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Article

Geochemistry of Waziristan Ophiolite Complex, Pakistan: Implications for Petrogenesis and Tectonic Setting

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Abstract: The Waziristan ophiolite complex (WOC), a segment of paleo-suture zone between the Indo-Pakistan plate to the south-east and the Afghan microplate to the north-west, is primarily composed of serpentized dunites and serpentinites after harzburgites, crosscut by pyroxenites. The crustal portion dominantly comprises basalts and dolerites, with less abundant plagiogranites. Whole-rock XRF and trace element ICP-MS analyses were undertaken to determine the degree of melt extraction and subsequent geochemical depletion or enrichment of peridotite protoliths. The investigated peridotites are extremely refractory and show high Mg# values (0.88–0.92), low Al₂O₃ (0.19–0.96 wt%), total alkali values (0.02 < Na₂O + K₂O ≤ 0.20 wt%), CaO (0.04–0.73 wt%), and TiO₂ (0.001–0.017 wt%), but are rich in Cr (up to 3550 ppm) and Ni (up to 2340 ppm). Bulk REE modelling suggests that Waziristan peridotites underwent a high degree (15%–25% melting) of melt extraction in the closed system of spinel-bearing peridotite facies at shallow depths above a subduction zone and, in their chemistry (Sc, REE, Al₂O₃, and MgO), resemble Izu-Bonin-Mariana (IBM) forearc peridotites. Their U-shaped REE patterns and trace elements resemble peridotites derived from supra-subduction zone (SSZ) settings, especially a forearc setting, and also reflect metasomatism by slab-derived fluids. The ultramafic rocks preserve depletion in REE content (0.03 < ΣREE_{CN} < 0.60), indicating the highly depleted nature of refractory peridotites. The basalts (Mg#, 0.48–0.68) are similar in composition to typical boninite and show low to moderate MgO (6.2–13.0 wt%), low total alkali content (0.01–4.45 wt%) and TiO₂ (0.13–0.17 wt%), but are higher in Al₂O₃ (≈11.9 wt%). They show a sub-alkaline affinity and possess geochemical signatures that are transitional from island arc basalt (IAB) magmas to boninitic magmas due to the changes from an extensional to a compressional regime during the initiation of subduction. These geochemical signatures suggest the formation of basalts from melts, resulting from the re-melting of the depleted mantle during intra-oceanic subduction initiation. The higher Th/Nb and V/Ti ratios of the studied basalts further confirm their generation in an SSZ setting characterized by subduction-derived fluids under higher oxidizing conditions. The mafic-ultramafic rocks of the WOC were, therefore, likely formed during intra-oceanic subduction initiation (forearc spreading) in the SSZ setting; they were exhumed along a thrust fault, and obducted onto the forearc region as result of the collision between the Indian plate and the Afghan microplate.

Keywords: Waziristan ophiolite; whole-rock chemistry; forearc peridotites; suprasubduction zone; boninite



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1. Introduction

The collision between the Indian and the Eurasian plates during the Early Paleogene, causing the Himalayan orogeny, resulted in the subsequent exposure of most of the ophiolitic sequences in south-central Asia [1]. Ophiolites, important depositories of Earth's evolutionary history, comprise temporally and spatially associated ultramafic, mafic, and felsic rocks that are interpreted as fragments of the tectonically obducted ancient oceanic

crust and the underlying upper mantle [2]. They are either preserved as dismembered sequences, i.e., ophiolitic melange zones [3], or as an intact section that consists of a complete stratigraphy of oceanic lithosphere [4–6]. A typical ophiolite sequence, from the bottom to the top, consists of residual peridotites ($\pm$ dunite $\pm$ chromite), ultramafic cumulates, layered to isotropic gabbros ($\pm$ troctolite), sheeted dikes, pillow lavas, and pelagic sediments [2,7–10]. Ophiolites display significant variations in their geochemical characteristics, internal structure, and emplacement mechanisms [2]. They represent a direct sample, allowing for the characterization of geochemical, tectonic, metasomatic, and magmatic processes associated with sea-floor spreading and subduction zones, e.g., [2,4,11–13].

Many geoscientists worldwide [4,14–24] have investigated the ophiolite complexes of Pakistan in terms of their age, emplacement, and tectonic history. A basic geological map of part of the Waziristan ophiolites was prepared on a 1:50,000 scale [25]. Petrological and geochemical investigations of the sheeted dykes and trondhjemites of the Waziristan ophiolite complex suggested a back-arc (suprasubduction zone) origin of these rocks [15,26]. Several studies [27,28] investigated the ultramafic and mafic rocks of the Waziristan igneous (ophiolite) complex in terms of the whole-rock major elements and mineral chemistry of silicates. Their findings suggested the island arc affinity of the complex.

Despite several studies of the ophiolite complexes in Pakistan, their exact mode of formation and whether they represent the oceanic lithosphere generated in a forearc basin, as opposed to a back-arc setting, remains a matter of debate. The previous petrogenetic studies [15,21,26,27] of the WOC were based on a very limited geochemical data. Hence, no conclusive interpretation has been made. This study deals with field and petrographic observations, coupled with detailed whole-rock majors and trace elements of ultramafic and mafic rocks from the WOC. The main aim of this study was to understand the petrogenesis of the WOC and place constraints on its geodynamic evolution, focusing on the global tectonics of collision between the Indian and the Eurasian plates during the Early Paleogene. This study also focuses on fluid–peridotite interactions and the behavior of elements during serpentinization processes.

2. Regional Geology

Most ultrabasic and basic rocks in Pakistan are ophiolitic in nature, which, together with ocean floor sediments and volcanic arc materials, are allochthonous bodies [29]. The ophiolite complexes are spread in a linear fashion (Figure 2b) and can be divided into two groups: (i) the northern ophiolitic belt, which includes the Shangla–Mingora ophiolite, the Jijal complex, the Chilas complex, the Sapat complex, the Dargai (Skhakot–Qila) complex, and the Dras ophiolites or igneous complexes, and (ii) the western ophiolitic belt, which consists of Bela, Muslim Bagh, Waziristan, and Zhob ophiolites (in Pakistan), with equivalent Khost and Kabul ophiolites exposed in eastern Afghanistan. The first three sequences, i.e., Bela, Muslim Bagh, and Waziristan ophiolites, constitute the megamelanges [21] and are briefly discussed below.

The Bela Ophiolite/Bela Ophiolite zone is located at the western boundary of the Indo-Pakistan continental plate. An intact ophiolitic section is observed in the northern part of the Bela Ophiolite, which is predominated by ultramafic rocks (harzburgites and dunites), a metamorphic sole, and gabbros (mainly foliated) [30]. Small-scale dykes of sodic plagiogranites are hosted within the peridotites. The tectonic environment for the formation of Bela ophiolite is interpreted as a fast-spreading mid-ocean ridge [31,32].

The Muslim Bagh ophiolite is one of the largest ophiolitic megamelanges, comprising two major tectonic massifs: (i) the western Jang Tor Ghar Massif (JTGM), which predominantly comprises mantle rocks, i.e., lherzolite, harzburgite, dunite, serpentinite, wehrnite, and pyroxenite, and (ii) the eastern Saplai Tor Ghar Massif (STGM), which represents an almost intact ophiolitic section (Figure 1a) comprising foliated peridotites at the base and crustal rocks at the top. The crustal section of the Muslim Bagh ophiolite, exposed in the eastern extremity of the STGM, is composed of the following: (i) cyclic successions (each 200–1500 m thick) of ultramafic-mafic cumulates with a basal dunite zone, grading into

wehrlite, clinopyroxenite, and gabbro towards the top [33], and (ii) a sheeted dyke complex (~1 km thick) that crops out in the east of the STGM [34–37]. The sheeted dyke complex is composed of dolerites; however, all of these underwent a metamorphism at green-schist to amphibolite facies [4].

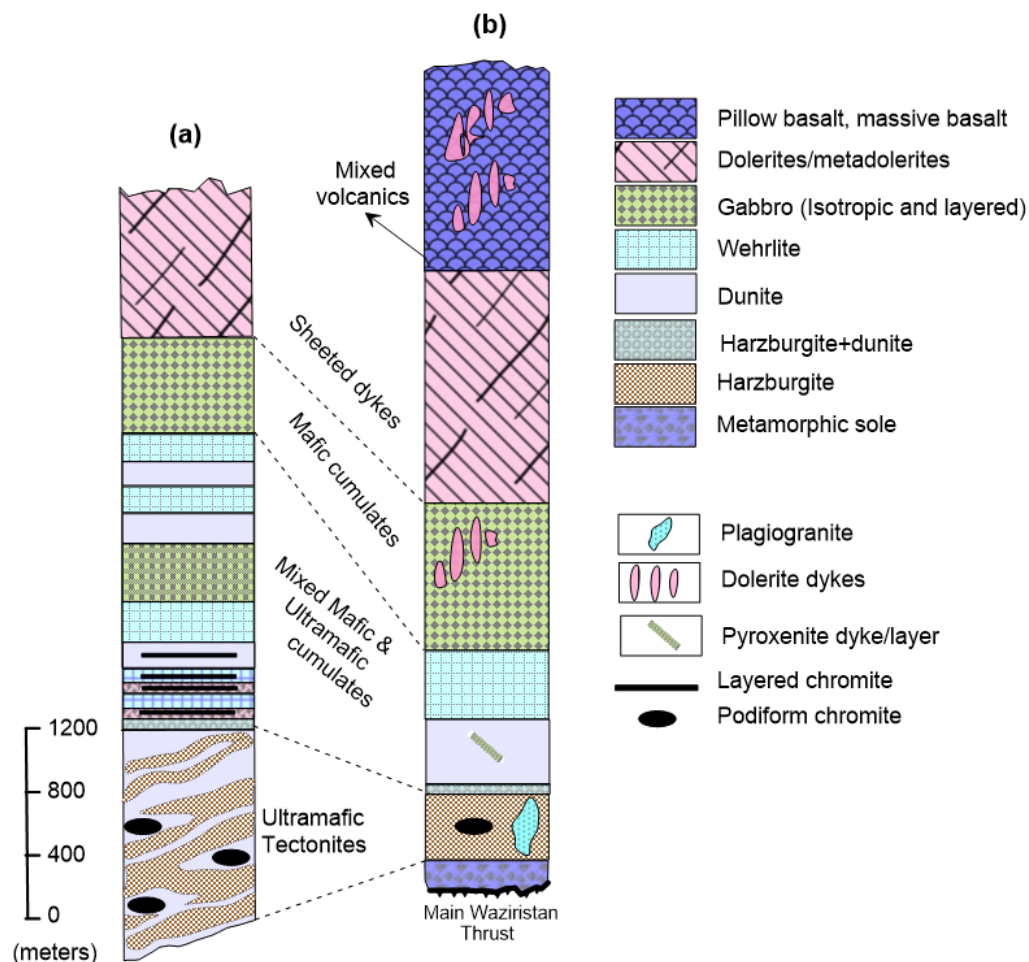


Figure 1. Geological sections. (a) Muslim Bagh ophiolite (redrawn after Siddiqui et al. [40]); (b) Waziristan Ophiolite complex (modified after Khan [25]).

The Waziristan ophiolite complex is the third largest ophiolite in Pakistan and represents part of the suture zone between the Indo-Pakistan plate to the south-east and the Afghan microplate to the north-west. It covers an area of ~2000 km² in the north and south Waziristan. The WOC consists of chaotically arranged thrust slices and imbricated blocks overridden by Jurassic–Cretaceous sediments. Due to severe deformation, the rocks of the complex are very dismembered and intensely folded, faulted, and in places, granulated and brecciated. Internally, the WOC is divided into three nappes or sheets. Located from east to west, these are as follows: (1) Vezhda Sar Nappe, which is primarily composed of pillow basalts. Ultramafic rocks and shelf-slope sediments exist in the form of exotic blocks engulfed within the pillow basalts. (2) The Boya Nappe represents the central body of the complex and consists of unevenly distributed blocks of ultramafic and gabbroic rocks that are exposed in the upper part of the nappe. However, a complete normal-order ophiolitic sequence (Figure 1b) is exposed at the Mami Rogha section in the basal part of the nappe, which consists of harzburgite, dunite, wehrlite, and gabbro-pyroxenite at the base, and grades upward into isotropic gabbros and pillow basalts capped by pelagic sediments at the top. (3) The Datta Khel Nappe, which marks the western extremity of the complex, consists of layered gabbroic rocks and a sheeted dyke complex. Small tectonic blocks of the

ultramafic rocks are only exposed along the Tochi River, located west of Datta Khel village (located at a distance of about 54 km from ‘Boya Kalay’ village) [15,25].

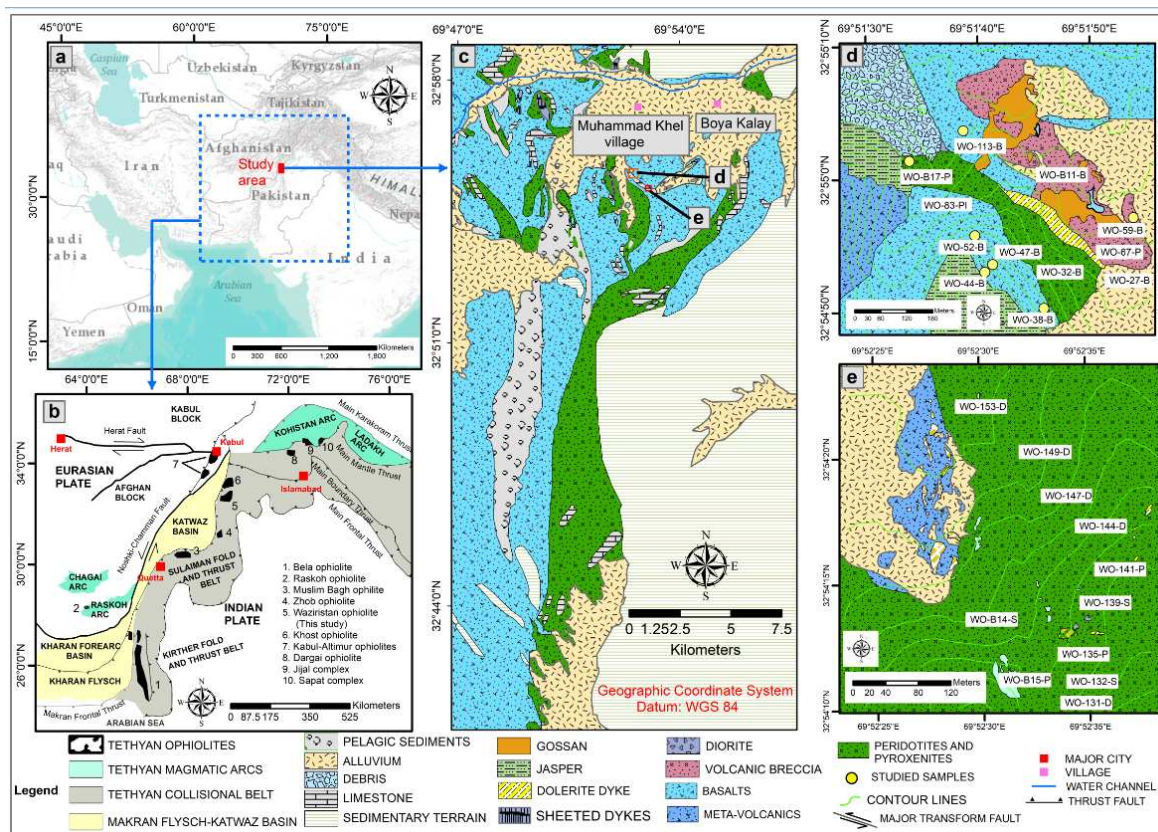


Figure 2. (a) General map showing the location of the study area; (b) Tectonic map showing the Neo-Tethyan sutures and ophiolite occurrences in Pakistan and adjacent regions (modified after [17,38,39]); (c) Simplified geological map of part of the Waziristan ophiolite complex (WOC) and surrounding region (modified after Badshah et al. [40]), showing locations of the studied two sections; (d,e) Local geological maps of the studied sections of the WOC showing spatial distribution and sample locations. See Supplementary Table S1 for coordinates of the studied samples.

3. Field Observations

The WOC constitutes the central segment of the western mountainous belt of Pakistan at the Pak–Afghan border region. It is located about 370 km south-west of Peshawar on the Indus Highway (N-55). It lies between a latitude $32^{\circ}19'12.85''$ N and longitude $69^{\circ}51'35.07''$ E, with an average altitude of 2000 m. Fieldwork was conducted on part of the Waziristan Ophiolite complex near the Muhammad Khel village. Two potential sites (Figure 2d,e), located at a distance of about 3 to 5 km south-west of Muhammad Khel village, were targeted for sample collection. A total of 162 outcrop and 18 borehole samples were collected. The sample locations, along with the sample numbers, are shown in Figure 2d,e and include mostly serpentinized dunite, serpentinite after harzburgite, pyroxenite, basalt, diorite, and less abundant felsic rocks (plagiogranite).

The studied area of WOC is dominated by mafic and ultramafic rocks (Figure 2c). The structure of ultramafic rocks is in the form of an elongated sinusoidal band, which comprises serpentinized peridotites and pyroxenites. This band is oriented in the north–south direction with a maximum lateral extension of 3500 m (Figure 2c). To the north, this band is disrupted in a number of variably thick (~20–80 m) discrete lenticular pieces within the mafic rocks. To the west, the ultramafics are bordered by a massive formation of pillow basalts. The ultramafics have a conformable upper contact with pillow basalts and a sharp lower contact with dolerites (Figure 2d,e) [41].

The pillow basalts generally range from brown to dark grey and light green, mostly jointed, and fractured and/or brecciated in places (Figure 3b). They display an elongated (deformed) form; however, circular and oval-shaped pillows are also observed in places. Turtle volcanics are found as irregular masses that show shearing and sub-aerial volcanism. Basic to intermediate and acidic dykes of very limited extension (<300 m) are hosted within the WOC. These include dolerite, diorite, rhyolite, and diabase dykes/sills. Dolerites display a granular texture with fine to medium-sized grains. These dykes are sporadically injected into the country rocks along a local thrust fault. The dolerite dyke has sheared contacts against brecciated volcanics in the east and ultramafics in the south-west. The dolerite dyke occurs in the form of patches (Figure 2d). It ranges from medium to coarse-grained and is stained with opaque minerals. Massive bodies of this dyke show various small, oxidized zones, capped by yellowish- to brownish-color gossans with limonite and goethite mineral assemblages, and are surrounded by mineralized and barren brecciated volcanics. These zones range in thickness from 2 to 5 m and are mostly associated with fracture filling or sheared zones [41].

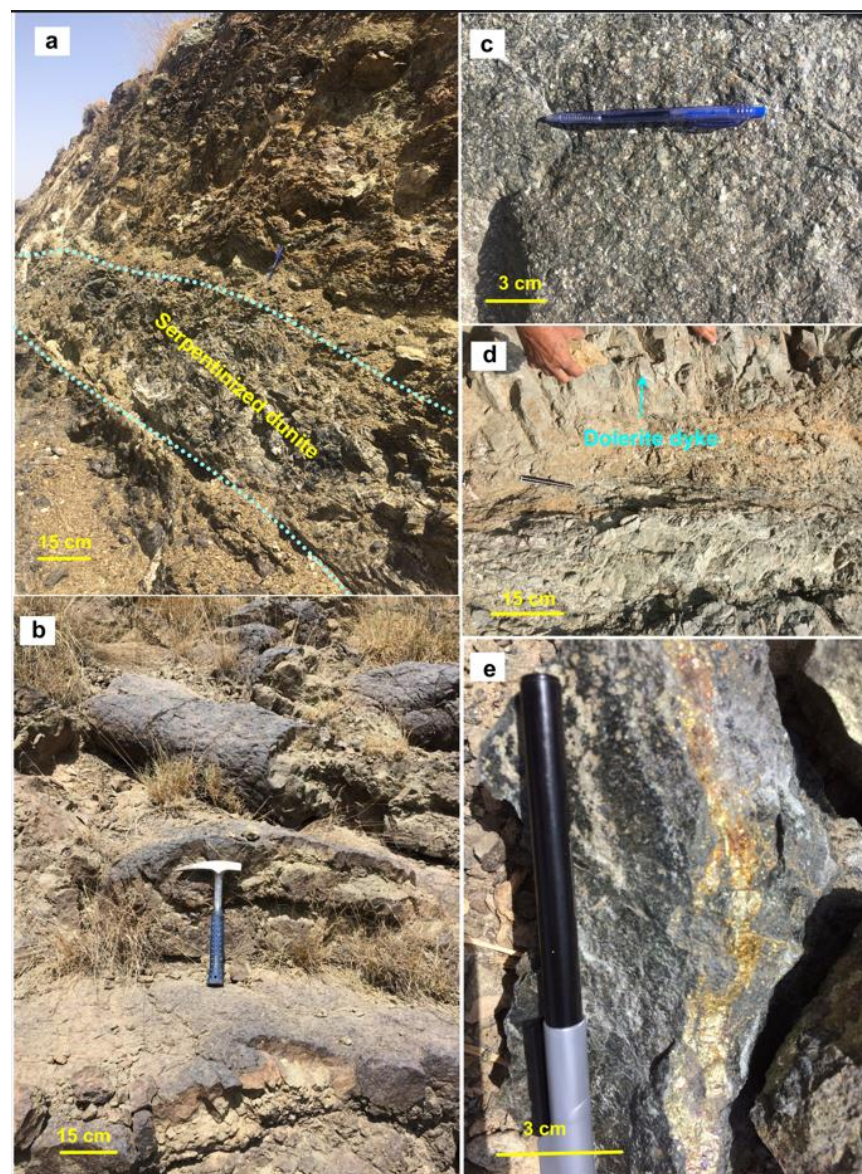


Figure 3. Field photographs showing different lithologies of the WOC. (a) Peridotite outcrop having a well exposed layer of serpentinized dunite; (b) Pillow lavas; (c) Close-up view of dunite outcrop; (d) Dolerite dyke; (e) Altered basalt having chalcopyrite mineralization as fracture filling.

4. Petrography

Based on the field observations, the collected samples were placed into different lithological groups and 50 representative samples from each group were selected for petrographic investigation. Photomicrographs of some of the thin sections are shown in Figure 4.

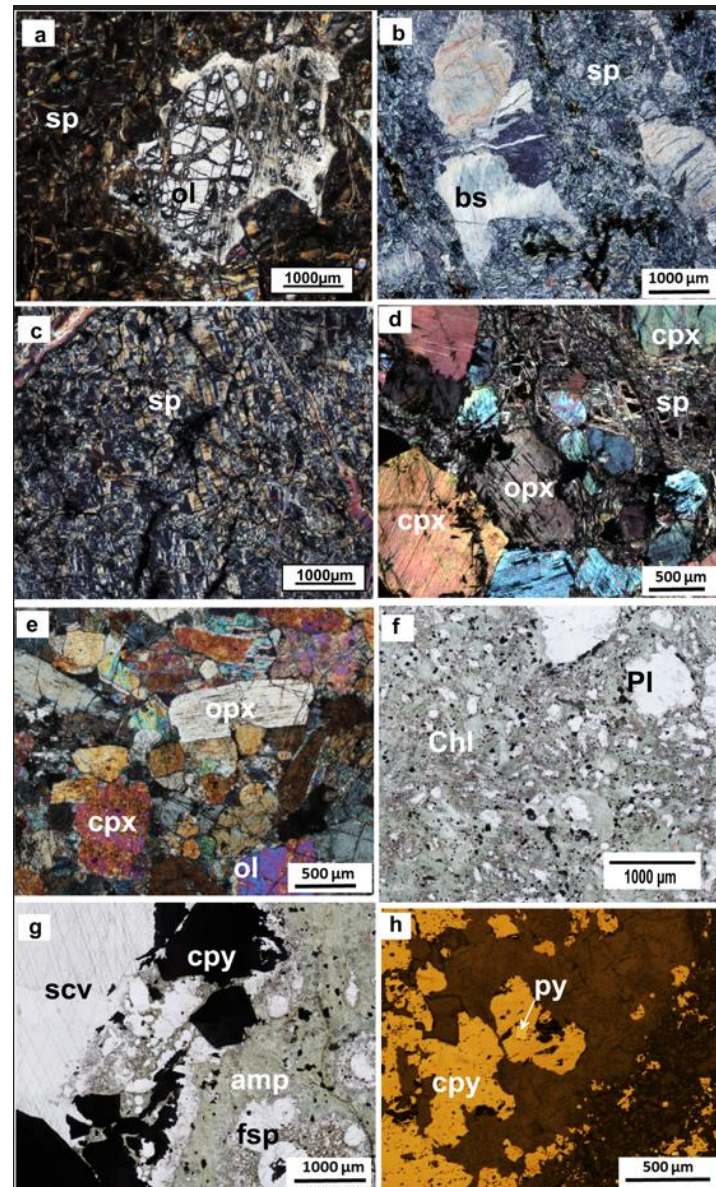


Figure 4. Photomicrographs of studied representative samples. (a) Serpentinized dunite with mesh texture showing olivine embedded in serpentine matrix (XPL); (b) Serpentinized harzburgites showing bastite pseudomorphs after orthopyroxenes (XPL); (c) Dunite sample showing invasive serpentinization; (d,e) Altered pyroxenite samples showing orthopyroxene, clinopyroxene, and relict olivine crystals (XPL); (f) Basalt showing fresh plagioclase, where chlorite (greenish color matrix) intermixed with plagioclase minerals in ground mass (PPL); (g) Basalt showing secondary calcite vein crosscut by chalcopyrite mineralization, where fresh feldspar (plagioclase) is dominant (PPL); (h) Altered basalt sample showing sulphide mineralization (RL). Abbreviations: Pl = plagioclase; sp = serpentinite; opx = orthopyroxene; cpx = clinopyroxene; scv = secondary calcite vein; cpy = chalcopyrite; py = pyrite; ol = olivine; fsp = feldspar; amp = chloritized amphibole; bs = bastite; XPL = cross-polarized light; PPL = plane polarized light; RL = reflected light.

Ultramafic rocks are mainly serpentized dunites with subordinate serpentized harzburgites, crosscut by pyroxenite dykes/layers. Some ultramafic samples are completely serpentized with relics of mesh and bastite texture, suggesting dunite and harzburgite protoliths, respectively. The investigated serpentized dunites are composed of olivine grains ranging from anhedral to subhedral (Figure 4a) embedded in a medium- to fine-grained serpentine matrix with/without rare bastite pseudomorphs of orthopyroxene, while serpentized harzburgites are rich in bastite pseudomorphs of orthopyroxene (15–20 Vol.%) (Figure 4b). Serpentinization is extremely invasive in dunite samples, where relict olivine is rarely observed (Figure 4c). Pyroxenites display medium to coarse-grained (from 0.4–1.2 mm) texture and mainly comprise orthopyroxene (40–55 Vol.%), clinopyroxene (25–30 Vol.%), and serpentine (5–10 Vol. %) with relict olivine (1–5 Vol.%). Orthopyroxenes (Opx) occur as equigranular crystals, showing parallel extinction, while clinopyroxenes (Cpx) are usually prismatic crystals with oblique extinction and a high interference color (Figure 4d,e). Euhedral Cpx crystals show exsolved lamellae of Opx (Figure 4d), suggesting magmatic origin. The serpentization of some pyroxenite samples is dominant along cracks and cleavages (Figure 4d). The crustal section of the WOC mainly consists of basalts that exhibit hypocrystalline and sub-porphyrific micro-textures (Figure 4f) and are composed of fresh plagioclase (15–20 Vol.%) and chlorite (55–75 Vol.%), with disseminated sulphides (1–5 Vol.%). Chlorite occurs as flaky (1–2 mm) grains and indicates the low-grade alterations in these rocks (Figure 4f). Few altered basalts lack primary minerals, and secondary crosscutting calcite veins (Figure 4g) are associated with chalcopyrite and pyrite clusters (Figure 4h).

5. Analytical Methods

After detailed petrographic investigations, the samples affected by alterations were filtered out and a total of 25 relatively fresh samples (Tables 1 and 2), including serpentized dunites, and serpentinites after harzburgites, pyroxenites, and basalts, were selected for whole-rock major and trace element analyses. All the analytical techniques listed below were performed at Macquarie Geo-Analytical (MQGA), Macquarie University, New South Wales, Australia.

The samples were pulverized using an agate ring mill. One gram of powdered sample was thoroughly mixed with 10 grams of pre-mixed flux (35.29% lithium tetraborate and 64.71% lithium metaborate) in a platinum crucible. The combination was then placed in a rocking furnace at 1050 °C for 25 min (one tablet of ammonium iodide was added after 20 min to release the surface tension) so that the sample was melted. The molten sample was then poured into a platinum mould to make the discs (diameter = 4 cm). The discs were analyzed for major element concentrations using a Panalytical AXIOS WDXRF (Wavelength Dispersive X-ray Fluorescence) operated at a maximum of 1 KW, using the United States Geological Survey (USGS) Basalt, Hawaiian Volcanic Observatory (BHVO-2) and Granodiorite, Silver Plume, Colorado (GSP-2) as reference materials (Supplementary Table S2). Four dispersive crystals—namely, LiF200, Ge111, PE002, and PX1—were used with the WDXRF.

Table 1. Whole rock major elements (in weight %) and trace elements including rare earth elements (in ppm) of the studied ultramafic rocks from part of the Waziristan ophiolite complex (WOC). $Mg\# = (MgO/Molar\ mass\ MgO)/(MgO/Molar\ mass\ MgO) + (0.8995 \times Fe_2O_3/molar\ mass\ of\ FeO)$. LOI: loss on ignition. BD: Below detection limit (<0.001).

Sample No	Serpentinized Dunites						Serpentinites					Pyroxenites			
	WO-153D	WO-131D	WO-144D	WO-147D	WO-149D	WO-95S	WO-104S	WO-132S	WO-139S	WO-B14S	WO-B17P	WO-141P	WO-67P	WO-135P	WO-B15P
SiO ₂	39.39	38.74	40.16	38.93	37.85	39.21	39.75	38.91	39.21	39.9	55.06	0.065	49.34	40.56	47.74
TiO ₂	BD	BD	BD	0.002	0.005	BD	BD	BD	0.001	0.017	0.211	4.72	0.14	0.1	0.065
Al ₂ O ₃	0.54	0.46	0.22	0.39	0.19	0.34	0.35	0.44	0.7	0.96	13.6	9.08	10.77	14.43	2.4
Fe ₂ O ₃	7.74	8.64	6.95	7.66	10.81	7.73	8.65	7.57	8.22	7.81	11.53	0.173	8.56	3.96	7.78
MnO	0.109	0.063	0.093	0.115	0.102	0.108	0.072	0.09	0.102	0.086	0.152	23.27	0.207	0.083	0.132
MgO	37.29	38.35	37.7	38.64	36.42	37.6	37.35	37.49	37.23	36.78	7.74	12.3	14.24	8.64	20.6
CaO	0.08	0.07	0.47	0.73	0.09	0.48	0.04	0.09	0.28	0.28	3.86	0.042	2.73	28.82	17.25
Na ₂ O	BD	BD	0.039	BD	0.048	0.214	0.119	0.159	0.011	BD	3.051	BD	1.088	0.096	0.07
K ₂ O	BD	BD	BD	BD	BD	0.009	BD	BD	BD	BD	0.318	0.036	0.057	BD	BD
P ₂ O ₅	0.043	0.046	BD	0.002	BD	BD	BD	0.006	BD	BD	0.055	0.086	0.055	BD	0.04
SO ₃	BD	0.161	BD	0.116	0.173	0.003	BD	0.006	0.003	0.21	0.138	4.2	0.01	0.049	2.427
LOI	14.1	12.5	13.8	12.8	13.3	13.7	12.4	14.6	13.6	13.3	7.9	97.7	14.1	3.3	4.4
Sum	99.3	99.1	99.4	99.4	99	99.4	98.8	99.3	99.4	99.3	104	0.85	101	100	103
Mg#	0.91	0.91	0.92	0.92	0.88	0.91	0.9	0.92	0.91	0.91	0.6	0.004	0.79	0.83	0.85
Cs	0.001	0.003	0.001	0.003	0.001	0.001	0.001	0.001	0.002	0.005	0.204	2.23	0.192	0.005	0.012
Rb	BD	0.069	BD	0.008	0.013	BD	BD	0.018	0.033	0.014	3.949	0.027	0.557	0.01	0.043
Ba	2.545	0.663	0.848	0.211	4.578	3.62	1.545	0.225	3.242	0.442	33.62	0.008	16.03	0.754	0.678
Th	0.002	0.006	0.001	BD	0.003	BD	BD	0.001	0.004	0.024	0.336	0.125	0.07	0.013	0.007
U	0.001	0.009	0.001	BD	0.015	0.001	0.002	BD	0.019	0.008	0.137	0.017	0.022	0.005	0.001
Nb	0.019	0.02	0.008	0.007	0.017	0.005	0.009	0.011	0.023	0.162	1.313	19.16	0.655	0.097	0.02
Ta	0.12	0.069	0.004	0.055	0.03	0.007	BD	0.008	0.196	0.01	0.073	1.87	0.033	0.043	0.068
Sr	2.29	1.478	1.08	1.234	2.234	3.346	1.056	1.145	2.421	6.338	78.14	421	25.25	5.885	10.45
Zr	0.202	0.164	0.159	0.118	0.214	0.11	0.141	0.149	0.296	0.68	13.01	2.656	6.671	1.398	0.921
Ti	24.7	27.41	20.19	11.51	29.58	12.94	15	17.98	46.45	73.88	1264	0.245	813	650	367
Y	0.08	0.039	0.038	0.022	0.054	0.021	0.044	0.053	0.24	0.335	8.215	0.275	21.73	3.015	2.132

Table 1. Cont.

Sample No	Serpentinized Dunites						Serpentinites				Pyroxenites				
	WO-153D	WO-131D	WO-144D	WO-147D	WO-149D	WO-95S	WO-104S	WO-132S	WO-139S	WO-B14S	WO-B17P	WO-141P	WO-67P	WO-135P	WO-B15P
Pb	0.142	0.203	0.167	0.155	1.251	0.15	0.166	0.103	0.273	0.231	0.375	0.72	0.348	0.198	1.462
La	0.01	0.031	0.005	0.002	0.02	0.007	0.028	0.007	0.062	0.112	1.193	0.103	1.435	0.421	0.161
Ce	0.017	0.052	0.009	0.003	0.032	0.007	0.042	0.014	0.095	0.216	2.576	0.472	2.775	0.828	0.531
Pr	0.002	0.005	BD	BD	0.004	BD	0.004	0.001	0.017	0.025	0.288	0.157	0.436	0.143	0.092
Nd	0.006	0.016	0.002	BD	0.016	BD	0.011	0.003	0.071	0.1	1.125	0.056	1.777	0.677	0.477
Sm	0.001	0.001	BD	BD	0.004	BD	0.002	BD	0.02	0.027	0.353	0.251	0.642	0.261	0.187
Eu	0.002	0.002	0.001	BD	0.004	0.001	0.008	0.001	0.01	0.013	0.127	0.05	0.199	0.141	0.066
Gd	0.002	0.005	0.002	BD	0.006	BD	0.002	0.002	0.025	0.04	0.64	0.389	1.264	0.397	0.28
Tb	BD	BD	BD	BD	0.001	BD	BD	BD	0.004	0.007	0.13	0.096	0.283	0.071	0.051
Dy	0.009	0.02	0.007	0.004	0.009	0.003	0.004	0.006	0.035	0.053	1.027	0.31	2.263	0.488	0.353
Ho	0.003	0.001	BD	BD	0.001	BD	0.001	0.001	0.008	0.012	0.258	0.368	0.563	0.11	0.079
Er	0.011	0.004	0.005	0.004	0.005	0.003	0.003	0.006	0.027	0.038	0.84	0.057	1.78	0.311	0.225
Yb	0.025	0.014	0.012	0.014	0.011	0.008	0.009	0.015	0.038	0.046	0.987	0.066	1.837	0.283	0.205
Lu	0.005	0.002	0.002	0.003	0.002	0.002	0.002	0.003	0.007	0.008	0.162	172.7	0.276	0.042	0.03
Hf	0.004	0.005	0.001	BD	0.002	BD	BD	0.001	0.006	0.016	0.369	46.86	0.13	0.058	0.04
V	39.02	20.37	24.86	37.64	22.18	30.44	26.28	36.36	43.41	31.64	267.5	1478	171.8	112.6	100.7
Sc	10.11	4.862	5.816	10.17	4.203	8.757	7.001	8.882	10.767	8.118	44.0	3.02	34.72	47.04	58.36
Cr	2317	3489	1337	1642	3551	1042	1167	1614	1504	1876	178	20.54	489	67	1946
Ga	0.728	1.411	0.431	0.501	0.662	0.351	0.334	0.454	0.828	1.313	10.82	39.86	7.214	5.65	3.051
Cu	17.08	9.054	5.831	5.679	657	3.53	3309	6.245	13.35	9.321	111.2	599	29195	24.09	1348
Zn	26.29	40.07	37.93	38.52	38.639	29.22	54.16	34.80	35.336	33.59	37.76	60.36	117.4	16.84	19.13
Ni	2217	2128	2341	2181	804	1986	2140	2011	2227	1633	57.50	BD	447	57	985
Co	97.81	119.7	94.34	95.31	157.13	86.47	102.6	87.03	96.56	86.99	30.8	7.171	113.2	31.62	98.3
Mo	BD	BD	0.09	0.02	0.05	0.074	0.053	0.049	0.071	0.023	0.664	0.045	0.067	0.055	0.019
Li	0.376	0.113	0.822	1.246	2.321	1.136	0.765	1.399	1.707	1.343	2.934	7.171	5.999	5.146	1.267
Be	BD	0.006	0.001	BD	BD	0.002	0.016	0.001	0.007	0.023	0.22	0.045	0.299	0.055	BD

Table 2. Whole rock major elements (in weight %) and trace elements including rare earth elements (in ppm) of the studied basalts from part of the Waziristan ophiolite complex (WOC). $Mg\# = (MgO/Molar\ mass\ MgO)/(MgO/Molar\ mass\ MgO) + (0.8995 \times Fe_2O_3/molar\ mass\ of\ FeO)$. LOI: loss on ignition. BD: Below detection limit (<0.001).

Rock	Basalts								
Sample No	WO-38-B	WO-44-B	WO-47B	WO-52-B	WO-59-B	WO-B11B	WO-113-B	WO-27-B	WO-32-B
SiO ₂	50.05	52.66	53.71	37.61	47.22	49.55	56.79	56.01	57.46
TiO ₂	0.155	0.148	0.174	0.14	0.173	0.163	0.171	0.145	0.13
Al ₂ O ₃	12.04	11.55	12.75	10.53	12.07	12.7	12.93	11.32	11.25
Fe ₂ O ₃	17.17	18.52	15.24	19.72	18.5	13.39	6.74	14.08	13.79
MnO	0.093	0.075	0.079	0.065	0.074	0.338	0.163	0.064	0.064
MgO	11.35	9.87	10.52	8.24	11.99	12.98	6.23	10.08	9.74
CaO	0.29	0.16	0.34	0.49	0.23	0.32	8.95	0.19	0.16
Na ₂ O	BD	BD	0.056	BD	0.014	1.582	4.433	0.024	0.01
K ₂ O	BD	BD	BD	BD	BD	BD	0.014	BD	BD
P ₂ O ₅	0.049	0.052	0.051	0.04	0.063	0.012	0.056	0.057	0.048
SO ₃	2.908	1.49	1.456	8.96	4.074	5.789	0.019	1.955	1.857
LOI	5.9	4.8	4	0.7	3.9	3	5.1	7.1	4.5
Sum	100	99.4	98.4	86.5	98.3	99.8	102	101	99
Mg#	0.59	0.54	0.6	0.48	0.59	0.68	0.67	0.61	0.61
Cs	0.03	0.005	0.008	0.003	0.032	0.005	0.004	0.047	0.037
Rb	0.043	0.063	0.047	0.031	0.045	0.078	0.05	0.135	0.077
Ba	3.072	2.87	3.932	2.094	1.409	1.901	5.057	5.634	5.867
Th	0.119	0.133	0.212	0.018	0.139	0.337	0.386	0.227	0.177
U	0.086	0.124	0.269	0.013	0.089	0.155	0.115	0.14	0.133
Nb	0.935	0.76	0.97	0.677	1.036	1.256	1.292	0.969	0.937
Ta	0.047	0.042	0.089	0.018	0.06	0.107	0.077	0.062	0.044
Sr	4.634	1.181	2.037	1.627	4.968	8.465	16.71	2.051	1.767
Zr	7.823	7.57	9.8	7.522	11.14	10.74	13.25	9.964	8.401
Ti	918	961	997	892	1037	898	1053	811	748
Y	3.386	9.564	4.61	8.314	4.293	4.959	7.519	5.792	3.844
Pb	0.16	0.147	0.28	0.12	0.173	2.133	1.496	0.27	0.282

Table 2. Cont.

Rock					Basalts				
Sample No	WO-38-B	WO-44-B	WO-47B	WO-52-B	WO-59-B	WO-B11B	WO-113-B	WO-27-B	WO-32-B
La	0.623	0.47	0.30	0.116	0.76	1.938	1.975	0.471	0.278
Ce	1.189	1.092	0.54	0.184	1.319	4.441	3.388	1.012	0.631
Pr	0.123	0.132	0.056	0.019	0.125	0.479	0.355	0.115	0.078
Nd	0.444	0.527	0.215	0.075	0.435	1.709	1.354	0.44	0.325
Sm	0.114	0.226	0.081	0.032	0.103	0.358	0.39	0.127	0.1
Eu	0.043	0.061	0.015	0.01	0.031	0.241	0.161	0.028	0.025
Gd	0.199	0.574	0.224	0.149	0.179	0.465	0.646	0.275	0.216
Tb	0.038	0.13	0.054	0.04	0.037	0.087	0.128	0.061	0.043
Dy	0.297	1.073	0.506	0.417	0.325	0.654	0.979	0.56	0.37
Ho	0.079	0.262	0.146	0.13	0.097	0.166	0.243	0.157	0.098
Er	0.266	0.818	0.523	0.462	0.351	0.539	0.782	0.54	0.318
Yb	0.348	0.881	0.637	0.488	0.449	0.644	0.9	0.634	0.372
Lu	0.062	0.135	0.109	0.075	0.081	0.111	0.146	0.102	0.063
Hf	0.16	0.17	0.224	0.087	0.201	0.309	0.385	0.22	0.183
V	200.2	214.7	219	146.3	222.8	207.2	204	191.1	183
Sc	45.78	42.53	37.24	32.37	42.84	37.63	36.10	35.84	36.46
Cr	338	442	143	190	525	289	176	110	156
Ga	9.5	10.90	7.794	5.741	10.32	8.962	14.33	7.595	7.451
Cu	11717	8584	5886	67680	15450	516	116	7370	7354
Zn	23.50	23.8	23.10	26.58	25.98	141.0	39.14	20.49	21.67
Ni	150	143	91.02	93.34	175	143.8	60.22	78.41	75.65
Co	69.92	70.92	67.21	61.22	76.2	40.18	26.18	53.64	53.96
Mo	4.054	0.204	4.227	10.02	0.575	0.556	BD	8.512	6.627
Li	4.137	4.877	19.64	6.539	3.116	4.047	2.689	9.292	12.89
Be	0.06	0.081	0.054	0.089	0.065	0.185	0.205	0.072	0.069

For trace element concentrations (ppm), approximately 100 mg of powdered sample was digested with a mixture of 50% concentrated HF (Merck, Suprapur grade) and 50% distilled HNO₃ (Merck, Darmstadt, Germany) in a clean 15 mL Savillex Teflon beaker for 24 h at 120 °C, then dried, and the process was repeated. The sample was then digested using a mixture of 2 mL HF (Merck, Suprapur) and 10 drops of perchloric acid HClO₄ (Merck, Suprapur) for 10 h, and then gradually dried at 150 °C, 170 °C, and 190 °C to remove fluoride complexes. The sample was further digested in a 6N HCl and 6N HNO₃ to remove any perchloric acid left in the sample. Finally, the sample was dissolved in a 10 mL mixture of 2% HNO₃ and 0.5% HF. Each sample solution (1:1000 dilution) was then individually spiked with a 0.02 mL aliquot of a ⁶Li, As, Rh, In, Tm, and Bi solution to monitor and correct for instrumental drift during analysis. The USGS reference material BCR-2 was used as a calibration standard. The spiked sample was then analyzed on an Agilent 7500cs quadrupole ICP-MS. The USGS standards, such as BHVO-2, GSP-2, BIR-1 (Icelandic basalt), and BCR-1 (the Columbia River Basalt Group), were also digested and analyzed. Two blanks were also included in the sample batch. All reported data were blank-corrected (Supplementary Table S2).

6. Results

6.1. Geochemical Characteristics of Ultramafic Rocks

Whole-rock chemical concentrations of both major and trace elements of the studied ultramafic rocks from WOC are listed in Table 1. The loss on ignition (LOI) values of the ultramafic section (i.e., peridotites and pyroxenites) range from 12.42 to 14.6 (wt%), reflecting a high degree of serpentinization. To obtain a better understanding of variably serpentinized rocks, major element data were recalculated (Supplementary Table S3) on an anhydrous basis to wt% [42]. Since CaO is highly mobile during serpentinization, while SiO₂ and Al₂O₃ are both very immobile [43,44], Al₂O₃ concentration was used as the denominator of a depletion index.

Ultramafic rocks (i.e., serpentinized dunites, harzburgites, and serpentinites) display very high Mg# values ($0.88 < \text{Mg\#} < 0.92$, Table 1), which are higher than the primitive mantle value of 0.89 [45]. They show similar MgO values (36.4–38.6 wt%) to depleted peridotites. The studied ultramafic rocks are very low in Al₂O₃ (0.19–0.96 wt%), CaO (0.03–0.28 wt%), Na₂O (0.002–0.21 wt%), and TiO₂ (0.001–0.017 wt%) contents, similar to those of supra-subduction zone (SSZ) peridotites [46]. Whole-rock major element oxides vs. Al₂O₃ (anhydrous) Harker diagrams of the studied ultramafic rocks are plotted within the fields of Tonga forearc peridotites (Figure 5a–f) [47], similar to Neoproterozoic forearc peridotites in the Arabian Nubian Shield [48] and suprasubduction zone peridotites from the Jijal complex [24]. However, they are more Al₂O₃-depleted when compared to primitive mantle values [45,49]. Major element oxides such as Al₂O₃ show a positive correlation with SiO₂ and a weak negative correlation with MgO (Figure 5a,b), which is characteristically observed in residual peridotites [50]. No correlation was observed in Al₂O₃ versus TiO₂ and Na₂O. Fe₂O₃ versus Al₂O₃ shows a contrasted behavior (positive correlation in dunites and a negative correlation in serpentinites). CaO shows a somewhat positive correlation with Al₂O₃, which is expected, and may suggest that, despite extensive serpentinization, the Al–Ca relationship was partially preserved.

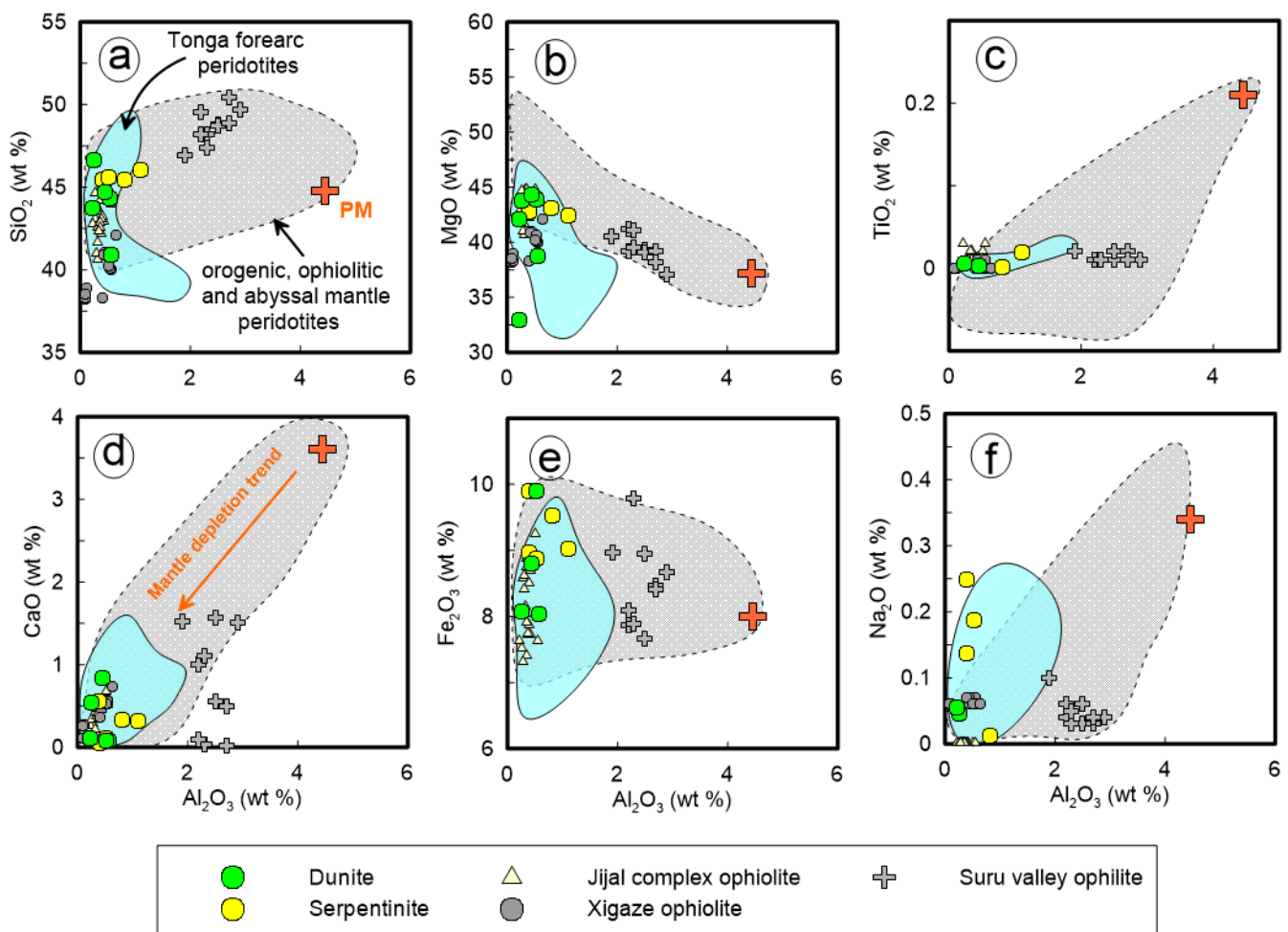


Figure 5. Variation diagrams of selected whole rock major element oxides against Al_2O_3 (anhydrous wt. %) for the studied peridotites of WOC. The grey fields reflect the orogenic, ophiolitic, and abyssal mantle peridotites of Bodinier and Godard [51]. The sky blue fields represent Tonga forearc peridotites of Birner et al. [47]. The supra-subduction zone peridotites of Ullah et al. [24], Bhat et al. [52], and Xiong et al. [46] are plotted for comparison. Primitive mantle (PM) values are from Sun and McDonough [45] and McDonough et al. [49].

The pyroxenites display intermediate Mg# values ($0.59 < \text{Mg\#} < 0.85$), moderate to low MgO values (7.8–23.3 wt%), moderate to high Al_2O_3 values (2.4–14.4 wt%), low total alkali content (0.04–3.37 wt%), and very low TiO_2 values (0.07–0.21 wt%), comparable to those of the SSZ pyroxenites of Çelik et al. [53].

Most of the investigated serpentinized dunites show an enrichment in Ni (2128–2340 ppm) and Cr (2317–3550 ppm) relative to fertile mantle (Ni, Cr ~2000 ppm), suggesting their refractory mantle origin [54].

The spider diagrams of the chondrite-normalized [45] rare-earth elements (REE) and the primitive mantle-normalized [49] trace elements of the ultramafic rocks in the WOC are shown in Figure 6. Relative to chondrite, the investigated ultramafic rocks have a low heavy REE content ($0.04 < (\text{Yb})_N \leq 0.4$). They show concave upward REE_{CN} patterns (Figure 6a,b), characterized by a depletion of the mid REE (MREE) relative to the heavy REE (HREE), with $(\text{Gd}/\text{Yb})_N$ as low as ≈ 0.004 . However, the light rare-earth elements (LREE) are enriched relative to the MREE, as reflected by their high La–Sm ratio (i.e., $1.9 < (\text{La}/\text{Sm})_N < 186$). These U-shaped REE patterns are characteristics of the peridotites that originated in the supra-subduction zone (SSZ) setting [55]. Such REE patterns can also be observed in fore-arc serpentinites and mantle wedge serpentinized peridotites [56]. Most of the studied peridotites display a close resemblance in their REE inventory to

the Izu-Bonin-Mariana [10] and South Sandwich forearc peridotites [57] (Figure 6a). It is worth noting that two of the serpentinite samples (WO-B14-S and WO-139-S) show flat but more REE enriched patterns, similar to Zildat (Tso Moriri-Himalaya) mantle wedge serpentinites [58] (Figure 6a).

The large ion lithophile element (LILE) content of the studied peridotites is very low relative to the primitive mantle [46] and is comparable to the depleted mantle peridotites [59]. The LILEs, however, show an enrichment relative to LREE ($27 < (Pb/Ce)_{PM} < 1458$ and $2 < (Sr/Ce)_{PM} < 40$).

The REE inventory (ΣREE) of the investigated pyroxenites ranges between 2.5 and 14.2 ppm. The pyroxenites show intermediate REE patterns, falling between a relatively flat REE pattern, from Lu to La (e.g., Sample WO-141-P and WO-B15-P), and a more complex pattern characterized by two segments, showing moderate depletion of the MREE relative to the HREE ($(Sm/Yb)_N \leq 0.4$), and then a very steady, slight enrichment of the LREE relative to the MREE ($2.1 < (La/Sm)_N$) (Figure 6b). This REE pattern resembles the one observed in the SSZ pyroxenites [53] (Figure 6b). However, the WOC's pyroxenites are slightly more enriched in light rare-earth elements (LREE).

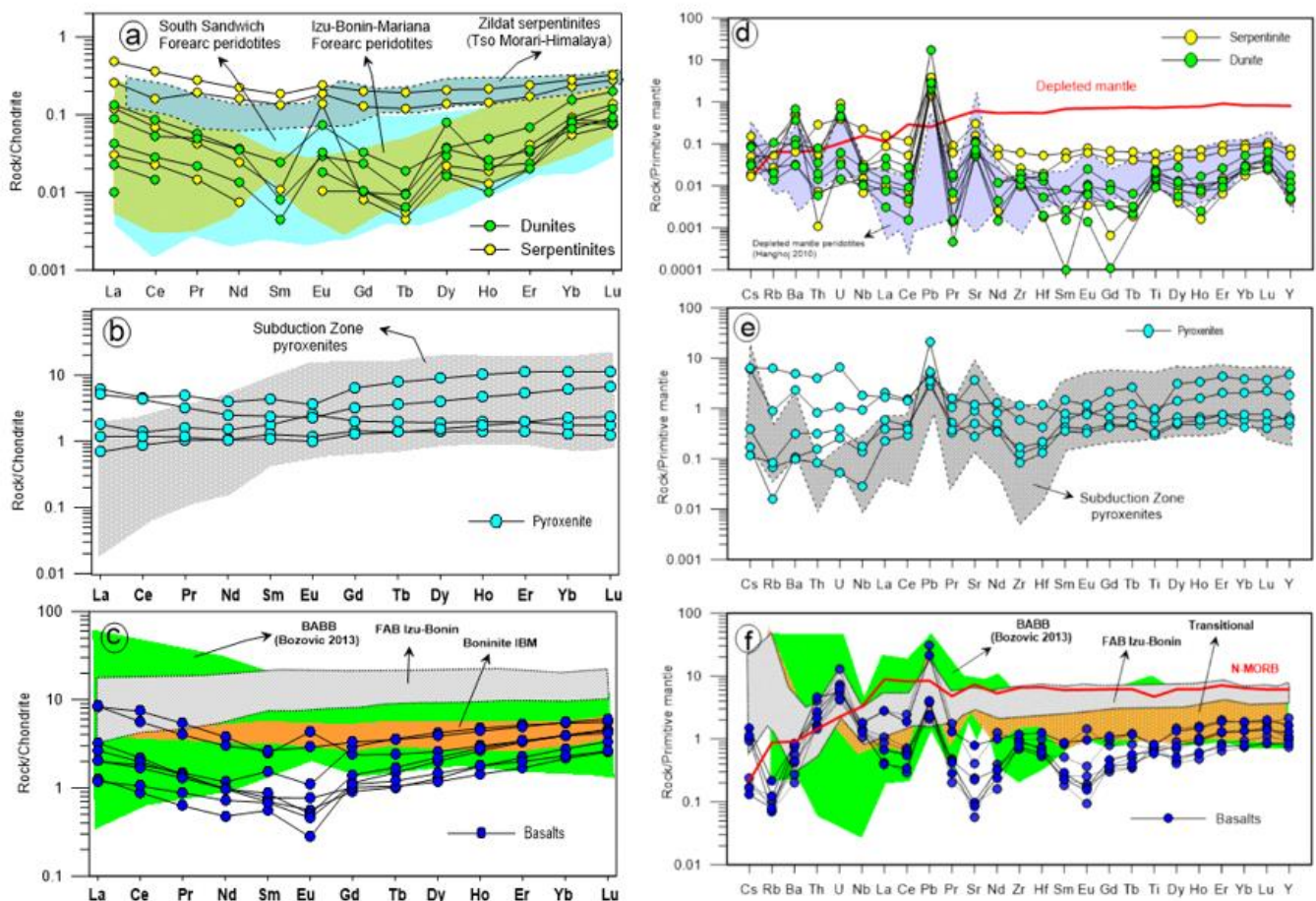


Figure 6. Rare-earth and trace element spider diagrams for different lithologies of the WOC. (a–c) Chondrite normalized [45,49] REE patterns; (d–f) primitive mantle normalized [45,49] extended trace elements' spider diagrams for the studied peridotites, pyroxenites, and basalts. Elements are arranged in terms of increasing compatibility (from left to right) in a peridotite–basaltic melt system [60]. Fields of Izu–Bonin–Mariana [10], South Sandwich forearc peridotites [57], Zildat forearc mantle wedge serpentinites [58], depleted mantle peridotites [59], subduction zone pyroxenites [61], back-arc basin basalts (BABB) [62], forearc basalts (FAB) Izu-Bonin, transitional, and boninite rocks of Mirdita ophiolite [63], and boninites [64] are shown for comparison.

High-field-strength elements (HFSE; Th, U, Nb, Ta, Zr, Hf, and Ti) are some of the most important trace elements used to decipher the subduction zone processes, on account of their unique geochemical behavior [65]. The studied pyroxenites are depleted in high-field-strength elements (HFSEs) relative to MREE, i.e., $0.2 < (\text{Ti}/\text{Tb})_{\text{PM}} < 0.8$; $0.2 < (\text{Zr}/\text{Sm})_{\text{PM}} < 0.5$. They also show depletions in HFSE relative to LREE ($0.1 < (\text{Nb}/\text{Ce})_{\text{PM}} < 0.5$), except sample WO-B17-P ($(\text{Nb}/\text{Ce})_{\text{PM}} = 1.3$). This characteristic depletion of HFSE relative to REEs, and other elements of similar compatibility, is commonly observed in subduction-related igneous rocks [66].

6.2. Geochemical Characteristics of Mafic Rocks

Whole-rock chemical concentrations of both major and trace elements of the studied mafic rocks from WOC are listed in Table 2. The loss on ignition (LOI) values in the mafic section of the WOC range from 0.6 to 7.1 (wt%), reflecting a low to moderate degree of serpentinization. The studied basalts of the mafic section of the WOC are marked by their low Mg# values ($0.47 < \text{Mg\#} < 0.68$, Table 2). These rocks display higher Al_2O_3 values (average = 11.90 wt%) and low to moderate MgO values (6.23–12.98 wt%), low total alkali content (0.01–4.45 wt%), and TiO_2 values (0.13–0.17 wt%).

Variations in whole-rock major oxides (wt%) and trace elements (ppm) vs. MgO (wt%) of the investigated basalts are shown in Figure 7. The SiO_2 (37.6–57.5 wt%) and P_2O_5 (0.01–0.06 wt%) contents negatively correlate with MgO (Figure 7a,c), showing geochemical characteristics that transition to forearc basalts [67] and back-arc basin basalt [68], similar to Oman ophiolitic mafic members, which have geochemical characteristics that transition between mid-ocean ridge basalts (MORB) and island arc tholeiites (IAT) [69]. The TiO_2 (0.13–0.17 wt%) remains constant for MgO. All the investigated basalts plot in the boninite field [70] (Figure 7b), except sample WO-113MB. A positive correlation can be observed in Al_2O_3 (0.13–0.17 wt%) against MgO (Figure 7d). Among the trace elements, Sc, Co and La exhibit the weak positive correlation (Figure 7e,f,h) while Zr and Th have no defined correlation against MgO in the studied basalts (Figure 7g,i).

In the total alkalis vs. silica (TAS) classification diagram (Figure 8a) [71], the basalts show a sub-alkaline affinity. The SiO_2 vs. FeO^*/MgO diagram (Figure 8a) [9] can further classify the sub-alkaline nature of the mafic rocks into tholeiite and calc-alkaline, wherein two of the samples are plotted in the tholeiitic field, and one sample has a somewhat transitional affinity, while two samples are plotted in the calc-alkaline field. In the AFM plot (Figure 8b) [72], these mafic rocks tend to show tholeiitic affinity, except one sample, which is plotted in the calc-alkaline field. The Th versus Co diagram—a more robust and potentially useful plot—can be used to classify both fresh and altered volcanic rocks [73], wherein the studied basalts show an affinity for the island arc tholeiites (Figure 8c).

The chondrite-normalized REE and primitive mantle-normalized trace element patterns of basalts are shown in Figure 6c,f. These rocks show a low overall REE inventory ($2 < \Sigma\text{REE}_{\text{ppm}} < 11.1$). A slight but noticeable MREE depletion can be observed relative to HREE ($0.07 < \text{Sm}_\text{N}/\text{Yb}_\text{N} < 0.48$). The LREE displays very limited enrichment relative to HREE ($0.17 < \text{La}_\text{N}/\text{Yb}_\text{N} < 2.08$), similar to boninitic and tholeiitic rocks (Figure 6c) from Cape Vogel, Papua new Guinea [64]. The primitive mantle-normalized trace element patterns of the studied basalts show geochemical characteristics that are transitional to back-arc basin basalts (BABB) [62] and forearc basalts (FAB) [63] (Figure 6f).

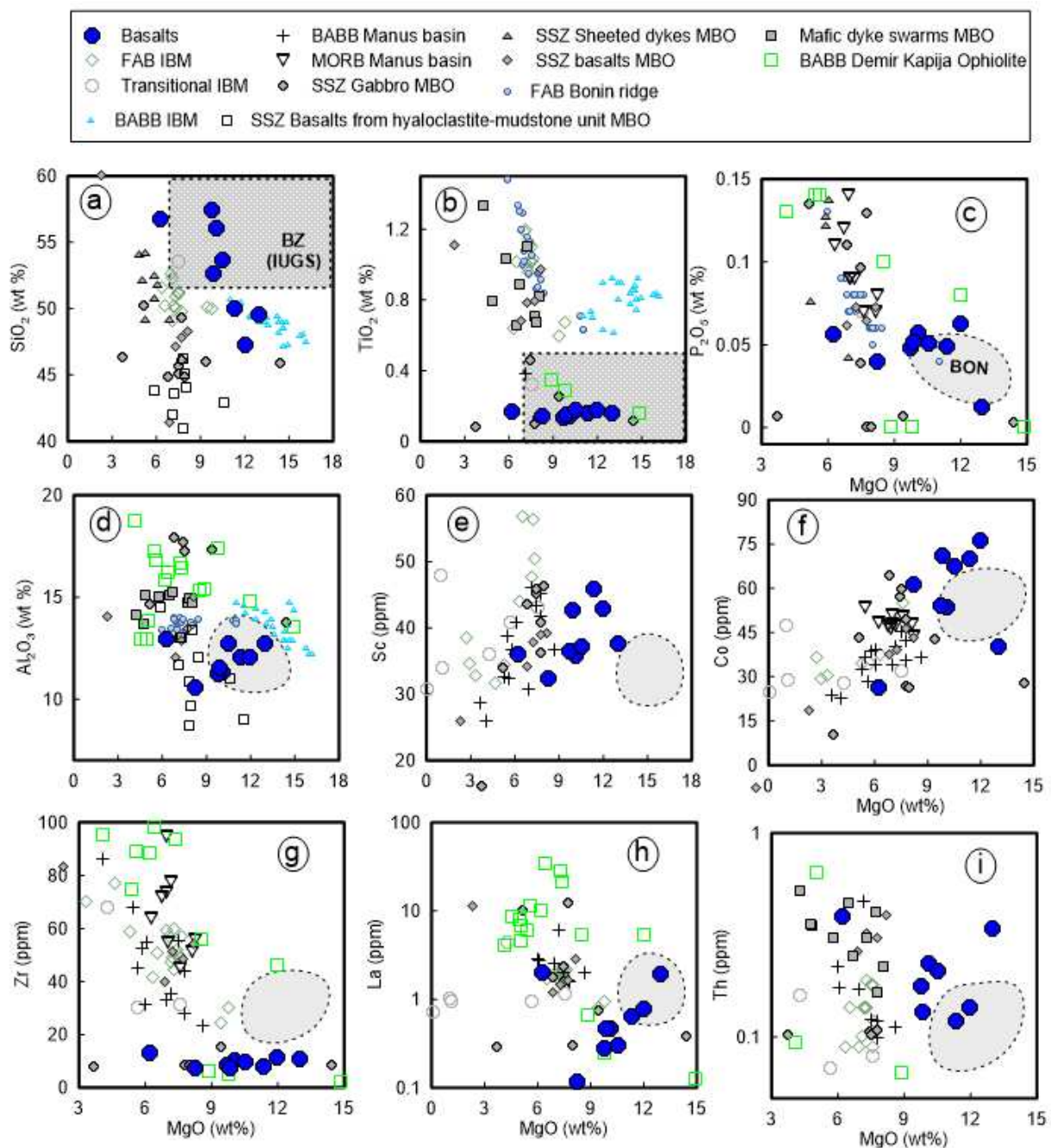


Figure 7. Harker diagrams of whole rock majors (wt%) and trace elements (ppm) against MgO (wt%) for the studied basalts of WOC. Field of boninite zone (BZ) International Union of Geological Association (IUGS) is from Le Bas [70]. Data of forearc basalts (FAB) Izu-Bonin-Mariana (IBM), boninites IBM (BON), and transitional basalts are from Reagan et al. [67] and Meffre et al. [74]. Data of back-arc basin basalt (BABB) Manus Basin and Mid-ocean ridge basalt (MORB) Manus Basin are from Beier et al. [75]. Data of suprasubduction zone rocks [4] from Muslim Bagh ophiolite (MBO), FAB from Bonin ridge [76], BABB from The Demir Kapija Ophiolite [62], and BABB from IBM [68] are shown for comparison.

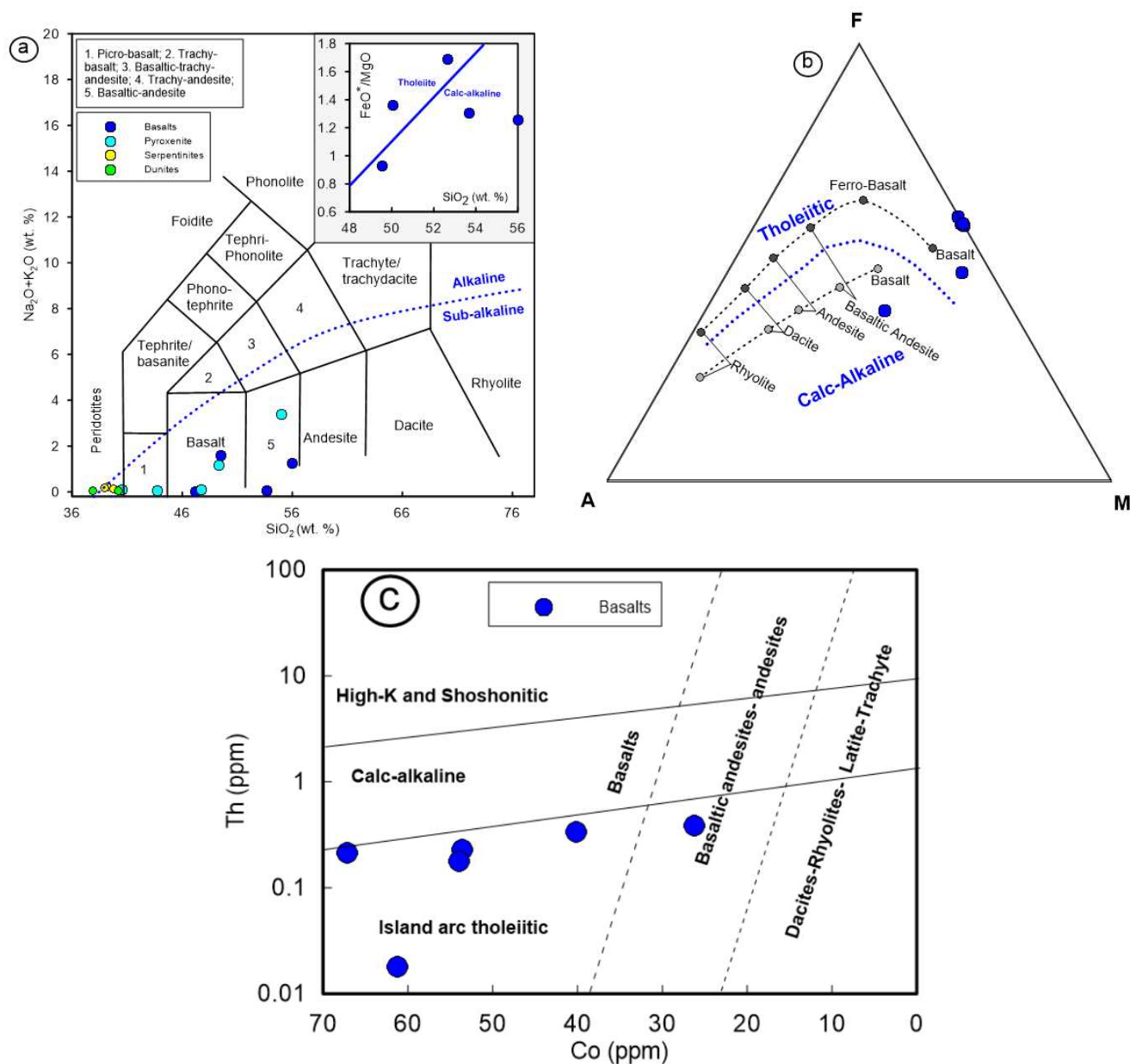


Figure 8. (a) Total alkalis vs. SiO_2 (TAS) classification diagram [71]. The dotted line indicates the boundary between alkaline and sub-alkaline fields (after Irvine and Baragar [72]). Inset shows SiO_2 vs. FeO^*/MgO plot with the solid blue line further classifying the sub-alkaline rocks into tholeiite and calc-alkaline respectively (after Miyashiro [9]); (b) AFM ternary diagram after Irvine and Baragar [72], where A are the sum of alkali oxides ($\text{Na}_2\text{O} + \text{K}_2\text{O}$); F, iron oxide (Fe_2O_3) and M, is magnesium oxide (MgO), the dotted line indicates the boundary between tholeiitic and calc-alkaline rocks; (c) The Th-Co discrimination plot [73] for the studied basalts. The dotted lines separate the geochemical boundaries of basalts, basaltic andesites-andesites, and dacites-rhyolites-latites-trachytes. The solid lines separate the compositional boundaries of Island arc tholeiites, calc-alkaline, and high-potassic schoshonites.

7. Discussion

7.1. Partial Melting of the Waziristan Ophiolitic Peridotites

Mantle peridotites within the ophiolitic complexes are one of the most important geological archives, which can provide a direct window to investigate the partial melting processes and the subsequent metasomatism [51]. Whole-rock major oxides and trace element geochemical characteristics, primarily controlled by partial melting processes

and fluid/melt-rock interactions, can be used to evaluate the degree of partial melting in ophiolitic peridotites. However, due to the complex and diverse nature of the mantle melting processes, a modelling approach is critical for evaluation [51]. The degree of partial melting can be estimated using whole-rock major and trace-element concentrations [50]. Low HREE contents relative to depleted MORB mantle (DMM; [77]) indicate a high degree of partial melting of the mantle source. We compared the very low HREE abundances of the investigated peridotites with the DMM melting curves in the spinel stability field [78,79], thereby indicating 15%–25% partial melting (Figure 9a). The MgO (whole-rock) content and Mg# of mantle-derived peridotites can be regarded as strong indicators of depletion, which positively correlate with their degree of partial melting [80,81]. Low concentrations of TiO₂, Al₂O₃, and CaO in peridotitic rocks relative to primitive mantle reflect a high degree of partial melting [12,82]. The WOC peridotites have a much higher MgO and much lower TiO₂, Al₂O₃, and CaO contents compared to primitive mantle sources, suggesting that they experienced a relatively higher degree of partial melting. In the Al₂O₃ versus MgO plots, the studied peridotites fall close to the end of the polybaric melting curves [83], thereby indicating a 15%–25% partial melting of the primitive mantle (Figure 9b); this is consistent with partial melting degrees derived from the DMM melting curves of HREE (Figure 9a). To obtain a better understanding of the partial melting of the WOC ophiolites, we modelled the whole-rock Ni and Yb concentrations based on the non-modal dynamic melting model [84]. Both Ni and Yb are regarded as fluid-immobile elements [10], whereas Ni is compatible and Yb is relatively incompatible in olivine and pyroxene during the melting processes [85,86]. Therefore, Ni/Yb versus Yb systematics of depleted peridotites can be used to determine the degree and type of partial melting [87]. In the Yb versus Ni/Yb diagram (Figure 9c), the studied peridotites reflect approximately 20%–31% closed-system-non-modal-dynamic melting of the primitive mantle (PM; [88]). Moreover, in the Yb (ppm) vs. Sc (ppm) plot (Figure 9d) for residual peridotites [89], the investigated peridotites indicate ~18–25 partial melting of the fertile MORB mantle (FMM), similar to forearc serpentinitized peridotites [48]. The high degree of partial melting, mainly 18–25% (up to 30%) of WOC residual peridotites, is evidence of the SSZ environment such as the forearc setting, wherein the amount of slab-derived fluids dominates relative to the back-arc setting, which causes a high degree of partial melting.

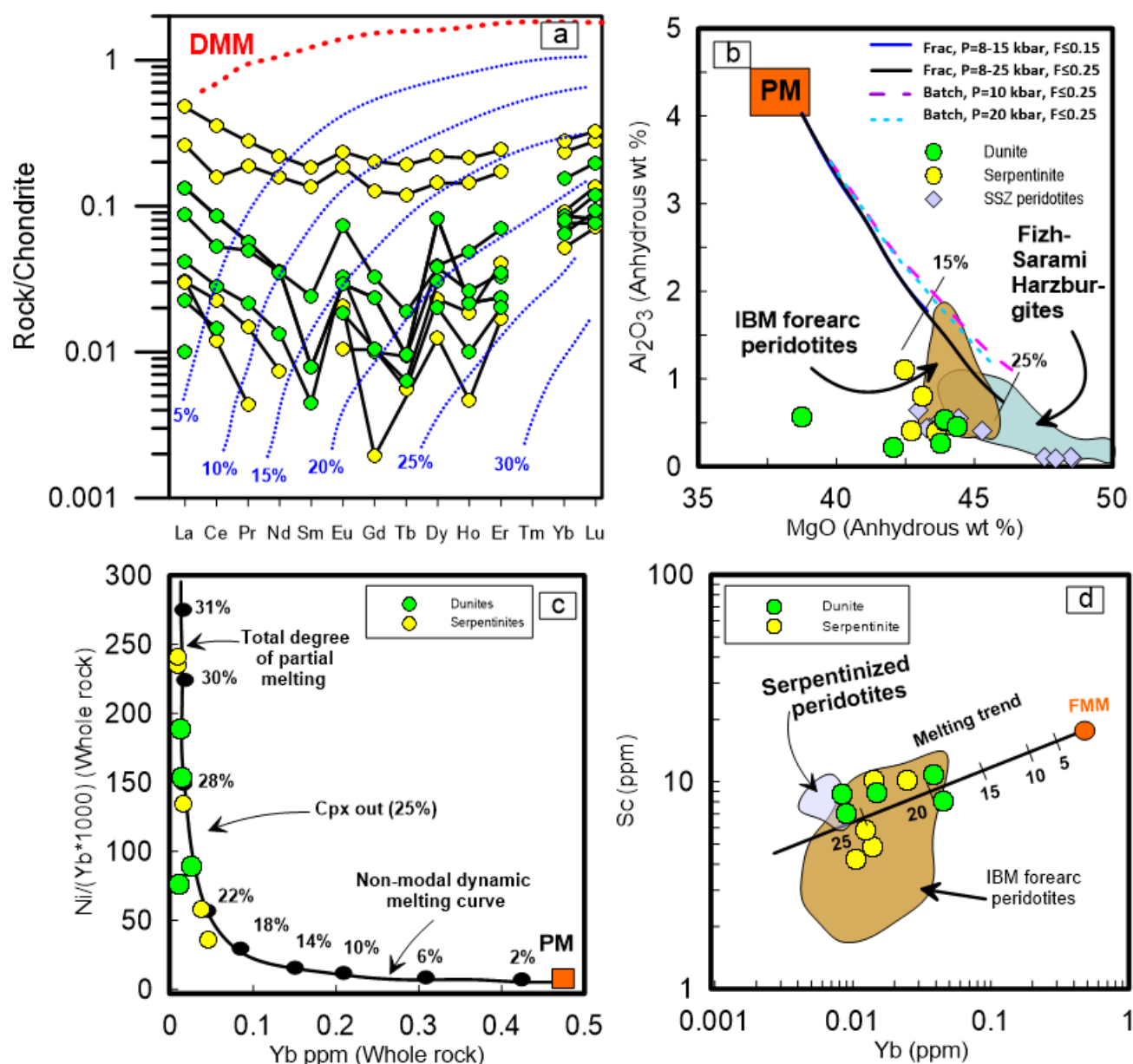


Figure 9. Estimation of partial melting degrees based on whole-rock chemistry. (a) Chondrite normalized [45] REE patterns of the studied dunites and serpentinites compared with the partial melting curves, supporting a source of depleted MORB mantle (DMM) composition [77] in the spinel stability field [78]; (b) MgO vs. Al₂O₃ for the studied dunites and serpentinites. The isobaric batch melting (broken lines) and near-fractional polybaric melting (solid lines) calculations are based on the mantle melting model [83]; (c) Non-modal dynamic melting of a primitive mantle (PM) source [88] (after Kapsiotis [84]) for the studied peridotites; (d) Yb vs. Sc binary plot for residual peridotites [89]. Data of Izu-Bonin-Mariana (IBM) forearc peridotites [10], serpentinized peridotites [48], suprasubduction zone peridotites [46], and Fizeh-Sarami (Oman) harzburgites [12,82] are used for comparison. The primitive mantle (PM) compositions are after McDonough and Sun [90] and Niu [43]. FMM = Fertile MORB mantle.

7.2. Fluid–Peridotite Interactions and Behaviour of Elements during Serpentinization Processes

Serpentinization is a post-magmatic ubiquitous process related to subduction zone peridotites [91,92]. It is believed that the alteration of peridotites to serpentinites changes the rheology and density of mantle rocks [93,94]. The WOC peridotites have experienced pervasive serpentinization, as indicated by their high LOI values (12.4 to 14.5 wt%). Their

LOI values are plotted against the selected major and trace elements to evaluate the behavior of elements and serpentinization stages of the studied peridotites. The negative correlations between Fe_2O_3 and MgO with LOI (Figure 10a,b) suggest that they are affected and slightly depleted during post-magmatic processes (e.g., sea-floor weathering). The fluid-mobile trace elements such as Sr and Ba show positive correlations with LOI (Figure 10c,d), suggesting their addition from slab-derived fluids during serpentinization. The HREE and selected trace elements exhibit a very good positive correlation with Zr (Figure 10e–h), indicating their immobile behavior during serpentinization processes.

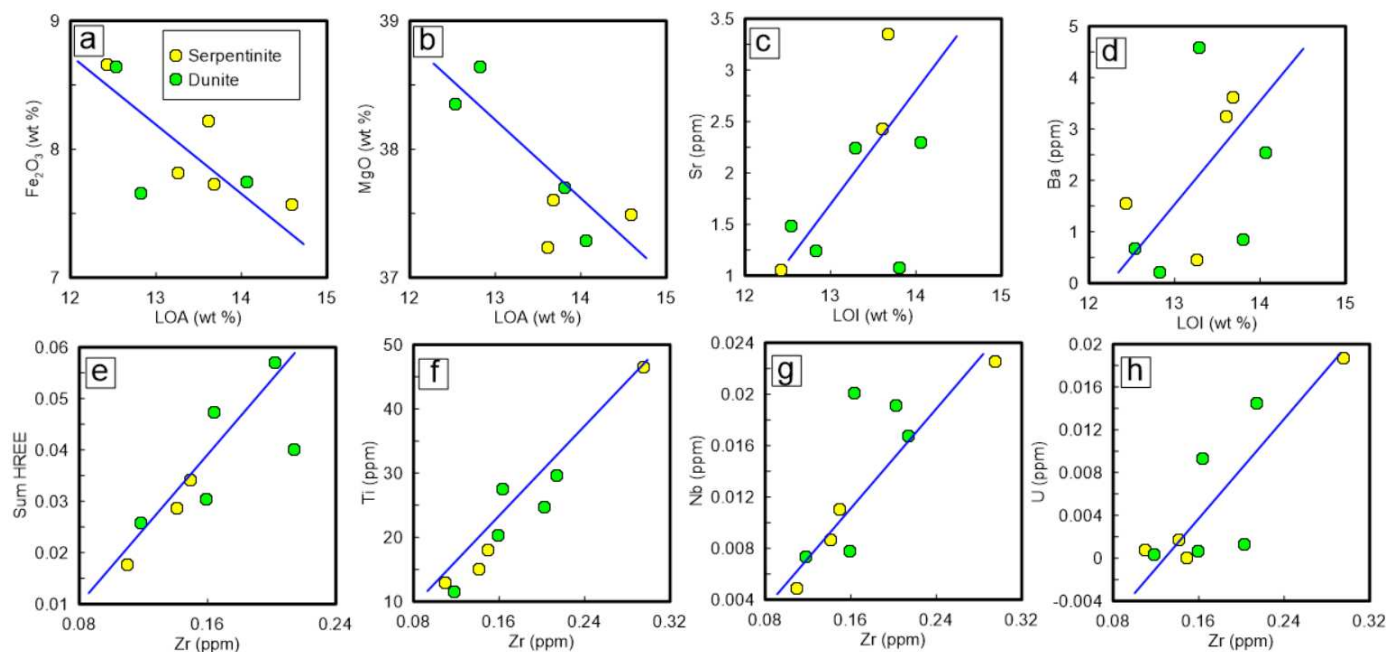


Figure 10. Binary plots showing variations in selected major and trace elements against LOI and Zr for the investigated WOC peridotites.

The studied serpentinized peridotites have very low $\text{Al}_2\text{O}_3/\text{SiO}_2$ (0.005–0.024) and MgO/SiO_2 (0.93–0.99) ratios. This depletion may reflect either MgO loss due to sea-floor weathering at low (<100 °C) temperatures [50] or SiO_2 enrichment during serpentinization in the presence of high fluid–rock ratios [95]. The MgO/SiO_2 ratio below the mantle fractionation array is commonly linked to the alteration process, coupled with magnesium leaching [44,96]. The much lower MgO/SiO_2 in our samples compared to the depleted mantle peridotites [59] reflects the higher degree of alterations. In the diagrams of $\text{Al}_2\text{O}_3/\text{SiO}_2$ versus MgO/SiO_2 (Figure 11a), some of the aforementioned peridotites fall in the overlapping fields of forearc and abyssal peridotites. These rocks show a depletion trend slightly below, but parallel to, the mantle array magmatic depletion or enrichment trend [97,98]. It is commonly observed that, despite the MgO loss, the overall budget of the protolith in terms of major oxides must be preserved during hydration processes [56]. As illustrated by Deschamps et al. [56] (Figure 11c), serpentinization preserves the $\text{SiO}_2/\text{sum oxides}$ ($\text{MgO} + \text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3 + \text{TiO}_2 + \text{CaO} + \text{Cr}_2\text{O}_3 + \text{MnO} + \text{NiO} + \text{Na}_2\text{O} + \text{P}_2\text{O}_5$) ratio (average = 0.81) [99]. The studied serpentinized peridotites have $\text{SiO}_2/\text{sum oxides}$ ratios ranging from 0.79 to 0.86 (average = 0.84). These rocks are plotted close to the theoretical serpentine minerals and are aligned between the average serpentinized peridotite [56] and UB-N [100] international standard compositions (Figure 11c).

In the $\text{Al}_2\text{O}_3/\text{SiO}_2$ versus vanadium (V, ppm) diagram (Figure 11b), the studied peridotites plot in the overlapping fields of abyssal and forearc peridotites; however, they follow the forearc depletion trend [44]. The vanadium concentrations of these peridotites are very low and show positive correlations with the $\text{Al}_2\text{O}_3/\text{SiO}_2$ ratios. Oxygen fugacity greatly affects the compatibility of V. It is moderately incompatible in relatively reducing

conditions (for example, mid-ocean ridge tectonic environments), while it behaves highly incompatibly in the relatively oxidizing suprasubduction zone (SSZ) tectonic setting [10]. Thus, V decreases more rapidly in SSZ tectonic environments as compared to mid-ocean ridge environments. This depletion can be observed in Figure 11c. It is believed that during the subduction of oceanic crust and overlying sediments, a significant amount of hydrous fluids (poor in V) are released from the subducting slabs [101,102]. Serpentine minerals incorporate the fluid-mobile trace elements, particularly the light rare-earth elements (LREEs), which are then recycled at subduction zones [56,58,103–106].

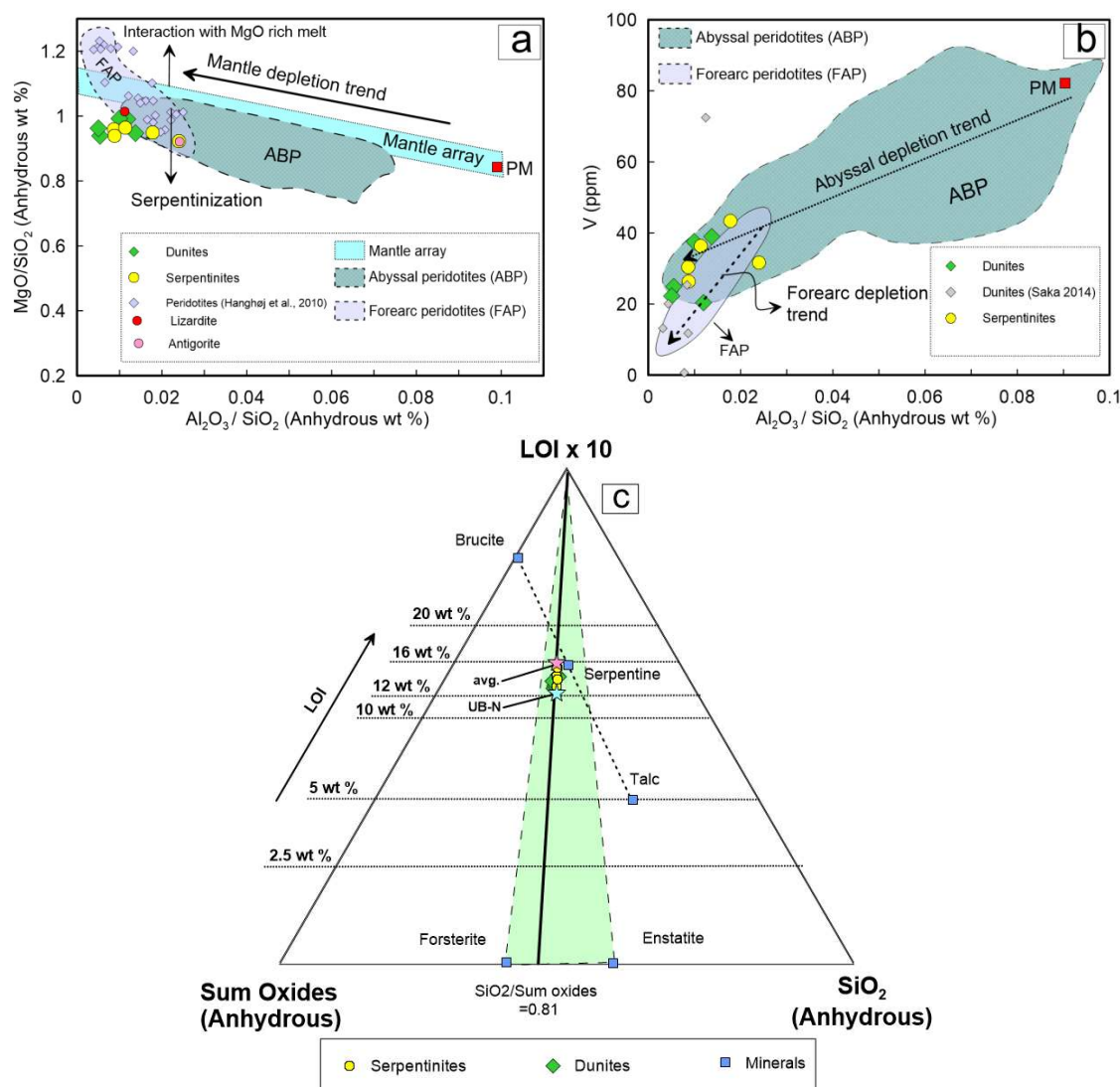


Figure 11. (a) SiO₂ normalized bulk rock Al₂O₃ vs MgO diagram of peridotites from WOC; (b) SiO₂ normalized Al₂O₃ contents plotted against immobile V (ppm). Grey colored samples are overlaid for comparison from Saka et al. [107]. The data for fore-arc peridotites (FAP) are from Parkinson and Pearce [10] and Lian et al. [108]. Abyssal peridotite fields reflect data from Niu [50] and Niu et al. [83]. Forearc depletion trend is from Snow and Dick [44]. Mantle array is from Jagoutz et al. [97] and Hart and Zindler [98]. Primitive mantle values are from Sun and McDonough [45] and McDonough et al. [49]; (c) Ternary plot of SiO₂, sum oxides (MgO + Fe₂O₃ + Al₂O₃ + TiO₂ + CaO + Cr₂O₃ + MnO + NiO + Na₂O + P₂O₅), and LOI x 10 for whole rock major oxides (anhydrous) after Deschamps et al. [56].

During fluid–rock interactions, the LREEs are more readily mobilized than HREE and HFSE, unlike the melt–rock interactions, whereby the REE and HFSE are transported

in almost similar proportions [50]. In the binary plots of La versus Nb (Figure 12a) and Gd/Lu versus Th (Figure 12c), Deschamps et al. [56] described two different positive trends: (i) melt–rock interaction trends, shown by blue arrows, which reflect conjoint enrichments in LREE and HFSE; (ii) fluid–rock interaction trends, shown by orange brown arrows, which reflect enrichments in LREE with a slight increase in HFSE. The studied serpentinized peridotites follow the fluid–rock interaction trends, thereby showing LREE enrichments with a minor increase in the concentration of HFSE (Figure 12a,c), similar to the depleted mantle peridotites from the Wadi Tayin Massif in Oman [59]. Similarly, these samples show a depletion in HREE as compared to LREE (Figure 12b), and are plotted in the overlapping field of global abyssal peridotites and mantle wedge peridotites, suggesting a transition from an extensional to a compressional regime [50]. This systematic relationship indicates that the hydrothermal alterations (fluid-dominated) largely affected LREE contents, while the effect on HREE and HFSE was lesser. The Yb (ppm) versus Ti (ppm) diagram [56] of the studied ultramafic rocks makes useful discriminations between mantle wedge serpentinities (with depleted compositions of Yb and Ti contents), subducted serpentinites (with relatively fertile compositions), and abyssal peridotites (with intermediate compositions). These ultramafic rocks are plotted in the overlapping fields of mantle wedge serpentinities and global abyssal peridotites due to the change from an extensional (e.g., forearc spreading) to a compressional regime of SSZ (Figure 12d).

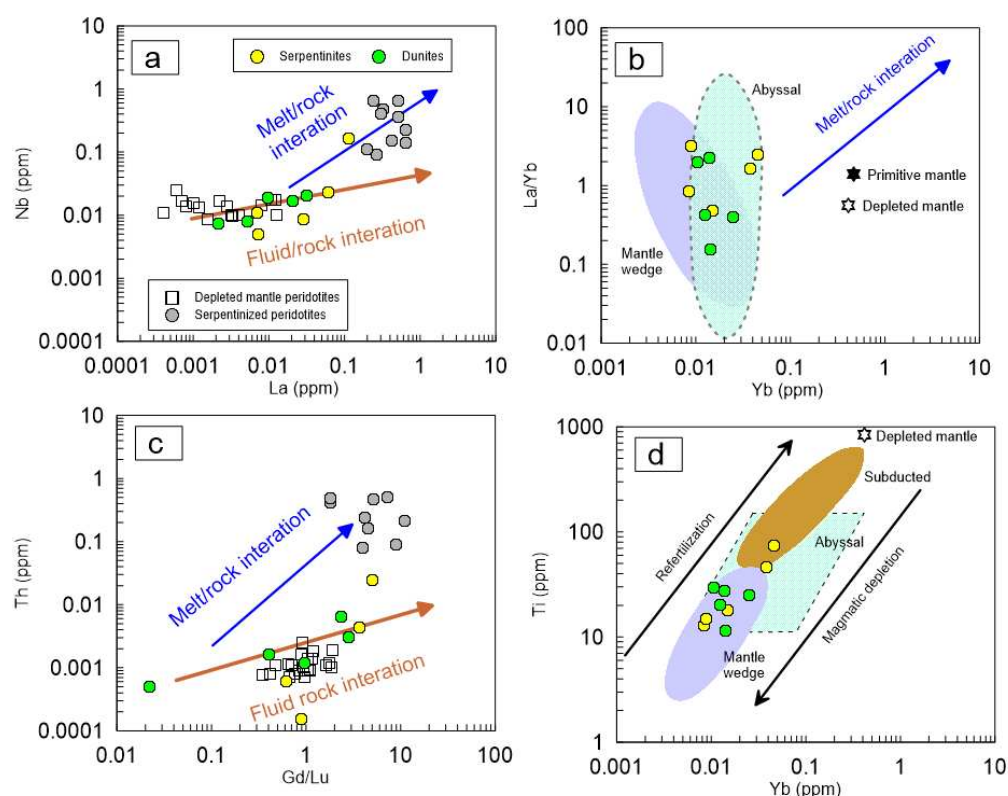


Figure 12. Binary plots of (a) La vs. Nb; (b) Yb vs. La/Yb; (c) Gd/Lu vs. Th; (d) Yb vs. Ti for the studied peridotites. The melt/rock interaction trends (blue lines) and the fluid/rock interaction trends (orange brown lines) in mantle peridotites are from Deschamps et al. [56]. Data of depleted mantle peridotites [59] and serpentinized peridotites [52] are shown for comparison. The fields of abyssal peridotites (turquoise green) are from Niu [50]. Compositional fields of mantle wedge (powder blue) and subducted serpentinites [56] are shown for comparison. Estimated compositions of the depleted mantle [109] and of the primitive mantle [90] are also presented for comparison.

7.3. Formation of Boninitic Magmas during Subduction Initiation

Boninites are subduction-related volcanic and hypabyssal rocks that originate from the re-melting of the already depleted residual mantle after the extraction of tholeiitic melts.

These rocks are an excellent window to the geochemical processes that control trace element mobility in subduction zones [64]. The studied basalts show strikingly concave rare-earth element (REE) patterns (Figure 6c). This REE inventory is interpreted to have been entirely inherited from an LREE-enriched slab component (subduction zone metasomatism) due to the depleted nature of their mantle source [110–112].

According to the International Union of Geological Sciences (IUGS), boninites are geochemically characterized by >52 wt% SiO₂, >8 wt% MgO, and <0.5 wt% TiO₂ [70]. We recalculated our oxides to a major-element sum of 100 % on a volatile-free basis for comparison with worldwide boninite data [42]. Boninites are classified, based on their major element systematics, into low-Ca (CaO/Al₂O₃ < 0.75) and high-Ca (CaO/Al₂O₃ > 0.75) [110]. The Cape Vogel in Papua New Guinea and the Troodos ophiolite in Cyprus are regarded as type localities for low- and high-Ca boninites, respectively. The CaO/Al₂O₃ ratio shows a negative correlation with the mantle source depletion due to the progressive extraction of clinopyroxene during prior melting events [113]. The studied basalts have an SiO₂ of up to 57 wt%, MgO up to 11.99 wt%, TiO₂ < 0.13 wt%, and CaO/Al₂O₃ ratios ranging from 0.01 to 0.69. These geochemical features, together with the lowest CaO/Al₂O₃ ratios, indicate a low-Ca boninitic affinity and confirm that the mantle source for the studied rocks was very depleted. In the TiO₂ vs. MgO diagram (Figure 13b), these rocks are plotted in the boninite field [114], suggesting their derivation in a suprasubduction zone during the initiation of subduction.

According to Pearce and Arculus [115], the above classification of boninites is unusual for rocks with MgO > 8% (both a high SiO₂ and low TiO₂ are prerequisites). If both the Si and Ti are low, the rock should be described as low-Ti basalt (LOTI). If both the Si and Ti are high, the rock should be termed as siliceous, high-Mg basalt (SHMB). The Si₈ and Ti₈ values of boninites [116] were calculated for a common MgO concentration of 8 wt % using the following equations.

$$\text{Si}_8 = \text{SiO}_2 + (\text{MgO} - 8) / 3.82, \text{ for MgO} > 8.$$

$$\text{Ti}_8 = 42 \times \text{TiO}_2 / (50 - \text{MgO}), \text{ for MgO} > 8.$$

Boninites can be divided into three groups: (1) subduction-related (i.e., subduction initiation and arc-basin systems), (2) intraplate, and (3) transitional type. The Izu-Bonin-Mariana subduction-initiation-type (type locality at Chichijima [117]) and Whundo-type boninites [118,119] provide a good example of oceanic subduction-related boninites. The Setouchi-type boninite [120] is the only intra-continental subduction-related example: (2) intraplate (i.e., mantle plume-sourced and subcontinental lithospheric mantle-sourced (SCLM) systems). The Whitney-type boninites [118,121] provide a typical example of plume-related boninite, while Mallina-type boninite [122] relates to SCLM-sourced boninites and (3) transitional type (plume-subduction interactions). Boninites in the northern edge of the Tonga subduction system [123] are of this type [124]. The investigated basalts are similar in chemistry to the IBM forearc, Setouchi proto-arc, and Whundo-type boninites, implying their formation in a subduction-related setting (Figure 13a). They are also plotted in the boninite field of IUGS (Figure 13b) and follow the fractionation trend of IBM proto-arc boninites [117]. These basalts also lie in the field of IUGS boninite and IBM proto-arc boninites (Figure 13c)—with the exception of one sample—that lie close to the Whitney-type boninite [118,121], suggesting their derivation from a mantle plume source.

Boninites are considered significant petrogenetic and paleo-tectonic tracers, particularly when delineating episodes of subduction initiation. However, they can also originate in a non-subduction setting such as intracontinental rifts, e.g., [125,126]. The formation of boninite magma is a process commonly described as second-stage melting [127]. Pearce and Arculus [115] explained the “two-stage” mechanism of boninite formation. The first stage initiates with the melting of a fertile mantle (e.g., lherzolite with 17% clinopyroxene (Cpx)), which results in the residue having less Cpx (e.g., harzburgite with Cpx < 5%), and the melt remains the Cpx-saturated (typically a basalt). The second stage of melting, when coupled

with the addition of fluids, heat and/or decompression, results in the further melting of the residue. Initially, the melt is Cpx-saturated; when Cpx is exhausted (and melts have composition A), the continued melting of the Cpx-poor residue results in Cpx-undersaturated melt with high Si and Mg (composition B) (Figure 13a). The aforementioned two stages of melting commonly occur at different tectonic settings: one at an ocean ridge or mantle plume and the other above a subduction zone. However, these two stages can occur in one tectonic setting (i.e., mantle plume or at a subduction zone [114]). Boninite generation occurs at shallow melting depths (ca. 30–50 km) and low pressure (0.5–2 GPa). This is in agreement with the investigated mafic rocks, whereas the basalts were formed at shallow depths and at low pressures (<0.5 GPa) in the forearc tectonic setting (Figure 13a).

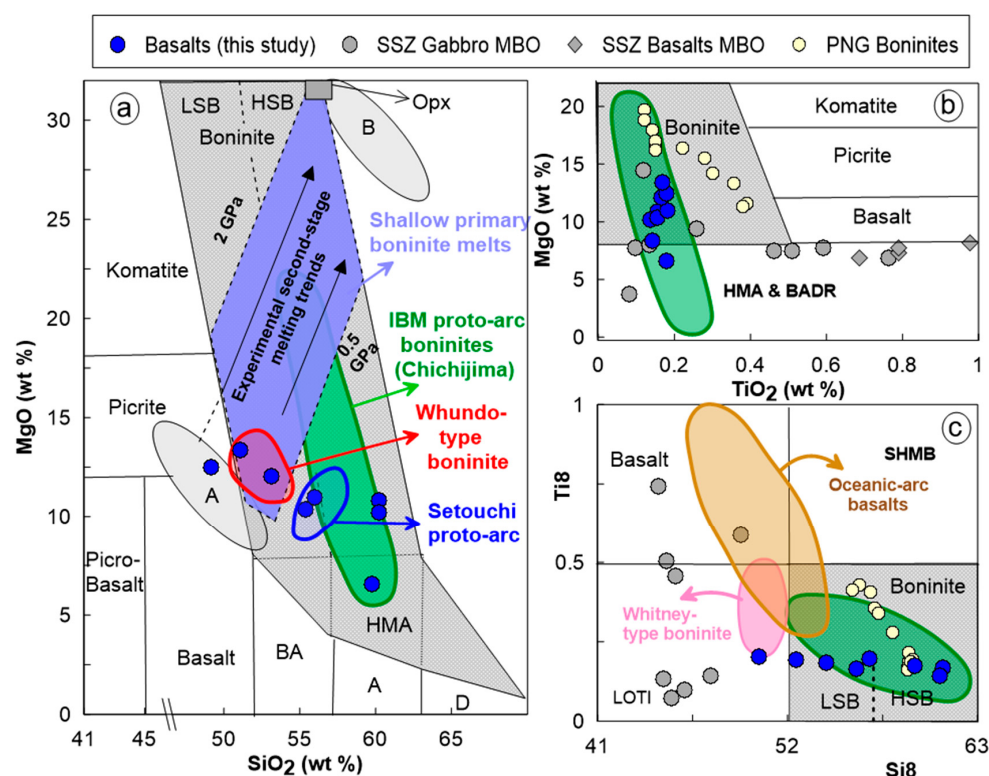


Figure 13. Boninite classification diagrams for identification of basalts. (a) MgO vs. SiO₂; (b) MgO vs. TiO₂; (c) Si8 vs. Ti8 projections, respectively. The geochemical boundaries (after Pearce and Reagan [126]) are parallel to fractionation trends of a typical boninite [117]. For references to the experimental data and further details, see Pearce and Reagan [124]. Data from Kakar et al. [4] and König et al. [64] are shown for comparison. Fields of Izu-Bonin-Mariana proto-arc [117], Whundo-type boninite [118,119], Setouchi protoarc [120], Whitney-type boninite [118,121], and oceanic-arc basalts [124] are presented for comparison. Abbreviations; LSB = low-Si boninite; HSB = high-Si boninite; HMA = high-Mg andesite; BA = basaltic andesite; A = andesite; D = dacite; BADR = basalt-andesite-dacite-rhyolite; SHMB = siliceous high-Mg basalts; LOTI = low-Ti basalts.

7.4. Tectonic Environment for the Formation of Waziristan Ophiolite

Researchers [2,128,129] have recently delineated various tectonic environments for ophiolite formation, which include subduction-related, i.e., supra-subduction zone (SSZ) and subduction-unrelated types. The subduction-related types include back-arc (BA), forearc (FA), back-arc to forearc (BA-FA), and volcanic arc (VA). The subduction-unrelated types include the mid-oceanic ridge (MOR), continental margin (CM), and plume (P). They presented discriminant diagrams that could be used for the evaluation of ophiolitic rocks and to decipher geodynamic provenance. The Nb/Yb–Th/Yb diagram (Figure 14a) is used to isolate subduction-related and subduction-unrelated ophiolites. Most of the

subduction-related (i.e., SSZ) lavas have higher Th/Nb values, because thorium (Th) is subduction-mobile, while niobium (Nb) is subduction-immobile, in most arc systems. Th/Nb ratios in subduction-unrelated lavas are plotted parallel to the MORB-OIB mantle array in the oceanic arc field. Most of the studied peridotites and basalts from WOC are displaced from the MORB-OIB mantle array (Figure 14a) to higher Th/Nb, indicating their generation in an SSZ setting in the presence of slab-derived fluids. In order to evaluate the extent of subduction influence on the SSZ lavas, the investigated ultramafic–mafic rocks are plotted on a Ti/1000–V diagram (Figure 14b) [130]. Ti is a highly incompatible element and is increasingly depleted in melts with the increase in the degree of partial melting. V is highly immobile and behaves very incompatibly in the presence of water under higher oxidizing conditions. Thus, subducted fluids lead to a melting regime that favors both Ti depletion and V enrichment. Ti/V ratios in lava compositions are higher (>20) in MORB, intermediate (10–20) in island arc tholeiites, and lower (<10) in boninites. The studied rocks have low Ti/V ratios (0.31–6.0) and are found in the space of the boninite data (Figure 14b), implying their formation during subduction initiation under higher oxidizing conditions. In Figure 13c of Pearce [131], these rocks plot in the overlapping fields of mid-ocean ridge basalts (MORB) and island arc basalts (IAB), indicating a transitional tectonic style from an extensional (incipient arc stage) setting during subduction initiation to the compressional setting and formation of highly depleted peridotites in the sub-arc mantle during the mature-arc stage (dominant calc-alkaline basalts, Figure 8b and boninite; Figure 13b,c) [48]. The changes from an extensional (formation of FAB or IAB or MORB) to the compressional (formation of boninites or FAB) regime during the formation of ophiolites in the SSZ setting have been discussed in some studies [48,62]. Th_{MORB} vs. Nb_{MORB} systematics can be used for the tectonic interpretation of ophiolitic basalts [132,133]. Most of the studied basalts are plotted in the overlapping fields of immature back-arc and forearc basalts (Figure 14d). However, the WOC peridotites were formed in the sub-arc mantle and emplaced in the forearc setting (Figure 15).

Their protoliths are refractory residues after a wide range (15%–30%) of partial melting (Figure 9), where highly hydrous fluids are available from the subducting slab in the forearc tectonic setting. Therefore, the WOC ophiolite represents a fragment of sub-arc mantle and oceanic crust that originated in an arc-related setting, wherein the depleted or residual peridotites were formed by decompression partial melting as a result of the asthenospheric upwelling during subduction initiation by proto-forearc spreading (extensional setting) (Figure 15a). The resultant melts (melt extraction after the partial melting of peridotites) from the decompression of peridotites have tholeiitic (MORB-like) affinity and were later crystallized as forearc basalts (FAB) (Figure 15a), whereas residual peridotites may have suffered from re-melting in the presence of slab-derived fluids to form boninitic melts and highly refractory peridotites. Therefore, the studied basalts were formed during the subduction initiation due to the extensional force in the forearc region and resemble both island arc basalt and the MORB of the extensional environment; they are chemically similar to forearc basalts and boninites (Figures 13 and 14b). This variation in the composition of the studied basalts is due to a transitional tectonic style from an extensional (MORB and FAB affinities) to a compressional regime (boninites or calc-alkaline basalts) during the SSZ setting.

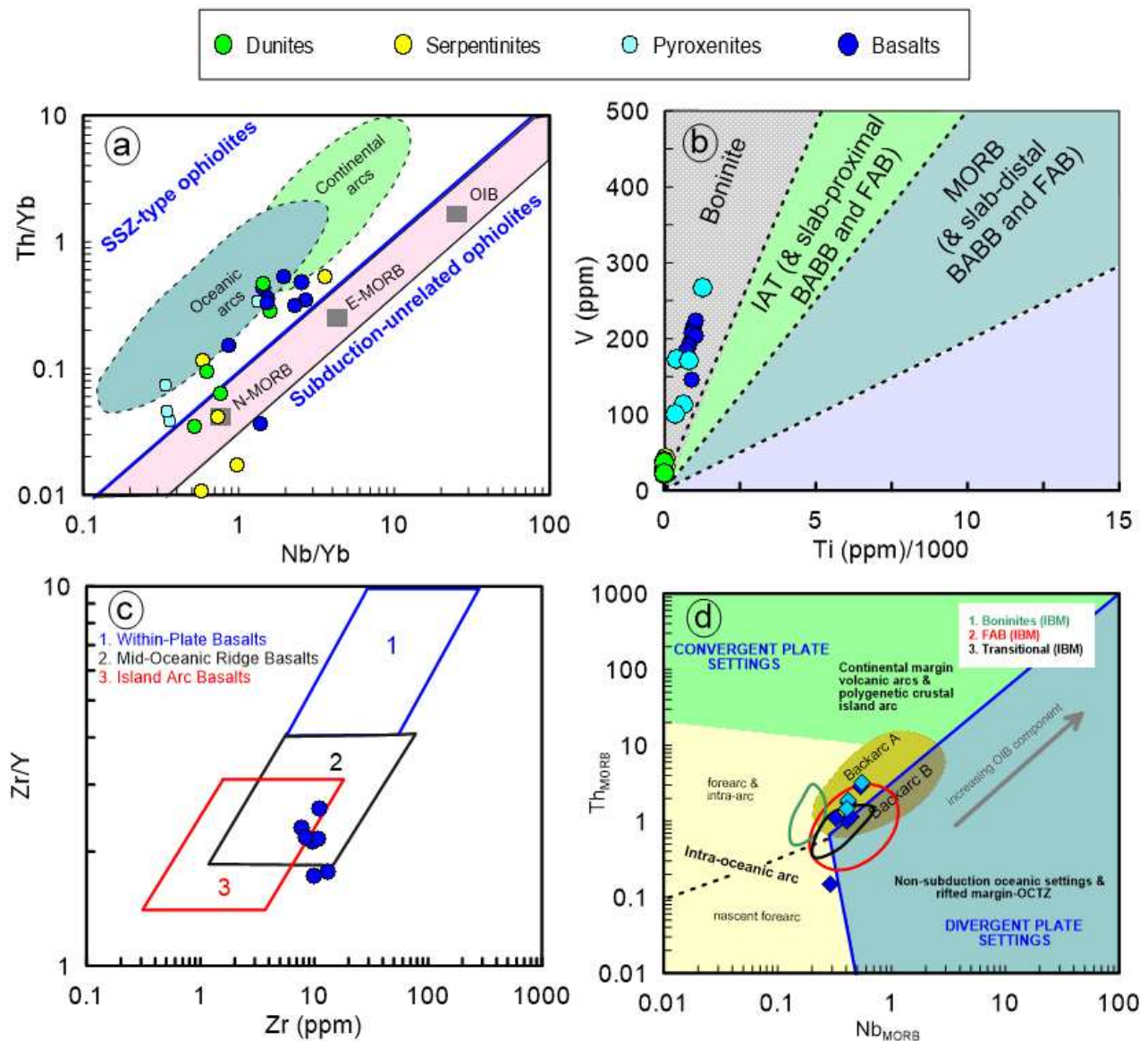


Figure 14. Tectonic discrimination diagrams. (a) Nb/Yb vs. Th/Yb plot [128,129] distinguishing suprasubduction zone (SSZ) ophiolites from mid-oceanic ridge ophiolites. Grey coloured rectangles represent average compositions of normal mid-oceanic ridge basalt (N-MORB), enriched MORB (E-MORB), and ocean island basalt (OIB) on a MORB-OIB mantle array. The fields of continental arcs and oceanic arcs lie above the mantle array; (b) Ti/1000 vs. V plot [129,130] separating MORB, island arc tholeiite (IAT), and boninite magma types; (c) Zr vs. Zr/Y plot [131] showing the fields of within-plate basalts, MORB, and island arc basalts; (d) NbMORB vs. ThMORB plot showing tectonic interpretation for ophiolitic basaltic rocks [132,133]. Back-arc A represents immature intra-oceanic or ensialic back-arc basin basalts (BABBs), whereas back-arc B indicates mature intra-oceanic BABBs. Fields of boninites, FAB IBM, and transitional basalts are from Reagan et al. [67]. MORB normalizing values are from Sun and McDonough [45].

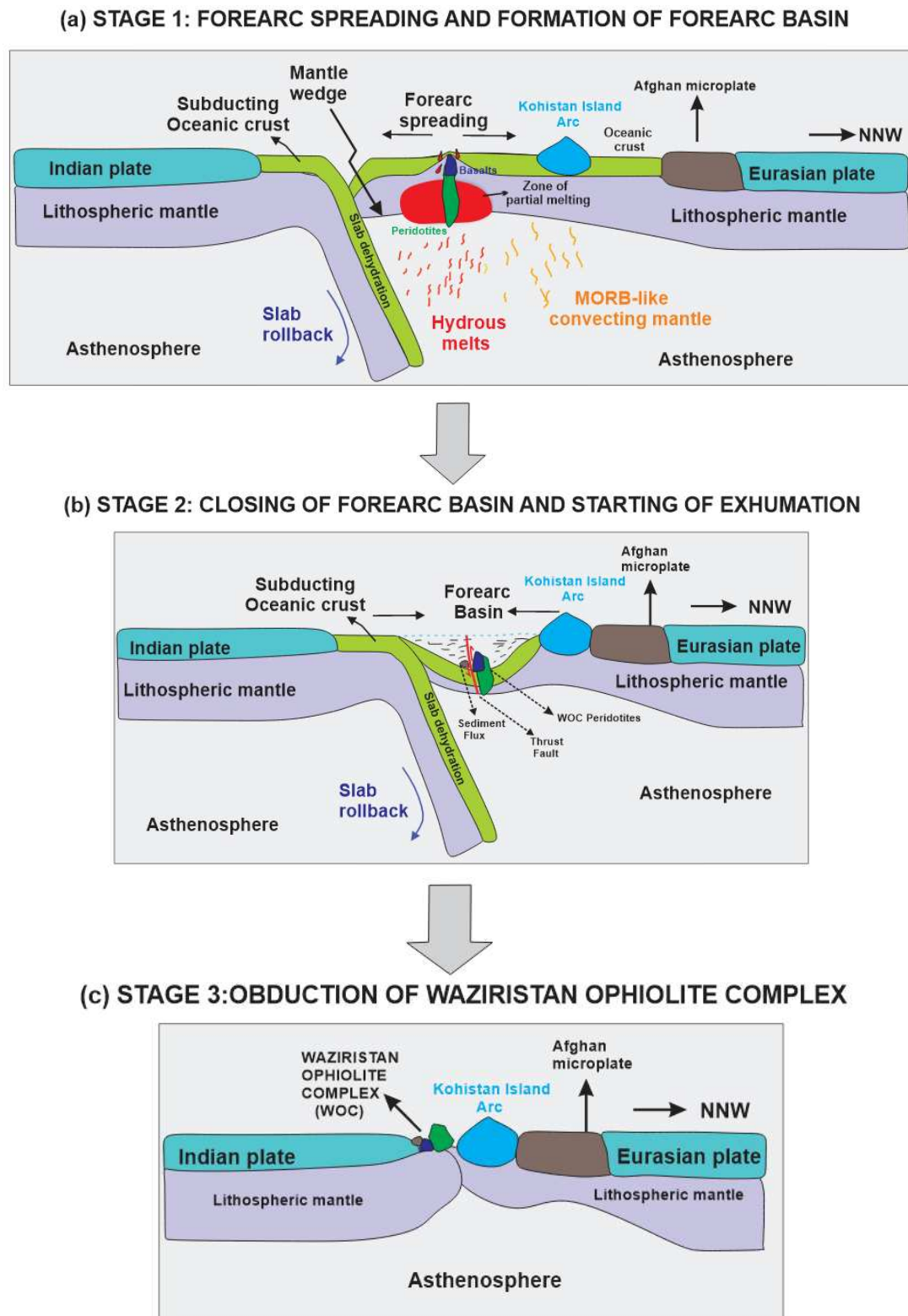


Figure 15. Schematic model (not to scale) showing the formation and emplacement of WOC. (a) Formation of WOC peridotites during forearc spreading (subduction initiation); (b) closing of forearc basin and exhumation of WOC along the thrust fault; (c) obduction of the WOC on the continental crust.

In summary, we propose a three-stage tectonic model for the formation and obduction of the WOC. Forearc spreading and formation of forearc basin (stage I): This stage

demonstrates the formation of the WOC during intra-oceanic subduction initiation triggered by proto-forearc spreading (Figure 15a). The residual peridotites were formed by decompression partial melting (15%–30% melting). The resultant melts, having a tholeiitic (MORB-like) affinity, were later crystallized as forearc basalts (FAB) (Figure 15a). Closing of forearc basin and starting of exhumation of WOC (stage II): This stage explains the closing of the forearc basin and the subsequent exhumation of WOC (Figure 15b). The exhumation of peridotites during subduction is more dominant along thrust faults than exhumation by uplifting processes (Figure 15b). Obduction of WOC (stage III): This stage explains the obduction of the WOC onto the continental crust due to collision between the Indian plate and Afghan microplate (Figure 15c). Finally, the studied peridotites and basalts were generated in the sub-arc mantle and emplaced in the forearc setting.

8. Conclusions

The ultramafic section of the Waziristan ophiolite complex (WOC) mainly consists of peridotites (serpentinized dunites and serpentinites after harzburgites) with subordinate pyroxenites. Peridotites are high in Mg# values (0.88–0.92), have a high degree of serpentinization (LOI, 12.4%–14.5%), have no marked HFSE anomalies, and show an extreme depletion in REE content ($0.03 < (\Sigma\text{REE})_N \leq 0.7$), similar to forearc peridotites in SSZ settings.

Partial melting models based on the major oxides and trace elements concentrations show that the studied peridotites underwent a high degree of partial melting (~15%–25%). Their enrichment in LREE relative to both HREE and HFSE indicates that the peridotites were formed in the forearc tectonic environment, where the depleted peridotites were re-enriched in the metasomatic fluids released from subducting slab.

Hypocrystalline and sub-porphyrific basalts show low Mg# (0.48–0.68) values and display concave REE patterns due to the enrichment of LREE from slab-derived fluids relative to immobile HREE.

The studied basalts exhibit geochemical signatures that transition from forearc basalts to boninites. Their lower Ti/V ratios (4.25–6.10) are similar to typical boninites ($\text{Ti}/\text{V} < 10$), implying their derivation during the initiation of subduction in an SSZ setting (e.g., forearc) characterized by highly subduction-derived fluids under higher oxidizing conditions. Furthermore, their higher Th/Yb ratios, plotted above the N-MORB-OIB mantle array in the oceanic arc field, suggest their origin in a subduction zone setting.

The WOC ophiolite represents a fragment of the sub-arc mantle and oceanic crust that originated in the arc-related setting, wherein the residual peridotites were formed in the sub-arc mantle during the proto-forearc spreading (subduction initiation). The melt extraction after the partial melting of peridotites was crystallized as forearc basalts. The residual peridotites may suffer from re-melting in the presence of slab-derived fluids, forming calc-alkaline basaltic/boninitic melts and highly refractory peridotites in the mature arc stage of the SSZ setting. Consequently, the WOC was formed in the sub-arc mantle and emplaced in the forearc setting.

Supplementary Materials: The following supporting information can be downloaded at <https://www.mdpi.com/article/10.3390/min13030311/s1>, Table S1: Table showing coordinates of the studied samples; Table S2: Table showing concentrations of the analyzed reference materials; Table S3: Table showing major oxides calculated on an anhydrous basis for the studied samples; Table S4: Showing the whole rock major and trace element concentrations of the analyzed samples.

Author Contributions: Conceptualization, R.J., O.A., M.Z.K. and M.T.S.; formal analysis, R.J. and O.A.; writing—original draft preparation, R.J.; supervision, O.A., B.S. and L.A.; writing—review & editing, O.A., B.S., M.Z.K. and M.N.A.; methodology, R.J., O.A. and B.S.; resources, R.J., L.A. and M.T.S.; investigation, R.J., L.A., M.S. and M.T.S.; software, R.J., O.A. and M.S. All authors have read and agreed to the published version of the manuscript.

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