Addis Ababa University
School Of Graduate Studies,
Faculty of Natural Sciences

Origin Of opal Hosted in Volcanic Rocks At Koste – Amba and Gift Mariyam, North Shoa (Central – Eastern Ethiopia)

A Thesis Submitted to
The School Of graduate studies of Addis Ababa University
In partial Fulfillment of the Requirements for the
Degree of Master of Science in Economic Geology

BY

Seid Ali

July 2006

ADDIS ABABA UNIVERSITY
DEPARTMENT OF EARTH SCIENCES
SCHOOL OF GRADUATE STUDIES

Origin of Opal Hosted in Volcanic Rocks At koste – Amba and Gift- Mariyam, North Shoa (Central – Eastern Ethiopia)

By

Seid Ali

Faculty of Natural Sciences
Department of Earth Sciences

Approval by board of examiners

Dr. Dereje Ayalew ______________________________
(Chairman)

Dr. Dereje Ayalew ______________________________
(Advisor)
Prof. Solomon Tadesse ______________________________
(Co – Advisor)

Dr. Worash Getaneh ______________________________
(Examiner)

Dr. Meseret T/Mariam ______________________________
(Examiner)

Declaration

This thesis is my original work and has not been presented for a degree in any other university, and that all sources of material used for the thesis have been duly acknowledged.

____
Seid Ali

Approved by____
Dr. Dereje Ayalew (Advisor)

Date: ____
Addis Ababa University

ACKNOWLEDGMENT

I wish to express my gratitude to Dr. Dereje Ayalew & Prof. Solomon Taddesse for that I received an extensive assistance of various types as well as in facilitating the rock samples analyses for their qualitative (X-ray diffraction method for clay minerals identification) and trace element composition analyses abroad. It is due to their thorough help that these rock samples have been analyzed in University of cagliari/Italy. My thank is also extended to this cooperative university. I would like also express my additional thanks to Dr. Dereje Ayalew for that all field studies and interpretation of all available data have been carried out under his guidance.

This research work had benefited from the contributions of many governmental organizations like the Mines and Energy Resources Development office for the Amhara National Regional State that facilitated the rock samples analyses in the Central laboratory of Ethiopian Geological Survey - Ministry of Mines. I am deeply indebted to this office for all his help. I also gratefully acknowledge the central laboratory of Ethiopian geological survey and the staff members of the mineralogy and petrography laboratory for their gracious laboratory works and professional assistances.

I'm very grateful to the examiners, Dr. Worash Getaneh and Dr. Meseret T/Mariam, for their constructive comments and suggestions that helped me in the preparation of the final research work.

(Seid Ali)

Table of content

Chapter One Introduction

Chapter Two Regional Geology

Chapter Three Local Geological Setting of Koste- Amba & Gift -Naryam

CHAPTER FOUR WHOLE – ROCK GEOCHEMISTRY

CHAPTER FIVE GEMMOLOGY AND GENESIS OF OPAL

List of Annexes

List of Figures

List of plates

List of Tables

Abstract

Gemstone- quality opal in North Shoa /koste - Amba & Gift – Maryam localities is found in small amount. The opal – bearing rhyolitic glass is found situated at the topmost part of the Ethiopian flood basalt. It is sandwiched between an underlying rhyolite and an overlying volcanic lava composed of some stacks of superimposed basalt flows at the immediate top / just next to the weathered mantle of the rhyolitic glass.

The main objective of the present study is to examine the origin of volcanic – hosted opal in Koste – Amba & Gift – Mariyam /North – Shoa, Amara - Region using petrographic description, major & trace element analysis, as well as x –ray diffraction(for samples collected from surficially altered part of the opal bearing rhyolitic glass/volcanic glass). Besides, it has been intended to establish the geological and geochemical conditions responsible for opal mineralization.

The deposit is associated with surfically altered rhyolitic glass, i.e. this lithologic unit has the same mineralogical composition with the rhyolite. A cliff forming rhyolite characterized by alternating vesicular subunit with finely laminated subunit on the same lithology underlies the opal – bearing rhyolitic glass. The size of the vesicles in this underlying rhyolite increases from bottom to top. However, these vesicles are not filled with any secondary minerals like opal.

Generally, opal accommodating lithologic unit of the study area is the rhyolitic glass/ volcanic glass, so that the mineralization seems to be highly influenced by lithology and other physico-chemical factors.

Features related to opal, like gemmology, genesis (formation environments, associated minerals and rocks) are elaborated based on cumulative global findings

Using results of major element analysis and TAS classification diagram, fresh rock samples are plotted in the field of basalt and rhyolite. Therefore, the host & parent rock

of amorphous silica ($SiO_2 . nH_2O$) seems to be the rhyolitic glass /volcanic glass that presently accommodate opal.

Samples have been taken from mantle material as well as from the fresh rhyolitic glass. According to the petrographic description, both fresh and mantle samples of the rhyolitic glass are found to have Sanidine and pyroxene main primary rock forming silicate minerals as well as zeolite. Pyroxene is found in trace amounts in the mantle material of the rhyolitIc glass but it is about 4% in the fresh rhyolitic glass. Besides both fresh & mantled rhyolitic glass contains high amount of volcanic glass and lesser amounts of opaque minerals & rock fragments.

X-ray diffraction analysis that has been done on samples from the highly altered top part of the rhyolitic glass shows clay minerals (montmorillonite and kaolinite/ halloysite), zeolite minerals (Philippsite & mordenite), as well as silica (quartz & cristobalite).

Deep surface weathering and a lack of detailed site investigations may obscure the difference between surface weathering process and post – volcanic hydrothermal activity. In the presence of this fact, (a) the formation of montmorillonite possibly from simultaneous surface weathering of sanidine and pyroxene that are contained in the rhyolitic glass or from the devitrification of volcanic glass fragments(shards) accompanied by the release of surplus silica to surrounding waters for the creation of opal mineralization in the study area ; (b) the occurrence of zeolite minerals(mordenite & philippsite) usually in earth surface weathering environments(with some exceptions where philippsite can occurs in saline - lake deposits, calcareous deep – sea sediments, hot – spring deposits) characterized by percolating ground water in acidic tephra; (c) the existence of opal – empted vesicular rhyolite and successive lava flows that underlies and overlies respectively the opal bearing horizon; all these together may exhibit that silica – rich waters derived from surface weathering processes can be the origin of opal in Koste – Amba & Gift – Mariyam localities.

Besides, recommendation as what is to be done regarding further research works on the deposit is forwarded.

CHAPTER FIVE

GEMMOLOGY & GENESIS

5.1 INTRODUCTION

Opal is a hydrated silicon dioxide, i.e. Sio_2. nH_2O. The “n” indicates that it contains an indefinite amount of water. On the other hand, the water content is around 6 to 10 percent in precious opal. The water content generally varies from between 1 and 13 to 34 percent, some of it being lost at ordinary temperatures. Opal is amorphous (cryptocrystalline) regarding the crystal system. It occurs in veins and seams botryoidal, reniform, and stalactitic. Commonly pseudomorphs after wood, shells, or bone. It is also often found in colloform crusts in vein lets, and as cavity filling or lining, more often; it is massive without any particular structure.

Specific gravity variable. 1.8-2.5. Hardness 5-61/2. Streak is white. Refractive index varies with water content usually in the range of 1.38-1.60. The specific gravity and refractive index decrease with increasing water content. Cleavage absent fracture is conchoidal. Specimens are transparent to translucent. Luster Waxy and vitreous, or matte in porous varieties. Most specimens fluoresce white or pale green, some phosphoresce, and all specimens can be very sensitive to impacts and low temperature. Opal, unlike quartz is soluble in alkalis. (Deer, & Zussman, 1963; Tennissen, 1974; Vasilievy & Arabaji, 1981; and Others).

Opal is made up of closely packed spheres of silica in hexagonal and/or cubic closest packing (see Fig. 4.1). Air or water occupies the voids between the spheres. In common, opal the domains of equal spheres with uniform packing are small or non-existent, but in precious opal, large domains are made up of regularly packed spheres of the same size. The sphere diameters vary from one opal to another and range from 1500A to 3000A. When white light passes through the essentially colorless opal and strikes planes of voids between Spheres, certain wavelengths are diffracted and flash out of the stone as nearly pure spectral colors (Klein et al., 1993).

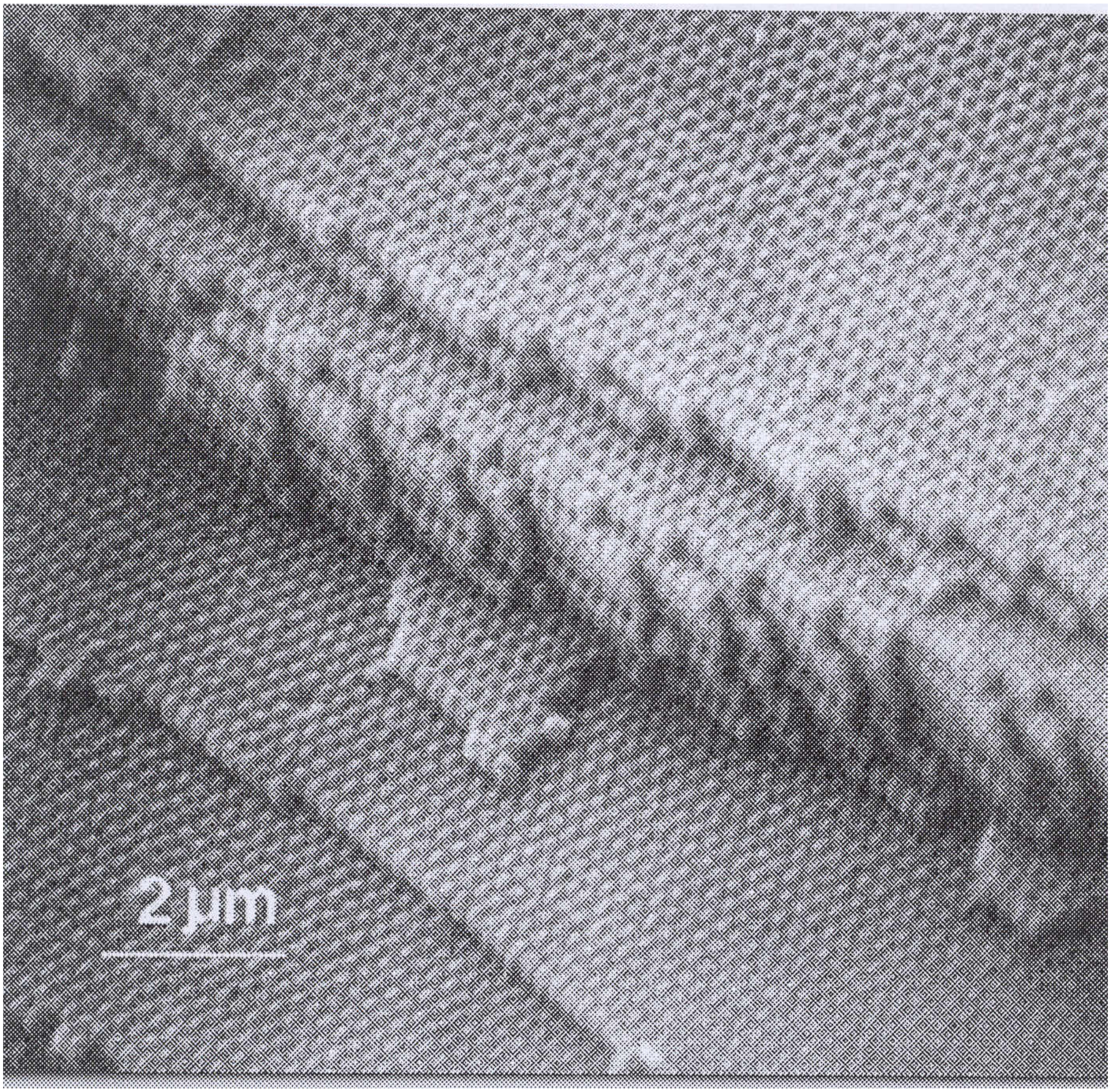


Figure 5.1 scanning electron micrograph of the silica spheres in opal, showing hexagonal closest packing of silica spheres (diameter of spheres is approximately 3000Å). Because of the weak bonding between the spheres, they are intact; in typical precious opal samples, many of the spheres are cleaved.[5a]

[5a]: http://www.samuseum.sa.gov.au./fossils/fgw4-3.htm
& Klein et al., 1993.

5.2 GEMMOLOGY

5.2.1 The causes and Colour Source of Opal

The color of an opal is a magnificent feature. Unlike any other gem, opals can display all the colour of the rainbow in an iridescent, moving pattern of red, green, blue, yellow, purple, aqua, pink, and any other colour you can imagine. The pattern and arrangement of the colour, which is displayed in an opal, can take on many beautiful forms, and the movement of color across the face of a stone is known as the play of colour.[5b]

Interference of light either at the surface or in the interior of a mineral may produce a series of colors as the angle of the incident light changes. The striking flashes of varied color against a white or black background, as seen in precious opal, are called play of colors. Electron microscopic study of opal has revealed that the underlying reason for the color play is the presence (in precious opal) of a regular three-dimensional array of equal –size spheres. These spheres consist of amorphous silica SiO_2, with small amounts of water; they are cemented together by amorphous silica with slightly different water content (see Figure. 5.1). In precious opal the uniformly packed spheres occur in patches (domains) ranging from less than a millimeter to more than a centimeter across. These regularly arrayed domains act as a diffraction gratings for white light, and resolve white light in the its spectral colors in accordance with the modified Bragg equation.

$$n\lambda = \mu 2d \sin \theta$$

Where n is small number (1, 2, or 3) and is known as the order of reflection, λ is the wave length of a specific spectral line, μ is the refractive index of opal (which must be considered because the process of diffraction takes place with in the SiO_2 of the opal), d is the spacing between the spheres in the precious opal and θ is the angle of incidence and reflection(Figure 5.2).The wavelength of the diffracted spectral color is determined by the value of d (interplanar spacing) and varies with the angle θ. Common opal lacks this regular internal stacking of spheres, and the scattered white light produces a milky opalescence (Klein et al., 1993).

[5b] http://www.opalsdownunder.com.au/articles/colour.htm

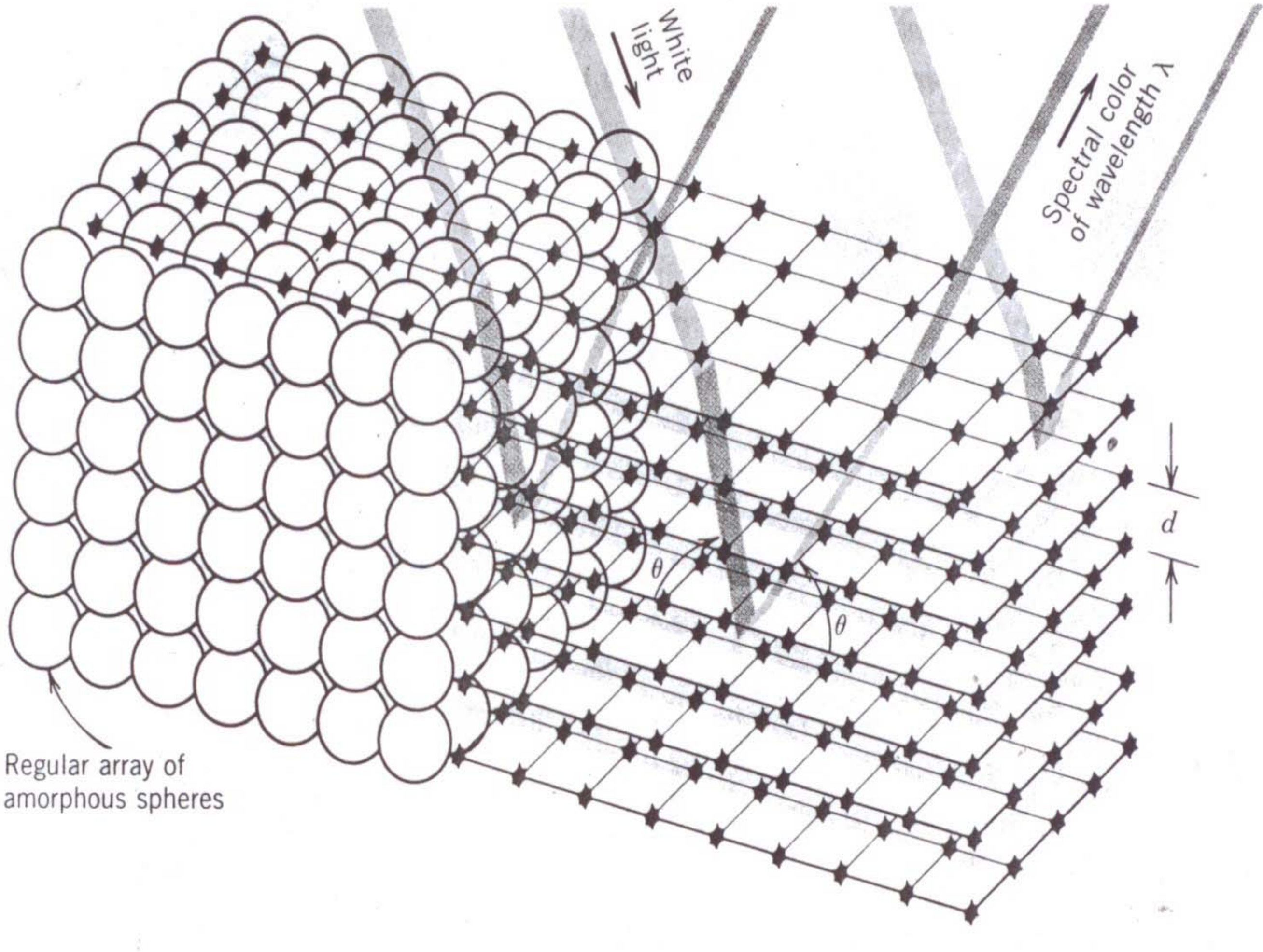


Figure 5.2 the spectral colors of precious opal are the result of diffraction by regularly spaced lattice planes. These planes result from amorphous spheres in a regular close packed array. The spacing of the lattice planes is shown as d. The λ of the diffracted spectral line is a function of d and the angle θ (Klein et al., 1993)

5.2.2 Valuing Opal – the value of opal

The value of an opal depends on many factors body tone, brilliance, pattern, colour bar thickness, faults, and the play of colour, play important roles in determining the value. Other important factors include the quality of the cut & polish, and the size of the stone.[5c]

Body tone: body tone is one of the most important factors in the classification and valuation of opals. Body tone refers to the background or the underlying colour of the opal, which ranges from black through dark to light. Generally, opals with a black or dark body tone are more valuable than those with a white, light, or crystal body tone. **Brilliance:** Brilliance describes the brightness and clarity of the colours displayed by opal, when the stone is viewed face – up. This ranges from brilliant, bright, to subdued or dull.

Pattern: the regular arrangement of colored segments, forming the play of colour of a precious opal, is unique to every individual opal. The distinctiveness and colour displayed by these segments determines the quality of the pattern of the opal.

Colour Bar: The thickness of the colour bar in opal is relative to the overall size and shape of the individual stone. Boulder opal typically has a very thin colour bar due to the way the opal is geologically formed.

Play of colour – The phenomenon known as the play of colour is the brilliant range of the full spectrum of colours by the diffraction of white light by the internal structure of orderly arrayed spheres of silica.

Faults – Various faults can detract the value of a finished opal. A crack in the face can render almost worthless an opal. Crazing, i.e. many small cracks in the opal's face will relegate the stone to worthless

5.2.3 Types of Opal – Different Types of Opal

Varieties of opals and the differences between the types of opals are depicted in accordance with the descriptions made by different authors (Hurlbut & Jr., 1949; Klein et al., 1993; Read, 1998).

5c: http://www.opalsdownunder.com.au/articles/colour.htm

A/Natural Opal

"**Potch" or Common opal (No opalescence):** Milk – white, yellow, green, red, etc., without internal reflections. Common opal is rather opaque or glassy.

Black opal (dark background with iridescence): Black opal is characterized by a dark body tone causing brightness of colour that is un matched by lighter opals.

White opal (White background with iridescence): It is also known as milky opal". white opal features light white body tones.

Fire opal: Transparent to translucent orange, occasionally with iridescence. Fire opal is a variety with intense orange to red reflections.

Boulder opal: Boulder opal forms on ironstone boulders in queen's land. This type of opal is usually out with the ironstone left on the back, as the opal seam is usually quite thin. Leaving the ironstone on the back means that boulder opal can be very dark and beautiful in colour.

Crystal opal: crystal opal is any of the above kind of opal (except common opal) which has a transparent or semi –transparent body tone. Forms of crystal opal include black crystal and white crystal.

Matrix opal: The opal occurs as a network of veins or infilling of voids or between grains of the host rock (ferruginous sand stone or ironstone). It generally shows pine fire colour in the natural state.

Water opal: Translucent to transparent colorless or pale brownish yellow with iridescence.

Hyalite: Transparent, colorless without iridescence and with globular or botryoidal surface.

Hydrophane: Opaque light – coloured, which becomes transparent and iridescent when soaked in water. Pink, yellow, green and blue opal –Translucent but with no iridescence.

Wood opal: Materials petrified by opal, opal pseudomorphs such as shells, bones and minerals.

Diatomite: Fine grained deposits, resembling chalk in appearance. Formed by sinking from near the surface and the accumulation on the sea floor of the siliceous tests of diatoms, also known as diatomaceous earth.

B/Synthetic or Man – Made Opal

These synthetics have chemical and physical properties, including a play of colour, that are essentially identical to those of natural precious opal.

The Gilson “synthetic opals are produced in both white and black versions of precious stones. Of these, the white opal is the most realistic imitations. The opals are thought to be made from a silicon ester solution. Many Gilson opals have a high porosity (this causes them to stick to the tongue, an effect not so marked in most natural opals).

The following differences can be observed between natural and synthetic opal;

- Synthetic opals usually show brighter colours, and colour patches are frequently larger than in natural opals.
- Colour grain boundaries are generally highly irregular in synthetic opal.
- Within each colour grain in synthetic opal, numerous sub-grains produce a distinctive snakeskin pattern.
- Synthetic material generally shows a more ordered array of colours since artificial does not duplicate the intricate pattern of natural opal.
- Synthetic opals are hydrophobic (a drop of water placed on the surface forms a hemispheric bead –natural opals are hydrophilic and water spreads rapidly across their surface).
- Any opals showing no signs of fluorescence are natural.

5.3 OPAL GENESIS

5.3.1 Formation Environments

Opal can be formed in some different environments in the earth. Hydration and hydrolysis are commonly regarded as the most important chemical reactions involved in rock decomposition, which facilitate the formation of opal, at or near the earth’s surface. Besides, hydrothermal solutions that originate from inside part of the earth and siliceous skeletons of micro – organisms can cause deposition of sediments at or near the earth’s surface, and in the oceans & lakes respectively followed by the creation of opal. The most common environments are examined as follows:

A/ Formation from Water near the Earth Surface

During the weathering process, feldspathic tuffs are readily kaolinzed and converted to soft earthy masses. One of the earliest changes in vitric tuff is the release of silica and the deposition of hydrated silica –opal and chalcedony that may convert these felsic tuffs to a dense flinty rock very much resembling chert (Pettijohn, 1984).

In a favorable situation /abundant atmospheric precipitation, high temperature and immense vegetative waste /the bond between aluminum and silica becomes completely disrupted in the process of hydrolysis of feldspars and of other aluminosilicates (mica, etc.) and there appear aluminum hydroxides (gibbsite or hydrargillite – a constituent of bauxite Al_2O_3. nH_2O) and of silica (water opal – SiO_2. nH_2O) and others, most stable in the superficial zone of the earth's crust (Gorshkov & Yakushova , 1977).

In hydrolysis, an Al-or Fe-bearing silicate is typically converted to a clay or Fe-oxide, accompanied by release of cations and incorporation of H^+. An example is the reaction of albite with weak acid to form clay, silica and Na+ ions.

$2Na\ AlSi_3O_8 + 2H^+ + H_2O = Al_2Si_2O_5COH_4 +$
Albite kaolinite
$4SiO_2 + 2Na^+$

Note that this reaction also involves hydration as well as the dissolution of Na+. The Al in this and many similar hydrolysis reactions may be released as well –crystallized clay mineral or as a colloidal, poorly crystalline aluminosilicate, and the SiO2 as colloidal silica, dissolved silicic acid (H_4SiO_4) or solid quartz, opal or other silica mineral. The released cation may be sorbed to the surface of the colloidal particles or released to solution. These adsorbed ions are then available for reaction and exchange with the passing solutions. Although hydrolysis can take place in pure water, the reaction is intensified in the presence of natural acids, of which the most common are carbonic acid and humic acid (Rose, 1977).

The relative small amount of dissolved carbon dioxide (carbonic acid) contained by rainwater, is enough to weather feldspars and dissolve great quantities of rock over a long time, for instance the full balanced form of the weathering reaction can be written:

Feldspar + Carbonic acid + Water $\longrightarrow$

$2KAlsi_3\ O_8$ $2H_2\ CO_3$ H_2O
Dissolved + Dissolved + Dissolved +Kaolinite Silica
Potassium
$Al_2\ Si_2O_5\ (OH)_4$ $4SiO_2$ 2K+

This simple weathering reaction illustrates the three main chemical effects of chemical weathering on silicates. It leaches, or dissolves away cations and silica. It hydrates, or adds water to the minerals, besides it makes the solutions less acidic. Specifically, the carbonic acid in rainwater helps to weather feldspar in the following way (Fig. 4.3): a small portion of carbonic acid molecules ionizes, forming hydrogen ions (H+) and bicarbonate ions (HCO3-) and thus making the water droplets slightly acidic; the slightly acidic water dissolves potassium ions and silica from feldspar, leaving a residue of kaolinite(solid clay); the hydrogen ions from the acid combine with the oxygen's of the feldspar to form the water in the kaolinite structure; the kaolinite becomes part of the soil or is carried away as a sediment; the solution becomes less acidic as the reaction goes on; the dissolved silica, potassium ions (K+) , and bicarbonate ions are carried away by rain and river waters and ultimately are transported to the ocean (Press & Siever 2001).

Opal is formed from a solution of silicon dioxide and water. As surface or ground water move through the earth in response to hydraulic or topographic gradient, it picks up silica from the product of the weathering reaction (solution), and carries this silica rich solution in the cracks and voids, i.e. primary and secondary openings, and veins, caused by natural faults, fractures, decomposing fossils, vughs and other verities of voids created by the weathering processes. As the water evaporates, it leaves behind a silica deposit. This cycle repeats over very long periods of time, and eventually opal is formed (Figure 5.3).

Under favorable conditions, spheres of silica, contained in silica rich solutions in the earth are formed and settle under gravity in a void to form layers of silica spheres. Silica spheres of uniform size may be formed through the process, i.e. precious opal commences to form. For precious opal, the sphere size is approximately from 150 to 400 nanometers. This type of opal can show a play of colour in the visible light range of 400 to 700 nanometers

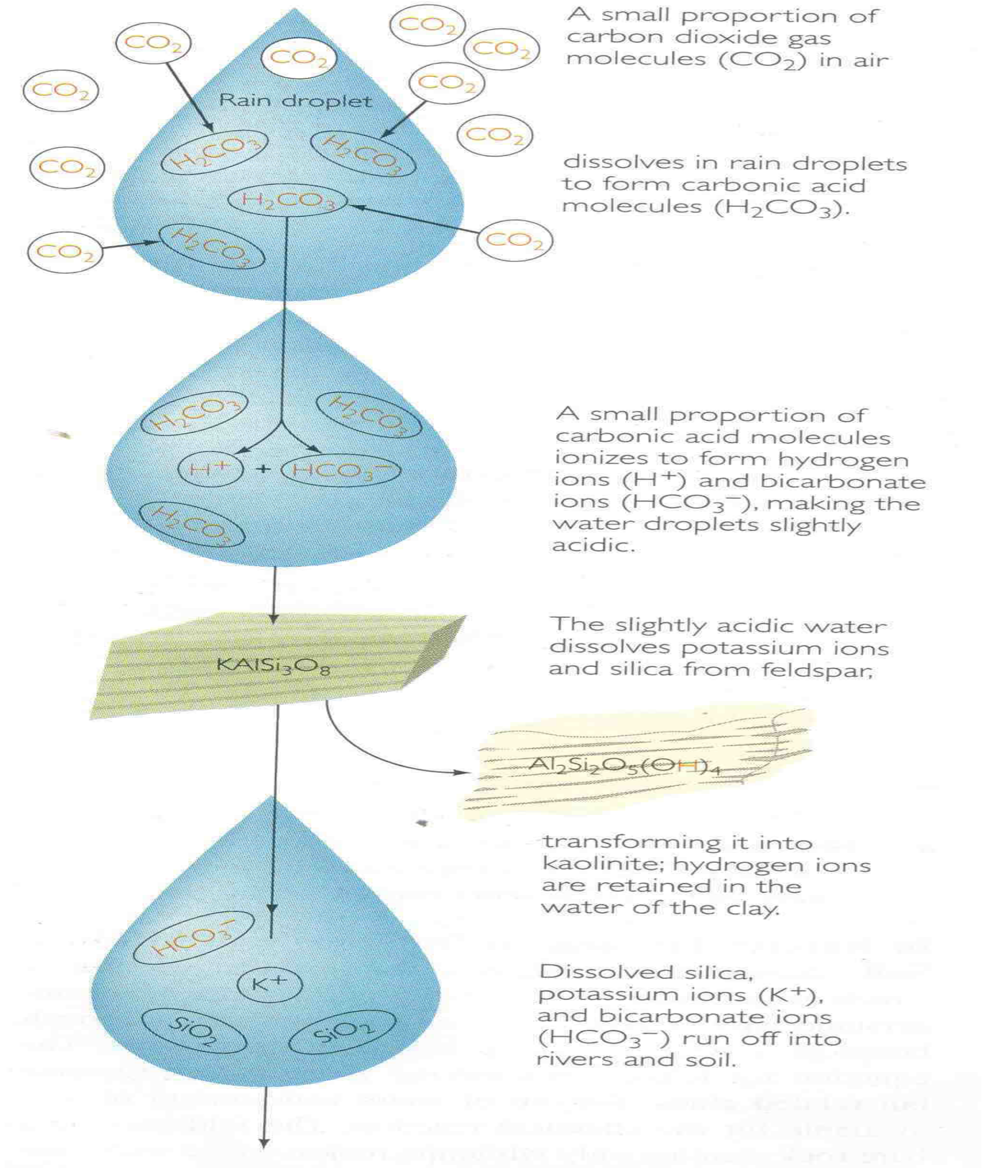


Figure 5.3 feldspar weathering when it is in contact with carbonic acid from rainwater containing carbon dioxide. Two products are formed: kaolinite clay and a solution containing dissolved silica, potassium ions, bicarbonate ions (After press & Siever 2001).

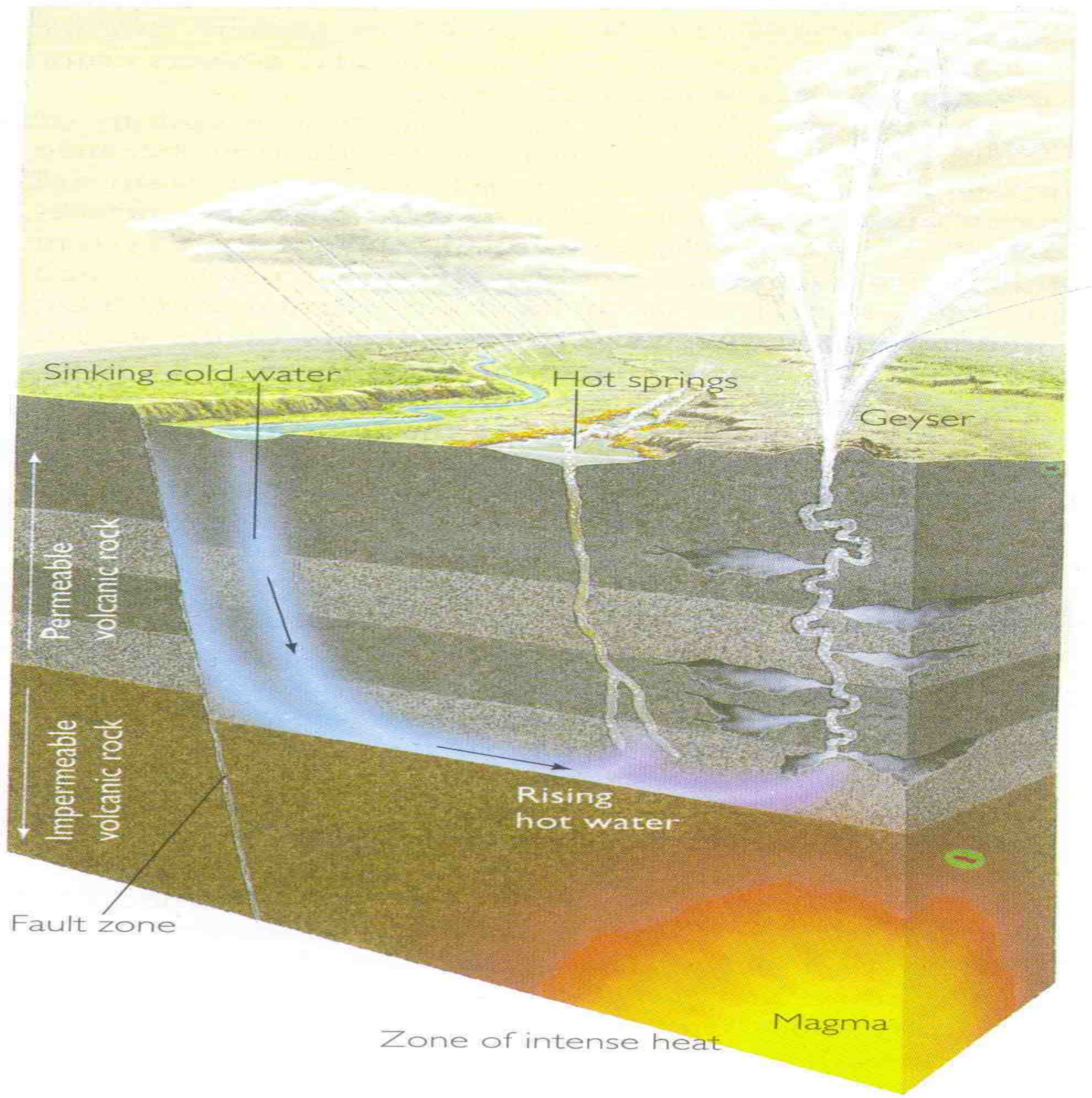


Figure 5.4 Circulation of water over a magma body produces geysers or hot springs. Cold rainwater soaks into the soil and filters down through permeable rocks. As it approaches the magma, it heats up and becomes less dense, thus setting up a circulation system that returns it to the surface. Hot springs rise more or less directly, whereas a geyser follows a much more irregular network of pores and cracks, which complicates the flow of water and leads to boiling and the production of steam and eruptions at intervals (After Press & Siever, 2001).

B/ Formations from Hydrothermal Solutions in the Earth's Crust

Hydrothermal waters are loaded with chemical substances dissolved from rocks at high temperatures. As long as the water remains hot, the dissolved material can remain in solution. However, as hydrothermal waters coming to the surface quickly cool, they may precipitate various minerals such as opal and calcite (Figure 5.4) (press & Siever 2001).

Hydrothermal solutions can originate from the dehydration of rocks during compaction and metamorphism, from cooling igneous intrusions, from earth's surface originating seawater, groundwater & rainwater but percolate downwards into the crust where it is heated and circulated. These fluids are highly mobile and chemically reactive, making them excellent solvents for silica (SiO_2) bearing rocks and minerals

C/Biogenic Formation (Marine or Lacustrine Environments)

Opaline silica (opal) is also a form of biologically produced silicon dioxide ($SiO_2 . nH_2O$) secreted as skeletal material by pelagic phytoplankton (diatoms) and one group of pelagic zooplankton (radiolarians). Opaline silica ($SiO_2 . nH_2O$) rich sediments cover about one third of the seabed, mainly in areas where sedimentation rates are high, associated with nutrient rich upwelling waters and polar areas particularly around Antarctica. See water is undersaturated with respect to silica and it is estimated that 95% of opaline silica dissolves as it sinks through the water column or at the sediment/water interface. Thus, the preservation of opaline silica only occurs where it is buried in rapidly accumulating sediment beneath the sediment /water interface. Subsequent dissolution of opal in the sediment saturates sediment pore waters with silica. The pore water cannot really exchange with open seawater and saturation prevents further opal dissolution. High sedimentation rates in the oceans can be caused by high mineral supply rates from the continents, but are usually caused by high production rates of biological particles. In high productivity areas, diatoms are the common phytoplankton species, and this enhances the importance of these regions as silica sinks (Andrews et al., 1996).

5.3.2 Main Minerals & Rock Associated With Opal

Together with the formation of secondary minerals (e.g. clays & zeolites), opal ($Si0_2.nH_20$) is formed through chemical weathering (hydration & hydrolysis) and hydrothermal alteration of primary silicate minerals such as feldspars, pyroxenes, hornblende and others. The main primary and secondary minerals that have close relationships with opal ($SiO_2.nH_20$) have been examined below in accordance with cumulative findings (Tennissen, 1974; Rose et al., 1974, Klein et al. 1993 and others).

A. Clay Minerals: They are part of the Phyllosilictates that contain large percentages of water trapped between the silicate sheets; they can absorb water or lose water from simple humidity changes. Clay minerals are formed chiefly by alteration or weathering of primary silicate minerals such as feldspars, pyroxenes and amphiboles.

Montmorillonite, $Al_2si_40_{10}$ $(OH)_2$. XH_20: where x represents the variable amount of water that this clay mineral could contain. In particular, magnesium, iron, and probably calcium are essential to build up the montmorillonite structure. Montmorillonite mineral is generally derived from simultaneous weathering of ferromagnesian silicate minerals, and feldspars that are the constituent elements of beds of volcanic glasses and volcanic ashes in water logged alkaline soils, whose PH is moderate but low Eh (Poorly oxygenated). The incomplete leaching of Na, Ca, Mg, K and trace metals favors the formation of this clay mineral.

The bases may be retained within the system as the result of impeded drainage or excessive evaporation. Montmorillonites are typical end products of weathering in waterlogged ground or in semi-arid climates. A high concentration of available Fe 2+ Mg2+ is naturally a strong predisposing factor in the formation of montmorillonite. Even in freely drained ground, montmorillonite may be a transient intermediate product in the course of the decay of the ferromagnesian constituents of mafic rocks to kaolinite. When drainage condition change and leaching becomes effective, montomorillonite may alter to kaolinite, as indicated in (Figure 5.5).

Kaolinite, $Al_2si_20_5(OH)_4$: It is well known as the stable end product of the laterization or latosols, produced by deep tropical weathering with PH of 5-7, but being well oxygenated, the Eh of its formation environment is neutral to high. It is generally formed by the decomposition of other aluminosilicates, especially the feldspars either by weathering or by hydrothermal alteration. An acid environment, with free drainage, favors kaolinite formation, thorough leaching of Na, Ca, Mg, and K, as well as many traces constituents. It develops most readily in relatively humid climates where rainfall exceeds evaporation and where downward percolation and lateral movement of underground water is active. Halloysite is like Kaolinite except for a layer of water between the sheets.

B. Zeolite minerals: They are a large group of white or colorless (some times red or yellow) frame work hydrous aluminosilicates that are analogous in composition to feldspars, with sodium, calcium and potassium (rarely barium or strontium) as their chief metals. Their frameworks are very open with large interconnecting spaces or channels.

Zeolites may be developed from magmatic solutions at a late stage of crystallization (e.g. analcime). More commonly, they are the products of hydrothermal activity or diagenesis. They are often the product of alteration of feldspars, feldspathoids, or volcanic tuff and volcanic glass. Especially these tuff and glass alteration-originating zeolites are the diagenetic products of silicic volcanic materials.

Philippsite$(K,Na,Ca)_{1-2}$ $(Si,Al)_8O_{16}$. $6H_20$ and **Mordenite (Ca, Na_2, K_2) $Al_2Si_{10}0_{24}$. $7H_20$** could be cited as examples of zcolites whose occurrence is strongly associated with earth’s surface weathering and percolating ground water (in acidic tephra).

Philippsite occurs in cavities in basalt, phonolite, and related rocks; saline lake deposits ;calcareous deep-sea sediments; hot spring deposits, where as **mordenite**, occurs filling cavities and veins in igneous rocks, in hydration product of glasses, authigenic deposits in sediments.

C. Silica

In terrestrial environment, silica necessary to form siliceous rocks may be derived directly through volcanic activity. This direct mechanism involves devitrification of volcanic glass fragments (shards). This process may result either in the formation of felsic fragment with no release of silica or in the formation of montmorillonite clay (bentonite) with release of surplus silica to surrounding surface or ground water. If the amount of silica released is sufficient to saturate the water with respect amorphous silica, opal will be precipitated and appeared to exist. The main varieties of silica that mostly associate earth opal are quartz, cristobalite, tridymite and chalcedony.

Quartz is stable over practically the whole range of geological conditions and because Sio_2 is the most abundant oxide in the earth's crust, it is a very common mineral. It is present in silica rich igneous rocks, both volcanic and plutonic, and makes up a large part of hydrothermal veins and granite pegmatite.

Cristobalite is present in crevices and cavities of siliceous volcanic rocks, both as the lining of cavities and as an important constituent in the fine grained groundmass. It is an abundant mineral.

Tridymite occurs commonly in certain siliceous volcanic rocks such as rhyolite, obsidian, and andesite, and for this reason it may be considered as an abundant mineral. Commonly associated with sanidine and cristobalite.

Chalcedony is a secondary mineral in the cavities of igneous rocks and is often associated with quartz, opal and zeolites. It is the principal constituent of chert and jasper. It occurs in diatomite as a replacement of opal. Chalcedony is more jasper. It occurs in diatomite as a replacement of opal. Chalcedony is more stable than opal and commonly appears to have re-crystallized from it.

D. Feldspars

They are the most abundant of all minerals. Feldspars fall in to two subgroups: potash feldspars (sanidine, orthoclase and microcline) and soda - lime feldspar (plagioclase series). Of these, the most common parent and associate silicate mineral of opal (Sio_2 $.nH_20$) is sanidine.

Sanidine (KAlSi3O8) is a high temperature mineral of the alkalifeldspar group. It is a high disordered monoclinic form, often tabular crystals embedded in un altered acid volcanic rocks such as trachyte and rhyolite. It appears to be stable under equilibrium conditions above approximately 5000c. Sanidine is characteristics of rocks that cooled quickly from an initial high temperature of eruption.

E. Volcaniclastic Sediments:

Volcaniclastic sediments are those composed chiefly of grains of volcanic origin like volcanic agglomerate, volcanic breccias, lapilli stone and tuff (vitric, lithic, crystal), derived from contemporaneous volcanic activity. A pyroclastic deposit is produced by explosive volcanic activity. Other volcaniclastic deposits result from different processes. Sediments derived from erosion of pre-existing volcanic rocks are types of lithic sandstones.

Volcanic glass is metastable so that except special conditions it is not reserved in rocks older than Mid-Teritiary. Volcanic glass is readily devitrified, altered and replaced during weathering and diagenesis. The common alteration products are clay minerals and zeolites. The clay minerals, which replace volcanic glass, are mainly montmorillonite in more basic ashes and kaolinite in feldspathic ashes. Silica is released on the alteration of glass to clays and zeolites. Some koalinite rich mud rocks are of volcanic origin. Apart from clay mineralogy the preference of some glass shards or their pseudomorphs, together with euhedral or zoned phenocrysts, especially of quartz, feldspar or pyroxene, will further confirm a volcanic origin.

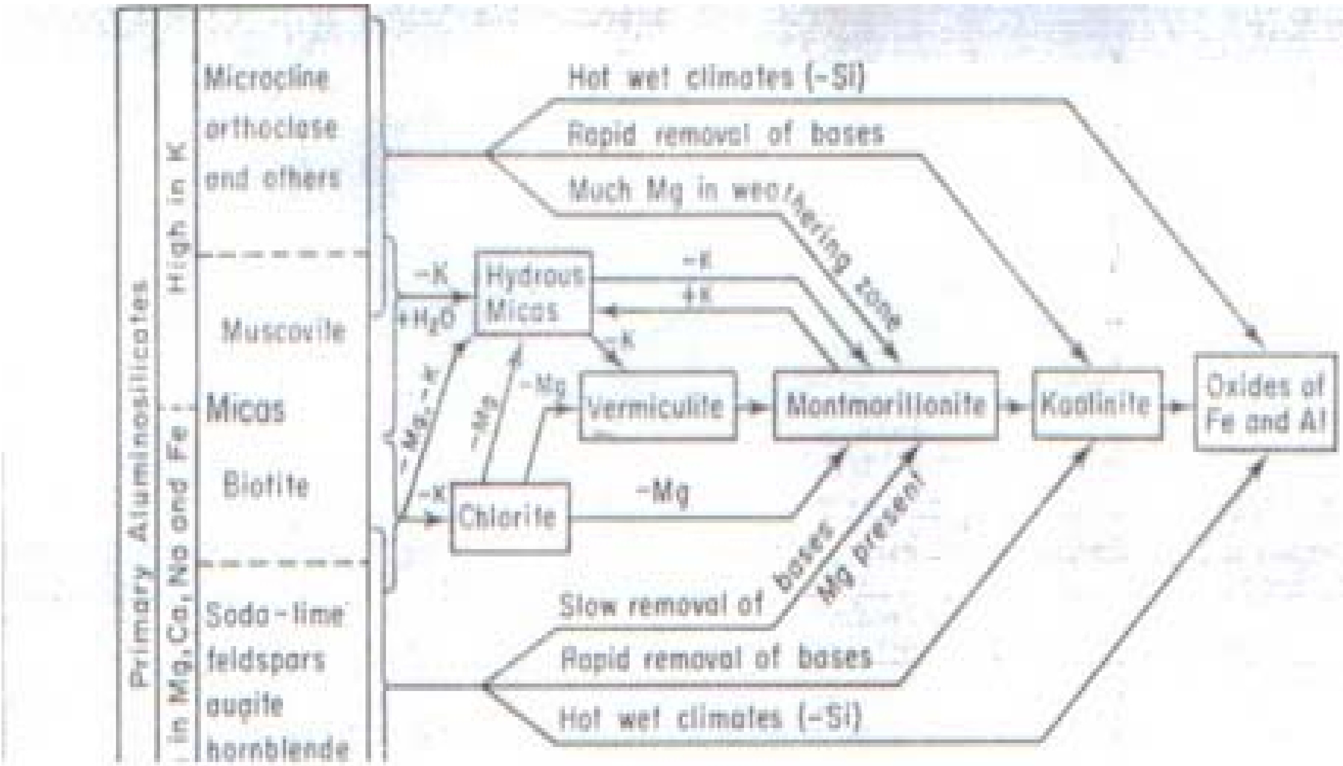


Figure 5.5 Weathering products of primary minerals, and sequence of forming clays (Rose, 1979).

CHAPTER FOUR

WHOLE- ROCK GEOCHEMISTRY

4.1 ANALYTICAL TECHNIQUES

Among 17 samples studied in thin section, 12 (twelve) were analyzed for major, trace & rare earth elements. Of these samples, 4 samples, i.e. they are altered products of rhyolitic glass/ volcanic glass, (SA-45/3, SA-47A, SA-52B & SA-52C), were also analyzed for clay minerals identification using x-ray diffraction analyzed. Generally, all the samples are collected from the prevailing hill slopes of the study area. Samples were crushed in steel jaw crushers and reduced to a fine powder in agate mortars. Major elements were analyzed by combined x-ray fluorescence and wet chemical analyses techniques and loss on ignition (LOI) at the main laboratory of geological survey-ministry of mines & energy.

Trace elements were analyzed by ICP-MS (inductively coupled plasma-mass spectroscopy) in the university of cagliari /Italy/. The results of major & trace elements compositions are presented in table 4.1. Besides, the analyses methods used by the University for trace elements determination is indicated in annex B.

4.2 MAJOR ELEMENTS

The rock sampled named here, as rhyoliic ignimbrite (SA-20) and rhyolitic glass /volcanic glass (SA-45/4 & SA-47B) are all rhyolites. Here after these rocks are referred to as rhyolite and rhyolitic glass respectively for simplicity.

The rhyolites (rhyolite & rhyolitic glass) consists of SiO2 (68.53-72.05 wt%), Al2O3 (12.48-13.33wt%), Fe2O3 (1.73-2.74wt%), MgO (0.04-0.041wt%), CaO(0.18-0.82wt%), Na_2O (3.09-4.72wt%), K_2O(6.95-7.48wt%), and P_2O_5 (0.018-0.088wt%), where as the basalts have SiO_2

(47.56-50.74 wt%), Al_2O_3(15.88-17.02 wt%), Fe_2O_3 (10.19-10.58 wt%), Mgo (3.3-6.87%) CaO (9.32-10.36wt), Na_2O (2.89-3.71wt%), K_2O(0.49-1.81wt%), and P_2O_5 (0.493-0.569wt%). Bimodal composition displayed by the volcanic rocks of the study area.Al_2O_3,Fe_2O_3 and K_2O decreases with increasing SiO_2 in rhyolite and rhyolitic glass. Recalculated to 100% on an anhydrous basis, the rocks plot as basalt and rhyolite on a total alkalies (K_2O+Na_2O) vs. silica (SiO_2) diagram in accordance with Lebas et al,1986 (figure 4.1).

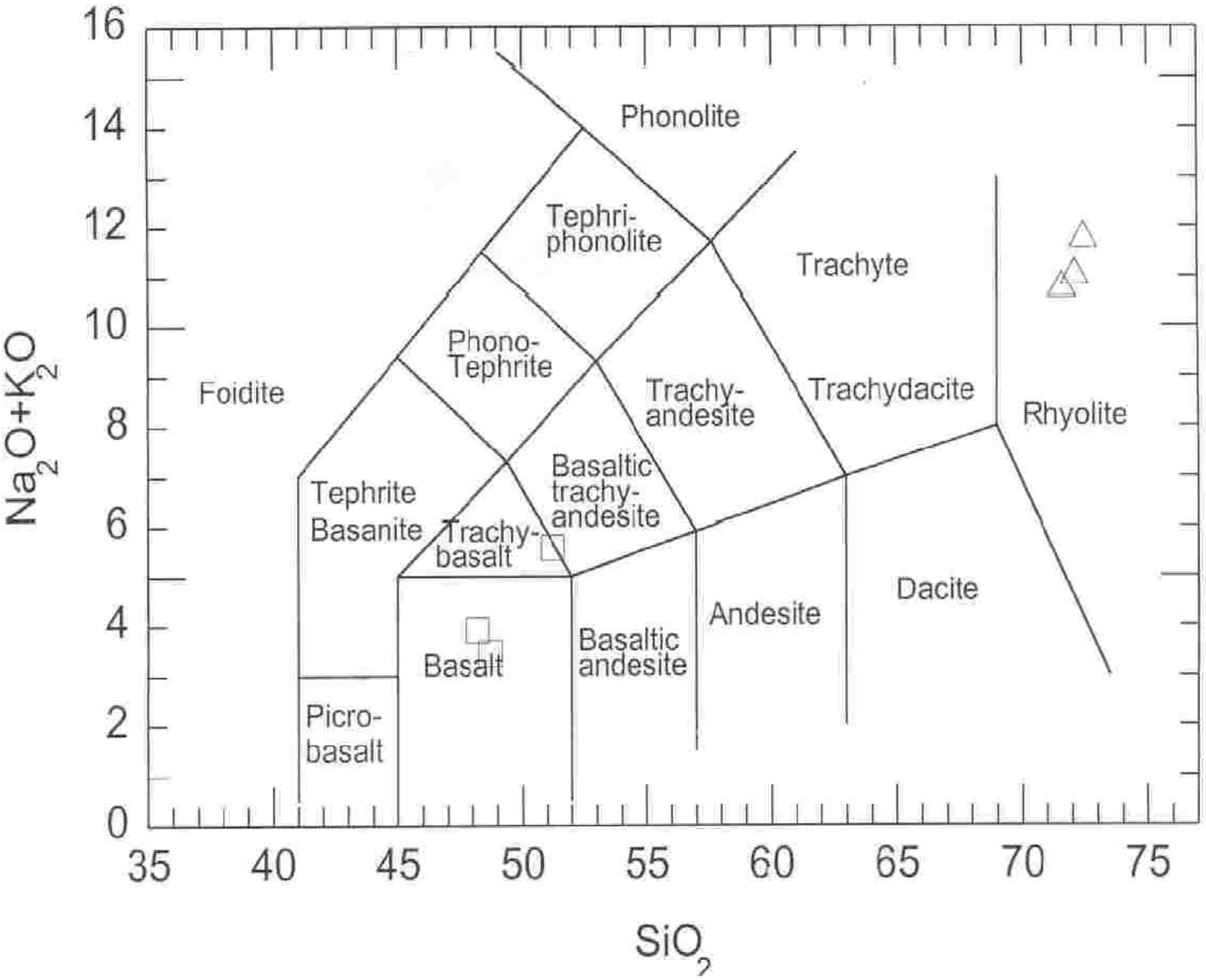


Figure 4.1 TAS classifications of volcanic rocks for the study area.

4.3 TRACE ELEMENTS

Volcanic rocks of the study area are slightly enriched in light rare earth elements (LREE), zinc (Zn), rubidium (Rb), niobium (Nb), zirconium (Zr) and yttrium (Y). Especially the rhyolite and the rhyolitic glass are more enriched in light rare earth elements (LREE). Besides, relatively high enrichment of light rare earth elements zinc, (Zn), niobium (Nb) and zirconium (Zr) are on display within the altered rhyolitic glass (figure 4.2).

The basaltic rock samples are characterized by the absence of pronounced negative or positive anomalies. They show almost gentle REE pattern from LREE to HREE distribution. As it is indicated in the two chondrite - normalized REE patterns (rhyolite & basalt), concentration of LREE increases during fractional crystallization of magma (basalt-rhyolite), where as HREE remain almost constant (smooth & flat pattern).

Fractionation of plagioclase feldspars generates a decrease in Eu, while the other REE are less affected. This produces a negative Eu anomaly in the REE pattern of residual liquids formed by extensive feldspar fractionation. This anomaly is typical of much evolved rocks such as the rhyolites of the study area, i.e. rhyolite & rhyolitic glass. Light rare earth element (LREE) concentration increase from basalt to rhyolite. The rhyolite shows somewhat steep normalized abundance of LREE & flat HREE patterns as well as negative Eu anomaly. The normalized abundance of LREE is significantly higher than the HREE ones. This is the result of ongoing fractional crystallization of magmas.

Table 4.1

Representative Whole Rock Major and Trace Element Analysis for Koste - Amba & Gift - Mariyam Volcanic Rocks(Hosting Opal)

		Weathering Condition											
		Fresh						Weatherd					
Rock type		Rhyolite	Rhyolitic Glass		Basalt			Clay					
Sample No.		SA-20	SA-45/4	SA-47B	SA-48A	SA-49	SA-51	SA-45/3	SA-47A	SA-48B	SA-52A	SA-52B	SA-52C
	Easting	579152	579203	578675	579133	579546	580943	579203	578675	579133	580162	580162	580162
Location	Northing	1105556	1105631	1105252	1105326	1106580	1107999	1105631	1105252	1105326	1108756	1108746	1108746
	Wt.%												
	SiO2	72.050	68.530	69.270	47.850	50.740	47.560	51.200	55.460	54.530	53.530	62.150	47.090
	TiO2	0.357	0.322	0.266	2.141	2.911	2.372	0.501	0.322	0.608	0.693	0.374	0.480
	Al_2O_3	13.330	12.540	12.480	16.830	15.880	17.020	30.870	28.480	27.510	28.570	19.400	34.820
	Fe_2O_3	1.730	2.740	2.670	10.190	10.580	10.550	4.430	2.100	4.410	4.910	3.360	4.190
	MnO	0.019	0.057	0.053	0.170	0.229	0.171	0.045	0.077	0.071	0.057	0.082	0.023
	MgO	0.040	0.410	0.280	6.870	3.300	6.280	1.630	2.150	1.890	1.660	2.960	0.730
	CaO	0.180	0.820	0.480	10.290	9.320	10.360	2.090	2.830	2.570	2.340	2.670	1.010
	Na_2O	4.720	3.230	3.090	2.890	3.710	3.200	0.160	0.170	0.760	0.710	1.090	1.010
	K_2O	6.950	7.050	7.480	0.490	1.810	0.660	0.190	0.310	0.810	0.890	1.490	0.540
	P_2O_5	0.088	0.030	0.018	0.493	0.569	0.532	0.060	0.081	0.076	0.079	0.036	0.082
	L.O.I	0.150	3.950	3.600	1.560	0.660	1.040	8.410	7.630	6.830	6.570	6.000	9.590
	SO3	0.010	0.020	0.010	0.000	0.050	0.020	0.020	0.010	0.020	0.010	0.010	0.010
	Total	99.624	99.699	99.697	99.774	99.759	99.765	99.606	99.620	100.085	100.019	99.622	99.575

…continued from table 4.1

		Weathering condition											
		Fresh						Weathered					
	Rock type	Rhyolite	Rhyolitic glass		Basalt			Clay					
	Sample No	SA-20	SA-45/4	SA-47B	SA-48A	SA-49	SA-51	SA-45/3	SA-47A	SA-48B	SA-52A	SA-52B	SA-52C
	Easting	579152	579203	578675	579133	579546	580943	579203	758675	579133	580162	580162	580162
Location	Northing	1105556	1105631	1105252	1105326	1106580	1107999	1105631	1105252	1105326	1108756	1108746	1108746
	Trace(ppm)												
	Cr	17.00	13.00	15.50	112.00	34.50	135.50	3.00	7.00	9.50	22.00	14.00	18.50
	Cu	0.50	1.00	2.00	35.50	25.50	42.50	44.50	4.00	16.50	11.00	9.50	10.50
	Zn	246.00	254.00	491.50	286.00	342.50	256.00	336.50	136.50	662.00	245.50	710.50	907.00
	Rb	103.00	104.00	115.50	2.50	19.00	3.00	2.50	4.00	5.50	6.50	19.50	6.50
	Cs	1.50	2.00	2.00	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	0.50	0.50
	Pb	24.00	14.50	9.00	<0.001	4.50	4.00	<0.001	10.50	6.00	17.00	18.50	35.50
	Ga	22.50	21.50	21.50	16.00	17.50	15.50	43.00	35.50	37.00	36.50	31.00	43.50
	Hf	2.00	12.50	11.50	3.00	4.50	3.00	26.00	20.50	1.50	14.50	17.50	26.50
	Nb	51.00	78.00	74.50	8.00	14.00	8.00	142.00	80.50	101.50	96.00	98.50	155.50
	Ta	3.00	5.50	4.50	0.50	1.00	0.50	10.00	9.00	6.50	6.00	7.00	11.00
	Th	12.00	16.00	12.50	1.00	2.50	0.50	36.00	24.00	18.00	14.50	18.00	24.00
	U	2.00	4.00	3.50	1.50	0.50	0.50	4.50	1.50	2.00	2.00	1.00	1.00
	Y	48.50	64.50	62.00	15.50	23.00	17.50	44.50	68.00	68.50	74.50	30.50	73.50
	Zr	33.00	315.50	407.50	125.50	18.50	117.50	635.50	500.50	518.50	465.00	489.00	651.50
	La	81.50	79.50	73.50	9.50	21.00	10.50	102.50	140.50	98.50	112.50	56.00	116.50
	Ce	161.00	145.50	159.50	22.50	43.50	24.00	225.50	254.00	192.00	189.50	126.50	402.00
	Pr	22.00	22.00	18.50	3.50	6.00	3.50	35.50	42.00	24.00	27.10	15.50	33.50
	Nd	80.50	93.50	74.50	16.00	25.50	18.00	133.50	162.50	103.00	104.00	54.50	171.00
	Sm	15.50	16.50	15.50	4.00	6.00	4.50	24.50	29.50	19.50	21.50	10.50	26.50
	Eu	1.00	0.50	0.50	1.00	1.50	1.50	1.00	1.50	2.00	2.50	0.50	2.00
	Gd	14.00	14.50	15.50	3.50	5.50	4.50	18.50	25.50	19.50	23.00	11.00	29.00
	Tb	2.00	2.00	2.00	0.50	1.00	1.00	2.50	3.50	2.50	3.50	2.00	4.00
	Dy	10.50	12.50	11.50	3.00	4.50	3.50	13.00	18.50	14.50	17.00	8.50	19.00
	Ho	2.00	2.50	2.00	0.50	1.00	0.50	2.00	3.00	2.50	3.00	1.50	3.50
	Er	4.50	7.00	7.00	2.00	2.00	2.00	5.50	8.00	7.50	8.50	4.00	11.00
	Tm	0.50	1.00	1.00	<0.001	0.50	<0.001	0.50	1.00	1.00	1.00	0.50	1.50
	Yb	4.00	6.50	6.00	1.50	2.00	1.50	4.50	5.50	6.50	6.50	3.50	10.50
	Lu	0.50	1.00	1.00	<0.001	0.50	<0.001	0.50	0.50	1.00	0.50	0.50	1.50

…continued from table 4.1

		Weathering condition											
		Fresh						Weathered					
Rock type		Rhyolite	Rhyolitic glass		Basalt			Clay					
	Sample No.	SA-20	SA-45/4	SA-47B	SA-48A	SA-49	SA-51	SA-45/3	SA-47A	SA-48B	SA-52A	SA-52B	SA-52C
	Easting	579152	579203	578675	579133	579546	580943	579203	758675	579133	580162	580162	580162
Location	Northing	1105556	1105631	1105252	1105326	1106580	1107999	1105631	1105252	1105326	1108756	1108746	1108746
	Trace(PPM0												
	Li	8.00	4.00	4.50	6.00	22.50	26.50	13.50	8.00	4.00	29.00	36.50	50.50
	Be	1.50	6.00	5.50	0.50	2.00	1.00	4.00	4.00	2.50	4.50	11.50	10.50
	As	1.00	3.00	2.50	3.50	0.50	5.50	2.50	<0.001	1.50	2.00	2.00	2.00
	Mo	0.50	3.50	3.50	0.50	1.00	0.50	0.50	0.50	0.50	0.50	0.50	1.00
	Cd	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
	In	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	0.50	<0.001	<0.001	<0.001	<0.001	<0.001
	Sb	0.50	<0.001	<0.001	<0.001	<0.001	0.50	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
	Sn	1.00	3.50	2.50	<0.001	<0.001	<0.001	8.00	14.00	3.50	2.50	4.00	6.00
	W	<0.001	1.00	1.50	<0.001	0.50	<0.001	<0.001	<0.001	<0.001	0.50	0.50	0.50
	Ti	<0.001	<0.001	0.50	<0.001	0.50	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	0.50
	Bi	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001

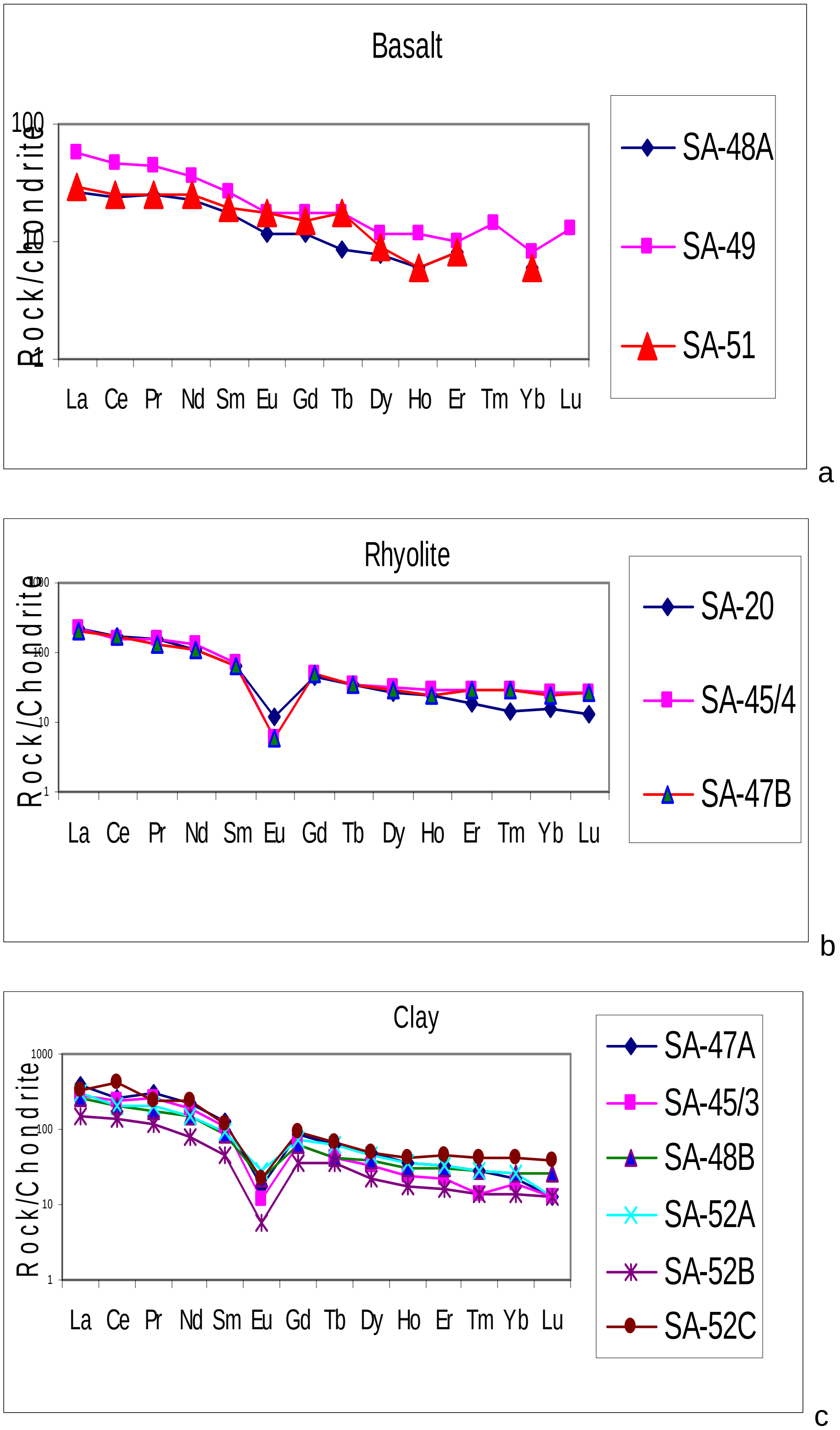


Figure 4.2 chondrite – normalized rare earth element diagrams for (a)basalt (b)rhyolite (c)clay material of the opal bearing mantle.

CHAPTER ONE

INTRODUCTION

1.1 BACKGROUND

Gem-quality opal with satisfactory structural stability, durability, play of color, color saturation and color patterns make people aspiration higher to use it as jewelers, personal adornment etc. Due to these demands, precious opal has become an important mineral commodity.

Both common and precious opal have been found to occur in North Shoa/Ethiopia and they are well known by the indigenous people since 1978 (Dowining, 1996). Later this gem has been discovered in South Gondar both of which are hosted in volcanic rocks. This gem-quality opal is proved to be similar to Mexico fire opal. However, the genesis of the opal remains poorly understood. How opal mineralization took place within the volcanic rocks of North Shoa/Ethiopia is currently a major scientific problem that needs to be investigated.

The principal goal of this research is therefore to understand the processes that led to the formation of opal in the volcanic succession in the above areas.

The study area is located on the central - Eastern plateau of Ethiopia adjacent to the western margin of Afar depression, about 210kms from Addis Ababa along the Debrebirhan-Molale /Mehal-Meda road.

This region is made up of thick sequence of flood basalts overlain by a major succession of pyroclastic products dominated by rhyolitic ignimbrites. Opal occurs within the flood basalt sequence, below the major contact separating the pyroclastic sequence from the flood basalts.

This project is intended to give scientific explanation for the natural processes that created favorable conditions for the opal formation. The study will be based on data that will be generated from petrographical and geochemical analysis of samples that have been systematically collected from the unit containing opal, and country rocks of the considered natural resource.

Initiation of the study came from the student and the Department of Earth sciences. It was from scientific interest to study opal origin in North Shoa /Ethiopia Koste - Amba and Gift -Maryam localities.

1.2 GLOBAL HISTORY OF OPAL

Opal is hydrated amorphous silica (3% to 20% water) containing aggregates of ordered or disordered microcrystallites of a –cristobalite. Electron microscopic studies show that opal is made up of close packed silica spheres ($SiO_{2.}$ nH_2O) and interstitial silica, water or CO_2 gas-vapor and air. Opal is characterized by a conchoidal fracture and it occurs in wide range of background colors. It is transparent to nearly opaque, and may be distinguished from chalcedony and cryptocrystalline varieties of quartz by its higher water content and lower hardness. Opal is brittle, sensitive to heat, and easily scratched. Furthermore, opal from some localities, is “unstable” and may crack or self-destruct through the loss of water. Despite these faults, opal’s beauty is supreme and for the past thousands years, it is recognized as a “highly prized” gemstone. [1a]

The history of opal /opals, the discoverer of opals, and the first time of opal discovery is expressed in accordance with literatures information. [1b]

Louis Leakey, the famous anthropologist discovered the earliest known opal artifacts that date back to about 4000 B.C., they are considered to come most likely from Ethiopia.

In the Old word, Hungary, mined opal for Europe and the Middle East, while Mexico, Peru, and Honduras supplied their own Native Empires with the gemstone.

Since the late 1800’s, opal production was dominated by Australia with more than 90% of the global out put. Opal of differing qualities occur in other countries such as Zambia, Ethiopia, Guatemala, Poland, Peru, Canada, New Zealand, Indonesia, the USA, Brazil, and Mexico.

The modern name of the gem opal is derived from ancient sources: the Sanskrit upala which means “precious stone”; the Latin opalus, and the Greek opallios both which means, “to see a color change”. Early races credited opal with magical qualities and traditionally, opal was considered to aid its wearer in seeing limitless possibilities. The early Greeks felt certain that the opal bestowed powers of foresight and prophecy upon its owner; while in Arabian folklore; it is believed that the stone fell from heaven in flashes of lightning. To the Romans, it was considered a token of hope and purity.

1a: htt://www.science.uwaterloo.ca/earth/waton/s984.html

1b: htt://www.opalsdownunder.com.au/articles/history.htm & others.

Ancient Romans provided the first real market for opal. With a rich powerful empire, wealthy citizens acquired disposable income and a passion for gems. Opal whose colors changed with every shift of light was rare than pearls and diamonds and destined to be the stuff of myths and dreams.

The Roman Pliny (79 A.D.) described opal as “Having a refulgent fire of the carbuncle ruby or garnet; the glorious purple of amethyst; the sea green of emerald; and all those colors glittering together mixed in an incredible way.”

The mines in Eastern Europe (Hungary) were the only source of European opal until the Spaniards returned from the new world with Aztec opal.

In the Middle Ages (from about AD 1000 to AD 1450), opal was known as the “eye stone” due to a belief that it was vital to good eyesight. Blonde women were known to wear necklaces of opal in order to protect their hair from losing its color. Some cultures thought the effect of opal on sight could render the wearer invisible.

In the late 18th and early 19th centuries, opal began to fall out of favor in Europe. It was wrongly branded as bringing bad luck (e.g. pestilence, famine and the fall of Monarchs). Nevertheless, Queen Victoria tried a lot to reverse the unfounded bad press. Queen Victoria was a lover of opal kept a fine personal collection and wore opals throughout her reign. Here friends and her five daughters were presented with fine opals. Opal became highly sought after because the Royal Court of Britain was regarded as the model for fashion around the world and fine quality opal had recently been discovered in far off Australia. In the latter years of her long reign, various Australian opal fields were discovered and worked.

Based on the study of written accounts, it is suggested that most of those early Australian discoveries were accidental - a horse’s hoof kicked up opal bearing rock, the run off from rainstorm-uncovered opal at lightning Ridge.

When Australian opals appeared on the world market in the 1890’s the Hungarian mines spread the idea that it was not genuine, probably due to gems with such brilliant fire had not been seen before. By 1932, the Eastern European mines were unable to compete with Australian high quality opal and ceased production, this event allowed Australia to become the mantle of premier opal producer of the world and famous for lightning ridge’s colorful and rare black and crystal stone.

Cooberpedy (1912), Andamooka (1930) and then Mintabie followed Angaston in South Australia. Now over 50% of world production comes from South Australia.

1.3 LOCATION AND ACCESSIBILITY

The study area is composed of Koste-Amba and Gift-Mariyam adjoing localities. These two research sites are situated in Amhara Administrative Region, North Shoa Zone, specifically in Tarmaber Woreda. They are naturally positioned by adjoining the Southwestern landmass edge of the Afar Triangle, i.e. near by the northern western part of the Main Ethiopian Rift Valley. The study area specifically lies at the eastern margin of the Western highlands, in the northern part of the Shoan plateau. Besides, the area is located within the grid reference of 578000 to 581000 Easting and 1104000 to 1109000 Northing. It lies in the Sela Dingay (1986) and Molale (1992) topo sub sheets having a scale of 1:50,000(Figure1.1).

The study area can be reached from Addis Ababa through 180km Asphalt road and 25km/30km all weather gravel road via Addis Ababa ________ D/Berehan _______ Termaber ____ Mezezo _____ Kob - Astil/Tiftif - Dinghy respectively. **Kob-Astil** is the place where turning the voyage due west is made so as to reach Koste - Amba locality through 3km trail rout, where as **Tiftif - Dingay** is the village where the West-ward turning could be made so as to reach Gift-Mariyam locality through about 1.5km trail route.

Because of the highly dissected and rugged nature of the terrain characterized by deep stream gorges and rolling plains, inter - field movement in the area was highly tire-some.

Most of the countryside dwellers have no considerable road access. Due to the low standard income of the people and the absence of enough access roads in the region, most every body use non-Motorized means for human and goods transportation. Walking, horses and mules for human transport the rural population themselves and pack animals for goods are common custom-made transport systems in the region.

1.4 PHYSIOGRAPHY AND DRAINAGE

The physiography and Drainage of the central eastern part of the northwestern highland plateau of Ethiopia, within which the study area lies, is described below as Doilicho et al. (1991) previously explains it.

The Shoan plateau, within which the study area situated, is the smallest sub-highland amongst the four groups of northwestern highlands (The Tigrean Plateau, North central massif, Shoan plateau and Southwestern high lands).

The Rift valley is both the eastern and Southeastern boundary of this plateau. Abbay and Omo gorges bound the northern and western limit of this plateau respectively. Almost three-fourth of this plateau area is located at an altitude of more than 2,000m. The largest proportion of elevated land in Ethiopia characterizes it. This sub-region is used as watershed (water divide) for rivers like Abbay, Awash, Ghibe and Omo river basins. The tributary streams of Abbay, Omo and Awash rivers drained the Shoan plateau out ward in all directions.

Mt. Abuye Meda (4000m), where the study area is found in the nearby vicinity and Mt. Guraghe (3721m) are the highest mountain peaks in the Northern and Southern parts of the Shoan plateau respectively.

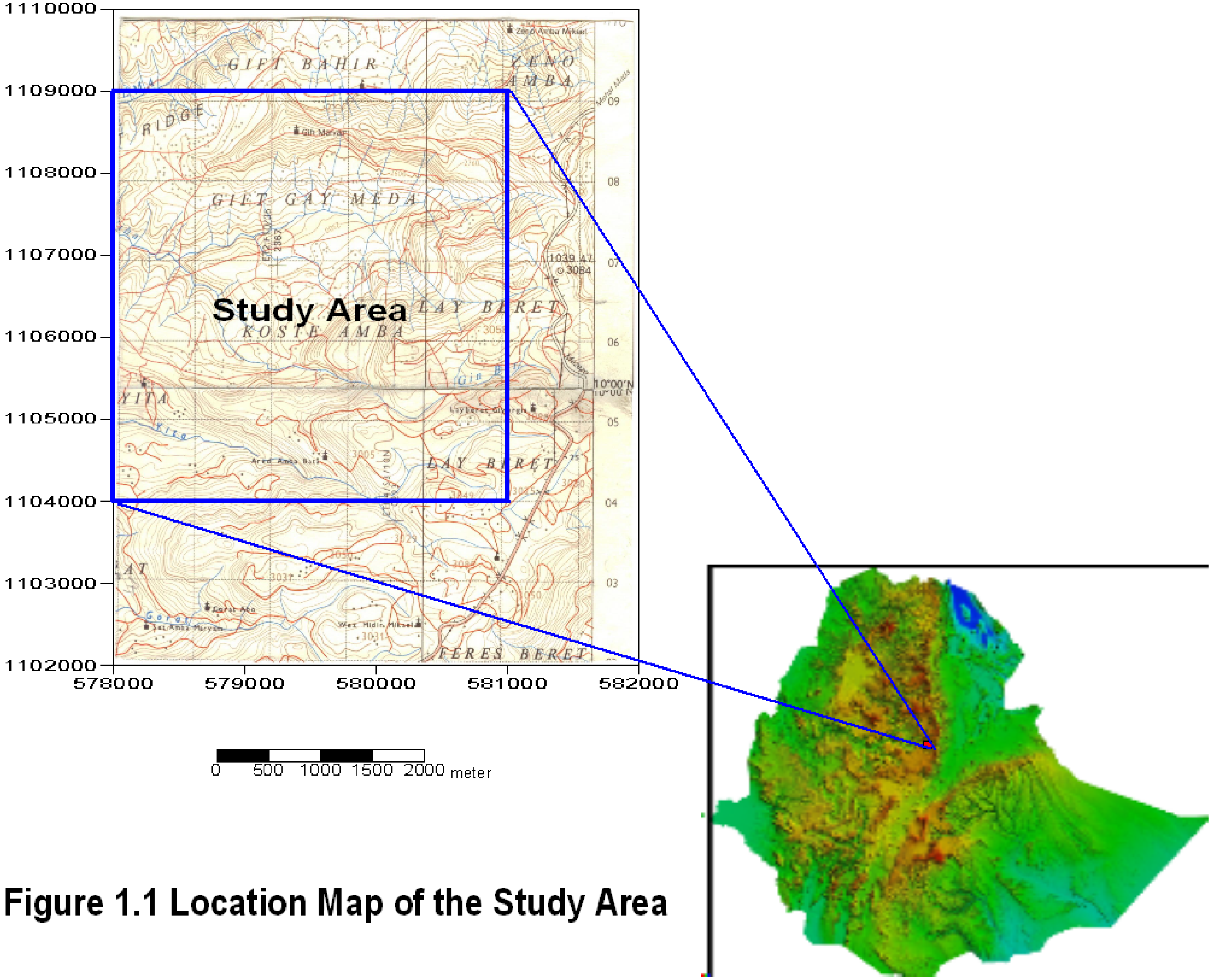


Figure 1.1 Location Map of the Study Area

1.5 CLIMATE AND VEGETATION

Climate and vegetation characteristics of the region (central - eastern Ethiopian plateau) within which the study area located is expressed in accordance with the information acquired from BCEOM (1999).

The central eastern Ethiopian plateau, where the study area found is predominantly characterized by warm temperature climate. This climate has distinct dry months in winter. The mean temperature of the coldest month is < 18^0c and for four months the mean temperature is > 10^0c with the mean annual rainfall (mm) > 20 X (T + 14), where T is the mean annual temperature in ^{0}c.

The study area is situated in the central and southeastern highland rainfall region specifically in the central eastern plateau of Ethiopia (in the northern part of the Shoan plateau). Ingeneral, this region has two rainy periods with quasi - double maxima (semi-bimodal) rainfall pattern and one dry period. The local names of the two rainy periods are kiremt (June to September) and Belg (February to May), they are the long and short rainy periods, respectively. The dry period, which characterizes the rest of the year (October to January), is named as Bega.

Farming /cultivation and grazing practices of the people have been continuously changing the original floral habitat of the region. By now, only remnant vegetation exists in a few localities. Large enough introduction of exotic species exists in the region through the agricultural and pastoral practices which could be either useful to the farmers or grow as weeds.

In general, shrub-land, i.e. composed of multi-stemmed wood species but usually less than 2m in height, is typical of the region. It is mostly mixed with grass. The shrub together with grass made the open shrub - land because the intensity of woody cover is somewhat low.

Eucalyptus plantation which is artificially introduced on a large scale into the region for aforestation or on small plots as village wood lots for fuel wood or poles exist in the highest land form of the region.

1.6 POPULATION AND SOCIO - ECONOMY

Almost all of the people in the region are Amharas; they are attached to the Christian orthodox religion. Concerning language, almost all peoples are characterized by Semitic (Amarigna). The region is densely populated. Food deficits occur. Meaning full resource degradation is continuously occurring due to the increasing number of human population pressure that by now severely causing and aggravating land degradation, soil erosion, deterioration of water quality (both surface and ground water), and loss of habitat for wildlife and loss of wildlife. In general, loss of forest resources, land degradation from agriculture and loss of habitat and biodiversity are the results of high population density and growth rates in the region.

The means of subsistence of human population is based on rain fed cultivation /agriculture combined with animal husbandry. Major growing crops are barely, wheat, sorghum, teff, pea, and lentil. The products of crop cultivation are for food staff and marketing. The agricultural activity is still traditional. It depends on animal. The most important livestock breeds of the region include cattle, sheep, goats, equine (horses, mules, and donkeys), poultry, and beehives. The livestock resource is mainly indigenous with some number of improved animals introduced in the region. Livestocks are bred for the source of power for plaughing, milk and meat production, hided and skins production, fuel manure and prestige.

The marketing of firewood and forest products (e.g. eucalyptus trees, very small number of cottage industries (e.g. weavers, carpenters, potters, blacksmiths, charcoal makers and tanners) supply the indigenous people with very small amount of extra cash income. Some of the local people are used to work as daily laborers in opal mining works of private licensees, and they hire their land plot for the licensee to use for opal mining.

1.7 PREVIOUS WORKS

Written or spoken account of past events about Ethiopian opal is presented below based on the information acquired from Abbay Natural Resources Development PLC, 2001; Ministry of Mines, 2002 and others.

Downing (1996) cited that the discovery of opal in North Shoa dates back to 1978 or before.

The illegal traditional mining of opal by the indigenous dwellers dates back to 1984 and by then smuggling of Ethiopian opals by outsiders were started (Abbay Natural Resources Development PLC., 2000).In the meantime, Ethiopian Mineral Resources Development Corporation conducted a preliminary investigation in the late 1980s in North Shoa area, where the opal gemstone has been investigated, and the corporation has come up with the acquisition of precious opal deposition in the region.

Then EMRDC offer the above rediscovery of opal in North Shoa and sent two samples of opal nodules to Sweden for further laboratory analyses. These opal specimens were opened and analyzed at Gutenberg gem laboratory and found to have the following characteristics:

Sample one (probably from Imbitata -North Shoa) - The nodule contained common white opal (potch) with a small area containing play of colors (precious white opal). Water content is found to be 21.5%. The opal crazed after 6:30 hours in the sunlight.

Sample two (probably from Gift-Bahir /Gift-Mariyam-North Shoa)-The nodule found to contain common red opal with out play of colors. Water content is approximately found to be 25%. This red opal crazed after 10 hours in darkness.

After the aforementioned work of EMRDC, the local farmers apparently collected and sold some opal, although it is not clear to whom they sold it.

Abbay Natural Resource Development PLC. Was may be the first insider investor to be granted an opal exploration license by Ministry of Mines and Energy in Yita Mikael area/North Shoa in 1994. Thenceforth other opal exploration and mining licenses have been given in the surroundings of the above-cited locality to other companies.

Since 1994, when the information about the discovery of opal in Ethiopia /North Shoa appeared for the first time in publication (Barot, 1994), a lot of researches (e.g. koivula et al., 1994; kammering et al., 1995; and Hoover et al., 1996), merchants and mining investors, who take part in gemstone industry, were interested to work on the Ethiopian opal.

There is no apparently known past production from North Shoa opal deposit. However, local indigenous people were aware that opal was present. Nevertheless, they were not aware for its gem potential. Interest created by the recent prospecting activity has resulted in some local farmers illegally mining material readily accessible at the surface of this large deposit. Small quantities of this contraband have reached Europe and the United States through Nairobi (Koivula et al. 1994 in Hoover et al. 1996).

Ethiopian / North Shoa precious opal is characterized by various base colors: colorless, translucent white, lavender, red, orange, Yellow, Green, and Blue. A single nodule can show various base colors and both precious and common opal. Both transparent and translucent precious opals have been found. The play of colour is manifested in the normal way or as contraluz, i.e. when the precious opal is held against the light. Inclusions such as dendrites of manganese oxide are occasionally found on natural fracture surfaces and within some opals. Air bubbles are sometimes found as well (Downing, 1996).

Hoover (1996) examined some characteristics of opals from North Shoa/Amhara Region and came up with the following results:

- Above one percent of the opal in the lithophysae has a play of color and much of the opall is crystal base;
- The refractive indices are found to be in the range of 1.439 to 1.448 - with hydrophane the lowest (1.439 to 1.441) ;
- Specific gravities ranged from 1.85 to 2.02, with hydrophane on the low side (1.85 to 1.87)
- All opals are found to be similar to that of other precious opal from volcanic sources.
- A small portion of the opal is found to be hydrophane, i.e. it gains water when soaked and loses it when left to dry in the air.

The overburden pressure and subsequent diagenesis caused the release of silica gel that was found in the opal bearing volcanoclastic deposit and later redeposited this solution within the void spaces of the seam and dehydrated to produce opal (Taffesse, 2002).

Precious opal is valued by carat (one carat being equivalent to 0.2 gram by weight) and presently the price of one carat of opal ranges from $5 to $ 700 USD. However, unprocessed opal is as low as a few dollars per kg (Ministry of Mines, 2002).

1.8 OBJECTIVES OF THE PRESENT STUDY

- To study the origin of opal hosted in Koste – Amba & Gift – Maryam volcanic rocks using major & trace element analysis, petrographic description as well as x –ray diffraction data.
- Establish the geological and geochemical conditions responsible for opal mineralization.

1.9 METHODS AND MATERIALS

To accomplish the objectives of the research, the methods that have been followed and the materials utilized include:

- Literature review
- Field work (geological study & sampling)
- Petrographic description of opal hosting and country rocks of the study area.
- Major & Trace element analysis as well as X-ray diffraction
- Utilization of soft wares such as global mapper, arc view and surfer
- Data interpretation
- Conclusions & recommendations have been made based on the results obtained.

1.10 LIMITATIONS OF THE STUDY

All physically and mentally tiresome and several time consuming efforts have been made so as to perform the study under consideration in accordance with previously submitted project proposal. However, this fatigued study has been brought to the result under limitations of financial and appropriate material resources for laboratory analysis. Besides, information about the origin of Ethiopian opal is almost non-existent. There were some prospecting, exploration and mining based quasi-research works on the origin of opal both by foreign and indigenous private companies but duplication of works could be inevitable unless result reports are published. Overall, data base management of the country is very poor and in effect, it was very difficult to get what has been done so far and where the gap is. Moreover, investigations of earth resources of an area from the beginning are financial and material consuming as well as time taking.

CHAPTER SEVEN

CONCLUSIONS AND RECOMMENDATIONS

7.1 CONCLUSIONS

- The topmost part of the flood basalt in the study area, overlain by enormous amount of ignimbrite, is characterized by cliff forming rhyolitic flow and rhyolitic glass (from bottom to top).
- The opal-bearing zone is confined to the rhyolitic glass, i.e. underlain by a rhyolite that has alternating vesicular and finely laminated unit.
- The basaltic unit just overlying the rhyolite (rhyolitic ignimbrite & the rhyolitic glass from bottom to top) is characterized by some stacks of superimposed basalt flows with reddish paleosols in between them. The bottom part of this pile of basaltic lava flows is intensely weathered. This weathered and unconsolidated rock material allows easy infiltration of rainwater towards the rhyolitic glass.
- The cliff forming rhyolite, that underlies the opal – bearing and hosting unit, is very finely laminated at its topmost part, so that it can be used as an impermeable medium and used as a barrier for the storage of certain amounts of water and silica solution within the rhyolitic glass. Therefore, the rhyolitic glass may be in a favorable condition for the weathering processes that may act up on it.
- The opal-bearing seam shows a rough zoning. An approximately 0.5m thick outer zone is a thin layer composed of clay (montmorillonite, kaolinite/halloysite); zeolite (mordenite & philippsite); cristobalite and quartz. An intermediate zone with an approximate thickness of 2.5m consists of agate, large and empted pockets of opal irregularly distributed within fresh or moderately weathered rhyolitic glass. The inner zone with its approximate thickness 1.0m consists of valuable opal nodules within its top most part. The lower most part of this zone is mostly fresh but some times contains densely populated macroscopic silica spheres nuclei/nucleation/ this may represent the stage in the growth of silica spheres (nucleation).

- In some places, there is no fresh rhyolitic glass except completely altered products like clayey residual materials. Conversely, only fresh rhyolitic glasses locally exist without altered top part (that may contain clayey material).
- The vesiculated rhyolitic – ignimbrite(rhyolite) consists of 10% sanidine crystals, 53% volcanic glass, 3% rock fragments, 20% chalcedony, 10% zeolite and 4% opaque minerals.
- The fresh Rhyolitic glass (opal bearing zone) consists of 10-13% sanidine crystals, about 10% opal and chalcedony, about 4% pyroxene, 1% opaque minerals and 68-80% volcanic glass.
- The altered rhyolitic glass (clayey material) consists of 10-13 sanidine, 5% zeolite 18% chalcedony, 60-70% volcanic glass, 2-5% rock fragments 2 – 15% opaque minerals and pyroxene in trace amounts.
- Relatively high concentration of light rare earth elements (LREE) are on display within the altered rhyolitic glass (clay materials). Both the fresh and altered rhyolitic glasses as well as the underlying rhyolite flow show somewhat steep normalized abundance of LREE and flat HREE patterns. These acidic rocks also reflect pronounced negative Eu anomaly.
- Altered rhyolitic glass/ clay materials, i.e. the topmost part of the rhyolitic glass is relatively more enriched in light rare earth elements (LREE) than both the underlying fresh rhyolite and rhyolitic glass. This may be due to the immobility of the light rare earth elements (LREE) during weathering (hydration and hydrolysis) on the surface environment.
- As it has been described in chapter six, deep surface weathering and a lack of detailed site investigations may obscure the difference between surface weathering process and post – volcanic hydrothermal activity. In the presence of this fact, (a) the formation of montmorillonite possibly from simultaneous surface weathering of sanidine and pyroxene that are contained in the rhyolitic glass or from the devitrification of volcanic glass fragments(shards) accompanied by the release of surplus silica to surrounding waters for the creation of opal mineralization in the study area ; (b) the occurrence of zeolite minerals(mordenite & philippsite) usually in earth surface weathering

environments(with some exceptions where philippsite can occurs in saline - lake deposits, calcareous deep – sea sediments, hot – spring deposits) characterized by percolating ground water in acidic tephra; (c) the existence of opal – empted vesicular rhyolite and successive lava flows that underlies and overlies respectively the opal bearing horizon; all these together may exhibit that silica – rich waters derived from surface weathering processes can be the origin of opal in Koste – Amba & Gift – Mariyam localities.

7.2 RECOMMENDATION

- The quality of geological information on any mineral deposit increases through progressive exploration activities. Whether they have direct or indirect relations with Ethiopian opals, global informations should be properly documented and interpreted to acquire the professional capability that upgrade the efficiency of modeling opal occurrences in Ethiopia as a whole.
- Henceforth, exploration activity should be carried out together with research woks so that the country will be benefited from the accumulated geological information. Therefore, this information can help us easily to understand the general genetic features of the deposit and it provides important prospecting and exploration guides for other mineral occurrences in similar geological settings.
- Detailed exploration geochemistry of the opal bearing seam materials should be carried out using recently developed and updated techniques as well as instruments of high precision and accuracy. The results of these studies will shade convincing light on genesis, physico – chemical conditions of opal producing phenomenon and many other features of the deposit.
- In searching for similar opal deposits in Ethiopia, it may be significant to consider the presence of surficially weathered or altered rhyolitic glass within the same geological setting and climatic conditions for overall exploration criteria.

CHAPTER SIX
RESULTS AND DISCUSSION

6.1 RESULTS

Previous studies show that Ethiopian opal from North Shoa has water content 21 - 25%, refractive index 1.439 – 1.448 and specific gravity 1.85 = 2.02. The lower values of refractive indices (1.439 – 1.441) and specific gravities (1.85 – 1.87) are found to be characteristics of hydrophane opal.

Opal occurs in the area commonly in seams of rhyolitic glass sandwiched between the underlying vesicular rhyolitic - ignimbrite and the overlying stack of successive basaltic lava flows. This gemstone mainly occurs as impregnations in the rhyolitic glass.

The interfaces between the overlying successive lava flows do not accommodate opal. The same is true for the vesicles of the rhyolitic ignimbrite that underlie the opal bearing volcanoclastic rock unit.

The opal – bearing seam shows a rough zoning:

An approximately 0.5m thick Outer zone is composed of almost horizontally layered and yellowish – gray and red colored secondary materials composed of montmorillonite, kaolinite/halloysite, subordinate quartz, cristobalite, zeolites(mordenite & philippsite).

An approximately 2.5m thick Intermediate zone consists essentially a mixture of moderately altered rhyolitic glass, agate, quartz and empty opal pockets. It consists of coarsely fragmented and partly weathered rhyolitic glass. State of decomposition decreases downward. Some clay materials leached from the outer zone are deposited in the intermediate zone.

An approximately 1.0m Inner zone is characterized by almost 0.5m precious opal bearing top most layer. Numerous nucleation of opal exist at the topmost part of this rhyolitic glass unit of inner zone.

Some basalt, ignimbrite, rhyolitic - ignimbrite, fresh & altered rhyolitic glasses have been petrographically examined so as to understand the mineralogical as well as textural set up of both opal hosting and country rocks of the study area. Their respective modal composition is forwarded below:

a/Basalt

22 – 50% lath shaped plagioclase feldspars.
30 – 38% anhedral to euhedral pyroxene.
10 – 17% opaque minerals.
1 – 13% volcanic glass.
3% calcite.
Groundmass mostly composed of plagioclase, pyroxene, Fe – oxide and volcanic glass.

b/Ignimbrite: The basal unit of the middle basalt.

about 30% sanidine.
about 59% volcanic glass.
Crystals of sanidine and rock fragments are suspended over the glassy groundmass. The glass shards are welded and flattened.

c/Rhyolitic – Ignimbrite

10% sanidine.
10% zeolite.
4% opaque minerals.
53% volcanic glass.
3% rock fragments.
groundmass is glass, i.e. vitrophyric texture.

d/Fresh – Rhyolitic glass(opal bearing zone)

12 – 13% sanidine.
about 4% pyroxene.
1 – 2% opaque minerals.
68 – 80% volcanic glass.
groundmass is composed of volcanic glass, i.e.vitrophyric texture

e/ Altered Rhyolitic glass(opal bearing zone)

10 – 15% sanidine.
5 – 7% zeolite.
2 – 15% opaque minerals.
60 – 70% volcanic glass.

trace amount of pyroxene.

The modal composition of pyroxene in fresh rhyolitic glass/volcanic glass is about 4%, but it is found in trace amounts in an altered rhyolitic glass. This may indicate that certain amounts of Mg, Fe and most probably Ca from pyroxene decomposition are utilized to build up the crystal structure of montmorillonite clay mineral.

According to the result of major element analysis, volcanic rocks of the study area display bimodal composition. Recalculated to 100% on an anhydrous basis, the rocks plot as basalt and rhyolite on a total alkalies vs. silica diagram in accordance with Lebas, et al., 1986.

Regarding trace element analysis, the rhyolite and the rhyolitic glass are enriched in light rare earth elements (LREE). Especially, altered rhyolitic glasses are more enriched in light rare earth elements (LREE) by comparison with the rhyolite and fresh rhyolitic glass. The basaltic rock samples show no pronounced negative or positive anomalies. They show almost gentle slope REE pattern from LREE to HREE distribution.

The x-ray diffraction analysis has come up with the following results:

Sample SA – 45/3: Clayey material mainly composed of montmorillonite and zeolite minerals (mordenite group) with kaolinite and subordinate quartz.

Sample SA – 47A: Clayey material composed of montmorillonite and zeolite minerals (mordenite group).

Sample SA – 52B: Clayey material composed of montmorillonite and zeolite minerals (mordenite group)

Sample SA – 52C: Clayey material composed of montmorillonite, halloysite(kaolinite group), zeolite (philippsite group) and cristobalite.

The samples generally characterize associated deposits of clay and zeolite mineral materials composed mainly of montmorillonite zeolite (mainly mordenite & philippsite in one sample), kaolinite, cristobalite and subordinate quartz.

6.2 DISCUSSION

Volcanic – hosted opal appears to be either related to post – volcanic hydrothermal activity, or to silica – rich waters derived from surface weathering processes similar to sedimentary – hosted deposits. The difference between these two processes may be obscured by deep surface weathering and a lack of detailed site investigations. Opal hosted by volcanic rock generally contains more water than opal formed in shallow sedimentary environments. Consequently, volcanic – hosted opal (with exceptions, i.e. Mexican fire opal) is generally less stable than opal recovered from sedimentary rocks and often exhibits a greater propensity for crazing(Barnes and others, 1992 cited in Hausel & Sutherland, 2005).

Opal deposition often occurs with rounded voids in volcanic rocks known as vesicles. This type of opal is deposited from siliceous solutions at temperatures higher than normal groundwater temperatures. Opal deposition under these conditions resulted in tiny silica spheres with close – packed arrays that exhibit almost no interstitial voids (Darragh and others, 11976). Kievlenko(2003) cites opal formation temperatures of 50o to 150o C for post – volcanic hydrothermal environments. Opal associated with siliceous sinter or geyserites is often attributed to post – volcanic hydrothermal activity (Hausel & Sutherland, 2005).

Primary silicate minerals such as feldspars & feldspathoids and ferromagnesian minerals like pyroxene & hornblende are common parent materials that can cause the release of silica through their alteration by weathering or hydrothermal processes.

Regarding associated deposits of opal in the study area(Koste – Amba & Gift – Mariyam localities), clay minerals (montmorillonite & kaolinite), zeolite minerals (mordenite & philippsite) and silica (quartz & cristobalite) are characteristics of opal bearing seams/zones.

Montmorillonite is the dominant clay mineral in bentonite, altered vocanic ash that could be the result of low temperature hydrothermal alteration and weathering, similarly kaolinite can be formed by weathering or hydrothermal alteration of aluminosilicates, particularly feldspars.

According to Blatt et al. (1972), devitrification of volcanic glass fragments(shards) may result either in the formation of a felsitic fragment with no release of silica or in the formation of montmorillonitic clay with release of surplus silica to surrounding waters. If the amount of silica released is sufficient to saturate the water with respect to amorphous silica, opal will precipitate.

Genetically, zeolites are formed by the reaction of pore water with materials such as volcanic glass, poorly crystalline clay, plagioclase or silica. Earth surface weathering and percolating groundwater in acidic tephra favor the geological synthesis and occurrences of some natural zeolites (mordenite & philippsite). These two zeolites appear to be associated with diagenesis by percolating groundwater and shallow burial.

Considering the deposit form, opal bearing horizon of the study area is completely stratabound. An occurrence of precious opal within this horizon is considered as erratic.

Post – Volcanic silica saturated hydrothermal solutions that may come from depth beneath the opal resource area could first encountered the vesicles of the cliff forming rhyolite, i.e. which underlies the opal bearing rhyolitic glass, for the accommodation of hydrated silica (opal – $SiO_2 . nH_2O$). Besides, hydrothermal solutions loaded with silica that may come from phreatomagmatic solutions(that may be related with the formation of the so – called base – surge deposit which is about 240m above the opal bearing zone) first could encountered the interfaces of basaltic lava flows before the existing opal bearing rhyolitic glass for the accommodation of the hydrated silica.

Silica – rich waters that may derived from surface weathering processes of the rhyolitic glass(i.e. similar to sedimentary – hosted deposits) most likely could be the cause for the creation of opal mineralization in the study area(Koste – Amba & Gift – Mariyam localities). However, the difference between the post – volcanic hydrothermal activity and surface weathering processes may be obscured by deep surface weathering and a lack of detailed site investigation, so that thorough research studies should be carried out so as to clearly know whether surface weathering process is the only source or post – volcanic hydrothermal activity is the cause for opal mineralization in the study area.

CHAPTER THREE

LOCAL GEOLOGICAL SETTING OF KOSTE - AMBA & GIFT - MARYAM

3.1 INTRODUCTION

Koste-Amba and Gift-Maryam localities of the study area are located in the Eastern segment of the North.-Central flood basalt plateau of Ethiopia by adjoining the South Western margin of the Afar Rift.

The regional stratigraphy is composed of Mesozoic sedimentary rocks of the Abbay gorge and flood basalts of the plateau area overlain by high summit shield volcanoes.

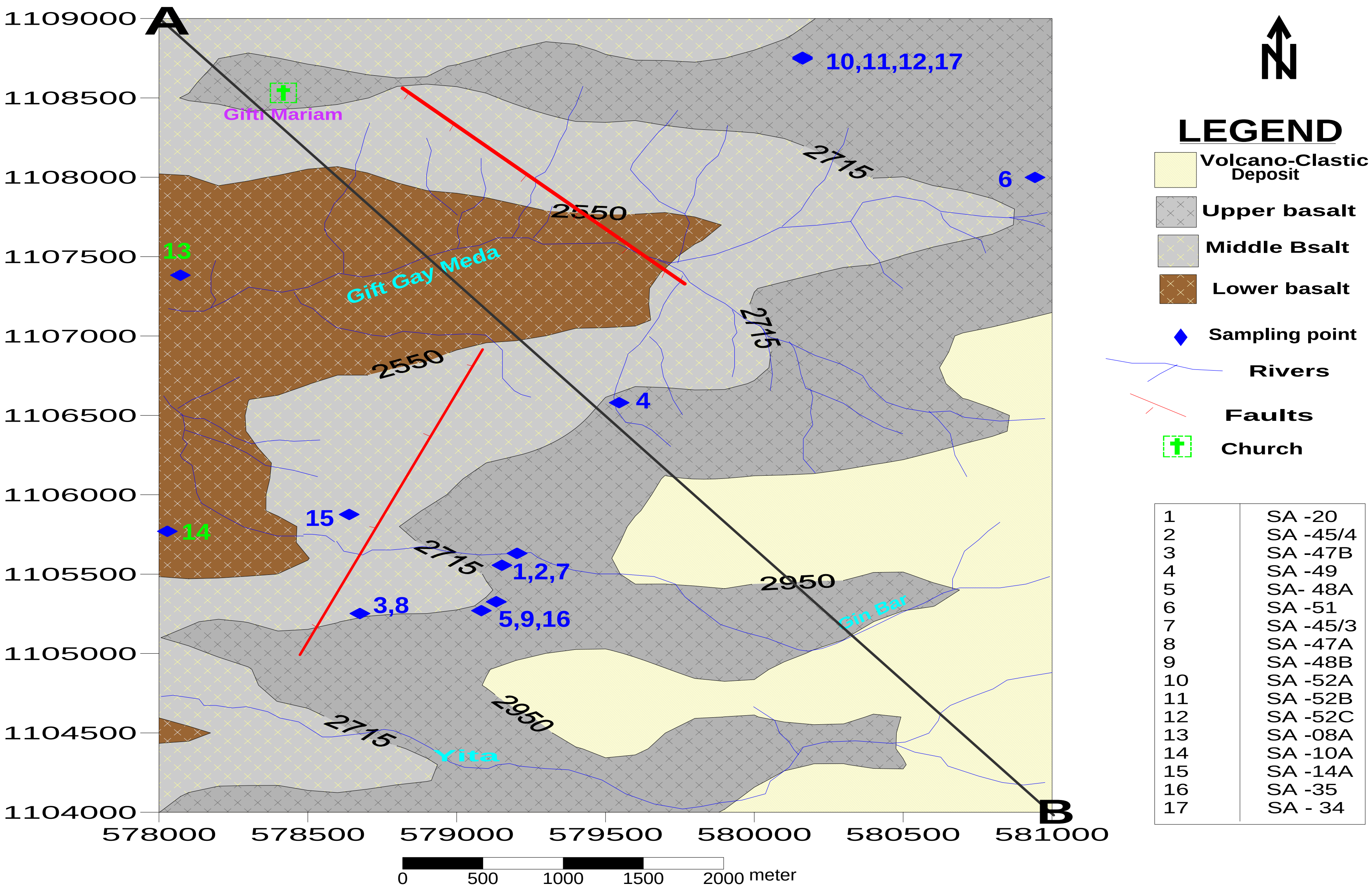
The voluminous outpouring of lava on the central part of Ethiopia built imposing stacks of superimposed basalt flows, as much as some hundreds of meters thick, i.e. maximum especially in the study area. Such like piles were believed to be fed from fracturing and fissuring linear zones in the continental crust through which basaltic magma emerge successive pulses, flooding out over the surrounding region. The high fluid nature of these volcanic basalt lavas resulted in the construction of a subdued or planar landform in the study region.

Many valleys filled with alluvial and colluvial deposits of recent age traverse the outcrops of the different rock units.

3.2 LITHOLOGY

Based on the stratigraphic relation ships among the various units, by taking ignimbrites & rhyolites as a basal unit of basalt lava flows, lithological, textural and volcanological variations as well as physical individuality, informal name like lower basal (LB), middle basalt (MB) upper basalt (UB) and volcanoclastic flow deposits (VFD) have been used for different formations so as to classify the vocanic composite unit of the study area (figure 3.1).

The topmost part of the local lithologic sequence is composed of an ignimbrite formation that offers plateau morphology for the landform of the study area. Conspicuous layer of rhyolite and/or ignimbrite is found midway through the underlying basalt sequence. By taking, this stratigraphic position in to consideration the local basaltic lava flow is subdivided into upper, middle and lower flood basalts. There is no interbedding of basalts within the rhyolite - ignimbrite successions, but there are occasional rhyolites within the basalt lithologic column.



1	SA -20
2	SA -45/4
3	SA -47B
4	SA -49
5	SA- 48A
6	SA -51
7	SA -45/3
8	SA -47A
9	SA -48B
10	SA -52A
11	SA -52B
12	SA -52C
13	SA -08A
14	SA -10A
15	SA -14A
16	SA -35
17	SA - 34

Fig. 3.1 Geological Map of the Study Area

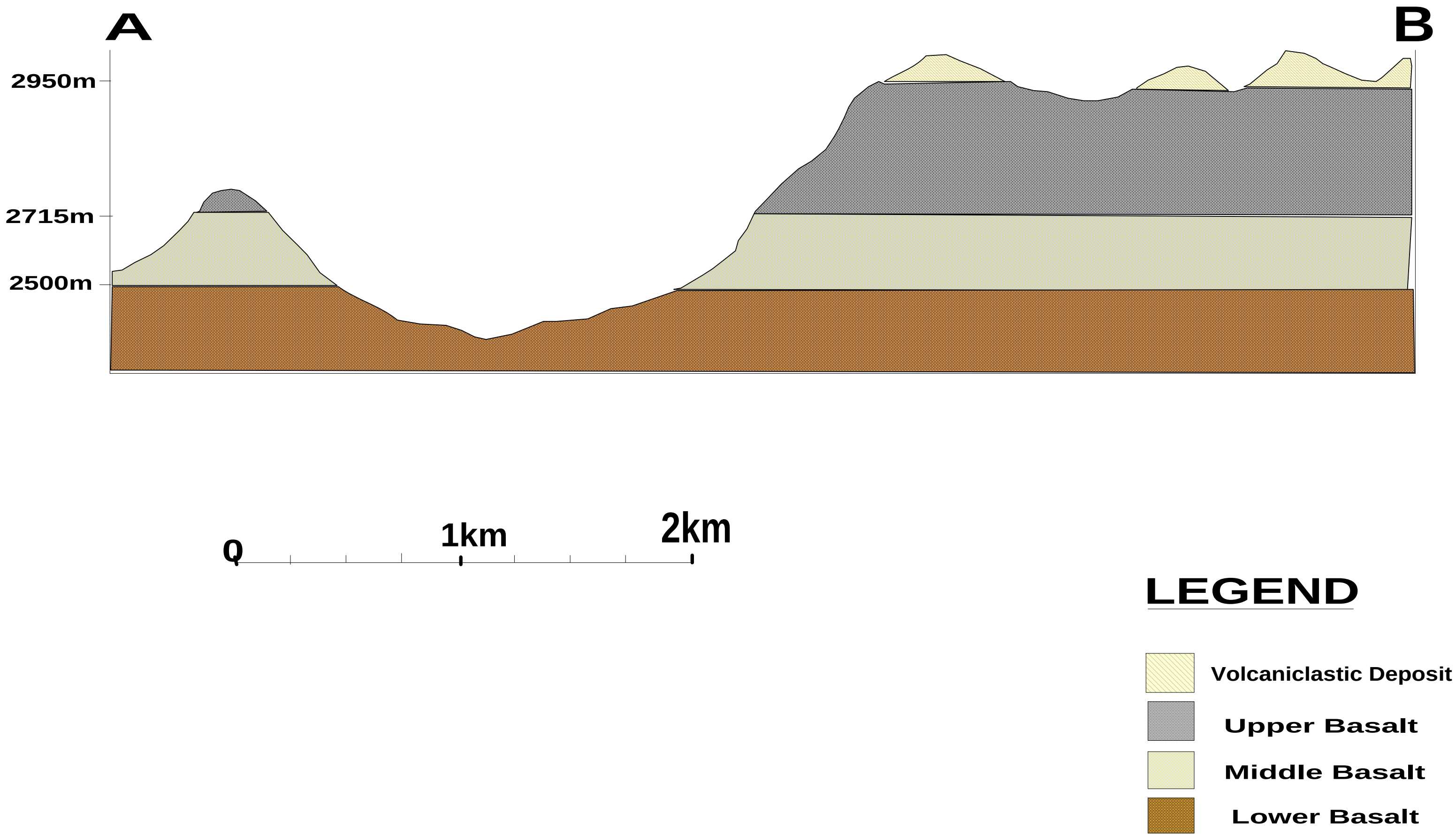


Figure 3.2 Geological Cross-Section Along Line A-B of the figure 3.1

A/ Lower Basalt (LB**)**

This formation is characterized by intrinsic dark-to-dark gray color, fine-grained texture. This may be due to olivine poor groundmass of the basaltic lava flow. The rock is outcropped along gully and stream channels. Less weathered and fresh outcrops are found along stream gorges.

The top part of this lava flow contains deeply weathered, altered and modified materials, which is typically colored in red, yellow and green by ferruginous clays iron oxide pigments. This part of the lower basalt may indicate an unconformity. This unconformity may results from a change that causes deposition to cease for a considerable span of time. It constitutes an unknown amount of geologic time that elapsed between the cessation of deposition of the underlying basaltic lava flow and the overlying middle basalt. The thickness of this formation within the study area is about 140m.

B/ Middle Basalt (MB)

This formation consists of stack of basaltic lave flows, ignimbrite & loosely welded tuff, in the typical locality within the study area. The thickness of this formation within the study area is about 165m.

The basaltic lithology of this formation is composed of successive lava flows up to 5 (five) in number and locally characterized by open to tight columnar jointing that may indicate variable stress released during emplacement. This unit is highly exposed along very steep hillsides and stream gorges. Macroscopic field observation of this basaltic unit generally encountered is aphanites or fine-grained basalts with phenocrysts of pyroxene and plagioclase crystals within the black matrix or groundmass of the rock. Almost the lower part of this basaltic stack/pile is inhibited by spherical vesicular cavities. These holes in the rock may be the result of gas bubbles being trapped in the rock as it cools.

Intercalated and somewhat welded glassy tuff (5-20 meters thick) characterizes almost the lowermost portion of the basaltic lava flows. It is yellowish gray dominated by glassy texture.

The ignimbrite is the basal unit of the middle basalt formation. Fresh ignimbrites show light greenish color with variable degrees of weathering. Columnar joints are common. There is generally a lack of internal stratification. The rock is dense. According to thin section description of this ignimbrite rock made by Taffesse (2002), phenocrysts of alkali feldspars, plagioclase feldspars and quartz are major constituents of this pyroclastic deposit. Hornblende, biotite and other opaque minerals also share the compositional skeleton of the rock.

C/ Upper Basalt (UB)

The upper basalt formation from bottom to top consists of vesicular & finely laminated light colored rhyolitic - ignimbrite, pitchy luster rhyolitic glass and dark - gray aphanitic basalt (plate 3.1).

The slightly weathered and cliff forming rhyolitic - ignimbrite with a thickness range of approximately 2-20m underlies the upper basalt formation. This lithostratigraphic unit is dense, fine –grained typically porphyritic and commonly exhibiting flow texture with phenocrysts of quartz and alkali feldspar (sanidine) in a glassy and cryptocrystalline ground mass. It is largely composed of volcanic glass. The upper part of this rhyolitic – ignimbrite (2-3m thick) inherited typical fine –flow –banded structure from its parent magmatic material and this gives the rock somewhat a platy cleavage. The lower most portion of this rhyolitic – ignimbrite rock unit (2-3m thick) is vesicular. As the rhyolite was extruded from deep within the crust, the sudden release of pressure caused gas to separate from the fluid magma and may form large vesicles or cavities.

Both the vesicular and very finely laminated textures of the same cliff forming rhyolitic – ignimbrite flow are observed alternating with each other from bottom to top. Size of vesicles (up to 10cm diameter) increases upward. They are not filled with opal (plate 3.2).

During feldspar decaying almost at or near the ground surface, clay and silica (SiO_2) bearing minerals should be constantly in contact with the small amount of water retained in spaces between grains in soils or loosely consolidated volcanic rocks. For the retention of rain water containing a relatively small amount of dissolved carbon dioxide (carbonic acid) in the spaces between grains or cleavage plains in the rhyolitic glass, the underlying rhyolitic - ignimbrite is very finely laminated and used as an impermeable/impervious (incapable of transmitting fluids under pressure) medium for downward percolation /infiltration of surface or groundwater.

The rhyolitic glass with the characteristic appearance of dull and/or pitchy luster, a rather flat fracture as well as completely decayed and altered of its top part (red and somewhat creamy colored) overlay the rhyolitic - ignimbrite rock unit. The top yellowish - gray and red colored clay mineralized material (outer zone) and the intermediate moderately weathered parts of the rhyolitic glass have an approximate thickness of 0.5m and 2.5m respectively. Both of them are formed by the break up and alteration of the primary rhyolitic glass. The top is usually completely weathered and the opal nodules within it are agatized (being a variegated chalcedony frequently mixed or alternating with opal/ and characterized by colors arranged in alternating stripes or bands), and some are empty opal pockets. Only the topmost part of inner zone rhyolitic glass part (almost 0.5m) is opal bearing though almost 70 - 95% of the nodules are completely weathered (plates 3.3&3.4).

The upper basalt formation is found overlying the rhyolitic glass. The base of this unit that has a thickness range of almost 2 – 10m and just next to the underlying mantle of the rhyolitic glass is intensely weathered (plate 3.6a). The color of this continuously weathering basaltic material is red, bluish and greenish gray. This weathered material allows easy infiltration of ground and surface water during rainy season. Besides, this pile of basalt flows forms cliffs, steep and gentle slopes. The waist of this unit is locally characterized by tight and near to open columnar jointing.

Consecutive lava flows of the lower most part of the upper basalt unit exhibit weathering of their respective upper surface characterized by red paleosols.

This unit is overlain by highly weathered trachytic basalt of 5 - 10 meters thickness range. Though the proportion is locally variable, the upper basalt contains somewhat coarse-grained phenocrysts of olivine, light colored feldspars, zeolites and quartz embedded in the matrix of microscopic crystals or grains/groundmass. This rock unit is said to be porphyritic in texture.

Plat 3.1 Panorama of Yita/Ketanit that shows the lithostratigraphic position of opal bearing zone.

Plate 3.2 Cliff forming rhyolitic - ignimbrite with alternating fine vesicles & finely laminated layers in Yita locality

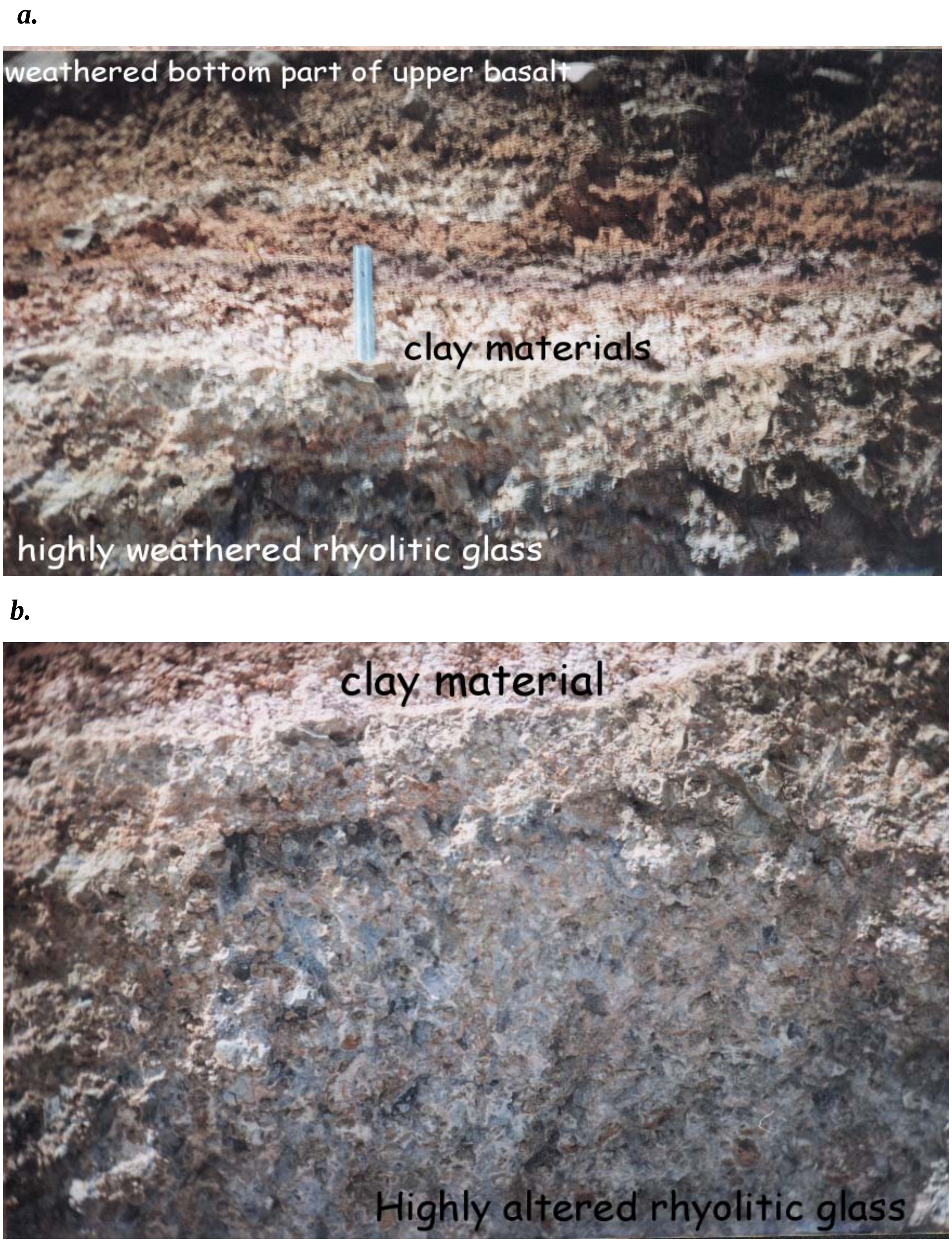


Plate 3.3 Depth section of highly altered rhyolitic glass (a&b) Yita locality

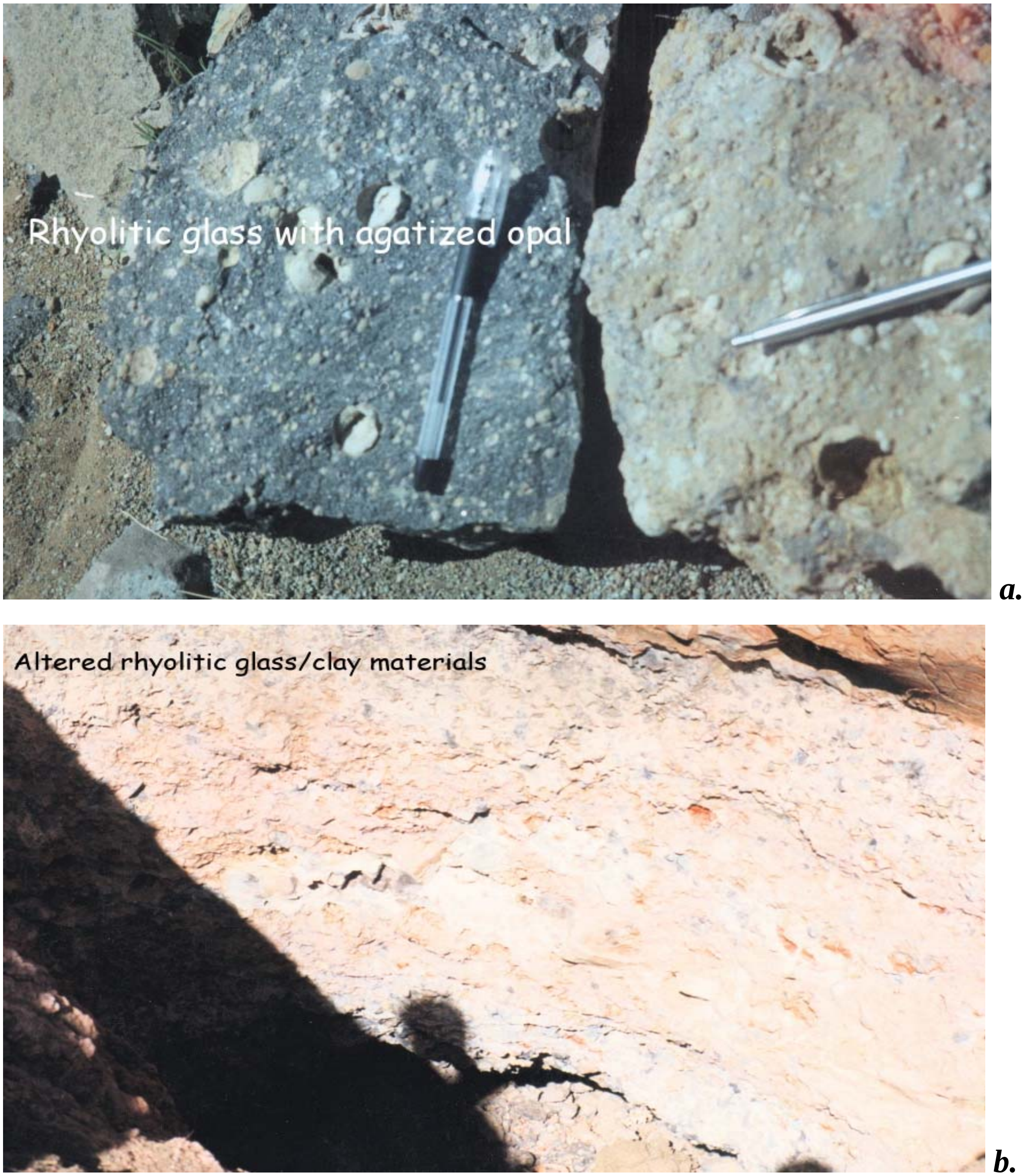


Plate 3.4 (a) Fresh rhyolitic glass spotted with some weathered opal nodules and opals nucleations (b) depth section of intensely altered rhyolitic glass.

D/Volcaniclastic Flow Deposits (VFD)

Substantial amount and alternating sequence of volcaniclastic flow deposit overlay the upper basal formation in the study area. These flow deposits are identified based on texture. Brief descriptions of the principal kind of deposits follow from bottom to top.

Thin bed base - surge deposit is the basal unit of volcanicalastic flow deposit formation in the study area. It shows somewhat well developed planar and cross bedding). According to Tucker (1988), base - surges are sub aerial flows formed by phreatic and phreatomagmatic eruptions (where magma comes into contact with water). The distinguishing feature for base - surge deposits is the presence of stratification, planar and cross bedding. There fore, the same is true with the deposits of the study area.

Lithified aggregates of poorly sorted angular fragments (blocks) and very fine material (with much ash), i.e. tuff - breccias, overlay the underlying base - surge deposits. The parent materials of the large rock fragments (blocks) embedded in the fine groundmass (ash) may be previously solidified lava flow. This tuff breccia is chaotic and unsorted and contains debris ranging from the finest ash to great blocks of either cognate or non-cognate accidental rocks. The size distribution of these several types of pyroclastic materials shows striking contrast. The rock fragments have about 80cm maximal sizes. Though there is local variation, the thickness range of this volcaniclastic flow deposit is 10-30 meters. An ignimbrite member of the clastic sediment formation that include rock types like welded tuff & non- welded tuff (sillar); intercalated rhyolites characterized by light color, aphanitic texture, smooth and curved surface fracture, fine grained ashes with light and yellowish gray color occurred at the top stratigraphic column of the volcaniclastic flow deposits.

3.3 STRUCTURES

The study area is situated at the southwest margin of the Afar Rift where the NNW – SSE trending oldest mega, fault structures are regionally very frequent. Faults /fracture – zones of the area under consideration are present as single planar units with parallel sets of planes along which movement has occurred. The faults are usually normal type features, i.e. the major dip – slip components that contain the hanging walls are on the down throw sides. Adjacent rock surfaces have obvious differential, displacements with a range of almost 30 - 50 meters. Fault occurrences are obviously observed within the ignimbrite and rhyolite lithologic units.

Three types of fault /fracture systems traverse the study area. These have NS, SW and NW general attitudes /directions. All have dip directions almost towards the west. Perennial springs in the study area occur within these fracture systems.

3.4 PETROGRAPHY

Several representative rock and opal samples have been collected in the field (annex A). The samples are made to cover the entire stratigraphic sections of the study area, out of which the rock samples composed of basalt (SA-08, SA-14, SA-45/2, SA-48A, SA-49, and SA-51), ignimbrite (SA-10A), rhyolitic ignimbrite (SA-20), fresh rhyolitic Glass /volcanic glass (SA-34, SA-35, SA-45/4, SA-47B) and altered products of rhyolitic glass, i.e. clay material (SA-45/3, SA- 47A and SA-48B) and opal samples (SA-55 and SA-56) have been examined for their mineral assemblages and textural characteristics using a petrographic microscope. Characteristic minerals of both volcanic rocks and mantle rocks of the weathering products have been identified. Major and trace element analysis have not made for some samples such as basalt (SA-08A, and SA-14A) ignimbrite (SA-10A) and fresh rhyolitic glass/ volcanic glass (SA-34 and SA-35), but they have been only microscopically examined. Besides, photomicrographs of all rock samples have been also taken.

Summary of petrographic description for 17 (Seven teen) volcanic rock samples of the study area, is presented in table 3.1.

Volcanic rocks of the study area (koste – Amba and Gift - Mariyam) can be divided into five main groups based on petrographically identified mineral assemblages and textural characteristics: (a) Basalt (b) Ignimbrite (c) Rhyolitic – Igmimbrite (d) Fresh Rhyolitic glass (e) Altered rhyolitic glass.

a) Basalt: All six samples (lower basalt, SA – 08A, middle basalt, SA – 14A, upper basalt; SA- 45/2, SA- 48A, SA- 49 and SA-51) contain in order of abundance plagio clase, pyroxene, opaque minerals and volcanic glass in common. Two samples from upper basalt such as SA – 48 and SA- 49 contain olivine somewhat to a greater and lesser modal volume respectively. Besides, SA-14A (middle basalt) and SA -49-upper basalt contain some amount of calcite as one of their altered products (secondary mineral). It is common that olivine is found in basalt in phenocrysts. Calcite is a common constituent of altered basic igneous rocks, where it develops by alteration of calcium silicates. Fluidal texture is characteristics of almost all samples. This shows that the flow continues during the cooling and crystallization of lava. The results of the petrographic analysis show alignment of platy feldspar laths. Cumulophyric (glomerophyric) texture. Plagioclase and pyroxene crystals are found clustered in groups, and it is exhibited in some basalt samples (plates 3.5 – 3.7)

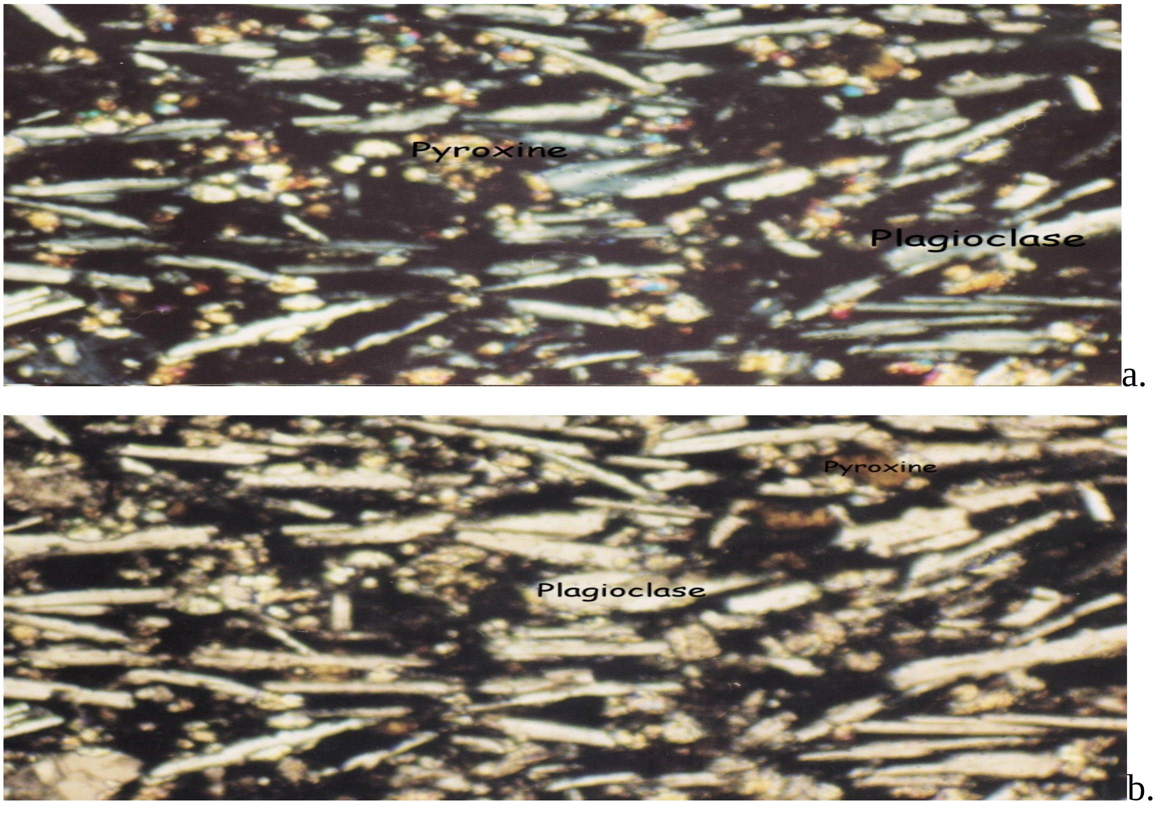


Plate 3.5 Photomicrographs of lath plagioclases that show sub-parallel to parallel alignments in a plagioclase, pyroxene, and opaque minerals groundmass, SA-08A, 10X, light – (a) PPL (b) XPL.

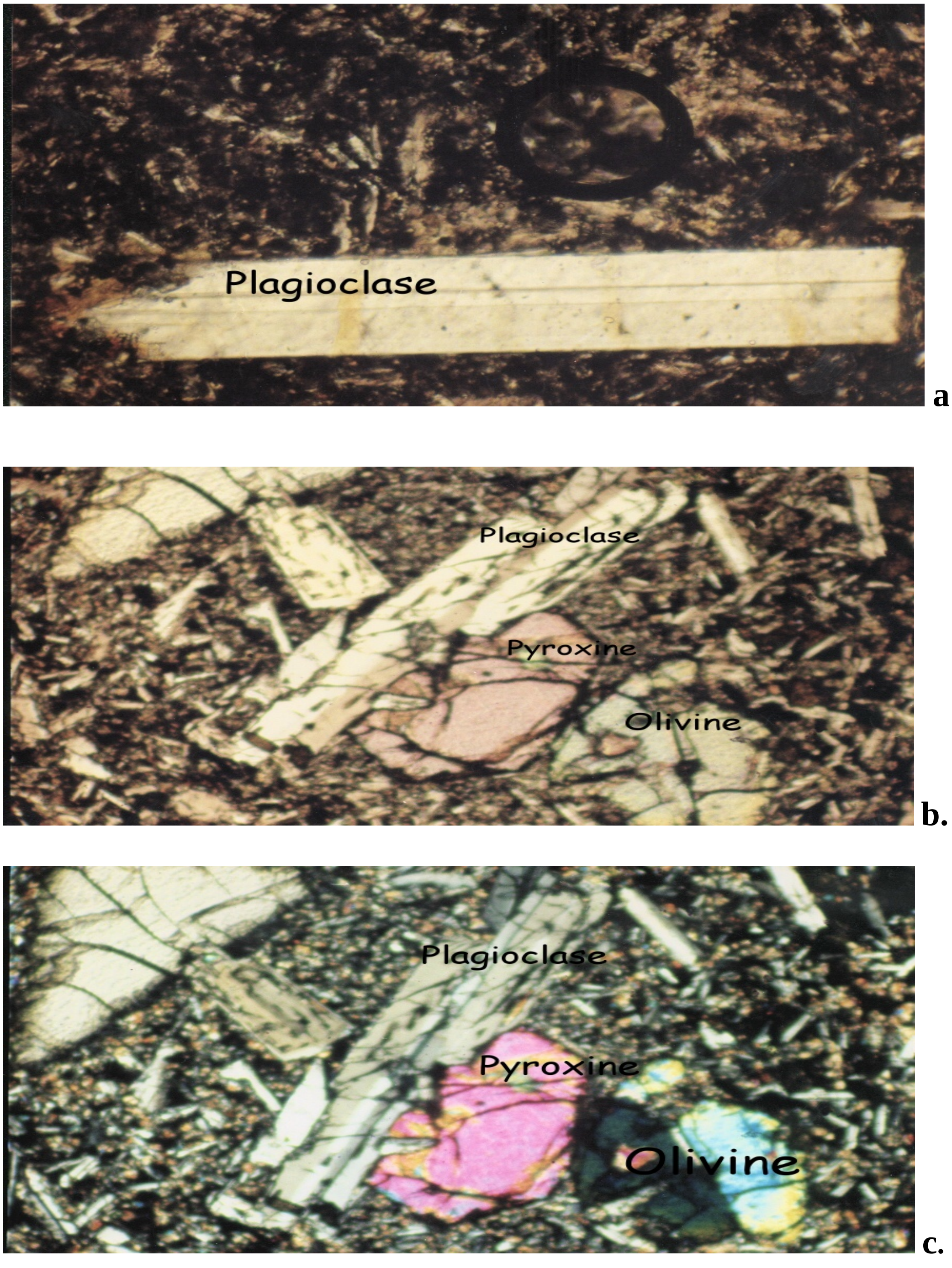
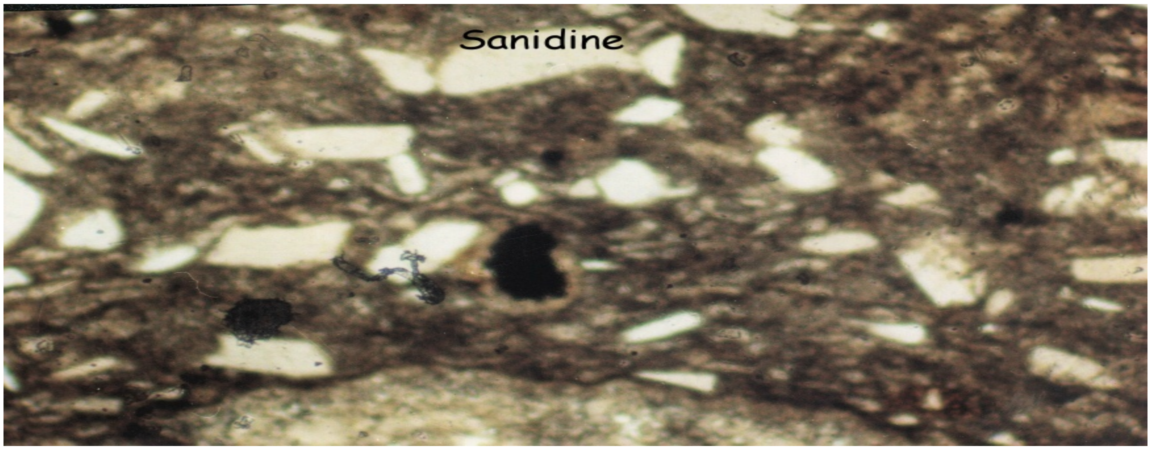


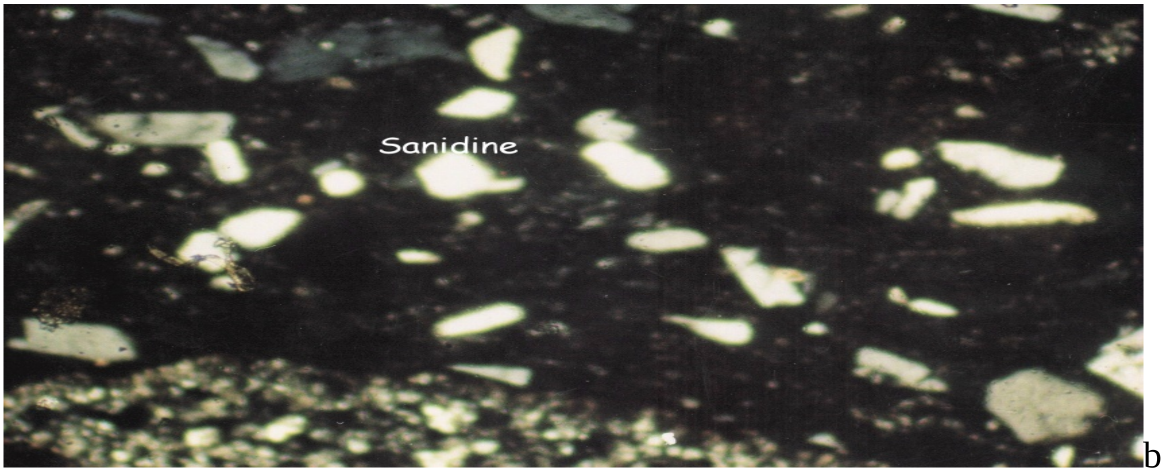
Plate 3.6 (a.) Photomicrograph of lath plagioclase embedded in a groundmass composed of plagioclase, pyroxene and opaque minerals (SA-14, magnification – 10X, light-ppl). (b&c) photomicrographs of plagioclase, pyroxene and olivine embedded in a groundmass composed of pyroxene, plagioclase, and opaque minerals(SA-48A, 5X , light – PPL & XPL respectively).

Plate 3.7 Photomicrographs of (a) plagioclase, pyroxene, and olivine crystals embedded in a groundmass, cumulophyric texture, SA-49, 10X,light-XPL; (b) plagioclase, pyroxene, and olivine crystals embedded in glassy groundmass, fluidal texture, SA-51, 10X,light-XPL; (c) calcite embedded in pyroxene, lath plagioclase, and opaque minerals made groundmass, SA-49, 10X,light-XPL.

b) Ignimbrite: This ignimbrite is the basal unit of the middle basalt. Petrographic examination of this pyroclastic rock shows irregularly distributed and flattened crystals and crystal fragments of sanidine embedded in almost fine-grained glassy ground mass. The examined rock sample (SA-10A) is found to contain 30% sanidine, 59% rock fragments, about 1% pyroxene and trace amount of hornblende. The glass shards that made the groundmass are flattened. It is characterized by vitrophyric texture (Plate 3.8).



a.



b.

Plate 3.8 Photomicrographs of sanidine embedded in a glassy groundmass, SA-10A, 5X, light – (a) PPL & (b) XPL.

c) Rhyotitic - Ignimbrite: This lithologic unit is characterized by alternating vesicular (fine – coarse from bottom to top) and very finely laminated textures /structures in the field. The thin section examined is found to contain, in order of abundance, volcanic glass 53%, sanidine 10%, rock fragment 3%, opaque minerals 4%, chalcedony /opal 20%, zeolite 10% and trace amount of sanidine. The glass shards are characterized by some curved surfaces of fractures, flattened and welded appearances. The sanidine crystal is found to be spotted with star- like fibrous crystals. Zeolites are considered to be developed at the expense of sanidine crystals. It is replacing sanidine crystal (plate3.9).

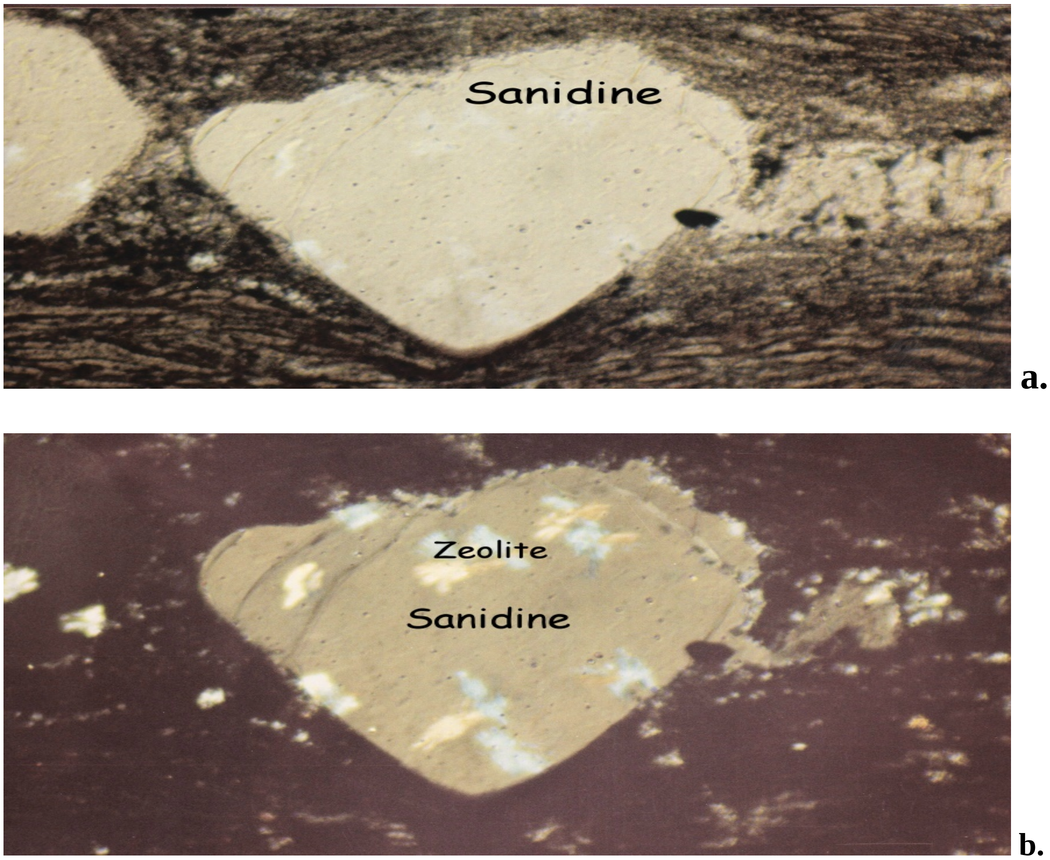


Plate 3.9 Photomicrographs of zeolite spotted sanidine embedded in a glassy groundmass of a rhyolitic – ignimbrite rock, SA-20, 10X, light – (a) PPL (b) XPL.

d) Fresh rhyolitic – glass: It is found to contain volcanic glass 68-80%, sanidine 5-13%, pyroxene about 4%, opaque minerals 1-2% and rock fragments about 2%. The glassy groundmass is characterized by phenocrysts of euhedral sanidine and subhedral pyroxene. The rim of the pyroxene crystal shows corrosion, i.e. characteristics of alteration. The volcanic glass is found to enclose crystals and crystal fragments of sanidine and pyroxene. The volcanic glass shards show fluidal texture of the rock (plate 3.10).

e) Altered Rhyolitic – glass: The alteration product is found to contain mainly volcanic glass 65% on average, sanidine 10-15%, opaque minerals 2-13%, zeolite 5-7%, rock fragments 2-10% and trace amount of pyroxene minerals. Pyroxene crystals (phenocrysts) are relatively more abundant in the fresh rhyolitic glass/volcanic glass than in the altered one. These phenocrysts are less abundant in the altered rhyolitic glass/volcanic glass. The main primary mineral sanidine crystal has a glassy appearance and it is tabular in shape. Large phenocrysts of sanidine crystals are observed. All the samples are found to have vitrophyric textures. The observed secondary fibrous zeolite minerals have crystallized at the expense of the primary mineral sanidine. Small granular and fibrous zeolite crystals are randomly enclosed within the large and tabular crystals of sanidine (plate 3.11).

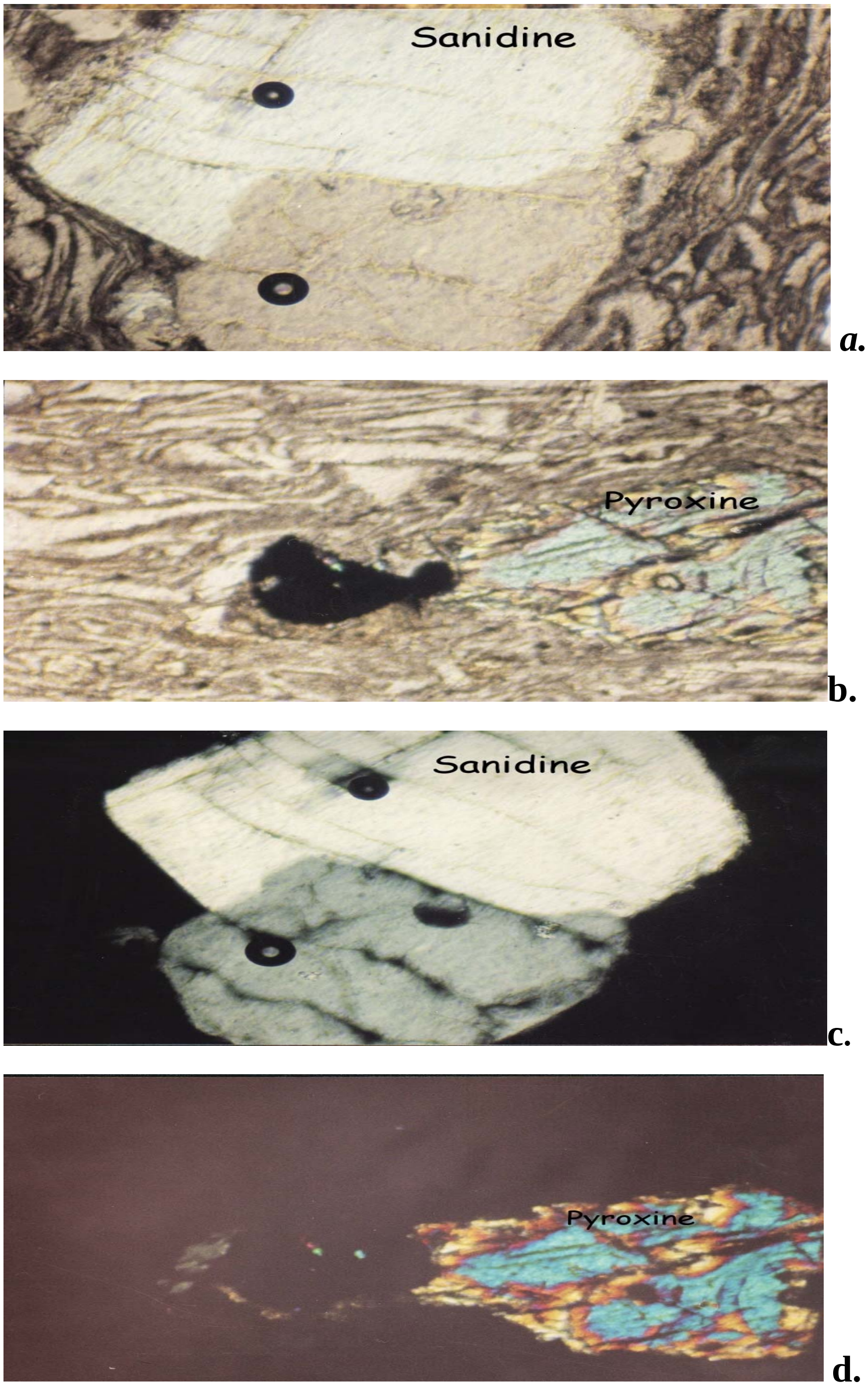


Plate 3.10 Photomicrographs of sanidine & pyroxene crystals embedded in a glassy groundmass, SA – 45/4(fresh rhyolitic glass), 10X, (a&b) PPL, (c&d) XPL.

Plate 3.11 Photomicrographs of sanidine crystals spotted with zeolite crystals embedded in a fine-grained groundmass, SA – 45/3(altered rhyolitic glass), 10X, (a) PPL, (b&c) XPL.

Table 3.1 Peterographic summary for representative volcanic rock samples (Fresh & weathered) of Koste – Amba & Gift -Mariyam localities.

Identification	Modal Composition
Sample No.-SA-10, SA- 20, SA-45/4,SA-47B, SA-34 (all are from ketanit/yita) & SA-35 (embachobert/gift). Rock type – Ignimbrite and/or Rhyolitic glass.	The rock is compositionally made up of 2-3% rock fragments, about 12% devitrified volcanic glass (SA -45/4 & SA-47B), about 4% pyroxene (SA-45/4 & SA-47B), 1-4% anhedral to euhedral Fe-oxide (opaque) (SA-45/4 & SA-47B), 53-15% volcanic glass, 5-13% euhedral sanidine, opal & chalcedony 10% (SA – 35). The special case is about 30% sanidine in SA-10A. Zeolites are developed at the expense of sanidine (SA-20). The rock fragments are of rhyolite and pumice. The whole –rock texture is found to be vitrophyric.
Sample No - SA-45/3 (yita/ zala bahir), SA-47A (yita/ketanit). Rock type – Clay material.	The rock samples are compositionally made up of 2 - 5% rock fragments, 2 -5% euhedral to subhedral Fe-oxide, about 5% radial zeolite (SA-45/3), 10-13% euhedral to subhedral sanidine, about 10% microcline (SA-47A), 60-70% volcanic glass and trace amount of subhedral to euhedral plagioclases as well as subhedral pyroxene (SA - 47A). The two samples are characterized by vitrophyric textures. The groundmass is mainly composed of welded glass shards. The rock fragments are pumice and rhyolite. Phenocrysts of sanidine and microcline exist in the groundmass. Zeolite crystals are developed at the expense of sanidine minerals.
Sample No. SA-48B (yita). Rock type – this highly weathered Product is considered to be recently formed sandstone.	This rock sample is made up of feldspar 25% clay 20% sanidine 15% Fe – oxide (opaque) 13% quartz 10%, zeolite 7% rock fragments 10% and trace amount of zircon. The texture of the rock sample is found to be grain supported. Grains are poorly sorted and not compacted. Clay materials and Fe-hydroxide are cementing elements in the framework of the rock. Rock fragments are Rhyolite and pumice. Zeolites crystallize at the expense of feldspars (mainly alkali).

Sample No - SA- 08A, SA-14A, SA-48A& SA- 49(all four are from yita & SA –51(gift). Rock type – Basalt.	The rock samples are composed of 1-13% volcanic glass, 10-17% euhedral – anhedral Fe – oxide, about 12-17% an hedral - euhedral olivine, 30-38% anhedral - euhedral pyroxene (excluding SA- 45/2), 22-43% lath shaped plagioclase feldspars, 3% chalcedony and 3% calcite (SA-14A). The textural composition is found to be porphyritic (SA-48&SA-49) and fluidal (SA – 08, SA – 45/2 & SA-51) textures. The groundmass is composed of pyroxene, plagioclase and Fe –oxide in both the preceding textural features. In fluidal texture, lath shaped plagioclase shows preferential parallel alignment. The groundmass of both textural features is made up of pyroxene, plagioclase and Fe – oxide. Phenocrysts are mostly made up of tabular plagioclase, euhedral olivine and pyroxene.
Sample No. SA-55 & SA-56 (yita/ketanit) Rock type – opal nodule	The two opal samples are composed of 88-95% opal (amorphous) and 5-12% rock fragments. The texture is found to be glassy. The groundmass is mad up of mono - mineral opal that is rimmed by ignimbrite rock fragments. The whole opal make up consists of glass shards (welded and flattened), pumice and crystals of quartz.

3.5 OPAL ASSOCIATED DEPOSIT TYPES

Four clay materials samples (SA - 45/3, SA - 47A, SA - 52B & SA - 52C), were sent to university of cagliari/Italy for qualitative analysis using x - ray diffraction techniques. These samples were collected from almost the surficial environment of highly altered topmost part of rhyolitic glass that characterizes koste - Amba & Gift - Mariyam localities of opal bearing zones/seams.

The x-ray diffraction analysis has come up with the following results:

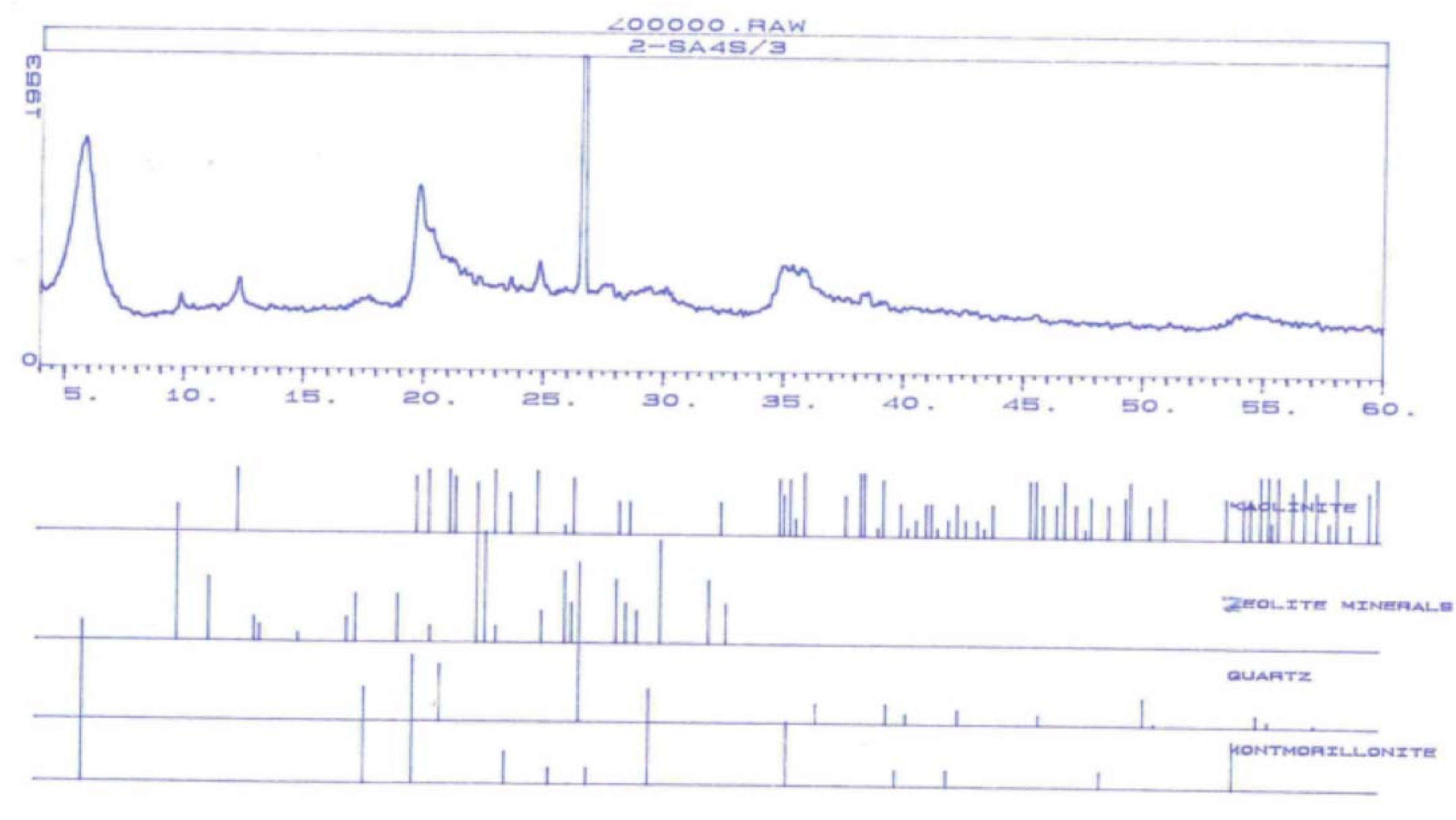
Sample SA – 45/3: Clayey material mainly composed of montmorillonite and zeolite minerals (mordenite group) with kaolinite and subordinate quartz.

Sample SA – 47A: Clayey material composed of montmorillonite and zeolite minerals (mordenite group).

Sample SA – 52B: Clayey material composed of montmorillonite and zeolite minerals (mordenite group)

Sample SA – 52C: Clayey material composed of montmorillonite, halloysite (kaolinite group), zeolite (philippsite group) and cristobalite.

The samples generally characterize associated deposits of clay and zeolite mineral materials composed mainly of montmorillonite, zeolite (mainly mordenite & philippsite in one sample), kaolinite, cristobalite and subordinate quartz (figure 3.3/a - d).



Z00000.RAW
2-SA4S/3
1953
0
5.
10.
15.
20.
25.
30.
35.
40.
45.
50.
55.
60.
KAOLINITE
ZEOLITE MINERALS
QUARTZ
MONTMORILLONITE

Figure 3.3a

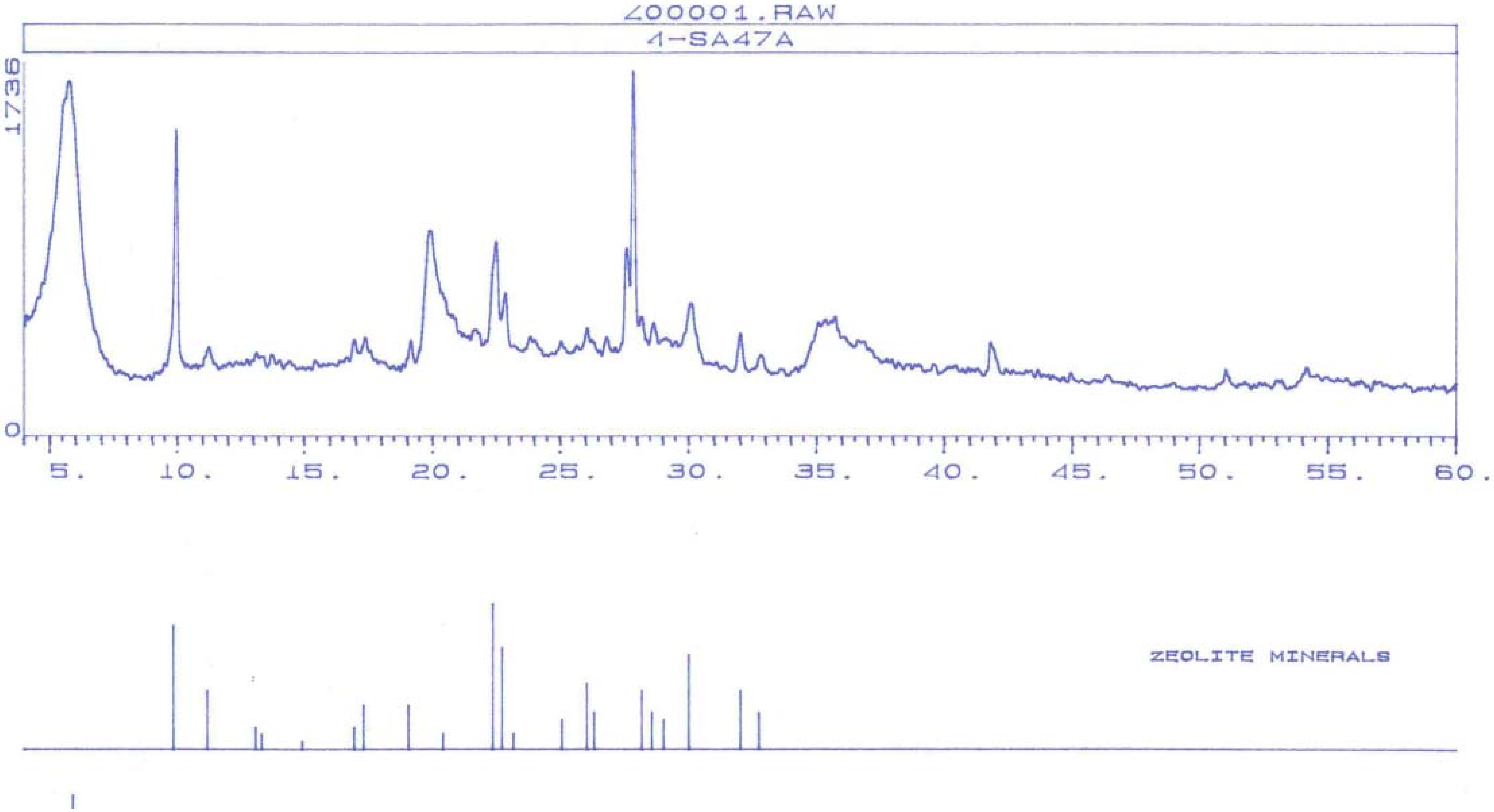

400001.RAW
4-SA47A
1736
0
5.
10.
15.
20.
25.
30.
35.
40.
45.
50.
55.
60.
ZEOLITE MINERALS

Figure 3.3b

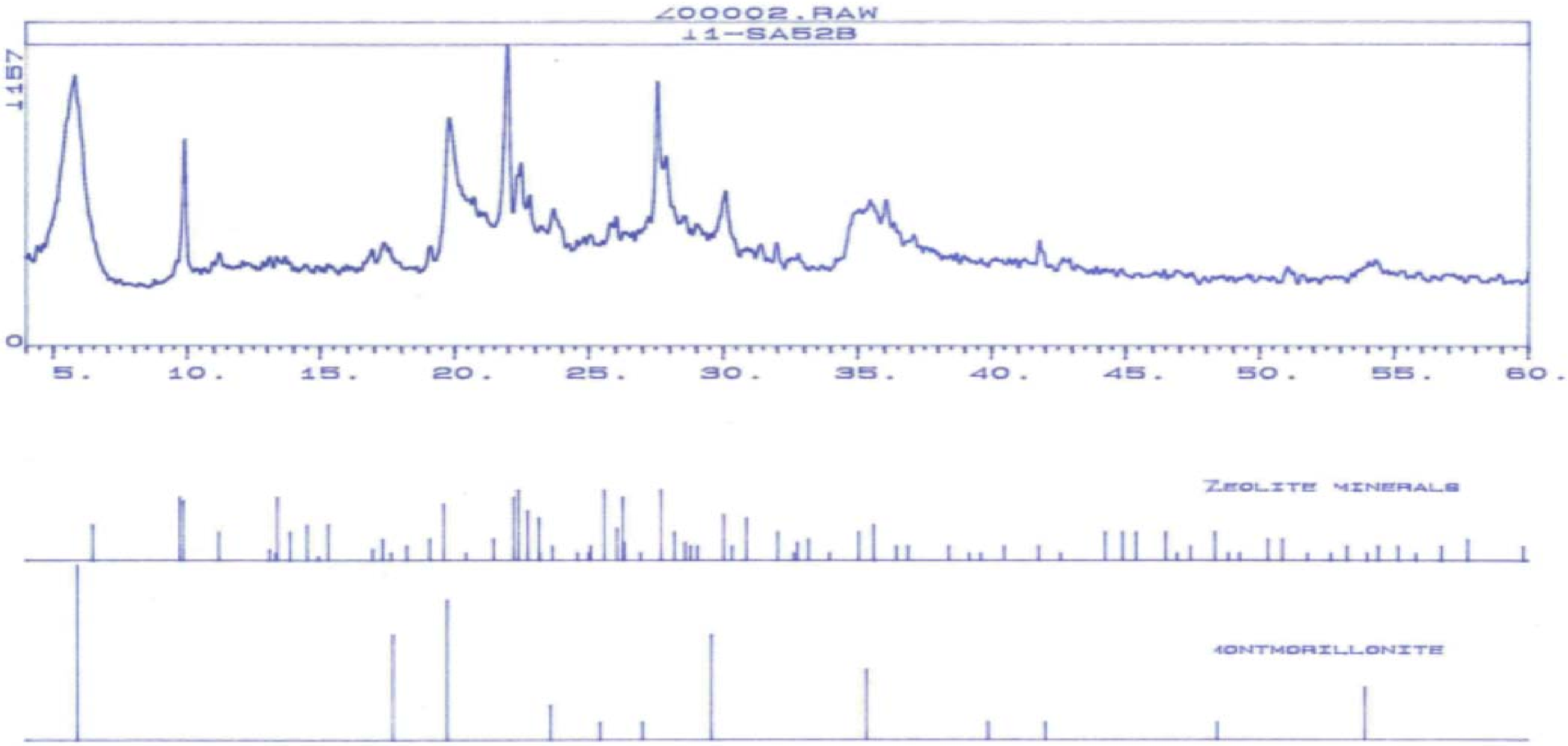

Z00002.RAW
11-SA52B
1157
0
5.
10.
15.
20.
25.
30.
35.
40.
45.
50.
55.
60.
ZEOLITE MINERALS
MONTMORILLONITE

Figure 3.3c

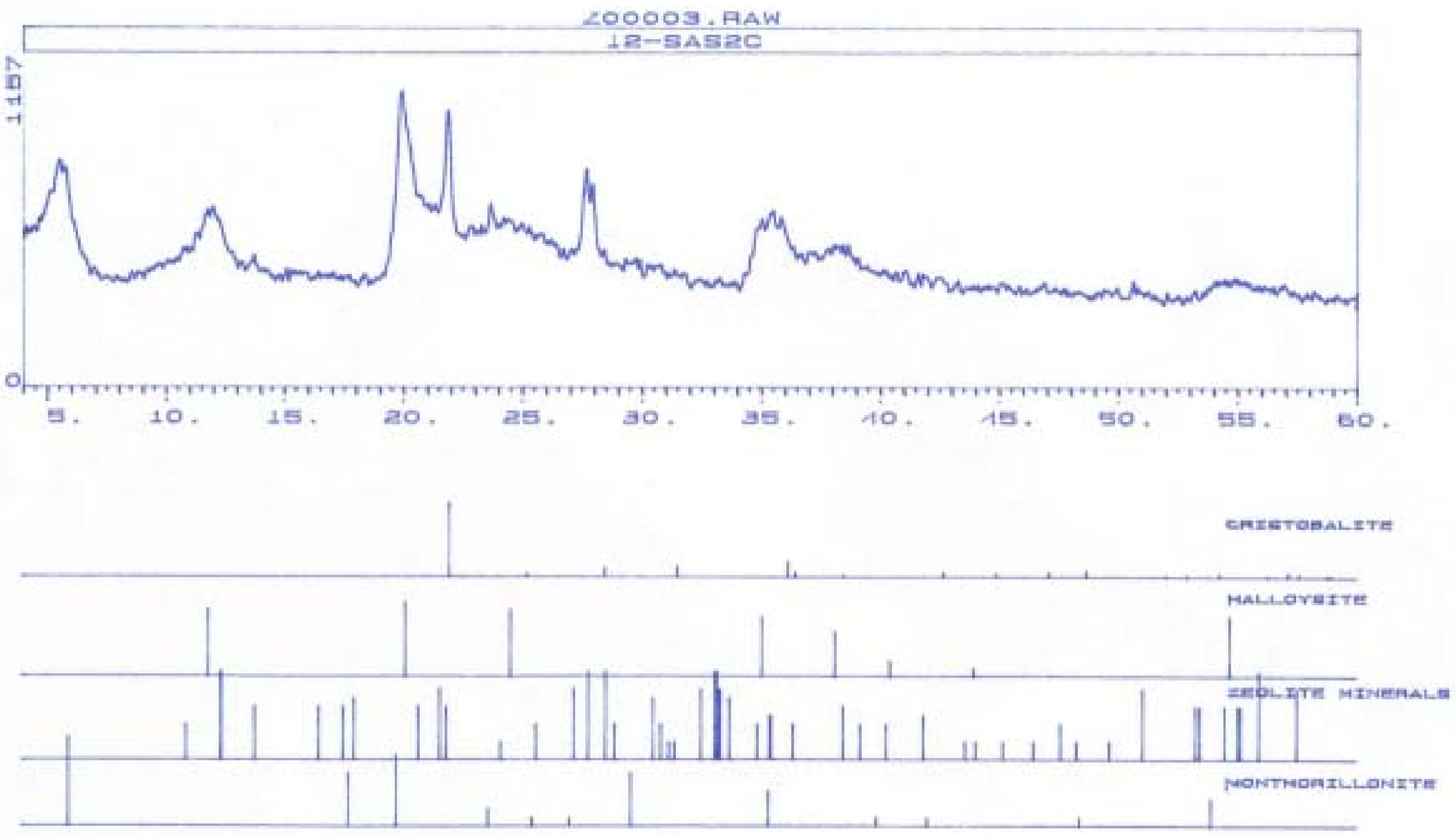

Z00003.RAW
12-SAS2C
1157
0
5.
10.
15.
20.
25.
30.
35.
40.
45.
50.
55.
60.
CRISTOBALITE
HALLOYSITE
ZEOLITE MINERALS
MONTMORILLONITE

Figure 3.3d

CHAPTER TWO

REGIONAL GEOLOGY

2.1 INTRODUCTION

Using previous studies as a springboard, four major rock units have been recognized in Ethiopia. They are itemized as the Precambrian metamorphic rocks along with associated syn - to - post tectonic intrusions which form the basement complex, the late Paleozoic to Mesozoic marine and continental sediments, the Cenozoic basic and felsic volcanics, the volcano-sedimentary and volcano-clastic rocks that are associated with the Cenozoic volcanic. These rock assemblages share 23%, 25%, 34% and 18% of the total surface area of the country respectively.

Lower - Middle Jurassic reactivation of Neoproterozoic structures has formed NW –SE faults bordering the Mesozoic Ogaden aborted rift. These faults have subsequently affected the propagation pattern of Cenozoic rift forming faults. The E-W to ENE- WSW striking fault system has also resulted from Cenozoic reactivation of Neoproterozoic structures. Among them, the E-W trending Ambo fault zone separates the east facing large fault zone forming the Afar western margin from the roll –over style of the western margin of the MER. The Wonji fault belt (WFB) is inherited from the Pan - African N-S to NNE-SSW shear and suture zones which were reactivated as dextral transtensional faults due to the NW-SE Cenozoic extension. It traverses the rift floor obliquely and sometimes extends up to the southeastern Ethiopian plateau (korme, 2003).

2.2 EVOLUTION OF THE NORTH – CENTRAL ETHIOPIAN VOLCANIC PLATUEA

The tectonic and volcanic activities that occurred in the Cenozoic era, i.e. the most recent of all the geologic eras, have a prominent influence in the building up of the existing landmass of Ethiopia and the surrounding area. Therefore, an immense uplifting of the Arabo - Ethiopian landmass that occurred at the beginning of Cenozoic era, i.e. the tertiary period, resulted in the terrestrial fracturing and out pouring of huge quantity of lava that form flood basalts in Ethiopia (Doilicho et al. 1991).

Eruption of the Ethiopian and east African plateaus started some 45Ma, before formation of the east African rift system, and they are generally attributed to one or two mantle plumes beneath northeastern Africa. The Afar plume, centered in northeastern Ethiopia, eventually resulted in the separation of Arabia from East Africa (Burke, 1996). The northeast African flood basalt plateaus are the largest of several Mid –Tertiary large igneous provinces (LIPS) in Africa, none of which has hotspot tracks - a feature due to the relatively small motion of the African plate during this time. Nearly 1 x 10^6 km^3 of mixed tholeiitic and alkaline mafic volcanic were erupted in this area in the last 45 Myr. The bulk of the Ethiopian and east African basalts, however, were erupted in ≤ 1Myr at 30Ma (Hofmann et al. 1997, Pik et al. 1998, 1999), and the remainder of those basalts was erupted chiefly at 17-23 Ma. The volcanic in these plateaus are mainly tholeiitic with some transitional alkaline members. Both plateaus are overlain by large, chiefly alkaline, shield volcanoes with ages ranging from 30 to 15 Ma (Condie, 2001).

Based on the aforementioned findings and in accord with Ayalew et al. (2002), Ethiopian continental flood basalt (CFB) province (~30Ma, > $3X10^5km^3$), within which the study area situated was formed as the result of the impingement of the Afar mantle plume beneath the Ethiopian lithosphere. This province includes major sequences of rhyolitic ignimbrites generally found on top of the flood basalt sequence. Their volume is estimated to be at least $6x10^4km^3$, which represents 20% of that of the trap basalts.

The Ethiopian plateaus bordering the rift and which includes the study region consists of a thick succession of flood basalts and lesser amounts of rhyolites overlain by a huge amount of ignimbrites.

According to Hofmann et al. (1997), immediately following the flooding of the vast volcanic plateau basalt, a number of large shield volcanoes developed on the surface of the volcanic plateau, after which subsequent volcanism was largely confined to regions of rifting (kieffer et al., 2004).

Melting in large hotter – than - average parts of the Ethiopian super swell produced the flood basalts; melting in small compositionally distinct regions produced the magmas that fed the shield volcanoes. [2a]

Regarding the tectonic evolution of central eastern Ethiopian plateau, lifting of plateau occurred “block by block” starting from northern regions. Each block is defined by faults

---

[2a] 2a: htt://petrology.oxfordjournals.org/cig/content/abstracts/45/4/793

parallel and transversal to escarpment. Fissured silicic volcanism died out in uplifted regions. While alkaline lavas built shield volcanoes along faults (Zanettin, 1992).

2.3 GEOLOGICAL SETTING OF NORTH - CENTRAL ETHIOPIAN PLATUEA

The study area is situated in the Cenozoic continental flood basalt province of North – Central part of Ethiopian plateau by adjoining the southwestern margin of Afar rift In Ethiopia, this huge volume of lavas (about 350,000 km^3) which forms a pile up to 2000m thick and covers more than 600,000km^2 (Mohr and Zanettin, 1988) were erupted 30 Ma, prior to significant extension (Fig 2.1) (Courtillot et al., 1987; Hempton, 1987; Justin and Hucho, 1992). Besides, the flood basalt province of Ethiopia includes major sequences of rhyolitic ignimbrites generally found on top of the flood basalt sequence.

The flood basalts have uniform mineralogical and chemical compositions. Most have aphyric to sparsely phyric textural characteristics, and contain phenocrysts of plagioclase and clino-pyroxene with or without olivine. Most have tholeiitic to transitional compositions (Mohr, 1983a; Mohr and Zanettin, 1988; Pik et al., 1998). Felsic lavas and pyroclastic rocks of rhyolitic, or less commonly, trachytic compositions are found interlay ered with the flood basalts, especially at upper stratigraphic levels (Ayalew et al., 1999). Pik et al., (1998, 1999) classified the basaltic rocks into various kinds based on trace element and Ti concentrations. They found out a suite of “low-Ti” basalts (LT) character sized by relatively flat rare earth element (REE) patterns and low levels of Ti and incompatible trace elements. These rocks are limited to the northwestern part of the flood basalt province. Alkali basalts with higher concentrations of incompatible elements and more fractionated REE patterns –“high-Ti” basalts (HT1 and HT2) are situated to the south and east(where the study area is situated)(fig 2.1). The HT2 basalts are slightly more Magnesia than the HT1 basalts and usually are rich in olivine ± clinopyroxene phenocrysts. They have higher concentrations of incompatible elements and show extreme fractionation of REE. The post Trap volcanism signatures, i.e. the shield volcanoes, are a conspicuous features of the Ethiopian plateau. The shields are found to be formed predominantly of volcanic rocks with alkaline compositions. The basal diameters of the shields range from 50 to 100 km and Ras Dashan (4533m a. s. l.)

is the present summit of the eroded simien shield, i.e. the highest point in Ethiopia. This peak soars almost 2000m above the top of the flood basalts, which lies at about 2700m in the northern part of the plateau. There are other smaller shields (in both diameter and height above the flood basalt plateau) with their respective ages (figure 2.1).

The lava flows of the shield volcanoes are thinner and less continues than the underlying flood basalts. Besides, they are more porphyritic, containing abundant and often large phenocrysts of plagioclase and olivine. Like the flood volcanic, the shield volcanoes are bimodal and contain sequences of alternating basalts, rhyolitic and trachytic lava flows, tuffs and ignimbrites, especially near their summits. The compositions of the lavas in some of the younger volcanoes (e.g. Mt Guna) are more variable and include nephelinites and phonolites (zanettin, 1993) in addition to alkali basalts.

The magmatic character of both the flood basalt and the shields varies from north to south and within each region, the character of the shield volcanoes match that of the underlying flood basalts.

The northern Ethiopian volcanic plateau is not a thick, monotonous, rapidly erupted pile of undiformed, flat-lying tholeiitic basalts but it consists of a number of volcanic centers of variable magmatic character and age.

The shield volcanoes are magmatically similar to the underlying flood basalts. The tholeiitic simien shield overlies tholeiitic flood basalts, and the alkaline choke and Guguftu shields overlie alkaline flood basalts. The change in volcanic style is driven not by a change in the compositions of the magma but probably by the tectonic setting and a decrease in magma flux.

As Zanettin (1974) has indicated it, a large iqnimberitic cover outcrops in the central - eastern portion of the Ethiopian plateau between Amba - Alaji and Debre - Berhan and along the Afar Margin. Its thickness is maximum in correspondence to the upper limit of the escarpment, and decreases until it disappear inland. As well as ignimbrite covers, the “Alaji Miocene Rhyolites”, within which the study area is situated, make up piles of thick compact flows stretching along the plateau/ escarpment boundary thinning rapidly both towards the plateau and towards the escarpment. The rhyolites and the basalts, which are interbedded among them in greater or lesser quantities, have been considered as products of a fissural volcanism (Oligocen – Miocene) linked to an approximately N-S tectonics and joined in a single series called “Alaji”. The Alaji volcanic, which characterize the surface geology of the study area, overlay and underlay respectively the continuously thick flood basalt and the huge volume of ignimbrite mass.

Rhyolites associated with high - Ti or low - Ti basalts are respectively enriched or depleted in titanium. Their trace element and isotope (Sr, Nd, O) Signatures (Nd^{143}/Nd^{144} and low $^{87}Sr/Sr^{86}$ ratios, compared to those of rhyolites from other CFB provinces) are clearly different form those of typical crustal melts and indicate that the Ethiopian rhyolites are among the most isotopically primitive rhyolites. Their major and trace element patterns suggest that they are likely to be derived from fractional crystallization of basaltic magmas similar in composition to the exposed flood basalts with only limited crustal contribution. Since Ethiopian high Ti-basalts have been shown to form from melting of a mantle plume, it is likely that Ethiopian ignimbrites, at least those that are Ti-rich, also incorporated material from the deep mantle (Ayalew et al., 2002).

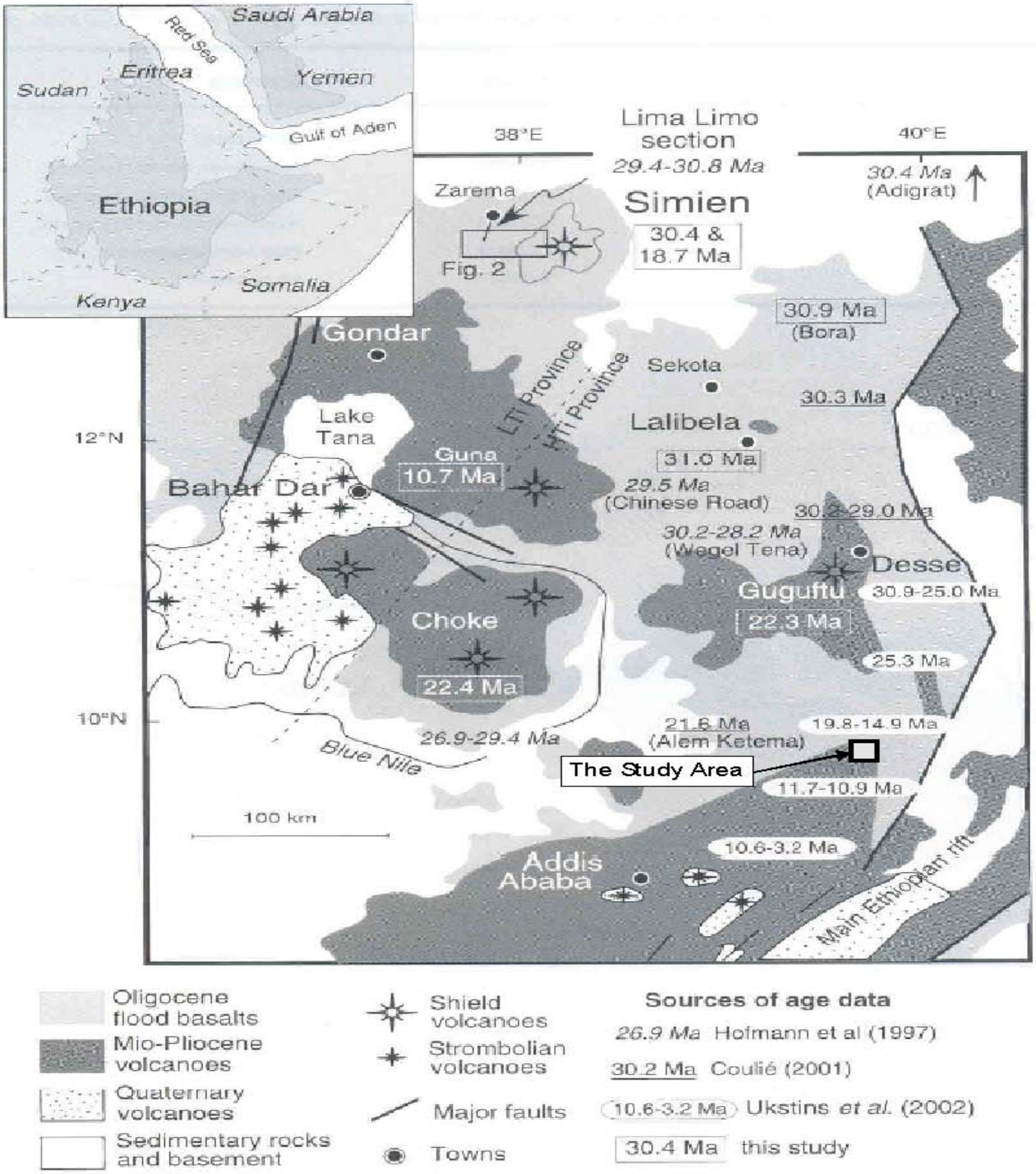


Figure 2.1 Geological map of the north - central part of Ethiopian plateau showing the extent of the flood volcanism and the location and ages of the major shield volcanoes. The dashed line shows the boundary between the LT and HT provinces. The inset shows the location of the Ethiopian volcanic plateau (gray) in the Horn of Africa (Adopted from Kieffer et al., 2004).

REFERENCES

Abbay Natural Resources Development PLC. (2000) Report on detail exploration of opal in Gift, Zeno and koste Amba of North Shoa (final), Addis Ababa, Unpublished.

Acocella, V., & Abebe, B. (2004) The Role of pre –existing structures, Origin,propagation and Architecture of Faults in the Main Ethiopian rift. **Gondwana Research, V. 7**, 467-479.

American Geological Institute (1987) Glossary of Geology. Robert L. Bates and Julia A. Jackson (eds), 3rd (edn), Virginia, p. 461.

Andrews, J.E., Brimblecombe, P., Jickells, T.D. & Liss, P.S. (1996) An introduction to Environmental Chemistry, School of Environmental Sciences, University of East Anglia, Blackwell Science, p. 136.

Arem, J. E. (1987) Color Encyclopedia of gemstones, 2nd (edn), Van Nostrand Reinhold, New York, pp. 139-142.

Ayalew, D., Barbay, P., Marty, B., Reisberg, L., Yirgu, G. and Pik, R. (2002) Source, genesis, and timing of giant ignimbrite deposits associated with Ethiopian continental flood basalts. **Geochimica et cosmo chimica Acta**. Vol. 66, No. 8, 1429-1448.

BCEOM (1999) Climatology, Abbay River Basin Integrated Development Master Plan project, Section 2, Volume 3, part 1, phase 2, pp. 1-22

BCEOM (1998) Environment: Abbay River Basin Integrated Development, master Plan project, phase 2, Section II, volume XIII, part 3, pp. 19-51.

BCEOM (1998) Land Resources Development, Abbay River Basin Integrated Development Master plans project, section 2, volume 10, parts 3, phase 2, pp. 27-49.

Blatt H., Middlton G. and Murray R. (1972) Origin of Sedimentary rocks, Prentice - Hall, Inc., Englewood Cliffs, New Jersey, pp. 348-541.

Carmichael, I.S.E., Turner, F.J. and Verhoogen, J. (1974) Igneous petrology, International Series in the earth and Planetary sciences, Kenneth D. Emery, Robert F. Legget, Bruce Murray and Lawrence L. Sloos (Eds), McGraw - Hill, pp. 1-50

Carozzi, A.V. (1960) Microscopic sedimentary petrography, John Wiley & Sons, Inc., pp. 8-14.

Chhatwal, M. (1987). Dictionary of Geology, Anmol Publications PVT. LTD. New Delhi, pp. 110-002.

Compton, R. R. (1962) Manual of field geology, John Wiley and Sons, Inc., New York, pp. 251 – 270.

Condie, K. C. (2001) Mantle Plumes and their record in Earth history. University of Cambridge, pp. 85 – 87.

Crystal Vine (2005) Ethiopian opal. http:// www. Crystalvine. Co - uk/Ethiopian opal.htm.

Dapples, E.C. (1967) Diagenesis of Sandstones. In: G. Larsen and G.V. Chilingar (editors), Diagenesis in sediments. Elsevier, Amsterdam, pp. 91-125.

Dapples, E.C. (1979) Diagenesis of sandstones. In: Gunnar Larsen & George V. Chilingar (Editors), Diagenesis in sediments and sedimentary rocks. Elsevier, Amsterdam, pp. 31-90.

Dapples, E. C. (1967) Silica as an agent in diagenesis. In: G. Larsen and G.V. Chilingar (Editors), diagenesis in sediments. Elsevier, Amsterdam, pp. 323-340.

Dapples, E.C. (1979) Silica as an agent in Diagenesis. In: Gunnar Larsen & George V. Chilingar (Editors), Diagenesis in sediments and sedimentary rocks. Elsevier, Amsterdam, pp. 99-137.

Davis, R. (1992) Depositional systems: an introduction to sedimentology and stratigraphy. 2nd (edn.), Prentice – Hall, Inc., a Simon & Schuster Company, New Jersey, p. 19.

Deer, W.A., Howie, R.A. and Zussman, J. (1963) Rock forming minerals: Framework Silicates, William Clowes and Sons, Limited, London and Beccles, Volume 4, p. 210.

Degens, E. (1965) Geochemistry of sediments: a brief survey, prentice –Hall, Inc., pp. 14 – 54.

Department of Earth Sciences, University of Oxford (1996) Sedimentary environments: processes, Facies and Stratigraphy, 3rd edition, H.G. Reading (Editor); Blackwell Science, Inc., pp. 400 & 401.

Doilicho B., Shahlu, E., Shewakena,F., Tekle,K., Serakhi,O., Shiferaw, T. and Tsishe, Z. (1992) Introduction to the Geography of Ethiopia: a preliminary teaching material; the Department of Geography College of Social Sciences, Addis Ababa University, pp. 10 – 90.

Downing, P. B., (1996) African Opal. Lapidary Journal, July 1996, pp. 39-42.

Einsele, G. (2000) Sedimentary Basins: Evolution, facies, and Sediment Budget, 2nd (edn), University of Tuebingen, Department of Geology and palaeontology, Germany, pp. 197 -201 and 679-698.

Fairbridge, R.W., (1967) Phases of diagenesis and authigenesis. In: G. Larsen and G.V. Chilingar (Editors), diagenesis in sediments. Elsevier, Amsterdam, pp. 19-89.

Faure, G. (1998) principles and applications of geochemistry, a comprehensive ext book for geology students, the Ohio State University, 2nd (edn), prentice – Hall, Inc., New Jersey, pp. 124-128.

Friedman, G.M., Sanders, J.E. and Kopaska Merkel, D.C. (1992) Stratigraphy and Sedimentology: Principles of Sedimentary Deposits, Macmillan, New York, pp. 69-106.

Gerra, S., (2000) A short introduction to the geology of Ethiopia. Chronique De La Recherche Miniere, NO. 540, pp. 3-10.

Gorshkov, G. & Yakushova, A. (1977) physical Geology, 2nd edn, translated from the Russian to English by V.V. Shiffer, Mir publishers, Moscow, pp. 116-118.

Greensmith, J.T. (1978) Petrology of the Sedimentary rocks, Queen Mary College, University of London, 6th (edn), Mackays of Chatham Ltd., Volume 2, p. 174.

Hausel, W.D.& Sutherland, W.M. (2005) Geology of the cedar rim opal deposit, granite mountains, central Wyoming: Metals and precious stones section, Wyoming state geological survey. http: //www.wsgs.uwyo.edu/metals/cedar Rimopal Field. aspx.

Heinrich, E.Wm. (1965) Microscopic Identification of Minerals, McGraw – Hill, New York, pp. 20&56-58.

Hershel Friedman (1997-2000) all varieties of opal. http://www.minerals. net/mineral/silicate/tecto/quartz/images/opal/opalvary. html

Hoover, D.B., Yohannes, T. Z. & Collins, D.S., (1996) Ethiopia: anew source for precious opal. Australian Gemologist, 26, 303-307.

Hyndman, D.W.(1972)Petrology of Igneous and metamorphic rocks(International series in the earth and planetary sciences), McGraw – Hill,Inc., Frank Press, M.I.T.C. (editor), pp. 31 – 238.

Johnson, M.L., Kammerling, R.C., Deghionno, D.G & Koivula, J.I. (1996) Opal from Shoa Province. Ethiopia. Gems & Gemology, Vol. 32, No. 2, pp. 112-120.

Kazmin, V. (1979a) Stratigraphy and Correlation of Volcanic Rocks in Ethiopia. Ethiopian Institute of Geological Survey, unpublished Note No. 106, Addis Ababa.

Jones, M.P. (1987) Applied Mineralogy: a quantitative approach, Mineral Resources Engineering Department, Imperial College, London, Alden Press, Oxford, pp. 7 & 54.

Justin - Visentin, E., Nicoletti, M., Tolomeo, L. & Zanettin, B. (1974) Miocene and pliocene volcanic rocks of the Addis Ababa Debraberhan area (Ethiopia). Bulletin of Volcanology 38, 237-253.

Keller, P.C. (1992) Gemstones of East Africa. Geosciences press, Inc., printed in Mexico, pp. 103-110.

Kerr, P.F. (1977) Optical Mineralogy, Robert H. Summersgill and James W. Bradley (eds), 4th(edn), McGraw - Hill, Inc., pp. 278-280.

Kieffer, B., Arndt, N., Lapierre, H.,Bastien, F., Bosch, D., Pecher, A., Yirgu, G., Ayalew, D.,Weis, D., Jerram, D. A., Keller, F., and Meugniot, C. (2004). Flood and Shield Basalts from Ethiopia: Magmas from the African superswell. Journal of Petrology, 45,793 – 834.

Klein, C. and Hurlbut, C.S. and JR. (1993) Manual of Mineralogy, Barry Harmon (editor), 21st (edn), John Wiley & Sons, Inc., pp. 266 - 267.

Lebas, M.J., Lemaitre, R.W., Streckeisen, A. and Zanettin, B. (1986) a chemical classification of volcanic rocks based on the total alkali - silica diagram. Journal of petrology, vol. 27, part 3, pp. 745-750.

Leeder, M.R. (1982) Sedimentology: Process and product, Department of Earth Sciences, University of Leeds, London,WCIAILU, UK , pp. 31-34 and 303-308.

Lowes, J.J. & Walker, M. J. C. (1984) Reconstructing Quaternary Environments, John Wiley & Sons, Inc., New York, p. 120.

Merla, G., Abatte, E., Azzaroli, A., Bruni, P., Fazzouli, M., Sagri, M. and Tacconi, P. (1979) Comment and a geological Map of Ethiopia & Somalia. Scale 1:2, 000, 000. Frienze, Italy. Consiglio Nazionale delle ricerche, p. 89

McLennan, S.M. (1989) Influence of provenance and sedimentary processes - Rare earth elements in sedimentary rocks, Geochemistry and Mineralogy of rare earth elements In: Lipin, B.R. & Mckay, G.A. (eds), volume 21, **Mineralogical Society of America**, pp. 169-195.

Minerals, British Columbia Ministry of Energy and Mines (2002) http://www.em.gov.bc.ca/Mining/Geolsurv/Metallicminerals/mineralDepositprofiles/proi…

Ministry of Mines - Mineral operations Department (2002) Gemstones – Investment Opportunities in Ethiopia.

Muller, G., (1967) Diagenesis in Argillaceous sediments. In: G. Larsen and G.V. Chilingar (Editors), Diagenesis in sediments. Elsevier, Amsterdam, pp. 129-172.

Paradis, S., Simandl, G.J. and Sabina, A. (1999) precious opal in volcanic sequences. In: opal deposits in volcanic sequences, in selected British Columbia Mineral Deposit profiles, G.J. Simandl, Z.D. Hora and D.V. Lefebure (eds.), volume 3, Industrial

Paradis, S., Townsend, J. and Simandl, G.J. (1999) Sedimentary Rock - hosted opal, in selected British Columbia Mineral Deposit profiles, G.J. Simandl, Z.D. Hora and D.V. Lefebure (eds), volume 3, industrial Minerals, British Columbia MinistryMines. http://www.em.gov.bc.ca/mining/Geolsurv/MetallicMinerals/MineralDeposit profiles /profi…

Peccerillo, A. & Yirgu, G. (1996) Introduction to geochemistry, Department of Geology and Geophysics, Addis Ababa University.

Pik, R., Denie, C., Coulon, C., Yirgul, G., Hoffmann, C. and Ayalew, D. (1998) the northwestern Ethiopian plateau flood basalts: classification and spatial distribution of magma types. **Journal of volcanology and Geothermal research 81**, 91-111

Pirsson, L. V. & Adolph Knopf (1947) Rocks and Rock – Minerals, 3rd (edn), New York, John Wiley & Sons, Inc. p. 67.

Pough, F.H. (1960) a field Guide to Rocks and Minerals, 3rd (edn), Houghton Mifflin, Boston, pp. 234 - 235.

Read,P.G.(1999) Gemmology, 2nd edition, Biddles Ltd,www.,CO.UK.

Rogers, A. F. & Kerr, P.F. (1933) Thin Section Mineralogy, McGraw –Hill, Inc., 1st (edn), the Maple press Company, New York, p. 165.

Rogers, A.F. and Kerr, P.F. (1942) Optical Mineralogy, McGraw – Hill, Inc., the maple press company, New York, 2nd (edn), pp. 189 & 190.

Rose, A.W. (1979) Geochemistry in Mineral Exploration, 2nd (edn), Edgewood Circle State College, PP. 129-146.

Sheapard, F.P., Inman, D.L. and Goldberg, E.D. (1963) Submarine Geology, Reycroneis (Editor), 2nd (edn), Harper & Row, New York 16, pp. 436-458.

Spencer, L.J. (1959) A key to precious stones, 2nd (edn), Emerson Books Inc., pp. 201-208.

Tadesse, S., Milesi, J.P., and Deschamps, Y. (2003) Geology and mineral potential of Ethiopia: a note on geology and mineral Map of Ethiopia. Elsevier, Journal of African Earth Sciences 36(2003) 273-313.

Tafesse, A. (2002) Geology and Opal Mineralization in Wedera – Zemamo, Master thesis, Addis Ababa University, un published.

Tefera, M., Chernet, T., and Haro, W. (1996) Explanation of the Geological Map of Ethiopia – Ethiopian Institute of Geological Survey, 1:2000, 000 scales, 2nd (edn).

Tefera, M., Chernet, T. and Haro, W. (1996) Geological Map of Ethiopia, 1:2,000,000, 2nd (edition), Geological survey of Ethiopia, Ministry of Mines and Energy, Addis Ababa.

Tennissen, A.C. (1974) Nature of Earth Materials, Department of Geology, Lamar University Prentice –Hall, Inc., Englewood cliffs, New Jersey, pp. 49-50.

Thaigem. Com (2004) Opal.http://www. thaigem. Com/dis-opal.asp

Tucker, M.E. (1988) Sedimentary petrology: an introduction, Department of Geological Sciences, University of Durham, Blackwell, and Alden press, oxford, pp. 210-226.

U.S. Department of the interior - US. Geological survey - Minerals information http://minerals.usgs.gov/minerals/pubs/commodity/gemstones/sp14-95/opal. html

Wahlstrom, E.E. (1960) Petrographic Mineralogy, Department of Geology, University of Colorado, 2nd (edn), John Wiley & Sons, Inc., p. 96.

Zanettin, B. (1992) Evolution of the Ethiopian Volcanic province. MemorieLincee Scienze Fisiche e Naturali 1, pp. 155-181.

Zanettin, B., Gregnanin, A., Justin – Visentin, E., Mezzacas, G. & Piccirillo, E. M. (1974a) Petrochemistry of the volcanic series of the Central Eastern Ethiopian plateau and relationships between tectonics and magmatology. Mem.1st Geol. Min. Univ. Padova, 31, 1-34.

Zanettin, B., Gregnanin, A., Justin –Visentine, E., Nicoletti, M., Ptrucciani, C., Piccirillo, E.M., and Tolomeol, L. (1974) Migration of the Oligocene – Miocene ignimbritic volcanism in the Central Ethiopian Plateau. N. Jb.Geol. Palaont. Mh. H.9, pp. 567 – 574.

Zanettin, B. & Justin - Visentin, E. (1974) the volcanic succession in Central Ethiopia. 2 The volcanic of the Western Afar and Ethiopia Rift Marigins. Mem.1st. Geol. Min. Univ. Padova,

Zanettin, B., Justin– Visentin, E. & Piccirillo, E.M. (1978) Volcanic succession, tectonics and Magmatology in Central Ethiopia. Allie Memorie dell' Accademia palavina discienze, Lettere ed Arli 90, pp. 5-19

Annex - A: List & Location of Fresh rocks and Weathered rock materials/Koste - Amba & Gift –Mariyam

Sample No.	Sampling Locality	Rock - Type	Location (UTM)	
			Easting	Nothing
SA - 08A	Gift - Gaymeda Stream	Basalt	578028	1107383
SA - 10A	Koste - Amba	Ignimbrite	578026	1105770
SA - 14A	Koste - Amba	Basalt	578639	1105876
SA - 20	Zala - Bahir	Rhyolitic - Ignimbrite	579152	1105556
SA - 34	Gift - Mariyam	Rhyolitic - Ignimbrite	580162	1108746
SA - 35	Yita/Ketanit	Rhyolitic - Ignimbrite	579083	1105270
SA - 45/3	Zala - Bahir	Clayey Material	579203	1105631
SA - 45/4	Zala - Bahir	Rhyolitic - Glass	579203	1105631
SA - 47A	Yita/Ketanit	Clayey Material	578675	1105252
SA - 47B	Yita/Ketanit	Rhyolitic - Glass	578675	1105252
SA - 48A	Yita/Ketanit	Basalt	579133	1105326
SA - 48B	Yita/Ketanit	Clayey Material	579133	1105326
SA - 49	Beret - Afer	Basalt	579546	1106580
SA - 51	Mehal - Belg	Basalt	580943	1107999
SA - 52A	Gift - Mariyam	Clayey Material	580162	1108746
SA - 52B	Gift - Mariyam	Clayey Material	580162	1108746
SA - 52C	Gift - Mariyam	Clayey Material	580162	1108746

Annex B. Techniques of Trace Element Analysis

a/ Sample preparation

Samples were dried at 105 ^{o}C in an electric oven and stored in a desiccator. Subsamples of 200 mg. were placed inside Teflon vessels and treated with 3 ml HF, 4 ml aqua regia (HNO_3- HCl 1: 3) and 1 ml Hcl O_4.The microwave heating program consisting of a three stage power and time settings.

- 30% power 10 min
- 45 % power 20 min.
- 30 % power 5 min.

After digestion the vessels were cooled at room temperature in a water bath and uncapped. The solution was transferred into 100 ml PFA evaporating dishes and takes to dryness on a hot plate at 150 ^{o}C. Then 1 ml HNO_3 Plus water were added and the content heated to dryness again The resulting residue were finally treated with 1 ml HNO_3 plus water and gently heated for 15 min. This clear solution was rinsed into 100ml volumetric flask and diluted to volume after the adding of 100 ppb of rhodium and rhenium as internal standards.

b/ Instrumentation

Microwave oven was a Milestone MLS system, which has a 100% power output of 1200 Watts.

Spectrometer was a Perkin-Elmer SCIEX ELAN model 5000 ICP – MS

c/ Instrumental operating conditions

Plasma Rf power ---- 1100 KW
Plasma gas flow ------ 15.0 L/min
Auxiliary gas flow ---- 1.40 L/min
Nebulizer gas flow ---- 0.85 L/min
Sample uptake flow --- 0.80 ml/min
Dwell time--------------- 50 sec
Sweeps-------------------1
Replicate ----------------- 3
Point across peak ------- 1

d/ Limits of Quantitation

The limit of Quantitation (LOQs) for the elements detected with ICP- MS were calculated for ten times the standard deviation (S) of the reagent blank, for 11 replicate determinations, divided by sensitivity at 5 μg/L concentration level, and multiplied by 500, that is , the diluted factor.

	LOQs		LOQs		LOQs
Element	PPm	Element	PPm	Element	PPm
Li	0.01	Cu	0. 05	Cd	0.001
Be	0.005	Ga	0,005	In	0.001
Sc	0.01	As	0.05	Sb	0, 01
V	0.01	Rb	0.005	Sn	0.05
Cr	0. 05	Y	0.01	Cs	0.01
Ni	0. 01	Zr	0.01	La	0.01
Zn	0. 01	Nb	0.01	Ce	0.01
Co	0. 01	Mo	0.01	Pr	0.01
Nd	0. 01	Tm	0.005	Bi	0.001
Sm	0. 01	Yb	0.005	Th	0.01
Eu	0.005	Lu	0.005	U	0.01
Gd	0.005	Hf	0.01		
Tb	0.005	Ta	0.01		
Dy	0.005	W	0.01		
Ho	0.005	Ti	0.01		
Er	0.005	Pb	0.05		

e/ Precision

The precision of the analysis is based on two independent sources of error, the uncertainty in the sample preparation procedure and instrumental precision. The precision of the analysis was evaluated by decomposing 11 replicate of a sample. For each set solutions analyzed, the average (X), standard deviation (S) and relative standard deviation (RSD) were calculated. To test instrumental fluctuations, one solution was run 11 times.

The precision of the sample decomposition procedure was then calculated to the following formula:

$$S\ sp = (S\ tot^{2} - S\ ins^{2})^{½}$$

Were Ssp = precision of the sample preparation

S_{tot} = precision of the analysis

S_{ins} = instrumental precision

Elem. ppm	X	S tot .	RSD %	S ins.	S sp
Li	87.4	1.062	1.23	0.821	0.675
Be	2.31	0,097	4.2	0.076	0.06
Sc	12.77	0.31	2.43	10.28	0.133
V	48.02	1.034	2.15	0.93	0.45
Cr	63.3	3.34	5.28	1.9	2.74
Ni	23.7	1.71	7.23	0.4	1.66
Zn	102.3	4.23	4.13	2.12	3.66
Co	8.61	0.21	2.42	0.13	0.16
Cu	16.97	0.42	2.47	0.16	0.38
Ga	16.55	0.3	1.81	0.23	0.19
As	5.51	0.146	2.66	0.11	0.096
Rb	10.31	0.456	4.42	0.22	0.39
Y	28.33	0.738	2.61	0.64	0.38
Zr	97.45	3.34	3.43	1.49	2.99
Nb	15.5	0.68	4.39	0.24	0.63
Mo	1.42	0.058	4.08	0.027	0.051
Cd	0.12	0.008	6.35	0.008	
In	0.1	0.009	9.13	0.0016	0.0088
Sb	0.9	0.085	9.4	0.08	0.028
Sn	2.91	0.096	3.24	0.061	0.074
Cs	2.5	0.065	2.61	0.054	0.036
	47.18	1.124	2.38	0.89	0.69
La					
Ce	87.81	2.53	2.88	1.18	2.23

Pr	10.27	0.23	2.25	0.21	0.093
Nd	32.08	0.6	1.86	0.51	0.32
Sm	5.66	0.434	2.37	0.16	0.403
Eu	1.08	0.025	2.29	0.039	
Gd	5.62	0.17	2.62	0.16	0.068
Tb	0.93	0.018	1.89	0.028	
Dy	4.87	0.068	1.41	0.11	
Ho	0.995	0.008	0.8	0.022	
Er	259	0.06	2.33	0.045	0.039
Tm	0.38	0.01	2.72	0.008	0.006
Yb	2.21	0.036	1.65	0.06	
Lu	0.36	0.011	3.14	0.006	0.001
Hf	3.87	0.147	3.79	0.097	1.11
Ta	1.11	0.068	6.08	0.022	0.064
W	2.67	0.116	4.12	0.062	0.044
Ti	0.3	0.007	2.34	0.009	
Pb	27.48	1.97	7.17	0.72	1.83
Bi	0.66	0.037	5.62	0.017	0.033
Th	16.26	0.517	3.18	0.35	0.38
U	4.46	0.153	3.43	0.13	0.08

f/Accuracy

The well-established reference standard materials Granite GSR-1 and Basalt GSR-3 were employed throughout the work to provide data quality assurance. Concentrations measured in each of the standard rocks were compared with available certificate values.

Er= Obv-Cev/Cev x 100

Where Er = Error %

Obv = Obtained value

Cev = Certified Value

	GSR-1			GSD-3		
	Certified	Obtained	Error	Certified	Obtained	Error
Elem.ppm	Value	Value	%	Value	Value	%
	CeV	ObV	Er	CeV	ObV	Er
Li	131	122	-6.87	9.5	10	5.26
Be	12.4	13	4.84	2.5	2.9	16.00
Sc	6.1	5.8	-4.92	15.2	15	-1.32
V	24	27	12.50	167	181	8.38
Cr	5	4 .2	-16.00	134	120	-10.45
Ni	2.3	2	-13.04	140	155	10.71
Zn	28	32	14.29	150	168	12.00
Co	3.4	3.02	-11.18	46.5	40.5	-12.90
Cu	3.2	4.1	28.13	48.6	52	7.00
Ga	19	17.2	-9.47	24.8	23.4	-5.65
As	2.1	2.6	23.81	0.79	0.83	5.06
Rb	466	448	-3.86	37	36.2	-2.16
Y	62	58	-6.45	22	20.6	-6.36
Zr	167	185	10.78	277	281	1.44
Nb	40	45	12.50	68	64.8	-4.71
Mo	3.5	402	14.86	2.6	2.3	-11.54
Cd	0.032	0.038	18.75	0.067	0.06	-10.45
In	0.02	0.018	-10.00	0.063	0.06	-4.76
Sb	0.21	0.23	9.52	0.083	0.1	20.48
Sn	12.5	13.6	8.80	2	2.52	26.00
Cs	38.4	37.6	-2.08	1.2	1	-16.67
La	54	55	1.85	56	53	-5.36
Ce	108	112	3.70	105	101	- 3.81
Pr	12.7	11.9	-6.30	13.2	12.88	-2.42
Nd	47	45	4.26	54	58.3	7.96
Sm	9.7	9.5	- 2.06	10.2	11.1	8.82
Eu	0.85	0.81	-4.71	3.2	3.1	-3.13

Gd	9.3	10.3	10.75	8.5	7.9	-7.06
Tb	1.65	1.62	-1.82	1.2	1.5	25,00
Dy	10.2	9.18	-10.00	5.6	5.5	-1.79
Ho	2.05	1.87	-8.78	0.88	0.95	7.95
Er	6.5	5.5	- 15.38	2	2.3	15.00
Tm	1.06	0.96	-9.43	0.28	0.23	- 17.86
Yb	7.4	7.1	-4.05	15	1.9	26.67
Lu	1.15	1.02	-11.30	0.19	0.14	-26.32
Hf	6.3	6.5	3.17	6.5	7.1	9.23
Ta	7.2	8.5	18.06	4.3	3.5	-18.60
W	8.4	7.2	-14.29	0.44	0.4	-9.09
Ti	1.93	1.6	-17.10	0.12	0.15	25.00
Pb	31	34	9.68	7.2	8.3	15.28
Bi	0.53	0.49	-7.55	0.045	0.05	11.11
Th	54	52	-3.70	6	5.2	-13.33
U	18.8	19.3	2.66	1.4	1.1	-21.43