2$ ($r = 0.71$), Al$_2$O$_3$ ($r = 0.83$), Fe$_2$O$_3$ ($r = 0.62$), TiO$_2$ ($r = 0.75$), and K$_2$O ($r = 0.80$), but correlates negatively with CaO and MgO ($r = -0.23$ and $-0.19$). These relationships imply the presence of smectite in the shale. Certain trace elements, such as Zr, Co, Rb, Ba, and Hf, have a positive correlation with Al$_2$O$_3$ ($r = 0.70, 0.71, 0.16, 0.34, and 0.24$, respectively), suggesting that they are likely fixed in K-feldspars and clays. On the other hand, some trace elements, such as V, Ni, Cu, Rb, Nb, Cs, and U, correlate positively with Al$_2$O$_3$ ($r = 0.04, 0.16, 0.17, 0.08, 0.16, 0.13, 0.01$, and $0.08$, respectively) and negatively with Sc, Sr, Sb, La, Ce, Nd, Sm, Eu, Gd, Tb, Yb, and Th ($r = -0.35, -0.41, -0.02$) [31].

Correlations between Ni, Cr, and Co may be utilized to determine the contribution of mafic minerals to the formation of rock. Between Cr and Ni, the correlation value is negative ($r = -0.15$), whereas Co is negatively connected with Cr ($r = -0.01$). This association indicates that acidic minerals are more prevalent than basic and ultrabasic minerals.

The concentration of large-ion lithophile elements (LILEs) varies significantly among examined samples. The alkali element Rb varies between 131–248 ppm with a mean value of 185 ppm, 119–193 ppm with a mean value of 167 ppm, and 151–227 ppm with a mean value of 192 ppm for Sections 1–3. Sr concentrations range from 130–211 ppm with an average of 163 ppm in Section 1, 124–234 ppm with an average of 152 ppm in Section 3, and 103–350 ppm with an average of 215 ppm in Section 2. The concentration of Ba in samples obtained from Section 3 ranges between 187 and 631 parts per million, with an average of 299 ppm. Its concentration ranges between 153–299 ppm with an average of 215 ppm in Section 1, whereas it fluctuates between 165–292 ppm with an average of 206 ppm in Section 2. The association between K$_2$O and Rb is negligible, i.e., $r = 0.03$. The positive value indicates that the abundance of these elements is primarily controlled by clay minerals containing potassium (i.e., illite, muscovite, and biotite) [45,51]. The association between Al$_2$O$_3$ and Rb is positive, indicating that phyllosilicates regulate the distribution of these elements. Similarly, Al$_2$O$_3$ and Ba exhibit a positive correlation, indicating that phyllosilicates control the distribution of these elements as well.

5. Discussion

The findings and their interpretation in our models indicate that the Chichali Formation sediments were derived from intermediate igneous rock, namely, granodiorite. This may be validated geologically since the deposition of shelf glauconitic sand and shale of the Chichali Formation was observed during the Late Jurassic [52]. This is related to the Tethys transgression in the Late Jurassic as a result of the Indian Plate’s northwestern margin expanding along rift faults. Flooding occurred during the Late Jurassic due to the rifting of the Indian Plate’s passive continental edge. Clasts from the exposed portion of the Indian Shield were deposited in the Chichali and Sembar Formations on the shelf as a result of the thermal rising of the Indian Shield’s eastern and southern margins [2,20].

The findings of U–Pb dating are consistent with the Tethyan and lower Himalayan values. The Indian Plate was believed to be the source of the Early Cretaceous Chichali Formation due to its similarities to the Tethyan and Lesser Himalayas. In this period, the present Higher Himalayas were not excavated because they were covered by Tethyan Himalayan sediments, which ruled out the possibility of the Chichali Formation being derived from them [53]. As a result of the detrital zircon provenance, the Indian Plate was the source of the Chichali Formation. The Indian Plate split apart from Gondwana between the Late Jurassic and Early Cretaceous period and began its journey north via the Somali and Mozambique basins [54,55]. The Indian Plate was also experiencing domal
uplift during this period when it passed through the Ninety-East Kerguelen [56]. As a result of domal uplift-induced erosion, the Indian Plate basins contain a significant amount of detrital sediment [57]. The evidence from the detrital record of the Chichali Formation supports erosion from Cambrian and Ordovician plutons that are common in the Tethyan and Lesser Himalayas [58]. Thus, the Aravalli Ranges might be considered a prospective source of sediment inside the Indian Plate during the Cretaceous period.

According to the interpretations made in this study, the source area experienced moderate weathering. This can be justified further by the fact that during the Late Jurassic, the study area was located at $-35^\circ$ paleo-latitude, which was a part of the sub-tropical climate belt, and a slightly humid to dry climate prevailed, resulting in moderate weathering in the source area. The Th/U ratio in the majority of upper crustal rocks is between 3.5 and 4. A Th/U ratio greater than 4 implies moderate to severe weather conditions in the source location. In the majority of instances, U is lost during weathering, increasing the Th/U ratio. The ratio of uranium to thorium in the Chichali Formation is more than 4, which means that the weathering of clasts from the parent rock happened in a somewhat wet-to-dry environment.

According to several tectonic setting discriminating diagrams, the Chichali Formation was deposited on the tectonically stable passive continental margin of the northern Indian Plate. At the period of the deposition of the Chichali Formation, the Indian Plate was in a state of calm, since no collisions with the Kohistan Island Arc (KIA) or the Eurasian Plate had occurred.

Nickel concentrations in typical soils have been reported to be as high as 40 ppm and as low as 25 ppm by various researchers [33,59]. Chromium levels in typical soils have been observed to range from trace to as high as 5.23% [60]. Cr concentrations of up to 4000 ppm are predicted in soils derived from igneous rocks, i.e., ultramafic rocks, while Cr concentrations of up to roughly 11 ppm are expected in sedimentary rocks [61]. The permitted limits for Zn, Ba, Ni, Cu, and Cr in drinking water are 5 ppm, 0.7 ppm, 0.02 ppm, and 0.05 ppm, respectively, as determined by Karasakal [62] (Table 3). This indicates that the average concentrations of Zn, Ba, Ni, Cu, and Cr in the examined sections that were looked at are higher than the acceptable limits set by US-EPA (1978) and Pakistan-EPA (1978).

| Parameter | Mean | Mean | Mean | Min–Max | Min–Max | Min–Max | Standard | (MCL) A | (MCL) B | (MCL) C | (MCL) D |
|-----------|------|------|------|---------|---------|---------|----------|---------|---------|---------|---------|
| Copper (Cu) | 65.6 | 36.8 | 52 | 65–67 | 18–57 | 32–66 | 20–40 | 1.3 | 1 | 1 | |
| Chromium (Cr) | 131.3 | 115.2 | 114 | 120–149 | 94–135 | 85–142 | 90 | - | 0.05 | 0.05 | |
| Nickel (Ni) | 9.33 | 18.1 | 17.5 | 44,814 | 44,887 | 44,923 | 40 | - | 0.02 | <0.02 | |
| Zinc (Zn) | 123.3 | 56 | 116.3 | 89–169 | 41–86 | 81–154 | 44,880 | 5 | 5 | 5 | |
| Barium (Ba) | 215.3 | 206.8 | 299 | 153–299 | 165–243 | 187–631 | - | - | 0.7 | 0.7 | |

The soil would be enriched with Cu, Zn, and Cr as a result of weathering and erosion. As Bowen [63] anticipated, weathering of the examined shale results in higher concentrations of Ba, Cu, and Zn than those seen in typical soils [64]. These elevated levels of trace elements have a toxic effect on soils. These are either agricultural or non-agricultural soils. If the soil formed by weathering is agricultural soil, it may be toxic to crops, and when these crops are consumed by living organisms, they may cause injury. The next section discusses
some of the hazardous impacts of enriching these elements in crops, plants, and soils. While copper is required in minimal amounts for both plants and animals, its excessive concentration may be hazardous. Copper concentrations over a certain level may result in stunted development and chlorosis [65]. Although chromium is neither needed nor useful for plants, it is necessary for trace amounts for mammals. It is poisonous and may cause cancer in animals when present at high concentrations [66].

If surface runoff rises and erodes the Chichali Formation sediments, they will have hazardous consequences if they reach the underground water, which percolates deep into the soil pores. If it combines with surface streams, it may be toxic to aquatic life.

Copper levels in the examined portion exceed WHO (2004) and US-EPA (1978) acceptable drinking water limits [67]. If the copper in the examined portion combines with surface water or percolates down into the subsurface water table, it may cause hazardous consequences in animals and humans, such as gastrointestinal tract stimulation, irritation of stomach nerve endings, and induction of the vomiting reflex [68]. Chromium concentrations within the allowable range are required for human nutrition to sustain proper glucose metabolism. When that level exceeds a particular threshold, poisoning occurs. The deleterious consequences of consuming a high concentration of Cr in drinking water might result in nephritis and glycosuria. Nickel is reasonably safe since the US-EPA (1978) does not propose any limitations for drinking water [69]. When water containing dissolved nickel comes into contact with the skin, it may cause dermatitis, and inhalation of the water can induce lung cancer. Taking into account all of the trace elements, it has been determined that if the Chichali Formation weathers and mixes with streams or reaches the water table, a high concentration of trace elements would pollute the water, rendering it unfit for residential use.

6. Conclusions

SiO$_2$ (17.89–60.14 wt%) is the primary major oxide in the Chichali Formation in the Hazara Basin, followed by Al$_2$O$_3$ (4.89–21.19 wt%), MgO (1–7.27 wt%), Fe$_2$O$_3$ (1.26–9.27 wt%), CaO (0.99–2.88 wt%), K$_2$O (0.61–5.75 wt%), Na$_2$O (0.01–0.17 wt%), and TiO$_2$ (0.5–1.48 wt%). We computed ratios such as Ba/Sc, Ba/Co, Th/Sc, Cr/Th, Cr/Zr, Th/Co, Th/Cr, and Sc/Th, bivariate plots such as Al$_2$O$_3$ (wt%) versus TiO$_2$ (ppm), TiO$_2$ (wt%) vs. Zr (ppm), and TiO$_2$ (wt% vs. Ni (ppm), and discriminant function (Df1–Df2). The bivariate plots of SiO$_2$ vs. K$_2$O/Na$_2$O and discriminant function (Df1–Df2) indicate that the Chichali Formation’s Early Cretaceous shales have mostly passive margin settings.

The computed values of CIA, ICV, Rb, and Cs indicate that the source regime experienced mild chemical weathering. The presence of heavy metals (Ba, Zn, Ni, Cr, and Cu) in the soils formed from Chichali Formation shale implies toxicity to agriculture and drinking water if the soils are combined with agricultural soils and/or drinking water.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/jmse10060800/s1, Table S1: Pearson correlation of major and minor oxides.

Author Contributions: Conceptualization, A.G.F. and M.U.; methodology, A.G.F.; software, A.G.F. and H.T.J.; validation, A.G.F., M.U. and H.T.J.; formal analysis, A.G.F., M.U. and H.T.J.; investigation, A.G.F., M.U. and H.T.J.; resources, A.G.F. and M.U.; data curation, A.G.F. and M.U.; writing—original draft preparation, A.G.F. and M.U.; writing—review and editing, H.T.J., F.S., M.A.F.M., G.K. and A.K.J.; visualization, M.U., H.T.J., F.S. and M.A.F.M.; supervision, M.U.; project administration, M.U.; funding acquisition, G.K. and H.T.J. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not Applicable.

Informed Consent Statement: Not Applicable.

Data Availability Statement: Not Applicable.
Acknowledgments: We would like to express our gratitude to Bestway Cements Limited in Hattar, Pakistan, for permitting us to utilize their facilities. The authors declare that they have no potential conflicts of interest related to the article’s authorship and publication. We would like to thank the editor and the anonymous reviewers for their thorough and helpful reviews, which made our study much more valuable.

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

References

1. Umar, M.; Sabir, M.A.; Farooq, M.; Khan, M.M.S.S.; Faridullah, F.; Jadoon, U.K.; Khan, A.S. Stratigraphic and sedimentological attributes in Hazara Basin Lesser Himalaya, North Pakistan: Their role in deciphering minerals potential. Arab. J. Geosci. 2015, 8, 1653–1667. [CrossRef]

2. Ali, S.K.; Janjuhah, H.T.; Shahzad, S.M.; Kontakiotis, G.; Saleem, M.H.; Khan, U.; Zarkogiannis, S.D.; Makri, P.; Antonarakou, A. Depositional Sedimentary Facies, Stratigraphic Control, Paleoclimatological Constraints, and Paleogeographic Reconstruction of Late Permian Chhidru Formation (Western Salt Range, Pakistan). J. Mar. Sci. Eng. 2021, 9, 1372. [CrossRef]

3. Abbasi, I.A.; Haneef, M.; Obaid, S.; Daud, F.; Qureshi, A.W. Mesozoic deltaic system along the western margin of the Indian plate: Lithofacies and depositional setting of Datta Formation, North Pakistan. Arab. J. Geosci. 2012, 5, 471–480. [CrossRef]

4. Janjuhah, H.T.; Ishfaque, M.; Mehmood, M.I.; Kontakiotis, G.; Shahzad, S.M.; Zarkogiannis, S.D. Integrated Underground Mining Hazard Assessment, Management, Environmental Monitoring, and Policy Control in Pakistan. Sustainability 2021, 13, 13505. [CrossRef]

5. Qasim, M.; Khan, M.A.; Haneef, M. Stratigraphic characterization of the Early Cambrian Abbottabad Formation in the Sherwan area, Hazara region, N. Pakistan: Implications for Early Paleozoic stratigraphic correlation in NW Himalayas, Pakistan. J. Himal. Earth Sci. 2014, 47, 25.

6. Ahsan, N. Facies modeling, depositional and diagenetic environments of Kawagarh Formation, Hazara Basin, Pakistan. Doctoral Dissertation, College of Earth and Environmental Sciences, Punjab University, Lahore, Pakistan, 2007.

7. Hasterok, D.; Gard, M.; Webb, J. On the radiogenic heat production of metamorphic, igneous, and sedimentary rocks. Geosci. Front. 2018, 9, 1777–1794. [CrossRef]

8. Armstrong-Altrin, J.S.; Lee, Y.I.; Verma, S.P.; Ramasamy, S. Geochemistry of Sandstones from the Upper Miocene Kudankulam Formation, Southern India: Implications for Provenance, Weathering, and Tectonic Setting. J. Sediment. Res. 2004, 74, 285–297. [CrossRef]

9. Armstrong-Altrin, J.S.; Lee, Y.I.; Kasper-Zubillaga, J.J.; Carranza-Edwards, A.; Garcia, D.; Eby, G.N.; Balaram, V.; Cruz-Ortiz, N.L. Geochemistry of beach sands along the western Gulf of Mexico, Mexico: Implication for provenance. Geochemistry 2012, 72, 345–362. [CrossRef]

10. Zaid, S.M. Integrated petrographic, mineralogical, and geochemical study of the Late Cretaceous–Early Tertiary Dakhla Shales, Quseir–Nile Valley Province, central Egypt: Implications for source area weathering, provenance, and tectonic setting. Arab. J. Geosci. 2015, 8, 9237–9259. [CrossRef]

11. Martini, A.M.; Walter, L.M.; Ku, T.C.W.; Budai, J.M.; McIntosh, J.C.; Schoell, M. Microbial production and modification of gases in sedimentary basins: A geochemical case study from a Devonian shale gas play, Michigan basin. AAPG Bull. 2003, 87, 1355–1375. [CrossRef]

12. Lin, N.H.; Guo, Y.; Wai, S.N.; Tamehe, L.S.; Wu, Z.; Naing, N.M.; Zhang, J. Sedimentology and geochemistry of Middle Eocene-Lower Oligocene sandstones from the western Salin Sub-Basin, the Central Myanmar Basin: Implications for provenance, source area weathering, paleo-oxidation and paleo-tectonic setting. J. Southeast. Asian Earth Sci. 2019, 173, 314–335. [CrossRef]

13. Ding, L.; Qasim, M.; Jadoon, I.A.; Khan, M.A.; Xu, Q.; Cai, F.; Wang, H.; Baral, U.; Yue, Y. The India–Asia collision in north Pakistan: Insight from the U–Pb detrital zircon provenance of Cenozoic foreland basin. Earth Planet. Sci. Lett. 2016, 455, 49–61. [CrossRef]

14. Jan, I.U.; Iqbal, S.; Davies, S.J.; Zalasiewicz, J.A.; Stephenson, M.H.; Wagreich, M.; Haneef, M.; Hanif, M.; Ahmad, S. A Periglacial Palaeoenvironment in the Upper Carboniferous-Lower Permian Tobra Formation of the Salt Range, Pakistan. Acta Geol. Sin. Engl. Ed. 2017, 91, 1063–1078. [CrossRef]

15. Khan, U.; Janjuhah, H.T.; Kontakiotis, G.; Rehman, A.; Zarkogiannis, S.D. Natural Processes and Anthropogenic Activity in the Indus River Sedimentary Environment in Pakistan: A Critical Review. J. Mar. Sci. Eng. 2021, 9, 1109. [CrossRef]

16. Ishfaque, M.; Dai, Q.; Haq, N.U.; Jadoon, K.; Shahzad, S.M.; Janjuhah, H.T. Use of Recurrent Neural Network with Long Short-Term Memory for Seepage Prediction at Tarbela Dam, KP Pakistan. Energies 2022, 15, 3123. [CrossRef]

17. Malkani, M.S. Stratigraphy, mineral potential, geological history and paleobiogeochemistry of Balochistan Province, Pakistan. Sindh Univ. Res. J. -SURJ (Sci. Ser.) 2015, 43. Available online: https://sujo-old.usindh.edu.pk/index.php/SURJ/article/view/1383 (accessed on 26 April 2022).

18. Garzanti, E.; Liang, W.; Ando, S.; Clift, P.D.; Resentini, A.; Vermeesch, P.; Vezzoli, G. Provenance of Thal Desert sand: Focused erosion in the western Himalayan syntaxis and foreland-basin deposition driven by latest Quaternary climate change. EarthSci. Rev. 2020, 207, 103220. [CrossRef]

19. Malkani, M.S.; Mahmood, Z. Revised stratigraphy of Pakistan. Geol. Surv. Pak. Rec. 2016, 127, 1–87.
