CHAPTER IV

DETRITAL CHROMIAN SPINELS

4.1 General statement

Chromian spinel is a ubiquitous accessory phase in basalts and peridotites, and with the exception of Cr_2O_3, does not contribute significantly to the total concentration of any element in the rock. Spinel is also extremely sensitive to bulk composition mineralogy and petrogenesis of the host rocks (e.g. Irvine 1965, 1967, 1976; Thayer 1970; Evans and Frost 1975; Dick 1977a; Fisk and Bence 1980). Spinel's principle constituents are very different during fractional crystallization or partial melting, with Cr and Mg strongly partitioned into the solid, and Al strongly partitioned into the melt. In addition, partition of Mg and Fe^{2+} between spinel and silicate melts and minerals is strongly temperature dependent and the ratio of Fe^{2+} to Fe^{3+} is sensitive to variations in fO_2. Due to these characteristics, the equilibrium spinel composition often undergoes large twins during various crystallization, melting or re-equilibration processes, which may produce only modest changes in the composition of the major silicate phases. Thus chromian spinel is effectively "petroloyic litmus paper" begin extremely sensitive to host rock petrogenesis, without itself palying any major geochemical role.

Irvine and others (1965, 1967) noted a pronounced positive correlation between Fe/Mg and Cr/Al ratios in chromian spinels in alpine-type peridotites and mafic layered intrusions. It was apparent that such correlations were crystallochemically based, because such rocks are characteristed by restricted ranges of Fe/Mg ratios of olivines and inferred temperatures of formation. In such rocks spinels typically have compositions close to the Al-Cr face of the so-called "spinel prism" defined by the verities of the $(Fe^{2+}, Mg)(Al, Cr, Fe^{3+})_2O_4$ composition space (Figure 4.1). 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 the spinel group in the oxides, which have two non-equivalent metal atom sites (AB_2O_4). The minerals of the spinel group usually show extensive solid solution between the various

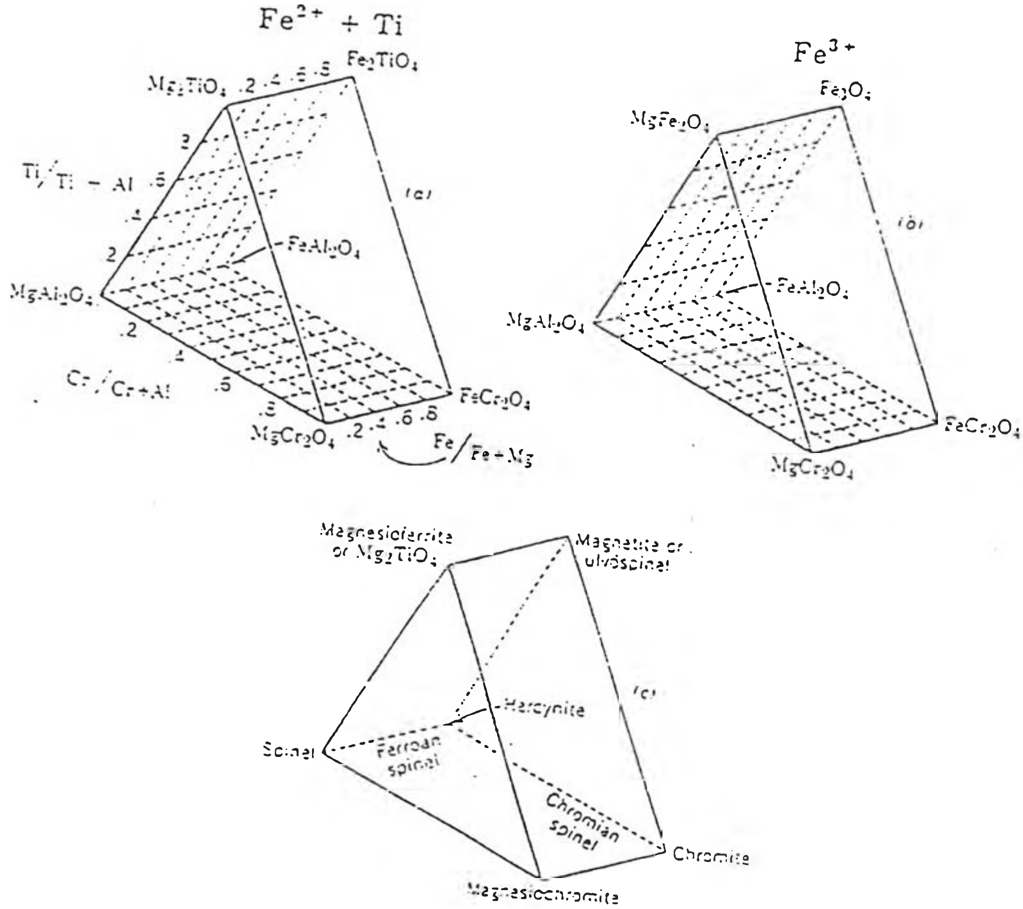


Figure 4.1 End member compositions in the spinel group as represented in a spinel prism.

end-member compositions. There is for example, the extensive solid solution between magmetite (Fe_3O_4) and ulvöspinel ($Fe^{2+}{}_2TiO_4$). Furthermore, there are substitution between chromite ($FeCr_2O$) and magnesiochromite ($MgCr_2O_4$), between spinel ($MgAl_2O_4$) and hercynite ($FeAl_2O_4$), and so on.

4.2 Previous works-significance of chromian spinels

Previous application 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 Alpine-type ophiolite instead of mid-oceanic ridge or stratiform intrusion. Pober and Faupl (1988) used spinels from heavy-mineral stream concentrates from a large area in the Eastern Alps, and on the basis of spinels in lherzolites and harzburgites established that pretest population of spinel data is in the abyssal harzburgite field, equivalent to Dick and Bullen (1984). Similarly, Arai and Okada (1991) use chemistry of detrital chromian spinels to compare the petrologic characteristics of the lost peridotite mass with those of currently exposed peridotite, and to discuss a tectonic history of the serpentine belt itself. Hisada and Arai (1993, 1994) studied the chemical composition of detrital chromian spinels in the Cretaceous Sanchu sandstone in Japan to relate serpentinite protrusion in the fore-arc region, and to determine the tectonic history of the Kanto Mountains. Recently Cookenboo et al. (1997) compared the composition range of spinels from the literature on ultramafic rocks. Bowser Basin spinels are compositionally matched those from Alpine-type peridotites emplaced by obduction of marginal-basin crust and island-arc complexes. This provenance interpretation was in a good agreement with earlier interpretation that related chert pebbles in the Bowser Basin and fitted in the detrital model analysis of sandstone, which called for obducted oceanic crust and island arc-source terrane.

4.3 Characteristics of detrital chromian spinels in sandstone

Detrital chromian spinel study is regarded as a single-mineral analysis applied to determine tectonic provenance. The study can increase tremendous confidence in provenance interpretation and simultaneously add the detailed secrets unavailable from normal approaches. The electron probe microanalysis (EPMA) of detrital chromian spinels in sandstones from the Mae Sariang Group is adopted to unravel the geological approach and geochemistry of the detrital chromian spinels are aimed to evaluate tectonic evolution of the Mae Hong Son area.

4.3.1 Accumulation and contribution

In the Mae Hong Son area, numerous detrital chromian spinels are discovered as one of the accessory minerals in sandstones from the Mae Sariang Group.

Generally the stratigraphy of the Mae Sariang Group is characterized by a bedded chert interbedded shale and limestone lens in some place in the lower part, conglomerate interbedded sandstone and sandstone interbedded shale in the middle part, and siliceous shale interbedded shale in the upper part. Although sandstones (Figure 4.2) were collected from the entire Mae Sariang Group along the Highway 1107 between km 20-20.5, detrital chromian spinels are usually found in the Tr_2 unit. In other area, sandstones were collected from streams at Ban Mae Leab (latitude 18^{O} 22' 49" N and longitudes 97^{O} 52' 10" E). It is important to note that these sandstones have been documented as parts of turbidite sequence (by Tofke et al., 1993). The successions often reveal graded bedding, cross-bedding, lamination and sole marking. Directions of currents, as measured from the flute casts, and cross-bedding for the probable source location of the detrital chromian spinels, varies from NW-SE ranging to N to S. As the Middle to Upper Triassic bivalve fauna including *Posidonia* and *Halobia* are reported in the associated Stopple et al. (1972, 1987).

4.3.2 Petrography of detrital chromian spinels

Chromian spinel grains discovered in this study area are generally deep brown to almost opaque under transmitted light corresponding to their Cr-Al-Fe^{3+} composition (see Bernier, 1990). These detrital chromian spinels are the most abundant in very fine- to fine-grained sandstones in turbidite sequences, especially in the Tr_2 unit. The detrital chromian spinels in the Mae Sariang Group are rather small. Their grains are varied between 20 μm

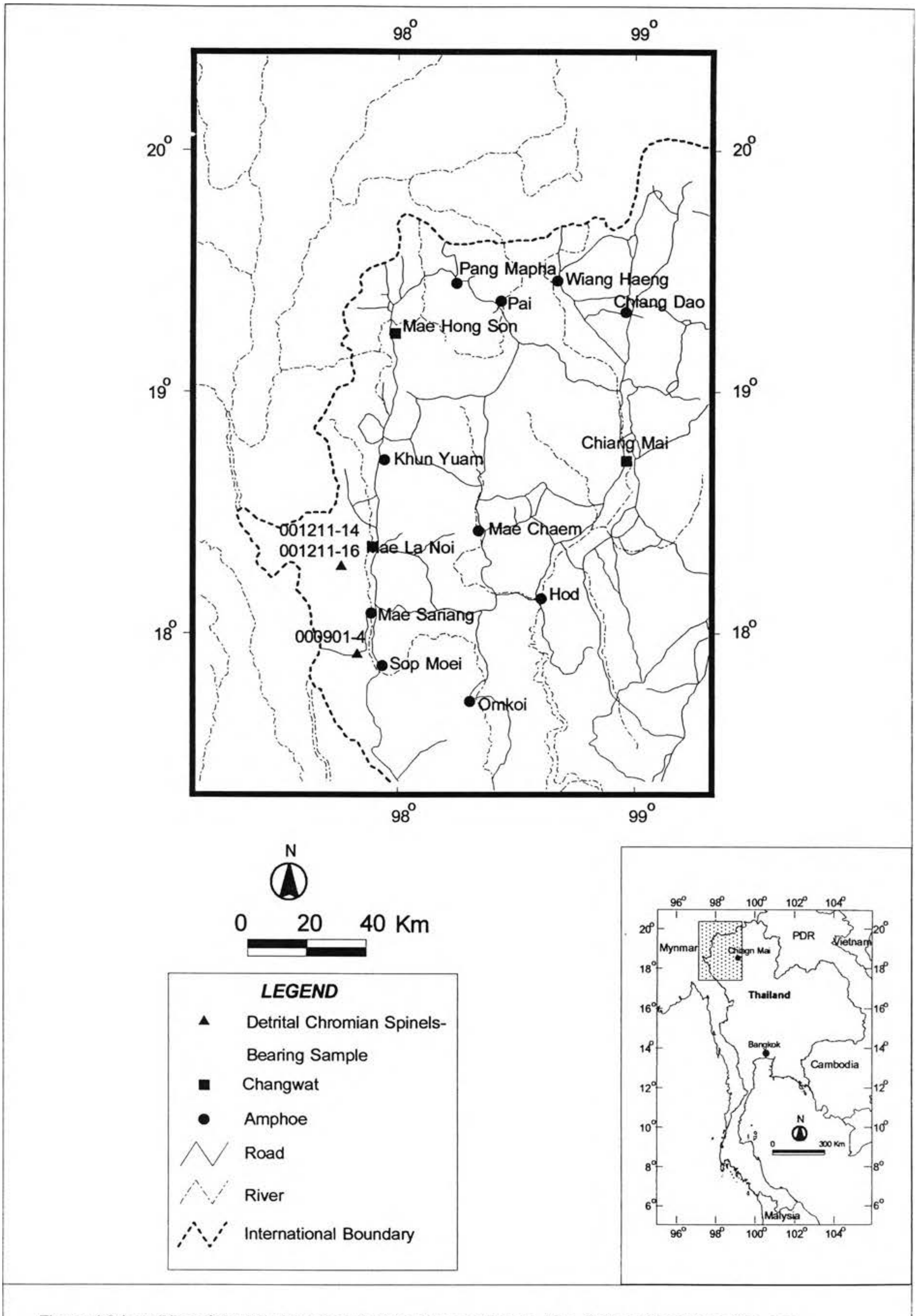


Figure 4.2 Localities of detrital chromianspinel-bearing sandstone, Mae Sariang-Mae Hong Son area, northern Thailand.

to 160 μm in size. Comparing with those of the detrital chromian spinels (75 μm to 150 μm in size) of the Alpine-type peridotite origin in the Bowser Basin in the Canadian Cordillera (Cookenboo et al., 1997), the spinels of the Mae Sariang sandstone one much smaller. Considering the grain size of detrital chromian spinels, however, they are too small to observe and identify in the hand specimens.

To comprehend of physical properties of small size chromian spinels that can not be noticed from hand specimens literature review was carefully performed. The physical properties of chromian spinels are intermediate between spinel and chromite. They resemble chromite but are more transparent. The minerals, spinel-chromite, are generally isometric. They are hard, and brittle minerals. The physical feature varies from chromite and spinel depending on their compositions. The hardness is about 5.5-8.0 and the specific gravity is about 3.6-4.8. 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 transmitted light, the occurrence of detrital chromian spinels in this study (Figure 4.3) as small, high refractive index (n=1.72-2.16) grains that are either opaque or deeply brown. Color serves to distinguish them from other minerals in sandstones. The translucent spinels are usually deep brown with darker thin edges. Both of them are mostly sub-angular to angular. Grains are generally homogeneous and show no obvious signs of zoning or twinning. Some of larger grains show very weak birefringence. As in reflected light, high Cr-spinels are often black or opaque with a sub-metallic to metallic luster in reflected light depending on the content of Cr and thickness of thin sections.

4.3.2.1 Ban Mae Leab Site

After the discovery of detrital chromian spinels in the middle part of the Mae Sariang Group around Huai at Ban Mae Leab. About 4 grains of detrital chromian spinels in Tr_2 unit (latitude 18° 22' 49" N and longitudes 97° 52' 10" E) are found in very fine- to fine-grained sandstones interbedded shale. Generally, they display brown to deep brown under

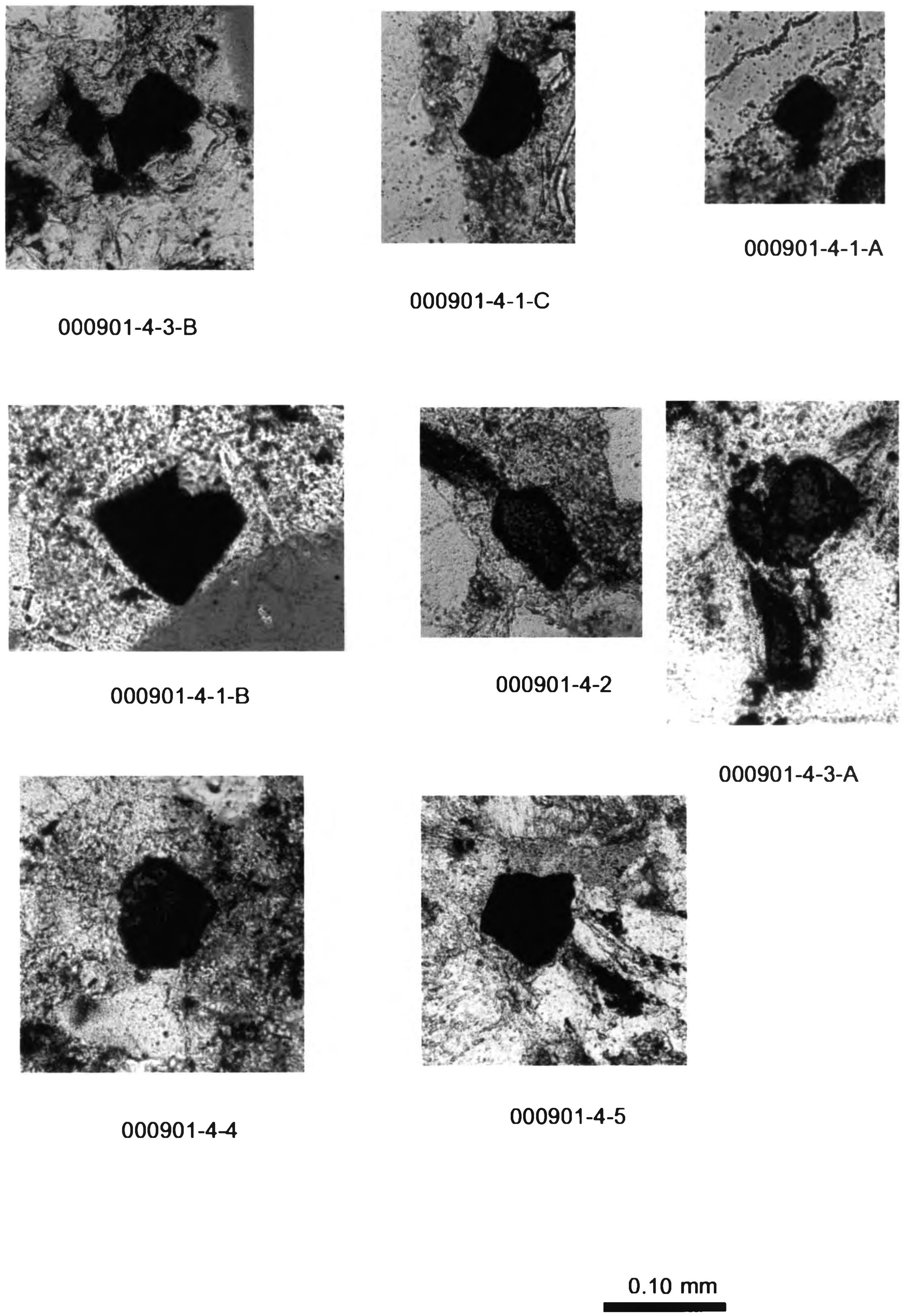
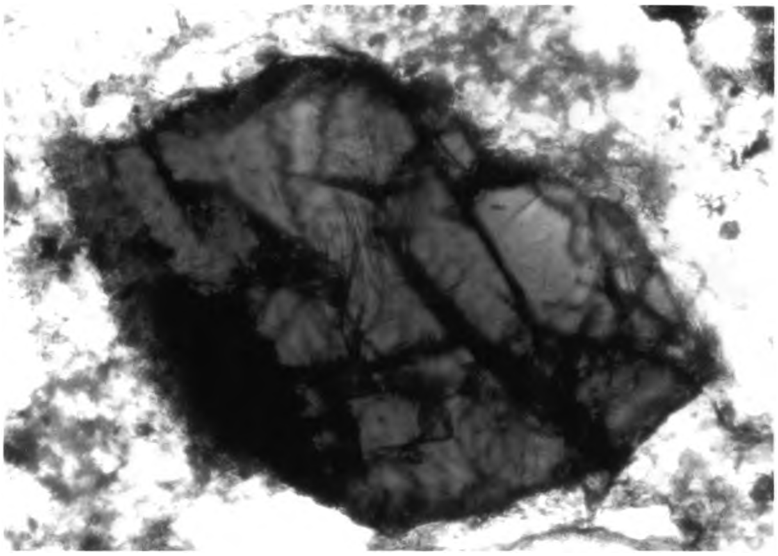


Figure 4.3 Photomicrograhps of detrital chromian spinels in sandstone, Mae Hong Song Group showing brown to dark brown-coloured, subhedral to euhedral habit. Polished-thin section without nicols.



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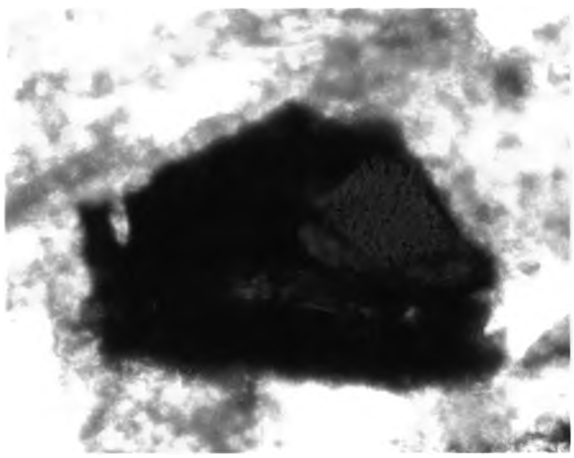

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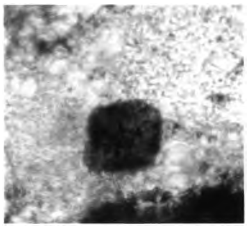

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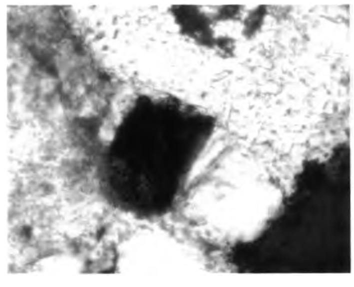

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0.05 mm

Figure 4.3 (cont.)

microscope. Their grains vary from 20 μm to 110 μm in size. The spinels exhibit mostly euhedral shape.

4.3.2.2 Ban Huai Pho Site

Eight grains of detrital chromian spinels were found in the Tr_2 unit, at Ban Mae Leab Site. Characteristically, the detrital chromian spinel grains are rather small in size ranging from 40 μm to 160 μm. Regarding the color of chromian spinels under microscope, two kinds of chromian spinels observed are brown and deep brown spinels. In general, the brown spinels displays subhedral and more variation in grain size (40-160 μm) comparing to the dark brown spinels.

4.3.3 Chemistry characteristics of detrital chromian spinels

4.3.3.1 Sampling and analytical technique

Thin-section examination indicates that chromian spinels are accessory (less than 1%) in the sandstone strata. Samples containing relatively higher concentrations of chromian spinels and distributing from several locations were selected during thin-section analysis for microprobe study. Several sandstones were chosen to represent all the sandstone strata from each rock unit exposed in the study area. More than 20 grains were identified for the representatives of chromian spinel for microprobe studies. Due to the constraints on available working time, only representative 12 grains from the Tr_2 unit were selected.

Geochemical data on major and minor elements of these detrital chromian spinels were obtained from polished thin-section using the electron probe microanalysis (EPMA). EPMA is a sophisticate technique for chemically analyzing small selected areas of solid or mineral samples, in which X-ray are excited by identifying the lines from their wavelengths. By comparison the intensities of these lines with those emitted from standards it is also possible to determine the concentration of major elements (quantitative analysis).

The preparation procedure is that for normal thin-section in the early stages. Because of the high stress of polishing, a strong adhesive (e.g. epoxy resin) should be used for attaching rock slices to glass slides. Individual rock slice were ground to a thickness greater than the 30 μm final thickness required, before starting the polish in the next step.

For EPMA analysis it is extremely desirable to avoid topographic effects, therefore the specimens made are flat and well polished. Starting with a flat ground surface, 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 samples being nonconductors of electricity, chromian spinels require a conductive coating to prevent charging under electron bombardment. For EPMA analysis, carbon is the preferred coating element in this study, since it has a minimal effect on the X-ray spectrum. The method of carbon coating is to place thin-section in a vacuum chamber with a current of around 100 μ passed through a cabon evaporation source consisting of carbon rods in contact under light pressure (normally less than ~10^{-4} torr). The optimum thickness of carbon is about 20 nm (Reed, 1996). This thickness can be controlled approximately by using a fixed current and evaporation time.

The quantitative major and minor element analysis of these detrital chromian spinels were carried out by a JEOL, model no. JXA-8621 Superprobe at the Chemical Analysis Center, the University of Tsukuba. Analysis of standards as unknowns 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 the method described by Arai and Hisada (1991), Arai (1992), Arai and Matsukage (1996), and Arai et al. (1997).

Regarding the analyzing resolution of the probed 10 μm diameter could be investigated. Total 12 representative chromian spinel grains were selected for geochemical data of detrital chromian spinels in the Mae Sariang Group.

4.3.4.2 Quantitative major element compositions

The result of the quantitative electron microprobe analysis was expressed in first instance as element mass concentrations (weight percent). The concentration of unanalyzed elements of O was obtained by computer calculation from the assumed valencies of the cations. The analyses, carried out by a JEOL Superprobe, were reported as both "weight percent oxide" and "number of atoms" (see Table 4.1).

Detrital spinels measured in this study vary widely in major-element concentrations. Compositionally chromian spinels have high values of Cr_2O_3 about 27% to 57%. The other major oxides of chromian spinels are Al_2O_3 ranging from 21.6% to 36.5%. FeO (total Fe) ranging from 13.0% to 23.9% and MgO ranging from 9.4% to 17.1%. As the important minor oxides. TiO_2 ranging 0.014% to 0.723%. NiO ranging from 0.030% to 0.194%, and MnO ranging 0.132% to 0.854%, make up only trace amounts.

Numbers of atoms derived from quantitative electron microprobe analysis were computer-normalized to 4 oxygen (which is appropriate for chromian spinels). The cation total is close to the theoretical value of three for chromian spinels. Detrital chromian spinels of the Mae Sariang Group have high Cr cation about 0.651 to 1.422, averaging about 0.950. The Al cations range from 0.503 to 1.204 and average about 0.950. The other major element is the Mg cations within the range of 0.454 to 0.757 and averages about 0.620. The Fe cation is the only element present that has dual valency, the proportions of Fe^{2+} and Fe^{3+} can be recalculated assuming ideal spinel stoichimetry following Arai and Hisada (1991) as previous mentioned. Recalculated iron cations of Fe^{2+} and Fe^{3+}, rang from

Table 4.1 EPMA analysis of detrital chromian spinels in the Tr_2 sandstone of the Mae Sariang Group, Mae Hong Son

Sample No.	001211-16-1-C	001211-16-2-C	001211-14-2-C	001211-14-3-C	000901-4-1-A	000901-4-1-B
SiO2	0.098	0.286	0.009	0.048	0.276	0.353
Al2O3	26.037	32.446	28.153	24.953	21.594	24.867
TiO2	0.454	0.723	0.098	0.397	0.678	0.612
Cr2O3	38.946	27.093	38.699	37.902	35.868	36.973
FeO	17.312	21.333	14.692	23.488	24.891	23.921
NiO	0.109	0.236	0.194	0.072	0.133	0.03
MnO	0.265	0.213	0.218	0.854	0.255	0.242
MgO	14.586	14.781	15.08	9.473	14.075	13.552
CaO	0	0.088	0	0.015	0	0.031
Na2O	0.009	0.07	0.054	0.028	0	0
K 2O	0.017	0.043	0.01	0.017	0.034	0.045
Total	97.832	97.313	97.206	97.246	97.804	100.626
cation	O=4	O=4	O=4	O=4	O=4	O=4
Si	0.003	0.009	0.000	0.002	0.009	0.011
Al	0.947	1.162	1.013	0.946	0.818	0.902
Ti	0.011	0.017	0.002	0.010	0.016	0.014
Cr	0.950	0.651	0.934	0.964	0.912	0.900
Fe	0.447	0.542	0.375	0.632	0.669	0.616
Ni	0.003	0.006	0.005	0.002	0.003	0.001
Mn	0.007	0.005	0.006	0.023	0.007	0.006
Mg	0.671	0.670	0.686	0.454	0.674	0.622
Ca	0.000	0.003	0.000	0.001	0.000	0.001
Na	0.001	0.004	0.003	0.002	0.000	0.000
K	0.001	0.002	0.000	0.001	0.001	0.002
Total	3.039	3.071	3.026	3.035	3.111	3.075
Fe*	0.43	0.51	0.38	0.64	0.64	0.59
Fe^{2+}	0.33	0.33	0.32	0.55	0.34	0.38
Fe^{3+}	0.10	0.19	0.06	0.09	0.30	0.21
Mg#(Mg/(Mg+Fe^{2+}))	0.67	0.67	0.68	0.45	0.66	0.62
Cr#(Cr/(Al+Cr))	0.50	0.36	0.48	0.50	0.53	0.50
Fe^{3+}3#(Fe^{3+}/Cr+Al+Fe^{3+}))	0.05	0.09	0.03	0.05	0.15	0.10
Al3#(Al/Cr+Al+Fe^{3+}))	0.47	0.58	0.50	0.47	0.40	0.45
Cr3#(Cr/(Cr+Al+Fe^{3+}))	0.47	0.33	0.47	0.48	0.45	0.45
TiO2wt%	0.45	0.72	0.10	0.40	0.68	0.61

Table 4.1 (cont.)

Sample No.	000901-4-2	000901-4-3-A	000901-4-3-B	000901-4-3-C	000901-4-4	000901-4-5
SiO_2	0	0	0.232	0	0.005	0
Al_2O_3	23.236	29.525	13.409	36.548	34.364	26.575
TiO_2	0.014	0.079	0.194	0.284	0.039	0.032
Cr_2O_3	47.719	38.457	56.583	36.724	37.745	42.321
FeO	19.235	13.047	20.483	13.933	15.614	20.235
NiO	0.043	0.124	0.039	0.144	0.067	0.094
MnO	0.325	0.207	0.416	0.132	0.309	0.365
MgO	12.034	17.085	11.174	15.121	16.453	11.509
CaO	0.031	0.016	0.035	0.028	0.039	0
Na_2O	0	0	0.019	0	0.037	0.013
K_2O	0.009	0.028	0.016	0.017	0.087	0.007
Total	102.646	98.568	102.6	102.931	104.759	101.151
cation	O=4	O=4	O=4	O=4	O=4	O=4
Si	0.000	0.000	0.007	0.000	0.000	0.000
Al	0.829	1.034	0.503	1.204	1.128	0.951
Ti	0.000	0.002	0.005	0.006	0.001	0.001
Cr	1.143	0.903	1.422	0.812	0.831	1.016
Fe	0.487	0.324	0.545	0.326	0.364	0.514
Ni	0.001	0.003	0.001	0.003	0.002	0.002
Mn	0.008	0.005	0.011	0.003	0.007	0.009
Mg	0.543	0.757	0.530	0.630	0.683	0.521
Ca	0.001	0.001	0.001	0.001	0.001	0.000
Na	0.000	0.000	0.001	0.000	0.002	0.001
K	0.000	0.001	0.001	0.001	0.003	0.000
Total	3.014	3.030	3.026	2.986	3.022	3.016
Fe*	0.49	0.33	0.55	0.32	0.37	0.52
Fe^{2+}	0.46	0.25	0.47	0.36	0.32	0.48
Fe^{3+}	0.03	0.08	0.08	-0.04	0.05	0.04
Mg#(Mg/(Mg+Fe^{2+}))	0.54	0.75	0.53	0.64	0.68	0.52
Cr#(Cr/(Al+Cr))	0.58	0.47	0.74	0.40	0.42	0.52
Fe^{3+}3#(Fe^{3+}/Cr+Al+Fe^{3+}))	0.02	0.04	0.04	-0.02	0.02	0.02
Al3#(Al/Cr+Al+Fe^{3+}))	0.41	0.51	0.25	0.61	0.56	0.47
Cr3#(Cr/(Cr+Al+Fe^{3+}))	0.57	0.45	0.71	0.41	0.41	0.51
TiO_2wt%	0.01	0.08	0.19	0.28	0.04	0.03

0.250 to 0.550 and from –0.04 to 0.210, respectively. Their averages are 0.038 for Fe^{2+} and 0.100 for Fe^{3+}.

After calculation of the cation fraction of major elements for the chromian spinel component, $(Mg, Fe^{2+})(Cr, Al, Fe^{3+})_2O_4$ of each sample grain, 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 TiO_2 content. The atomic ratios Cr/(Cr+Al) or Cr# vary considerably from 0.360 to 0.740, but mostly above 0.4 and with the average about 0.500. The atomic cations $Mg/(Mg+Fe^{2+})$ or Mg# also range widely from 0.45 to 0.75 and average about 0.62, with Mg concentration generally decreasing as Fe increases. The Fe^{3+} concentration is considerably low. The atomic ratios $Fe^{3+}/(Cr+Al+Fe^{3+})$ in detrital chromian spinels are mostly below 0.15 with the average of about 0.05. Only one out of twelve grains analyzed had the atomic ratios $Fe^{3+}/(Cr+Al+Fe^{3+})$ almost down to 0.