

Article

Identification and Origin of Jurassic (~182 Ma) Zircon Grains from Chromitite within the Peridotite of the Jijal Complex, Kohistan Arc in North Pakistan

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Abstract: The Jijal ultramafic–mafic complex in Pakistan probably preserves the most complete fragments of the petrological Moho. However, a few studies argue for multiple origins (including petrogenetic speculations and tectonic reconstructions) for different lithologies. One of the main reasons for this dispute is the lack of direct age information of the ultramafic rocks. Zircon grains, despite generally being exotic in ultramafic rocks, can provide significant insights into the petrogenetic process of the host ultramafic rocks. This study reports the first zircon U-Pb age and Lu-Hf and trace element data for zircon grains separated from chromitite lenses within the peridotite, which is commonly considered the lowermost part of the Jijal complex. These zircon grains yield concordant 206 Pb/ 238 U ages of ~182 ± 3 Ma, which is much older than the late Early Cretaceous age (<120 Ma) of the Jijal complex, and lying above it, the other complexes of the Kohistan paleo-arc. Furthermore, these Jurassic zircon grains present radiogenic ϵ Hf(t) values (+9.7 to +6.0) which are obviously lower than the values for the Cretaceous zircon grains of the Kohistan arc. From integrated analysis of the zircon trace element signatures (e.g., high Th, U, Th/U, and U/Yb ratios) and regional geology, we speculate that these zircon grains came from a 'missing' Early Jurassic arc akin to the Gangdese belt to the east, and entered the mantle by oceanic subduction processes. Although these Jurassic zircon grains cannot actually constrain the formation age of the chromitite as well as the peridotite, it reminds us that some cryptic pre-Cretaceous complexes and geodynamic processes were incorporated in building the oceanic crust of the Jijal intra-oceanic arc, or the mantle section (at least part of it) should probably belong to the Indus ophiolite mélange. Further research, particularly chronological studies on mantle (or ultramafic) rocks, as well as detailed geological mapping, should be carried out in the future for solving this issue.

Keywords: Pakistan; zircon U-Pb age and Lu-Hf isotopes; chromite; mantle rock; Jijal complex; Jurassic

1. Introduction

The 3 km-thick Jijal ultramafic–mafic complex in northern Pakistan is comprised of a series of rocks ranging from ultramafic to mafic in composition from south to north. They have attracted vast numbers of studies on their formation age and petrogenetic processes because they probably represent a rare preservation of the most complete fragments of the lowermost arc crust and contiguous uppermost sub-arc mantle, namely the petrologic Moho (e.g., [1–4]). Despite this, debate remains on whether these ultramafic to mafic rocks formed by crystallization and accumulation of genetically related melt, by multistage magmatic melt inflation and interaction at the mantle–crust transition, or if



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they represent modified, sub-arc, residual mantle (e.g., [1–5]). The general consensus is that they were formed at the late Early Cretaceous time (younger than ~117 Ma; e.g., [6,7]). More importantly, a few studies suspect that the mantle section, at least part of it, potentially belongs to the Indus ophiolite mélange (e.g., [8]). Thus, the origin and tectonic affinity of ultramafic rocks in the Jijal complex are still highly enigmatic, largely hindering our knowledge of the processes of continental crust formation as a result of accretion and metamorphism of oceanic arc complexes. The dispute is mainly related to the fact that the formation age and interpretable isotope values for ultramafic rocks are very hard to obtain.

Zircon (ZrSiO₄) is a common accessory mineral in many types of rocks and is resistant to a wide range of chemical and physical conditions, such that zircons can even survive temperatures and pressures up to 1500 °C and 20 GPa (equivalent to ~600 km deep in the Earth), as demonstrated by experimental work and zircon grains obtained from ultra-high pressure (diamond-related) metamorphic terranes ([9] and references therein). More importantly, the U–Pb isotope age, coupled with trace element, Lu–Hf, and stable isotopes (O and Li), makes this mineral an unmatched tool to study the formation of various geological processes, including the age and source of igneous and sedimentary rocks, metamorphic P-T (Pressure and Temperature) condition hydrothermal alteration, mantle–crustal interaction and recycling, and metasomatism (e.g., [9,10]). Zircon is theoretically unable to crystallize from primary peridotite due to its low bulk-rock Zr content and Si-undersaturated affinity, but an increasing number of studies have demonstrated that mantle rocks, including chromitite, peridotite, and pyroxenite, sometimes contain abundant zircon grains (e.g., [10–17]). In general, these zircon grains are thought to be exotic and thus could not represent the formation age of the mantle rocks, but they do provide important access to detect the deep geodynamic processes and origin of the mantle rocks.

This study presents U–Pb dating and Lu–Hf isotope analyses, as well as trace element data, for zircon grains separated from chromitite lenses within peridotite that is generally regarded to be from the lower part of the Jijal complex, in an attempt to reveal the mechanism of zircon occurrence in the chromitite and further explore the petrogenesis of the ultramafic rock suite and its relationship with 'overlying' mafic–felsic rocks. This achievement could provide new insights into the building of the Kohistan intra-oceanic arc.

2. Geology Background and Field Occurrence

The Indus–Zangbo suture zone marks the boundary between the Indian and Asian plates, but in Pakistan and western Himalaya there is a Cretaceous island arc, i.e., the Kohistan arc, wedged in the two plates (Figure 1) [5,6]. The Kohistan arc can be correlated with the Ladakh, Gangdese and Dianxi–Burma arcs in the east, which collectively comprise a more than 3000 km long granitoid-dominant arc belt resulted from the subduction of Neo-Tethyan lithosphere (e.g., [18]). However, here are two aspects that make the Kohistan arc relatively distinct. First, the arc represents an intra-oceanic arc formed during the Mesozoic northward intra-oceanic subduction of the Neo-Tethyan lithosphere, mainly based on the absence of continental basement and continental-derived sediments (e.g., [1,5,6,19]). Second, and more importantly, the arc accretion to the Karakoram plate at around 85 Ma and subsequent obduction onto the India plate during India–Asian collision(~50 Ma) [5,20], with the result that they probably preserve one of the most intact profiles of the lower crust–Moho zone, which offers us an interesting subject to understand crustal growth at an intra-oceanic arc (e.g., [1,5,6,19]).



Figure 1. (a) Distribution map of the Transhimalayan batholith (modified after Ji et al. [18]); (b) Simplified geological map showing the location of the Jijal complex of the Kohistan island arc complex, northern Pakistan (after Burg et al. [1]); (c) Geological section of the Jijal mafic–ultramafic complex (modified after Burg et al. [21]).

The Kohistan arc is mainly made up of three parts, including the Glight complex, the Chilas complex, and the Southern plutonic complex (including the Kamila amphibolites and the Jijal complex). As the southernmost part of the Kohistan arc, the ~150-km² Jijal complex lies in the hanging wall of the Indus suture (Figure 1) [1,22], which was tectonically emplaced over the gneisses of the Indian plate at 50–45 Ma (e.g., [1,6]). The Jijal complex consists of an upper gabbroic section overlying a thick ultramafic section (Figure 1c). The northern part of the complex is a gabbroic section that contains the main mass of the complex and consists of garnet granulites derived from gabbros, troctolites, pyroxenites, and anorthosites (Figure 1c).

The southern part of the complex consists of a 10 km \times 4 km slab of chromite-bearing dunite, peridotite, and pyroxenite, which are commonly layered. Chromitite samples for this study were collected from nearly the southernmost part of the ultramafic section in northern Jijal country (north of the Indus valley), where they are interbedded with dunite layers as lenses or disseminated occurrences. The samples investigated in this study are located (GPS: 72°56′16.66″ E, 35°2′32.41″ N) close to the Indus suture zone. The rocks exposed there are primarily composed of peridotite, and are mostly serpentinized. Compared with the surrounding peridotite and dunite, the chromitite samples are much fresher and only some olivine has altered to serpentine along the crack and rim. The structure of the chromitite samples is massive and disseminated, in a coarse-grained structure, and they are black in color. The chromitite comprises mainly chromite with variable portions of olivine and minor pyroxene; the chromite grains are generally euhedral to subhedral in shape, 0.4–3 mm in length, and black in color (Figure 2).



Figure 2. (a) Hand specimen of the chromitite, massive, black in color; (b) and (c) microphotograph in cross-polarized light of the chromitite, euhedral to subhedral chromite; (d) microphotograph in transmitted light of (c). Abbreviations: Chr = chromite; Ol = olivine; Px = pyroxene.

3. Analytical Methods and Results

3.1. Analytical Methods

All the relevant analyses in the present study were finished at the Key Laboratory of Continental Collision and Plateau Uplift, Institute of Tibetan Plateau Research, Chinese Academy of Sciences (LCPU, ITP CAS). Zircon grains were separated from ~20 kg chromitic samples by using standard magnetic and heavy liquid separation and were individually hand-selected under a binocular microscope. The cathodoluminescence (CL) images were obtained using a JEOL JXA-8100 Super Probe to reveal the internal structures of individual zircon grains. These zircon grains we selected for U-Pb isotope and trace element analyses were generally euhedral to subhedral, colorless, with oscillatory zones, and a lack of complex internal structure. Zircon U–Pb isotope and trace element analyses were conducted using a New Wave UP193FX excimer laser coupled with an Agilent 7500a ICP-MS. During our analysis, the standard zircon 91500 (1064 Ma) [23] and Plešovice (337 Ma) [24] were used as external and internal standards for the U-Pb isotopes, respectively, and NIST 612 glass was used as the external standard for trace elements. The offline isotope ratios and trace element concentrations were calculated using GLITTER 4.0 [25]. We used all the measured isotope ratios of 91500 during our experiment to calculate the external precision (2σ) , which was input into the GLITTER. Then the software automatically propagated the standard uncertainty into each spot data during data processing. The common Pb was corrected following the method of [26] and data reduction was performed using the Isoplot/Ex V.3.0 program [27].

Zircon Lu–Hf isotope analyses were performed using a Nu Plasma II multi-collector inductively coupled plasma mass spectrometer (MC-ICPMS, Nu Instruments Ltd., North Wales, UK) equipped with a 193 nm New Wave laser ablation system (New Wave Instruments, Provo, UT, USA). The Lu–Hf isotopic analyses were made on the spots which previously were analyzed for U–Pb ages, as much as possible. The isotope ratio ¹⁷⁶Hf/¹⁷⁷Hf was normalized to ¹⁷⁹Hf/¹⁷⁷Hf = 0.7325 using an exponential law for mass bias correction. Correction for isobaric interference of ¹⁷⁶Lu on ¹⁷⁶Hf and ¹⁷⁶Yb on ¹⁷⁶Hf was performed using the recommended ¹⁷⁶Lu/¹⁷⁵Lu ratio of 0.02655 and the ¹⁷⁶Yb/¹⁷¹Yb ratio of 0.90184. During the analysis, the Plešovice zircon standards were analyzed as unknown samples. The ¹⁷⁶Hf/¹⁷⁷Hf values for 20 Penglai zircon grains (the analytical procedure includes samples that are not reported in this study) are from 0.282868 ± 11 to 0.282916 ± 14 with an average of 0.282893 ± 12, which are in good agreement with the published values, within the experimental errors [28]. The detailed analytical procedures for zircon U–Pb and Lu–Hf isotope and trace element analysis are described in Cai et al. [29] and Wang et al. [30].

Chrome spinel chemistry analyses were performed using a JEOL JXA-8230 electron microprobe. The parameters during our analysis were as follows: probe diameter = $5 \mu m$, accelerating voltage = 15 kV, specimen current = 20 nA, counting times for peaks = 10 s, and counting times for upper and lower background levels per element = 5 s. The analytical precision is better than 1-2%.

3.2. Zircon Trace Element and Isotope Composition

Separated zircon grains from the Jijal chromitite occur as moderate grains (~20–50 µm in length with length–width ranging from 1:1 to 2:1; Figure 3) characterized by colorless and somewhat rounded and subhedral shapes (Figure 3a). They are dominantly smoky or black on cathodoluminescence (CL) images with oscillatory zones and the absence of a complex internal structure (Figure 3a). The zircon U–Pb isotope data are listed in Table A1. All the analyses were performed on the rim of the zircon grains and thirteen data points were obtained (Table A1). As shown in Figure 3a, all of the analyses are concordant and present individual ages ranging from 201 ± 3 Ma to 170 ± 3 Ma, with mean average (concordant 206 Pb/ 238 U ages) values of 182 ± 3 Ma (MSWD = 3.5; Figure 3a).

0.0

10

100



Figure 3. (a) Zircon U–Pb concordant diagram and representative cathodoluminescence images; (b) chondrite-normalized REE patterns of zircon grains (composition of chondrite according to Sun and McDonough [31]); (c) zircon Y versus U/Yb diagram (based on Grimes et al. [32]); (d) zircon U versus Th diagram (based on Grimes et al. [32] and Li et al. [13]).

0.1

0.1

1

10

100 U(ppm) 1000

10,000

LILL

100,000

1111

10,000

1000

Y(ppm)

The zircon trace element data are listed in Table A2. All of the analyzed zircon grains have high Th, U, and Th/U ratios (Table A2 and Figure 3d), and their chondrite-normalized rare earth elements (REE) patterns (Figure 3b) are remarkably homogeneous and characterized by strong depletions in La, pronounced positive Ce and negative Eu anomalies, and enrichment in heavy REEs (HREEs). Additionally, on U/Yb versus Y plots, all of them fall in the field of continental zircon grains (Figure 3c) [32].

The zircon Lu–Hf isotope data are listed in Table A3 and plotted in Figure 4. The analyzed zircon grains yielded low ¹⁷⁶Lu/¹⁷⁷Hf ratios (<0.002), suggesting an ignorable radiogenic Hf in-growth after zircon formation. They exhibit a narrow spread in ¹⁷⁶Hf/¹⁷⁷Hf values of 0.282436–0.282600, and age-corrected (¹⁷⁶Hf/¹⁷⁷Hf) i values of 0.282836–0.282935, ε Hf(t) values of 6.0–9.7, and Hf model ages (TDM) of 448–600 Ma.



Figure 4. Zircon U–Pb age (Ma) versus ε Hf(t) value for zircon grains from the Jijal chromitite. Literature data for zircon ε Hf(t) values of the Kohistan (Jagoutz et al. [19] and reference therein) and south Gangdese [18,33] paleo-arcs are shown for comparison.

3.3. Chromite (Chrome Spinel) Chemistry

The in-situ major element compositions for the analyzed chrome spinel grains are listed in Table A4. They are characterized by high Cr_2O_3 , moderate MgO and Al_2O_3 , and low TiO₂ contents with chrome spinel Cr numbers (Cr# = Cr/(Cr + Al)) ranging between 0.59 and 0.84, and Mg numbers (Mg# = Mg/(Mg + Fe²⁺)) between 0.50 and 0.75, typical of Type-I high-Cr chrome spinels. Our new data for chrome spinel composition fall within the range of compositions reported previously [34].

4. Discussion

4.1. Age of the Jijal Complex and Kohistan Arc

Bosch et al. [7] reported zircon U–Pb ages of 97.7 \pm 0.7 Ma for the metatonalite and ages of 100.9 \pm 0.6 Ma to 89.9 \pm 0.5 Ma for the mafic (garnet-bearing) rocks that were located about ~10 km north of the samples investigated in this study, yet precise ages for the Jijal gabbroic rocks are still lacking, let alone for the ultramafic section. However, we note that the previous isochron isotopic ages of the mafic section appear to be consistent with the zircon U–Pb age result, as Sm–Nd isochron ages for the Jijal garnet gabbros and Sarngar gabbros are 98.9 \pm 0.4 Ma to 91 \pm 6 Ma [34–39]. Nevertheless, the Sm–Nd isochron ages for clinopyroxene in pyroxenites from the ultramafic section of the Jijal complex yield a notably older age of 117 \pm 7 Ma, which has been interpreted as dating the first episodes of slab dehydration fluids metasomatism in the lithospheric mantle [6], and is therefore a minimum age for initial subduction of the Neo-Tethyan Oceanic lithosphere. This hypothesis needs further exploration (in terms of both the geochronological precision and the tectonic interpretation) because the time interval is too long from subduction initiation to first appearance of arc magmatic rocks. On a larger scale, within the Kohistan arc, zircon U–Pb ages (except those for ultramafic rocks) reveal an overall similar formation age of the late Early Cretaceous (<120 Ma) and all analyzed zircon grains show depleted mantle-like Hf isotope values [7,19,40]. These previous studies collectively suggest

the Jijal complex, as well as the Kohistan arc as a whole, mainly formed at the late Early Cretaceous (<120 Ma).

Nonetheless, although the Kohistan arc is generally believed to have formed in the late Early Cretaceous intra-oceanic subduction zone, it probably does contain ancient materials, as demonstrated by single Jurassic zircon grains or small Jurassic dikes. To be specific, Schaltegger et al. [41] and Jagoutz et al. [19] both reported concordant zircon ages of ~155 Ma for the Matum-Das tonalite of the Chilas Complex, so far the oldest rock within the Kohistan arc, which was interpreted as a proto-arc. However, the zircon ²⁰⁶Pb/²³⁸U ages of this late Jurassic granitic dike are not very concordant, with a wide range between 128 and 173 Ma (Jagoutz et al. [19]). Similarly, Bosch et al. [7] discovered a ~175 Ma old zircon grain from leucogranite at a location ~10 km northeast of the study area. Our study provides the first identification of Jurassic zircons within the mantle part of the Jijal complex, which provide new insights into the perplexing results of previous studies as to why intra-oceanic arc magmas yield inherited zircon grains much older than the arc system itself.

4.2. Parent Magma Equilibrium with Chrome Spinel

It has been shown that chrome spinel is very resistant to alteration, weathering, and metamorphism, and its original composition primarily depends on the makeup of the parent magma (see Zhou et al. [42] for reviews). For instance, based on a large and global dataset, Kamenetsky et al. [43] found a relationship between chrome spinel Al₂O₃ and TiO₂ contents and parent magma—(TiO_{2melt}) = 0.708 $\ln(TiO_{2 \text{ spinel}}) + 1.6436$, (Al₂O_{3 spinel}) = 0.035 (Al₂O_{3 melt})^{2.42} for high-Al chrome spinel; (TiO_{2 melt}) = 1.0897 (TiO_{2 spinel}) + 0.0892, and (Al₂O_{3 melt}) = 5.2253 $\ln(Al_2O_{3 \text{ melt}}) + 1.1232$ for high-Cr chrome spinel; see also Zhou et al. [42] and reference therein. As the Jijal chrome spinel belongs to the high-Cr chrome spinel, we use the high-Cr chrome empirical formula to compute these values.

On the other hand, since Mg and Fe are balanced between silicate minerals and non-silicate minerals, the melt FeO/MgO ratio can also be estimated using the empirical formulation proposed by Maurel and Maurel [44]: ln (FeO/MgO)_{spinel} = $0.47 - 1.07 [Al/(Cr+Al+Fe^{3+})]_{spinel} + 0.64 [Fe^{3+}/(Cr+Al+Fe^{3+})]_{spinel}$. Moreover, another common indicative function of spinel is the source melting degree of the parent magma, reflected by the correlation between the Cr# and Mg# numbers. The computed parent TiO₂, Al₂O₃, and FeO/MgO contents of the equilibrium with the Jijal chrome spinel range from 0.28 to 1.09 wt.%, 8.66 to 11.83 wt.% and 1.22 to 1.42, respectively. Comparison with spinel from various settings demonstrated the boninitic arc-related affinity of studied spinels (Figure 5) [45,46].



Figure 5. (a) Variations in chrome spinel Mg# versus Cr# (based on Xiong et al. [45]) and (b) spinel Cr# versus TiO₂ (wt.%) diagrams. Literature data for the Jijal chromitite are from Arif and Jan [34].

4.3. How Did Crustal Zircon Grains Enter the Jijal Chromitite?

One explanation for the source of the zircon grains in the mantle (ultramafic rocks) is that these were introduced during sample processing. This possibility can be precluded because the zircon grains were independently separated by two times, in spite of sparse numbers of grains being obtained each time (six and nine, respectively). Zircon grains in this study present similar concordant $^{236}\text{U}/^{208}\text{Pb}$ ages (Figure 3) and show somewhat plausible magmatic features, such as high Th/U ratios, strong HREE-enriched patterns with depletion in La, positive Ce and negative Eu anomalies, and a lack of complex internal structure (Figure 3) [47]. They still should be termed 'exotic' given the low Zr and SiO₂ contents of the chromitite. This is shown by the generally round zircon grains, and they contain mineral inclusions of quartz, plagioclase, and apatite (Figure 4), which are significantly different from the constituent minerals of chromitite. There are three possible mechanisms that can introduce zircon grains into mantle rocks, as described in detail below.

First, zircon can crystallize from the fluids, hydrous melt, and supercritical fluids released from the down-going slab that metasomatizes the mantle peridotite [48,49]. However, the grains formed in this model generally have complex internal structures, such as a dark core rounded by a white rim in CL images (e.g., [13]). Regardless of the SiO₂ and TiO₂ activities, the low crystallization temperature attested by the overall low Ti values of the investigated zircon grains [50,51] is inconsistent with the relatively hot hydrous melt-related metasomatism (generally >800 °C). In addition, zircon grains that crystallized from supercritical fluids would be characterized by a spongy texture and consistent enrichment with light rare earth elements (LREE), Th, U, and high-field strength elements (HFSE) [13,52], which are absent in the metasomatic zircon grains from the Jijal chromitite. Furthermore, it has been demonstrated that in fluid, U is much more mobile than Th [53]. Thus, the high Th/U ratios of the analyzed zircon grains roughly argue against an origin from metasomatic fluid (Figure 3; e.g., [13]). Consequently, we dispute a metasomatic origin for the zircon grains identified in the Jijal chromitite.

Second, zircon grains are likely to be contaminated from continental crust during the emplacement of the mantle rocks [11,48]. Nevertheless, no Cretaceous zircon grains have been found in the studied rocks, whereas Early Cretaceous magmatism is intensive before Eocene emplacement. For the same reason, although there might be a missing Jurassic arc, as we speculate in the following text, it is not precipitated from inflated granitic melts after emplacement, as raised by, e.g., Belousova et al. [11]. On the other hand, the exotic zircon grains in mantle rocks could derive from recycled crustal materials, as they are suggested to be stable at the ultra-high temperature and pressure of the mantle environment. Crustal materials can enter the mantle by subduction or delamination (e.g., [9,16,42]). Irrespective of mechanisms, that lack of Cretaceous and younger zircon grains recognized in the chromitite indicates that the recycling event(s) happened between the early Jurassic and late Early Cretaceous (from ~180 to 120 Ma). As an overthickened crust is a premise for delamination, this hypothesis is disproved by the lack of geological record. Therefore, we infer the zircon grains were recycled into the mantle by subduction. Another fundamental issue is where these exotic minerals ultimately came from, as we will discuss in more length below.

4.4. Where Zircons Came from and Tectonic Implications

Although the zircons investigated in this study are exotic minerals in chromitite, the presence of only one age population led us to advocate that the zircon grains were derived from eroded magmatic rocks instead of sediment/surface rocks, unless the sediment was deposited in the fore-arc basin, a situation that is analogous to the magmatic arc. Importantly, the composition and rock-type of the parent melt that the zircon crystallized from, if not entirely correct, can be approximately inferred from the trace elements and Lu–Hf isotope values (e.g., [10,31,54]). First and foremost, their positive and uniform ε Hf values suggest any mixing of different source materials, if it happened, would have occurred at the source region. Thus, the parent melt should be derived by partial melting of the juvenile crust or depleted mantle. Crystallization from mafic (mantle-derived) melt is less likely given that their morphologies are akin to zircon grains in felsic (crust-derived) rocks, such as is suggested in Corfu et al. [55]. Their extremely high Th and U contents are more common in granitic rocks rather than in mafic rocks [10]. Besides, their high U/Yb ratios resemble continental zircon grains (including island arc crust) rather than oceanic crust (Figure 3) [10,31], and preclude precipitation from depleted

mantle-derived melts while ascending. To our knowledge, with the exception of the aforementioned detrital zircon grains, the Jurassic igneous rocks in the Kohistan area are only limited to ophiolite [56]. After evaluating the potential sources, Bosch et al. [7] also argued for a magmatic origin for the Jurassic zircon grains, but limited it to the oceanic lithosphere, which has been excluded by their trace element composition. Here we propose two alternative explanations for their origin.

First, there are some "missing" Jurassic arcs that are akin to the Jurassic magmatism in the Gangdese arc to the east (e.g., [18,32,57]). We boldly speculate this hypothesis because Jurassic zircon grains have been identified in the Jijal complex and elsewhere in the Kohistan arc, from ultramafic to felsic rocks. If this is the case, the missing Jurassic arc should have been either underlain by the Cretaceous arc or have been almost entirely eroded away (Figure 6; see the figure captions for more details). This means that some cryptic pre-Cretaceous materials and the geodynamic processes have not been realized in building the Jijal intra-oceanic arc, similar to some studies advocating that the proto-arc started after the Jurassic [19]. Another possibility is that the mantle peridotite, or at least part of it, belongs the Indus ophiolite mélange [34]. We are more in favor of the former hypothesis, as the Jurassic arcs are also limited to the eastern part but are missing in the western part of the ~2000 Km long Gangdese belt (see Kang et al. [57]).

Additionally, since thus far no Hf isotope data exist for any unit from the Jijal complex, and no Hf isotope data have been determined directly on mafic lithologies from any of the plutonic root fragments, the only available data for comparison are compiled from the rutile *ɛ*Hf values for the Jijal complex and the zircon ε Hf of other segments of the Kohistan arc. Based on the indistinguishable weighted mean ε Hf (11.4 ± 3.2 to 20.1 ± 5.7) of rutile across the mafic section of the Jijal complex, Ewing and Müntener [3] suggest a consistent source of depleted mantle without the requirement of more enriched materials for the magmas that made up the entire thickness of the gabbros mafic section. However, the zircon grains in chromitite have obviously lower ε Hf values than those in leucogranite, probably reflecting different source regions. Thus, regardless of which of the two cases we raised, or other possibilities, it reminds us the Kohistan arc is not 'pure', and might be composite. In other words, the ultramafic section is chemically decoupled from the mafic section. This view is backed by the high Cr# and low TiO_2 values of the chrome spinel in chromitite, as well as the very low TiO_2 and total REE concentrations of clinopyroxene in the pyroxenite within the peridotite, which consistently indicate a depleted parent magma, such as boninite melt, and/or they resulted from melt inflation and interaction (Figure 5) and are not cogenetic with the mafic plutonic rocks [5,45,58]. More future work, particularly chronological studies on ultramafic (e.g., bulk-rock and mineral Re–Os and Lu–Hf isotope, spinel U–Th–Pb) rocks, will be instructive in solving this issue to help us to better understand the building of an intra-oceanic arc and/or tectonic evolution of northern Pakistan.



Figure 6. Hypotheses for the origin of Jurassic zircon grains within the chromitite of the Jijal complex. Hypothesis 1: The Jurassic Kohistan arc was formed during the Jurassic subduction of the Tethyan lithosphere, which was subducted into the mantle during the second stage subduction responsible for the origin of the Early Cretaceous Kohistan arc. The Jurassic zircon grains of crustal materials (i.e., granite) were recycled to the mantle source of the Early Cretaceous arc. Hypothesis 2: The Jurassic and Cretaceous Kohistan arcs were formed by the Jurassic and Cretaceous subduction of the Neo-Tethyan lithosphere, respectively, while the Jurassic arcs (mostly the lower part, as the upper counterparts are easily eroded) probably now underlay the Cretaceous arcs caused by their accretion to the Asian margin and subsequent Indian–Asian collision.

5. Concluding Remarks

First reported here, zircon grains of the chromitite lenses within the peridotite of the Jijal complex yield concordant 206 Pb/ 238 U ages of $\sim 182 \pm 3$ Ma, which is much older than the widely accepted late Early Cretaceous age. From integrated analyses of the zircon U–Pb age, ε Hf(t), and trace element values with regional geology, we speculate that they should be derived from a 'missing' Early Jurassic arc that entered the mantle by subduction, or underlaid the Cretaceous arcs during the Indian and Asian blocks' convergence. These new data led us to advocate that some cryptic pre-Cretaceous materials and unrealized geodynamic processes have been incorporated in building the Jijal intra-oceanic arc

crust, or the mantle section (at least the part of it in the Jijal complex) should probably belong to the Indus ophiolite mélange.

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Appendix A

Enat	Th	U	ть /I I	Isotopic Ratio						Age					
Spot	(ppm)	(ppm)	I N/U	²⁰⁷ Pb/ ²⁰⁶ Pb	1σ	²⁰⁷ Pb/ ²³⁵ U	1σ	²⁰⁶ Pb/ ²³⁸ U	1σ	²⁰⁷ Pb/ ²⁰⁶ 1	Pb 1o	²⁰⁷ Pb/ ²³⁵ U	1σ	²⁰⁶ Pb/ ²³⁸ U	1σ
2016PD51-01	292	316	0.9	0.0514	0.0033	0.2055	0.0126	0.0290	0.0004	259	113	190	11	184	3
2016PD51-02	2131	1717	1.2	0.0494	0.0020	0.1989	0.0077	0.0292	0.0003	168	72	184	7	185	2
2016PD51-03	802	778	1.0	0.0517	0.0037	0.2090	0.0145	0.0293	0.0005	271	129	193	12	186	3
2016PD51-04	674	954	0.7	0.0498	0.0017	0.1864	0.0058	0.0271	0.0002	187	56	174	5	173	2
2016PD51-05	784	1080	0.7	0.0507	0.0020	0.1960	0.0072	0.0281	0.0003	226	67	182	6	178	2
2016PD51-06	671	1021	0.7	0.0538	0.0041	0.2101	0.0155	0.0283	0.0005	363	135	194	13	180	3
2016PD51-08	204	278	0.7	0.0548	0.0026	0.2273	0.0105	0.0301	0.0004	405	81	208	9	191	2
2016PD51-09	409	537	0.8	0.0536	0.0030	0.2025	0.0110	0.0274	0.0004	353	98	187	9	174	2
2016PD51-10	369	302	1.2	0.0519	0.0038	0.1914	0.0137	0.0268	0.0005	279	131	178	12	170	3
2016PD51-11	317	1016	0.3	0.0530	0.0018	0.2092	0.0066	0.0286	0.0003	329	55	193	6	182	2
2016PD51-12	217	2333	0.1	0.0520	0.0021	0.2116	0.0083	0.0295	0.0003	285	71	195	7	188	2
2016PD51-14	87	90	1.0	0.0486	0.0043	0.2038	0.0176	0.0304	0.0006	128	154	188	15	193	4
2016PD51-15	767	1011	0.8	0.0523	0.0034	0.2287	0.0143	0.0318	0.0005	297	115	209	12	201	3

 Table A1. Zircon U–Pb data of Jijal chromitite.

Table A2. Rare earth elements composition (ppm) of zircon in Jijal chromitite.

Spot. No	2016PD 51-01	2016PD 51-02	2016PD 51-03	2016PD 51-04	2016PD 51-05	2016PD 51-06	2016PD 51-08	2016PD 51-09	2016PD 51-10	2016PD 51-11	2016PD 51-12	2016PD 51-14	2016PD 51-15
Ti	4.39	6.77	3.645	3.4	3.42	5.367	8.94	5.712	6.6	8.66392	7.48	9.98	11.81
Y	2067	4049	3101	4657	6287	2339	1889	3002	2402	2486	2656	976	4768
Nb	9.54	15.36	11.82	30.07	22.38	8.64	6.71	14.61	7.73	13.86	9.30	3.09	34.44
La	0.23	0.15	0.13	0.42	0.16	1.13	3.24	1.64	0.67	2.01	2.15	0.07	4.57
Ce	25.26	97.97	42.42	57.30	46.43	34.59	25.30	31.57	31.98	23.33	7.28	10.68	60.85
Pr	0.34	0.68	0.38	0.47	0.51	0.55	1.12	0.82	0.87	0.90	0.56	0.37	2.13
Nd	5.23	11.51	6.28	7.05	8.36	6.64	11.37	9.45	12.79	8.96	4.03	3.95	22.28
Sm	10.10	21.19	14.00	20.43	24.72	11.48	14.46	16.56	21.60	14.37	7.74	7.30	33.52
Eu	0.15	0.29	0.15	0.13	0.16	0.18	0.23	0.30	0.30	0.41	0.23	0.17	0.97
Gd	51.3	94.1	73.5	117.1	148.3	53.0	53.9	85.1	83.2	73.1	43.5	31.8	171.8
Tb	18.31	35.21	27.64	43.18	57.04	20.18	17.67	28.48	25.27	23.68	20.39	10.24	49.37
Dy	207	418	328	515	686	240	199	328	271	270	254	111	549
Но	71	145	115	177	242	83	66	111	89	89	89	37	174

Spot. No	2016PD 51-01	2016PD 51-02	2016PD 51-03	2016PD 51-04	2016PD 51-05	2016PD 51-06	2016PD 51-08	2016PD 51-09	2016PD 51-10	2016PD 51-11	2016PD 51-12	2016PD 51-14	2016PD 51-15
Er	288	603	457	679	938	349	264	424	348	352	419	144	627
Tm	56.03	132.08	92.55	135.09	182.09	79.19	56.97	85.17	71.00	81.83	114.34	31.35	130.75
Yb	465	1303	838	1201	1583	795	560	785	688	853	1274	293	1315
Lu	78.2	169.9	111.9	148.6	199.6	111.0	71.1	102.4	95.0	122.7	202.3	49.0	163.1
Hf	9464	10,671	7095	8365	8245	8696	6850	6608	7300	10,344	18,864	7599	8483
Ta	2.13	8.74	3.7175	5.76	4	8.6687	1.816	3.5592	1.883	11.79264	29.07	0.92	9.85
U	316	1717	778	954	1080	1021	278	537	302	1016	2333	90	1011
Th	292	2131	802	674	784	671	204	409	369	317	217	87	767

Table A2. Cont.

Table A3. Lu–Hf isotopic composition of zircon in Jijal chromitite.

Spot No	¹⁷⁶ Yb/ ¹⁷⁷ Hf	¹⁷⁶ Lu/ ¹⁷⁷ Hf	¹⁷⁶ Hf/ ¹⁷⁷ Hf	2σ	¹⁷⁶ Hf/ ¹⁷⁷ Hf(t) _i	εHf(t)	TDM1(Ma)
2016PD51-01	0.033	0.001	0.282847	0.000027	0.282842	6.5	580
2016PD51-02	0.050	0.002	0.282877	0.000028	0.282869	7.5	547
2016PD51-03	0.031	0.001	0.282879	0.000026	0.282875	7.7	532
2016PD51-04	0.034	0.001	0.282841	0.000031	0.282837	6.1	587
2016PD51-05	0.041	0.002	0.282940	0.000039	0.282935	9.7	450
2016PD51-06	0.023	0.001	0.282936	0.000025	0.282933	9.6	448
2016PD51-08	0.048	0.002	0.282922	0.000035	0.282916	9.3	479
2016PD51-10	0.046	0.002	0.282842	0.000028	0.282836	6.0	594
2016PD51-11	0.048	0.002	0.282839	0.000028	0.282832	6.1	600

 Table A4. Major element composition (wt.%) of spinel in Jijal chromitite.

Spot. No	K ₂ O	CaO	TiO ₂	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	Cr ₂ O ₃	MnO	FeO	NiO	Total
2016PD51-01	0.00	0.03	0.15	0.01	14.95	11.38	0.06	58.62	0.30	13.08	0.02	98.60
2016PD51-02	0.01	0.07	0.42	0.02	13.67	10.74	0.05	59.16	0.26	14.29	0.10	98.80
2016PD51-03	0.02	0.05	0.37	0.03	11.34	11.36	0.03	59.36	0.33	16.53	0.03	99.44
2016PD51-04	0.01	0.04	0.41	0.02	10.40	11.11	0.03	59.02	0.24	18.36	0.04	99.68
2016PD51-05	0.00	0.01	0.36	0.01	10.34	6.51	0.05	63.41	0.26	18.49	0.05	99.49
2016PD51-06	0.00	0.01	0.58	0.02	8.81	6.98	0.05	62.61	0.64	19.79	0.06	99.53
2016PD51-07	0.00	0.03	0.44	0.02	10.68	6.74	0.02	62.54	0.56	18.81	0.00	99.83

Table A4. Cont.

Spot. No	K ₂ O	CaO	TiO ₂	Na ₂ O	MgO	Al_2O_3	SiO ₂	Cr ₂ O ₃	MnO	FeO	NiO	Total
2016PD51-08	0.00	0.08	0.32	0.02	10.78	7.94	0.04	59.49	0.45	19.34	0.04	98.50
2016PD51-09	0.01	0.01	0.18	0.07	11.77	10.61	0.24	57.67	0.48	17.40	0.06	98.49
2016PD51-10	0.01	0.00	0.22	0.00	11.27	9.92	0.23	59.40	0.53	17.06	0.12	98.75
2016PD51-11	0.01	0.01	0.45	0.00	12.61	10.04	0.22	58.93	0.48	16.58	0.10	99.43
2016PD51-12	0.00	0.04	0.35	0.01	10.68	8.31	0.05	60.86	0.51	17.60	0.06	98.45
2016PD51-13	0.00	0.00	0.46	0.03	11.23	7.13	0.10	61.24	0.33	18.54	0.05	99.12
2016PD51-14	0.00	0.02	0.21	0.03	10.08	8.73	0.18	61.98	0.42	17.95	0.06	99.65
2016PD51-15	0.02	0.09	0.39	0.00	12.24	13.83	0.16	54.62	0.38	17.00	0.07	98.80
2016PD51-16	0.00	0.00	0.21	0.01	13.84	12.04	0.21	58.40	0.49	13.41	0.02	98.62
2016PD51-17	0.01	0.05	0.24	0.02	12.76	11.69	0.19	59.76	0.33	14.81	0.09	99.94
2016PD51-18	0.00	0.01	0.16	0.01	14.27	10.67	0.02	60.06	0.45	13.88	0.08	99.61
2016PD51-19	0.01	0.01	0.33	0.04	13.02	10.65	0.01	59.61	0.53	14.99	0.00	99.20
2016PD51-20	0.00	0.00	0.26	0.02	13.60	11.93	0.06	59.12	0.34	13.47	0.08	98.89
2016PD51-21	0.00	0.00	0.15	0.06	11.17	11.50	0.20	57.38	0.25	18.24	0.08	99.01
2016PD51-22	0.00	0.03	0.32	0.00	12.48	9.74	0.12	60.30	0.40	15.56	0.12	99.08
2016PD51-23	0.01	0.05	0.39	0.00	13.99	11.52	0.11	57.53	0.51	14.98	0.09	99.16
2016PD51-24	0.02	0.04	0.29	0.00	12.46	9.29	0.14	59.96	0.42	15.45	0.10	98.16
2016PD51-25	0.00	0.03	0.35	0.01	12.67	10.65	0.17	59.17	0.43	16.02	0.10	99.59
2016PD51-26	0.01	0.04	0.37	0.00	12.87	10.12	0.00	59.30	0.52	15.67	0.10	98.99
2016PD51-27	0.00	0.02	0.22	0.02	13.84	10.63	0.07	59.81	0.59	14.17	0.05	99.40
2016PD51-28	0.01	0.02	0.44	0.00	13.00	11.04	0.05	58.85	0.36	15.49	0.14	99.41
2016PD51-29	0.00	0.01	0.32	0.05	12.44	12.21	0.05	56.93	0.39	17.12	0.16	99.68
2016PD51-30	0.00	0.00	0.35	0.01	12.87	11.09	0.18	57.28	0.49	16.58	0.06	98.91

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