

Article

Petrology and Geochemistry of Mesoarchean Sukinda Ultramafics, Southern Singhbhum Odisha Craton, India: Implications for Mantle Resources and the Geodynamic Setting

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Abstract: The Sukinda ultramafic complex in India comprises precisely two areas: Kaliapani (KLPN) and Katpal (KTPL). These areas consist of a sequence of lithotypes, including orthopyroxenite, dunite, serpentinite, and chromitite, displaying a rhythmic layering of rocks. These rocks exhibit a cumulate texture and stand out due to their elevated Mg# (78.43–93.20), Cr (905.40–58,799 ppm), Ni (193.81–2790 ppm), Al₂O₃/TiO₂ (27.01–74.06), and Zr/Hf (39.81–55.24) ratios, while possessing lower TiO₂ contents (0.01–0.12 wt%). These ultramafics, characterized by low Ti/V (0.83–19.23) and Ti/Sc (7.14–83.72) ratios, negative anomalies of Zr, Hf, Nb, and Ti in a primitive mantle-normalized spider diagram, indicate that the ultramafics originate from a depleted mantle source. Furthermore, the presence of enriched LREE compared to HREE, a negative Eu anomaly, and enrichment of Th, U, and negative Nb anomalies suggest a subduction setting. The whole-rock geochemical data reveal high levels of MgO, Cr, and Ni, as well as low TiO₂ and CaO/Al₂O₃ ratios and high Al₂O₃/TiO₂ ratios. Moreover, the mineral chemistry data of the ultramafic rocks show high-Mg olivine (Fo 90.9–94.1) in dunite, high-Mg orthopyroxene (En 90.4–90.7) in orthopyroxenite, and high Cr# (0.68–0.82) and low Mg# (0.40–0.54) in chromite, alongside significant Al₂O₃ (9.93–12.86 wt%) and TiO₂ (0.20–0.44 wt%) contents in the melt. Such geochemical characteristics strongly suggest that the Sukinda ultramafic originates from the fractional crystallization of a boninitic parental magma, which is derived from the second-stage melting in a depleted metasomatized mantle source within a supra-subduction zone tectonic setting.

Keywords: boninites; chromites; Singhbhum Craton; Sukinda ultramafic complex; supra-subduction zone

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1. Introduction

Mafic and ultramafic rock formations have proven to be significant hosts for precious mineral deposits, including chromium minerals (chromites), nickel–copper sulfides, iron oxides, and elements from the platinum group (PGEs) [1]. Chromite deposits, known as chromites, have experienced mineralization from the Precambrian to the Phanerozoic era, with notable occurrences in Mesoarchean times. These chromite deposits are frequently located within sill-shaped ultramafic rock formations in greenstone belts across diverse regions of the globe. Some notable examples of Archean chromiferous layered sill-like ultramafic provinces include the Kaapvaal Craton [2] and Bushveld Layered Igneous intrusion in South Africa [3], Emeishan Large Igneous Province in southwest China [4,5], Zimbabwe Craton [6–8], and the Singhbhum and Dharwar Cratons of the Indian shield [9,10].

Chromiferous ultramafic deposits are found in the Singhbhum Craton (Sukinda–Nuasahi–Jojohatu area) and Dharwar Craton (Nuggihalli–Krishnarajpet–Holenarsipur–Nagamangala–Javanhalli area) within the Indian shield. These deposits occur as sill-like ultramafic deposits within Archean greenstone belts [9–14]. They are genetically associated with high-Mg lithotypes, such as komatiites, komatiitic basalts, siliceous high-Mg basalts (SHMBs), picrites, and boninites [10,15]. Significant chromiferous layered ultramafic rocks are accommodated within the Archean greenstone belt in the Singhbhum Craton [10,16]. The Nuasahi and Sukinda areas of the Odisha state and the Roro–Jojohatu area of Jharkhand state host significant ultramafic–mafic igneous complexes that intrude into the iron ore group [17–19]. The largest ultramafic body in the Singhbhum Craton is the Sukinda massif, a layered complex composed of rhythmic layers of orthopyroxenite–dunite–serpentinite–chromitite. The Sukinda ultramafic complex has intruded into the Archean iron ore group (IOG) of rocks (cherty quartzite and banded magnetite quartzite) in the Singhbhum Craton. It has intruded at a width of 2–5 km and extends nearly 25 km in an ENE–WNW direction from Kansa (east) to Maruabil (west) and beyond [10]. In order to conduct a comprehensive study of the Sukinda ultramafic complex, rock samples were collected from two distinct regions: Kaliapani (KLPN) and Katpal (KTPL).

Previous studies of the Sukinda ultramafic complex have focused on the chromite mineralization associated with ultramafics [10,20–22] and suggested that the Sukinda ultramafics are part of an Archean ophiolite complex based on a limited platinum-group element (PGE) analysis. Ref. [16] stated that the chromiferous ultramafic cumulates of Sukinda are part of the conformable and tectonically overlying Archean greenstone sequence and can be compared to the present-day oceanic crust. However, based on chromite chemistry, Ref. [10] proposes that the Sukinda ultramafics are formed from boninitic or siliceous high-Mg basalts in a supra-subduction zone setting.

However, limited efforts have been dedicated to investigating the comprehensive chemical composition of whole rocks and individual minerals within the Katpal and Kaliapani regions of the Sukinda ultramafic complex. This study focuses on scrutinizing the characteristics of Sukinda ultramafic rocks and the associated minerals. It aims to present insights into the origin and evolutionary history of the Sukinda ultramafic complex. By analyzing the geochemical datasets and mineral makeup of the rocks in these specific areas, a more comprehensive understanding of the evolution of the Earth's crust during the Archean period and its geographical interrelationships will emerge. Achieving an improved comprehension of the geological conditions in which ultramafic rocks hosting chromite were formed offers valuable insights for future explorations of chromite and platinum deposits within the Archean greenstone belts.

2. Geological Setting

2.1. Regional Geology

The Indian shield consists of five Archean cratonic nuclei, i.e., the Singhbhum Odisha Craton (SOC), Baster Craton, Dharwar Craton, Aravali Craton, and Bundelkhand Craton. The Sukinda ultramafic complex (present study area) is accommodated within the Singhbhum Odisha Craton. The SOC, composed of Archean–Palaeoproterozoic rocks, spreads over 40,000 km² in the Singhbhum district (Jharkhand) and the northern part of the Odisha state (Figure 1a) having (1) a supra-crustal sequence of an older metamorphic group (OMG) and older metamorphic tonalitic gneiss (OMTG); (2) different phases of granitoid batholiths (e.g., Singhbhum granite, Nilgiri granite, Bonai granite, Chakradharpur granite–gneiss, and Mayurbhanj granite); (3) younger supra-crustals of the iron ore group (IOG), which accommodates a banded iron formation (BIF) of economic interest; and (4) the SOC also contains basic volcanic formations (i.e., Simlipal, Dhanjori, and Dalma), and some mafic-ultramafic complexes, i.e., the Baula–Nuasahi and Sukinda ultramafic complex, Mayurbhanj gabbro–anorthosite complex, and newer mafic dolerite dyke swarms. The oldest recognizable litho-unit of the Singhbhum Orissa Craton (SOC)

is the OMG, dated using zircon U-Pb at 3500 Ma [23]. The OMG is exposed in the Keonjhar district, west of the Champua areas [24]. The lithology of the OMG comprises various types of rocks, such as pelitic schists, quartz–magnetite–cummingtonite schists, quartzites, banded calc-gneiss, and ortho and para-amphibolites [25]. An intrusion in the OMG rocks led to the formation of the OMTG, which led to the formation of the OMTG, which is predominantly tonalitic–trondhjemitic with some granodioritic rocks. After the formations of OMG and OMTG, the emplacement of Singhbhum granites (SBGs) occurred in three phases, i.e., SBG I, SBG II, and SBG III [26]. SBG is the most widespread rock type in the SOC, occurring in an N-S elongated trend in the central part of the craton, covering an area of around 8000 Km² [26]. SBG hosts various rocks, such as biotite granodiorite, granite adamellitic, biotite trondhjemite, and leucogranite. At the boundary of the SBG, different rocks, such as chlorite epidote granodiorite and pyroxene diorite, have been found [26–28].

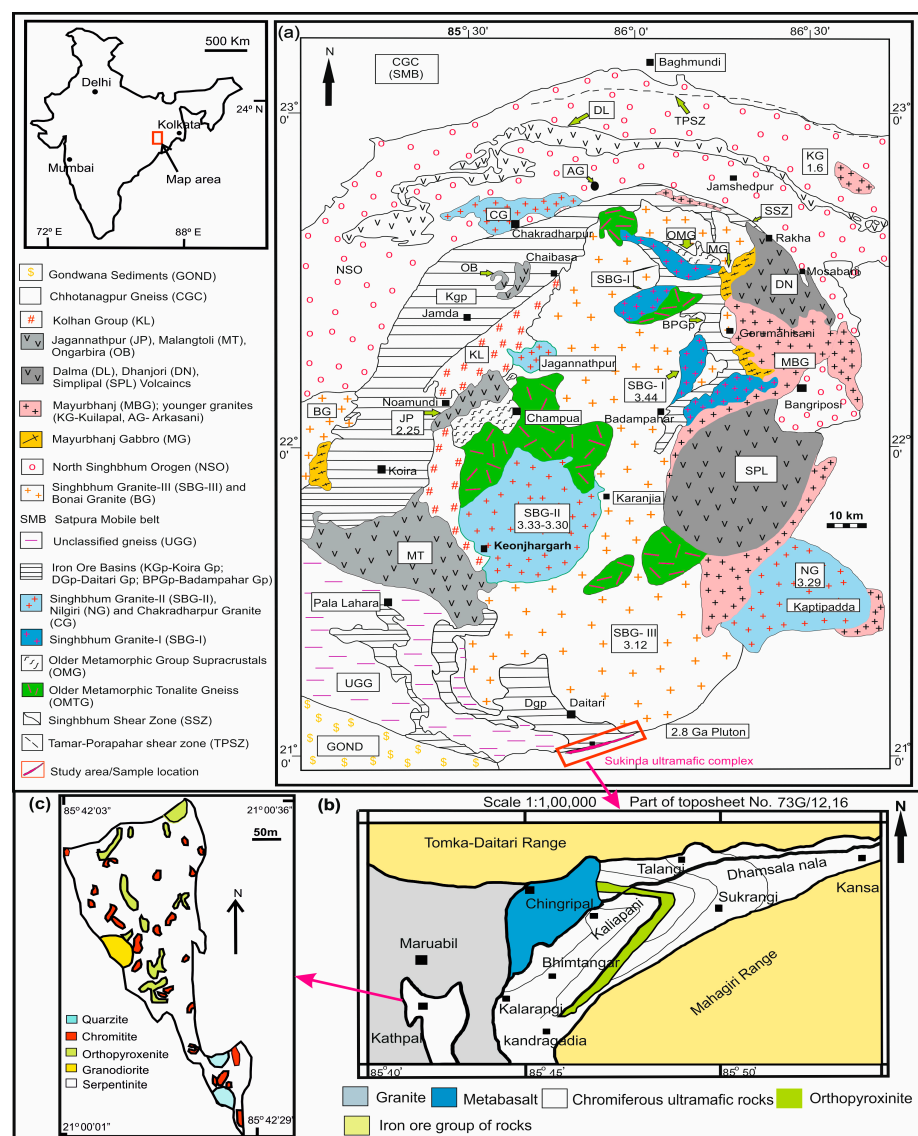


Figure 1. (a) Simplified geological map of Singhbhum Craton [10,13,26,28] and the location of the study area (box). (b) Geological map of Sukinda ultramafic complex [19,29]. (c) Geological map of Katpal area [29].

The Iron ore group (IOG) and Jagannathpur–Malangtoli–Simlipal–Dhanjori–Dalma lavas are volcanic–sedimentary formations bordering the Archean SBG batholith. The IOG supra-crustal successions consist of low-grade metamorphic sediments, including

meta-pelites, phyllites, tuffaceous shales, quartzites, and carbonates associated with mafic and felsic meta-volcanic and banded iron formations [26,30]. IOG formations also contain different forms of intrusive and extrusive igneous rocks, such as high-Mg rock varieties, komatiite, boninites, picrites, and siliceous high-Mg basalts [10,12,19,31–33]. The plutonic ultramafic suites are in a tabular form with economic chromite deposits and are associated with the Tomka–Daitari–Nuasahi–Sukinda belt [10]. The mafic intrusive bodies are found in the Nuasahi–Nilgiri–Gorumahisani–Badampahar areas [12]. Komatiites are present in the eastern IOG belt, such as Patharkata [34], Dhipasai (Tua Dungri hillock; [35]), and Kapili [36]. The subject of our current study, the Sukinda ultramafic complex, is located within the southeastern sector of the Tomka–Daitari basin, a component of the iron ore group formation [12,30]. Our study entailed a methodical collection of rock samples from two specific regions: Kaliapani (KLPN) and Katpal (KTPL).

There is a lack of geochronological data on the IOG and its age of formation; however, based on the intrusive field relationship, it is found that the period would have 3.2–3.1 Ga [23,37]. The U-Pb SHRIMP zircon age of dacite lava in the Tomka–Daitari basin is reported as 3.5 Ga [30]. The older rock formations of the SOC are intruded by newer mafic-ultramafic dyke (2600–950 Ma); this mafic-ultramafic intrusive is called ‘newer dolerite dyke swarms’ [24,38].

2.2. Local Geology

The Sukinda ultramafic complex is restricted within the eastern Ghats mobile belt and IOG and exposed along the southern margin of the Singhbhum Craton. These ultramafic suites intrude along the marginal fracture of Singhbhum crustal rocks in successive phases, and they are regional folds, forming a plunging synform. The plunging synform’s northern limb shows a moderate dip, whereas the southern limb appears as sub-vertical [29,39]. The Sukinda ultramafic rocks consist of dunites, serpentinite, chromitite, and pyroxenite (Figure 1b). The exposed serpentinite in the Sukinda area is the low-grade metamorphic equivalent of dunites. Relatively fresh and unaltered pyroxenites are a late-stage intrusion into the early formed dunite and chromitite rock sequence. However, the regional disposition and relation with IOG suggest that the Sukinda ultramafic complex may be from the Precambrian age [22].

The rock samples were collected from the Kaliapani and Katpal areas of the Sukinda ultramafic complex for the present study. The Katpal area (Figure 1c) of the Sukinda ultramafic complex is situated in the southwestern part of the Kaliapani ultramafic unit (Figure 1b). In the Katpal area, dunite, serpentinites and chromitites are the major lithologic units. They are distributed randomly in fragments of different shapes within the coarse-grained gabbroic to granodioritic matrix, forming tectonic breccias [29]. The chromite grains of Katpal are dark black to dark brown. The Katpal chromites are texturally similar to Kaliapani chromites. The Katpal breccia of the gabbroic matrix consists of medium- to coarse-grained plagioclase, clinopyroxene, serpentine, amphibole, talc, quartz, and some chromites [29]. The studied ultramafic rocks were systematically sampled from different chromite host lithologies, specifically in the Kaliapani and Katpal chromite mines (Figure 2a,b). Field observations confirmed that dunites (Figure 2c) and serpentinitized dunites were the predominant litho-unit in the area. Pyroxenites (Figure 2d) were associated with the serpentinitized dunites as intrusive. Chromite ore bodies were interbedded within these two litho-units. The pyroxenite band contained fewer chromite minerals than the dunites. The fresh and unweathered samples (hand specimens), weighing several kilograms each, were collected from different mine sections.



Figure 2. (a,b) Field photographs of ultramafic rocks exposed in Sukinda chromite mines. (c,d) Ultramafic hand specimens collected from the Kaliapani area. (e,f) Ultramafic hand specimens collected from the Katpal area.

3. Samples and Analytical Methods

The samples of the Sukinda ultramafic complex were collected from the Kaliapani and Katpal areas, avoiding secondary veins (quartz and carbonates). The rock samples were powdered in a Retsch Vibratory Disc Mill RS 200 to a 300 mesh size in the Department of Applied Geology, IIT(ISM) Dhanbad. Major elements were determined by using pressed pellets in an X-ray fluorescence spectrometer (XRF; Rigaku ZSX Primus IV) at the Central Research Facility (CRF), IIT(ISM) Dhanbad, India. Pressed pellets (40 mm diameter) were prepared using collapsible aluminum cups. These cups were filled with boric acid, and about 2 g of the finely powdered sample was evenly sprayed and pressed under a hydraulic press at a 15-ton pressure to create a pellet (Hydraulic Press, Herzog, Germany). The rock standards used for the analysis were JH-1 and JGb-2. A duplicate analysis of the rock standard and certified values is given in Supplementary Table S1. The detection limits of the major and minor elements were ~0.001%, and the analytical precision and accuracy are given in Table S1. The major and minor oxides were recalculated on an anhydrous basis and presented in Table 1.

Table 1. Selected element (oxide) contents in weight percent (wt%) by XRF, or parts per million (ppm, $\mu\text{g}\cdot\text{g}^{-1}$) by HR-ICP-MS, in bulk whole-rock samples from Katpal. Kaliapani area of the Sukinda ultramafic complex. $\text{Fe}_2\text{O}_3^{\text{T}}$ represents total iron (oxide) content.

Species	Katpal						Kaliapani				
	1A	3A	5A	2A	4A	8-11A	12-13A	X2A	21A	7A	X4A
Main-element oxide contents in weight percent (wt%)											
SiO ₂	42.14	42.31	44.76	46.44	54.31	37.83	40.06	40.26	47.5	50.21	53.79
TiO ₂	0.12	0.1	0.06	0.02	0.1	0.02	0.01	0.01	0.02	0.02	0.03
Al ₂ O ₃	3.23	3.08	1.86	1.1	3.11	1.13	0.74	0.79	1.22	0.92	1.16
Fe ₂ O ₃ ^T	5.12	8.84	3.24	10.94	4.23	8.15	10.56	10.08	9.4	8.21	8.07
MnO	0.09	0.09	0.06	0.09	0.07	0.09	0.1	0.09	0.1	0.1	0.11
MgO	41.33	41.41	44.41	39.79	32.32	47.94	47.48	47.36	39.42	37.87	34.54
CaO	0.2	0.05	0.04	0.2	3.85	0.05	0.1	0.15	0.55	0.28	0.69
K ₂ O	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.01	n.d.	n.d.
Na ₂ O	0.16	0.15	0.15	0.15	0.15	0.17	0.17	0.16	0.18	0.16	0.18
P ₂ O ₅	0.03	0.03	0.03	0.02	0.03	0.03	0.03	0.02	0.03	0.03	0.03
Cr ₂ O ₃	7.29	3.01	4.27	1.05	1.05	4.59	0.75	0.8	1.16	1.08	1.1
NiO	0.13	0.09	0.7	0.04	n.d.	n.d.	n.d.	0.01	n.d.	0.91	n.d.
LOI	9.92	10.7	11.78	11.65	4.69	12.28	13.01	13.81	12.64	11.12	3.61
Analytical sum	109.76	109.85	111.37	111.47	103.91	112.29	113	113.55	112.22	110.9	103.3
Trace-element contents in parts per million (ppm, $\mu\text{g}\cdot\text{g}^{-1}$)											
Cr	58,799	28,159	26,785	7166	5492	18,778	3719	6370	5242	4140	905.4
Co	100.87	122.64	58.21	116.56	48.69	110.57	149.7	123.57	99.7	89.16	18.66
Ni	1660	1627	2311	1334	832	2225	2790	1947	1124	2759	193.81
Rb	1.93	1.4	7.75	0.98	1.23	27.31	45.94	10.92	8.71	27.27	3.58
Sr	11.98	4.22	204.83	3.74	7.05	188.04	257.42	227.53	127.73	227.41	20.44
Cs	0.13	0.1	0.17	0.08	0.13	0.84	1.4	0.25	0.09	0.45	0.06
Ba	11.84	20.06	65.28	9.77	7.13	60.19	87.67	64.07	42.36	92.12	16.33
Sc	9.91	9.31	7.4	8.69	15.68	7.09	8.5	4.77	7.14	7.38	2.31
V	150.57	104.95	94.55	49.87	85.34	104.25	73.54	41.88	32.94	39.33	10.05
Ta	0.02	0.02	0.01	0	0.07	0.02	0.01	0.01	0.01	0.01	0.02
Nb	0.15	0.14	0.14	0.08	0.53	0.12	0.1	0.07	0.04	0.07	0.57
Zr	7.07	5.9	2.99	1.75	4.85	6.16	5.65	0.96	0.6	1.27	2.23
Hf	0.16	0.14	0.07	0.04	0.12	0.15	0.13	0.02	0.01	0.03	0.04
Th	0.25	0.19	0.55	0.09	0.25	1.72	1.66	0.27	0.09	0.26	1.02
U	0.73	0.11	5.43	0.08	0.12	6.03	5.94	5.84	2.19	3.27	3.06
Y	3.36	1.46	4.77	0.77	5.1	9.48	10.84	2.43	0.89	6.14	1.96
Rare-earth element (REE) contents in parts per million (ppm, $\mu\text{g}\cdot\text{g}^{-1}$)											
La	1.19	0.52	3.92	0.56	0.56	16.25	19.16	4.04	1.07	4.69	2.93
Ce	2.63	1.09	8.05	0.63	1.48	34.98	40.49	8.19	1.87	7.4	6.59
Pr	0.34	0.14	1.05	0.13	0.24	4.65	5.29	1.07	0.25	1.17	0.73
Nd	1.39	0.58	4.23	0.49	1.28	18.82	21.24	4.29	0.95	4.66	2.93
Sm	0.34	0.14	0.93	0.11	0.44	3.75	4.19	0.82	0.19	1.05	0.56
Eu	0.09	0.03	0.19	0.03	0.12	0.72	0.75	0.16	0.05	0.25	0.12
Gd	0.47	0.21	0.9	0.14	0.66	2.99	3.42	0.7	0.16	1.11	0.45
Tb	0.08	0.03	0.15	0.02	0.13	0.42	0.47	0.09	0.02	0.18	0.04
Dy	0.57	0.22	0.83	0.16	0.87	1.94	2.23	0.45	0.13	1	0.25
Ho	0.13	0.05	0.17	0.03	0.19	0.36	0.43	0.09	0.03	0.21	0.05

Er	0.39	0.16	0.5	0.1	0.55	0.93	1.07	0.24	0.08	0.57	0.13
Tm	0.06	0.03	0.08	0.02	0.08	0.12	0.14	0.04	0.01	0.08	0.01
Yb	0.4	0.2	0.44	0.12	0.5	0.66	0.75	0.18	0.08	0.45	0.15
Lu	0.06	0.03	0.07	0.02	0.07	0.09	0.11	0.03	0.02	0.07	0.01
Cu	15.37	8.29	46.31	5.96	6.11	120.61	144.75	54.06	32.87	62.57	120.67
Zn	80.2	71.85	396.68	48.24	42.82	355.11	755.22	221.36	337.46	574.29	759.94
Pb	22.16	11.03	24.16	8.3	5.73	32.54	38.86	16.01	13.99	23.94	9.96
Calculated values and element (oxide) ratios											
Mg#	88.99	82.41	93.2	78.43	88.42	85.46	81.81	82.46	80.75	82.19	81.07
Al ₂ O ₃ /TiO ₂	27.01	30.21	30.88	64.47	31.69	49.32	74.06	66	56.48	54.94	35.97
CaO/TiO ₂	1.66	0.47	0.58	11.59	39.29	2.32	9.84	12.17	25.14	17	21.36
CaO/Al ₂ O ₃	0.06	0.02	0.02	0.18	1.24	0.05	0.13	0.18	0.45	0.31	0.59
Ti/Sc	72.33	65.65	48.9	11.73	37.47	19.44	7.14	15.09	18.18	13.53	83.72
Ti/V	4.76	5.83	3.83	2.04	6.88	1.32	0.83	1.72	3.94	2.54	19.23
Ti/Zr	101.37	86.47	51.18	14.41	83.08	19.48	8.48	10.17	18.37	14.12	27.33
(La/Yb) _{CN}	3.12	0.93	5.5	2.08	2.5	7.08	3.11	15.49	17.46	16.7	1.13
(La/Sm) _{CN}	2.51	0.8	3.3	2.3	2.21	2.79	2.4	3.09	2.86	2.71	2.51
(Gd/Yb) _{CN}	0.96	0.84	1.64	0.95	1.07	3.66	3.71	3.2	1.69	1.98	2.43
(Ce/Yb) _{CN}	1.74	1.44	4.79	1.39	0.77	13.9	14.27	12.13	6.22	4.31	11.61
(Tb/Yb) _{CN}	0.93	0.75	1.47	0.87	1.11	2.81	2.84	2.36	1.33	1.82	1.26
(Sm/Yb) _{CN}	0.92	0.76	2.3	1.02	0.95	6.18	6.12	5.01	2.66	2.54	4.1
Ti/1000	0.72	0.61	0.36	0.1	0.59	0.14	0.06	0.07	0.13	0.1	0.19
Th/Ce	0.09	0.17	0.07	0.14	0.17	0.05	0.04	0.03	0.05	0.04	0.15
La/Yb	2.99	2.6	8.88	4.75	1.11	24.59	25.7	22.81	13.52	10.42	19.63
Dy/Yb	1.44	1.11	1.87	1.32	1.73	2.93	2.99	2.55	1.62	2.21	1.66
Nb/Zr	0.02	0.02	0.05	0.05	0.11	0.02	0.02	0.07	0.07	0.06	0.26
Th/Zr	0.04	0.03	0.19	0.05	0.05	0.28	0.29	0.28	0.15	0.21	0.46
Nb/Y	0.05	0.1	0.03	0.1	0.1	0.01	0.01	0.03	0.05	0.01	0.29
Rb/Y	0.57	0.96	1.62	1.26	0.24	2.88	4.24	4.5	9.83	4.44	1.83
Sc/Y	2.95	6.39	1.55	11.23	3.07	0.75	0.78	1.97	8.06	1.2	1.18
Zr/Hf	43.11	41.51	45.13	39.81	40.16	42.4	44.89	51.42	55.19	45.29	55.24
U/Th	2.98	0.59	9.84	0.93	0.48	3.5	3.59	21.65	23.92	12.41	3.01
Eu/Eu*	0.71	0.58	0.62	0.81	0.68	0.65	0.6	0.65	0.78	0.71	0.75
(Th/Yb) _{PM}	3.41	5.23	6.93	4.05	2.73	14.45	12.34	8.43	6.44	3.25	37.78
(Th/Eu) _{PM}	5.08	11.21	5.79	5.08	3.96	4.67	4.3	3.24	3.9	2.02	15.88
(Eu/Yb) _{PM}	0.67	0.47	1.2	0.8	0.69	3.1	2.87	2.6	1.65	1.61	2.38
(Nb/Nb*) _{PM}	0.1	0.16	0.03	0.13	0.49	0.01	0.01	0.02	0.05	0.02	0.11
(Ta/Ta*) _{PM}	0.22	0.35	0.04	0.12	1.17	0.02	0.01	0.07	0.11	0.03	0.06
(Zr/Zr*) _{PM}	0.7	1.41	0.1	0.51	0.44	0.05	0.04	0.03	0.1	0.04	0.12
(Hf/Hf*) _{PM}	0.6	1.26	0.08	0.47	0.4	0.04	0.03	0.03	0.06	0.03	0.08
(Ti/Ti*) _{PM}	0.71	1.49	0.16	0.34	0.42	0.02	0.01	0.04	0.32	0.04	0.21

(n.d.) not detectable (below detection limit); (CN) chondrite-normalized and (PM) primitive-mantle-normalized distributions; normalization factors after [40]. Note that the analyses are reported on an anhydrous basis and LOI values are presented for informational purposes.

The trace and rare-earth element (REE) concentrations were determined by high-resolution inductively coupled plasma mass spectrometry (HR-ICP-MS; Nu Instruments Atom[®], Wrexham, UK). The analysis was performed in jump-wiggle mode at a resolution of 300, allowing all the analytes of interest to be measured accurately. The instrument was optimized using a 1 ppb tuning solution, and the sensitivity of ¹¹⁴In was about 1 million

cps. The samples were prepared by using a closed-vessel digestion method. A total of 0.05 g of powdered samples were dissolved using an HF-HNO₃ acid mixture in a proportion of 7:3 in Savillexscrewtop vessels, and the acid mixture was kept on a hot plate at ~150 °C for 48 h. Following this, the vessels were opened and then we added one or two drops of HClO₄, which were evaporated at 150 °C for about 1 hour to near-dryness. The remaining residues were dissolved by adding 10 mL of 1:1 HNO₃ and kept on a hot plate for 30–45 min at 80 °C to dissolve all the suspended particles. We transferred the prepared solution in a 250 mL standard flask, added 10 mL of 1:1 HNO₃ and 5 mL of Rh (Rhodium) solution as an internal standard, and the volume was made to reach 250 mL with Millipore water. Subsequently, the solution was finally stored in polyethylene bottles for the HR-ICP-MS analysis. A couple of procedural blanks were also prepared with the sample batch by adopting the same protocol described above to negate any errors due to the reagent and handling issues. Certified reference materials UB-N (ANRT, France) and BHVO-1 (USGS) were dissolved simultaneously following the method described above and analyzed along with the samples. A duplicate analysis of the rock standard and certified values is given in Table S1, and the major element oxide in weight percentage (wt%) and trace-element and REE contents are presented in Table 1. The detailed analytical technique, instrument setting, analytical condition, and lower detection limit refer to [41].

The mineral chemistry of the silicate minerals and chromite grains was analyzed by CAMECA SX five electron probe micro-analysis (EPMA) at the Central Research Facility (CRF), IIT(ISM) Dhanbad, Jharkhand. This instrument was equipped with four wavelength-dispersive spectrometers (WDSs). Before the EPMA analysis, the polish sections were coated with ~20 nm of carbon in a Cressington 108 carbon/A coater to minimize the electron beam's charging rate. The analysis was performed at a high-vacuum setting (10⁻⁶ Torr), with a 1–3 μm electron beam diameter at the point of incidence, operated at an accelerating voltage of 15 KeV, and the beam used a 20 nA probe current as measured using the Faraday cup. Spectra were collected for 30 s at the peak and 10 s in the background. The internal mineral standards used for the calibration were periclase (Mg), orthoclase (K, Al), apatite (Ca, P), hematite (Fe), albite (Si, Na), synthetic rutile TiO₂ (Ti), synthetic eskolaite Cr₂O₃ (Cr), rhodonite (Mn), and Ni (NiO). Raw data were corrected using proprietary CAMECA software applying a ZAF algorithm. The structural calculation of the analyzed minerals was performed by a stoichiometry process. The amounts of Fe³⁺ and Fe²⁺ in the chromites were calculated according to the charge balance equation [42]. Net lower limits of detection (LLDs) for the relevant concentration intervals were listed per oxide species in a separate column in the data, as per [43]. The selected mineral chemistry data are presented in Tables 2–5.

Table 2. Selected main-element oxide contents in weight percent (wt%) by EPMA in olivine from the Sukinda ultramafic complex. Calculated Fe₂O₃ and FeO (cf. guidelines from Droop (1987)) [42]. Oxide contents recast into numbers of cations in atoms per formula unit (cf. Deer et al. (2013)) [44]. Further explanation in the text. (n.d.) not detectable (below detection limit).

LLD%	X7-1	X7-5	X6-10	X6-13	X2-11	X2-9	X5U-13	X9-3	X5U-15	X2-7	X9-10	
Main-element oxide contents in weight percent (wt%)												
SiO ₂	<0.07	40.93	41.42	41.30	41.07	41.88	41.54	40.89	41.17	41.01	41.87	40.89
Al ₂ O ₃	<0.05	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.05	0.05	n.d.	n.d.	n.d.
Fe ₂ O ₃		0.84	0.63	0.92	0.97	0.97	0.96	0.93	0.88	0.84	0.99	0.94
FeO	<0.22	6.80	5.11	7.46	7.87	7.83	7.81	7.52	7.14	6.79	8.00	7.60
MgO	<0.06	49.70	51.40	49.86	49.57	49.97	49.61	49.16	49.40	49.98	50.26	48.96
MnO	<0.24	n.d.	n.d.	n.d.	n.d.	0.24	n.d.	n.d.	0.31	n.d.	n.d.	n.d.
NiO	<0.04	0.40	0.44	0.19	0.24	0.11	0.25	0.23	0.49	0.40	0.13	0.23
CaO	<0.05	0.09	0.07	0.15	0.11	0.09	0.03	0.17	0.11	0.12	0.03	0.10
Analytical sum		98.76	99.07	99.88	99.83	101.09	100.21	98.95	99.55	99.13	101.28	98.71
Numbers of cations in atoms per formula unit (apfu) on the basis of 4O												

Mg	1.817	1.858	1.808	1.802	1.792	1.792	1.801	1.799	1.821	1.797	1.797
Fe ²⁺	0.14	0.104	0.152	0.16	0.157	0.158	0.155	0.146	0.139	0.161	0.156
Ca	0.002	0.002	0.004	0.003	0.002	0.001	0.004	0.003	0.003	0.001	0.002
Mn	n.d.	n.d.	n.d.	n.d.	0.005	n.d.	n.d.	0.006	n.d.	n.d.	n.d.
Ni	0.008	0.009	0.004	0.005	0.002	0.005	0.005	0.01	0.008	0.003	0.005
Al	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.001	0.001	n.d.	n.d.	n.d.
Fe ³⁺	0.015	0.012	0.017	0.018	0.017	0.018	0.017	0.016	0.015	0.018	0.017
Σ	1.982	1.985	1.985	1.988	1.975	1.974	1.983	1.981	1.986	1.98	1.977
Si	1.004	1.004	1.005	1.002	1.007	1.007	1.005	1.006	1.002	1.004	1.007
Σ	1.004	1.004	1.005	1.002	1.007	1.007	1.005	1.006	1.002	1.004	1.007
Calculated values											
Mg#	0.929	0.947	0.923	0.918	0.919	0.919	0.921	0.925	0.929	0.918	0.92
Forsterite	92.14	94.16	91.47	91	91.1	91.06	91.29	91.74	92.2	90.97	91.18

Table 3. Selected main-element oxide contents in weight percent (wt%) by EPMA in orthopyroxene from Sukinda ultramafic complex. Fe₂O₃ and FeO calculated (cf. guidelines from Droop (1987)). Oxide contents recast into numbers of cations in atoms per formula unit (cf. Deer et al. (2013)). Further explanation in text. (n.d.) not detectable (below detection limit).

	LLD%	X1-16	X2-20	X3-27	X4-16	X5-26	A-17	B-22	C-31	D-39
Main-element oxide contents in weight percent (wt%)										
SiO ₂	<0.07	57.72	58.07	57.56	57.72	57.59	58.41	57.88	58.18	58.19
TiO ₂	<0.05	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.06
Al ₂ O ₃	<0.05	0.71	0.75	0.8	0.71	0.68	0.7	0.69	0.73	0.72
Cr ₂ O ₃	<0.04	0.64	0.67	0.51	0.64	0.58	0.56	0.54	0.59	0.56
Fe ₂ O ₃		n.d.	n.d.	0.461	0.767	n.d.	n.d.	n.d.	n.d.	n.d.
FeO	<0.22	5.52	5.56	5.425	4.831	5.68	5.43	5.41	5.31	5.46
MgO	<0.06	34.52	34.34	34.82	34.52	34.48	34.12	34.41	34.1	34.49
MnO	<0.24	0.3	n.d.	n.d.	0.3	n.d.	n.d.	n.d.	n.d.	n.d.
NiO	<0.04	n.d.	n.d.	0.18	n.d.	0.09	n.d.	n.d.	n.d.	n.d.
Na ₂ O	<0.06	n.d.	n.d.	n.d.	n.d.	0.06	n.d.	n.d.	n.d.	n.d.
CaO	<0.05	0.6	0.68	0.65	0.6	0.62	0.75	0.76	0.76	0.69
Analytical sum		100.01	100.07	100.41	100.09	99.78	99.97	99.69	99.67	100.17
Numbers of cations in atoms per formula unit (apfu) on the basis of 6O										
Si	-	1.985	1.991	1.972	1.989	1.984	2.003	1.99	1.999	1.993
Al ^{IV}	-	0.015	0.009	0.028	0.011	0.016	0	0.01	0.001	0.029
Σ		2	2	2	2	2	2.003	2	2	2
Al ^{VI}	-	0.014	0.021	0.004	0.018	0.012	0.028	0.018	0.029	0.022
Cr	-	0.017	0.018	0.014	0.017	0.016	0.015	0.015	0.016	0.015
Ni	-	n.d.	n.d.	0.005	n.d.	0.002	n.d.	n.d.	n.d.	n.d.
Fe ³⁺	-	n.d.	n.d.	0.012	0.02	n.d.	n.d.	n.d.	n.d.	n.d.
Ti	-	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.002
Mg	-	1.769	1.755	1.778	1.773	1.771	1.744	1.764	1.746	1.761
Fe ²⁺	-	0.159	0.159	0.155	0.139	0.164	0.156	0.156	0.153	0.156
Mn	-	0.009	n.d.	n.d.	0.009	n.d.	n.d.	n.d.	n.d.	n.d.
Ca	-	0.022	0.025	0.024	0.021	0.023	0.028	0.028	0.028	0.025
Na	-	n.d.	n.d.	n.d.	n.d.	0.004	n.d.	n.d.	n.d.	n.d.
Σ		1.99	1.978	1.992	1.997	1.992	1.971	1.981	1.972	1.981
Calculated values										
Mg#	-	0.918	0.917	0.92	0.927	0.915	0.918	0.919	0.92	0.918
Cr#	-	0.377	0.375	0.3	0.377	0.364	0.349	0.344	0.352	0.343

Table 4. Selected main-element oxide contents in weight percent (wt%) by EPMA in chromite from the Kaliapani area. Calculated Fe₂O₃ and FeO (cf. guidelines from Droop (1987)). Oxides content recast into numbers of cations in atoms per formula unit (cf. Deer et al. (2013)). Further explanation in text. (n.d.) not detectable (below detection limit).

	LLD%	X6-17	X2-4	X2-5	X8-9	X8-13	X8-27	X2-2	X2-4	X2-4/1	X2-6/1	X9-8	X9-9
Main-element oxide contents in weight percent (wt%)													
SiO ₂	<0.07	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.08	0.1
TiO ₂	<0.05	0.17	0.17	0.14	0.19	0.18	0.15	0.20	0.18	0.17	0.19	0.18	0.17
Al ₂ O ₃	<0.05	8.92	15.30	15.12	12.13	12.04	12.36	13.15	13.57	15.14	13.68	14.50	14.51
Cr ₂ O ₃	<0.04	60.45	55.33	55.15	57.50	57.92	58.63	55.57	55.44	55.22	54.24	55.17	54.90
Fe ₂ O ₃		2.84	0.25	0.95	1.90	1.22	0.31	2.24	1.93	0.88	3.38	1.19	0.86
FeO	<0.22	18.06	17.09	17.43	19.19	20.06	20.46	20.60	19.52	17.33	19.45	16.90	17.87
MgO	<0.06	9.90	11.15	10.72	9.72	9.00	8.83	8.92	9.65	11.16	9.79	11.33	10.62
MnO	<0.24	0.42	n.d.	0.30	0.35	0.47	0.39	0.37	0.29	0.34	n.d.	0.25	0.26
NiO	<0.04	0.16	0.07	n.d.	n.d.	0.10	0.25	n.d.	n.d.	n.d.	0.08	n.d.	n.d.
CaO	<0.05	n.d.	n.d.	0.05	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Analytical sum		100.92	99.37	99.86	100.98	100.98	101.37	101.05	100.58	100.24	100.81	99.52	99.19
Numbers of cations in atoms per formula unit (apfu) on the basis of 4O													
Si	-	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.003	0.003
Al	-	0.347	0.58	0.573	0.465	0.464	0.475	0.505	0.519	0.571	0.521	0.551	0.555
Cr	-	1.575	1.407	1.403	1.479	1.498	1.51	1.43	1.423	1.396	1.386	1.406	1.409
Fe ³⁺	-	0.07	0.006	0.023	0.047	0.03	0.008	0.055	0.047	0.021	0.082	0.029	0.021
Ti	-	0.004	0.004	0.003	0.005	0.004	0.004	0.005	0.004	0.004	0.005	0.004	0.004
Σ		1.996	1.997	2.002	1.996	1.996	1.997	1.995	1.993	1.992	1.994	1.993	1.992
Mg	-	0.487	0.535	0.514	0.471	0.439	0.429	0.433	0.467	0.532	0.472	0.545	0.514
Fe ²⁺	-	0.498	0.46	0.469	0.522	0.549	0.557	0.561	0.53	0.464	0.526	0.456	0.485
Ni	-	0.004	0.002	n.d.	n.d.	0.003	0.007	n.d.	n.d.	n.d.	0.002	n.d.	n.d.
Mn	-	0.012	n.d.	0.008	0.01	0.013	0.011	0.01	0.008	0.009	n.d.	0.007	0.007
Ca	-	n.d.	n.d.	0.002	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Σ		1.001	0.997	0.993	1.003	1.004	1.004	1.004	1.005	1.005	1	1.008	1.006
Calculated values													
Mg#	-	0.494	0.538	0.523	0.474	0.444	0.435	0.436	0.468	0.534	0.473	0.544	0.514
Cr#	-	0.82	0.708	0.71	0.761	0.763	0.761	0.739	0.733	0.71	0.727	0.719	0.717
Fe ³⁺ ratio	-	0.035	0.003	0.011	0.023	0.015	0.004	0.028	0.024	0.011	0.041	0.015	0.011
(Al ₂ O ₃) _{melt}	-	9.93	12.82	12.76	11.58	11.54	11.68	12.01	12.18	12.76	12.22	12.53	12.54
(TiO ₂) _{melt}	-	0.27	0.27	0.23	0.30	0.29	0.25	0.31	0.29	0.27	0.30	0.29	0.27

Table 5. Selected main-element oxide contents in weight percent (wt%) by EPMA in chromite from the Katpal area. Calculated Fe₂O₃ and FeO (cf. guidelines from Droop (1987)). Oxide contents recast into numbers of cations in atoms per formula unit (cf. Deer et al. (2013)). Further explanation in the text. (n.d.) not detectable (below detection limit).

	LLD%	2A	9	13	14	22	23	26	33	36	39	40	41	43
SiO ₂	<0.07	n.d.	n.d.	0.09	0.07	0.1	n.d.	n.d.	n.d.	0.07	n.d.	0.09	n.d.	n.d.
TiO ₂	<0.05	0.25	0.21	0.29	0.19	0.27	0.30	0.27	0.21	0.20	0.16	0.24	0.21	0.24
Al ₂ O ₃	<0.05	12.98	13.63	12.74	15.42	14.42	15.25	13.06	13.05	12.01	11.59	11.32	12.51	11.92
Cr ₂ O ₃	<0.04	53.07	52.56	54.05	50.27	51.50	50.17	52.91	53.70	55.64	56.76	56.14	54.72	56.05
Fe ₂ O ₃		3.44	3.21	3.43	4.09	3.38	4.23	3.98	3.61	3.39	3.48	3.92	4.22	3.84
FeO	<0.22	21.40	21.17	21.66	21.26	21.31	21.44	21.12	18.23	18.22	17.94	17.52	18.18	18.12
MgO	<0.06	8.19	8.40	8.18	8.40	8.21	8.44	8.24	10.09	10.21	9.78	10.24	10.36	9.88
MnO	<0.24	0.41	0.29	0.51	0.58	0.56	0.38	0.44	0.36	0.30	0.47	0.24	0.40	0.29
NiO	<0.04	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.12	n.d.	n.d.	0.09	0.09	n.d.	0.10

Na ₂ O	<0.06	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.09	0.09	n.d.	0.10
CaO	<0.05	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Analytical sum	99.74	99.47	100.86	100.22	99.64	100.21	100.13	99.25	99.97	100.36	99.80	100.60	100.54	
Numbers of cations in atoms per formula unit (apfu) on the basis of 4O														
Si	n.d.	n.d.	0.003	0.002	0.003	n.d.	n.d.	n.d.	0.002	n.d.	0.003	n.d.	n.d.	
Al	0.507	0.531	0.493	0.592	0.559	0.587	0.508	0.505	0.463	0.447	0.438	0.479	0.459	
Cr	1.39	1.374	1.403	1.295	1.34	1.294	1.381	1.395	1.44	1.47	1.458	1.405	1.447	
Fe ³⁺	0.086	0.08	0.085	0.1	0.084	0.104	0.099	0.089	0.084	0.086	0.097	0.103	0.094	
Ti	0.006	0.005	0.007	0.005	0.007	0.007	0.007	0.005	0.005	0.004	0.006	0.005	0.006	
Σ	1.989	1.99	1.991	1.994	1.993	1.992	1.995	1.994	1.994	2.007	2.002	1.992	2.006	
Mg	0.405	0.414	0.4	0.408	0.403	0.411	0.405	0.494	0.498	0.478	0.502	0.502	0.481	
Fe ²⁺	0.593	0.585	0.595	0.58	0.587	0.585	0.583	0.501	0.499	0.491	0.481	0.494	0.495	
Ni	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.003	n.d.	n.d.	0.002	0.002	n.d.	0.003	
Mn	0.012	0.008	0.014	0.016	0.016	0.011	0.012	0.01	0.008	0.013	0.007	0.011	0.008	
Ca	0	0	0	0	0	0	0	0	0	0	0	0	0	
Na	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.006	0.006	n.d.	0.006	
Σ	1.01	1.007	1.009	1.004	1.006	1.007	1.003	1.005	1.005	0.99	0.998	1.007	0.993	
Calculated values														
Mg#	0.405	0.414	0.402	0.413	0.407	0.412	0.410	0.497	0.500	0.493	0.510	0.504	0.493	
Cr#	0.733	0.721	0.740	0.686	0.706	0.688	0.731	0.734	0.757	0.767	0.769	0.746	0.759	
Fe ⁺³ -ratio	0.043	0.040	0.043	0.050	0.042	0.052	0.050	0.045	0.042	0.043	0.049	0.052	0.047	
(Al ₂ O ₃) _{melt}	11.94	12.20	11.84	12.86	12.50	12.80	11.97	11.97	11.52	11.33	11.21	11.74	11.48	
(TiO ₂) _{melt}	0.38	0.33	0.43	0.30	0.40	0.44	0.40	0.33	0.31	0.26	0.36	0.33	0.36	

4. Results

4.1. Petrography

The studied ultramafic rocks were systematically sampled from different chromite host lithologies, specifically in the Kaliapani and Katpal chromite mines (Figure 2a,b). Field observations confirmed that the dunites and serpentinized dunites were the predominant litho-unit in the area. Pyroxenites were associated with the dunite and serpentinized dunite as intrusive. The chromite ore bodies were interbedded within these two litho-units. The pyroxenite band contained less chromite minerals than the dunites. The fresh and unweathered samples (hand specimens), weighing several kilograms each, were collected from different mine sections. Thin sections were analyzed for a petrographic study and prepared using Struers and Buehler equipment [45]. Epoxy additives were used in to create the thin sections. The 30 µm thin sections were polished using diamond pastes at 6–4–3–0.25 µm on cloth. In incident- and transmitted-illumination settings, the polished sections were studied using an optical Nikon Eclipse E200 petrographic microscope.

4.1.1. Dunite

The fresh and unaltered dunite samples were collected from the mine sections for petrographic and geochemical studies. The dunites appeared as dusty green in the hand specimen (Figure 2c,e). The primary mineral phases of the dunite are olivines, which are rarely altered to serpentine in some places but retain the protolith's primary cumulate structure. The mineral grains in the dunite were medium to coarse in size and subhedral to euhedral in shape (Figure 3b). The large euhedral to subhedral grains of olivine were highly deformed and fractured (Figure 3b). The dunite host disseminated chromite grains as an accessory mineral phase. The chromite grains were fine to medium in size and euhedral in shape, which could be observed under the microscope. Chromite grains were observed along with cumulus olivines. The rounded shape of poikilitically included chromite grains within the olivine was primarily attributed to the process of resorption. They appeared as either opaque or a dark reddish-brown color (Figure 3b).

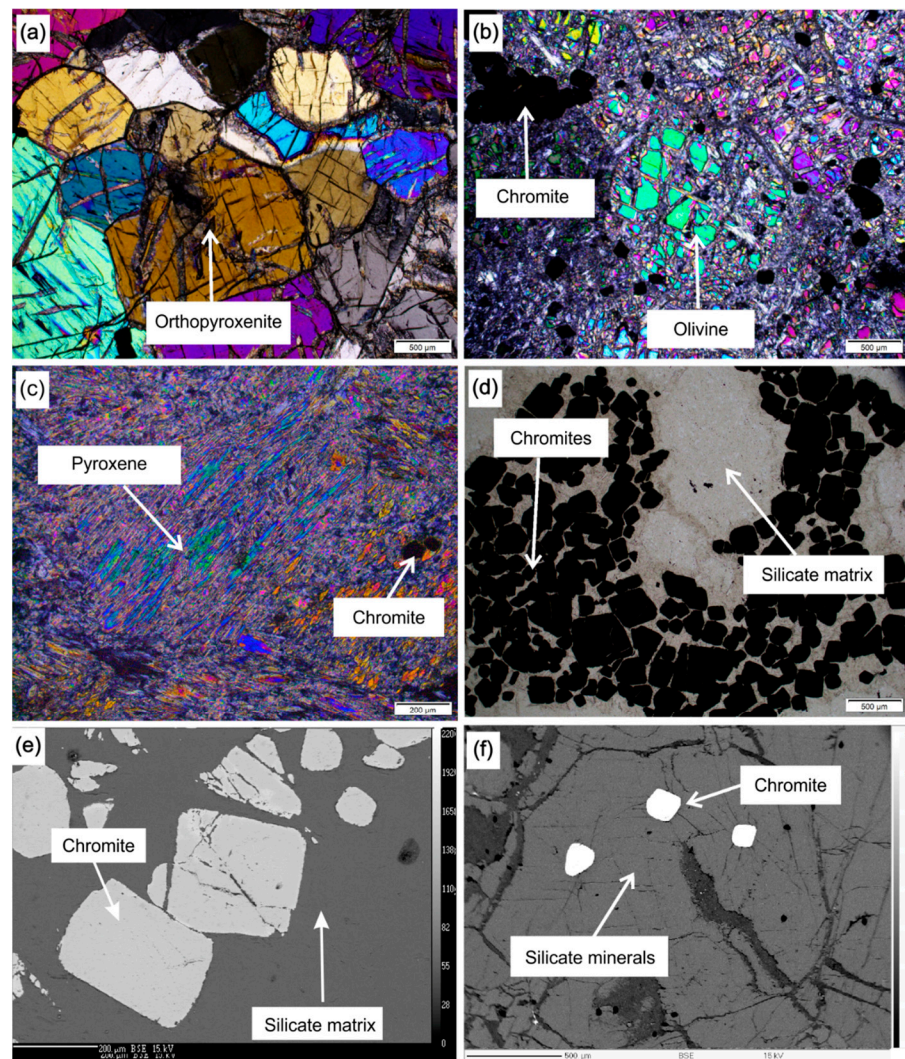


Figure 3. (a) Orthopyroxenite (enstatite mineral grains with much fewer chromite grains). (b) Dunite (olivine grain surrounded by chromite grains and the serpentine minerals developed in the fractures). (c) Pyroxene (larger grains of pyroxene with small patches of chromite). (d) Traces of weathered silicate mineral grains surrounded by chromite grains. (e) BSE image of chromite grains surrounded by silicate matrix. (f) BSE image of orthopyroxenite, gray minerals are enstatite, and the light-colored mineral grains are chromite.

4.1.2. Orthopyroxenite

In the hand specimen, the orthopyroxenite appeared dark greenish and coarse-grained (Figure 2d). The orthopyroxenites were relatively less altered. Under the microscope, the orthopyroxenites were medium to coarse grained and showed euhedral to sub-hedral orthopyroxene grains with a granoblastic texture. The orthopyroxenite primarily comprised the enstatite orthopyroxene mineral phases (Figure 3a,c). In the photomicrograph, the pyroxenes showed exsolution lamellae. These lamellae resulted from the exsolution of a separate pyroxene phase due to sub-solidus re-equilibrium occurring during successive slow cooling. Accessory chromite mineral phases were rarely observed in the orthopyroxenite compared to dunite.

4.1.3. Serpentinite

The original cumulate textures from previous stages were still evident in the serpentinite (Figure 2f), where remnants of olivine could be observed dispersed throughout the matrix. The serpentinization process occurred more extensively along the fractures and

fissures (Figure 3b). As serpentinization progressed, it gradually removed the bulk of olivine and orthopyroxene, leaving only their skeletal structures behind. In the later stages, these skeletal structures were no longer present in the final mineral compositions of the serpentinite (Figure 3d). However, the serpentinite litho-types were not considered for the geochemical analysis and interpretation.

The observed textures in the Sukinda area's ultramafic rocks provide valuable insights into the sequence of crystallization events. These rocks exhibit a distinct pattern of mineral formation, starting with olivine, followed by a combination of olivine and chromite, then a mix of olivine and orthopyroxene, and, finally, orthopyroxene. As olivine continues to crystallize, the composition of the magma gradually shifts towards the olivine–chromite cotectic point, leading to the simultaneous precipitation of both olivine and chromite phases. In the Sukinda region, once chromite formation and the primary ultramafic mass crystallization occurred within the upper mantle conditions, the remaining magma underwent a further evolution, reaching a composition dominated by orthopyroxene.

4.2. Whole-Rock Geochemistry

4.2.1. Major-Element Geochemistry

The Sukinda ultramafics of the KTPL area showed high Mg# (78.43 to 93.20 wt%) and low to moderate Fe₂O₃^t (3.24 to 10.94 wt%), CaO (0.04 to 3.85 wt%), SiO₂ (42.14 to 54.31 wt%), TiO₂ (0.02 to 0.12 wt%), Al₂O₃ (1.10 to 3.23 wt%), and Na₂O contents (0.15 to 0.16 wt%), whereas the Cr₂O₃ concentration varied from 1.05 to 7.29 wt% and NiO from 0.04 to 0.70 wt%.

The KLPN area showed high Mg# (80.75 to 85.46 wt%) and low Fe₂O₃^t (8.07 to 10.56 wt%), CaO (0.05 to 0.69 wt%), SiO₂ (37.83 to 53.79 wt%), TiO₂ (0.01 to 0.03 wt%), Al₂O₃ (0.74 to 1.22 wt%), and Na₂O contents (0.16 to 0.18 wt%), whereas the Cr₂O₃ concentration varied from 0.75 to 4.59 wt%. and the NiO concentration ranged between 0.01 and 0.91 wt%.

While the KTPL samples exhibited a broad spectra of Cr₂O₃, Fe₂O₃, and CaO contents, the KLPN samples demonstrated a more restricted range of these oxides. The KTPL samples exhibited elevated Ti values, primarily attributed to the presence of Ti-V-bearing iron oxide minerals, while the KLPN samples presented higher Fe values due to the presence of magnetite iron oxide as an accessory phase.

The samples from the Sukinda ultramafic complex showed distinct major and minor oxide distributions. The bi-variant diagrams of MgO versus other major and minor elements were plotted for Sukinda ultramafic rocks (Figure 4). The Sukinda ultramafic samples displayed a negative trend between MgO vs. SiO₂, a scattered pattern between MgO and Fe₂O₃^t, and a negative trend between MgO vs. TiO₂ (Figure 4). The negative correlation between MgO versus SiO₂, TiO₂, and Al₂O₃ suggested the fractional crystallization of the parental magma from which the Sukinda ultramafic rocks were formed. The positive correlation of MgO versus Cr (ppm) and Ni (ppm) was due to the fractionation of early cumulus olivine and chromite crystals from the parental magma.

4.2.2. Trace-Element Geochemistry

The ultramafics of the Katpal samples showed different compatible trace-element concentrations for Cr (5492 to 58,799 ppm), Ni (831.75 to 2311 ppm), and V (49.87 to 150.57 ppm), and the incompatible elements showed variations in Zr (1.75 to 7.07 ppm), Sr (3.74 to 204.83 ppm), Cs (0.08 to 0.17 ppm), U (0.08 to 5.43 ppm), Th (0.09 to 0.55 ppm), Y (0.77 to 5.10 ppm), Nb (0.08 to 0.53 ppm), and Rb (0.98 to 7.75 ppm).

The total REE value of the Katpal ultramafics showed a narrow range of variation from 2.56 to 21.50 ppm, with there was limited REE fractionation. The (Ce/Yb)_{CN} ratios varied from 0.77 to 4.79, LREE values varied from (La/Sm)_{CN} = 0.79 to 3.17, MREE values varied from (Sm/Yb)_{CN} = 0.76 to 2.30, and presented a limited fractionation of HREE (Gd/Yb)_{CN} = 0.84 to 1.64 with a negative Eu anomaly (Eu/Eu* = 0.58 to 0.81). The chondrite-

normalized REE distribution diagram (Figure 5a) of the Katpal ultramafics was characterized by a weak enrichment of LREE, flat HREE, and negative Eu anomalies ($\text{Eu}/\text{Eu}^* = 0.58$ to 0.81).

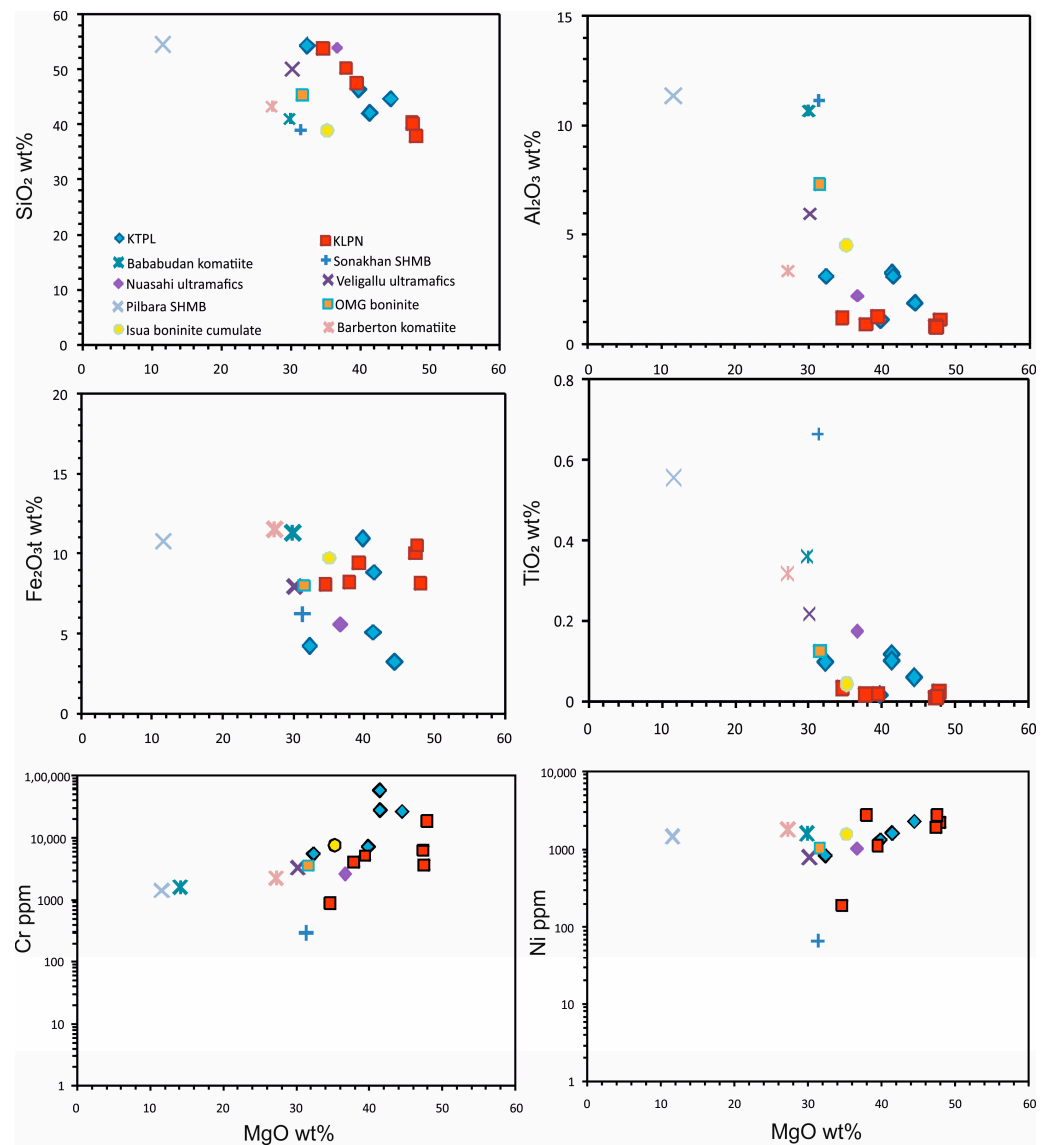


Figure 4. Variation diagram of MgO versus Al_2O_3 , SiO_2 , Cr, Ni, TiO_2 , O, and Fe_2O_3^t in Sukinda ultramafic complex and different high-Mg rocks (i.e., boninites, siliceous high-Mg basalts, and komatiites) in the world. The data are obtained after OMG boninite [46], Nuasahi boninite [9], Bababudan komatiite [47], Veligallu ultramafic [48], Sonakhan SHMB [49], Barberton komatiite [50], Pilbara SHMB [51], and Isua boninite cumulate [52].

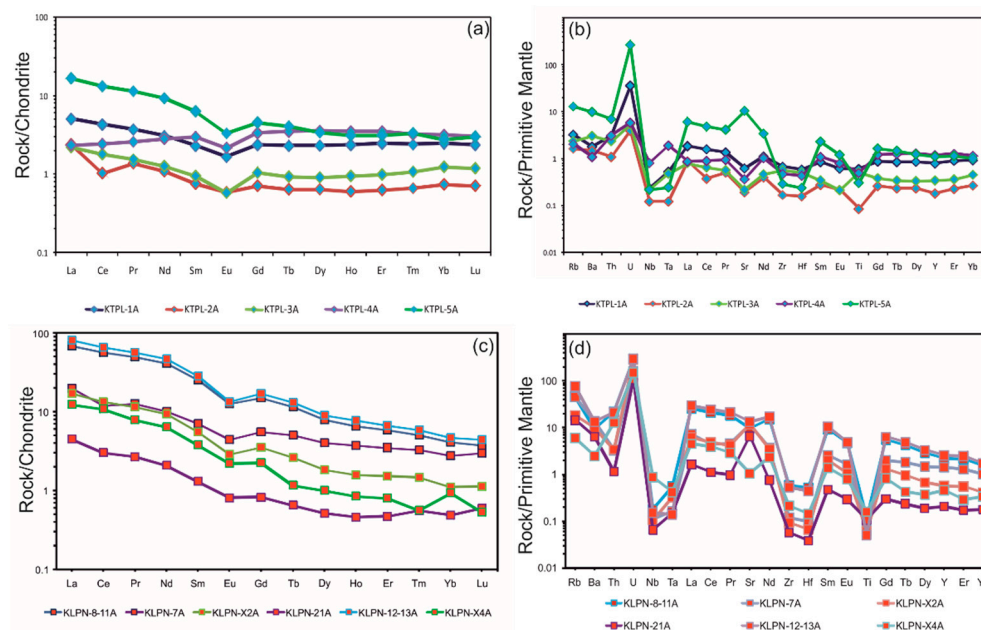


Figure 5. Chondrite-normalized rare-earth element patterns and primitive mantle-normalized multi-element plots of Sukinda ultramafic rocks. (a,b) Plotted for Kaliapani and (c,d) Katpal samples. For normalization, chondrite and primitive mantle values are taken from McDonough et al. (1995) [45].

In the primitive mantle-normalized trace-element plots (normalization values were obtained from McDonough et al. (1995) [40] (Figure 5b), the incompatible elements of Katpal rocks displayed a negative correlation ($[\text{Th}/\text{Yb}]_{\text{PM}} = 2.73$ to 6.93) ($[\text{Th}/\text{Eu}]_{\text{PM}} = 3.96$ to 11.21), and the compatible elements displayed a relatively positive to flat pattern ($[\text{Eu}/\text{Yb}]_{\text{PM}} = 0.47$ to 1.20). The primitive mantle-normalized trace-element plot displayed significant negative anomalies for several elements, including Nb ($[\text{Nb}/\text{Nb}^*] = 0.03$ to 0.49), Ta ($[\text{Ta}/\text{Ta}^*] = 0.04$ to 0.35 , except for one sample that showed 1.17), Zr ($[\text{Zr}/\text{Zr}^*] = 0.10$ to 0.70 , except for one sample, KTPL-3A, which showed 1.41), Hf ($[\text{Hf}/\text{Hf}^*] = 0.08$ to 0.60 , except for one sample, KTPL-3A, which showed 1.26), and Ti ($[\text{Ti}/\text{Ti}^*] = 0.16$ to 0.71 , except for one sample, KTPL-3A, which showed 1.49). These negative anomalies indicated depletions in these elements relative to the primitive mantle.

The total REE value of Kaliapani ultramafics varied from 4.89 to 99.72 ppm, with limited REE fractionation ($\text{Ce}/\text{Yb}_{\text{CN}}$ ratios varying from 4.31 to 14.27 , LREE values varying from $(\text{La}/\text{Sm})_{\text{CN}} = 2.70$ to 3.45), MREE values varying from $(\text{Sm}/\text{Yb})_{\text{CN}} = 2.54$ to 6.18 , and HREE values varying from $(\text{Gd}/\text{Yb})_{\text{CN}} = 1.69$ to 3.71) with a negative Eu anomaly ($\text{Eu}/\text{Eu}^* = 0.60$ to 0.78). The chondrite-normalized diagram (Figure 5c) of the Kaliapani ultramafics shows a negative-sloping REE pattern with LREE enrichment and a slightly negative Eu anomaly ($\text{Eu}/\text{Eu}^* = 0.60$ to 0.78).

Relative to the Katpal samples, the Kaliapani samples were characterized by a high REE concentration and LREE enrichment. Relative to the Katpal samples, the trace elements in the Kaliapani samples were characterized by low concentrations of Zr (0.60 to 6.16 ppm); Cr (905.40 to $18,778$ ppm); Ni (193.81 to 2790 ppm); and V (10.05 to 104.25 ppm), and high concentration of Sr (20.44 to 257.42 ppm), Cs (0.06 to 1.40 ppm), U (2.19 to 6.03 ppm), Th (0.09 to 1.72 ppm), Y (0.89 to 10.84 ppm), Nb (0.04 to 0.57 ppm), and Rb (3.58 to 45.94 ppm).

The primitive mantle-normalized trace-element plots (Figure 5d) of the Kaliapani rocks displayed a negative sloping pattern ($[\text{Th}/\text{Yb}]_{\text{PM}} = 3.25$ to 37.78), the incompatible elements had negative slopes ($[\text{Th}/\text{Eu}]_{\text{PM}} = 2.02$ to 15.88), and the compatible elements displayed a relatively flat to negative pattern ($[\text{Eu}/\text{Yb}]_{\text{PM}} = 1.61$ to 3.1). The primitive mantle-normalized trace-element plot showed prominent negative anomalies of Nb ($[\text{Nb}/\text{Nb}^*] = 0.01$ to 0.11), Ta ($[\text{Ta}/\text{Ta}^*] = 0.01$ to 0.11), Zr ($[\text{Zr}/\text{Zr}^*] = 0.03$ to 0.12), Hf ($[\text{Hf}/\text{Hf}^*] = 0.03$ to 0.08), and Ti ($[\text{Ti}/\text{Ti}^*] = 0.01$ to 0.32).

The Kathpal ultramafics displayed a limited range of variation in their total REE values, ranging from 2.56 to 21.50 ppm, with minimal REE fractionation. On the other hand, the Kaliapani ultramafics exhibited a broader spectrum in total REE values, spanning from 4.89 to 99.72 ppm, signifying significant variability. In contrast to the Kathpal samples, the Kaliapani samples were characterized by elevated REE concentrations and a preferential enrichment of LREE. The Kathpal ultramafics demonstrated a mild LREE enrichment, a relatively uniform distribution of HREE, and negative Eu anomalies ($\text{Eu}/\text{Eu}^* = 0.58$ to 0.81). In comparison, the Kaliapani ultramafics presented a descending REE pattern with LREE enrichment and a slightly negative Eu anomaly ($\text{Eu}/\text{Eu}^* = 0.60$ to 0.78). The high trace-element concentration, higher range in total REE values, and elevated LREE concentration of the KLPN samples relative to KTPL samples suggested that the KLPN samples may have interacted with more evolved melt during the secondary melting phase or the fractionation process.

4.3. Mineral Chemistry

4.3.1. Chromite

Chromite grain occurred as an independent phase in the Sukinda ultramafic rocks. The analyses of chromites from dunites were taken into consideration in this study. The Cr numbers, $\text{Cr}\# = [\text{Cr}/(\text{Cr} + \text{Al})]$, molar ratio], of chromites in the dunite in the Kaliapani and Kathpal areas varied from 0.70 to 0.82 and 0.68 to 0.76; the Mg number, $\text{Mg}\# = [\text{Mg}/(\text{Mg} + \text{Fe}^{2+})]$ molar ratio], of chromites in the dunite varied from 0.43 to 0.54 and 0.40 to 0.51; and the iron number ($\text{Fe}\# = \{\text{Fe}^{3+}/(\text{Fe}^{3+} + \text{Cr} + \text{Al})\}$ molar ratio) varied from 0.003 to 0.041 and 0.04 to 0.052, respectively. The inclusions of chromite grains in the ultramafics did not show any compositional variations from the core to the rim. All the data considered for the present research are chromite core compositions.

4.3.2. Orthopyroxene

Orthopyroxene in the Kaliapani area contained enstatite ($\text{En}_{90.4}$ to $\text{En}_{90.7}$) (Figure 3f). Enstatite has a low Al_2O_3 content (0.68–0.80 wt%), with low CaO (0.60 to 0.76 wt%) and TiO_2 contents (<0.06 wt%). Cr_2O_3 content ranges from 0.51 to 0.67 wt%. The Cr# [$\text{Cr}/(\text{Cr} + \text{Al})$ molar ratio] and Mg# [$\text{Mg}/(\text{Mg} + \text{Fe}^{2+})$ molar ratio] contents of enstatite in orthopyroxene vary from 0.30 to 0.37 and 0.91 to 0.92, respectively.

4.3.3. Olivine

The analyses of the olivine obtained from dunite showed it was high in magnesium (MgO 48.96 to 51.40 wt%) and low in Al_2O_3 (<0.05 wt%), CaO (<0.17 wt%), TiO_2 , and Cr_2O_3 (all the samples showed trace concentrations). The olivines in the dunites were identified as forsterite, and the forsterite concentration varied from $\text{Fo}_{90.9}$ to $\text{Fo}_{94.1}$.

5. Discussion

5.1. Role of Crustal Contamination

To comprehend the petrogenesis and tectonic contexts of the Sukinda ultramafic rocks, assessing the potential influence of crustal components on their composition was crucial. Throughout the phases of mantle melting, magma ascent, and temporary lodgment of melts, there was a chance of incorporating crustal elements into the magma, especially within a continental environment [53,54]. Nevertheless, the Sukinda ultramafic rocks exhibited substantial levels of Mg# (averaging 84 wt%), Ni (averaging 1709 ppm), Cr (averaging 15,050 ppm), V (averaging 71.5 ppm), and Sc (averaging 8 ppm), alongside diminished concentrations of Al_2O_3 (averaging 1.67 wt%), Na_2O (averaging 0.16 wt%), K_2O (occurring in trace amounts), and TiO_2 (averaging 0.05 wt%). These compositional characteristics provided no indication of potential crustal influence or contamination within the Sukinda ultramafic rocks.

Notably, crustal materials are typically enriched in LILEs and LREEs and depleted in Nb, Ta, and Ti [55]. Minor crustal contamination in the magma can manifest as a negative Nb and Ta anomaly; however, it also results in positive Zr and Hf anomalies in adjacent elements [56].

In the primitive mantle-normalized multi-element plot (Figure 5), a negative Nb anomaly was observed in the Sukinda ultramafic rocks. Additionally, the enrichment of LREEs in the REE plot suggested some crustal contamination (Figure 5). However, it is important to note that this geochemical evidence is not unique to crustal contamination alone. Similar signatures are also evident in mantle-derived boninite and norite magmas, contradicting the presumption of crustal contamination within the parent magma [57–61]. The enrichment of LREEs can potentially occur from certain processes, such as the subduction of continental or oceanic materials into the mantle or metasomatism of the mantle.

If the Sukinda ultramafic rocks underwent crustal contamination, a positive Zr and Hf anomaly would have been observed in the primitive mantle-normalized multi-element plot (Figure 5). Crustally contaminated rock samples usually exhibit disturbed REEs and spider plot patterns, while Sukinda ultramafic rocks display a parallel to sub-parallel pattern (Figure 5). Moreover, the Earth's continental crust is typically enriched in thorium (Th), characterized by higher ratios of Th/La (~0.30) [62] and Th/Ce (~0.15) [63], when compared to magmas originating from the Earth's mantle. These ratios are around ~0.12 for Th/La and 0.02–0.05 for Th/Ce in mantle-derived magmas [64]. In contrast, the Sukinda ultramafic samples exhibited Th/La and Th/Ce ratios averaging 0.18 and 0.09, respectively. These values suggest that there is no evidence of significant crustal contamination during the process of magmatic evolution in Sukinda ultramafic rocks.

5.2. Classification and Parent Melt Composition

Cr-spinel (chromite) occurs as the primary mineral phase in chromitite and as an accessory mineral phase in several mafic-ultramafic litho-types [51,65–67]. Chromite ore deposits are genetically linked to mafic-ultramafic magmatism occurring in particular period and tectonic settings (10, 11), and the chromite chemistry reflects the composition of parent magma. Chromites are considered as the earliest phase to crystallize from mafic-ultramafic magma and are used to determine the primary magma/melt composition. Therefore, the geochemical signature of chromites is widely used to understand the genesis of parent magmas and the tectonic settings of the host rock [65,68–75].

Various authors [68,74,76,77] have established a link between chromite's Al_2O_3 and TiO_2 contents and the composition of the surrounding melt. Ref. [77] proposed the idea that Al_2O_3 and TiO_2 contents within chromite remain unaltered, even in the presence of subsolidus re-equilibration with olivine or post-cumulus reactions. As a result, these particular components can be relied upon as consistent indicators for deciphering the geochemical composition of the melt from which the chromite originally crystallized. Ref. [68] pointed out this relationship by studying chromite–olivine and melt inclusion–chromite pairs in oceanic arc and intraplate tectonic settings. The study revealed that the Al_2O_3 and TiO_2 components could be effectively utilized to determine the tectonic setting in which the chromite formed.

In order to determine the Al_2O_3 and TiO_2 chromite–parent melt relationship of Sukinda ultramafics, a set of equations was formulated by [78] using the data of ref. [68]; the TiO_2 and Al_2O_3 contents of spinels (chromites) were exclusively the function of TiO_2 and Al_2O_3 in the melt. The best-fit logarithmic expression for the (Al_2O_3) spinel versus (Al_2O_3) melt and the power regression line for (TiO_2) spinel versus (TiO_2) melt were used to estimate the Al_2O_3 and TiO_2 contents of the parent melt. The spinel–melt compositional relationship is generally used in petrogenetic studies due to its independence from temperature variations or post-cumulus reactions between olivine and chromite. The equations for the (TiO_2) and (Al_2O_3) melts are as follows:

$$\text{Al}_2\text{O}_3 \text{ wt\% in melt} = 5.356 \ln (\text{Al}_2\text{O}_3) \text{ wt\% in spinel} - 1.7852 \quad (1)$$

$$\text{TiO}_2 \text{ wt\% in melt} = 1.1993(\text{TiO}_2 \text{ wt\% in chromite})^{0.8259} \quad (2)$$

The calculated Al_2O_3 wt% melt ranged from 9.93 to 12.54 wt% (Avg. 11.04 wt%) for KLPN samples and 11.21 to 12.86 wt% (Avg. 11.95 wt%) for KTPL samples. The calculated TiO_2 wt% in the melt ranged from 0.20 to 0.31 wt%. (Avg. 0.27 wt%) for KLPN and 0.26 to 0.44 wt% (Avg.

0.35 wt%) for KTPL samples. The calculated values of (Al_2O_3) and (TiO_2) melts indicated a boninitic affinity of the parent melt (Figure 6a). These calculated values are also comparable to boninites in the SSZ setting ($\text{Al}_2\text{O}_3 = 10.06\text{--}14.41$ wt%, $\text{TiO}_2 = 0.10\text{--}0.52$ wt%) [10,72,79–81]. The calculated parental melt of the Sukinda chromites and chemical characteristics of boninites in the Sukinda complex were compared with the other Archean–Paleoproterozoic mafic–ultramafic magmas in the Peninsular Indian shield and are presented in Table S3.

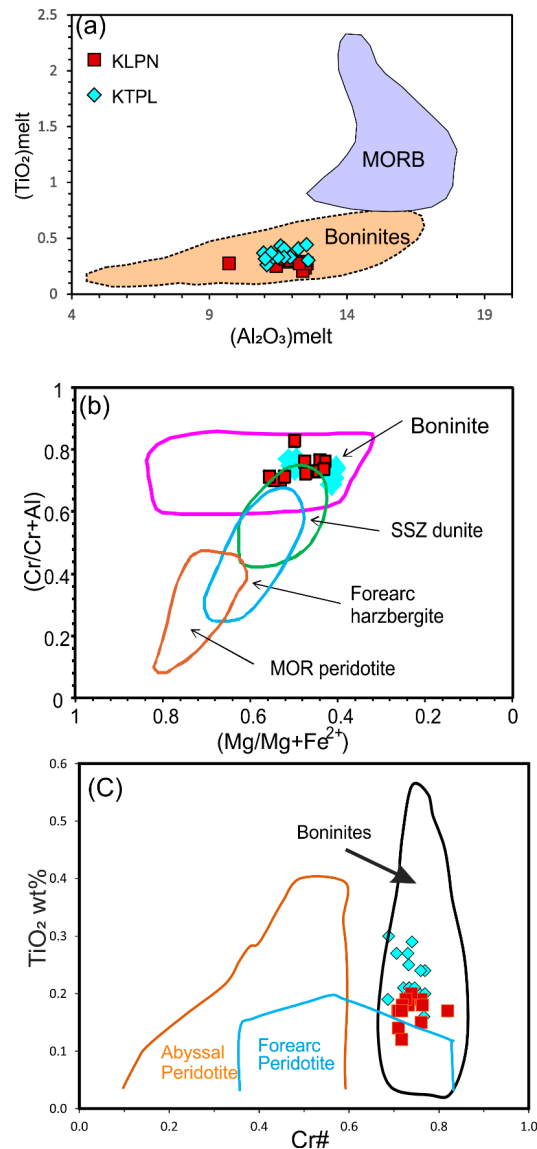


Figure 6. (a) Calculated TiO_2 vs. Al_2O_3 composition of melt that was in equilibrium with chromites from the Sukinda complex compared with MORB [82,83] and boninitic compositions [57,84]. (b) $\text{Mg}\#$ ($\text{Mg}/\text{Mg} + \text{Fe}^{2+}$) vs. $\text{Cr}\#$ ($\text{Cr}/\text{Cr} + \text{Al}$) diagram for spinels from Sukinda ultramafic rocks. Fields are drawn after [85–88]. (c) The compositional plot of TiO_2 vs. $\text{Cr}\#$ showing Sukinda ultramafics indicates a boninitic affinity. The general boninitite field taken after [88–92], the abyssal peridotite field taken after [67,87] and the forearc peridotite field taken after [85,93].

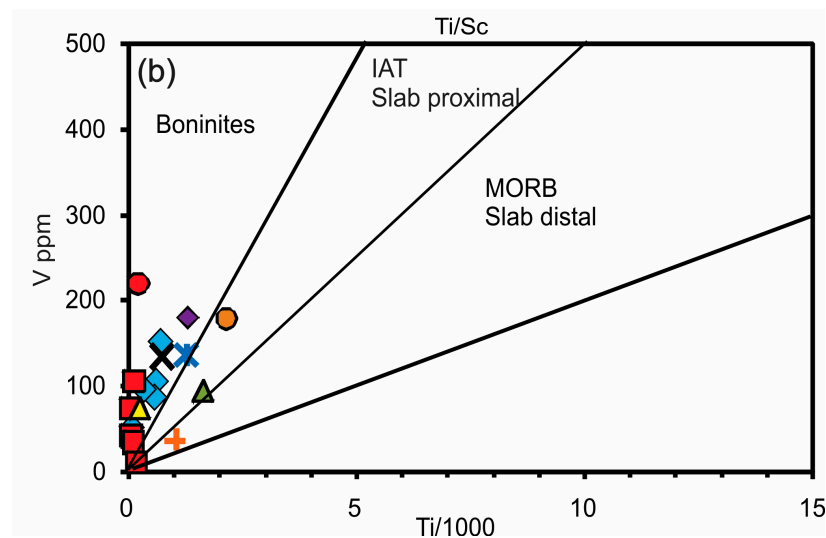
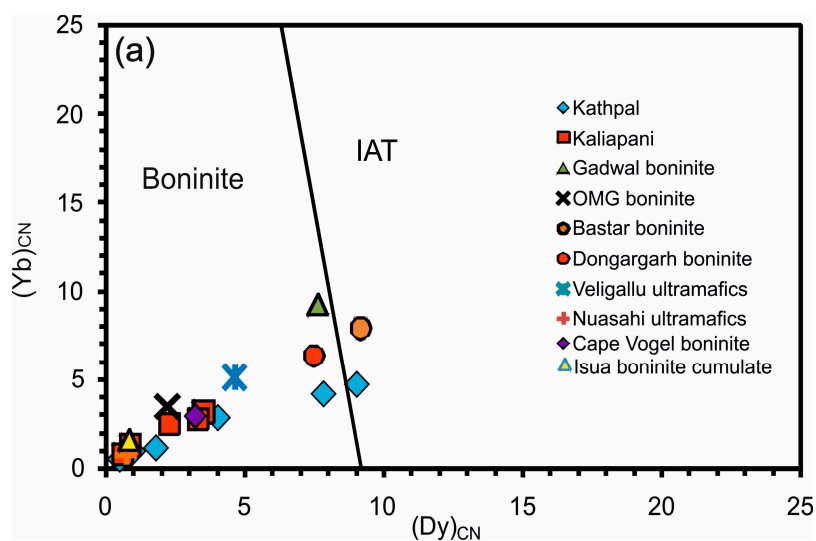
The Mg number ($\text{Mg}/\text{Mg} + \text{Fe}^{2+}$) versus Cr number ($\text{Cr}/\text{Cr} + \text{Al}$) plots are presented in Figure 6b (field of forearc harzburgites/peridotites and SSZ dunites were obtained from [85,86,92]). The abyssal peridotite field was obtained from [87] and the boninitite field was from [93]), depicting that the chromites fell within the boninitite field. In the geochemical plot of TiO_2 versus the Cr number (Figure 6c), all the chromites showed a boninitic parentage. The TiO_2 wt% and Al_2O_3 wt% in the melt of the Sukinda samples were comparable with the Singhbhum boninitic melt composition (Table S2).

The Sukinda ultramafic rocks are characterized by high Mg-olivine (Fo 90.5–94.1), Mg-orthopyroxene (En 90.4–90.7), and Cr-chromite (cr# 68–82) contents. Orthopyroxenes also showed a low aluminum content ($\text{Al}_2\text{O}_3 = 0.68\text{--}0.80$ wt%). This assemblage is typical of a boninite melt [94]. A highly fractionated PGE pattern of Sukinda chromites, demonstrated by Page et al. [22], and crystallization from S-undersaturated magmas [95] are features of boninitic magmas [96,97].

The mineral chemistry data of olivine, orthopyroxene, chromite, TiO_2 and Al_2O_3 melt calculation, and from previous studies strongly suggest that Sukinda ultramafic rocks derive from a boninitic parent magma.

Sukinda ultramafic rocks are primarily composed of dunites, partially serpentinized dunites, and pyroxenites. During the ultramafic rocks' residence and evolution process, Na_2O , K_2O , and large ion lithophile elements (LILs) (K, Sr, Cs, Rb, Ba) were possibly mobilized and did not reflect their initial distributions. Hence, high-field-strength elements (HFSEs) (Ti, Zr, Y, Nb, Ta, Hf, Th), REEs, and transitional elements (Cr, Ni, Cs, V) are used to classify the Sukinda ultramafic rocks. On the $(\text{Yb})_{\text{CN}}$ vs. $(\text{Dy})_{\text{CN}}$ diagram (Figure 7a), the samples occupy the field of boninites; one sample falls within the transition of boninite and island arc tholeiite (IAT) field. The samples from the Sukinda ultramafic complex with low V vs. $\text{Ti}/1000$ contents clustered in the "boninite" field (Figure 7b).

The La/Sm vs. TiO_2 distribution (Figure 7c) was narrow and lay within or close to the Phanerozoic boninite field. In the Ti/V vs. Ti/Sc plot (Figure 7d) (one sample close to the SHMB field), most Sukinda samples were close to the fields of boninite.



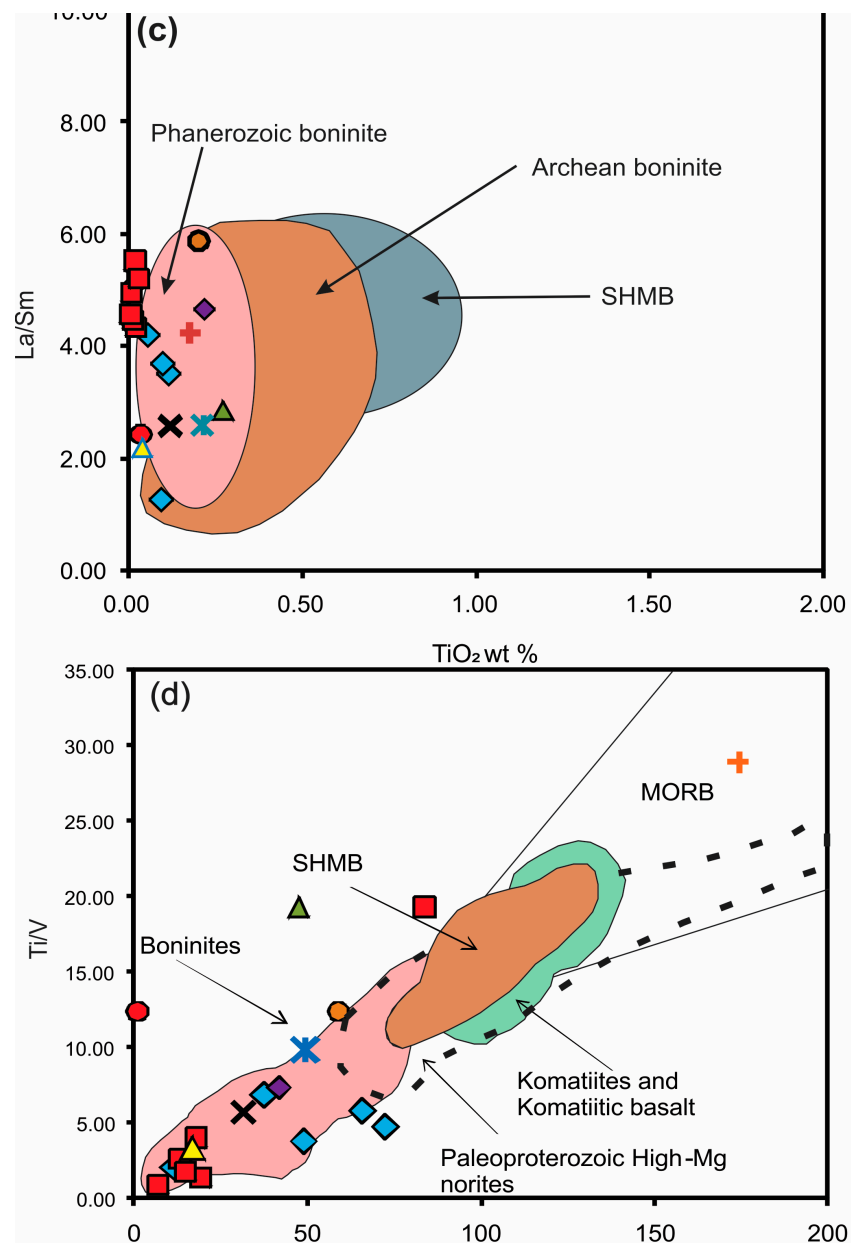


Figure 7. (a) $(Yb)_{CN}$ vs. $(Dy)_{CN}$ plot [98] showing distinct fields for boninites and island arc tholeiites (IATs), where most of the Sukinda rock samples cluster in the boninite field. (b) Ti/1000 vs. V diagram (after [99]) illustrating the studied samples occupying the fields of boninite. (c) La/Sm vs. TiO₂ classification diagram of [58,100,101]. (d) Ti/Sc vs. Ti/V diagram for Sukinda ultramafics; the samples occupy the fields of boninites, which differentiate from komatiites, komatiitic basalts, SHMBs, and Palaeoproterozoic high-Mg norite fields after [54,55,102]. The data of the Sukinda ultramafic complex are plotted along with different high-Mg rocks of the world for comparison purposes. The data are obtained after Gadwal boninite [103]; OMG boninite [46]; Bastar boninite [104]; Dongargarh boninite [105]; Nuasahi ultramafic [9]; Veligallu ultramafics [48]; Cape Vogel boninite [106], and Isua boninite cumulate [52].

5.3. Comparison and Distinction of Sukinda Boninites from Komatiites, Siliceous High-Mg Basalts, Picrites, and Other Ultramafic Formations

Compositional overlaps were seen between boninite, komatiites, siliceous high-Mg basalts, high-Mg norite, and picrite (Table S2). There was a minor geochemical difference between these high-Mg mafic–ultramafic rocks. However, these mafic–ultramafic rocks were identified by their different petrogenesis and distinct geochemical characterization. Geochemically, these high-Mg mafic–ultramafic rocks have high-silica, high-Mg, low-Ti,

and low-HFSE levels. Immobile trace-element concentrations, such as Ti, Zr, V, Sc, Yb, and REEs, are essential for discriminating high-Mg mafic–ultramafic rocks, such as boninites and siliceous high-magnesium basalt, komatiites, and picrite [61,107]. The chemical composition of boninite can be recognized by $\text{SiO}_2 > 53$ wt%, its high Mg number (Mg#), $\text{Al}_2\text{O}_3/\text{TiO}_2$, characteristic U-shaped REE and inclined LREE pattern, and low concentrations of Nb, Ta, and Ti [103].

Higher TiO_2 and lower Al_2O_3 levels chemically characterized picrites and showed an MREE-enriched REE pattern compared to LREE and HREE with positive Zr and Nb anomalies [47]. The plume-generated Archean picrites [108] were characterized by high Nb > 12 ppm contents, Nb/Th > 8 ratio, and positive Nb anomalies. The abovementioned geochemical characterization of picrites was not similar to Sukinda ultramafic rocks.

The high MgO and Mg# concentrations with low Al_2O_3 , CaO, and TiO_2 contents and low HFSE (Nb, Zr, Y) and Yb in the Sukinda boninites overlapped with Al-depleted komatiites [109,110]. The high MgO wt% may be due to the second-stage partial melting of a refractory and depleted mantle source [111]. Compared to Bababudan komatiites, the chondrite-normalized rare-earth element pattern showed a depleted LREE and enriched HREE pattern; the negative Nb anomaly observed for the komatiite samples was attributed to the assimilation of lower crustal materials. The Bababudan komatiites also showed positive Zr, Hf, and Ti anomalies on the mantle normalized multi-element diagram, suggesting the derivation of parent magma by melting under anhydrous conditions in the shallow mantle domain, and the garnet entered the melt phase [112].

The $\text{Al}_2\text{O}_3/\text{TiO}_2$ ratio is the most distinguishing ratio between komatiites and boninites. Komatiites ($\text{Al}_2\text{O}_3/\text{TiO}_2 < \sim 20$) are generated by the dry melting of mantle plumes, and boninites ($\text{Al}_2\text{O}_3/\text{TiO}_2 > 20$) are formed by the wet melting of the refractory mantle wedge in a subduction complex [94,103]. The Katpal samples showed a range of $\text{Al}_2\text{O}_3/\text{TiO}_2$ ratio range (27.0 to 64.47) and the Kaliapani samples showed a $\text{Al}_2\text{O}_3/\text{TiO}_2$ ratio range (35.9 to 74.06). Hence, the samples from the Katpal and Kaliapani areas had boninitic characteristics. According to [59,61,94,104,113,114], the Archean komatiites ($\text{CaO}/\text{Al}_2\text{O}_3 > 0.85$) and Phanerozoic boninites ($\text{CaO}/\text{Al}_2\text{O}_3 < 0.85$) can be distinguished based on the $\text{CaO}/\text{Al}_2\text{O}_3$ ratio. The $\text{CaO}/\text{Al}_2\text{O}_3$ ratio of Kaliapani samples varied from 0.05 to 0.59, and the Katpal samples varied from 0.02 to 0.18 (one sample showed a ratio of 1.24). Hence, the samples were from the Katpal and Kaliapani areas of a Phanerozoic boninite affinity. However, some studies propose that komatiites or komatiitic basalts are the Archean equivalents of boninites and form the partial melting of mantle under hydrous conditions [103,115–117].

Siliceous high-magnesium basalt is another variety of high-Mg rocks found in the Archean–Proterozoic boundary in and around granite greenstone terranes [49]. The genesis of SHMB has different theories: (a) according to [118], SHMBs are the Archean equivalent of modern boninites, (b) SHMBs are the volcanic equivalent of Late Archaean high-Mg norites [59,64], (c) and SHMBs are the products of crustal assimilation and the fractional crystallization (AFC) of komatiite magma, [64,119]. SHMBs and boninites have some geochemical differences: SHMBs have a low $\text{Al}_2\text{O}_3/\text{TiO}_2$ and Sc/Y ratio and a high Ti/Zr and Ti/Sc ratio than boninites; however, these two have larger overlapping values [64,120] (Table S2). In comparison to Sonakhan SHMBs (Bastar craton, Manu [72]), the $\text{Al}_2\text{O}_3/\text{TiO}_2$ (10.18 to 20.71) and Sc/Y (0.23 to 1.16, avg. 0.55) ratios are lower than the Sukinda boninitic rock ratios ($\text{Al}_2\text{O}_3/\text{TiO}_2 = 27.0$ to 74.06) and (Sc/Y = 0.75 to 11.23 avg. 3.56), and the Ti/Zr (126.4 to 397.3 avg. 218.7) and Ti/Sc (265.8 to 475.3 avg. 372.7) ratios of Sonakhan SHMBs are higher than Sukinda boninitic rock ratios (Ti/Zr = 10.74 to 215.33 avg. 90.37), (Ti/Sc = 7.14 to 83.72 avg. 35.74).

The trace-element and mineral chemistry study shows that Sukinda ultramafic rock is boninitic in nature. Significantly high MgO, Mg#, and low SiO_2 contents do not comply with the standard classification schemes for boninite [113,121]. On the other hand, the high Mg# (78 to 93) content in the Sukinda ultramafics suggests that the rocks may be of a cumulate origin. In contrast, Phanerozoic boninites rarely exceed 18% MgO

[106,122,123], and the SiO₂ content in Archean boninites, in contrast to modern boninites, is typically < 52 wt% (e.g., [102,103,120,124,125]). The boninitic rocks in the Singhbhum Craton are characterized by low SiO₂ levels of 42 to 46 wt%, high Mg# levels of 80 to 83 wt%, and MgO levels of 30 to 32 wt% (e.g., [46]), and in the Dharwar Craton, the reported boninite composition is characterized by low to medium SiO₂ levels of 45 to 52 wt%, high Mg# levels of 70 to 82 wt%, and MgO levels of 12 to 24 wt%, e.g., [103]). Neoproterozoic Abitibi greenstone belt boninite rocks show a maximum MgO content of 24.5 wt%, Mg# 83, with a minimum of 44 wt% SiO₂ (Kerrick et al., 1998) [124]. These boninite formations are comparable to Sukinda boninitic rocks. A broader geochemical comparison of different high-Mg mafic rocks and boninites from various Archean and Phanerozoic tectonic settings is presented in Table S2. The Mg# of Sukinda boninite is consistent with boninites from Singhbhum (OMG), Dharwar, Bastar, Abitibi, and Isua formations; however, they show higher values than those derived from Archean boninites. The Al₂O₃/TiO₂ ratios for Sukinda boninites conform to Singhbhum (OMG), Bastar, Abitibi, Isua, and Archean boninites, while relatively lower Al₂O₃/TiO₂ ratios characterize Dharwar boninites.

We compared primitive melts from different tectonic settings and Archean–Paleoproterozoic mafic–ultramafic magmas from Peninsular India presented with Sukinda boninitic rocks based on Al₂O₃ and TiO₂ melt contents by the chromite mineral chemistry data (Table S3).

5.4. Petrogenesis of Sukinda Ultramafic Rocks

The generation of boninitic magmatism has been examined by different experimental studies and trace-element modeling. The primary components of boninite magmatism are a high hydroxyl content, higher mantle temperature, and mantle decompression [89,123,126,127]. According to [94,128–130], boninitic magma generation is achieved through a high degree of partial melting, which is metasomatized by slab-derived fluids/melts in a subduction zone at high temperatures (1130–1275 °C) and shallow depths (0.3–1.7 GPa).

The following models were suggested to account for the petrogenesis of boninite magma:

1. Partial melting of serpentinized harzburgite at the time of subduction initiation along a transform fault [131].
2. Subsequent melting of the mantle begins at a mid-oceanic ridge and continues above a subduction zone in response to the addition of water or extension [132,133].
3. Mantle melting is associated with subduction underneath an active or dying oceanic ridge system [93] or beneath a young, hot, oceanic lithosphere [134,135].
4. Partial melting of the mantle wedge in response to the subduction of young, hot, oceanic crust in the early stages of the subduction process [136,137].
5. Partial mantle wedge melting due to the subduction of an active spreading center trending sub-parallel to an intra-oceanic arc-trench system [94].
6. Contact melting of the hydrous mantle wedge due to the introduction of a hot mantle diapir during arc rifting [137].

Hence, the two essential factors of boninite magma generation are: (a) the partial melting of the depleted mantle source and (b) the addition of subducted slab components to the mantle wedge.

5.4.1. Partial Melting of the Depleted Mantle Source

Sukinda ultramafic rocks primarily comprise olivine, pyroxene, and chromite with serpentines. The serpentines are the product of the retrograde metamorphism of olivine and pyroxene. The mineralogical composition of unaltered ultramafics from Sukinda indicates that they evolved from a peridotitic source, most likely spinel-harzburgite. HFSEs (Nb, Zr), REEs (Gd, Yb, Y), and transition elements (Ti, V, and Sc) are considered insoluble in an aqueous fluid. At the time of the lithosphere subduction, the lithospheric slab melts

by flux melting simultaneously with the mantle wedge. These insoluble elements are retained in the subducted slab; therefore, the concentrations of these elements in the mantle wedge are unchanged. Thus, the concentration of these elements in the arc magma is predominantly controlled by the mantle wedge [138–140]. Hence, these elements' concentrations and ratios can be used to demonstrate the nature of the mantle source.

The notably low Ti/V (2.04–6.88, avg. 4.67) and Ti/Sc (11.73–73.33, avg. 47.21) ratios in the Katpal samples and Ti/V (0.83–19.23, avg. 4.93) and Ti/Sc (7.14–83.72, avg. 26.18) ratios in the Kaliapani block relative to the average N-MORB (Ti/V = 29, and Ti/Sc = 190 [94] show that the mantle source of the Sukinda ultramafic rocks is comparatively more depleted than the average N-MORB. The typical, very high MgO concentrations in the Katpal (32.32 to 44.41 wt%; avg. 39.85 wt%) and Kaliapani areas (34.54 to 47.94 wt%; avg. 42.44 wt%) and very low TiO₂ (<0.03 wt%; avg. 0.02 wt %), Al₂O₃ (<1.22 wt%; avg. 0.99 wt%), and CaO (<0.69 wt%; avg. 0.30 wt%) levels in the Kaliapani and Katpal areas (TiO₂ (<0.12; avg. 0.08 wt %), Al₂O₃ (<3.23 wt%; avg. 2.48 wt%), CaO (<3.85 wt%; avg. 0.87 wt%)) suggest that the ultramafic samples were derived from a highly depleted mantle source [80,133]. The high Mg#, Cr, Ni, and low Nb, Zr, and Y concentrations, and their Zr/Y (avg. 1.24) and Nb/Y (avg. 0.07) ratios and negative Nb anomalies relative to the neighboring trace elements (Figure 5) further suggest that the melts are derived from a relatively high-degree partial melting of a depleted peridotitic mantle source. Indeed, boninite magma's genesis needs a depleted upper mantle source by basaltic melt abstraction in single or multiple episodes, which implies that the mantle harzburgite is the source [80,81,132,133].

Several models were considered to demonstrate the mantle's source composition and geochemical stability field from which the residual magma was derived. Dy/Yb ratios can serve as an indicator to differentiate between the spinel and garnet stability domains during the partial melting of the depleted mantle source [141,142]. In general, partial melting within the garnet stability field tends to produce melts with high Dy/Yb ratios (>2.5), while melting within the spinel stability field produces melts with low Dy/Yb ratios (<1.5). Sukinda boninites, on the other hand, have Dy/Yb ratios ranging from 1.11 to 2.99. This suggests that they are formed through mantle-melting conditions, including spinel peridotite facies and garnet peridotite facies. In the Dy/Yb vs. La/Yb diagram (Figure 8a) [143], most of the Kaliapani samples (Dy/Yb = 1.62–2.99) fall in the garnet peridotite facies zone and the Katpal samples (Dy/Yb = 1.1–1.8) fall in the spinel peridotite zone, respectively. A garnet-bearing source is suspected if $(\text{Gd}/\text{Yb})_{\text{N}} > 2$ (four samples from Kaliapani and no samples from Katpal show garnet-bearing sources) or $(\text{Tb}/\text{Yb})_{\text{N}} > 1.8$ (four samples from Kaliapani and no samples from Katpal show garnet-bearing sources) [144]. In the $(\text{La}/\text{Sm})_{\text{CN}}$ vs. $(\text{Gd}/\text{Yb})_{\text{CN}}$ diagram (Figure 8b), Katpal samples show the affinity of a spinel-bearing source and Kaliapani samples from a garnet-bearing one. These relationships constrain the melting depth, and the spinel/garnet limit is between 80 and 90 km. Hence, the Kaliapani samples are generated at a greater depth than the Katpal samples.

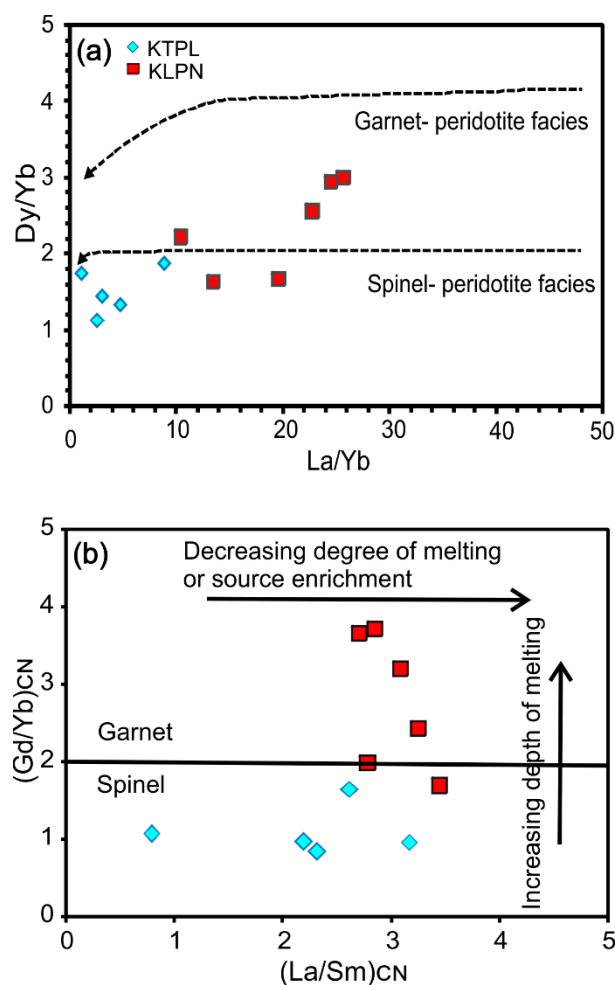


Figure 8. (a) Dy/Yb vs. La/Yb diagram [143] suggests mantle melting in spinel peridotite for Sukinda ultramafics. (b) (La/Sm)_{CN} vs. (Gd/Yb)_{CN} diagram points to a spinel-bearing source and a garnet-bearing source, and then to a decreasing depth of melting. Normalization values of the chondrite C1 after [40].

5.4.2. Addition of Subducted Slab Components to the Mantle Wedge

The rocks formed in a subduction zone environment start from the early decompression melting of a depleted mantle peridotite to the fluid-fluxed hydrous melting of fertile peridotite mantle that has been remarkably changed by subduction-derived fluids/sediments/melts due to the melting of the subducted slab. The changes are seen in the magma composition, which is regulated by the collaborated effect of melt depletion, metasomatism, enrichment of the mantle wedge by hydrous fluxes, and mantle wedge hybridization by slab melts. This gives rise to tholeiitic forearc basalt in the early stage, followed by the subsequent eruption of boninites, calc-alkaline arc basalts, high-Mg andesites, Nb-enriched basalts, and adakites [145].

During the early subduction process, the hydroxyl components are released from the subducted slab by the dehydration process in shallow mantle conditions and the mantle wedge metasomatism by the addition of slab-derived fluids and water, which leads to boninite magmatism [94,129,130,146]. The boninite magmas are significantly enriched in LILE and LREE compared to HFSE. The Sukinda ultramafics indicate significant negative anomalies at Nb, Ta, Zr, Hf, and Ti on primitive mantle-normalized trace-element plots (Figure 5), which suggests a significant LILE enrichment relative to the HFSE in the mantle. This significant characteristic feature suggests the infiltration of hydrous fluid from the slab into the mantle source from where the boninite melt is formed [94,129,147–150]. During the flux melting of the subduction slab, the mobile elements, i.e., LREEs and LILEs,

are released from the slab and added to the mantle wedge; however, the high-field-strength elements, due to their immobile nature, are retained in the dehydrated slab in a subduction regime [106,129,150]. The released fluid from the subducted slab promotes the migration of elements and decreases the melting temperature of the mantle, which contributes to 3%–25% of the melting of the mantle wedge at a depth of 30–50 km and a 1250–1350 °C mantle temperature [151,152]. The enrichment of Th, U, and LILEs (Figure 5), and the LREE values for Katpal and Kaliapani indicate that the parental magma is subsequently metasomatized by the infiltration of subducted fluids and/or melts during the melt generation process.

In summary, we believe that the geochemical characterization of Sukinda boninites is derived from (i) multiple episodes of extraction of basaltic melt from depleted peridotite sources more refractory than residua from MORB generation; (ii) hydrous fluids/melts derived from a subducting slab enriched in incompatible elements (LILE, LREE); and (iii) the flux-induced re-melting of a metasomatized mantle wedge generating boninitic melts. Overall, it appears that boninitic parental magma is derived from a high degree of partial melting of a depleted mantle source in a subduction zone environment. The ultramafic cumulates were formed due to the early removal of cumulus phases, such as chromite, olivine, and orthopyroxene, during fractional crystallization of the parental boninitic magma.

6. Pressure Condition and Thermal History

The Mg-Fe charge transfer equation between olivine and chromite was used to determine the crystallizing temperature of Sukinda ultramafic rocks. This equation was used as a good geothermometry for chromite-bearing ultramafic rocks [70,153]. In the present study, the forsterite concentration was very high (Fo% = 90 to 94%); therefore, calibration [154] was essential. The thermometry equation is:

$$T^0 (\text{K}) = (4250 Y^{\text{SpCr}} + 1343) / (\ln K^{\text{D}} + 1.825 Y^{\text{SpCr}} + 0.571) \quad (3)$$

where K^{D} denotes the apparent distribution coefficient $K^{\text{D}} = \ln K^{\text{D}} - 4.0 Y^{\text{SpFe3+}}$ [155] $K^{\text{D}} = X^{\text{Olivine}} X^{\text{SpFe}} / X^{\text{Olivine}} X^{\text{SpMg}}$ and $Y^{\text{SpCr}} = (\text{Cr} / \Sigma \text{ octahedral cations})^{\text{sp}}$.

From this equation, the calculated temperature of the Sukinda ultramafic complex ranged from 1258 °C to 1370 °C (average 1329 °C).

The Olivine+chromite+orthopyroxene mineral assemblage indicated the crystallization of rocks with a pressure range of 1 to 2 Gpa, equivalent to pyrolite's melting condition in the spinel peridotite field [87]. The P-T figure (Figure 9) of melting pyrolite [156] indicates the possible crystallization of Sukinda ultramafic rocks at about ~1.7 Gpa and 1300 °C, representing the spinel peridotite field.

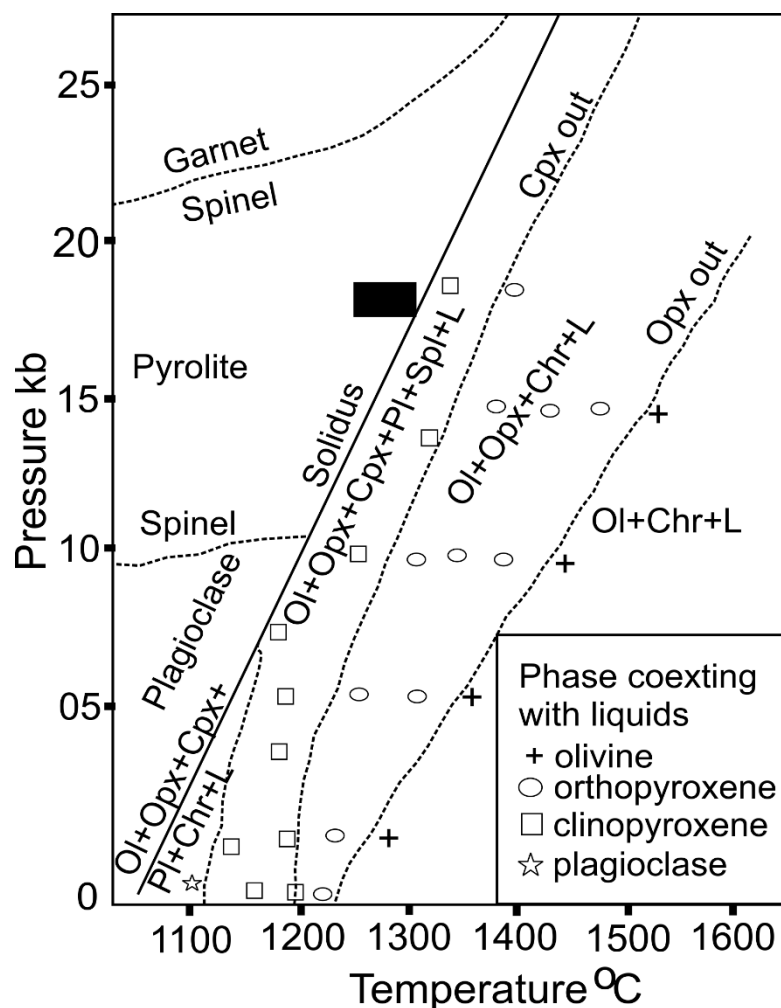


Figure 9. P–T diagram for melting of pyrolite (after [156]). Ol: olivine, Opx: orthopyroxene, Cpx: clinopyroxene, Spl: spinel, Chr: chromite, pl: plagioclase, L: liquid, the rectangular black box indicates the possible pressure condition of Sukinda ultramafic rocks.

7. Tectonic Framework of the Sukinda Complex

The mafic–ultramafic rocks are formed in diverse tectonic environments, such as large layered igneous complexes (stratiform type), subduction allied tectonic settings (Alaskan type), and ophiolites in active orogenic settings (podiform type). The above mentioned varieties of tectonic settings have their characteristic geochemical features, which can be used to recognize the tectonic environment [79,87,157].

A high U/Th ratio (0.48–23.9) and negative Nb-Ta-Ti anomalies in the primitive mantle normalized multi-element diagram indicate the significant role of subduction-related melts/fluids associated with boninite magma genesis. If the mantle plume (komatiitic affinity) mixed up in the genesis of boninites, there would have been a positive Zr anomaly in the multi-element-normalized diagram [127,158–160].

Sukinda ultramafic rocks are characterized by high Mg-olivine (Fo 90–94), high-Mg, and low-Al orthopyroxene (En 90.4–90.7, Al₂O₃ < 0.80 wt %) concentrations, and a high-Cr concentration in chromites (Cr# 68–82) is typical of boninite melts in supra-subduction zone environments [94]. According to [57], boninitic magmas are associated with subduction and arc-related settings, and the bivariate Al₂O₃ versus TiO₂ plots (Figure 10a) indicate that chromites fall in the field of supra-subduction zone peridotites and high-Ti arc settings. The Al₂O₃ versus Fe²⁺/Fe³⁺ plot (Figure 10b) also suggests chromites are linked to either the supra-subduction zone or volcanic settings. The chromite chemistry of Sukinda ultramafics suggests that chromite host rocks are associated with the SSZ environment,

which further indicates that they are formed during the initial stages of subduction. The evidence from the SSZ rocks suggests that the early formed magma is of a boninitic composition, which is derived in response to the intra-oceanic subduction resulting in the partial melting of the hydrated oceanic lithosphere in the mantle wedge [148,161].

The plausible model, which is schematically shown (Figure 11), can be illustrated and described; Sukinda ultramafics in the Singhbhum Craton are formed from multiple episodes of extraction of basaltic melt from a depleted peridotite source. The mantle wedge generating boninitic melts intrudes further into the iron ore group of rocks in a supra-subduction zone setting. Cumulates of olivine and pyroxene are developed, and chromite mineralization occurs in the intercumulus space in the Sukinda ultramafic complex.

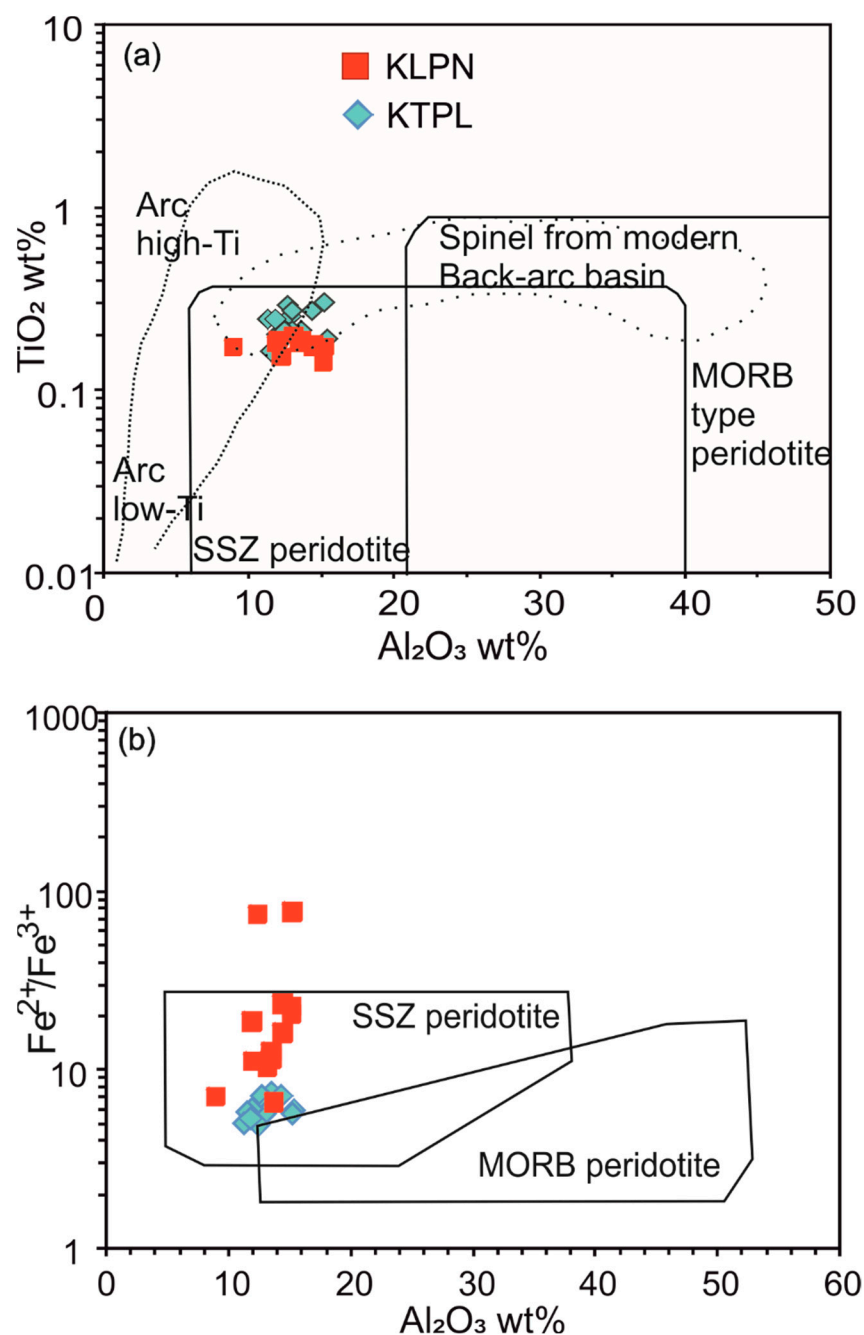


Figure 10. (a) TiO₂wt% vs. Al₂O₃wt% and (b) Fe²⁺/Fe³⁺ vs. Al₂O₃ wt% diagram for chrome spinel in Sukinda ultramafics indicate supra-subduction zone tectonic settings; field after [62].

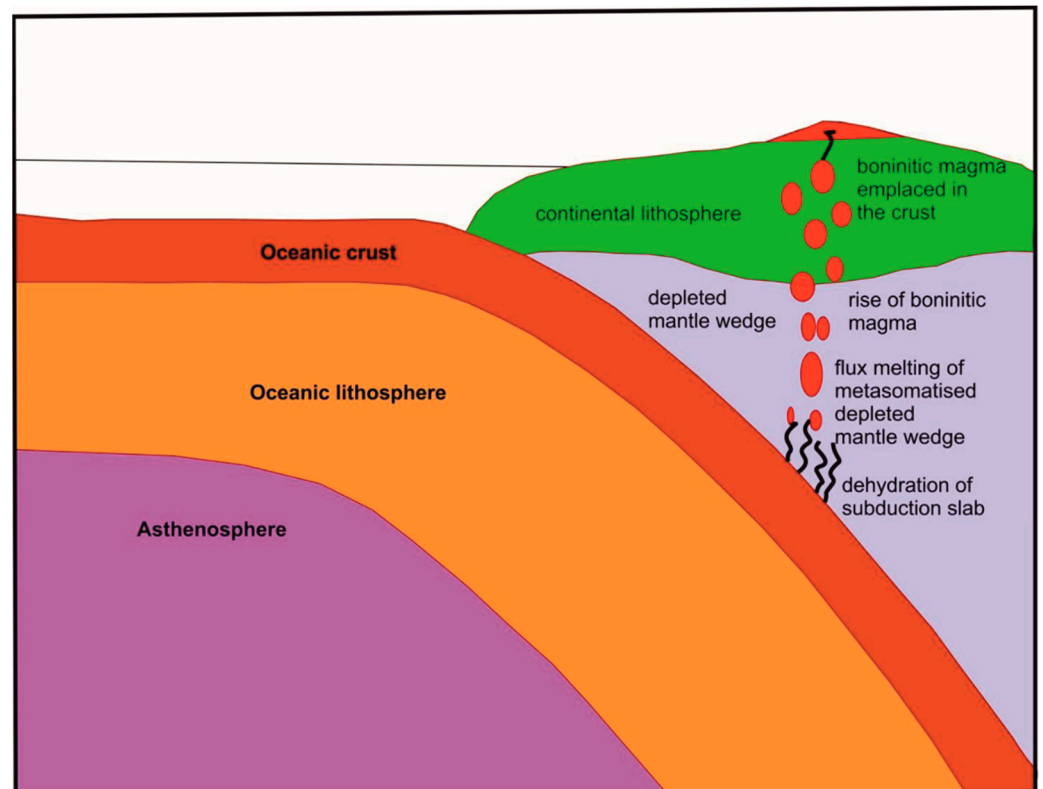


Figure 11. Schematic representation of possible tectonic setting for forming chromiferous ultramafic rocks in the Sukinda complex.

8. Conclusions

The study extensively examined the Sukinda ultramafic complex in the Kaliapani and Katpal areas, encompassing comprehensive petrology, whole-rock geochemistry, and mineral chemistry analyses. The primary conclusions drawn from this research are as follows:

Firstly, the Sukinda ultramafic rocks found within the Singhbhum Odisha Craton exhibit distinctive major and trace-element geochemistry data. By employing melt calculations based on unaltered chromite mineral chemistry data, we ascertained that the original composition of the parent magma responsible for the Sukinda ultramafic complex aligned with a boninitic parentage.

Additionally, the chemical makeup of the chromites within the ultramafic rocks from the Sukinda complex provided compelling evidence that their formation occurred within the context of a supra-subduction zone arc tectonic setting.

Furthermore, the insights achieved from mineral chemistry analyses of Sukinda ultramafics indicate a crystallization temperature of approximately ~ 1300 °C, as determined through olivine spinel thermometry. This process occurred under a pressure exceeding 1.0 GPa, signifying that the Sukinda ultramafic rocks originated from upper mantle conditions.

Moreover, the ultramafic rocks distinctly exhibited a boninitic affinity, characterized by an enrichment in fluid mobile elements, alongside conspicuous negative anomalies in elements, such as Nb, Zr-Hf, and Ti. These features collectively point towards a genesis process deeply rooted in subduction-related environmental conditions.

Finally, the formation of ultramafic cumulates can be attributed to the early elimination of cumulus phases, such as chromite, olivine, and orthopyroxene. This phenomenon is attributed to the fractional crystallization process of the initial boninitic magma.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/min13111440/s1>, Table S1: Main element oxide contents by XRF (wt%), trace element and REE contents (ppm, $\mu\text{g}\cdot\text{g}^{-1}$) by HR-ICP-MS, and relative standard deviations (%RSD) for reference materials JH-1, JB-3, BHVO-1, UB-N. $\text{Fe}_2\text{O}_3\text{T}$ represents total iron content. Certified values from GEOREM (<http://georem.mpch-mainz.gwdg.de>, accessed on 17 July 2023). Further explanation in text; Table S2: The geochemical comparison of different high-Mg mafic rocks and boninites from various Archean and Phanerozoic tectonic setting [46,58,59,64,102–104,112,124,162,163]; Table S3: Calculated parental melt of the Sukinda ultramafic complex chromites and chemical characteristics of boninites compared with other Archean-Paleoproterozoic mafic-ultramafic magmas of Peninsular India and primitive melts of different tectonic settings [10,35,46,68,75,78,80,86,101,103,104,114,164–176].

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