CHAPTER I

INTRODUCTION

1.1 General Statement

It becomes broadly accepted that gem corundums, i.e. ruby and sapphire, associated with basaltic fields appear to have their own exotic origins and are unlikely to involve a direct crystallizing process from the host basaltic magma (i.e. Coenraads *et al.*, 1995; Guo *et al.*, 1996; Pisutha-Arnond *et al.*, 1998; Sutherland *et al.*, 1998; Berg, 2000; Yui *et al.*, 2003; Sutthirat *et al.*, 2001; Promprated *et al.*, 2003; Chualaowanich *et al.*, 2005). However, understanding on the detailed genetic processes of corundum, especially ruby, still remain vague. A prime factor is obligated to a lack of ruby-bearing xenoliths for detail investigation.

In 2007, a relatively fresh ruby-bearing xenolith obtained from Nguu Hill basaltic subterrane, which is situated in the vicinity of Simba, a small town, in SE Kenya region, was firstly mentioned (Sutthirat *et al.*, 2007). This ruby-related basaltic area was under a preliminary stage of gemstone exploration by that time (Kamwathi, 2007 *pers. comm.*) (see Figure 1.1). In addition, ruby-bearing xenoliths were also found in another basaltic subterrane in the vicinity of Ngulai Hills Ranch area, about 12 km northwesterly of the Nguu Hill basalt (Chualaowanich *et al.*, 2008). These basaltic subterranes are settled in the northernmost part of the Cenozoic Chyulu Hills volcanic field (e.g. Baker, 1954; Saggerson, 1963; Walsh, 1963 *cited in* Spä̈th *et al.*, 2000; Haug and Strecker, 1995). Within these unspoiled terranes, a suite of rare ruby-bearing mafic granulite, together with pyroxenite and peridotite, xenoliths can be observed easily. This crucial evidence indicates that the discovered rubies are *in-situ* derived from the exposed basalt bodies. There are only few studies on the xenoliths of the Chyulu Hills volcanic field available so far, including a work by Henjes-Kunst and Altherr (1992) comparing xenoliths from Kenya to those of northern Tanzania and additional few works done on some aluminous websterite and Mg-Al sapphirine- and Ca-Al Hibonite-bearing granulite xenoliths collected from the northwestern part of the Chyulu Volcanic Province by Ulianov *et al.* (2005, 2006) and Ulianov and Kalt (2006). However, none of these works specifically mentioned about ruby-bearing mafic granulite xenoliths exposed in the Nguu Hills area in the vicinity of Simba.

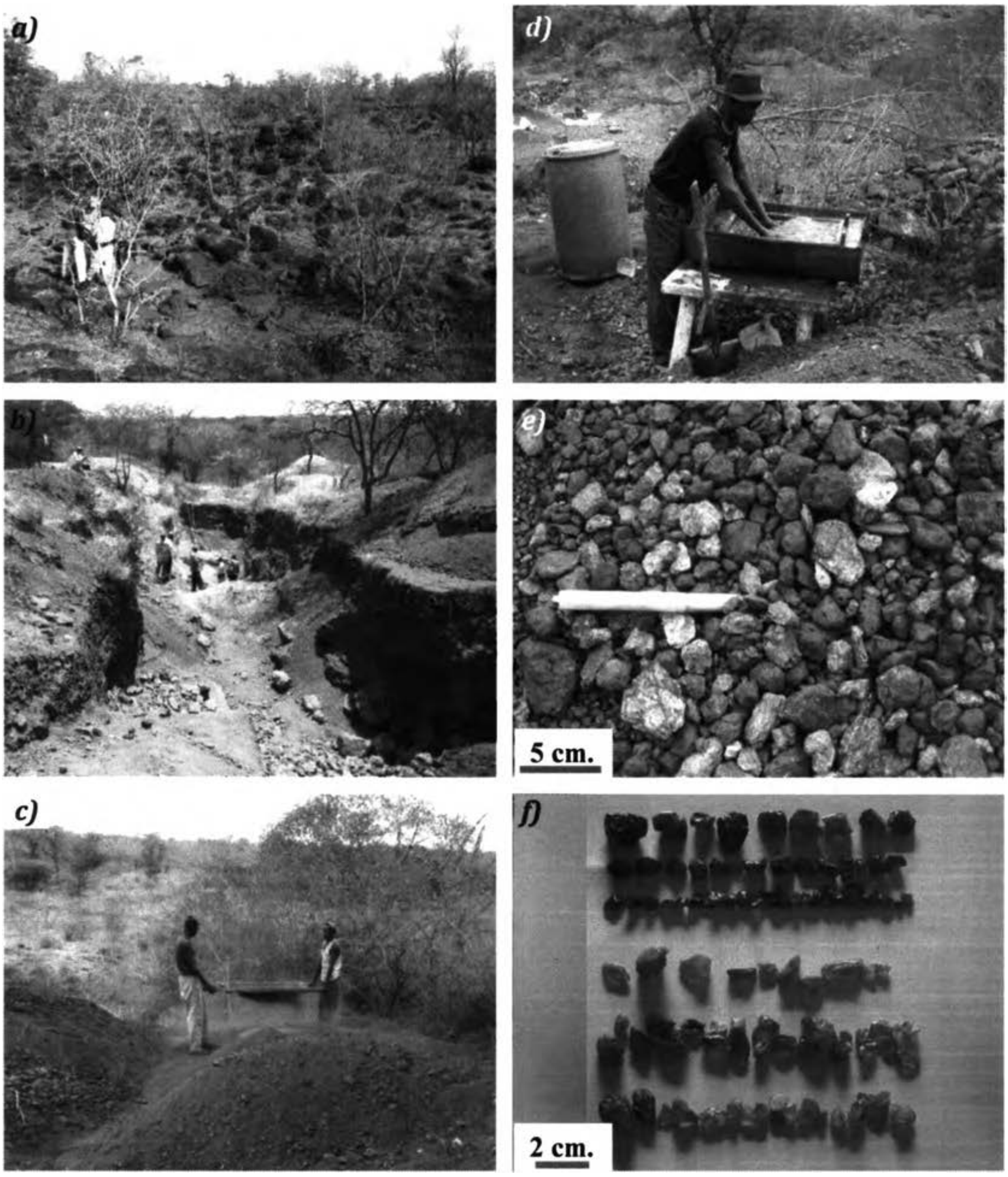

Figure 1.1 Ruby exploration area, licensed to Gemstone International Mining Ltd., at Nguu Hills. *a*) Topography of the area covered by basaltic flow. *b-d*) Prospecting activities, with primitive tools, along stream branches. e) Left over gravels comprising basalt, xenoliths and basement fragments. *f*) Color varieties of ruby and purple sapphire retrieved from the Nguu area.

rift zone, and to obtain a better understanding on genetic aspects of the basalt-associated ruby via the ruby-bearing xenoliths suite.

1.2 Objectives and Aims

The main objectives of this study are:

1. To characterize and compare ruby-bearing xenoliths and other associated xenoliths as well as the basaltic hosts collected in the vicinities of Simba and Emali, SE Kenya.

2. To determine a petrogenesis and P-T condition of the ruby-bearing xenoliths and the interaction with the hosts.

3. To confine the timing of the ruby-related eruption event.

The main intention of this study is to provide fundamental data on physical and chemical characteristics of the xenoliths and their hosts and to better understand the genesis of the basalt-related ruby. A study of petrography and petrochemistry of the full range of observed xenoliths as well as of the host basalts is a prerequisite for interpretation of their genesis. Thermobarometry of well equilibrated assemblages found in xenoliths would yield additional information on P-T conditions of the latest environment before being picked up by the basaltic magma. The result of this study would probably shed the light on the provenance of xenoliths; some could be of very deep-seated origin, possibly from the upper mantle or lower crust underneath the southeast region of Kenya.

1.3 Geologic Setting

The study area is located around the mid-way between Nairobi and Voi. It occupies 2 adjoining basaltic areas. The first area is the Nguu Hills basaltic subterrane, located about 5 km northeast of Simba town. The other is the Ngulai Hills basaltic subterrane located northeast of Emali town, about 10 km northwesterly from Simba. Within each subterrane, several small volcanic centers can be clearly observed on a satellite image. The Nguu Hills volcanic field is composed of one large cone and four satellite vents whereas the Ngulai Hills field is made up of at least 6 smaller cones to form a cluster of 5 hills, namely Kwa Mbiti, Kwa Nthuku, Kwa Kali, Kyanduini (Chanduini), and Kwa Ngeta. The Ngulai Hills study area also includes an isolated cone of Ol Doinyo Orkaria (Ndumoto), located about 3 kilometers south of the main clustered hills (Figure 1.2).

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The Chyulu Hills Volcanic Province (CHVP) is located on the eastern flank of the Kenya Rift Valley, more than 100 km away from the rift axis. Geology of the CHVP has been described and mapped by several workers since the early 1950s (e.g. Baker, 1954; Searle, 1954 and Temperley, 1960 *cited in* Saggerson, 1963, 1968; Walsh, 1963; Goles, 1975; Haug and Strecker, 1995; Omenge and Okelo, 1992 *cited in* Späth *et al.*, 2000). However, there are limited data on the xenoliths associated with this volcanic province available (e.g. Henjes-Kunst and Altherr, 1992; Ulianov *et al.*, 2005, 2006; Ulianov and Kalt, 2006). The study area consists of two small separated volcanic fields within the province and is situated approximately 100 km north of Mt. Kilimanjaro. The simplified geologic map for the study volcanic fields is shown in Figure 1.3.

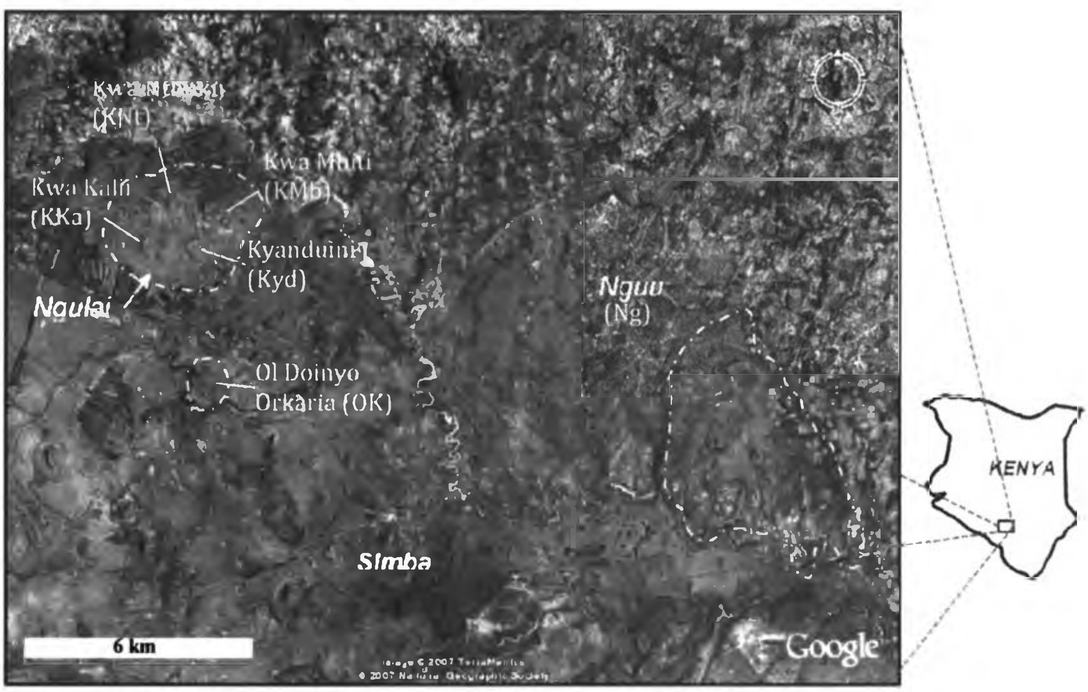

Figure 1.2 Satellite image displaying topographic features around the study area in the vicinity of Simba town, SE Kenya. Dashed bounders and abbreviations in blankets represent areas where xenoliths were collected. (Image source: downloaded from GoogleEarth, 2007)

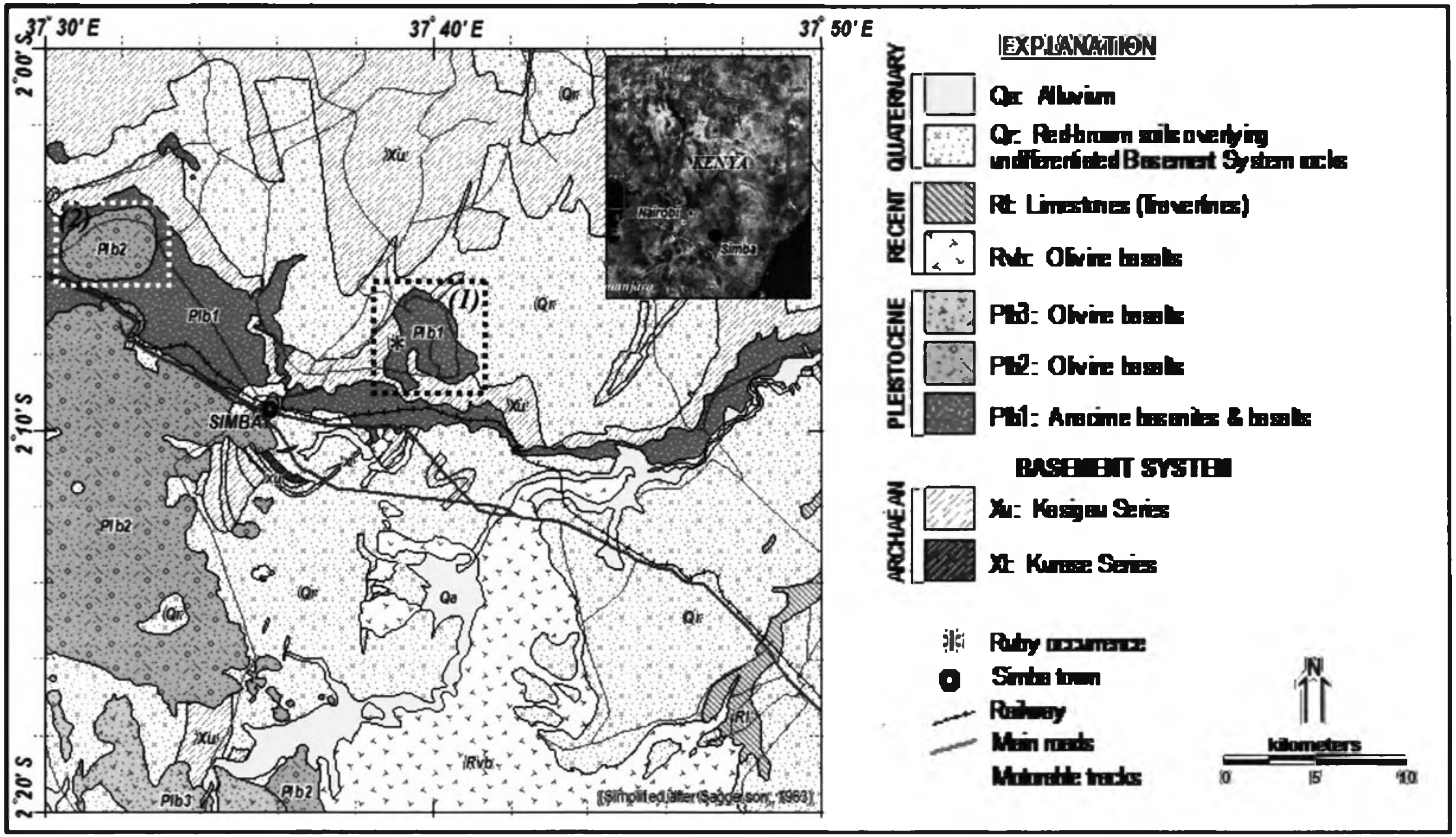

Figure 1.3 Simplified geological map showing the distribution of the Cenozoic volcanic units in the northernmost part of the Chyulu Hills volcanic field that crop out in the vicinity of Simba town (modified from Saggerson, 1963). Rectangles mark the study sub-areas: (1) the Nguu Hills and (2) the Ngulai Hills volcanic subterranes.

to basanite and rare nephelinite (Volker and Altherr, 1989). Main rock types of the suite are foidite, less-silica undersaturated basanite and fractionated alkaline basalt (Huag and Strecker, 1995; Späth *et al.*, 2000). The CHVP lavas comprise 2 main parts. According to Saggerson (1963), the lavas in the northern part (Pleistocene in age) are divided into 3 subunits, which are analcime basanites (Plb1), olivine basalts (Plb2) and olivine basalts (Plb3). The Plb1 unit is composed of 2 main basaltic bodies, which are the Sultan Hamud-Emali-Simba lavas and the Nguu lavas. The Sultan Hamud-Emali-Simba lavas outpoured eastwardly from the Mwani crater in the Sutan Hamud area through the Emali area, and continued flooding over the old Muoni river to the east of Simba. The Nguu lavas is a small part of the Plb1 unit cropped out as a small basaltic patch on the northern flank of the recent Muoni river, where the Nguu Hills situated, apart from the main Plb1 body (see Figure 1.3). The Plb2 unit is also composed of 2 main basaltic bodies distributed in the area between Emali and Simba in north-south direction. The Ngulai lavas, where the Ngulai Hills situated, are a small portion of the Plb2 unit separately located just north of the main patch. The Ngulai basaltic body is encircled within the Sultan Hamud-Emali-Simba lavas (see Figure 1.3). The Plb3 unit, named Ngatatema lavas, exposed on th east of Merueshi town further south of the main Plb2 patch. The southern part, Holocene in age, the lavas are distinguished into the Mzima-type lavas and the Southern Chyulu Hills suite (Späth *et al.*, 2000). Stratigrapically, the basanites and basalts around Simba town is considered to be the oldest (Lower Pleistocene), whereas the lavas erupted in the Ngatatema area, south of Simba, is presumably younger (Upper Pleistocene) and the 'Chyulu basalts' is the youngest (Holocene) (Saggerson, 1963). The absolute age of Chyulu basalts exposed along the area between Simba and Kibwezi is around 480± 200 years, based on a radiocarbon age from a sample of carbon beneath a lava flow near Kibwezi (Dodson, 1960 *cited in* Saggerson, 1963). In addition, Haug and Strecker (1995) reported an Ar-Ar age of about 1.4 Ma for a lava flow in the vicinity of Emali.

The CHVP overlies the Proterozoic formations of the Kurase and the Kasigau Series, comprising a variety of meta-sedimentary and metamagmatic rocks, of the Mozambique Belt Complex. Several studies suggest high grade metamorphic conditions for this basement complex (e.g. Coolen *et al.*, 1982; Pohl *et al.*, 1980; Key *et al.*, 1989; Appel *et al.*, 1998; Möller *et al.* 2000; Muhongo *et al.*, 2001; Johnson *et* *al.*, 2003; Sommer *et al.*, 2003; Kröner *et al.*, 2003; Hauzenberger *et al.*, 2004; Tenczer *et al.*, 2006). Along the Belt, a number of localities of ophiolitic rocks are also documented as evidence for a supra-subduction zone (in Baragoi) or a back-arc environment (in Moyale) in the northern region (Berhe, 1990) and a suture zone (in Voi) in the SE region of Kenya (Frisch and Pohl, 1986). Within the Voi suture zone, several ultramafic bodies are associated with gem corundum, e.g. at Kinyiki Hill and in the Taita Hills. These bodies appear to have been tectonically emplaced the surrounding country rocks and mineralization of the associated corundum may have taken place under granulite facies conditions (Mercier *et al.*, 1999).

Nevertheless, the Kasigau Series is predominant in the study area and composed of garnetiferous and muscovite-rich rocks intercalated with abundant hornblende-biotite gneisses and graphite gneiss, subordinate garnet amphibolites and rare quartz-silimanite gneisses and calc-silicate granulites (Saggerson, 1963). Lithologically, none of these exposed basement rocks is similar to the corundum-bearing granulitic and ultramafic xenoliths studied herein.

According to seismic tomography studies using seismic refraction and wide angle reflection surveys, there is no evidence of recent asthenospheric upwelling or upwarping of the Moho underneath the CHVP observed. The Moho is detected at approximate depth of 40-44 km with a 20-24 km-thick lower crust (Novak *et al.*, 1997; Ritter and Kaspar, 1997). A low velocity anomaly beneath the CHVP, which was detected at depth from ~30 to 40 km by seismic surveys, may imply the existing of a partially melting zone directly above the Moho below the region (Savage and Long, 1985; Novak *et al.*, 1997; Ritter and Kaspar, 1997). However, this low velocity body would possible correspond to an anorthositic body or the plagioclase-rich differentiates if a completely solid crust is assume (Novak *et al.*, 1997). In addition to seismic data, there are geothermobarometric estimates from high-P porphyroclastic garnet lherzolite and depleted garnet-spinel harzburgite xenoliths from the Chyulu volcanic field which provide a P-T range of 1,300-1,350°C and 3.3-3.6 GPa, suggesting that an apparent lithosphere-asthenosphere boundary possibly lies at a depth between 107 and 120 km with a lithospheric thickness of about 105 km (Henjes-Kunst and Altherr, 1992). As indicated by chemical diffusion profiles observed in orthopyroxene grains in most garnet-free spinel harburgitic xenoliths and some garnet pyroxenitic xenoliths, these xenoliths were considerably heated before they were taken to the surface by the host magmas. This suggests magma stagnation in the uppermost lithospheric mantle below.

Unlike the NW Kenya region where both the crust and the lithosphere have been intensively thinned as indicated by seismic studies (Keller *et al.*, 1994) and thermobarometric data on mantle xenoliths (Henjes-Kunst and Altherr, 1992), the lithosphere thinning has not been observed in the area of the Chyulu province (Novak et al., 1997). The Quaternary lavas of NW Kenya have been interpreted to be generated as a consequence of a mantle plume interacting with an already thinned lithosphere (70-80 km) (Class *et al.*, 1994), whereas the volcanism within the Chyulu volcanic field have been explained as a result of tectonic and pre-existing structural controls (Bosworth, 1987, 1989) together with diapirs of mantle plumes (e.g. Burke, 1996; Mechie *et al.*, 1997; Ritter and Kaspar, 1997; Späth *et al.*, 2000).

1.4 Methodology

The main steps of this study were started with searching and reviewing related literatures. After background information had been gathered, field investigation was conducted to obtain crucial field data and specimen for laboratorial works. Then, the laboratorial works including sample preparation, petrographic investigation, whole-rock geochemical analyses, mineral chemical analyses, and geochronology were carried out. Next, all the obtained data were compiled to construct a petrogensis model. The final step was literature task of article publication, dissertation writing, and wrapped up with oral defense. The methodology framework is summarized in Figure 1.4 and detail of fieldwork and laboratorial task are described below.

Sample Collection: Field investigation and specimen collection were undertaken during 8-30th October, 2007. Most of rock specimens were collected from two adjoining ruby-related basaltic subterranes, Nguu Hills and Ngulai Hills. Few basalt specimens from nearby basaltic exposures outside these subterranes in vicinity of Kiboko were also collected for comparison. The collection strategy was to sample all observed xenolith types as well as the host basalts; however, ruby-bearing xenoliths are the main focus.

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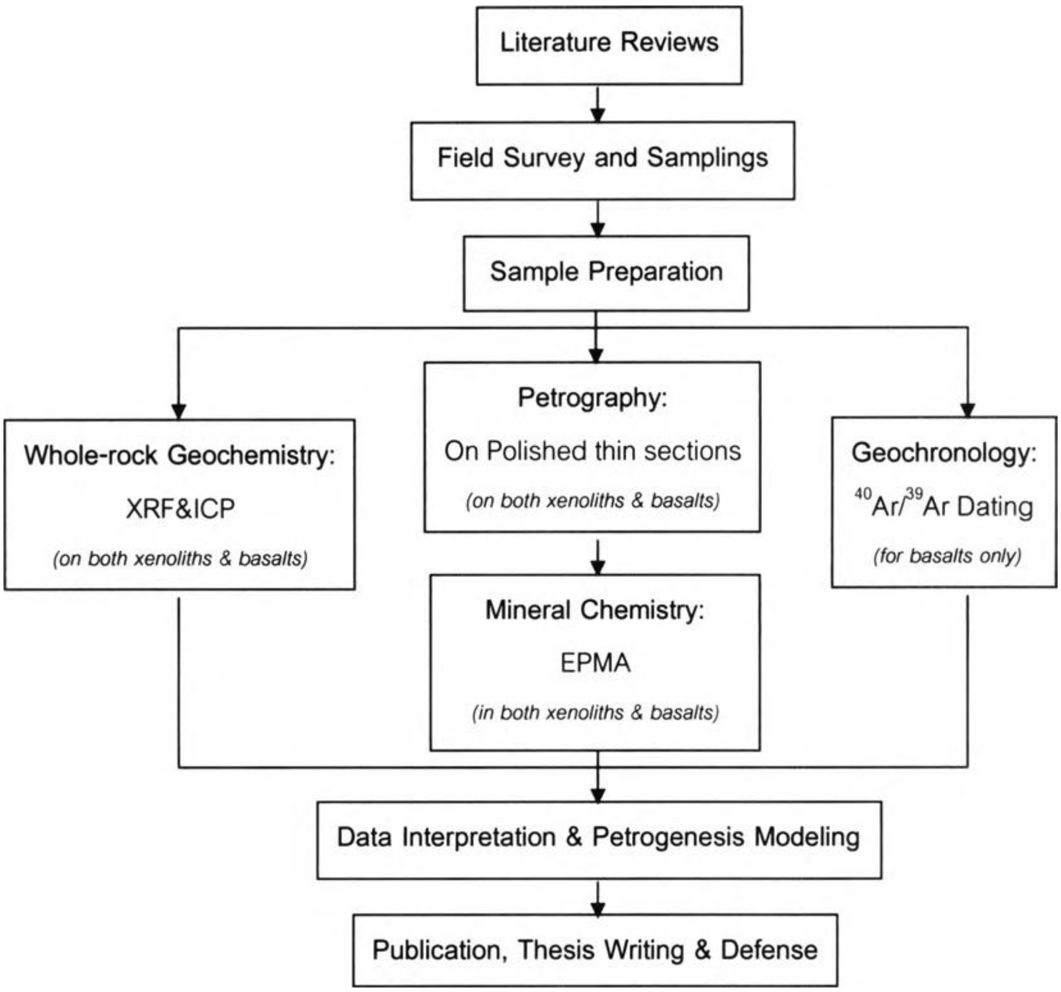

Figure 1.4 Schematic diagram showing methodology framework of this study.

Sample Preparation: Selected specimens, both xenoliths and basalts, were cut into slabs and prepared as polished thin sections for petrographic investigation and Electron Probe Micro-Analysis (EPMA). Some representative specimens, for whole-rock chemical determination by X-ray Fluorescence Spectrometry (XRF) and Inductively-Coupled Plasma-Emission Mass Spectrometry (ICP-MS) were crushed and ground to -200 mesh using a tungsten carbide mill. For geochronological study, the freshest basalt samples of each body were crushed and sieved to 1-2 mm sizes,

Petrographic Investigation: The polished thin sections were examined under an optical microscope to describe mineral assemblages and textures, in order to classify the xenoliths. The petrographic task was carried out before taking photomicrographs and purforming chemical analyses

Whole-Rock Geochemical Analysis: In this part, two main analytical techniques were employed including X-Ray Fluorescence (XRF) Spectrometer for major oxide determination and Inductively Coupled Plasma-Mass Spectrometer (ICP-MS) for trace element determination. In addition, titration technique was utilized to determine FeO content.

The XRF analyses were measured on fused glass disks at the Department of Mineral Resources (DMR) of Thailand using a PANalytical WD-XRF (Axios advanced) spectrometer. Each glass disk was made of 1 gram of a powdered sample fused with 5 grams of a fluxing agent, which is a 66:34 combination of di-lithium tetraborate and lithium metaborate. The XRF analytical conditions for all analyses were set at an accelerating voltage of 40 kV and 15 mA sample current. Two rock standards, including JB-1a (Basalt) and MRG-1 (Gabbro), were used for calibration. The detection limits in these routine tasks are 0.01 wt% for MnO, K_2O and P_2O_5; 0.02 wt% for TiO_2, $Fe_2O_3^t$ and CaO; 0.05 wt% for Al_2O_3 and 0.1 wt% for SiO_2, MgO and Na_2O. Prior to L.O.I determination, most specimens were analyzed for moisture (H_2O^-) contents by being heated at 105-110°C until the sample weight unchanged (~1-2 hrs). The samples were further heated in a muffle at 950-1100°C for about half an hour to obtain L.O.I values. The FeO contents were acquired through a wet chemical task at DMR. Then, weight percent of Fe_2O_3 of each specimen were recalculated using equation: $Fe_2O_3 = Fe_2O_3^t - 1.1113 \times FeO$.

The ICP-MS analyses were facilitated in 2 laboratories. The first set of samples was performed at the Department of Geosciences, National Taiwan University (NTU). The analyses were carried out using an Agilent 7500s spectrometer. Here, the powdered samples, about 20 mg each, were dissolved with a 1:1HNO_3/HF (3:5) mixture in screw-top Teflon beakers heated to 45V for overnight, followed by drying (~1.5hrs at 50V.). Then, the samples were re-dissolved with a 1:1HNO_3/HF (2:3) mixture and heated at 45V for 7-10 days. Next, after having been dried, the samples were again dissolved with 1:2HNO_3 and heated overnight and, finally, the sample solutions were diluted by 2% HNO_3. An internal standard solution of 5 ppb Rh and Bi mixture was added and the spiked solution was diluted with 2% HNO_3 to a sample/solution weight ratio of 1:2000. AGV-2, BHVO2, WIR1, and W2 were utilized as rock standards. Detailed analytical procedures were similar to those described in Yang *et al.* (2005).

The second set of samples was sent to SGS Toronto laboratory in Canada for analyzing with ICM 90A package. Here, the powdered samples, approximately 0.1 gram each, were fused by sodium peroxide in graphite crucibles and later were dissolved using diluted HNO_3. Then, each digested sample solution was split into two portions. One half was given to ICP-MS for measuring using Elan 6100 and the other half was given to ICP-OES using Perkin Elmer Optima 5300DV. The ICP-MS and ICP-OES were calibrated with each work order and an instrument blank, and calibration check was analyzed with each run. Solutions with 50 ppb Re and 10 ppb Rh were used as internal standard for the ICP-MS and 5 ppm Lu solution was used for the ICP-OES. The detection limits are 0.05 ppm for Dy, Er, Eu, Gd, Ho, Lu, Pr, Tb, Tm and U; 0.1 ppm for Ce, Cs, La, Nd, Sm, Sr, Th and Yb; 0.2 ppm for Cd, In and Rb; 1 ppm for Ga, Ge, Hf and Nb; 5 ppm for Be, Cu, Ni, Pb, Sc, V and Zn; 10 ppm for Cr. Two rock standards of SO3 and SY4 were employed. All quality controlled samples were verified using LIMS (Laboratory Information Management System). All the graphical presentations of the obtained whole-rock data were done through the Igpet2007 program.

In principle, the combined whole-rock analytical methods could provide overall chemical characteristics of the examined specimens, which normally are used for rock classification and nomenclature. To compare the obtained chemical data, a genetic linkage among xenoliths could possibly be revealed, leading to a genetic model of the rock suite.

Mineral Chemical Analysis: This task is performed using a JEOL-JXA8100 Electron Probe Micro-Analyzer (EPMA) equipped with five wavelength-dispersive spectrometers at the Geology Department, Faculty of Science, Chulalongkorn University. The microprobe was operated at a condition of 15 kV accelerating voltage and about 24 nA beam current with a focused beam (<1μm) for all mineral phases. Before analyzing, all polished thin sections were thoroughly coated on the surface with thin-film carbon. Natural minerals and synthetic pure oxides were used as standards for calibration. The results were automatically processed using ZAF4 correction software. Fe^{2+}/Fe^{3+} ratios were recalculated for orthopyroxene, clinopyroxene, spinel, and garnet/kelyphite according to the method of Droop (1987).

In principle this analytical method could yield insight chemical characteristics of crucial mineral phases. Several grains of each mineral, i.e. pyroxene, plagioclase, garnet, corundum, etc., of the same sample were selected for analysis. The chemical data obtained from some mineral assemblages may in turn be applicable for P-T condition estimation of the rocks at the last equilibration.

Geochronology: $^{39}Ar/^{40}Ar$ dating for 7 basalt specimens, i.e. *KNg05, KNg06, KNg08, KKNt01, KMb01, KKb01* and *KKb02*, was performed at the Department of Geosciences, NTU under supervision of Professor Dr. Ching-Hua Lo. The selected basalt specimens were crushed and sieved to about medium- to coarse-sand particles (~0.5-1 mm), rinsed and cleaned with 10%HCl acid, and handpicked under a binocular microscope for only fresh chips, free of any xenoliths/xenocrysts. The handpicked specimen was then cleaned with acetone and deionized water in an ultrasonic bath, dried, weighted (~2-3 grams), and encapsulated in an aluminum foil socket, await for neutron irradiation procedure. All encapsulated samples were stacked up and irradiated in VT-C position with and two aliquots of standard Km3-biotite using the Tsing-Hua Open-Pool Reactor (THOR) for 30hrs. Subsequently, the irradiated samples were individually heated in an incrementally step manner to extract isotopic argon gases. The released gases were purified and passed through a Varian-MAT VG1200 mass spectrometer for determination of relative abundances of each argon isotope. The whole detailed procedure was described by Lo *et al.* (2002). Every $^{40}Ar/^{39}Ar$ value obtained from each heating step was recalculated to yield an apparent age. Finally, all the apparent ages were plot against % cumulative ^{39}Ar release to get a plateau age of the specimen.

1.5 Organization of Thesis Report

This thesis report consists of 5 chapters which orderly include introductory sections, followed by the main works of this study on basalts and their xenoliths, and ended with discussions and recommendations for further study. Chapter I is an introduction to provide basic information related to this study. This chapter comprises aspects, objectives, geologic setting, and methodology. Then, Chapters II and III handle about the primary set of data collected during the course of the study. Petrographic description, geochemistry, mineral chemistry and Ar/Ar dating results of whole-rock basalts are presented in Chapter II, whereas petrographic description, whole-rock geochemistry and mineral chemistry of represent xenoliths are reported in Chapter III. Thermobarometry is then carried out for significant assemblages of both basalts and xenoliths as revealed in Chapter IV. In Chapter V, all data from previous chapters are then discussed in the particular aspects focusing on petrogenetic model of xenoliths and host basalts and proposing a simplified genesis model of ruby in the study area. Suggestions for further works will be included in the last part of this chapter.