CHAPTER 3

Methodology

3.1 Sample Selection

Eighty samples of felsic to mafic volcanic/ hypabyssal rocks were collected from many localities in the areas of Nakhon Sawan and Uthai Thani Provinces. The felsic to mafic volcanic/ hypabyssal rocks in the study areas have experienced variable degrees of alteration and metamorphism. Accordingly, their chemical compositions are not to represent the original magmas. A number of fresh, least-altered igneous samples (volcanic/ hypabyssal rocks) were collected from both outcrops and in situ float rocks in the study areas for original chemical compositions analysis. However, the volcanic/ hypabyssal samples presented in this study are only those considered to be least-altered under the petrographic microscope. The least-altered samples in this account generally exclude the samples with

- extensive development of mesoscopic domains of secondary minerals such as quartz resulted from silicification, epidote minerals and chlorite,
- 2) well-developed foliation or mineral layering,
- 3) abundant vesicles/amygdales, xenocrysts and xenoliths, and
- quartz, epidote or calcite veining and/or patches totally more than 5 modal %. Occasional samples had some that more than 5 modal % secondary calcite and/or quartz but were included in this study in the absence of betterpreserved rocks.

Using the above criteria, fifty-four least-altered felsic to mafic volcanic rocks were selected to represent magma prior to eruption. The locations of these least-altered samples are shown in Figure 4.1 (see Chapter 4).

3.2 Petrographic Study

Eighty samples of felsic to mafic volcanic/ hypabyssal rock samples were prepared for the standard thin sections (0.03 mm thick) and then studied at the Department of Geological Sciences, Faculty of Science, Chiang Mai University. The thin sections were studied to characterize primary mineral compositions, alterations and textures. Rock names are applied, on the basis of both geochemical and textural characteristics. The results of lithologic and petrographic study are summarized in Chapter 4 and individually reported in Appendix A.

3.3 Whole Rock Chemical Analyses

The fifty-four carefully selected felsic to mafic volcanic/ hypabyssal rocks were prepared for whole-rock chemical analysis by powdering. These powder samples were chemically analyzed for major oxides, trace elements, rare-earth elements (herein REE) and loss on ignition (herein LOI). The representatives of the least altered samples were analyzed for U – Pb zircon geochronology analysis.

3.3.1 Powder Sample Preparation

The fifty-four carefully selected felsic to mafic volcanic/ hypabyssal rocks were prepared for whole-rock chemical analysis by cutting off the weathering surfaces of the least-altered samples, splitting into conveniently sized fragments, and then crushing to small chips (approximately 5 mm across), using a Rocklabs Hydraulic Splitter/Crusher. The chips (~ 200 g) were cautiously chosen to avoid those containing vesicles, amygdale minerals, veinlets, xenoliths and weathering surfaces. The compressed air was used to remove dusty materials from the selected chips. The cleaned rock chips were divided by quartering into approximately 50-80 g of the cleaned chips and then were pulverized for a few minutes by a Rocklabs Tungsten-Carbide Ring Mill. All the described procedures were done at the Department of Geological Sciences, Faculty of Science, Chiang Mai University.

3.3.2 Major Oxides Elements Analysis

Chemical analyses of major oxides (SiO₂, TiO₂, Al₂O₃, total iron as Fe₂O₃, MnO, MgO, CaO, Na₂O, K₂O and P₂O₅) were carried out on fifty-four carefully selected felsic to mafic volcanic/ hypabyssal rocks powder, using an Automated Philips PW 1480 X-Ray Fluorescence (herein XRF) Spectrometer with a Phillips MagixPro PW 2400 Wavelength Dispersive Sequential X-ray Spectrometer, installed at the Department of Geological Sciences, Faculty of Science, Chiang Mai University, Chiang Mai, Thailand.

The major oxides were measured from fusion discs, prepared by mixing 0.800 g sample powder with 4.000 g lithium tetraborate ($Li_2Br_4O_7$) and 0.060 g lithium bromide (LiBr) in a platinum crucible. The mix was fused by Bunsen Burner, and then cool down in a 3 cm platinum mold. All the fusion discs were prepared by the author and were analyzed by Dr. Apichet Boonsoong.

The instrumental parameters are made up of (1) Rhodium (Rh) tube with a lithium fluoride 200 crystal (used in an elemental range of K – Ru), and scintillation and flow proportion detectors, and (2) X- ray tube operated at 60 kV and current of up to 125 mA; at a maximum power level of 4 kW. The net (background correlated) intensities were measured, and the concentrations were calculated against the calibrations derived from eight international standards reference rock sample as AGV-2, BIR-1, RGM-1, BCR-2, DNC-1, W-2, BHVO-2, and GSP-2. The interelements matrix corrections were done by the Super Q version 3.0 program. The reporting detection limit is about 0.01 wt% for major oxides. The accuracy and precision for most of the elements are better than 5%.

3.3.3 Trace and Rare Earth Elements Analysis

The trace elements (Li, Be, Co, Cu, Zn, Ga, Mo, Cs, Ba, Rb, Sr, Y, Zr, Nb, Ni, Cr, V, Sc, Hf, W, Pb, Ta, Th and U) and the REE (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu) were determined on fifty-four carefully selected felsic to mafic volcanic/ hypabyssal rocks powder, using a

Thermo Scientific XSERIES 2 Inductively Coupled Plasma Mass Spectrometry (herein ICP-MS) installed at the Key Laboratory of Isotope Geochronology and Geochemistry, the Guangzhou Institute of Geochemistry, Chinese Academy Sciences (CAS), Tianhe, Guangzhou, Guangdong, China. The ICP-MS analytical procedure is described in Qi et al. (2000). The analytical precision is better than 5% for elements > 10 ppm, less than 8% for those < 10 ppm, and about 10% for transition metals. Solutions for ICP-MS analysis were prepared with Qi et al. (2000) digestion technique. Analytical reagent-grade HF and HNO3 were used and purified prior to use by sub-boiling distillation. The screw-top PTFE Teflon Beaker bombs were cleaned using 20% HNO₃ (v:v) heated to 100°C for 1 hour. Dissolution of felsic to mafic volcanic/ hypabyssal rocks powdered samples were started with 35-45 mg of samples and weighed into 25 ml screw-top PTFE bomb. 0.6 ml (30 drops) HNO₃ and HF (1:1, BVIII grade, Beijing Institute of Chemical Reagents) and 0.3 ml (15 drops) HClO₄ (1:3) were slowly added to each sample bombs and were treated in an ultrasonic cleaner/bath for 60 minutes. Then bombs were placed on a hot plate with 100 °C for 48 hours. After that each bomb were opened, solution evaporated to dryness for remove most of silica. Next step, 0.8 ml (40 drops) HNO₃ (1:1, BVIII grade, Beijing Institute of Chemical Reagents) were slowly added to each sample bombs and put on hot plate with 110 °C for 1 hour. After that 0.8 ml (40 drops) HF (1:1, BVIII grade, Beijing Institute of Chemical Reagents) and 0.3 ml (15 drops) HClO₄ (1:3) were slowly added to each sample bombs. Then bombs were sealed and lined in stainless steel bombs (high pressure bomb). Next, they were placed in an electric oven and heated to 190°C for 48 hours. After cooling, the bombs were washed outside and opened before placed on a hot plate with 150 °C for 12 hours (overnight) for evaporated to incipient dryness. The final digestion residue was re-dissolved by adding 4 ml 4 N HNO₃ to each bomb and closed. Resealed and lined in stainless steel bombs and returning them to the electric oven heated at 170 °C for a period of 4 hours. After cooling, the bombs were washed outside under and placed on the hot plate with 115 °C

for 1 hour. The final solution was transferred into polypropylene bottles and weight for add 3% HNO₃ 2,000 time of sample weight. In addition, separate bulk sample aliquots were added 1 mgml⁻¹ Rh and Re solution as an internal standard with 1:1 before ICP-MS analysis. The reagent blanks were treated exactly as were the samples.

In addition, separate bulk sample aliquots were leached with 2 M HCl and 0.5 M HNO₃ for 24 hours under the room temperature to extract the leachable fraction. REEs in the leachable fraction were also analyzed by ICP-MS following a similar procedure as described above.

Analytical calibration was accomplished using aqueous standard solutions to correct for matrix effects and instrument drift. The standards used in ICP-MS analysis were the international standards (W-2, SY-4, GSR-1, GSR-2, GSR-3, BHVO-2, SARM-4, GDS-9 and AGV-2) and the internal standard (10 ppb Rh). The preparation for standards solution, Single-element 1000 mgl⁻¹ stock solutions were prepared using pure metals or pure metal oxides. Four multi-element stock solutions were prepared, containing 10 mgl⁻¹ of each analyze: (1) Li, Be, V, Cr, Co, Ni, Cu, Zn, Ga, Rb, Sr, Cs, Ba, Pb, Th, U; (2) Sc, Y and 14 REEs; (3) W, Mo; (4) Nb, Ta, Zr, Hf. The stock standard solution containing W and Mo was prepared in 2% NH₃.H₂O, whereas the stock standard solution containing Zr, Hf, Nb and Ta was prepared in 2% HNO₃ and 0.2% HF. The multi-element working standard solutions were prepared (using the reagent blank solution as diluents) from the above mentioned stock solutions to span the concentration range from 10 to 100 mgl⁻¹. At these concentration levels, all elements could be mixed together. Working standard solutions were found to be stable over a period of 2 weeks. The detection limit for each element (in solution) was calculated as three times the S.D. of the ion counts obtained for the sample blank (measured for ten replicate determinations), divided by the sensitivity of 10 mgl⁻¹ multi-element standard solutions. For Li, Be, Sc, V, Cr, Co, Ni, Cu, Zn, Ga, Rb, Sr, Zr, Mo, Cs, Ba and Pb the detection limits ranged from 0.01 to 0.2 mgl⁻¹. For Y, Nb, Hf, Ta, W, Th, U and REE the detection limits ranged from 0.001 to 0.005 mgl⁻¹. Detection limits for these elements in the solid (rock) can be estimated to be much higher that calculated for the sample blank, corresponding to the dilution factor used. The recoveries for most of these elements ranged from 90 to 110%. The solutions for ICP-MS analysis were prepared by the author and analyzed by Mr. Ta Xianglin. The analytical results other than Co were illustrated in Chapter 5 and standard analyses listed in Appendix B. The amount of Co is omitted in this report because the ring mill used was made from tungsten carbide.

3.3.4 Loss on Ignition Determination

Loss on ignition was carried out at the Department of Geological Sciences, Faculty of Science, Chiang Mai University by the author via gravimetric method, heating about 1 g of each sample powder at 1000°C for 12 hours in mafic rock sample and 10 hours in felsic rock samples.

3.4 U – Pb zircon Geochronology Analysis

Four samples of felsic to mafic volcanic/ hypabyssal rocks from different localities in the areas of Nakhon Sawan and Uthai Thani Provinces showed some zircon grains under the petrographic microscope. However, only two carefully selected, representative, felsic to mafic volcanic/ hypabyssal rock samples were analyzed for U, Th and Pb isotopic data by Laser Ablation Inductively Coupled Plasma Mass Spectrometry (herein LA-ICPMS) method, installed at the University of Tasmania, Australia. Measuring procedures and evaluation of the data followed the descriptions of Dr. Sebastien Meffre.

Approximately 100 g of rock was repeatedly sieved and crushed in a Cr-steel ring mill to a grain size <400 microns. Non magnetic heavy minerals were then separated using a gold pan and a Fe-B-Nd hand magnet. The zircons were handpicked from the heavy mineral concentrate under the microscope in cross-polarised transmitted light. The selected crystals were placed on double sided sticky tape and epoxy glue was then poured into a 2.5 centimeters diameter mould on top of the zircons. The mount was dried for 12 hours and polished using clean sandpaper and a clean polishing lap. The samples were then washed in distilled water in an ultrasonic bath.

The analyses in this study were performed on an Agilent 7500cs quadrupole ICP-MS with a 193 nm Coherent Ar-F gas laser and the Resonetics M50 ablation cell at the University of Tasmania, Hobart, Australia. The downhole fractionation, instrument drift and mass bias correction factors for Pb/U ratios on zircons were calculated using 2 analyses on the primary (91500 standard of Wiendenbeck *et al.*, 1995) and 1 analysis on each of the secondary standard zircons (Temora standard of Black *et al.*, 2003 and JG1 of Jackson *et al.*, 2004) analysed at the beginning of the session and every 12 unknown zircons (roughly every 1/2 hour) using the same spot size and conditions as used on the samples. Additional secondary standards (The Mud Tank Zircon of Black and Gulson, 1978) were also analysed. The correction factor for the ²⁰⁷Pb/²⁰⁶Pb ratio was calculated using 3 large spot of NIST610 analysed at the beginning and end of the day and corrected using the values recommended by Baker *et al.* (2004).

Each analysis on the zircons began with a 30 second blank gas measurement followed by a further 30 seconds of analysis time when the laser was switched on. Zircons were sampled on 32 micron spots using the laser at 5 Hz and a density of approximately 1.5 J/cm². A flow of He carrier gas at a rate of 0.6 litres/minute carried particles ablated by the laser out of the chamber to be mixed with Ar gas and carried to the plasma torch. Isotopes measured were ⁴⁹Ti, ⁹⁶Zr, ¹⁴⁶Nd, ¹⁷⁸Hf, ²⁰²Hg, ²⁰⁴Pb, ²⁰⁶Pb, ²⁰⁷Pb, ²⁰⁸Pb, ²³²Th and ²³⁸U with each element being measured every 0.16 s with longer counting time on the Pb isotopes compared to the other elements. The data reduction used was based on the method outlined in detail in Meffre *et al.* (2008) similar to that outlined in Black *et al.* (2004) and Paton *et al.* (2010).

Element abundances on zircons were calculated using the method outlined by Kosler (2001) using Zr as the internal standard element, assuming stoichiometric proportions and using the 91500 to standard correct for mass bias. LA - ICP - MS U - Pb isotropic and trace element data for standard zircons from this study are given in Appendix C.