CHAPTER 4

DETRITAL CHROMIAN SPINELS

4.1 General statement

In the sandstone provenance studies, the approaches of single-mineral analysis are extremely diverse, such as the petrographic classification of detrital quartz (Basu et al., 1975), the compositional analysis of detrital feldspars (Trevena and Nash, 1981), or heavy minerals (e.g. Morton, 1991), and the advanced laboratory methods of radiogenic decay or fission-track dating of detrital zircon (e.g. Ross and Parrish, 1991). In spite of their restrictions, each of these approaches can increase important detail and confidence in provenance interpretation based on bulk composition techniques such as detrital-mode analyses.

Compositional analysis of chromian spinels is applied for the petrological studies of spinel-bearing mafic and ultramafic rocks (such as Irvine, 1965, 1967, 1977; Dick and Bullen, 1984; Haggerty, 1991; Arai, 1992, 1994a, 1994b; Arai and Matsukage, 1996). Since the composition of chromian spinels is a sensitive indicator of physio-chemical conditions of the parent melt during the crystallization (Irvine, 1965; Dick and Bullen, 1984). Furthermore, chromian spinel is also chemically and physically more durable than other ultramafic minerals, which are invariably always major phases in the parent rocks. Chromian spinels is

regard as the only one remnant mineral unaltered by the sub-greenschist facies serpentinization common in sea-floor environment (Hekinian, 1985; Arai and Okada, 1991) as olivine and most other mafic minerals are altered swiftly at near-surface.

Concerning the geochemical analysis of detrital chromian spinels for the provenance determination of sources, such a subject has studied widely during this decade. Detrital chromian spinels are essential to provenance studies as same as common applications of spinels in petrologic studies of parent ultramafic-mafic rocks (Arai and Okada, 1991; Arai, 1992; Hisada and Arai, 1993, 1994; Cookenboo et al, 1997; Hisada et al., 1998; Lee, 1999). Recent chemical data accumulation of chromian spinels in ultramafic-mafic rocks facilitates the precise comparison between detrital grains in clastic rocks and their parent source rocks. Despite the widespread use of chromian spinels in petrologic studies, the application of detrital chromian spinels in provenance studies has been limited and is now in progress.

4.2 Previous works – Significance of chromian spinels

Previous applications of chromian spinel chemistry to support the provenance interpretation includes a study by Press (1986), who used the morphology and composition of detrital chromites to relate the sediments of the Rhenish Massif to an Apline–type ophiolite instead of mid-oceanic ridge or stratiform intrusion. Pober and Faupl (1988) used spinels in stream concentrates of heavy minerals from a large area in the Eastern Alps, and established that the greatest population of spinel data is in the abyssal harzburgite field, equivalent to Dick and Bullen (1984) on the

basis of spinels in lherzolites and harzburgites. Similarly, Arai and Okada (1991) used the chemistry of detrital chromian spinels to compare with those of currently exposed peridotite, and to discuss a tectonic history of the serpentinite belt itself. Hisada and Arai (1993, 1994) studied the chemical compositions of detrital chromian spinels in the Cretaceous Sanchu sandstone in Japan to relate the serpentinite protrusion in the fore-arc region, and to unravel the tectonic evolution of the Kanto Mountains.

Cookenboo et al. (1997) compared the composition of detrital chromian spinels in volcanic lithic sandstones from the Bowser Basin with the compositional ranges of spinels from the literature (e.g. Dick and Bullen, 1984) on ultramafic rocks. The Bowser Basin spinels matched compositionally those from Alpine-type peridotites emplaced by the obduction of marginal-basin crust and island-arc complexes. This provenance interpretation was in a good agreement with earlier interpretation from the studies of chert pebbles in the Bowser Basin, and this provenance interpretation was also fitted in the detrital model analysis of sandstone, which called for the obducted oceanic crust and island arc-source terrane.

Most recently, Chutakositkanon (1999) and Chutakositkanon et al. (2001) studied the characteristics of detrital chromian spinels from sandstones of turbiditic sequences of the Permian Nam Duk Formation, central Thailand. Geochemistry of detrital chromian spinels compared with the compositional fields of chromian spinels from the literature (e.g. Arai, 1992) indicates that the Nam Duk chromian spinels are related to mafic-ultramafic rocks of arc region. The result newly reveals that the

arc-related tectonic setting was probably developed in this area during the Permian; not being a passive margin like other Permian sequences in central Thailand. Considering these studies, it is valuable to note that the detrital chromian spinel studies can be a suitable approach to solve the tectonic evolution of Thailand.

4.3 Detrital chromian spinels in the Sa Kaeo-Chanthaburi Accretionary Complex

Detrital chromian spinel study is regarded as a single-mineral analysis applied to determine the tectonic provenance. The study can increase tremendous confidence in provenance interpretation and simultaneously add the detailed evidence unavailable from normal approaches. The electron probe microanalysis (EPMA) of detrital chromian spinels in the sandstones from the Pong Nam Ron Formation, the sandstone blocks in mélange, and the volcaniclastic rocks of the Sa Kaeo-Chanthaburi accretionary complex (SKCB-AC) is adopted to unravel the geological history of the SKCB-AC in this research. Detailed studies of basic geological approach and geochemistry of the detrital chromian spinels are aimed to evaluate the tectonic evolution of the western margin of Indochina in the eastern Thailand.

4.3.1 Definition of chromian spinels

Spinel, in general, means an isometric mineral that has the general formula $MgAl_2O_4$. The mineral spinel ($MgAl_2O_4$) is also an end-member of spinel group in the oxides expressed by AB_2O_4, in which A represents divalent cations (R^{2+}) and B trivalent cations (R^{3+}). The

minerals of the spinel group usually show extensive solid solution between the various end-member compositions. There is, for example, the extensive solid solution between magnetite (Fe_3O_4) and ulvöspinel ($Fe^{2+}{}_2TiO4$). Furthermore, there are substitution between chromite ($FeCr_2O_4$) and magnesiochromite ($MgCr_2O_4$), between spinel ($MgAl_2O_4$) and hercynite ($FeAl_2O_4$), and so on. The complexity of the chemical substitutions in this spinel group makes it very difficult to use triangular composition diagrams for expression of the various solid solutions extent; instead, a "spinel prism" (Kerr, 1977; Klein and Hurlbut, 1993) is used for such chemical representations (Fig. 43).

Following the general literature on the chromian spinel studies (e.g. Irvine, 1965, 1967; Dick and Bullen, 1984; Arai, 1992), "chromian spinel" as definition in this study is a term used in the broadest sense to denote composition which are Cr-rich but which extensive solid solubility among members on the base of the so-called spinel prism defined by the most natural vertices of the $(Mg, Fe^{2+})(Cr, Al, Fe^{3+})_2O_4$ + $(Mg, Fe^{2+})_2TiO_4$ composition space (Irvine, 1965, 1967; Haggerty, 1976, 1991; Dick and Bullen, 1984; Ghiorso and Sack, 1991; Sack and Ghiorso, 1991). Generally the chromian spinel occurs in the intermediate mode among hercynite ($FeAl_2O_4$), spinel ($MgAl_2O_4$), magnesiochromite ($MgCr_2O_4$), and chromite ($FeCr_2O_4$) at or near the base of the spinel prism (Kerr, 1977; Klein and Hurlbut, 1993). The chromian spinel is generally a disseminated accessory mineral in basalts and peridotites.

4.3.2 Accumulation and contribution

Numerous detrital chromian spinels are newly discovered as

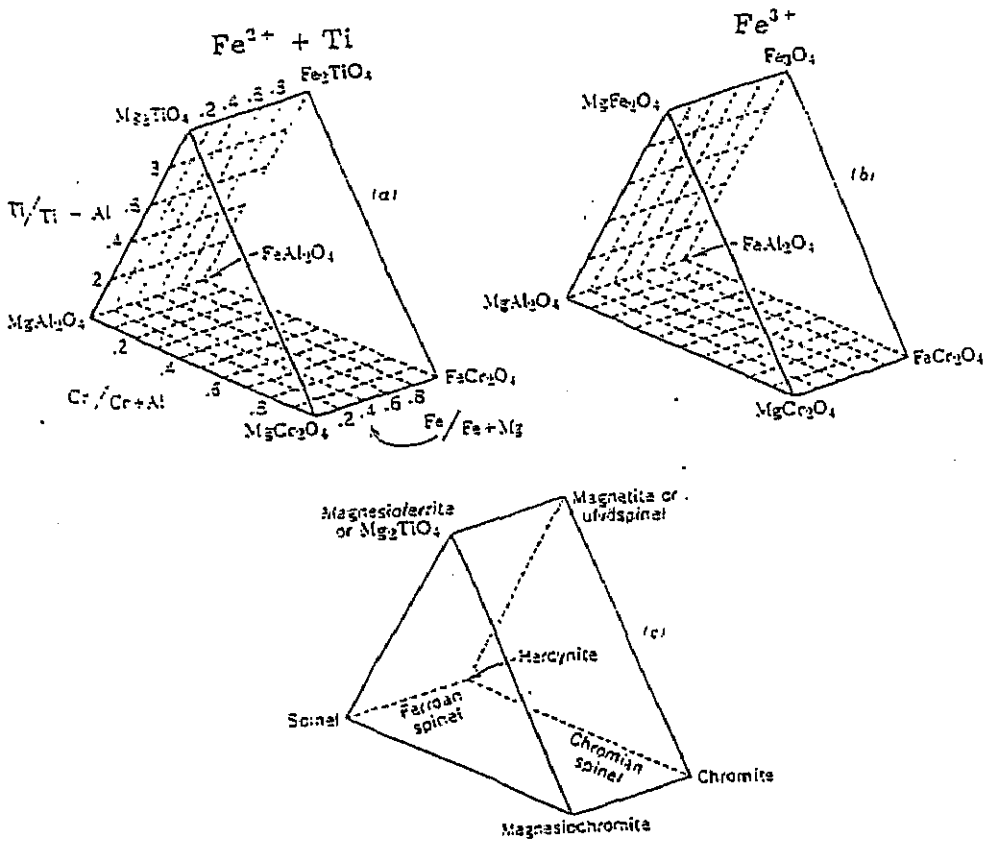

Fig. 43 End member compositions in the spinel group as represented in a spinel prism (Klein and Hurlbut, 1993).

one of the accessory minerals in sandstones and volcaniclastic rocks from the SKCB-AC, eastern Thailand. Such a discovery can provide the first and pioneering information for the chromian spinel studies in eastern Thailand.

The SKCB-AC includes various units of mélanges and covering sediments (i.e. Pong Nam Ron Formation). In this study, detrital chromian spinels can be discovered in three groups of rocks; sandstones of the Pong Nam Ron Formation, sandstone blocks in mélanges, and volcaniclastic rocks in mélanges. It is noted that detrital chromian spinels in the alternated shale of chromian spinel-bearing turbidite sequences are too small to observe and identify under the microscope (Chutakositkanon, 1999).

4.3.2.1 Pong Nam Ron Formation

Detrital chromian spinels are usually discovered in greywacke sandstones under the microscope. They occur as an accessory mineral (less than 1%) in greywacke sandstones. These sandstones have been documented as turbidites from their characteristics of succession. Several indicators for deposition by turbidity current can be observed. The successions often revel graded bedding, cross bedding, lamination and sole marking. Direction of currents measured from the flute casts, groove casts and cross lamination for the probable source location of detrital chromian spinels indicates sediments were derived mainly from south and southeast.

4.3.2.2 Sandstone blocks in mélange

After the discovery of detrital chromian spinels from sandstone blocks in the mélange of the Ban Nong Bon unit, special attention was paid to find the new locations for understanding the accumulation and distribution of detrital chromian spinels in mélange. Detrital chromian spinels of the Ban Nong Bon unit are probably new interesting data for the studies of detrital chromian spinels, which are firstly discovered in sandstone and conglomerate blocks from the mélange unit in Thailand. Chromian spinels are usually found as the accessory mineral in the tectonic sandstone and conglomerate blocks in shale matrix.

Extending from the Ban Nong Bon unit, detrital chromian spinels are also discovered in sandstone and conglomerate blocks in other tectonic mélange units of the Khao Hleam and Soi Dao units.

4.3.2.3 Volcaniclastic rocks in mélange

Abundant chromian spinels are found in volcaniclastic rocks in both Khao Hleam and Soi Dao units. Generally these volcaniclastic rocks are formed as tectonic blocks in mélange.

Volcaniclastic rocks associated with basaltic pillow lavas of the Khao Hleam unit contain abundantly detrital chromian spinels in matrix. Almost clasts in these volcaniclastic rocks are fragments of basaltic pillow lavas. Matrix is probably hyaloclastite.

In the Soi Dao unit, abundant detrital chromian spinels are discovered from greenish gray matrix of volcaniclastic rocks, possibly basaltic clast-bearing hyaloclastites. Purplish brown basaltic clasts display aphanitic, porphyritic, and amygdaloidal textures. These volcaniclastic rocks are in fault contact with Middle Permian limestones (age given by Fontaine and Salyapongse, 1997; Fontaine et al., 1997).

4.3.3 Petrography of detrital chromian spinels

Detrital chromian spinel grains discovered in this study area are generally deep brown to almost opaque in transmitted light (Plates 16 to 24) corresponding to their Cr-Al-Fe^{3+} composition (Bernier, 1990). These detrital chromian spinels are the most abundant in volcaniclastic rocks, sandstones and conglomerate. Comparing with the detrital chromian spinels of the Alpine-type peridotite origin in the Bowser Basin in Canadian Cordillera (Cookenboo et al., 1997), the detrital chromian spinels in the Pong Nam Ron Formation are rather smaller. Their grains vary between 20 to 400 μm in size (Plates 16, 17 and 18). Some of them rise to more than 1 mm across especially in conglomerates blocks of the Ban Nong Bon unit (Plates 19, 20 and 21).

The physical properties of chromian spinels are intermediate between spinel and chromite. They resemble chromite but are more transparent under the microscope. The minerals, spinel-chromite, are isometric. They are hard, brittle minerals. The physical feature varies from them of chromite and spinel depending on their composition. The hardness is about 5.5 to 8.0 as the specific gravity is about 3.6 to 4.8

(Vanders and Kerr, 1967). The chromian spinels are usually black minerals with brown streak. Some of them are translucent to transparent minerals with varied colors. Luster is sub-metallic. Weakly magnetic feature usually in granular masses that are frequently associated with serpentine is sometimes recognized (Vanders and Kerr, 1967).

In the transmitted light, the occurrence of detrital chromian spinels in this study as small, high refractive index (n=1.72 to 2.16) grains serves to distinguish them from other minerals in sandstones. The translucent spinels are easier to be microscopically recognized for chromian spinels than opaque spinels. Both of them are mostly sub-angular to angular. Several grains exhibit sub-hedral to euhedral suggesting the preservation of original crystal shape. Grains are generally homogeneous and show no obvious signs of zoning or twinning. Some of larger grains show very weak birefringence. Several spinel grains contain inclusions with unknown composition. As in reflected light, high Cr-spinels (often black or opaque) display a sub-metallic to bright metallic luster depending on the content of Cr and thickness of thin sections.

4.3.4 Geochemical characteristics

4.3.4.1 Sample preparation - Sampling and analytical techniques

Thin-section examination indicates that chromian spinels are the accessory mineral (less than 1%) in the sandstones and conglomerates. Samples, containing relatively higher concentrations of

chromian spinels and collected from several locations, were selected during thin-section analysis for the microprobe study. More than 500 grains were identified for the representatives of chromian spinels for microprobe studies. Due to the constraints on available working time, only representative 37 grains from sandstones of the Pong Nam Ron Formation, 44 from terrigenous clastic blocks of the Ban Nong Bon and the Soi Dao units, and 109 from volcaniclastic rocks of the Khao Hleam and the Soi Dao units, were analyzed (see Appendix B).

Geochemical data on major and minor elements of the detrital chromian spinels were obtained from polished thin sections using the electron probe microanalysis (EPMA). EPMA is a technique for chemically analyzing small selected areas of solid samples, in which X-rays are excited by a focused electron beam (about 10 μm in diameter). Theoretically the X-rays spectrum contains lines that are characteristic of the elements present; hence a qualitative analysis is easy to obtain by identifying the lines from their wavelengths. By comparing the intensities of these lines with those emitted from standards, it is also possible to determine the concentration of element (quantitative analysis).

The preparation procedure is the same as normal thin sections in the early stage, but because of the high stress of polishing, a strong adhesive (e.g. epoxy resin) should be used for attaching the rock slice to the glass slide. The rock slice was ground to a thickness greater than the 30 μm final thickness required, before starting the finer polish in next step.

For X-ray analysis, it is extremely desirable to avoid topographic effects; therefore the specimens are made flat and well polished. Staring with a flat ground surface, the polishing is carried out with progressively finer grades of abrasive (carborundum or emery in the coarser grades and diamond in the late stage). Woven nylon lap is preferable to clothe with a nap, since it has fewer tendencies to produce surface relief between minerals of different hardness.

As most geological specimens being nonconductors of electricity, chromian spinels require a conductive coating to prevent charging under electron bombardment. For the X-ray analysis, carbon is the preferred coating element in this study, since it is minimal effect on the X-ray spectrum. The method of carbon coating is to place thin sections in a vacuum chamber with a current of around 100 Å passed through a carbon evaporation source consisting of carbon rods in contact under light pressure (should be less than $\sim 10^{-4}$ torr). The optimum thickness of carbon is about 20 nm (Reed, 1996). The thickness can be controlled approximately by using a fixed current and evaporation time.

The quantitative major and minor element analyses were carried out by a JEOL, JXA-8621 Superprobe at the Chemical Analysis Center, the University of Tsukuba. Analysis of standards was done at the beginning and the end of analytical runs to ensure proper calibration throughout. All Fe are expressed as FeO. In this investigation, cationic ratios were calculated, assuming spinel stoichiometry.

It is visualized that the Cr-rich spinel grains are the solid solutions of the chromian spinel component, (Mg, Fe^{2+})(Cr, Al,

$Fe^{3+})_2O_4$, and the ulvöspinel component, $Fe^{2+}{}_2TiO_4$. All Mn was added to total Fe before the calculation. All Ti was combined with Fe as the ulvöspinel component ($Fe^{2+}{}_2TiO_4$). After that, the cation fraction of Mg, Fe^{2+}, Al, Cr and Fe^{3+} were calculated for the chromian spinel component following Arai and Hisada (1991), Arai (1992), Hisada and Arai (1993), Arai and Matsukage (1996), Arai et al. (1997), Chutakositkanon (1999) and Chutakositkanon et al. (2001).

Regarding the analyzing resolution of the probe (about 10 μm in diameter), many detrital spinels are much smaller than detection limit. Only chromian spinel grains that have a polished flat surface larger than 10-μm diameters could be investigated. Total 190 representative chromian spinel grains were selected for geochemical data of detrital chromian spinels in the Pong Nam Ron Formation, sandstone blocks in mélange, and volcaniclastic rocks.

4.3.4.2 Results - Quantitative major element compositions

The result of the quantitative electron microprobe analysis was expressed as element mass concentrations (weight percent). The concentration of unanalyzed elements of O was obtained by computer calculation from the assumed valencies of cations. The analyses, carried out by a JEOL Superprobe, were reported as both "weight percent oxide" and "number of atoms".

Detrital chromian spinels measured in this study vary widely in major-element concentrations. Compositionally chromian spinels have high values of Cr_2O_3 about 24% to 60%. A few grains have

lower Cr_2O_3 contents less than 20%. The other major oxides of chromian spinels are Al_2O_3 ranging widely from 2.08% up to 43.56%, FeO (total Fe) ranging from 15.39% to 52.82%, and MgO ranging from 0.04% to 16.34%. As the important minor oxides, TiO_2 ranging less than virtually nil to 11.03%, NiO ranging virtually nil to 0.31%, and MnO ranging 0.14% to 2.77%, make up only trace amounts. Generally ZnO also displays as a trace element ranging from nil to 0.30%. But some of detrital chromain spinels have ZnO content rising to 8.41%.

Numbers of atoms derived from quantitative electron microprobe analysis were computer-normalized to 4 oxygens (which is appropriate for chromian spinels). Considering the stoichiometry, the cation total is close to the theoretical value of three for chromian spinels. Detrital chromian spinels of the SKCB-AC have high Cr cations about 0.478 to 1.838, averaging about 1.008. The Al cations are ranging from 0.091 to 1.458 and averaging about 0.750. The other major element is the Mg cations within the range of 0.002 to 0.707 and average about 0.473. The Fe cation is the only element present that has dual valency, the proportions of ferrous iron (Fe^{2+}) and ferric iron (Fe^{3+}) can be recalculated assuming ideal spinel stoichiometry following Arai and Hisada (1991) as mentioned before. Recalculated iron cations, Fe^{2+} and Fe^{3+}, are ranging from 0.293 to 1.059 and 0.037 to 0.809, respectively. Their averages are 0.519 for Fe^{2+} and 0.223 for Fe^{3+}.

After calculating the cation fraction of major-element for the chromian spinel component, $(Mg, Fe^{2+})(Cr, Al, Fe^{3+})_2O_4$, of each sample grains, atomic ratios are used herein for the chromian spinel component, unless weight percent oxide is specified. The notation Cr# is

used for atomic ratios of Cr/(Cr+Al), and Mg# is used for atomic ratios of $Mg/(Mg+Fe^{2+})$, following common practice in petrologic literatures (e.g., Dick and Bullen, 1984; Arai and Matsukage, 1996; Cookenboo et al. (1997). Characteristically these spinels have high Cr content and relatively vary in TiO2 content. The atomic ratios Cr/(Cr+Al) or Cr#s vary considerably from 0.25 to 0.95, with the average about 0.58. The atomic ratios $Mg/(Mg+Fe^{2+})$ or Mg#s range widely from virtually nil to 0.70 and average about 0.47, with Mg concentration generally decreasing as Fe increases. The Fe^{3+} concentration is consistently low. The atomic ratios $Fe^{3+}/(Cr+Al+ Fe^{3+})$ in detrital spinels are mostly below 0.15 with the average about 0.11. Some of them have the atomic ratios $Fe^{3+}/(Cr+Al+ Fe^{3+})$ about 0.25. As a few grains almost rise to 0.38.

4.3.4.2.1 The Pong Nam Ron Formation

Representative 35 grains of detrital chromian spinels discovered from sandstones of the Pong Nam Ron Formation have high values of Cr_2O_3 about 33.01% to 57.37%. The other major oxides recognized are Al_2O_3 ranging from 9.83% to 27.77%, FeO (total Fe) ranging mostly from 18.32% to 33.89%, and MgO almost ranging from 7.67% to 14.71%. The minor oxides are TiO_2 ranging nil to 2.67%, NiO ranging virtual nil to 0.30%, MnO ranging 0.20% to 0.53%, and ZnO ranging nil to 0.30%.

Based on appropriately 4 oxygens, the representative 35 chromian spinels of the Pong Nam Ron Formation have high averaged Cr cations about 1.133 within the range of 0.810 to 1.550. The Al cations are ranging from 0.396 to 1.019 and averaging about

0.689. The Mg cations are ranging 0.383 to 0.701 with the average about 0.499. Recalculated Fe^{2+} and Fe^{3+} cations are ranging from 0.310 to 0.997 and 0.045 to 0.353, respectively. The averages of recalculated ferrous iron and ferric iron cations are 0.520 and 0.190.

Considering to the cation fractions, detrital chromian spinels from this unit are generally high in Cr# with the average about 0.62. The Cr#s are ranging from 0.44 to 0.80. As the Mg#s range from 0.00 to 0.69 and average about 0.48. The atomic ratios $Fe^{3+}/(Cr+Al+Fe^{3+})$ are ranging from 0.02 to 0.18 with the average about 0.09.

On the other hand, the specimens 2-1-2+9 and 2-1-2+12, two out of thirty-seven grains analyzed of detrital chromian spinels from the Pong Nam Ron Formation, have different geochemistry from the majority. They have Cr_2O_3 (38.48% and 33.29%) and TiO_2 (0.72% and 0.68%) contents within the range of majority. Focusing on the other oxides, they have contrarily recognized lesser value of Al_2O_3 (7.15% and 4.64%) and MgO (0.53% and 0.09%), and larger value of FeO or total Fe (47.14% and 52.82%), MnO (1.12% and 2.15%), and ZnO (0.97% and 1.64%). Their cations Al (0.33 and 0.23) and Mg (0.03 and 0.01) based on 4 oxygens are lower than the compositional range of majority. Other cations Fe^{2+} (1.01 and 1.06), and Fe^{3+} (0.54 and 0.81) have higher value. Both grains have Cr# about 0.78 and 0.83 and much lower Mg# about 0.03 and 0.01. The atomic ratios $Fe^{3+}/(Cr+Al+Fe^{3+})$ are higher about 0.26 and 0.38.

4.3.4.2.2 Sandstone blocks in mélange

Compositionally, 44 detrital chromian spinels from blocks of terrigenous sandstones and conglomerates in the mélange of the Ban Nong Bon and the Soi Dao units have probably very wide values of Cr_2O_3 about 21.31% to 62.39%. Al_2O_3 ranging from 2.08% to 43.56%, FeO (total Fe) ranging from 15.39% to 38.60%, and MgO wide ranging from 0.57% to 16.34%, are measured as the major components of these spinels. As the minor oxides are TiO_2 ranging from 0.03% to 2.53%, NiO ranging from virtually nil to 0.31%, MnO ranging from 0.17% to 2.35%, and ZnO ranging from virtually nil to 2.93%.

After calculating based on properly 4 oxygens, the chromian spinels from sandstone and conglomerate blocks in mélange have high averaged Cr cations about 1.220 within the range of 0.478 to 1.838. The Al cations are ranging from 0.091 to 1.458 with the average about 0.603. The Mg cations are ranging from 0.031 to 0.707 and averaging about 0.449. Recalculated Fe^{2+} and Fe^{3+} cations are ranging from 0.305 to 0.978 and 0.047 to 0.339, respectively. The averages of recalculated ferrous iron and ferric iron cations are 0.557 and 0.189.

Generally detrital chromian spinels from sandstone and conglomerate blocks have the atomic ratio Cr#s range widely from 0.25 up to 0.95 and average about 0.67. The atomic ratio Mg#s are about 0.03 to 0.70, with the average about 0.45. The atomic ratios of $Fe^{3+}/(Cr+Al+ Fe^{3+})$ are also widely ranging from 0.02 to 0.17, with the average about 0.09.

4.3.4.2.3 Volcaniclastic rocks in mélange

In the SKCB-AC, detrital chromian spinels are discovered from volcaniclastic rocks in mélanges of both Khao Hleam and Soi Dao units. Selected 109 grains of detrital chromian spinels are analyzed for their representative geochemistry.

Totally detrital chromian spinels in the matrix of volcaniclastic rocks have values of Cr_2O_3 about 18.21% to 59.80%. The other major oxides are Al_2O_3 ranging from 8.03% to 42.47%, FeO (total Fe) ranging mostly from 18.72% to 52.08%, and MgO almost ranging from 0.04% to 14.77%. The minor oxides are TiO_2 ranging 0.02% to 11.03%, NiO ranging nil to 0.30%, MnO ranging 0.14% to 2.77%, and ZnO ranging nil to 8.41%.

Based on the theoretically 4 oxygens, total 109 detrital chromian spinels from volcaniclastic rocks have averaged Cr cations about 0.880, within the range of 0.539 to 1.624. The Al cations are ranging from 0.331 to 1.423 and averaging about 0.838. The Mg cations are ranging 0.002 to 0.695 with the average about 0.483. Recalculated Fe^{2+} and Fe^{3+} cations are ranging from 0.293 to 0.912 and 0.037 to 0.488, respectively. The averages of recalculated ferrous iron and ferric iron cations are 0.495 and 0.238.

Focusing to the cation fractions, detrital chromian spinels from volcaniclastic rocks are generally high in Cr# with the average about 0.52. The Cr#s are ranging from 0.27 to 0.83. The Mg#s range from 0.00 to 0.70 and average about 0.49. The atomic ratios

$Fe^{3+}/(Cr+Al+ Fe^{3+})$ are ranging from 0.01 to 0.31, with the average about 0.12.

4.3.4.2.3.1 The Khao Hleam unit

Generally 31 detrital chromian spinels from blocks of volcaniclastic rocks in the mélange of the Khao Hleam unit have probably wide values of Cr_2O_3 about 22.56% to 41.60%. Al_2O_3 ranging from 8.03% to 24.30%, FeO (total Fe) ranging from 23.34% to 47.42%, and MgO wide ranging from 0.19% to 14.77%, are measured as the major components. The minor oxides are TiO_2 ranging from 1.03% to 8.71%, NiO ranging from 0.13% to 0.30%, MnO ranging from 0.15% to 2.77%, and ZnO ranging from 0.01 to 8.41%.

After calculation based on properly 4 oxygens, the chromian spinels in volcaniclastic rocks of the Khao Hleam unit have high averaged Cr cations about 0.945 within the range of 0.707 to 1.111. The Al cations are ranging from 0.371 to 0.892 with the average about 0.672. All Mg cations are ranging from 0.011 to 0.688 and averaging about 0.553. Recalculated Fe^{2+} and Fe^{3+} cations are ranging from 0.300 to 0.699 and 0.214 to 0.451, respectively. The averages of recalculated ferrous iron and ferric iron cations are 0.402 and 0.294.

The detrital chromian spinels from volcaniclastic rocks in the Khao Hleam unit have the atomic ratio Cr#s range highly from 0.50 to 0.73 and average about 0.59. The atomic ratio Mg#s are about 0.02 up to 0.70, with the average about 0.57. The atomic ratios of $Fe^{3+}/(Cr+Al+ Fe^{3+})$ are also widely ranging from 0.11 to 0.26,

with the average about 0.16.

4.3.4.2.3.2 The Soi Dao unit

Total 78 detrital chromian spinels in volcaniclastic rocks from two localities, Khao Pun (15 grains) and Khao Khlong Pun (63 grains), in the Soi Dao unit are analyzed for their characteristics of the geochemistry in this study.

Characteristically chromian spinels from the matrix part of volcaniclastic rocks of the Soi Dao unit have the values of major components of Cr_2O_3 about 18.21% to 59.80%, Al_2O_3 ranging from 8.18% to 42.47%, FeO (total Fe) ranging from 18.72% to 52.08%, and MgO ranging from 0.04% to 14.22%, are measured as the major components. As the minor oxides are TiO_2 ranging from 0.02% to 11.03%, NiO ranging from virtually nil to 0.30%, MnO ranging from 0.14% to 2.48%, and ZnO ranging from nil to 3.54%.

Based on computer-normalized to 4 oxygens, detrital chromian spinels in volcaniclastic rock of the Soi Dao unit have high averaged Cr cations about 0.854 within the range of 0.539 to 1.624. The Al cations are ranging from 0.331 to 1.423 with the average about 0.904. The Mg cations are ranging from 0.002 to 0.695 and averaging about 0.455. Recalculated Fe^{2+} and Fe^{3+} cations are ranging from 0.293 to 0.912 and 0.037 to 0.488, respectively. The averages of recalculated ferrous iron and ferric iron cations are 0.532 and 0.216.

Considering to the cation fractions, totally 78 detrital chromian spinels from volcaniclastic rocks in the Soi Dao unit have the atomic ratio Cr#s range from 0.27 to 0.83 and average about 0.49. The atomic ratio Mg#s are widely ranging about 0.00 up to 0.70, with the average about 0.46. The atomic ratios of $Fe^{3+}/(Cr+Al+Fe^{3+})$ are also widely ranging from 0.02 to 0.31, with the average about 0.11.

4.4 Chromian spinels from serpentinites in the Sa Kaeo-Chanthaburi Accretionary Complex

From the field investigation in this study, several new location of serpentinite are discovered. Outcrop of serpentinites in the SKCB-AC can be exposed as large bodies and tectonic blocks in mélanges in the present. For understanding the possible provenance rocks for detrital chromian spinels, the chromian spinel studies on these serpentinites are suitable (Plates 25 to 28).

Compositionally, 56 chromian spinels from the serpentinite bodies of the Khao Prik, Khao Hleam, and Soi Dao units (see Appendix B) have probably wide values of Cr_2O_3 about 26.07% to 62.78%. Al_2O_3 ranging from 1.18% to 34.26%, FeO (total Fe) ranging from 22.04% to 47.89%, and MgO wide ranging from 2.93% to 9.92%, are measured as the major components of these spinels. The minor oxides are TiO_2 ranging from 0.02% to 0.38%, NiO ranging from virtually nil to 0.26%, MnO ranging from 0.30% to 0.77%, and ZnO ranging from virtually nil to 0.67%.

Based on computer-normalized to 4 oxygens, chromian spinels in serpentinite of the SKCB-AC have high averaged Cr cations about 1.365 within the range of 0.632 to 1.809. The Al cations are ranging from 0.056 to 1.238 with the average about 0.477. The Mg cations are ranging from 0.178 to 0.482 and averaging about 0.357. Recalculated Fe^{2+} and Fe^{3+} cations are ranging from 0.527 to 0.908 and 0.056 to 0.734, respectively. The averages of recalculated ferrous iron and ferric iron cations are 0.659 and 0.189.

Considering to the cation fractions, totally chromian spinels from serpentinite have the atomic ratio Cr#s range highly from 0.34 to 0.97 and average about 0.74. The atomic ratio Mg#s are widely ranging about 0.16 up to 0.48, with the average about 0.35. The atomic ratios of $Fe^{3+}/(Cr+Al+ Fe^{3+})$ are also widely ranging from 0.03 to 0.34, with the average about 0.09.

4.4.1 The Khao Prik Unit

Generally, 11 chromian spinels from the biggest serpentinite body of the SKCB-AC in the Khao Prik unit have values of Cr_2O_3 about 40.81% to 45.84%. Al_2O_3 ranging from 2.55% to 19.26%, FeO (total Fe) ranging from 22.04% to 47.89%, and MgO wide ranging from 2.93% to 9.78%, are measured as the major components. As the minor oxides are TiO_2 ranging from 0.02% to 0.14%, NiO ranging from virtually nil to 0.26%, and MnO ranging from 0.35% to 0.56%.

After the calculations based on properly 4 oxygens, the chromian spinels in this serpentinite have high averaged Cr cations about

1.195 within the range of 1.161 to 1.31. The Al cations are ranging from 0.123 to 0.757 with the average about 0.684. All Mg cations are ranging from 0.178 to 0.482 and averaging about 0.423. Recalculated Fe^{2+} and Fe^{3+} cations are ranging from 0.527 to 0.908 and 0.056 to 0.734, respectively. The averages of recalculated ferrous iron and ferric iron cations are 0.594 and 0.153.

The chromian spinels from serpentinite in the Khao Prik unit have the atomic ratio Cr#s range from 0.61 to 0.91 and average about 0.64. The atomic ratio Mg#s are about 0.16 up to 0.48, with the average about 0.42. The atomic ratios of $Fe^{3+}/(Cr+Al+ Fe^{3+})$ are also widely ranging from 0.03 to 0.34, with the average about 0.07.

4.4.2 The Khao Hleam Unit

Totally 10 chromian spinels in blocks of the serpentinite mélange have values of Cr_2O_3 about 26.07% to 34.88%. The other major oxides are Al_2O_3 ranging from 19.52% to 34.26%, FeO (total Fe) ranging mostly from 27.47% to 37.28%, and MgO almost ranging from 6.29% to 9.92%. The minor oxides are TiO_2 ranging 0.15% to 0.38%, NiO ranging 0.03% to 0.10%, MnO ranging 0.34% to 0.55%, and ZnO ranging 0.25 to 0.67%.

Based on the theoretically 4 oxygens, chromian spinels from serpentinite mélange have averaged Cr cations about 0.853, within the range of 0.632 to 0.937. The Al cations are ranging from 0.803 to 1.238 and averaging about 0.897. The Mg cations are ranging 0.321 to 0.453 with the average about 0.360. Recalculated Fe^{2+} and Fe^{3+} cations are

ranging from 0.556 to 0.703 and 0.150 to 0.393, respectively. The averages of recalculated ferrous iron and ferric iron cations are 0.668 and 0.304.

Focusing to the cation fractions, chromian spinels from serpentinite mélange in the Khao Hleam unit are generally high in Cr# with the average about 0.49. The Cr#s are ranging from 0.34 to 0.54. The Mg#s range from 0.31 to 0.45 and average about 0.35. The atomic ratios $Fe^{3+}/(Cr+Al+Fe^{3+})$ are ranging from 0.07 to 0.19, with the average about 0.15.

4.4.3 The Soi Dao Unit

Compositionally, 35 chromian spinels from the serpentinite bodies of the Soi Dao unit have very high values of Cr_2O_3 about 45.86% to 62.78%. Low Al_2O_3 ranging from 1.18% to 14.17%, FeO (total Fe) constantly ranging from 24.15% to 44.25%, and MgO wide ranging from 3.14% to 9.23%, are measured as the major components of these spinels. The minor oxides are TiO_2 ranging from 0.08% to 0.25%, NiO ranging from virtually nil to 0.19%, MnO ranging from 0.30% to 0.77%, and ZnO ranging from 0.11% to 0.47%.

Based on computer-normalized to 4 oxygens, chromian spinels in serpentinite of the Soi Dao unit have very high averaged Cr cations about 1.565 within the range of 1.336 to 1.809. The Al cations are ranging from 0.056 to 0.566 with the average about 0.293. The Mg cations are ranging from 0.188 to 0.459 and averaging about 0.335. Recalculated Fe^{2+} and Fe^{3+} cations are ranging from 0.551 to 0.879 and

0.069 to 0.623, respectively. The averages of recalculated ferrous iron and ferric iron cations are 0.677 and 0.167.

Considering to the cation fractions, totally chromian spinels from serpentinite have the atomic ratio Cr#s range from 0.703 to 0.967 and average about 0.845. The atomic ratio Mg#s are widely ranging about 0.176 up to 0.454, with the average about 0.332. The atomic ratios of $Fe^{3+}/(Cr+Al+ Fe^{3+})$ are also widely ranging from 0.035 to 0.292, with the average about 0.082.