

Chromian-spinel compositions from the Hiep Duc serpentized peridotite, central Vietnam: implications for early Paleozoic tectonics of the Indochina block

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Abstract: The Hiep Duc serpentized peridotites are parts of the ophiolitic complexes that have long been considered as remnants of Paleo-Tethyan oceanic lithosphere between the Kon Tum massif and Truong Son belt. Our analytical data using electron microprobe analysing system showed that the serpentized peridotites contain some relicts of mantle-derived Cr-spinel, and a later metamorphic mineral assemblage composed by talc, serpentine-group minerals, and magnetite. The primary compositions of the Cr-spinels from the serpentized peridotites are used to deduce their petrogenesis and tectonic environments. These spinels are characterized by medium Cr₂O₃ content (31.53–37.01 wt.%), high contents of Al₂O₃ (20.01–33.94 wt.%), FeO (18.13–28.76 wt.%) and MgO (9.71–13.47 wt.%), and very low TiO₂ content (0.17–0.32 wt.%) with medium Cr# (0.44–0.47) and Mg# (0.62–0.71). They also show low Fe³⁺ and Fe²⁺ of (0.03–0.09) and (0.40–0.60), respectively. Evaluating all characteristics of the Cr-spinel in the serpentized peridotites indicate that the rocks are of supra-subduction peridotites. The Cr-spinel compositions combined with Al₂O₃ and TiO₂ contents of parental melts as well as available data within the TPSZ suggest that the rocks probably of back-arc tectonic setting that was triggered by a Paleo-Tethys underneath the Kon Tum Massif during the early Paleozoic.

1. Introduction

Crustal growth through successive subduction and accretion generates well-defined suture zones marked by ophiolites in a supra-subduction zone setting. The Indochina block is a Gondwana-derived terrane that is separated by the opening of different branches of the Paleotethyan Ocean, and is marked by the presence of various suture zones such as the Song Ma, Sra Keao, Nan-Luang Prabang Suture Zones (Metcalf, 2013). In central Indochina, the Tam Ky – Phuoc Son Suture Zone (TPSZ) extends from Tam Ky to Phuoc Son areas (Vietnam) over a distance of >100 km (Tran et al., 2014) (Figure 1a). The suture zone is considered to separate the Truong Son Belt (TSB) to the North from the Kon Tum Massif (KTM) to the South (Tran et al., 2014).

Along the TPSZ in Vietnam, numerous lenticular-shaped, metamorphosed peridotites (dunite and harzburgite), meta-gabbros, pyroxenites, and plagiogranites are observed over a few meters to several kilometers in length. Based on the composition of the relict minerals (e.g. Cr-spinel, clinopyroxene) from the serpentized rocks, Pham et al. (2006) and Izokh et al. (2006) proposed the rocks are of the Alpine-type ophiolitic complex. All the rock types in the TPSZ have been tectonically juxtaposed by foliated meta-extrusive rocks that are intercalated with marbles, meta-siliceous shales, and volcanogenic metapelites, tentatively defined as the early Paleozoic ages of the Kham Duc complex (Figure 1b) (Faure et al., 2018; Tran

et al., 2014).

Although the complexity of lithology within the TPSZ has been preferred as an ophiolitic signature that represents amalgamation zone between the TSB and KTM during the early Paleozoic (Nguyen et al., 2019; Tran et al., 2014), the tectonic origin of the ultramafic rocks of the Hiep Duc complex within the TPSZ remains controversial. In this paper, we present new petrology of serpentinized rocks in the Hiep Duc area in order to define the tectonic setting of the rocks.

2 Geological background

The TPSZ is composed of five main complexes: The Kham Duc, Ngoc Hoi, Dieng Bong, Hiep Duc, and Nui Vu Complexes. The Nui Vu, Ngoc Hoi, and Dieng Bong Complexes are dominantly observed in southern and southwestern part of the TPSZ. The Kham Duc Complex is composed of meta-extrusive rocks (mafic to felsic components) intercalated with meta-siliceous, metapelite (Nguyen et al., 2019) while the Dieng Bong and Ngoc Hoi Complexes are characterized by intrusive rocks of meta-pyroxenite, meta-gabbro,

plagiogranite, tonalite and usually exposed as small to moderate block or lenticular shapes. All the rocks display oriented-structures, and are conformably distributed within surrounding foliated metamorphic rocks of the Nui Vu volcanic complex (Nguyen et al., 2019; Tran and Vu, 2011). Magmatic zircon ages of 518 Ma and 502 Ma dated for a trondjemite-tonalite suite of the Dieng Bong complex have been reported for the northeastern part of the TPSZ. Their geochemical characteristics suggest the existence of a Cambrian island arc in the northern part of the TPSZ (Nguyen et al., 2019). The Nui Vu complex consists of metapelite, metapsammite, paragneiss, amphibolite of greenschist- to amphibolite-facies. A clockwise P-T path for the pelitic gneiss in this complex got peak temperature at ca. 570–700 °C pressure at ca. 7.9–8.6 kbar (Nakano et al., 2007; Osanai et al., 2004). Usuki et al. (2009) reported the high pressure/medium temperature metamorphism occurred before HT/medium pressure metamorphic event at ca. 450 Ma that overprinting by the Permo-Triassic metamorphic event.

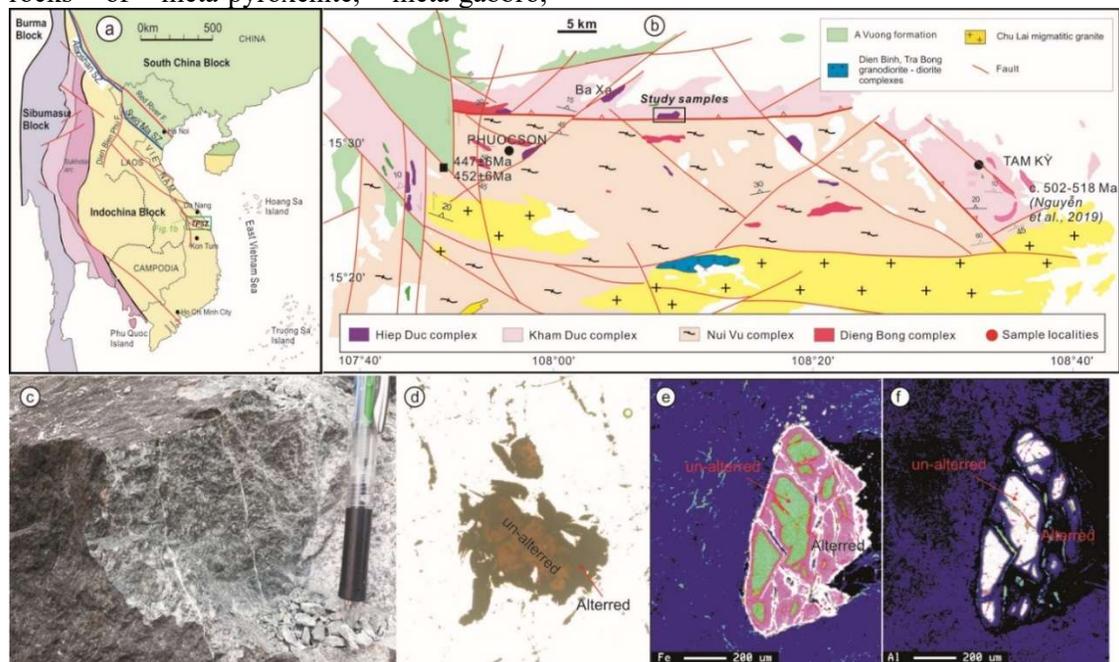


Figure 1. (a) Simplified tectonic map of Southeast Asia (Faure et al., 2018; Metcalfe, 2013), (b) Simplified geological map of the TPSZ showing distribution of lithology and sample localities, (c) Field photo of the Hiep Duc serpentinite, (d) Representative Cr-spinel under microscope, and elemental mapping of Fe (e) and Cr (f) of a Cr-spinel shows primary igneous core and the secondary rim domains.

The Hiep Duc ultramafic complex is mainly exposed in northern and western KTM, along the TPSZ and Po Ko Suture zone in the north and west margin, respectively (Figure 1b). The Hiep Duc Complex is just exposed as small lenticular shape mélanges within the Kham Duc and Nui Vu Complexes. Most of the rocks demonstrate highly mylonitic texture. These ultramafics are spatially associated with the mafic intrusive and monzo-gabbro, which do not show typical ophiolitic features (Tran, 2005). The Cr-spinel compositions from some serpentinites of the Hiep Duc have been reported, suggesting an alpine-type ophiolitic components (Pham et al., 2006). However, their tectonic features have not been well discussed. In addition, some high Cr# values of the Cr-spinel were products of metamorphic magnetite, which was not fully examined.

3. Samples description

Serpentinite samples of the Hiep Duc complex were collected from the Hiep Duc area (Figure 1b), where it occurs in associated with meta-gabbros and basalts. The samples were strongly serpentinitized and metamorphosed that no other primary peridotite minerals (Figure 1c) are preserved except for some Cr-spinel grains (Figure 1a). The serpentinitized peridotites contain some relicts of the mantle-derived Cr-spinel, and a later metamorphic mineral assemblage composed of talc, serpentine-group minerals, and magnetite. All the serpentine grains have been brecciated. Cr-spinels demonstrate anhedral to subhedral with relatively coarse-grained crystals (Figure 1d). All the grains have been altered into ferritchromite and Cr-magnetites in their rims and along with the granular fractures. The reddish brown to dark-brown primary igneous Cr-spinels (Figure 1d) are preserved in some core parts of the coarse-grained particles.

4. Electron microprobe analyses and results

Electron microprobe analyses of minerals were carried out at Okayama

University of Science using a JEOL JXA-8900R. The quantitative analyses on mineral chemistry were performed with 15 kV accelerating voltage, 12 nA beam current and 3 μ m beam size. Natural and synthetic silicates and oxides were used for calibration. The ZAF method (oxide basis) was employed for matrix corrections. Estimating Fe²⁺ and Fe³⁺ contents from total FeO is based on the charge balance using stoichiometric criteria (Droop, 1987). Elemental mapping (Cr, Fe) analyses were carried out to check how post metamorphism/magma affected to the alteration of Cr-spinel grains. Figure 1e, f shows a representative Cr-spinel grain, which is rich Fe and low Cr components in the rim parts, while the core parts show relatively higher Cr and lower Fe than the rim parts, their contributions are homogeneous in the core part of the Cr-spinels.

The representative original compositions of the Cr-spinels are listed in Table 1, and their core compositions are characterized by medium in Cr₂O₃ content (31.53–37.01 wt.%), high contents of Al₂O₃ (20.01–33.94 wt.%), FeO (18.13–28.76 wt.%) and MgO (9.71– 13.47 wt.%), and very low TiO₂ content (0.17–0.32 wt.%). The Cr# [Cr/(Cr + Al)] and Mg# [Mg/(Mg + Fe²⁺)] have minor ranges from 0.39 to 0.47 and from 0.42 to 0.60, respectively. The Fe³⁺ and Fe²⁺ contents are very low (0.03 – 0.09) and (0.40 – 0.60), respectively. The altered Cr-spinel domain (black color under microscope) was not dated in this study. Further insights into the chemistry of the parental melts for the studied Cr-spinel can be obtained using an equation from Maurel and Maurel (1982) to calculate Al₂O₃ and TiO₂ contents of parental melts. Representative calculations of Al₂O₃, TiO₂ values are given in Table 1. The Al₂O₃ and TiO₂ parent melt contents were estimated between 14.68 - 16.87 wt.% and 0.38 – 0.84 wt.%, respectively.

Table 1: Representative chemical analyses of Cr-spinel cores of the Hiep Duc serpentinite.

Sample N	01	01	01	01	02	02	02	03	03	03	05	05	05	05	06	06	06	06	06
TiO ₂	0.20	0.26	0.32	0.31	0.31	0.17	0.21	0.23	0.19	0.29	0.28	0.28	0.17	0.18	0.25	0.24	0.26	0.23	0.2
Al ₂ O ₃	32.74	32.60	32.05	32.35	32.86	28.95	31.72	30.41	31.39	34.49	33.94	34.71	30.94	31.51	25.08	32.1	31.39	31.18	30.36
Cr ₂ O ₃	34.24	34.35	33.80	33.66	33.93	37.37	35.26	35.35	35.48	32.92	32.02	32.52	34.72	33.51	36.08	33.27	34.99	35.52	35.99
FeO	19.76	19.37	19.43	19.45	19.77	21.54	19.47	19.47	20.31	18.13	19.60	18.35	24.29	23.29	28.76	22.47	20.26	20.26	20.16
MnO	0.29	0.27	0.25	0.27	0.25	0.32	0.32	0.27	0.32	0.27	0.30	0.21	0.38	0.32	0.71	0.35	0.28	0.3	0.3
MgO	12.08	12.16	12.37	12.00	12.10	10.06	11.86	11.51	11.60	13.24	13.20	13.47	8.68	9.71	8.85	10.48	11.39	11.34	11.14
NiO	0.06	0.07	0.06	0.07	0.10	0.03	0.04	0.06	0.01	0.09	0.08	0.09	0.03	0.03	0.04	0.05	0.06	0.05	0.04
<u>Total</u>	99.37	99.10	98.28	98.11	99.31	98.45	98.87	97.28	99.31	99.42	99.42	99.64	99.20	98.55	99.77	98.96	98.63	98.88	98.19
O	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00
Ti	0.00	0.01	0.01	0.01	0.01	0.00	0.00	0.01	0.00	0.01	0.01	0.01	0.00	0.00	0.01	0.01	0.01	0.01	0.00
Al	1.18	1.14	1.13	1.15	1.15	1.05	1.12	1.09	1.11	1.19	1.19	1.19	1.12	1.09	0.84	1.12	1.11	1.10	1.09
Cr	0.78	0.81	0.80	0.80	0.80	0.91	0.84	0.86	0.84	0.76	0.75	0.75	0.85	0.83	1.04	0.83	0.84	0.85	0.87
Fe	0.50	0.50	0.50	0.50	0.51	0.57	0.50	0.51	0.52	0.46	0.49	0.46	0.63	0.63	0.85	0.57	0.53	0.53	0.53
Mn	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.02	0.01	0.01	0.01	0.01
Mg	0.55	0.56	0.57	0.55	0.55	0.48	0.55	0.54	0.53	0.59	0.58	0.60	0.40	0.47	0.31	0.48	0.53	0.52	0.52
Fe ³⁺	0.05	0.05	0.07	0.05	0.05	0.05	0.05	0.05	0.06	0.05	0.07	0.06	0.03	0.09	0.15	0.05	0.05	0.05	0.05
Fe ²⁺	0.45	0.45	0.44	0.45	0.45	0.53	0.45	0.46	0.47	0.41	0.42	0.40	0.60	0.54	0.70	0.52	0.48	0.48	0.48
Mg#	0.55	0.55	0.57	0.55	0.55	0.48	0.55	0.54	0.53	0.59	0.58	0.60	0.40	0.47	0.31	0.48	0.52	0.52	0.52
Cr#	0.40	0.41	0.41	0.41	0.41	0.47	0.43	0.44	0.43	0.39	0.39	0.39	0.43	0.43	0.55	0.42	0.43	0.43	0.44
Al ₂ O ₃ melt	16.72	16.57	16.50	16.54	16.61	16.07	16.46	16.28	16.41	16.81	16.87	16.84	16.49	16.15	14.70	16.51	16.41	16.38	16.27
TiO ₂ melt	0.49	0.70	0.83	0.81	0.81	0.40	0.53	0.60	0.48	0.77	0.74	0.73	0.38	0.44	0.66	0.62	0.70	0.60	0.51

5. Discussions

Cr-spinel $[(\text{Mg}, \text{Fe}^{2+})(\text{Cr}, \text{Al}, \text{Fe}^{3+})\text{O}_4]$ is an ubiquitous accessory mineral in peridotites, and its composition reflects geotectonic environments, magma chemistry, degree of partial melting, fractional crystallization, temperature-dependent partitioning, and variations in oxygen fugacity (Barnes, 2000; Dick and Bullen, 1984). Primitive Cr-Spinels are generally altered by serpentinization and/or metamorphism, and later magmatism (Barnes, 2000; Burkhard, 1993). The Cr-spinel compositions are plotted on a diagram proposed by (Barnes and Roeder, 2001; Roeder, 1994) in order to re-examine their primary igneous characteristics (Figure 2a). The Cr-spinels concentrate on Field I (Figure 2a), which represents Cr-spinels in primitive basalt, mantle peridotite, and chromitite, which are used for petrogenesis discussion (Figure 2a).

5.1. Petrogenesis

The primary Cr-spinel core compositions from the Hiep Duc serpentinites are characterized by Al_2O_3 and Cr_2O_3 plotting on the mantle array field (Figure 2b), indicating the peridotites of the mantle component. Mantle components commonly experienced various melting degrees that depend on their tectonic setting, e.g. mantle of MOR have lower melting degree than those in the supra-subduction zone (SSZ), which is believed to form in the fore-arc, back-arc, or proto-arc tectonic settings. The low TiO_2 and high Al_2O_3 content of the Cr-spinel are plotted overlapping MOR- and SSZ-peridotite fields (Figure 2c). On the Al_2O_3 vs. $\text{Fe}^{2+}/\text{Fe}^{3+}$ diagram (Figure 2d) all of the Cr-spinel compositions plot on the SSZ peridotite field. These indicate that the Cr-spinels were formed in a supra-subduction zone tectonic setting (Kamenetsky et al., 2001), instead of MORB-peridotite (Pearce et al., 2000). Despite the fact that Ti content in Cr-spinel is minor, it is a very important indicator for tectonic discrimination of parental magma. Cr-spinels from the oceanic plateau and back-arc have distinctive TiO_2 and $\text{Fe}^{3+\#}$ relationship; the intraplate basalts show the highest TiO_2 content while the arc magmas are

the lowest (Arai, 1992). The melts of peridotite that is affected by fluid and/or melts from sediment will increase TiO_2 content by increasing melting degree (Hellebrand et al., 2001). The positive relationship of TiO_2 and Cr# of Cr-spinel indicates the addition of sediment fluid/melt during the mantle melting (Figure 2e). These clearly indicate that the Cr-spinels from the Hiep Duc were derived from an SSZ tectonic setting. On the Mg# vs. Cr# diagram (Figure 2f), the primary Cr-spinel compositions plot within the back-arc field rather than those from the fore-arc tectonic setting. The Hiep Duc serpentinized peridotites show characteristics similar to both MORB- and arc-like components. The MORB- and arc-like basic rocks are commonly believed to be products of fore-arc (Reagan et al., 2010; Tomoaki et al., 2011) or back-arc (Ngo et al., 2016; Ngo et al., 2014) tectonic settings.

The high-Al contents in Cr-spinel illustrate low degree of partial melting of parental melt (Rollinson, 2008). Very low Fe^{3+} contents in the Cr-spinels indicate relatively low oxygen fugacity conditions of their primary source that is typical characteristics of Cr-spinel formed in an SSZ (Murck and Campbell, 1986). The parental melts Al_2O_3 and TiO_2 contents overlap boninites and MOR Cr-chromitites lava overlapping arc-type magmatism (Figure 3a,b) (Rollinson, 2008). These data (Al_2O_3 melt and TiO_2 melt) indicate that the Cr-spinels in the region are derived from MOR- and Arc-like melts. This value is similar to those from Oman harzburgites, which is ranged from 11.9 to 16.3 (Auge, 1987), and is different from those in mid-oceanic ridge (Wilson, 1989).

In summary, the primary igneous Cr-spinel compositions from the Hiep Duc serpentinized ultramafics have characteristics of those derived from mantle origin that experience a moderate degree of partial melting in an SSZ tectonic environment and are different from the parageneses in Alaskan-type and arc-related mafic-ultramafic complexes (Eyuboglu et al., 2010; Eyuboglu et al., 2011a). The features that we reported in this study suggest partial melting with the involvement of subduction-related and MORB

mantle of magma components that might form in a back-arc environment (Stern and

Bloomer, 1992).

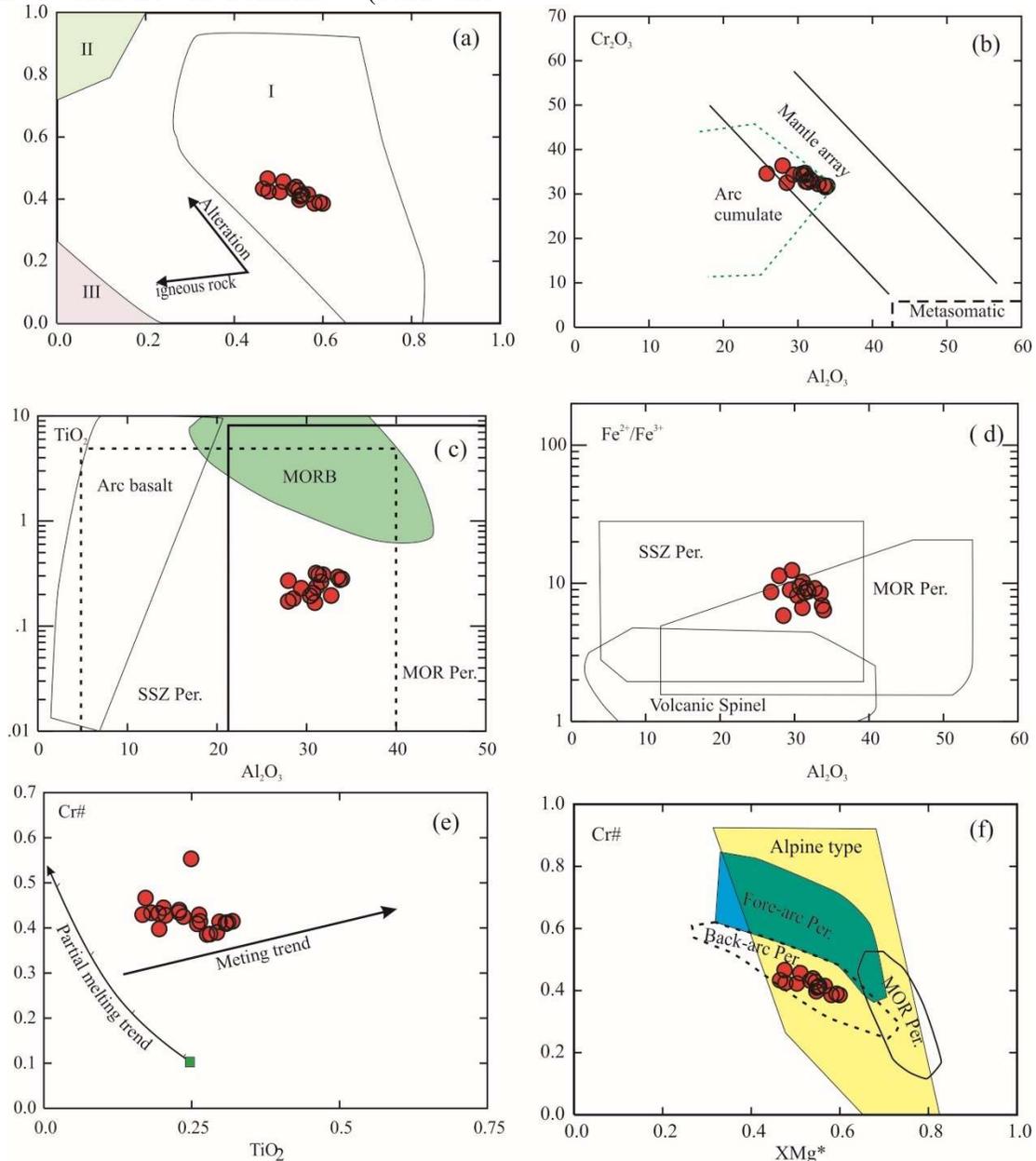


Figure 2. (a) $Mg/(Mg + Fe^{2+})$ vs. $Cr/(Cr + Al)$ variation diagram: field I represents Cr-spinels in primitive basalt, mantle peridotites and chromitites, field II represents magnetite from metamorphic rocks, field III is magnetites from un-metamorphosed igneous rocks (fields are from Roeder (1994)) (b) Plot of Cr-spinels on Al_2O_3 vs. Cr_2O_3 diagram (after Franz and Wirth (2000)). (c) Composition of the Cr-spinels compared to the field of Cr-spinels from the supra-subduction zone (SSZ) and mid-ocean ridge (MOR) mantle peridotites (Barnes and Roeder, 2001). (d) Al_2O_3 vs. Fe^{2+}/Fe^{3+} diagram showing the fields of supra-subduction zone (SSZ) and mid oceanic ridge (MOR) peridotite after Kamenetsky et al. (2001). (e) Plot of Cr# vs. TiO_2 in Cr-spinel. (f) Cr# vs. Mg# diagram for the Cr-spinel cores. The field boundaries are from Dick and Bullen (1984).

5.2. Regional tectonic implications

The mafic and ultramafic rocks from the

TPSZ have been regarded as fragments of an ophiolite suite representing the remnant of MORB crust of the Paleotethyan Ocean

between the TSB and KTM (Pham et al., 2006; Tran and Vu, 2011). Pham et al. (2006) used mineral composition of Cr-spinel, olivine, clinopyroxene, suggested that the serpentinite bodies with associated MORB-like gabbros in the TPSZ represent a remnant of Paleooceanic lithosphere. The low to very low TiO_2 content along with medium Cr# and high $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio of the Cr-spinel from this study suggest an SSZ tectonic setting. In addition, the MOR-/arc-like chemical composition of the mafic complex of the Nui Vu complex is

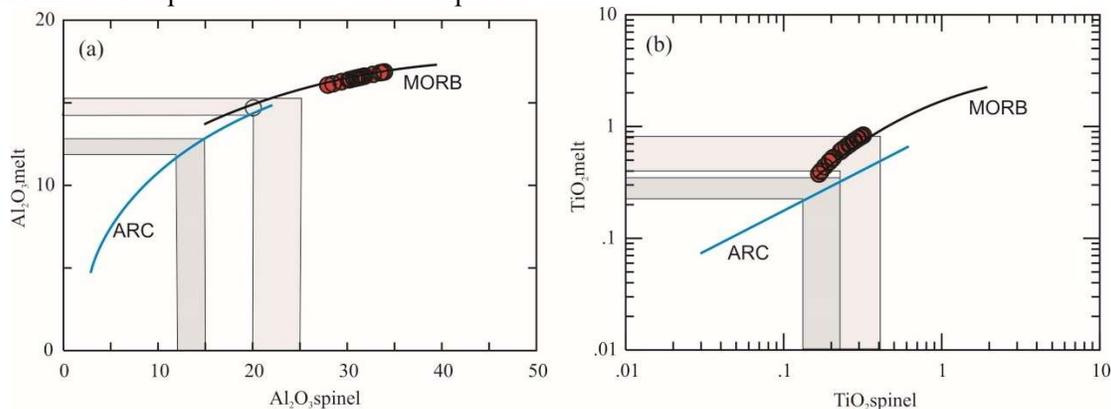


Figure 3. Estimated composition of the Al_2O_3 and TiO_2 parental melt in equilibrium with Cr-spinel from the Kham Duc serpentinite. The regression lines are derived from the experiment study of Maurel and Maurel (1982) and Cr-spinel, melt inclusion studies in MORB, OIB, LIP and Arcs (Kamenetsky et al., 2001; Rollinson, 2008). Grey field represent Cr-spinel composition from Oman boninite (Kamenetsky et al., 2001; Rollinson, 2008).

In the northern part of the TPSZ, complex rocks of plagiogranite ages of ca. 500 – 520 Ma island arc have been reported (Nguyen et al., 2019). Similar ages of ca. 500 Ma of gabbro and plagiogranite were also reported from Hiep Duc area (Ngo Xuan Thanh. et al., 2020). Furthermore, recent studies have reported the early Ordovician (ca. 485–473Ma) and late Ordovician (ca. 457–453 Ma) continental arc-related diorite and granodiorite of the Ben Giang and Dien Binh complexes, respectively are observed within the KTM (Nguyen et al., 2021). The data are consistent with the Ordovician – Silurian granodiorite and granite of the Tra Bong complex within the KTM, which have been dated to be ca. 470–444 Ma and favored as continental arc-related magmas (Carter et al., 2001; Maluski et al., 2005; Nagy et al., 2001; Sanematsu et al., 2011; Shi et al., 2015; Tran et al., 2020; Tran and Vu, 2011). The recent research for

reported to be formed in an arc-/back-arc tectonic setting (Huynh and Dinh, 2014). This indicates that these serpentinitized peridotites may be derived from the same tectonic environment. The Nui Vu complex is exposed mostly in the southern part of the TPSZ and is consists of metapelite, metapsammite, paragneiss, and amphibolite associated with black schists and thin-layered marbles, which was interpreted as a back-arc complex (Izokh et al., 2006).

complex dioritic and granodiorite rocks at Tra My and Phuoc Son areas also showed that the magmatic rocks associated with the continental arc/back-arc that formed around 450 Ma ago (Ngo Xuan Thanh. et al., 2020). Thus, complex rocks with back-arc affinity in the TPSZ may be products of subduction of Paleooceanic lithosphere underneath the KTM during the middle Cambrian to Middle Ordovician.

Conclusion

In conclusion, the primary Cr-spinels from the Hiep Duc serpentinite provide compelling evidence to support an SSZ tectonic setting for the supra-subduction zone ophiolites. The integrated data based on field observation, textural examination, and mineralogical analyses of the Hiep Duc serpentinitized peridotites in Hiep Duc area are firmly to support an SSZ tectonic setting for the supra-

subduction zone ophiolites. The Cr-spinel composition show low Mg# and moderate Cr# is the most favorable geodynamic setting for such Cr-spinel in a back-arc basin. The Cr-spinel characteristics are combined all the available evidence suggests that parts of the Tam Ky – Phuoc Son ophiolite formed in an early Paleozoic SSZ, probably in a back-arc tectonic setting. This, together with the magmatic evolution of KTM, is marked by southward subduction of the Paleo-Tethys beneath the KTM during Cambrian to Silurian, forming a series of subduction-related plutons within the KTM.

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