Research Article

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Geochronology, trace elements and Hf isotopic geochemistry of zircons from Swat orthogneisses, Northern Pakistan

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Abstract: In this study, zircon grains are applied for U–Pb dating, Hf isotopes and trace elements to reveal the origin of magmatism and tectonic evolution of Late Paleozoic rocks of the Indian plate, Northern Pakistan. Most of the zircons are characterized by oscillatory zoning, depletion of light rare earth elements (LREE) and enrichment of heavy rare earth elements (HREE) with Ce and Eu anomalies. The yielded ages for these rocks are 256 ± 1.9 Ma and are plotted in the zones defined for the continental setting with few deviated toward the mid-oceanic ridge and the oceanic arc setting. Deviated zircons are recognized as inherited zircons by displaying a high concentration of normalized primitive La and Pr values, while others are plotted in the continental zones. Rare earth elements (REE) and trace elements including Th, Hf, U, Nb, Sc and Ti discriminate Swat orthogneisses into the within plate setting and the inherited zircons are plotted in the orogenic or the arc-related setting. The LREE discriminated these zircons into a magmatic zone with inherited zircons deviated toward the hydrothermal zone. The temperature calculated for these rocks based on the Ti content in zircon ranges from 679 to 942°C. The $\varepsilon_{\text{Hf}}(t)$ ranging from –11.1 to +1.4 reveals that the origin is

the continental crust with the minute input of the juvenile mantle.

Keywords: Late Paleozoic, zircon trace elements, Hf isotopes, anorogenic, Northern Pakistan

1 Introduction

Traditionally, the importance of zircon (ZrSiO_4) is known for its geochronological dating, but zircon trace element geochemistry is an emerging field to interpret tectonic settings [1–3]. Titanium present in the zircon can help calculate the temperature of the rocks, and the Hf isotopic study can play a significant role to unravel crustal recycling [4–7]. LREE depletion and HREE enrichment with Eu and Ce anomalies are used to know the magmatic and metamorphic origins of the rocks from the zircon study [8,9]. Zircon occurs in several igneous, sedimentary and metamorphic rocks as an accessory mineral [5]. It is due to its high durability and stability to harsh physical and chemical weathering as well as due to its dominant role in the growth with granitoid petrology that it is regarded as the most common mineral used in igneous, metamorphic and sedimentary petrology [10,11]. Trace element geochemistry in zircon is an emerging field to interpret the origin and the tectonic setting of igneous rocks [2,12,13], and this technique is applied for the first time on the Swat orthogneisses, Northern Pakistan. The REEs like Ce and HREE present in zircons display unique enrichment normalized trends, which are used to find the protolith of the rock [3,14]. As hafnium is most compatible with zircon, the ages determined by the U–Pb dating are also used for the Lu–Hf isotope system, which is the best choice for determining the evolution of igneous and metamorphic rocks in collisional zones [15]. Lu is least compatible with the zircon, while hafnium and zirconium are geochemically similar, and 1–4% of hafnium is present in the zircon, which is geotectonically very

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important. The zircon is a very resistant mineral to harsh chemical and physical weathering, and during physical weathering, the zircon moves to the sand portion along with hafnium, while the Lu is discarded into the clay portion, which is the basis for finding the geochemical settings [5,16]. Although the importance of Hf as a geochemical tracer was recognized in the early 1980s, Hf separation was very difficult, and later the MC-ICP-MS technique was adopted to determine the accurate ratios of Hf isotopes in the zircon, which is a revolution to study the mantle crust processes in detail as a geochemical tracer in subduction settings [17,18]. The Hf isotopic record in the zircons is the best decipher for source rocks as well as plays important roles in the magma mixing, assimilation and petrogenesis [9,19–22]. It is noted that the geochemical behavior of Zr and Hf during magma crystallization is the same, and all the zircons have 0.4–4 wt% Hf, which is a part of the zircon lattice [5]. The Lu is not compatible with zircon, and hence, the initial Lu/Hf ratio is much less (<0.001) compared to the continental crust with the high Lu/Hf ratio. The crust/mantle differentiation in the context of $^{176}\text{Hf}/^{177}\text{Hf}$ is different, and this specific characteristic of Hf is used as the trace for differentiation [5,23]. The technique to determine the Hf isotopic ratio from the same spot that is used for finding the age is a new development in the petrochronology [24–26]. The previous ages determined for Swat orthogneiss were 268 ± 7 Ma, 265 ± 2 , 278 ± 4 by U–Pb and Rb/Sr techniques [27,28]. Crustal and mantle processes are particularly studied in detail by using the evolution of hafnium in zircon [29]. The morphology and the chemistry of trace elements of the zircon combined with the Hf isotope composition help interpret petrogenetic information [11]. In this article, Swat orthogneisses (Figure 1) of zircons are analyzed for Hf isotopes, U–Pb dating and trace elements to find the origin and the evolution of magma. The zircon morphology, trace elements in zircon and Hf isotopes from the zircon were determined by using cathodoluminescence (CL) imaging, laser ablation inductively coupled plasma mass spectrometry (LA-ICPMS) and laser ablation multicollector inductively coupled plasma mass spectrometry (LA-MC-ICPMS).

2 Geological setting

Northern Pakistan is tectonically divided into three terranes from the south to the north, i.e., Indian plate rocks in the south, Kohistan–Ladakh Island arc in the

middle and Karakoram plate rocks in the north [30,31]. The main mantle thrust (MMT) separates the Indian plate rocks (Figure 1) from the Kohistan island arc in the north [32–34]. The Kohistan Island in the north is bounded by the main Karakoram thrust or the northern suture zone. The part of the Indian plate in Pakistan is further divided into three tectonic bodies by the main central thrust (MCT), main boundary thrust and salt range thrust. The zone between the MCT and the MMT (Figure 1) is a part of greater Himalaya [35–38]. The Indian plate rocks in the south are metamorphosed as a result of initial subduction phases and later on collision with the Kohistan–Ladakh island arc in Cretaceous to Cenozoic Himalayan orogeny [37]. The Greater Himalayan zone consists of pelitic-psammitic schists, gneisses, amphibolites, meta-carbonates and intrusion of plutonic bodies ranging in age from Archean to recent (ca. 1,847–47 Ma) [28,39,40]. The Himalayan orogeny has great effects in the context of sedimentation, metamorphism and plutonism on the Indian plate rocks, which are formed as early as the Archean era. Granitic rocks are the most abundant intrusive bodies ranging in size from plutons to smaller size sills and dykes in northern Pakistan [41]. The granitic rocks from northern Pakistan were grouped based on their radiometric ages, but the data available for these extensive rock bodies are limited [35,42]. Swat orthogneisses were metamorphosed to greenschist and amphibolite facies during Eocene–Oligocene [43,44]. These orthogneisses are divided into seven groups starting from Early Proterozoic (ca. $>2,175$ Ma) to Late Quaternary (ca. 10 Ma). This study focuses on Late Paleozoic (ca. 350–268 Ma) orthogneisses by interpreting the trace elements from zircon grains. Swat orthogneisses were explored by using whole-rock major and trace element geochemistry, as well as geochronological studies were reported from this terrane, but zircon trace element geochemistry is limited [3,5,14]. The felsic plutonic activity is the main cause of crustal differentiation, but to correlate felsic magma with the crust development, knowledge of magmatic evolution is required, which is difficult from the whole rock composition. Hf isotopes extracted from the zircons are the best tracers for finding the magma evolution in continental granitoids, continental arcs and subduction zones [19,45]. Hf isotopes in the zircons are selected as it is highly compatible with the zircon. The precise ages determined by the U–Pb system in zircon can accurately provide the isotopic evolution of Hf. Both Hf and Lu are incompatible elements, but Hf segregated more strongly into the melts than Lu during magma differentiation stages. The concentration of $^{176}\text{Hf}/^{177}\text{Hf}$ is increased in

Figure 1: Geological map of the study area [after Refs. 37,38].

the mantle compared to the crust. Granitic magmas with high $^{176}\text{Hf}/^{177}\text{Hf}$ are the indication of magma intruded directly from mantle or by melting of the lower crust. The lower concentration of $^{176}\text{Hf}/^{177}\text{Hf}$ is determined for magma from crustal reworking [19,45].

3 Analytical techniques

3.1 Zircon U–Pb dating and Hf isotope

Zircons grains were extracted from coarsely crushed orthogneisses (80 mesh). These zircons were separated by using the combined technique of magnetic separation

and heavy liquid before handpicking under a binocular microscope. These separated zircons were mounted in epoxy resins and were polished to half size to best expose grain interiors. The CL images and transmitted and reflected images of the polished zircons were obtained (Figure 2a–f). Detailed interpretation of all these images was carried out to select those areas that have no cracks and inclusions for laser ablation. The zircon U–Pb dating was performed at the state key Laboratory of Geological Processes and Mineral Resources, China University of Geosciences, Beijing (GPMR-CUGB). Zircon standard 91500 was used as an external standard as described in Ref. [46]. The standard was run two times after every eight samples. The first 20 s were used for blank gas followed by 50 s for sample. The laser ablation was performed by using a GerlasPro

Figure 2: (a and b) Representative cathodoluminescent images displaying the sector and oscillatory zoning for igneous zircons. Most of the zircons display the typical euhedral prismatic shape, while few are of the oval shape with a 1:1 length to width ratio. The spot size of 35 μm is used to hit the zircons for U–Pb, trace elements and Hf isotope analysis. Red circles show the U–Pb dating, while yellow circles show the Hf isotopic analysis. (c–f) Backscatter and transmitted images are interpreted to locate those areas with no fracture and inclusions to get accurate results for age and Hf isotopes. The very thin white rims in these zircons represent metamorphic zones.

laser ablation system comprising a COMPexPro 102 ArF excimer laser with a wavelength of 193 nm and a maximum energy of 200 mJ and a MicroLas optical system. The laser ablation was done with a ablation spot size of 35 μm , and ion signal intensities were taken by the ICPMS instrument (Agilent 7700 $\times$). Helium gas was applied as a carrier gas, and Argon was used as a make-up gas that mixes with the carrier gas through a T-connector prior entering the ICP. The standards of the U–Pb dating analysis are Plešovice, 91500, GJ-1 and SRM 610, which were used as external standards [46]. The concentrations of U–Pb and trace elements obtained from the LA-ICPMS analysis were interpreted for results on the ICPMS-Data-Cal 10.8 software by using the method defined in Ref. [47]. The common lead correction was carried out by following the method designed in Ref.

[48]. U–Pb Concordia and the weighted average mean were obtained through Iso-plot version 2003 by using the method described in Ref. [49]. The REE and trace elements obtained during this research work are listed in Table 1.

The *in situ* Hf isotopic analysis of zircon was carried out by using LA-MC-ICPMS at GPMR-CUGB. The Lu–Hf zircon isotopic analysis was performed by using the 35 μm spot size. The geo-standards follow those given in Ref. [50], including 91500 ($^{176}\text{Hf}/^{177}\text{Hf}$ value 0.282306 ± 30) and Plešovice ($^{176}\text{Hf}/^{177}\text{Hf}$ value 0.282477 ± 30). The isotopic concentrations of $\varepsilon_{\text{Hf}}(i)$ and $\varepsilon_{\text{Hf}}(t)$ were determined by using the chondrite uniform reservoir standards defined in Ref. [19,51,52]. The concentrations of these are as follows: $(^{176}\text{Lu}/^{177}\text{Hf})_{\text{CHUR}} = 0.0336$,

Table 1: LA-ICP-MS analytical results of rare earth elements and trace elements from Swat orthogneisses

Zircon spots	REE (ppm)													
	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
KIA-17-03-02	0.56	40	0.19	1.06	1.6	0.29	10	5	66	30	162	39	420	92
KIA-17-03-03	0.12	75	0.10	1.37	2.8	0.50	20	9	122	54	295	74	806	181
KIA-17-03-04	5.25	63	2.65	14.91	6.1	0.77	22	9	118	50	257	61	610	131
KIA-17-03-05	—	14	0.10	1.92	5.6	0.27	43	21	306	134	685	160	1,571	320
KIA-17-03-06	16	78	4.35	21	9.8	2.09	43	15	182	70	334	74	714	145
KIA-17-03-10	15	211	3.90	18	14.7	2.40	75	27	342	131	603	128	1,181	231
KIA-17-03-13	0.53	76	0.24	2.00	3.3	0.70	24	11	147	64	335	81	837	184
KIA-17-03-15	0.01	50	0.05	0.79	1.9	0.35	12	5	80	37	213	57	652	156
KIA-17-03-16	0.03	41	0.23	3.42	5.6	2.11	28	8	102	38	174	37	348	72
KIA-17-03-18	0.08	20	0.10	1.75	4.4	0.85	25	10	124	51	245	55	550	119
KIA-17-03-19	—	3	0.07	1.40	4.8	0.33	36	15	199	80	389	89	852	163
KIA-17-03-20	0.03	49	0.07	1.50	4.4	1.15	33	16	224	96	511	132	1,420	304
KIA-17-03-21	0.01	33	0.04	0.80	2.4	0.50	18	8	120	52	279	71	753	168
KIA-17-03-22	0.03	39	0.31	5.46	8.2	3.74	38	12	133	49	211	44	404	81
KIA-17-03-23	0.03	44	0.14	2.45	6.5	0.72	41	17	229	93	452	102	977	190

Zircon spots	Trace elements (ppm)								
	Sc	Ti	Fe	Y	Zr	Nb	Hf	Ta	SiO ₂
KIA-17-03-02	283	6	191	937	4,34,393	15	16,455	9	39
KIA-17-03-03	398	7	48	1,837	4,33,210	29	14,958	10	39
KIA-17-03-04	316	8	763	1,550	4,18,869	18	14,491	8	41
KIA-17-03-05	479	6	66	4,221	4,20,660	7	17,365	5	40
KIA-17-03-06	359	27	78	2,195	4,33,485	9	14,382	5	39
KIA-17-03-10	334	14	114	4,090	4,22,761	34	13,200	14	40
KIA-17-03-13	353	6	58	2,063	4,27,837	29	15,689	12	39
KIA-17-03-15	356	5	54	1,282	4,30,231	26	17,119	11	39
KIA-17-03-16	274	21	32	1,129	4,34,938	5	12,704	3	39
KIA-17-03-18	390	57	785	1,519	4,30,396	6	14,401	3	40
KIA-17-03-19	548	9	23	2,576	4,39,006	2	16,219	2	38
KIA-17-03-20	405	50	300	3,288	4,31,386	24	17,995	15	38
KIA-17-03-21	493	10	184	1,673	4,35,580	15	17,232	8	38
KIA-17-03-22	301	40	2	1,401	4,41,454	4	10,869	2	39
KIA-17-03-23	361	8	228	2,963	4,36,050	16	15,732	7	38

$(^{176}\text{Hf}/^{177}\text{Hf})_{\text{CHUR}} = 0.282785$ and $(^{176}\text{Lu}/^{177}\text{Hf})_{\text{mean crust}} = 0.015$. Initially, the zircons were run for U–Pb dating, and the best concordance results were then interpreted for the Hf isotopic study. The calculation of the initial and final values of the Hf isotopic composition followed the method defined in Ref. [4] and is presented in Table 2.

4 Results

4.1 Rock petrography

The Swat orthogneisses are essentially composed of potash feldspar, quartz and muscovite with accessory

minerals including epidote, apatite, plagioclase, clinopyroxenes and rutile (Figure 3a–d). The modal percentage of potash feldspar including both orthoclase and microcline ranges from 45% to 65% in different views. The microcline displays the coarsed grain texture with anhedral to subhedral shape. The grain size of the microcline ranges from 1 to 2.5 mm with hatched twinning. The microcline shares its boundaries with the muscovite and recrystallized quartz. The quartz is a second dominant phase, and it ranges in modal composition from 15% to 25%. Quartz is mostly anhedral, and the smaller grains display strains that are easily visible from the undulose extinction. The orthoclase displays simple twins and mostly represented by a cloudy surface in the plane light due to sericitization.

Table 2: Hafnium isotopic analysis of zircons for those spots that are initially run for determining the U–Pb ages

Zircon spots	Age (Ma)	$^{176}\text{Lu}/^{177}\text{Hf}$	$^{176}\text{Hf}/^{177}\text{Hf}$	$^{176}\text{Hf}/^{177}\text{Hf}_i$	$\epsilon_{\text{Hf}}(0)$	$\epsilon_{\text{Hf}}(t)$	TDM	TDM(Hf)C	fLu/Hf
KIA-17-03-02	258	0.0009	0.2826	0.2826	−6.33	−0.74	911	1,306	−0.97
KIA-17-03-03	257	0.0011	0.2826	0.2826	−7.57	−2.04	967	1,388	−0.97
KIA-17-03-04	255	0.0015	0.2826	0.2826	−5.45	−0.03	891	1,258	−0.96
KIA-17-03-05	257	0.0033	0.2825	0.2825	−8.42	−3.27	1,062	1,465	−0.90
KIA-17-03-06	258	0.0011	0.2825	0.2825	−8.35	−2.81	998	1,437	−0.97
KIA-17-03-10	256	0.0039	0.2827	0.2827	−3.57	1.47	870	1,163	−0.89
KIA-17-03-13	256	0.0031	0.2827	0.2826	−4.53	0.65	892	1,216	−0.91
KIA-17-03-15	256	0.0012	0.2826	0.2826	−6.58	−1.10	930	1,327	−0.96
KIA-17-03-16	249	0.0014	0.2827	0.2827	−3.93	1.38	827	1,164	−0.96
KIA-17-03-18	257	0.0012	0.2826	0.2826	−6.19	−0.68	914	1,301	−0.96
KIA-17-03-19	257	0.0002	0.2823	0.2823	−16.13	−10.45	1,277	1,921	−0.99
KIA-17-03-20	257	0.0014	0.2826	0.2826	−6.19	−0.72	920	1,303	−0.96
KIA-17-03-21	256	0.0013	0.2823	0.2823	−16.62	−11.15	1,332	1,964	−0.96
KIA-17-03-22	256	0.0013	0.2827	0.2826	−4.70	0.77	856	1,208	−0.96
KIA-17-03-23	255	0.0019	0.2825	0.2825	−8.88	−3.53	1,040	1,480	−0.94

Figure 3: (a) Field exposure of the Swat orthogneisses from the southern margin of Kohistan island arc. GPS location is (E 72° 23' 40''; N 34° 47' 34.4''). (b–d) The petrographic analysis mainly displays alkali feldspar, quartz and micaceous minerals like muscovite and biotite. Kfs (K-feldspar), Mc (microcline), Qtz (quartz), Ep (epidote), Ms (muscovite), Ser (sericite), Pl (plagioclase) and Rt (rutile).

Muscovite is less than 10% in these rocks and is characterized by the tabular appearance. The dominance of muscovite over biotite in these rocks represents its peraluminous nature. Biotite is less abundant in most views, and its percentage is <5% but mostly associated with muscovite grains. The laths of tabular muscovite exhibit truncated contact with microcline. Megacrysts of potash feldspar (microcline) are the common mineral in these rocks. Inclusions of biotite grains are present in the potash feldspars. The graphic texture is observed where quartz shares a boundary with a microcline. Quartz grains with the anhedral to subhedral shape are clear, while the alkali feldspars have minute input of sericitization and saussuritization in the form of sericite, muscovite and epidote. Biotite and muscovite display subhedral to euhedral shape, and topotaxial growth is also observed in small grains where muscovite is crystallized at the expense of biotite. Clusters of epidotes occur in these rocks with dominant zoning, which are bluish and orange that represent metamorphic stages in these rocks. Biotite is fresh looking with perfect one set of cleavage with some spots altered to greenish color chlorite in the center. Recrystallized quartz grains mostly of the anhedral shape are present along the boundary of microcline, and these are developed during high-grade metamorphism. The rock is characterized by hypidiomorphic texture with most of the minerals represented by anhedral with few euhedral shapes. The biotites are less than 0.5 mm, and muscovite is coarse grained with an average size of 0.5–1 mm. The quartz grains are less than 0.5 mm to more than 2 mm in different views. The recrystallized quartz grains are represented by smaller anhedral shapes, and the grain boundaries are sutured. Traces of rutile as an euhedral mineral are also observed in these rocks. The regional stress direction is represented by the orientation of muscovite, biotite and quartz grains in these rocks.

4.2 Zircon morphology and age

The zircons extracted were mostly 100–150 μm in length and exhibit cracks as examined in the CL images. Those zones that display igneous zoning in CL images and display no inclusions in transmitted light were selected, and the care was also taken to select those areas, which were not diluted by Pb loss due to internal stresses and fractures. These zircons have preserved the oscillatory zoning, which is the characteristic of igneous zircons, and the broad zoning without visible cores reveals that

these zircons were developed during one stage of the magmatic growth [10]. Prismatic grains in these zircons display weak oscillatory zoning, while nonprismatic subhedral elliptical grains are characterized by good oscillatory zones. There are lighter zones that display their metamorphic history, while the magmatic sector and oscillatory zones are preserved in almost all zircons (Figure 2). Most of them are subhedral to euhedral, and due to the long tectonic history, some are split into pieces as a result of tectonic forces. The uranium content in these zircons ranges from 74 to 3,192 ppm, while the Th/U content of the analyzed zircons ranges from 0.087 to 1.15, which display its magmatic age [53]. The concordant age (Figure 4a and Supplementary Table 3) determined for this sample is 256 ± 1.9 Ma (mean square weighted deviation (MSWD) = 2.7, $n = 15$). The age is calculated based on 15 zircons in which the concordance of most of the grains is more than 95%. The range of time calculated for the granitic rocks from this study is 249–256 Ma based on the $^{206}\text{Pb}/^{238}\text{U}$ ratio. The $\text{Lu}_{(n)}$ values in these zircons range from 2,940 to 13,010, similar to the range

Figure 4: (a) U–Pb Concordia displaying Late Paleozoic age (256 ± 1.9 Ma). (b) The zircons are plotted in the zone defined for the continental crust similar to the zone plotted in Ref. [14]. The normalized values are taken from Ref. [60].

defined in Ref. [54] for the igneous-type granitoids. The Y concentration in these zircons is 937–4,220 ppm, which is similar to granitoids (500–4,534 ppm) reported in Ref. [55].

4.3 Zircon trace elements and Hf isotopes

Zircons were analyzed for REE and trace elements including Sc, Ti, Y, Zr, Nb, Hf and Ta to find out the tectonic setting of Swat orthogneisses (Table 1). The concentrations of trace elements are as follows: Sc, 274 to 547 ppm; Ti, 4.6–57.4 ppm; Y, 937–4,220 ppm; Nb, 1.6–34.4 ppm; Hf, 10,869–17,994 ppm; and Ta, 1.8–14.5 ppm. All the zircons were characterized by negative Eu and positive Ce anomaly (Figure 4b) as plotted on the normalized primitive values in Ref. [56]. The concentration of REE in these zircons was dominated by the enrichment of HREE and depletion of LREE. The Ti content was variable and converted to a temperature range of 679–942°C. The highest temperature of >800°C was displayed by the metamorphic region that has a high concentration of Ti, and the zircons having a temperature range of <750°C are all the magmatic zircons with a low titanium content [7]. The composition of Hf in the context of the $^{176}\text{Hf}/^{177}\text{Hf}$ ratio ranges from 0.282315 to 0.282684, and $\varepsilon_{\text{Hf}}(t)$ for this composition is –11.15 to +1.47.

5 Discussion

5.1 Tectonic setting of Swat orthogneisses

The origin of granitic rocks based on multiple trace elements like Hf, U, Th, Y and HREE easily distinguished the island arc setting, within plate orogeny and convergent plate orogeny [3,14]. Trace elements in zircons, i.e., U, Y and Hf, are used to distinguish the continental and oceanic setting [14]. The REE normalized pattern of zircon in this study is shown in Figure 4b. Zircons from Swat orthogneisses are characterized by continental granitoids as plotted in Ref. [14] the normalized pattern of REE. The LREE depletion with prominent positive Ce anomaly and the enrichment of HREE discriminated these zircons into typical magmatic origin [57]. The pattern is compared with the standard given in Ref. [14] for zircons, and it is found that the zircons are plotted on the continental zone with less or no contamination of the oceanic island setting. Few of the zircons are noted with high La (>5 ppm) and Pr

(>10 ppm) from the LREE, and these are included in the inherited zircons as the enrichment of La and Pr is a dominant feature in the inherited zircons [58]. Granitic rocks are further classified into I-type, S-type and A-type on the basis of REE patterns, and in this study, zircons show the I-type concentration of REE [59]. The Eu-negative anomaly in the REE pattern normalized to [60] primitive values is the characteristic feature of plagioclase crystallization in these rocks. The Th/U and Nb/Hf [61] ratios are critical to distinguish orogenic within the plate setting from the arc-related orogenic setting (Figure 5a). The zircons from the Swat orthogneisses have a high concentration of the Nb/Hf ratio, which is a clue for these zircons to have originated in the anorogenic stable within the plate setting as a result of plutonic magma in the continental crust. The inherited zircons with a low concentration of Nb/Hf are plotted in the zone for arc or orogenic setting. The high concentration of Th than Nb and similarly the high concentration of Hf than Nb are characteristic features of zircon from the continental arc-related orogenic setting. The zircons in this study are plotted in the anorogenic within the plate zone [62] with the low concentration of Hf and Nb compared to the arc-related setting, while the inherited zircons are deviated toward the zone or the arc setting (Figure 5b). The Hf content in the zircons in this study is higher (>10,000 ppm), which reveals that the origin of magma for these rocks is from more evolved felsic magma [63]. The heavy REE element Yb in the zircon has a characteristic to be differentiated into the oceanic zone and the continental zone correlated with the uranium content [14]. The zircons in this study have a high concentration of uranium and are plotted in the zone defined for the continental survey. The rocks are plotted in the zone of anorogenic within the plate setting in the figures of Refs. [61,62] on the basis of Th/Nb versus Hf/Th and Th/U versus Nb/Hf ratios (Figure 5a and b).

It is noted that multiple trace element ratios are more efficient to discriminate the tectonic setting compared to the single element. The ratio of trace elements like Nb/Yb versus U/Yb (Figure 5c) is helpful to define the tectonic setting for Swat orthogneisses to have originated in the continental arc-type setting, and the similar setting is determined for these rocks as plotted on the binary (Figure 5d) Sc versus U [3]. U/Yb is used for distinguishing the zircons from the continental and oceanic settings as major changes are observed in the ratio for these tectonic settings [64,65]. The average U/Yb values for N-MORB, primitive arc basalts, average lower and upper crust are ~0.01, 0.3, 0.13 and 1.35, respectively. Based on these values, the tectonic settings

Figure 5: (a) The rocks are plotted in the anorogenic/within plate zone similar to that in Ref. [61] based on concentration of Th/U and Nb/Hf in the zircons. (b) The anorogenic zone is attributed for Swat orthogneisses similar to the discriminatory plot in Ref. [62]. Inherited zircons are plotted in the arc-related environment, which are inherited zircons. (c) The continental arc field is defined for the zircons based on Nb, U and Yb figure from Ref. [3]. (d) The concentration defined for the continental zone has high Sc and U values, while the mid-oceanic ridge has a very narrow zone of Sc values (>10 and <100). Zircons from Swat orthogneisses on the basis of Sc and U are plotted in the continental arc compilation after [3].

are easily distinguished. The Swat orthogneisses have the U/Yb ratio ranging from 0.18 to 3.47 and the high values indicating the enriched crust, which have influence on the mature arc. The higher ratio (>0.1) discarded the phenomenon of these rocks to have originated from the mid-ocean ridge basalt (MORB) setting [14]. Zircon is characterized by partitioning Yb compared to U, and thus, the concentration of U in the magma increased in the later stages of magma is increased [66]. This increasing trend is used to differentiate the primary magma from the MORB and the later secondary stages of magmas.

Niobium [67] is the tracer for interpreting the subduction zones by its normalized negative anomaly, but in the zircons trace element geochemistry, the enrichment of Nb is plotted for felsic igneous within plate rocks and alkali-rich magmas. The zircons are plotted in the field of the continental arc setting based on Nb/Yb and U/Yb discrimination (Figure 5c), and the crystallization of these granitic rocks in the continental setting is confirmed. Trace elements from the zircons are used to correlate with rock types, and the concentration is documented for classifying the igneous rocks [2].

The dominant trace elements used for discriminating igneous rocks into different fields include Y, U, Yb, Sm, Nb and Ta, and the number of rocks recognized based on these elements from zircons ranges from ultramafic to felsic compositions, i.e., kimberlites to leucogranites. The Yb/Sm versus Y composition of zircons from Swat orthogneisses is used to know the rock type on the plot [2], and the zircons are plotted in the field of granodiorites (Figure 6). The Ta and Nb as well as Ce/Ce* versus Y plot discriminate the zircons into the same granodiorites. Similarly, Nb/Ta versus Y plot also discriminates the zircons from Swat orthogneisses into the granodiorite field. It is confirmed from the trace element concentration that the original rock in which these zircons grow is granodiorite as shown in all the

discriminatory figures. The granitoid field in the previous study [2] is further divided into three zones, namely, (1) aplites and leucogranites, (2) granites and (3) granodiorites and tonalites. The rocks are plotted in the granodiorites, which is subfield 3 from the discrimination diagram [2]. The rock classification figures of the trace elements are shown in Figure 6. The ratio of Nb/Ta analyzed in this study ranges from 0.9 to 2.73 with an average value of 2 and the chondritic Nb/Ta ratio [68] is 17. The high ratio is found in most fractionated rocks like granites, while the low ratio is reported in kimberlites. The Nb/Ta and Y are positively correlated as the ionic size of Nb is larger than Ta, and thus, Ta is most compatible with zircon during magma differentiation. The normalized pattern of trace elements is used to

Figure 6: (a–d) Zircon trace elements are used to know the parent magma from which the rock originally crystallized [2]. Based on trace elements like Yb, Sm, Ta, Nb, Y and Ce, the zircons are plotted in the granitoid field with few inherited zircons deviated toward different fields. The fields mentioned in the figures are as follows: (1) aplites, leucogranites, (2) granites, (3) granodiorites and tonalites, (4) larvikites, (5) nepheline syenite and syenite pegmatite, (6) syenite pegmatites, (7) carbonatites, (8) syenites, (9) kimberlites, (10) lamproites and (11) mafic rocks.

distinguish between the magmatic and the hydrothermal zircons [57]. The LREE (La and Sm) normalized values are plotted versus La [57], and most of the zircons in this study are plotted in the magmatic zone with few deviated toward the hydrothermal zone (Figure 7a). The deviated zircons also have high contents of La and Pr on the normalized spider pattern (Figure 4b) and are included in the inherited zircons. The deviation of magmatic zircons toward the hydrothermal zone is also documented in Ref. [57] as the inclusion of apatite, monazite and titanite, which can greatly enhance the composition of LREE and thus deviates from the magmatic zone to the hydrothermal zone. The hafnium concentration of this study zircons plotted versus U/Yb has the characteristic of the enriched mantle zone or crustal input in the continental zone (Figure 7b). The Hf concentration is >10,000 ppm, and the ratio of U/Yb is more than 0.1. The Yb plotted versus Ti (Figure 7c) shows

the input of the mid-oceanic ridge setting with most of the zircons plotted in the continental zone compilation with the arrow marking toward the amphibole absent zone. Most of the zircons have Ti content less than 10 ppm plotted in the continental compilation with few having a Ti content greater than 10 ppm in the mid-oceanic ridge compilation [3].

The boundary between the continental and oceanic crust setting is best explained by U/Yb and Th/Yb ratios from zircons [3,14]. The average U/Yb ratios for N-MORB, primitive basalts, lower and upper crust are 0.01, 0.3, 0.13 and 1.35, respectively [64,65]. This ratio calculated for the Swat orthogneisses ranges from 0.18 to 3.47 with an average value of 1.72, which is for the upper crustal setting. Few zircons are recognized as hydrothermal based on a flattened normalized light REE pattern [5]. The Sc/Yb ratio from the zircon is used as a proxy for tectonic settings including continental arc, mid-ocean

Figure 7: (a) The zircons from this study are plotted in the igneous zone as discriminated based on normalized La and Sm values [56]. The inherited zircons are deviated from the field of igneous toward the hydrothermal zone [57]. (b) Hafnium and U/Yb trace elements plotted the Swat orthogneisses into the continental survey [3]. (c) The high concentration of Ti is reported from the inherited zircons, while the igneous zircons display their origin in continental compilation [3]. (d) Most of the zircons are plotted in the temperature zone (~700°C). The temperature values are calculated from the Ti content in the zircon by following the method defined in Ref. [7].

ridge and ocean island arc. The high silica crustal island arcs have a high concentration of Sc/Yb (>0.1), and the zircons extracted from the Swat orthogneisses have the same concentration, i.e., 2.6–7.4 with an average value of 5.2. The mid-ocean ridge and oceanic arcs have less than 0.1 concentration reported for Sc/Yb [3,14]. LREE enrichment is commonly related to hydrothermal alteration, and Swat orthogneisses also have this pattern for few zircons as shown in Figure 4b. The roles of inclusions like apatite, titanite and allanite can also enhance the LREE concentration [69,70]. The enrichment pattern of LREE is also associated with sub-solidus condition during metamorphism, and Swat orthogneisses displayed the normalized enrichment pattern of few zircons due to the regional metamorphism [71]. The Swat orthogneisses are metamorphosed from granitic protolith, which are plotted in the anorogenic plot in Ref. [14], but few zircons deviated toward the arc-related orogenic setting. The deviated zircons that display arc-related settings are characterized by the high concentration of LREE.

5.2 Temperature of Swat orthogneisses

Temperature calculation of the Ti content present in the zircon is a technique to evaluate the minimum crystallization temperature of the rock [6,7,72,73]. For high-grade metamorphic rocks, the techniques defined in Refs. [74,75] are used to determine the temperature of Ti in the zircon. The titanium content in the zircons from the Swat orthogneisses ranges from 4.6 to 57.4 ppm, and there is a temperature variation from 679 to 942°C. The temperatures calculated for the lowest and highest values in Ref. [7] are 678.8 and 942.4°C. The variation in temperature calculated for these zircons is due to the magmatic origin and metamorphism, and the inherited zircons also have a high concentration of Ti, which is converted to high temperature. Igneous zircons have Ti concentration in the range of 4–10 ppm, and displayed temperature ranges from 700 to 800°C. These zircons display a temperature range above granitic rocks solidus and thus are characterized by the actual temperature of the zircon crystallization [76]. These zircons are also plotted in the continental zones on different variation figures as discussed in the discrimination portion of trace element. Inherited zircons have Ti content ranging from 20 to 30 ppm, and they have a temperature range of $>800^{\circ}\text{C}$. The inherited zircons with the variable Hf content and the high Ti content display very high temperature, and these values are not related to the

bulk rock crystallization conditions, but either they later on mixed with the magma or the variation is also due to inclusion of Ti bearing minerals in the zircon like ilmenite and rutile. The Hf versus the increasing temperature trend is shown in Figure 7d.

5.3 Hafnium isotopic evolution

The Lu–Hf system in zircon is the best choice for interpreting the geological setting as a geochemical tracer. Hf isotope from the zircon is used to know the magma mixing and the composition of magma in the crystallization of granitoids. The Lu–Hf system is also characterized by tracking back the chemical composition of crust and mantle as Lu is fractionated from Hf during crust mantle differentiation [61,62]. The half-life of this system is approximately 35.7 billion years, and the initial $^{176}\text{Hf}/^{177}\text{Hf}$ ratio in the zircon is preserved due to the high incompatibility of Hf than Lu during mantle melting [18,77]. The ϵ_{Hf} value for the rocks derived from mantle obtained in Ref. [16] is +14, while the ϵ_{Hf} value of the current oceanic basaltic magma is +23. These values show high variation, and the magma sources for these mantle rocks are characterized into different sources [78]. The negative values of ϵ_{Hf} (–10 and –12) are recognized for the lower crust by the previous pioneer works [78,79]. Another source for the enriched ϵ_{Hf} is the subduction of the oceanic crust beneath the continental or oceanic plate. The variation in Hf isotopic composition is highly variable, and it is noted from the results that there is an input of the juvenile crust with time in the Swat orthogneisses. Two sources are concluded from the isotopic composition, i.e., initially, the crust derived magma is later on mixed with the juvenile crustal input material with the positive Hf values from negative ones. The zircons from this study have dominantly negative values with some partially positive input, i.e., $\epsilon_{\text{Hf}}(t)$ –11.5 to +1.47. The high variation in the values of $\epsilon_{\text{Hf}}(t)$ is due to inherent heterogeneity in the source magma from which these rocks are crystallized. The age versus $\epsilon_{\text{Hf}}(t)$ plot in Figure 8 shows that most of the zircons are clustered at $\epsilon_{\text{Hf}}(t) = -4$ to +1 and shows the igneous evolution of magma, which is dominant from the crustal input toward the juvenile mantle. The age versus $^{176}\text{Hf}/^{177}\text{Hf}$ ratio displays that these zircons are formed below the depleted mantle zone within the zone of the lower crust in the ranges of >0.282 and <0.283 . The inherited zircons are deviated in the $\epsilon_{\text{Hf}}(t)$ plot and deviated from the main magmatic cluster showing highly

Figure 8: The Swat orthogneisses are interpreted to be originated in the continental crustal environment based on $\epsilon_{\text{Hf}}(t)$ (–2 to +1) as plotted against the age.

variable values. The $\epsilon_{\text{Hf}}(t)$ values of the inherited zircons show that these are from the upper crust of the juvenile mantle. The Hf evolution reveals that the Swat orthogneisses rocks have negative values, which is confirmed for its origin from the crustal section, but partial addition of positive values is either from the magma mixing or exposure of these rocks to continental collision. The Hf composition from the zircon spots revealed that the recycled crustal material played a role to generate plutonic magma in this terrane, as well as with time, the Hf composition changes to positive values, which is a clue for mixing of juvenile mantle material in the already generated crustal section [23,77,80].

6 Conclusions

On the basis of trace elements in zircon, Hf isotopic analysis and geochronology, the following conclusions are presented:

1. The age (256 ± 1.9 Ma) determined for these rocks in the current research work is younger from the previous calculated ages (i.e., 268 Ma).
2. The Swat orthogneisses have akin their geochemical behavior similar to upper crustal level rocks based on concentration determined by U/Yb and Sc/Yb ratios.
3. These rocks are formed in the anorogenic/within plate setting based on trace element concentration reported in this study on zircons.
4. The average temperature calculated for these rocks ranges from 700 to 800°C based on the Ti content present in the zircons.

5. $\epsilon_{\text{Hf}}(t)$ has mainly negative values, which confirmed the fact that these rocks originated in the continental setting, and slightly positive $\epsilon_{\text{Hf}}(t)$ addition is either due to magma mixing or from the juvenile mantle zone.

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