Article

Petrogenesis of Neoproterozoic Ultramafic Rocks, Wadi Ibib–Wadi Shani, South Eastern Desert, Egypt: Constraints from Whole Rock and Mineral Chemistry

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Abstract: This contribution deals with new geology, petrography, and bulk-rock/mineral chemistry of the poorly studied ultramafics of Wadi Ibib–Wadi Shani (WI–WS) district, South Eastern Desert, Egypt. These ultramafics are dismembered ophiolitic rocks that can be subdivided into serpentinites and serpentinitized peridotites. Primary minerals such as olivine and pyroxene are absent in serpentinites, but relics of them occur in serpentinitized peridotites. Pseudomorph after olivine is indicated by common hourglass textures with less mesh, whilst schistose bastites reflect a pyroxene pseudomorph. Chromite can be subdivided into Cr-spinel and Al-spinel. Cr-spinel ranges from chromite to magnesiochromite in composition, whereas Al-spinel belongs to the spinel field. Cr-spinel includes YCr ($Cr/(Cr+Al+Fe^{+3})$), YAl ($Al/(Al+Cr+Fe^{+3})$), and YFe^{+3} ($Fe^{+3}/(Fe^{+3}+Al+Cr)$), similar to forearc peridotite, whilst Al-spinel is more similar to abyssal peridotite, and may be formed during inactivation of subduction processes in proto forearc environments. The main secondary minerals are tremolite, talc, and chlorite—which is subdivided into pycnochlorite and diabantite—and their temperature ranges from 174 to 224 °C. The examined rocks had undergone high partial melting degrees (>25%), as indicated by the Cr# of their unaltered cores (Cr-spinel, >0.6), whole rocks (Al_2O_3 , SiO_2 , CaO, and MgO), trace and REEs, depleted Na_2O , Al_2O_3 , and Cr_2O_3 of clinopyroxene, and high forsterite content ($Fo = 100 \text{ Mg}/(\text{Mg} + \text{Fe})$, av. 95.23 mol%), consistent with forearc settings.

Keywords: serpentinitization; element mobility; partial melting; forearc affinity

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1. Introduction

Neoproterozoic ultramafic rocks are commonly distributed in central and southern sectors of the Egyptian Eastern Desert (ED) in the northern Nubian Shield. The Nubian Shield is considered the western side of the Arabian Shield, both of which are juvenile crusts forming the Arabian–Nubian Shield (ANS) of the northern East African Orogeny (EAO) [1]. These rocks constitute 5.3% of Egypt's crystalline outcrops, mostly as allochthonous nappes [2–6]. The field and geochemical signatures of the ultramafic magma provide clues as to the different tectonic settings. They are either older, dismembered ophiolitic fragments—which are partially or completely metamorphosed to serpentinite, mostly consisting of chromitites and magnesites of mid-ocean ridges or supra-subduction settings—or younger, unmetamorphosed ones [7,8]. The latter, with an age > 640 Ma [9], encompass fresh, concentrically arc-zoned dunites and clinopyroxenites of Alaskan type, mostly consisting of PGEs, Ni–Cu sulfide deposits, and fresh layered intrusions hosting Fe–Ti oxides [10,11].

Ophiolites are slices of the oceanic lithosphere thrust on the continental plates, which help in recognizing the tectonic processes in the mantle [12]. Serpentinites, carbonatized

serpentinites, talc-carbonates, and listwaenite series (carbonate-rich, silica-carbonate, and birbirites) rocks are the main alteration products of the ophiolitic harzburgite/dunite fragments, due to interaction with CO_2 - and SiO_2 -rich fluids [13]. These processes are widely observed along faults and shear zones. Ultramafic rocks are enriched with magnesium and iron silicate minerals; therefore, carbonation processes take place via the hydrolysis of these minerals, through evicition of Si and combination of these cations with carbonates [3,14]. The tectonic setting of Egyptian ophiolitic mantel rocks (ultramafics) is still a subject of debate; some authors suggest mid-ocean ridge (MOR), while others suggest supra-subduction zone (SSZ) [4,15].

MORs form abyssal mantle rocks of anhydrous melting at low degrees (5–15%), whilst more than 20% represents a high degree of melting, forming refractory or depleted rocks in SSZs [16]. The melting degree of the first type depends on the interaction between mantle rocks and melts, as well as the temperature and pressure at melting depth. Conversely, the melting degree of the latter represents a complex process, and depends on the interaction between melts and fluids generated from the subducted slab [17]. In this paper, new geological, mineralogical, and geochemical data are discussed, with a view to detecting the hydrothermal effects, origins and tectonic setting of the studied ultramafic rocks.

2. Geological Setting

The Neoproterozoic Era was an important period of crustal growth—especially in the ANS [1], where the Gondwana supercontinent merged. Ophiolites are oceanic lithosphere remnants formed during the Tonian–Cryogenian in mid-ocean ridges (MORs) or through successive subduction and accretion in supra-subduction zone (SSZ) settings during the closing of the Mozambique Ocean [1–8,18]. In Egypt, the ANS Pan-African ophiolites comprise serpentinites from the ED's central and southern sectors (CED and SED, respectively), extending across the Sudanese border (Figure 1a,b). Neoproterozoic ophiolitic rocks of the Wadi Ibib–Wadi Shani (WI-WS) district represent the southwestern extension of the largest Gerf nappe—a dismembered ophiolite sequence covered by metamorphosed, lowered units of ultramafic, metagabbro, and metasedimentary rocks (Figure 1c).

Figure 1. Cont.

Figure 1. (a) Regional geological map of Egypt. (b) Distribution of Tonian ophiolite rocks [15]. In addition, location of the examined area, and (c) detailed geological map of Wadi Ibib (WI)–Wadi Suwawrib (WS) [19].

The examined ophiolitic ultramafic rocks are represented by the dominant serpentinite and less serpentinitized peridotites, which are usually metamorphosed to greenschist facies. Field observations reveal that the examined ultramafic rocks cover $\sim 100 \text{ km}^2$, forming an extended N–S ridge with a high relief (950–1100 m above sea level) at the north–south side of G. Abu Hadeida. They are exposed as mountainous blocks, which are mainly massive and grey–black in color. Furthermore, they exhibit a closely spaced system of joints trending NE–SW and NW–SE along the fault plane. They are thrust over the metasediments (Figure 2a), as indicated by dip directions, with some shearing and tightness of foliation close to the contact. These metasediments are fine-grained, highly foliated, laminated, and exhibit alternating mafic-rich and -poor layers of schists (Figure 2b). Ultramafics are partially to extensively sheared and highly altered to foliated (asbestiform), buff colored, talc–carbonate, carbonate-rich (listwaenite), and magnesite rocks—especially along fault planes and shear zones. These alteration products (listwaenite) occur either as patches or as dike-like with high relief relative to the host (serpentinite)—especially along fault planes.

Figure 2. (a) Thrust contact between serpentinites and metasediments, and (b) pod of talc-carbonate within serpentinites along the shear zone.

3. Materials and Methods

Representative samples were crushed and pulverized using a vibration mill. Loss of ignition (LOI) was measured by the difference in weight after ignition. Whole-rock analysis (major, trace elements, and rare earth elements) of 25 samples was carried out via inductively coupled plasma emission spectrometry (ICP-ES) at Acme Lab, Vancouver, Canada. Detection limits for trace elements and major oxides were 0.01–0.5 ppm and 0.001–0.04 wt.%, respectively. The analytical precision, as calculated from replicate analyses, was 0.5% for major oxides, and varied from 2% to 20% for trace elements. Some samples were selected and analyzed for major elements (as a test) using fused pellets prepared as described in [20], using lithium tetraborate as a flux at the laboratories of the Nuclear Materials Authority (NMA), Cairo, Egypt. The mineral chemistry was carried out at the Microscopy and Microanalyses Facility, University of New Brunswick (UNB), Fredericton, New Brunswick, Canada. Samples were analyzed with a JEOL JXA-733 Electron Microprobe, equipped with ds spec and dQant32 automation (Geller Micro Analytical Labs, Canada). An accelerating voltage of 15 kV and a probe current of 30 nA were used. Peak counting times were 30 s (Al and Si), 90 s (Ti, V, Cr, and Cs), and 120 s (Na, Mg, K, Ca, Mn, Fe, and Ni). High and low backgrounds were counted for one-half of the peak counting times.

4. Petrography

Generally, the examined mantle units can be divided into serpentinites and serpentinized peridotites, based on their mineralogical composition. Petrographic examination of 31 samples was carried out at NMA using a polarizing microscope (Olympus bx53). Serpentinites are commonly sheared (carbonatized), and exhibit pseudomorphic textures after olivine and pyroxene minerals. Pseudomorph after olivine is indicated by common hourglass textures with less mesh, whilst bastite reflects pyroxene pseudomorph. Primary minerals such as olivine and pyroxene are completely replaced by antigorite, magnetite, and carbonate minerals. Antigorite occurs as dense sherds of fibro-lamellar, irregular aggregates, ranging from colorless to pale green, fractured, and occupied by iron oxides and carbonates. Abundance of bastites suggest pyroxene pseudomorph, providing evidence for harzburgite protolith (Figure 3a). Scattered patches of carbonate are the main component in the examined serpentinites. Opaque minerals are essentially represented by magnetite (Figure 3b). Magnetite is disseminated as fine, black, anhedral crystals.

Figure 3. Photomicrographs of serpentinites—(a) sherds of antigorite (Atg) forming a bastite texture after pyroxene; (b) patches of carbonates (Cb) associated with disseminated magnetite (Mag)—and serpentinitized peridotites: (c) fibro-lamellar antigorite enclosed between olivine (Ol) crystals; (d) perfect veinlet of chrysotile (Ctl); (e) replacement of olivine by antigorite; (f) schiller structure of orthopyroxene (Opx); (g) two porphyroblasts of green spinel (Al-Spl) engulfing apatite (Ap); and (h) fresh core of Cr-spinel (Cr-Spl) rimmed by secondary Cr-magnetite (Cr-Mag).

On the other hand, serpentinitized peridotites are essentially composed of serpentines (antigorite and chrysotile) with variable relics of orthopyroxene, clinopyroxene, olivine,

and spinels. Tremolite, carbonates, and talc are the main secondary minerals. Fibro-lamellar, irregular aggregate of antigorites form asbestiform and hourglass, reflecting their olivine pseudomorph (Figure 3c). Chrysotile commonly occurs as veinlets crosscutting olivine crystals (Figure 3d). Olivines reveal significant cracks, and are replaced partially to completely by serpentine, magnetite, and talc along their peripheries, forming iddingsite (Figure 3c–e). Orthopyroxene is replaced by serpentine, chlorite, tremolite, and magnetite, forming schiller structures (Figure 3f). Magnetite and red and green spinels are the main opaque minerals (Figure 3g). Red spinels occur as euhedral, unfractured grains, and are commonly zoned with fresh Cr-spinel cores (red) rimmed by Cr-magnetite (black in color, Figure 3h).

5. Results

5.1. Mineral Chemistry

Electron microprobe analysis (EMPA) results of the examined olivine are listed in Table 1. They contain forsterite (Fo = 100 Mg/Mg + Fe) ranges from 91.94 to 98.13, with a mean value of 95.23 mol%. The Fo content of the examined olivine is higher than those reported in [21] (88–92 mol%), and similar to those of Egyptian ophiolitic peridotites (89–96 mol%) [22]. Moreover, they possess NiO and MnO contents (0.28–0.92; 0.087–0.92 wt.%) similar to olivine mantle array (plot in and close to mantle array field; Figure 4a).

Table 1. Representative microprobe analysis of olivine.

Serpentinized Peridotites																				
No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
SiO ₂	41.79	41.98	40.97	39.12	40.12	42.15	40.66	41.31	42.33	40.66	40.29	40.36	41.69	41.36	40.59	42.32	42.77	41.36	40.62	41.68
TiO ₂	0.01	0.02	0.01	0.03	0.01	0.02	0.01	0.02	0.01	0.01	0.01	0.02	0.01	0.02	0.02	0.02	0.03	0.02	0.01	0.02
Al ₂ O ₃	0.00	0.00	0.04	0.05	0.02	0.01	0.00	0.00	0.01	0.03	0.26	0.46	0.45	0.72	0.52	0.22	0.18	0.15	0.36	0.24
Cr ₂ O ₃	0.08	0.07	0.06	0.06	0.06	0.04	0.03	0.09	0.08	0.08	0.03	0.26	0.39	0.58	0.64	0.72	0.67	0.82	0.53	0.47
FeO*	3.75	4.92	5.88	7.32	5.46	5.73	4.98	4.31	1.69	1.87	3.92	3.75	3.12	4.19	3.72	3.62	2.96	4.06	4.31	3.59
MnO	0.67	0.59	0.43	0.79	0.99	0.09	0.63	0.49	0.18	0.17	0.61	0.69	0.54	0.48	0.46	0.29	0.27	0.43	0.58	0.42
MgO	52.51	51.66	52.19	51.94	52.14	50.30	52.56	52.71	55.22	55.92	51.36	52.72	52.13	51.66	52.92	51.17	52.46	52.33	52.12	52.62
NiO	0.35	0.32	0.29	0.36	0.42	0.29	0.28	0.36	0.34	0.37	0.33	0.89	0.92	0.55	0.62	0.41	0.35	0.29	0.37	0.44
CaO	0.01	0.01	0.02	0.02	0.03	0.01	0.01	0.01	0.01	0.02	0.02	0.04	0.05	0.06	0.03	0.02	0.03	0.05	0.07	0.09
Na ₂ O	0.01	0.01	0.01	0.02	0.03	0.03	0.02	0.03	0.06	0.05	0.02	0.03	0.02	0.03	0.03	0.03	0.02	0.06	0.04	0.07
K ₂ O	0.01	0.01	0.01	0.02	0.02	0.02	0.01	0.01	0.02	0.02	0.01	0.02	0.04	0.01	0.01	0.01	0.01	0.03	0.02	0.05
Total	99.19	99.59	99.92	99.73	99.30	98.69	99.08	99.35	99.95	99.19	99.25	99.24	99.36	99.73	99.56	98.83	99.75	99.60	99.03	99.69
Si	1.01	1.01	0.99	0.96	0.98	1.03	0.99	1.00	1.00	0.98	1.00	0.98	1.00	0.98	1.02	1.02	1.00	0.99	1.00	1.00
Ti	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Al	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.01	0.02	0.02	0.01	0.01	0.00	0.01	0.01
Cr	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.01	0.01	0.01	0.01	0.02	0.01	0.01
Fe(ii)	0.08	0.10	0.12	0.15	0.11	0.12	0.10	0.09	0.03	0.04	0.08	0.08	0.06	0.08	0.08	0.07	0.06	0.08	0.09	0.07
Mn	0.01	0.01	0.01	0.02	0.02	0.00	0.01	0.01	0.00	0.00	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Mg	1.89	1.86	1.88	1.90	1.90	1.82	1.90	1.90	1.95	2.00	1.89	1.91	1.87	1.86	1.90	1.84	1.86	1.88	1.89	1.88
Ni	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.02	0.02	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Ca	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Fo	95.48	94.35	93.64	91.94	93.50	93.91	94.35	95.13	98.13	98.00	95.28	95.48	96.20	95.17	95.75	95.89	96.66	95.40	94.99	95.90
Fa	3.83	5.04	5.92	7.27	5.49	6.00	5.01	4.36	1.69	1.84	4.08	3.81	3.23	4.33	3.78	3.81	3.06	4.15	4.41	3.67
Tp	0.69	0.61	0.44	0.80	1.01	0.09	0.64	0.51	0.18	0.17	0.64	0.71	0.57	0.50	0.47	0.31	0.28	0.45	0.60	0.44

Unfortunately, pyroxene minerals are observed only in serpentinized peridotites. Orthopyroxenes are typically enstatite (Supplementary Materials, Table S1), whilst clinopyroxenes (Supplementary materials Table S2) are classified as augites based on nomenclature [23] (Figure 4b). Orthopyroxenes contain (En_{89.65–93.18}, Fs_{6.13–9.23}, Wo_{0.59–2.62}) and Mg# ranges from 89.65 to 93.18, with a mean value of 91.03, and low contents of Al₂O₃ and TiO₂ (1.22–3.23; 0.01–0.04, respectively), similar to forearc peridotites [24]. Clinopyroxenes (En_{49.89–61.71}, Fs_{1.94–5.33}, Wo_{34.89–46}) contain CaO ranges from 17.87 to 23.14 wt.% and low TiO₂ contents (0.02–0.08 wt.%), reflecting their non-alkaline affinity [25]; in addition, they have Al₂O₃ contents of more than 1 wt.%, suggesting their magmatic affinity [26]. Orthopyroxenes and clinopyroxenes have Cr₂O₃ less than 1 wt.%, similar to those in forearc settings (Figure 4c,d).

Figure 4. (a) Fo vs. NiO binary variation of olivines. Fields of olivine mantle array [27], ophiolite [22], forearc peridotite (FAP) [24], and layered intrusions [7]. (b) Enstatite (En)–ferrosilite (Fs)–wollastonite (Wo) nomenclature diagram of pyroxene minerals [23]. (c) Na₂O vs. Al₂O₃ and (d) Cr₂O₃ vs. Al₂O₃ binary diagrams [24]. Field of forearc peridotite (FAP) and abyssal basin peridotite (ABP) obtained from [24], and back-arc peridotite (BAP) [28].

Spinel is predominantly composed of opaque minerals, and reveals heterogenetic composition; it can be distinguished into Cr-spinel (Supplementary Materials, Table S3) and Al-spinel (Supplementary Materials, Table S4). Al-spinel is found in the picotitic field, whilst Cr-spinel straddles the chromite field, and both are related to ophiolitic spinels [29,30] (Figure 5a). Furthermore, Cr-spinel can be classified into chromite and magnesochromite, whereas Al-spinel is classified as spinel according to the Cr# versus Mg# binary discrimination diagram [31] (Figure 5b). Al-spinels contain high contents of Al₂O₃ (33.55–38.55, av. 35.77 wt.%), MgO (12.37–16.12 av. 14.84 wt.%), and Mg# (Mg/(Mg+Fe²⁺)) (0.55–0.69, av. 0.64 wt.%), and low contents of FeO (11.98–20.16, av. 16.66 wt.%), Cr₂O₃ (28.48–34.17, av. 31.46 wt.%), and Cr# (Cr/(Cr+Al)) (0.34–0.39; av. 0.37), compared to those of Cr-spinel. In addition, they are found in the mantle array field, suggesting their magmatic nature (Figure 5c). The Cr# contents of Cr-spinel are similar to those of the Egyptian Eastern Desert [32]. Cr-spinels contain YCr (Cr/(Cr+Al+Fe³⁺), YAl (Al/(Al+Cr+Fe³⁺)) and YFe³⁺ (Fe³⁺/(Fe³⁺+Al+Cr)), similar to forearc peridotites [32], whilst the contents of Al-spinel are similar to those of abyssal peridotites, which may be formed during inanition of subduction processes in proto-forearc environments (Figure 5d).

Figure 5. Spinel variation diagrams: (a) Cr-Al-Fe³⁺ ternary diagram [29,30]; (b) Cr/(Cr+Al) vs. Mg/(Mg+Fe²⁺) [31]; (c) Cr₂O₃ vs. Al₂O₃ binary diagram [32]; and (d) Cr-Al-Fe³⁺ ternary diagram [18].

EPMA results of serpentine minerals are shown in the Supplementary Materials (Table S5). Chrysotile exhibits low Al₂O₃ content (1.29–3.79, Figure 6a) and high MgO (43.36–47.35 wt.%) and SiO₂ (44.67–49.35 wt.%) relative to the antigorite phase in serpentinites (4.33–5.66 wt.%; 41.69–45.55 wt.%; 43.18–45.78 wt.%, respectively) and serpentinized peridotites (4.55–5.44 wt.%; 41.69–43.77 wt.%; 43.79–45.89 wt.%, respectively), which is consistent with the findings of [33] (Figure 6b–d). The chrysotile phase has a chemical affinity similar to that of olivine, whilst antigorite comes from orthopyroxene and olivine, reflecting a dunite protolith for the former, and both harzburgite and dunite for the latter phase (Figure 6e). The abundance of antigorite rather than chrysotile in the examined ultramafic rocks reflects prograde metamorphism [33,34].

Chlorite represents one of the main alteration products of the primary minerals (pyroxenes) in serpentinized peridotites. EPMA results show that the examined chlorites contain SiO₂ ranges from 33.98 to 37.45 wt.%, Al₂O₃ from 19.45 to 21.89 wt.%, MgO from 24.62 to 2.45 wt.%, Si from 6.05 to 6.52 apfu, Al^{iv} from 1.47 to 1.94 apfu, Fe# from 0.22 to 0.28, and Mg# from 0.72 to 0.78 (Supplementary Materials, Table S6). On the Si (apfu) vs. Fe²⁺+Fe³⁺ (apfu) binary diagram [35], the examined chlorite is classified as pycnochlorite and diabantite (Figure 7a). Al^{iv} can be used to determine the chlorite temperature [36].

Using the equation in [37] ($T = 106.2 \cdot Al^{iv} + 17.5$), the temperature of chlorite ranges from 174 to 224 °C.

Figure 6. Serpentine binary variations: (a) MgO vs. Al₂O₃; (b) MgO vs. FeO; (c) MgO vs. NiO; (d) MgO vs. MnO; and (e) Cr₂O₃ vs. NiO. Fields of antigorite and chrysotile are from [38]; serpentine after olivine and orthopyroxene fields are from [39].

Likewise, chlorite and tremolite represent the main alteration products of pyroxene. The examined tremolites (serpentinized peridotites) have SiO₂ ranges from 48.34 to 59.81 wt.%, MgO from 23.33 to 24.71 wt.%, and CaO from 13.17 to 14.63 wt.% (Supplementary Materials, Table S7). They are classified as tremolite according to [40] (Figure 7b). They have Ti contents ranging from 0.003 to 0.014 apfu, with a mean value of 0.0036 apfu, reflecting their metamorphic nature. Furthermore, greenschist facies of the examined rocks are indicated by low Na and K contents of tremolite (av. 0.003 apfu) [41].

The investigated magnetites (serpentinites and serpentized peridotites) were composed mainly of high FeO* contents (av. 93.76), whilst their TiO₂ (av. 0.055), MnO (av. 0.42), CaO (av. 0.017), Na₂O (av. 0.027), K₂O (av. 0.015), Cr₂O₃ (av. 0.29), NiO (av. 0.18), and ZnO (av. 0.031) contents are less than unity (Supplementary Materials, Table S8). They possess ulvöspinel of less than 0.5 mol%, based on [42]. They are classified mainly as magnetites

by using the FeO-TiO₂-Fe₂O₃ ternary diagram (Figure 7c). In addition, the abundance of magnetites—either as patches, or filling fractures as veinlets—reflects the high degree of alteration of primary minerals, such as olivine [43].

Figure 7. (a) Nomenclature diagram of chlorite from [35]; (b) TSi (apfu) vs. Mg# discrimination diagram [40]; and (c) FeO-TiO₂-Fe₂O₃ discrimination diagram of magnetite and ilmenite.

EPMA of the examined talcs reveals that they consist mainly of SiO₂ ranges from 56.35 to 60.99 wt.%, Na₂O from 12.77 to 15.44 wt.%, Al₂O₃ from 18.47 to 23.45 wt.%, Mg# from 13.84 to 24.34, K# from 0.001 to 0.015, and Fe# from 75.65 to 86.16 (Supplementary Materials, Table S9). It is widely known that the talc forms as an alteration product after primary minerals (olivine and serpentine), suggesting high-temperature metamorphism.

5.2. Whole-Rock Geochemistry

The whole-rock (major, trace, and REEs) compositions of serpentinites and serpentized peridotites are given in Table 2. Loss on ignition (LOI) varies from 5.27 to 11.5 wt.% for serpentinites, and from 4.16 to 10.7 wt.% for serpentized peridotites, indicating a various and extensive degree of hydration and serpentinization. Therefore, bulk major oxides were recalculated to 100 wt.% based on an anhydrous to compensate for the variable serpentinization effect [18,44]. The average contents of major oxides in serpentinites and serpentized peridotites reveal that the TiO₂, Al₂O₃, MnO, Na₂O, K₂O, and P₂O₅ contents are less than 1 wt.%. In addition, the low CaO (av. 1.48 and 1.09 wt.%, respectively)

and Al_2O_3 (av. 0.76 and 0.59 wt.%, respectively) contents of the examined serpentinites and serpentinitized peridotites are similar to forearc peridotites and Pan-African serpentinites [18,45]—especially those in the Egyptian Eastern Desert [8,19,22]—suggesting their refractory origin [19] (Figure 8a,b).

Table 2. Abundances of major (wt.%), trace, and rare earth elements (ppm) in ultramafic rocks.

	Serpentinites											
	IA1	IA2	IA3	IA4	IA5	IA6	IA7	IA8	IA9	IA10	IA11	IA12
SiO ₂	43.10	42.02	42.18	43.57	41.63	41.14	43.45	42.66	40.64	43.06	40.93	42.09
TiO ₂	0.01	0.01	0.02	0.02	0.01	0.01	0.01	0.01	0.01	0.01	0.03	0.01
Al ₂ O ₃	0.65	0.31	0.48	0.56	0.31	0.77	0.31	0.28	1.82	0.58	1.16	1.36
MgO	44.72	43.44	44.10	44.30	44.86	44.73	45.36	46.36	46.39	43.65	42.94	42.77
CaO	1.06	1.77	1.78	1.35	2.04	1.85	0.45	0.39	1.72	1.64	2.05	2.14
MnO	0.10	0.12	0.09	0.08	0.14	0.13	0.10	0.16	0.14	0.15	0.14	0.09
Fe ₂ O ₃	10.29	12.21	11.29	10.05	10.94	11.28	10.24	10.07	9.15	10.83	12.68	11.49
Na ₂ O	0.02	0.05	0.02	0.02	0.03	0.04	0.04	0.03	0.08	0.02	0.01	0.02
K ₂ O	0.02	0.02	0.01	0.01	0.01	0.02	0.01	0.02	0.01	0.03	0.04	0.01
P ₂ O ₅	0.02	0.02	0.01	0.01	0.04	0.01	0.02	0.01	0.03	0.01	0.01	0.01
LOI	9.10	8.40	11.50	10.21	10.80	9.30	5.27	9.10	8.10	8.70	8.23	8.40
Ba	4.24	4.93	5.66	5.41	6.22	5.17	5.83	6.92	4.51	5.40	3.61	5.53
Rb	0.39	1.43	0.52	0.59	0.82	0.91	0.81	1.36	1.24	1.45	1.56	0.59
Sr	5.91	4.84	4.56	2.39	2.87	2.97	3.81	3.52	3.11	3.32	2.91	2.66
Cs	1.12	0.14	0.11	1.15	0.17	0.27	0.24	0.25	1.33	0.41	0.45	1.49
Ga	1.96	0.82	0.75	0.86	1.02	1.09	1.13	1.79	0.82	0.84	1.63	1.48
Ta	1.22	1.36	0.92	0.81	0.41	0.32	0.35	0.21	0.27	0.17	0.18	0.99
Nb	3.12	2.24	2.19	1.27	0.37	1.41	0.49	2.15	2.09	1.72	1.65	1.15
Hf	0.12	0.23	0.16	0.15	0.11	0.10	0.09	0.10	0.01	0.01	1.12	1.77
Zr	2.75	1.32	1.09	1.02	2.59	0.52	1.75	0.87	2.12	1.29	1.15	1.25
Y	2.59	1.66	1.71	0.79	0.87	1.95	0.98	1.54	0.42	2.34	2.29	1.45
Th	1.05	0.06	0.05	0.04	0.03	1.06	0.09	0.08	1.05	0.03	0.04	1.05
U	0.02	0.01	0.01	0.01	0.02	0.05	0.01	0.02	0.08	0.01	0.01	0.08
Ni	2459.00	2510.00	2422.00	1265.00	2456.00	2325.00	1382.00	2319.00	1566.00	1376.00	2435.00	1455.00
Co	148.00	92.00	132.00	139.00	142.00	99.00	106.00	109.00	122.00	146.00	152.00	158.00
Sc	17.00	18.00	10.00	17.00	8.00	9.00	5.00	14.00	16.00	10.00	11.00	9.00
V	46.00	136.00	42.00	99.00	32.00	129.00	25.00	34.00	22.00	119.00	14.00	25.00
Cu	15.00	28.00	14.00	19.00	38.00	17.00	25.00	32.00	30.00	15.00	12.00	13.00
Pb	4.00	3.00	3.00	4.00	3.00	2.00	1.00	2.00	1.00	4.00	4.00	3.00
Zn	66.00	46.00	39.00	45.00	52.00	62.00	71.00	79.00	82.00	33.00	30.00	49.00
Bi	0.11	0.15	0.19	0.24	0.39	0.39	0.29	0.21	0.13	0.08	0.16	0.25
Cd	0.20	0.20	0.40	0.20	0.20	0.30	0.10	0.10	0.30	0.10	0.20	0.20
Sn	0.91	0.86	1.37	1.22	1.09	1.19	0.75	0.78	0.61	1.50	3.00	2.00
W	1.30	1.75	1.62	1.35	1.50	1.77	1.31	0.97	0.86	1.39	1.45	0.75
Mo	1.51	2.71	2.53	2.22	3.44	3.63	3.94	3.15	3.81	5.66	5.24	3.45
As	1.88	0.75	0.68	0.91	0.04	0.05	0.09	0.76	0.89	1.09	1.15	1.12
Sb	0.31	1.39	0.49	1.45	0.51	0.59	1.15	0.17	0.09	0.06	1.08	0.19
La	0.65	0.58	1.44	0.16	0.12	0.79	0.66	0.15	0.13	0.88	0.56	1.27
Ce	0.87	0.95	0.34	0.27	0.22	0.14	0.99	0.85	0.35	0.33	0.91	0.89
Pr	0.21	0.32	0.27	0.39	0.45	0.35	0.66	0.59	0.32	0.35	0.11	0.42
Nd	0.88	0.82	0.79	0.72	1.39	1.49	1.52	1.69	1.75	0.92	1.29	0.32
Sm	0.39	0.36	0.45	0.56	0.47	0.58	0.51	0.33	0.37	0.27	0.42	0.37
Eu	0.14	0.19	0.17	0.22	0.37	0.26	0.16	0.75	0.69	0.07	0.09	0.32
Gd	0.52	0.45	0.49	0.59	0.69	0.28	0.32	0.35	0.46	0.51	0.53	0.41
Tb	0.12	0.19	0.14	0.16	0.42	0.49	0.62	0.78	0.52	0.93	0.17	0.08
Dy	0.57	0.63	0.69	0.61	0.15	0.99	0.37	0.15	0.31	0.02	0.19	0.22
Ho	0.12	0.14	0.17	0.27	0.39	0.44	0.52	0.77	0.75	0.92	1.34	0.19
Er	0.39	0.31	0.46	0.49	0.32	0.39	0.72	0.61	0.22	0.15	0.27	0.66
Tm	0.08	0.09	0.12	0.19	0.29	0.45	0.35	0.52	0.59	0.74	0.79	0.81
Yb	0.39	0.44	0.48	0.51	0.57	0.62	0.46	0.59	0.11	0.05	0.65	0.12
Lu	0.06	0.08	0.09	0.15	0.29	0.39	0.07	0.45	0.09	0.07	0.05	0.61
LREEs	3.00	3.03	3.29	2.10	2.65	3.35	4.34	3.61	2.92	2.75	3.29	3.26
HREEs	2.39	2.52	2.81	3.19	3.49	4.31	3.59	4.97	3.74	3.46	4.08	3.42
LREEs/HREEs	1.26	1.20	1.17	0.66	0.76	0.78	1.21	0.73	0.78	0.79	0.81	0.95
ΣREEs	5.39	5.55	6.10	5.29	6.14	7.66	7.93	8.58	6.65	6.21	7.37	6.68
Eu/Eu*	1.00	1.40	1.10	1.20	2.00	1.80	1.10	6.70	5.10	0.60	0.60	2.50
(La/Yb) _{cn}	1.10	0.90	2.00	0.20	0.10	0.90	1.00	0.20	0.80	11.90	0.60	7.20
(Gd/Yb) _{cn}	1.10	0.80	0.80	0.90	1.00	0.40	0.60	0.50	3.30	8.30	0.70	2.80
(La/Sm) _{cn}	1.00	1.00	2.00	0.20	0.20	0.90	0.80	0.30	0.20	2.10	0.80	2.20

Table 2. Cont.

Serpentinized Peridotites													
	AP1	AP2	AP3	AP4	AP5	AP6	AP7	AP8	AP9	AP10	AP11	AP12	AP13
SiO ₂	45.33	45.51	46.50	44.71	47.96	44.97	44.19	43.64	44.08	44.42	44.83	47.77	47.22
TiO ₂	0.01	0.01	0.01	0.01	0.03	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Al ₂ O ₃	0.55	0.82	0.71	0.38	1.27	0.67	0.79	0.44	0.20	0.42	0.39	0.30	0.49
MgO	43.61	43.46	42.88	43.17	39.03	43.02	42.69	43.01	44.01	45.02	45.19	42.52	43.15
CaO	2.05	1.52	1.42	1.24	0.02	0.96	1.49	0.75	0.65	0.93	0.95	0.99	1.35
MnO	0.10	0.10	0.17	0.15	0.20	0.14	0.09	0.14	0.11	0.15	0.14	0.09	0.10
Fe ₂ O ₃	8.28	8.53	8.25	10.24	11.43	10.13	10.61	11.93	10.85	9.00	8.43	8.26	7.61
Na ₂ O	0.03	0.02	0.02	0.04	0.02	0.05	0.07	0.05	0.06	0.03	0.01	0.01	0.02
K ₂ O	0.01	0.01	0.01	0.01	0.01	0.01	0.03	0.01	0.01	0.01	0.01	0.03	0.03
P ₂ O ₅	0.02	0.01	0.02	0.03	0.02	0.02	0.02	0.01	0.01	0.01	0.03	0.02	0.01
LOI	10.70	6.00	6.22	7.46	4.16	6.90	5.30	6.40	5.00	5.82	5.90	7.12	8.12
Ba	9.70	10.00	9.00	5.00	6.00	3.00	4.00	4.00	5.00	4.00	10.00	6.00	5.00
Rb	0.67	1.12	0.19	0.25	1.75	1.85	0.49	1.22	0.27	0.35	0.27	0.33	1.40
Sr	4.52	3.62	4.91	5.21	2.34	3.61	2.93	2.81	3.24	5.11	4.26	3.78	3.99
Cs	0.41	0.19	0.11	0.13	0.22	0.32	0.18	0.27	0.36	0.14	0.28	0.37	0.49
Ga	1.75	2.36	3.72	3.92	4.11	4.56	3.22	1.39	1.98	4.97	2.48	3.47	5.64
Ta	1.22	1.36	0.86	0.55	0.45	0.36	0.24	0.26	0.22	0.33	0.44	0.66	0.99
Nb	1.25	1.77	1.84	2.11	0.46	1.57	1.57	0.92	1.19	1.15	0.97	1.13	1.69
Hf	0.91	1.25	1.19	0.87	0.15	0.11	0.13	1.22	1.45	1.69	1.89	1.25	1.10
Zr	1.55	1.66	1.99	1.88	1.77	1.33	1.44	1.66	1.99	1.45	2.10	2.20	1.88
Y	2.69	1.89	2.99	2.78	2.56	2.36	2.45	0.88	0.99	0.87	0.69	0.74	0.55
Th	0.09	0.08	0.07	0.06	0.11	0.15	0.19	0.22	0.07	0.05	0.07	0.08	0.09
U	0.02	0.01	0.02	0.03	0.02	0.01	0.02	0.02	0.01	0.04	0.03	0.04	0.02
Ni	1590.0	1756.0	1816.0	1975.0	2632.0	1453.0	1415.0	1356.0	1466.0	2341.0	2566.0	1586.0	1439.0
Co	99.00	133.00	170.00	122.00	109.00	95.00	87.00	76.00	132.00	145.00	121.00	102.00	75.00
Sc	10.00	11.00	6.00	5.00	22.00	6.00	9.00	7.00	14.00	22.00	5.00	4.00	9.00
V	49.00	69.00	75.00	99.00	106.00	110.00	59.00	67.00	84.00	93.00	87.00	118.00	37.00
Cu	10.00	24.00	35.00	49.00	57.00	22.00	10.00	92.00	14.00	19.00	35.00	66.00	42.00
Pb	2.00	4.00	6.00	2.00	10.00	12.00	11.00	3.00	7.00	5.00	6.00	4.00	4.00
Zn	34.00	28.00	45.00	64.00	49.00	24.00	72.00	69.00	86.00	91.00	40.00	39.00	54.00
Bi	0.36	0.35	0.24	0.11	0.36	0.58	0.45	0.16	0.13	0.69	0.45	0.36	0.78
Cd	0.10	0.20	0.30	0.50	0.60	0.10	0.20	0.30	0.50	0.60	0.80	0.20	0.40
Sn	1.00	2.00	1.00	2.00	2.00	1.00	1.00	1.00	1.00	2.00	1.00	2.00	2.00
W	1.55	1.99	1.66	1.45	1.33	1.69	1.75	1.56	1.44	1.22	1.66	1.88	1.48
Mo	2.60	4.20	4.90	5.60	3.40	1.50	1.80	1.40	2.30	4.20	6.20	5.70	3.10
As	1.23	1.09	0.66	0.78	0.34	0.56	0.78	1.59	1.89	2.45	2.46	2.15	2.14
Sb	0.12	0.14	0.47	0.39	1.58	1.26	1.11	1.10	0.78	0.78	0.65	0.73	0.42
La	0.77	0.69	0.89	0.45	0.36	0.11	0.45	0.45	0.78	0.66	0.88	0.99	0.77
Ce	0.99	0.68	0.45	0.47	0.78	0.66	0.78	0.86	0.65	0.78	0.48	0.78	0.89
Pr	0.66	0.28	0.32	0.77	0.84	1.24	1.35	0.37	0.45	0.92	0.75	1.55	0.69
Nd	0.12	0.09	0.07	0.08	0.05	0.52	0.65	0.73	0.09	0.24	0.45	0.98	1.48
Sm	0.25	0.29	0.38	0.69	0.75	0.45	0.51	0.24	0.55	0.66	0.66	0.77	0.89
Eu	0.46	0.29	0.27	0.05	0.14	0.29	0.87	0.69	0.34	0.23	0.14	0.11	0.08
Gd	0.03	0.02	0.14	0.05	0.04	0.15	0.18	0.27	0.32	0.42	0.56	0.88	0.64
Tb	0.27	0.05	0.03	0.08	0.02	0.04	0.03	0.28	0.68	0.44	0.33	0.11	0.28
Dy	0.03	0.19	0.14	0.13	0.23	0.35	0.29	0.15	0.44	0.19	0.36	0.45	0.56
Ho	0.17	0.26	0.19	0.62	0.22	0.07	0.05	0.14	0.66	0.79	0.69	0.84	0.46
Er	0.14	0.06	0.13	0.02	0.07	0.16	0.32	0.15	0.24	0.17	0.36	1.26	0.45
Tm	1.06	0.05	0.04	1.03	0.12	0.14	1.06	0.03	0.04	0.05	0.36	0.45	0.22
Yb	0.12	0.04	0.03	0.11	0.02	0.05	0.06	0.03	0.13	0.22	0.14	0.58	0.69
Lu	0.11	0.12	0.13	0.24	0.06	0.18	0.15	0.08	0.07	0.14	0.15	0.22	0.36
LREEs	2.79	2.03	2.11	2.46	2.78	2.98	3.74	2.65	2.52	3.26	3.22	5.07	4.72
HREEs	2.39	1.08	1.10	2.33	0.92	1.43	3.01	1.82	2.92	2.65	3.09	4.90	3.74
LREEs/HREEs	1.17	1.87	1.92	1.05	3.02	2.08	1.24	1.46	0.86	1.23	1.04	1.03	1.26
ΣREEs	5.18	3.11	3.21	4.79	3.70	4.41	6.75	4.47	5.44	5.91	6.31	9.97	8.46
Eu/Eu*	9.00	5.00	3.00	0.40	1.00	2.70	7.20	8.30	2.30	1.30	0.70	0.40	0.30
(La/Yb) _{cn}	4.30	11.70	20.00	2.80	12.20	1.50	5.10	10.10	4.10	2.00	4.20	1.20	0.80
(Gd/Yb) _{cn}	0.20	0.40	3.80	0.40	1.60	2.40	2.40	7.30	2.00	1.50	3.20	1.20	0.70
(La/Sm) _{cn}	1.90	1.50	1.50	0.40	0.30	0.20	0.60	1.20	0.90	0.60	0.80	0.80	0.50

The SiO₂/MgO ratio of the studied rocks ranges from 0.87 to 1.22, similar to the ophiolitic peridotites in [45] (Figure 8c). In terms of the CaO-Al₂O₃-MgO ternary diagram, the studied rocks are located in the dunite field, with a few samples in harzburgite (Figure 8d). Lack of alteration of clinopyroxene is associated with dissolution of Ca [27] in the examined rocks; therefore, they have very low CaO contents, below the values of the depleted (DM, 3.5 wt.%) [46] and primitive mantle (PM, 3.7 wt.%) [47]. Furthermore, the Al₂O₃ contents of the studied rocks are less than that of the PM (Al₂O₃ ca. 4.5 wt.%) [47]. Likewise, the average MgO content is high relative to PM composition, suggesting that the mantle melting is more than 20%. Conversely, SiO₂ and Fe₂O₃ concentrations are lower than the values of the PM.

Figure 8. (a) Al_2O_3 of the examined rocks compared to Pan-African serpentinites [22] and others from [48]; (b) CaO vs. Al_2O_3 of bulk rock [49]; (c) Al_2O_3 vs. SiO_2/MgO diagram [45]; and (d) CaO - Al_2O_3 - MgO ternary diagram [50].

The incompatible trace elements of the examined mantle rocks are depleted in high-field-strength elements (HFSEs)—such as Zr (0.52–2.75 ppm), Hf (0.01–1.89 ppm), Nb (0.37–3.12 ppm), and Ta (0.17–1.36 ppm)—and low-field-strength elements (LFSEs), including Rb (0.19–1.85 ppm), Ba (3–10 ppm), and Sr (2.34–5.91 ppm) (Table 2). Multiple elements of the primitive mantle (PM)-normalized diagram [51] (Figure 9a) show a strong negative Ta anomaly and slight enrichment of LFSEs relative to HFSEs, which are consistent with SSZ geochemical affinity [52]. Furthermore, they reveal a slightly positive Pb anomaly, similar to forearc peridotites [44]. This may be related to the effects of percolation of fluid during serpentinization processes [18]. They also possess high concentrations of transition elements, such as Ni and Co. Ni (1265–2510, av. 1982 ppm) and Co (92–158, av. 128 ppm) contents are higher in serpentinites than in serpentinized peridotites (Ni, av. 1825; av. Co, 114 ppm). Wide variation of Ni may be related to the dissemination of Ni in ferromagnesian minerals by serpentinization processes [53]. In addition, Ni^{2+} substitutes Mg^{2+} in olivine, and holds with Mg^{2+} even during and after serpentinization processes.

Figure 9. (a) Trace elements of the examined ultramafics normalized to the primitive mantle; and (b) chondrite-normalized rare earth elements [51].

Furthermore, we noticed a narrow range of Co contents, which may be related to the substitution by Fe^{+2} —due to the similarity of ionic radii—and Mg^{+2} [53]. REEs are variable even in the same rock units, and reveal zigzag patterns (Figure 9b). The examined serpentinites are depleted in REEs (av. $\Sigma\text{REEs} = 6.6$ ppm), since their light rare earth element (LREE) contents range from 0.2 to 2.2, and their heavy rare earth element (HREE) contents range from 0.5 to 8.3 [51]. Likewise, the examined serpentinitized peridotites contain ΣREEs ranging from 3.11 to 9.97 ppm, and slightly less fractionated LREEs ($(\text{La}/\text{Sm})_{\text{N}} = 0.2\text{--}1.9$) relative to HREEs ($(\text{Gd}/\text{Yb})_{\text{N}} = 0.2\text{--}7.3$), which is consistent with forearc serpentinites [18].

6. Discussion

6.1. Protolith Changes and Element Mobility

Slight changes in the bulk major oxides are estimated from the $(\text{TiO}_2 + \text{MgO} + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3 + \text{CaO} + \text{MnO} + \text{K}_2\text{O} + \text{Na}_2\text{O} + \text{P}_2\text{O}_5)/\text{SiO}_2$ ratios [18]. The calculated sum oxides/ SiO_2 ratio (1.08–1.46) is similar to those of [54]. The investigated rocks represent some of the metamorphosed Egyptian ultramafic rocks with variable amounts of serpentine, tremolite, and talc, and fewer chlorite minerals. The presence of antigorite and talc suggest high temperature [55]. REEs and HFS elements are considered immobile, especially during alteration, in comparison with LFSEs—such as Cs, Rb, K, Sr, and U—even during low alteration [18]. Serpentinites represent as an alteration products of low temperature of ultramafic rocks, making some changes of the protolith chemical composition by water addition [3,18,56]. In addition, some major oxides—such as CaO and SiO_2 [49]—can be remobilized during serpentinization processes. According to [49], the completely serpentinite rocks are more depleted in CaO relative to partially serpentinitized rocks. Some physical properties of the protolith—such as density and magnetism—are also changed by serpentinization processes. Protoliths have higher density and lower magnetism than serpentinites [56], due to magnetite formation by serpentinization, as represented by the following equation:

There are two types of serpentinites based on the major serpentine minerals: (1) chrysotile is formed by retrograde metamorphism of primary minerals (olivine, orthopyroxene, and clinopyroxene) at low temperatures (<300 °C), and (2) antigorite serpentinites are formed by prograde metamorphism of lizardite and chrysotile at temperature ranges from 320 °C and 390 °C, and become stable above 390 °C [56]. Lizardite represents the most common serpentine mineral, whereas chrysotile is the least common [34]. They crystallize at identical temperature and pressure, but in different modes, where chrysotile precipitates a void

space from a liquid state, whilst lizardite precipitates from a solid state on the surface of olivine [56]. Transition of lizardite or chrysotile to antigorite within water-saturated open systems takes place according to the following equation:

Major oxides (Al_2O_3) and some trace elements—especially HFSEs (e.g., Zr, Th, Nb, Hf)—of serpentinites and serpentinized peridotites exhibit little change, tending to be immobile during the different metamorphic conditions, whilst LFSEs are expected to be mobile [13,57]. Fluid mobile elements (FMEs), encompasses LFSEs (Rb, Sr, Ba, U & Cs) and semi-volatile elements (e.g., Pb) are enriched in serpentinites relative to other of the same compatibility either serpentinites developed at supra-subduction or MOR [29]—due to high concentrations of these elements as a result of fluid–rock interaction leverage [17].

Serpentinization of mantle rocks is achieved via the formation of serpentine minerals and the addition of H_2O at theoretical contents of up to $12.38\text{ wt.}\% \pm 2.99\text{ wt.}\%$ [18]. For this reason, the degree of serpentinization can be assessed by LOI. According to [57], samples with LOI of more than 6 wt.% are considered to be altered. LOI reached up to 11.5 wt.% in the studied serpentinites, and 10.7 wt.% in serpentinized peridotites, supporting the role of hydrothermal alteration. There was a varying degree of serpentinization processes in all samples, where LOI varied from 4.16 to 11.5 wt.%, reflecting moderately to completely serpentinized samples.

6.2. Partial Melting Processes

Whole-rock geochemistry and mineral chemistry of primary mantle minerals can be used to manifest different processes affecting the protolith, including partial melting and metasomatism [44,58]. It is noticeable that the examined rocks contain low concentrations of TiO_2 , ranging from 0.01 to 0.03 wt.%, suggesting a high degree of partial melting [59].

On the other hand, systematic changes in primary minerals (olivine, pyroxene, and spinel) can be used as a key to deduce historical processes such as metasomatism and melting degree [60]. It is noteworthy that Cr-spinels are more resistant primary minerals and can be used to infer the degree of partial melting [60]. The examined Cr-spinels of serpentinized peridotites have high Cr# (more than 6; av. 0.754), $\text{TiO}_2 < 0.3$, and Mg# (av. 0.42), reflecting a high degree of partial melting (>35%) (Figure 10a) that developed in a forearc setting [22,38,61,62]. In terms of Cr# vs. TiO_2 in Cr-spinel, they exhibit depleted mantle, and the examined sample was located in the fresh Cr-spinel of the Egyptian Eastern Desert and forearc fields (Figure 10b).

The Cr# content of both spinel types (especially Cr-rich) can be used to detect the degree of partial melting in the host rocks [62]. The degree of partial melting in spinel mantle can be calculated using the equation described in [60] ($F = 10 \times \text{Cr\#} + 24$), where F is the melting degree (wt.%). Based on this empirical equation, the examined rocks had experienced partial melting degrees ranging from 13.32 to 14.63% for Al-spinel, and from 17.34 to 24% for Cr-spinel, which is consistent with forearc affinity [61]. Moreover, the analyzed Al-spinels contained Al_2O_3 ranges from 33.55 to 38.55 wt.%, and Cr# from 0.34 to 0.39, which may be related to decompression melting in the asthenosphere (Al content decreases with increases in the degree of partial melting) according to [17,38].

In addition, depletion of Na_2O (av. 0.12 wt.%), K_2O (av. 0.013 wt.%), Al_2O_3 (av. 2.1 wt.%), Cr_2O_3 (av. 0.628 wt.%), and TiO_2 (av. 0.048 wt.%) in the examined Cpx (Figure 4c,d), and the high forsterite (Fo = 91.94–98.13, Figure 4a) content of the analyzed olivine relics, reflect depleted mantle that had been subjected to high partial melting in a forearc setting [38].

6.3. Protolith and Tectonic Setting

The presence of primary orthopyroxene, olivine, and spinel relics in the examined rocks, as well as enrichment of transition elements such as Ni (1265–2632 ppm) and Co (75–170 ppm), reflect their mantle origin. Bulk major contents of SiO_2 and Al_2O_3 are

immobile during alteration processes relative to CaO and LFSEs; therefore, they can be used as indices of mantle depletion [44,61]. The tectonic setting of the ultramafic rocks is still a subject of debate. Some of the earliest authors suggested a mid-ocean ridge origin for the Egyptian ophiolites, based on the geochemistry of their basaltic units [63,64]. Geochemical studies of the Egyptian ophiolites recognize a supra-subduction zone, which have a geochemical nature of spreading centers in back-arc basin [65] or fore-arc basin [8,22].

Al_2O_3 concentration in the bulk-rock chemistry and mineral chemistry of spinel, olivine, and pyroxene can be used to determine typical tectonic settings via various discrimination diagrams [66].

Harzburgite–dunite complex protoliths are indicated by bastite and mesh textures, in addition to high contents of compatible elements such as Ni and Co. Ultramafics of supra-subduction zone affinity (forearc) are characterized by low TiO_2 contents (<0.05 wt.%), MgO/SiO_2 ratios (<1.4), Al_2O_3 contents (<0.78 wt.%), and $\text{Al}_2\text{O}_3/\text{SiO}_2$ ratios (<0.02), according to [17,49]. The $\text{Al}_2\text{O}_3/\text{SiO}_2$ ratios of the examined rocks show very narrow variance, ranging from 0.004 to 0.04, with an average of 0.014—lower than that of PM composition (~ 0.1) [67], but close to that of depleted mantle harzburgite (~ 0.02) [63]—suggesting that they underwent partial melting before serpentinization processes [17]. Conversely, the average of MgO/SiO_2 ratio of these rocks ranged from 0.81–1.14, with an average of 0.99—higher than that of PM (~ 0.85). $\text{Al}_2\text{O}_3/\text{SiO}_2$ and MgO/SiO_2 ratios were not affected during hydration processes or peridotite metamorphism [46]. The studied samples lie above the trend of mantle terrestrial arrays and abyssal peridotites straddling the forearc field (Figure 10a). In addition, they have $\text{Al}_2\text{O}_3/\text{SiO}_2$ (0.004–0.04) and MgO/SiO_2 (av. 0.99) ratios similar to those of forearc peridotites [61]. Among the HFSEs, the studied peridotites are variably depleted in Nb, consistent with an SSZ geochemical signature [52]. According to the Zr vs. Nb binary diagram in [68], the examined rocks plot among depleted mantle sources (Figure 10b).

On the other hand, the mineral chemistry of Cr-spinel can be suggestive of a forearc setting. The ternary Cr–Al–Fe diagram [18] (Figure 5d), Mg# vs. Cr# [1] (Figure 10c), and Cr# vs. TiO_2 [69] (Figure 10d) reveal a forearc signature. In addition, there is a positive relationship between the Cr# content of spinels and the partial degree of melting or melt/rock reaction, where those with $\text{Cr\#} > 6$ are formed in supra-subduction (mostly forearc) environments with a high degree of partial melting, whilst those with $\text{Cr\#} < 6$, with tholeiitic magma, are formed in abyssal zones such as mid-ocean ridges (MORs) [66,70]. The average Cr# of the examined Cr-spinels was more than 0.6 (av. 0.689), which is consistent with those of modern forearc serpentinites [22]. Furthermore, high Fo content (av. 95.23 mol%) also reflects their forearc origins [22] (Figure 4a). The clinopyroxene compositions of the examined ultramafic rocks plot in the field characteristic of forearc settings, due to depletion of Al_2O_3 , Na_2O , and Cr_2O_3 [70] (Figure 4c,d). Likewise, orthopyroxenes are moderate in Al_2O_3 (<3.23 wt.%) and low in Na_2O (<0.04 wt.%), TiO_2 (<0.04 wt.%), and Cr_2O_3 (<0.92 wt.%), consistent with forearc peridotite orthopyroxenes [24,28] (Figure 4e).

The current results of the examined ultramafics suggest that they are relics of the oceanic lithosphere that were emplaced in a forearc environment (Figure 11).

Figure 10. (a) $\text{Al}_2\text{O}_3/\text{SiO}_2$ vs. MgO/SiO_2 in the studied ultramafic samples. Abyssal peridotite, primitive mantle, and depleted mantle are from [44,46,67], respectively. Mariana forearc and forearc are from [44,61], respectively. The thick yellow line represents a terrestrial array [71]. (b) Zr vs. Nb diagram from [68]; (c) Mg# versus Cr# binary diagram from [1]; partial melting degree is from [72]. (d) 100Cr# vs. TiO_2 of the examined spinels (Cr- and Al-spinel). Boninites, MORB, forearc peridotites, and depleted and highly depleted peridotites are obtained from [28,73–75], respectively. The pink field represents fresh Cr-spinels of the Egyptian Eastern Desert [22].

6.4. Geothermometry

Different thermometer methods can be used to deduce the temperature of equilibrium of the examined serpentinized ultramafics (Supplementary Materials, Table S10). These methods include olivine–spinel thermometry using the calibrations described in [76,77], as well as Al in orthopyroxene–olivine–spinel thermometry [75]. The obtained average temperature of the studied serpentinized peridotites using the olivine–spinel thermometry [77] method was 781 °C, which is lower than the average temperature (852 °C) calculated using the calibration described in [76]. On the other hand, the average temperatures of the studied serpentinized peridotites calculated using the calibrations described in [75] (Al content in the orthopyroxene) was 859 °C, similar to the estimated average in [76]. In comparison with Pan-African forearc peridotites using the calibration described in [77], the estimated average temperature of the studied serpentinized peridotites (781 °C) is very similar to those found in Um Khariga (778 °C) [78]. In addition, the average temperature of the examined rocks obtained using Al in orthopyroxene thermometry (859 °C) is close to the average of Um Khariga peridotites (984 °C) using the same calibration.

Figure 11. Schematic illustration showing the tectonic setting of the examined ultramafic rocks, modified from [79].

7. Conclusions

Wadi Ibib–Wadi Shani (WI–WS) ultramafics represent relics of dismembered ophiolitic rocks in the southwestern extension of the largest Gerf ophiolitic nappe, South Eastern Desert, Egypt. Based on their petrographic description, the ultramafic rocks can be divided into serpentinites and serpentinitized peridotites; the former consist mainly of serpentine minerals, whereas the latter comprise serpentine minerals with relics of primary minerals such as pyroxene, Cr-spinel, and olivine. These primary minerals are completely replaced by serpentine, magnetite, and carbonate minerals in serpentinites. The abundance of mesh and bastite textures reflects dunite and harzburgite protoliths. The composition of primary mantle minerals such as orthopyroxene ($Mg\# (Mg/(Mg+Fe^{2+}))$, 89.65 to 93.18), clinopyroxene (depletion of Al_2O_3 , Na_2O , and Cr_2O_3), high Fo content of olivine, and high Cr# of Cr-spinel reflect a forearc setting. The calculated temperatures of the WI–WS serpentinitized peridotites using olivine–spinel (av. 781 °C) and Al in orthopyroxene (av. 859 °C) thermometer calibrations are consistent with those of Egyptian forearc mantle rocks.

Supplementary Materials: The following are available online at <https://www.mdpi.com/article/10.3390/app112210524/s1>: Table S1: Representative microprobe analysis of orthopyroxene in serpentinitized peridotites; Table S2: Representative microprobe analysis of clinopyroxene in serpentinitized peridotites; Table S3: Representative microprobe analysis of Cr-spinel in serpentinitized peridotites; Table S4: Representative microprobe analysis of Al-spinel in serpentinitized peridotites; Table S5: Representative microprobe analysis of serpentine; Table S6: Representative microprobe analysis of chlorite in serpentinitized peridotites; Table S7: Representative microprobe analysis of tremolite in serpentinitized peridotites; Table S8: Representative microprobe analysis of magnetite; Table S9: Representative microprobe analysis of talc in serpentinitized peridotites; Table S10: Average temperatures of serpentinitized peridotites calculated using different calibrations.

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