Petrographic and Geochemical Study of Low Grade Metamorphic Rocks around Negash with Reference to Base Metal Mineralization and Groundwater Quality, Tigray, Northern Ethiopia

*K. Bheemalingeswara and Nata Tadesse
Department of Earth Science, College of Natural and Computational Sciences, Mekelle University, Mekelle, Ethiopia (*kbheema@hotmail.com)

ABSTRACT
The paper presents preliminary petrography and geochemical data of Precambrian low grade metamorphic rocks from Tsaliet Group around Negash and discusses their mineralization potential and effects on groundwater quality.

Petrographic data suggest that among the three types of metamorphic rocks (metavolcanic, metavolcaniclastic and metasediments present in the study area), metavolcaniclastics shows the presence of clasts set in a fine grained tuffaceous groundmass and indicates a significant compositional contrast between these, probably volcanic derived, groundmass and the clasts. The clasts vary in size and shape. They vary from angular, rounded to sub-rounded and elliptical shape (due to shearing). Metavolcanics are massive, non-foliated. They show the presence of relicts of plagioclase feldspar and pyroxenes which are set in a fine grained matrix. Phyllite, the predominant lithounit of metasediments is composed of fine grained muscovite, quartz and chlorite with incipient foliation and at places well developed crenulations. The presence of chlorite together with not well developed muscovite and biotite (rare) suggests low grade metamorphic conditions in the area. Geochemical data of metavolcanics indicate variation in their composition from basalt to andesite. Metavolcaniclastics are relatively enriched in alkalis and silica and deficient in MgO compared to metavolcanics. Phyllite, on the other hand, is enriched in K2O and silica compared to metavolcanics. Development of chlorite, sericite and others due to low grade metamorphism and hydrothermal alteration have modified the chemistry of the rocks particularly MgO by chlorite in phyllite.

Shear zones are common in the area, trending N-S and showing the presence of clasts with non-ideal tails, relatively higher amount of quartz veins, malachite stains, Cu anomalies and sericitisation. These stains and anomalies strongly suggest a shear zone-controlled copper mineralization. Island arc setting, bimodal volcanism, intrusive granitic plutons and similar type of shear zone –controlled Zn-mineralization in the nearby Abhra Atsbha area indicate the possible presence of a similar kind of mineralization elsewhere in the basement rocks around these plutons.

Hydrogeochemical data indicate that groundwater is relatively fresh. Among major elements Na, Ca and Mg show relatively higher values compared to K. Water from metasediments is relatively harder among others. Na, though shows higher values compared to Ca and Mg, does not indicate any particular trend. Ca and Mg in water are related to the primary mafic and plagioclase feldspar minerals. Among trace elements, iron, nickel and lead show relatively higher values compared to other analyzed elements. Fe and Ni are related to metavolcanics and metavolcaniclast, and Pb to metapelitic.
Key words: Low grade metamorphites, Base metal mineralization, Petrography, Hydrogeochemistry, Negash, Ethiopia

1. INTRODUCTION

The need for natural resources in the development of a country is an undisputable issue. The resources are available either on the surface or subsurface of the Earth. Search for these resources whether mineral or water thus mainly targets the Earth’s crust. The resources are the result of a particular or combination of geological processes and occur in a suitable geological condition. A variety of exploration methods such as geological, geochemical and geophysical either single or in combination are employed in search of these resources, keeping in view the geology of the area and type of resource. The basement or Precambrian terrains which are invariably metamorphosed, tectonically disturbed and affected by intrusive plutons are some of the potential targets for a variety of mineral deposits e.g. base metal sulphides, native gold, skarn, greisen, pegmatite etc). Use of metallogenic/ deposit genetic models has become an important step in outlining prospective areas regionally in the search of mineral resources. A preliminary investigation related to geological mapping, petrography, alterations, and geochemistry provides the information whether to undertake a detailed survey or not. It is very common that in majority cases the ore deposits that we come across may be of low grade and uneconomical. Though the deposits would commercially be uneconomical, they could contribute high quantities of metals to the percolating meteoric water and circulating groundwater. The constant interaction of water with ores and gangue minerals facilitate leaching and release of metals into the aquifer system, depending on the nature of solubility of different minerals and geochemical condition, thus influencing the quality of groundwater and in turn causing problems to the end users in various ways.

The abundance of minor and trace elements, which will be generally below 1% of the total, can often get enriched to significant levels, depending on the geochemical conditions. For example, decrease of pH by one unit may lead to an increase of more than one order of magnitude in the concentration of certain metals like Al, Be (Edmunds and Smedley, 1996). Increase in the acidity of groundwater is a common feature particularly in non-carbonate areas (e.g. granite) or in areas where oxidation of sulphides (e.g. pyrite) is common. This increases the solubility of many metals like Al, Be, Cd, Pb, Cu etc. Such changes are also common when there is a change from
oxidizing to reducing conditions (e.g. Fe). Some metals like Cu, Zn and As are favoured in oxidizing conditions and are facilitated to have their mobility where as others like Fe and Mn become mobile under reducing conditions. Hardness of water is one of the parameters, which depends on the concentration levels of Ca and Mg. It is reported that many metals are soluble in soft water resulting in the enrichment of metals in water (Edmunds and Smedley, 1996). Any one or combination of these may cause mobility and concentration of metals. Such changes often enhance the concentration of many elements, particularly trace metals to intolerable proportions and become a serious threat to human health. The quality requirement of groundwater depends on its purpose of use i.e. for drinking, industry, irrigation etc. So, the suitability is generally tested on the basis of hardness, sodium absorption ratio, total dissolved solids, conductivity etc. So, the mineral deposit whether of high or low grade affects the groundwater quality. The effects on health will be more intense in the case of metallic deposits compared to the non-metallic.

In this light, an area around Negash and Wukro in Tigray region of northern Ethiopia, a Late Proterozoic metamorphic terrain, was chosen for study with the purpose of evaluating the metamorphites; their potential to host mineral deposits and their effects on groundwater quality. To achieve this objective, the metamorphic rocks were probed for petrographic and geochemical characteristics so as to derive the following information.

a) primary mineralogy; b) textural relations; c) alterations or changes in the primary mineralogy due to hydrothermal or meteoric water activity; d) metal concentrations associated with shear zones and possible relation to mineralization; e) presence of secondary minerals like limonite or malachite; and f) trace metal geochemistry of groundwater to define its quality and utility value.

The area of study around Negash is located about 45 km from Mekelle towards north on the way to Adigrat and forms part of Tigray region, northern Ethiopia. It is located between 13°50’20” to 13°58’34” E and 39°33’20” to 39°38’15” N (Fig.1). It is spread in an area of about 144 Km². The area is connected by an asphalt road which makes it accessible in all weather conditions. Interconnecting cross roads though are of gravel, are also accessible for vehicles even during rainy season.

2. REGIONAL GEOLOGY
The Precambrian basement rocks of northern Ethiopia are predominantly composed of metavolcano-sedimentary assemblage (Kazmin, 1973; Tadesse, 1996; Drury and De Souza, 1998). They form part of the southern part of the Arabian Nubian Shield (ANS) (Kazmin et al., 1978; Vail, 1983, 1988), which in turn constitute a large segment of juvenile Neoproterozoic crust formed by accretion of oceanic arc terrains (Stoeser and Camp 1985; Stern 1994; Genna et al., 2002; Johnson and Woldehaimanot 2003). The ANS is flanked by the older basement, which was remobilized during the Pan-African orogenic cycles (850–550 Ma) and eventually led to the formation of Gondwana. The Precambrian basement rocks of Ethiopia including northern Ethiopia have been studied by many workers. They include, Kazmin et al. (1978) on stratigraphy and evolution; Shackleton (1994, 1996), Stern (1994), Abdeselam and Stern (1996), Tadesse (1996), Tadesse and Allen (2002), Genna et al. (2002), and Johnson and Woldehaimanot (2003) on sutures and shear zones; Ayalew et al. (1990), Gichile (1992), Teklay et al. (1998) and Gerra (2000) on geochronology. Studies are also conducted on the metamorphic rocks of northern Ethiopia by Tadesse et al. (1999) and Alene et al. (2000) on geochemistry and tectonic setting.

Kazmin et al. (1978) have divided the Precambrian basement of Ethiopia into Upper, Middle and Lower Complexes on the basis of the grade of metamorphism. The low grade rocks belonging to Upper Complex and high grade to Lower Complex and medium to Middle Complex. They also considered the Upper Complex rocks to be Late Proterozoic in age and Middle and Lower Complexes to be Middle and Early Proterozoic (or Late Archean). But recent studies on the basis of the geochronological and isotopic data (Gerra, 2000, Teklay et al., 1998 and others) have suggested that the Precambrian basement rocks are dominantly Neoproterozoic in age and have experienced different grades of metamorphism. In tune with the geochronological and other data, the basement rocks are regrouped into two major blocks, Volcanic-sedimentary terrain (including the younger metasediments) and the Gneisic – migmatitic terrain, separated by numerous Ophiolitic sutures (Asrat et al., 2001).

3. GEOLOGY OF THE STUDY AREA
The rocks of the study area form part of the basement and belong to Upper Complex of Kazmin et al. (1978) and have experienced low grade metamorphic conditions and Neoproterozoic in age (Gerra, 2000, Ayalew et al., 1998, Teklay et al., 1998). The rocks mainly trending N-S to NE-NW are predominant in the north though present in northern, western and southern parts of the country. The rocks indicate greenschist facies metamorphism and represent a volcano-sedimentary succession (Kazmin et al., 1978). They are invaded by felsic plutons such as granodiorite/ granite rocks in the west (Negash pluton) and granite in the eastern part of the study area (Fig.1). The emplacement of Negash pluton has taken place, on the basis of U-Pb dating of
Figure 1. Geological, rock, water sample location map around Negash, Tigray, Northern Ethiopia (modified after Arkin et al., 1971).

LEGEND

A Alluvium
B Adigrat Sandstone
C Enticho Sandstone
D Granite
Tambien Group
E Diamictite
F Black Limestone
G Meta Limestone/Dolomite/Marble with minor Phyllite
H Phyllite/Slate/Meta Limestone
Tsaiyet Group
I Phyllite/Metavolcanoclast
J Metavolcanics/Metavolcanoclast with minor Phyllite

Rock Sample
Water Sample
Shear/Alteration Zone
Reverse Fault (Negash Fault)
Normal Fault (Wukro Fault)
Cu anomalies in rock

A Abrha Atsba Zinc Prospect

> 6300 ppm
200 - 500 ppm

© CNCS 111 Mekelle University
zircons, around 608 ±7 Ma (Asrat, 2002) and marks the end of Proterozoic. This emplacement represents the last of the three granitic magmatism episodes: 800-885 Ma, 700-780 Ma and 540-660 Ma that have taken place in Ethiopia (Garland, 1980; Miller et al., 1967; Mock et al., 1999; Alemu, 1998; Tadesse, et al., 2000; Ayalew et al., 1990; Rogers et al., 1965; Jelene, 1996; Gilboy, 1970; Teklay et al., 1998). These ages are also considered to be related to the major structural and metamorphic events in different terrains in Ethiopia (Teklay et al., 1998; Ayalew et al., 1990; Tadesse, et al., 2000). The basement rocks in the study area are classified under Tsaliet and Tambien Groups (Kazmin et al., 1978). Tsaliet Group rocks are older and dominated by metavolcanics (MV), metavolcaniclastics (MVC) and metasediments/metapelite (MP). MV is the oldest and MP is the youngest. The younger Tambien Group consists of only metasediments. They are, in the order of older to younger, phyllite-marble-dolomite intercalation, meta-limestone (black limestone), slate and diamictite (pebbly slate) and form part of Negash syncline (Miller et al., 2003) (Fig.1).

The area is also marked by the presence of two prominent faults: Negash fault trending N-NE and the younger Wukro fault trending E-W (Fig.1). Negash fault is a thrust fault where the younger Tambien Group rocks have thrust over the older Tsaliet Group rocks (Fig.1). Since the fault is involved between the Tambien and Tsaliet Group rocks and also confined to the basement rocks, it may be related to the age of the Negash pluton. Wukro fault is a normal fault and much younger in age and involved in the upliftment of the basement rocks (Negash) with relation to the Mesozoic sedimentary rocks (Wukro) of the Mekelle basin. The intrusive granitic plutons and related tectonic activity has facilitated generation and mobility of ore-forming hydrothermal fluids within the basement rocks. Further, the fluid-wall rock interaction has produced alterations e.g. epidotisation, sericitisation by modifying the primary mineral assemblages. Among the rocks of Tsaliet and Tambien Groups, only the rocks of Tsaliet Group are considered for the present study and discussed in the paper. Brief description of the rocks is given below.

3.1 Metavolcanics

These rocks are dominated by metabasalts with subordinate meta-andesites and metarhyolites. The metabasalts are massive, non-foliated, and fine grained. They typically show green color
whereas the meta-andesites are dark grey and metarhyolites light pink in color. Development of alterations such as epidotisation and chloritisation are common. MV is dominant in the central part of the study area. Kaolinisation is also common in the metarhyolites. Metabasalt being the dominant rock type in the area, it is considered for detailed petrography and geochemistry.

3.2 Metavolcaniclastic
These rocks are relatively predominant in the area and occupy a large part of the study area. MVC shows significant variation in the size, shape and chemical composition of the clasts and in turn overall rock composition. The clasts vary in size from very coarse in the east to fine in the west. They also vary in shape from angular, elongated (elliptical), sub-rounded to round. The clasts are mainly lithic and mineral fragments varying in composition from mafic (amphiboles/pyroxenes) to felsic (feldspars and quartz). The matrix consists of fine grained material at places shows green color. The clasts in general show random orientation and at places show alignment indicating fluvial transport. On the basis of the field association, lack of proper sedimentary characteristics, fine grained matrix and clasts with varying composition and random orientation, the rock is considered to be volcanic-derived with limited amount of sedimentary input. Pyrite crystals are common in the rock but mostly are altered to limonite.

3.3 Metasediments
These are represented by phyllite and slate. Megascopically, the rocks are fine grained and show well developed foliation in phyllite and slaty cleavage in slate. These rocks are more prominent in the eastern and western parts of the study area and show a range of colors such as light grey, dark grey, green and brown/red. Development of crenulation cleavage is prominent at places. Schistosity though is poorly developed, is seen along the contacts with the intrusive pluton where development of muscovite is quite prominent. Presence of pyrite crystals with cubic outline is quite conspicuous in these rocks. In majority cases, these are altered to limonite (pseudomorphs) and show red color.

3.4 Shear Zones
The zones trending N-NE are characterized by the presence of tails of non-ideal simple stress. The rigid clasts (lithic fragments) show rotation and developed cracks during the shearing of the
matrix. The tails or the pressure shadows extend on either side of the clasts and the rotation of the clasts is marked by the layers/tails being rolled around the rigid clasts (David, 1993). In the field, these zones are common in MVC and MP. The rigid clasts also show breakdown producing cracks possibly due to stretching and rotation. They are later filled by the fine grained matrix. Relatively well developed foliation/schistosity/crenulations, increased quartz vein activity, sericitisation and malachite stains are some of the common features associated with these zones. Presence of green colored malachite is quite conspicuous in these zones indicating base metal mineralization. These zones vary in width from less than a meter to few meters and most common along the contacts between MV, MVC and MP. It is interesting to note that these zones are prominent only in Tsaliët Group rocks not in Tambien Group in the area.

Precambrian stratigraphic succession of the rocks in the study area from younger to older is as below (Kazmin et al., 1978; Miller et al., 2003).

---------Granit and, Granodiorite (Negash pluton) (Intrusive Plutons)-----

**Tambien Group**

*[Undifferentiated units (Negash Syncline) (~1750m thick)]*

- Diamictite (pebbly slate)
- Black limestone
- Metalimestone- dolomite-marble- minor phyllite
- Phyllite- slate- metalimestone

**Tsaliët Group**

*[Metapelites and Metavolcanics (~1500m thick)]*

- Slate / Phyllite
- Metavolcaniclastics
- Metavolcanics

**4. METHODOLOGY**

A detailed geological map has been prepared in the scale of 1:50,000. 100 rock samples covering the three lithounits (MV, MVC and MP) and 28 water samples were collected during the field work around Wukro and Negash for geochemical analysis. The sample locations are given in fig.1. Out of 100 rock samples, 39 samples were selected for geochemical analysis. The rock samples were crushed and ground to obtain fine rock powders (~200 mesh size). Whole rock geochemical analysis was performed on the powdered samples. Major, minor and trace elements data was generated using X-ray Fluorescence Spectrophotometer (XRF) (Phillips PW 2024) in the Geochemical Laboratories of the Department of Applied Geology at Technical University, Berlin, Germany. Major oxides were analysed using fused beads following fusion with LiBO3.
and trace elements by pressed powder pellets using boric acid as binder. The spectrometer was calibrated with a set of 30 - 35 International reference materials (rock standards), covering a wide range of composition and detection limits.

30 rock samples were chosen for petrographic studies. Rock thin sections were prepared for petrographic investigations at Geology Department, Delhi University, India and studied using petrological Leica Orthoplan Microscope attached with Image Analyser. 28 groundwater samples about one liter each were collected in pre-cleaned and numbered plastic bottles. The samples were analyzed for pH and EC in the site. They were acidified and later submitted for geochemical analysis using Flame Atomic Absorption Spectrophotometer (Varian Spectra, 50B) in the Geochemistry Laboratory, Department of Earth Science, Mekelle University. Elements such as Ca, Mg, Na, K, Cu, Pb, Zn, Mn, Fe, Ni and Co were analyzed after setting the instrument, using the prescribed standard conditions. Chemical standards in the range of 1 to 10ppm for each element were used for constructing standard working curve and also as reference. The detection limits for all the elements except Pb was 0.1 ppm. For lead, it is 1.0 ppm. The precision range for these elements was within ± 5-10%. The petrographic data is given in table.1 and whole rock and water sample data are given in tables 2 to 4. All rock and water sample locations are shown in figure.1.

5. RESULTS
5.1 Petrography
Among 30 samples studied for petrographic details, 15 are from MVC, 10 from MV and 5 from MP. On the basis of the petrographic investigation (Table. 1), the rocks are described below. They are 1) metavolcanic – consists of plagioclase feldspar, hornblende, inequigranular quartz, relict and reaction textures with poorly developed schistosity indicated by chlorite. Green colored hornblende and colorless needle shaped tremolite showing random distribution and sometimes wrapping the relict pyroxenes indicate decussate texture; 2) metavolcaniclastic-quartz, chlorite, muscovite, biotite, lithic fragments with different compositions, with well developed schistosity (at places), the fragments are being wrapped by the sheet silicates. The matrix comprises of fine grained material possibly volcanic derived tuff (glass)? The fragments sometimes show orientation indicating flow structure and also elongation due to stretching.
fragments are irregularly distributed and vary in composition from mafic (pyroxenes) to felsic (feldspars); Mineral associations and field relations suggest that the rock is metavolcaniclastic rock. 3) phyllite- consists of fine grained quartz, chlorite and muscovite with well developed foliation and crenulations; and 4) slate- consists of similar mineralogy as in phyllite but with very fine and poorly developed foliation.

Table.1 Petrographic description of selected metamorphic rocks, Negash.

| # no. | Minerals present (%) | Description | Rock type |
|-------|----------------------|-------------|-----------|
| ND 31 | Plagioclase(40) Quartz (30) Calcite (15) Hornblende/ Chlorite (10) Opaque (5) | The rock (plagioclase, quartz, calcite, hornblende/ chlorite and opaque shows medium grained plagioclase feldspar laths together with few coarse- grained rounded to sub-rounded quartz clasts in fine grained quartz dominated matrix. The mafic minerals though not very prominent seem to have undergone alteration to produce secondary chlorite. Younger, relatively more intense, calcite veins cut across the primary minerals (also incipient schistosity). Opaque minerals are randomly distributed in the rock and unrelated to these secondary veins and suggest that they are produced due to chemical break down of the primary mafic minerals. | MV (Metaandesite) |
| ND 71 | Tremolite/ Hornblende (25) Pyroxene (10) Quartz (15) Plagioclase (20) Muscovite (10) Chlorite (15) Opaque (5) | The section is of highly altered metabasalt. It shows presence of randomly oriented minerals (decussate texture) such as green color hornblende and colorless tremolite (?) needles and plagioclase laths and quartz with undulose extinction. The pyroxene (mostly relics) and amphibole minerals show alteration to chlorite. Muscovite is also present together with quartz particularly along the veins. Opaques are mainly primary related to magnetite, ilmenite? Opaques related to alteration of mafic minerals are also present but in minor amounts. | MV (meta-basalt) |
| ND 63 | Muscovite (45) Quartz (25) Chlorite (20) Opaque (10) | The rock consists of predominantly muscovite and followed in the order of abundance are quartz, chlorite, and opaque minerals. The minerals are fine grained and show a well developed foliation. Three sets of foliation trends are observed as indicated by the alignment of fine grained muscovite, chlorite and quartz. Minor amounts of opaque minerals are seen associated with later quartz veins probably indicating mobilized ore minerals. Due to crenulation, common in phyllite, preferential dissolution of quartz takes place at higher angle to the shortening direction; relict quartz grains become increasingly in-equidimensional. Precipitation of quartz is seen taking place predominantly in the fractures cutting across the crenulations. Opaque minerals do follow the trend of foliation. | Phyllite (Quartz-mica schist?) |
| ND 21 | Quartz (60) Plagioclase (10) Muscovite (10) Chlorite (15) Opaque (5) Lithic fragments(20) | The rock is composed of quartz, muscovite, chlorite, feldspar and opaque minerals. It is dominated by the presence of medium to coarse grained clasts of quartz and feldspar minerals. Quartz is irregular to sub-round in shape and feldspars occur as laths. The clasts show elongation due to deformation, parallel to the schistosity. Because they are competent, produce cracks which are later filled by the incompetent sheet silicates, secondary quartz, feldspar and opaque minerals. The lithic fragments are mostly mafic (mostly pyroxene) and hence are highly altered and produced iron oxides. Opaque minerals fine to coarse in size (probably pyrite) and are mainly in association with quartz veins. These opaques often show alteration to secondary iron hydroxides. The matrix is fine grained and consists of volcanic derived tuff (glass)? On the basis of the nature of the clasts and associated mineralogy and field association the rock is metavolcaniclast. | MVC |
The rock shows presence of lithic fragments (like lenses), comprising of fine grained aligned mica-rich mineral within quartzose matrix. The fragments show an alignment indicating a flow and also stretching indicating shearing effects and are wrapped by the quartzose matrix. The clasts are originally mafic rock fragments altered to secondary minerals like chlorite, biotite and muscovite. Equigranular quartz and calcite are also present in association with the clasts (mafic) as secondary products. They are produced after the chemical breakdown of the mafic minerals (clasts). Absence of feldspars in the section amply suggest that the parentage is sedimentary not igneous. The matrix is fine grained and consists of volcanic derived tuff (glass)? On the basis of the nature of the clasts and associated mineralogy and field association the rock is metavolcaniclast.

| ND 58  | Quartz (35) | Chlorite (15) | Muscovite (25) | Calcite (10) | Lithic fragments (15) |
|--------|-------------|---------------|----------------|-------------|-----------------------|
|        |             |               |                |             | MVC                   |
Figure 2. Microphotographs of basic metavolcanic (MV) and phyllite (MP) rocks. [MV rock (#ND-31) (A) under PPL and (B) under cross, is relatively fresh with limited alteration showing decussate texture; MV rock (#ND 71) (C) under PPL and (D) under cross, showing randomly distributed tremolite, muscovite, chlorite and opaques; Phyllite (#ND 63) rock showing development of crenulation cleavage due to the alignment of fine grained muscovite and chlorite and is cut across by the later quartz vein (F) under PPL and (G) under cross position; (Note: Hbl- Hornblende; Chl- Chlorite; Pl. Felds- Plagioclase Feldspar; Tre – Tremolite; Opq-Opaque;Qtz-Quartz; Mus-Muscovite)]
5.2 Rock Geochemistry

Major oxide data indicates significant variation in major element concentrations in the three rock types (Table.2). Metavolcanic rocks show maximum values for MgO (upto 14%), Fe₂O₃ (upto 13.3%), and CaO (upto 10.39%). Similarly, metavolcaniclastic rocks show maximum values for SiO₂ (upto 70%), Al₂O₃ (upto 18%) and Na₂O (upto 9%). In the case of metapelites, though SiO₂ and Al₂O₃ and MgO values range up to 70%, 17% and 10% respectively, they show very low values for CaO (0.2 to 1%) and Na₂O (0.1 to 2%). Among different oxides, MgO and CaO show inverse relation with SiO₂ (Fig.4). K₂O and Na₂O values, on the other hand, show large variation in values and at the same time, do not suggest any particular pattern.
Table 2. Major oxide data (wt%) of Negash metamorphites, Tigray, northern Ethiopia.

| S.No. | # no. | SiO₂ | Al₂O₃ | Total Fe as Fe₂O₃ | MnO | MgO | Na₂O | K₂O | TiO₂ | P₂O₅ |
|-------|-------|------|-------|-------------------|-----|-----|------|-----|------|------|
|       | Metavolcanic Rocks |       |       |                   |     |     |      |     |      |      |
| 1     | ND13  | 66.03| 15.30 | 4.91             | 0.08| 1.76| 3.35 | 3.71| 1.94 | 0.50 |
| 2     | ND15  | 60.70| 18.20 | 5.44             | 0.08| 1.95| 3.26 | 5.20| 2.02 | 0.69 |
| 3     | ND16  | 65.85| 14.32 | 4.22             | 0.09| 1.61| 3.83 | 5.61| 0.65 | 0.45 |
| 4     | ND26  | 60.89| 17.16 | 9.39             | b.d.l.| 1.15| 0.20 | 0.10| 5.18 | 0.92 |
| 5     | ND27  | 50.03| 15.14 | 13.30            | 0.25| 3.22| 10.39| 2.55| 0.10 | 1.40 |
| 6     | ND28  | 62.46| 15.51 | 7.23             | 0.11| 2.91| 1.51 | 5.33| 1.21 | 0.87 |
| 7     | ND31  | 63.39| 12.41 | 6.15             | 0.15| 3.70| 5.49 | 3.53| 0.70 | 0.63 |
| 8     | ND32b | 55.93| 15.84 | 6.85             | 0.15| 4.58| 1.89 | 4.65| 1.29 | 0.68 |
| 9     | ND51A | 51.17| 16.02 | 8.90             | 0.12| 6.25| 7.14 | 3.67| 0.51 | 0.56 |
| 10    | ND68  | 49.88| 18.68 | 11.64            | 0.07| 6.81| 0.34 | 4.44| 0.91 | 0.69 |
| 11    | ND71  | 50.96| 14.82 | 7.73             | 0.18| 13.74| 3.19 | 4.08| 0.07 | 0.67 |
| 12    | ND74  | 48.38| 17.01 | 7.85             | 0.15| 12.44| 2.56 | 5.41| 0.15 | 0.50 |
| 13    | ND75  | 49.95| 17.02 | 10.28            | 0.21| 7.24| 5.18 | 5.58| 0.10 | 0.69 |
| 14    | ND76  | 50.20| 17.30 | 8.88             | 0.16| 9.45| 3.94 | 5.91| 0.10 | 0.67 |
|       | Metavolcanoclastic Rock |       |       |                   |     |     |      |     |      |      |
| 15    | ND1   | 65.43| 14.19 | 7.27             | 0.09| 1.37| 0.54 | b.d.l.| 5.98 | 0.97 |
| 16    | ND5   | 69.47| 13.30 | 4.00             | 0.04| 0.39| 2.04 | 5.87| 1.78 | 0.40 |
| 17    | ND6   | 57.91| 15.11 | 7.33             | 0.08| 2.44| 3.29 | 8.72| 0.18 | 0.72 |
| 18    | ND18  | 57.57| 14.77 | 4.32             | 0.05| 0.52| 3.15 | 7.01| 1.56 | 0.56 |
| 19    | ND21  | 63.95| 14.77 | 4.32             | 0.05| 0.52| 3.15 | 7.01| 1.56 | 0.56 |
| 20    | ND33  | 65.80| 14.12 | 5.27             | 0.08| 3.00| 1.56 | 6.59| 0.58 | 0.60 |
| 21    | ND39  | 50.49| 14.82 | 7.73             | 0.18| 13.74| 3.19 | 4.08| 0.07 | 0.67 |
| 22    | ND51  | 48.38| 17.01 | 7.85             | 0.15| 12.44| 2.56 | 5.41| 0.15 | 0.50 |
| 23    | ND57  | 65.88| 14.95 | 5.35             | 0.13| 1.17| 4.81 | 2.42| 2.50 | 0.49 |
| 24    | ND58  | 65.10| 14.50 | 5.56             | 0.08| 1.73| 3.11 | 5.05| 1.10 | 0.47 |
| 25    | ND66  | 64.48| 14.52 | 10.44            | 0.03| 1.00| 0.20 | 0.10| 4.40 | 0.92 |
| 26    | ND72  | 68.19| 16.15 | 5.04             | b.d.l.| 0.72| 0.20 | 0.10| 4.43 | 0.87 |
| 27    | ND98  | 66.46| 13.67 | 7.95             | 0.05| 3.31| 0.25 | 0.49| 2.77 | 0.68 |
| 28    | ND99  | 62.71| 17.92 | 7.06             | 0.11| 2.97| 0.33 | 2.43| 3.06 | 0.62 |
|       | Phyllite |       |       |                   |     |     |      |     |      |      |
| 29    | ND42  | 59.61| 14.20 | 6.03             | 0.11| 2.22| 6.30 | 1.62| 2.45 | 0.51 |
| 30    | ND45  | 65.19| 13.63 | 6.54             | 0.10| 2.71| 2.04 | 4.53| 1.25 | 0.58 |
| 31    | ND49  | 58.07| 19.09 | 6.96             | 0.08| 4.02| 0.78 | 1.92| 3.32 | 0.79 |
| 32    | ND55  | 62.75| 16.30 | 8.16             | 0.03| 3.25| 0.20 | 0.10| 3.29 | 0.91 |
| 33    | ND55A | 69.56| 14.39 | 6.38             | 0.18| 1.08| 0.95 | 1.68| 1.62 | 0.46 |
| 34    | ND63  | 54.94| 17.04 | 6.45             | b.d.l.| 9.97| 0.27 | b.d.l.| 4.61 | 0.93 |
| 35    | ND65  | 67.63| 14.18 | 7.58             | 0.03| 0.84| 0.20 | 0.10| 3.41 | 1.02 |
| 36    | ND72A | 69.92| 11.52 | 5.28             | 0.06| 1.17| 3.12 | 3.70| 1.65 | 0.47 |
| 37    | ND96  | 67.74| 13.29 | 8.06             | 0.05| 3.39| 0.26 | 0.48| 2.77 | 0.69 |
| 38    | ND100 | 64.91| 17.14 | 5.49             | 0.03| 1.26| 0.20 | 0.12| 4.75 | 0.92 |
|       | Slate  |       |       |                   |     |     |      |     |      |      |
| 39    | ND60  | 66.24| 14.62 | 8.22             | 0.03| 1.36| 0.31 | 0.17| 4.06 | 0.91 |
|       |   |      |       |                   |     |     |      |     |      |      |

© CNCS
Figure 4. Showing variation in major oxide (wt%) and trace element (ppm) concentrations in metavolcanic (# 1-14), metavolcaniclastic (#15-28), phyllite (#29-38) and slate (#39): (A) SiO₂, Al₂O₃ and Fe₂O₃; (B) MgO, CaO, Na₂O and K₂O; (C) TiO₂ and P₂O₅; (D) Ba and Mn; (E) Cr, Ni, V and Co; (F) Zn, Zr, Rb and Sr; and (G) Cu.

Various trace elements analysed (Table.3), only Cu, Zn, Ni, Co, Cr, V, Zr, Ba, Rb, Sr show large variation in the three rock types. Copper values show above 6500 ppm in both MV and MVC and up to 170 in MP. Other base metals, such as zinc and lead are conspicuously low 24-205 ppm and 10-20 ppm respectively. Ba values are relatively higher in MVC and MP (> 800 ppm) compared to MV. Other elements like Ni, Cr and V are expectedly show higher values up to 151, 838 and 474 ppm respectively in MV and Zr values (179 ppm) in MP (Fig. 4). Similar
values for trace elements in different rocks were also reported by Alene et al. (2000) and Dwivedi (2003).

Table 3. Trace element data (ppm) of Negash metamorphites, Tigray, northern Ethiopia.

| S.No | # No. | Ba  | Co  | Cu  | Cr  | Mn  | Ni  | Rb  | Sr  | V   | Zn  | Zr  |
|------|-------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| Metavolcanic Rocks |
| 1    | ND13  | 460 | 1   | 1   | 108 | 638 | 1   | 40  | 434 | 103 | 49  | 111 |
| 2    | ND15  | 478 | 12  | 23  | 111 | 716 | 1   | 44  | 361 | 136 | 67  | 150 |
| 3    | ND16  | 175 | 1   | 44  | 100 | 792 | 1   | 16  | 275 | 73  | 73  | 117 |
| 4    | ND26  | 706 | 11  | 1   | 197 | 150 | 26  | 99  | 11  | 223 | 1   | 158 |
| 5    | ND27  | 23  | 30  | 151 | 1   | 1815| 1   | 11  | 306 | 474 | 108 | 72  |
| 6    | ND28  | 355 | 11  | 1   | 66  | 913 | 1   | 16  | 99  | 16  | 93  | 81  |
| 7    | ND31  | 245 | 18  | 1   | 838 | 1204| 81  | 12  | 183 | 122 | 51  | 68  |
| 8    | ND32b | 149 | 18  | 6500| 1   | 1815| 1   | 14  | 229 | 248 | 34  | 47  |
| 9    | ND31  | 171 | 30  | 456 | 1   | 149 | 715 | 1   | 123 | 111 | 1   | 139 |
| 10   | ND68  | 117 | 11  | 1   | 66  | 913 | 1   | 14  | 14  | 200 | 175 | 38  |
| 11   | ND71  | 37  | 43  | 6359| 479 | 1405| 1   | 72  | 237 | 100 | 50  | 99  |
| 12   | ND74  | 70  | 36  | 342 | 372 | 1340| 1   | 72  | 209 | 204 | 74  | 38  |
| 13   | ND75  | 79  | 38  | 209 | 1   | 1806| 23  | 1   | 138 | 442 | 84  | 36  |
| 14   | ND76  | 35  | 46  | 1   | 188 | 1375| 50  | 1   | 111 | 251 | 79  | 34  |
| Metavolcaniclastic Rock |
| 15   | ND1   | 880 | 16  | 1   | 195 | 881 | 1   | 104 | 20  | 167 | 48  | 97  |
| 16   | ND5   | 436 | 1   | 75  | 154 | 330 | 17  | 33  | 35  | 47  | 1   | 137 |
| 17   | ND6   | 30  | 16  | 1   | 149 | 715 | 1   | 123 | 111 | 1   | 139 |
| 18   | ND18  | 614 | 17  | 25  | 119 | 976 | 1   | 36  | 57  | 120 | 49  | 159 |
| 19   | ND21  | 250 | 11  | 27  | 100 | 475 | 22  | 32  | 62  | 97  | 1   | 130 |
| 20   | ND33  | 336 | 12  | 90  | 161 | 701 | 19  | 1   | 118 | 126 | 67  | 97  |
| 21   | ND39  | 51  | 1   | 1   | 168 | 545 | 1   | 66  | 84  | 49  | 76  | 56  |
| 22   | ND51  | 35  | 25  | 6500| 1   | 123 | 111 | 1   | 111 | 251 | 79  | 34  |
| 23   | ND57  | 546 | 12  | 1   | 149 | 715 | 1   | 123 | 111 | 1   | 139 |
| 24   | ND58  | 348 | 13  | 155 | 51  | 725 | 1   | 21  | 216 | 120 | 30  | 74  |
| 25   | ND66  | 613 | 16  | 1   | 196 | 150 | 57  | 81  | 26  | 204 | 1   | 152 |
| 26   | ND72  | 793 | 15  | 110 | 215 | 150 | 19  | 87  | 21  | 233 | 1   | 160 |
| 27   | ND98  | 664 | 18  | 1   | 210 | 541 | 16  | 54  | 36  | 187 | 99  | 105 |
| 28   | ND99  | 553 | 19  | 474 | 65  | 819 | 1   | 45  | 42  | 130 | 110 | 103 |
| Phyllite |
| 29   | ND42  | 342 | 22  | 73  | 87  | 921 | 1   | 41  | 126 | 128 | 54  | 90  |
| 30   | ND45  | 516 | 17  | 131 | 190 | 868 | 23  | 23  | 131 | 159 | 97  | 93  |
| 31   | ND49  | 826 | 19  | 278 | 126 | 766 | 37  | 61  | 39  | 259 | 132 | 130 |
| 32   | ND55  | 441 | 1   | 39  | 161 | 311 | 51  | 63  | 19  | 177 | 159 | 169 |
| 33   | ND55A | 473 | 1   | 1   | 85  | 1605| 1   | 28  | 115 | 77  | 1   | 75  |
| 34   | ND63  | 97  | 21  | 1   | 140 | 150 | 69  | 98  | 1   | 227 | 104 | 162 |
| 35   | ND65  | 430 | 1   | 170 | 187 | 150 | 33  | 63  | 23  | 162 | 152 | 74  |
| 36   | ND72A | 306 | 11  | 22  | 211 | 543 | 1   | 32  | 125 | 108 | 34  | 80  |
| 37   | ND96  | 648 | 20  | 1   | 195 | 539 | 16  | 52  | 32  | 176 | 96  | 104 |
| 38   | ND100 | 777 | 25  | 141 | 161 | 212 | 68  | 74  | 27  | 201 | 75  | 168 |
| Slate |
| 39   | ND60  | 669 | 14  | 1   | 125 | 150 | 54  | 77  | 32  | 162 | 40  | 159 |

According to Dwivedi (2003) (on ten samples) Cu values varied from 1.44 to 2.6% in MV and 26 to 6440 ppm in phyllite and alteration zones. Lead concentrations are high in metapelites and varied from 288 to 5380 ppm. Zinc is interestingly low and varied from 16 to 254 ppm in the
area. Iron from 2.53 to 42.62% particularly is very high in alteration zones. Manganese varied from 43 to 2012; nickel and cobalt from 16 to 51 and 8 to 65 ppm respectively. Silver and arsenic are also reported from the study area, the values varied from 1.4 to 21.3 and 24 to 145 ppm respectively (Dwivedi, 2003). According to Alene et al. (2000), Ni varied from 22 to 146 ppm in metavolcanic rock and 14 to 36 in metavolcaniclasts; Co from 37 to 45 in metavolcanics and 12 to 30 ppm in metavolcaniclasts.

Figure 5. Major and trace elements variation in groundwater samples collected from MV, MVC and MP rock dominated areas: (A) major element concentration (ppm) in groundwater (#1-16) from MV area; (B) major oxides (wt%) in rock (MV); (C) trace element concentration (ppm) in groundwater (#1-16) from MV area and (D) trace element concentration (ppm) in the rock (MV); (E) major element concentration (ppm) in groundwater (# 17-28) from MVC and MP area; (F) major oxides (wt%) in the rock (MVC & MP); (G) trace element concentration (ppm) in groundwater (# 17-28) from MVC & MP area and (H) trace element concentration (ppm) in the rock (MVC & MP).
Table 4. Hydrogeochemical data (ppm), Negash, Tigray, northern Ethiopia (Bheemalingeswara and Nata, 2006).

| S.No. | # No. | Rock    | E.C (µS) | TDS (ppm) | SAR Hardness | Na  | K  | Ca | Mg  | Cu | Pb | Mn | Fe | Ni |
|-------|-------|---------|----------|-----------|--------------|-----|----|----|-----|----|----|----|----|----|
| 1     |      | NR2     | ---      | 6         | 270          | 40  | 19 | 57 | 31  | bd | 4  | bd | 11 | 9  |
| 2     |      | NR4     | ---      | 6         | 329          | 44  | 8  | 74 | 35  | bd | 3  | bd | 5  | 10 |
| 3     |      | NR7     | ---      | 7         | 387          | 59  | 3  | 104| 31  | bd | 5  | bd | 9  | 8  |
| 4     |      | NR9     | ---      | 7         | 225          | 43  | 6  | 57 | 20  | bd | 5  | bd | 5  | 10 |
| 5     |      | NR14    | ---      | 13        | 229          | 77  | 16 | 60 | 40  | bd | 4  | bd | 7  | 11 |
| 6     |      | NR22    | ---      | 7         | 221          | 37  | 13 | 53 | 21  | bd | 5  | bd | 9  | 11 |
| 7     |      | NR25    | ---      | 6         | 219          | 35  | 14 | 50 | 21  | bd | 4  | bd | 10 | 8  |
| 8     |      | NR28    | ---      | 5         | 207          | 28  | 0  | 55 | 17  | bd | 1  | bd | 8  | 9  |
| 9     |      | NR30    | ---      | 5         | 168          | 26  | 8  | 46 | 13  | bd | 4  | bd | 11 | 11 |
| 10    |      | NR31    | ---      | 5         | 283          | 34  | 7  | 72 | 25  | bd | 5  | bd | 7  | 8  |
| 11    |      | NR34    | 420      | 294       | 6           | 216 | 29 | 5  | 48  | 28 | 2  | 6  | 2  | 1  |
| 12    |      | NR35    | 600      | 420       | 5           | 235 | 29 | 2  | 48  | 28 | 2  | 8  | 4  | 5  |
| 13    |      | NR40    | 390      | 273       | 4           | 164 | 22 | 3  | 41  | 15 | 2  | 8  | 4  | 5  |
| 14    |      | NR41    | 410      | 287       | 6           | 182 | 35 | 4  | 35  | 23 | 2  | 9  | 5  | 6  |
| 15    |      | NR56    | 350      | 245       | 5           | 134 | 25 | 5  | 29  | 15 | 2  | 8  | 2  | 5  |
| 16    |      | NR57    | 150      | 105       | 20          | 63  | 58 | 0  | 4   | 13 | 1  | 6  | 1  | 4  |
| 17    |      | NR43    | MVC+MP   | 340       | 238         | 7   | 137| 31 | 7   | 27 | 17 | 2  | 8  | 3  |
| 18    |      | NR44    | MVC+MP   | 470       | 329         | 9   | 156| 44 | 6   | 28 | 21 | 2  | 9  | 5  |
| 19    |      | NR46    | MVC+MP   | 590       | 413         | 4   | 264| 24 | 6   | 48 | 35 | 2  | 8  | 2  |
| 20    |      | NR47    | MVC+MP   | 330       | 231         | 2   | 241| 16 | 6   | 67 | 18 | 2  | 8  | 4  |
| 21    |      | NR48    | MVC+MP   | 410       | 287         | 3   | 154| 17 | 7   | 32 | 18 | 2  | 7  | 2  |
| 22    |      | NR49    | MVC+MP   | 710       | 497         | 5   | 242| 34 | 3   | 54 | 26 | 2  | 7  | 3  |
| 23    |      | NR50    | MVC+MP   | 810       | 567         | 6   | 303| 40 | 8   | 54 | 41 | 2  | 7  | 3  |
| 24    |      | NR51    | MVC+MP   | 1140      | 798         | 5   | 414| 36 | 5   | 67 | 60 | 2  | 8  | 3  |
| 25    |      | NR52    | MVC+MP   | 740       | 518         | 5   | 278| 33 | 6   | 57 | 33 | 2  | 8  | 4  |
| 26    |      | NR53    | MVC+MP   | 590       | 413         | 4   | 232| 27 | 4   | 50 | 26 | 2  | 7  | 3  |
| 27    |      | NR54    | MVC+MP   | 970       | 679         | 22  | 460| 168| 4   | 25 | 97 | 1  | 6  | 1  |
| 28    |      | NR33    | MVC+MP   | ---       | 6           | 216 | 34 | 5  | 47  | 24 | 2  | 9  | 5  | 5  |

Note: bd: below detection; MV= Metavolcanic; MP= Metapelite; MVC= Metavolcaniclast

5.3 Water Geochemistry

Na shows high values as compared to other major ions, varying from 16 to 168 ppm, Ca from 4 to 104 ppm, Mg from 13 to 97 pm and K < 19 ppm. Na and Mg shows high values in
groundwater collected from MVC and MP dominated area. On the other hand, Ca shows higher values in the water collected from MV (Table 4, Fig. 5). Potassium shows low values and insignificant variation. Among trace elements, Fe values vary from 1 to 12, Ni ~13 and Pb 1 to 9. Other elements such as Mn vary from < 5, Cu < 2 and Co and Zn are in below detection level. Fe, Ni and Mn show higher values in the samples collected from MV dominated area and Pb, Ni and Mn in those collected from MVC and MP dominated area.

6. DISCUSSION
6.1 Petrography
On the basis of the dominant mineral phases that are present in different rock types in the study area and their textures, the rocks are named as metavolcanic, metavolcaniclastic, phyllite and slate. The presence of chlorite, muscovite and biotite (rare) and development of foliation indicates low grade metamorphism in the area. At the same time, development of schistosity at places is observed due to the localized effects but only in MVC, MP as compared to MV. On the basis of the nature of alignment, texture, size and type of minerals identified in these rocks, it is possible to conclude that the rocks have experienced only low grade greenschist facies metamorphism. However, the presence of minerals like tremolite and biotite (rare) in some sections suggests low-medium grade metamorphic conditions though their identification is somewhat difficult because they are mostly fine grained. Since they are not common minerals, it is possible that they are developed due to the increased temperatures locally provided by the later intrusive bodies or hydrothermal activity or shearing.

Among the three types of rocks such as MV, MVC and MP, metavolcanics being dominated by metabasalts clearly shows fine grained matrix with few coarse mafic and plagioclase minerals (Figs. 2A-D) and corresponding geochemistry in figure 4 and tables 1 and 2. Similarly, MP is characterized by the fine grained matrix and with well developed foliation and crenulations (Fig. 2E-F) and corresponding geochemistry in figure 4 and tables 1 and 2. In the case of MVC, the rocks show variation in matrix as well as composition of clasts (Fig. 3A-D) and geochemistry (Fig. 4 and Tables 1 and 2). Matrix varies from grey/white colored volcanic tuff (+fine argillaceous) with fine clay/ash/muscovite to green colored fine grained mafic composition. There are also indications of the presence of glassy material (glass shards?) in the section
indicating volcanic source. The clasts, on the other hand, vary from dominant quartz, feldspar to rare green colored mafic rock fragments and show angular, rounded, sub-rounded and irregular shapes. The source for such variation in composition in clasts and matrix is assumed to be due to arc related volcanic activity with limited sedimentation. On the basis of the petrographic data, it may be said that the source for MVC is primarily volcanic with subordinate sediments. The clasts often show elongation/stretching, indicating shearing effects and are typically related to the shear zones in the field. The size variation of the clasts from east (coarse) to west (fine) in the study area seems to indicate the direction of the source of supply to be in the east. However, these rocks being subjected to later folding and faulting, such relationship needs to be established only after regional correlation. Secondary quartz is more prominent in metavolcaniclastic rock as compared to others. Quartz and calcite veins are common in all types of rocks and often cut across the schistosity and represent different episodes.

Among opaque minerals, pyrite is common often showing cubic outlines. It is also visible in hand specimen, often showing alteration to limonite. Association of opaques within the primary minerals, alteration products and quartz and calcite veins of different generation indicates difference in their genesis and emplacement conditions. The first variety in association with primary minerals is seen distributed randomly and in relation to the primary magmatic minerals e.g. magnetite, ilmenite (common in MV). The secondary variety is the one which is formed due to chemical breakdown of the primary mafic minerals (common in MV). The clasts of mafic variety in MVC also show similar alterations. The third is in association with the hydrothermal cross cutting quartz and calcite veins (Figs. 2A-D). In the case of MVC and MP, the opaques are mainly related to euxinic environment or hydrothermal activity. The pyrite related to euxinic environment is a sedimentary pyrite and is also quite visible in the hand specimen. The hydrothermal variety is fine grained and associated with hydrothermal veins and is quite prominent in shear zones. Interestingly, chalcopyrite, though not identified under microscope, is the dominating sulfide ore mineral in shear zones as compared to pyrite as indicated by the presence of green malachite stains and anomalous concentrations for copper (Table 2). Absence of any indications of development of gossan, which is common in base metal sulfides, is quite conspicuous in the area. Anyone or more of the following reasons may explain the absence or non-development of gossan- i) the base metal mineralization is of very low grade, ii) pyrite
mineral (dominantly gossan producing mineral) is very low among sulfides, iii) the mineralization is subsurface and not exposed for intense weathering, iv) the mineralization is shear zone-related and dispersed.

Finally, uplift of the basement rocks has facilitated meteoric water-rock interaction in addition to the hydrothermal solutions-rock interaction and has resulted in kaolinisation, sericitisation etc. So, the mineralogy and related textural properties suggest that the rocks have experienced low grade regional metamorphism and emplacement of granitic plutons have facilitated ore-forming fluids that are dominant in the shear zones.

6.2 Geochemistry of Basement Rocks and Mineralisation

Tectonic discrimination diagram (Fig.6) drawn between TiO\(_2\) and Zr for metavolcanic rocks suggests an island arc tectonic setting. Basic metavolcanic unit is the dominant unit among MV which is calc-alkaline in composition and related to volcanic arc setting environment (Alene et al., 2000). Major oxide data indicates lower values for K (Fig.4) suggesting that the metavolcanics are not only calc-alkaline in composition but also low –K type. Erratic behavior and low values of K seems to be a common feature in metamorphosed rocks due to the mobility of K either through diffusion, albitionisation of plagioclase or loss due to mobility during metamorphism (Alene et al., 2000).

Phyllite rocks show high silica values with marginally increased Al\(_2\)O\(_3\). Some of the samples show relatively higher values for Mg as compared to MV and MVC (Table.2). Higher values for Mg are ascribed to mineral chlorite. Significant variation in trace element content in phyllites is well reflected by the colors that it displays. The colors include grey, green, violet, and red. Higher values for iron in phyllite are ascribed to the dominantly present sedimentary pyrite. Along the shear zones, both in phyllites and MVC, the presence of grey or silvery white colored sericite indicating sericitisation is quite conspicuous. Sericitisation seems to indicate input of potassium.

![Figure 6. Tectonic setting discrimination diagram, metavolcanics of Negash (Pearce, 1980).](image)
(alkali metasomatism?) that is leached by hydrothermal solutions from the country rock MV which clearly indicate lower values for K⁺. Other elements like Mn and Ba, though relatively high in phyllite, do not suggest any abnormal behavior and any trend.

The metavolcaniclastics typically show quite variable concentrations for SiO₂, Al₂O₃, MgO and Fe₂O₃. These values seem to be related to the varying size and composition of clasts from east to west and at the same time, to the varying matrix composition from tuffaceous to argillaceous and mixed. Interestingly, some of the samples show relatively higher values for Ba and anomalous concentrations for copper (>6500 ppm), particularly along shear zones (Table 2).

On the basis of the present and published petrological, geochemical and structural data, it is possible to construct a sequence of events that have taken place in the area. Sedimentation and development of linear sedimentary belts in intra oceanic basins (Tadesse, 1999) was accompanied by bimodal volcanism during Middle to Late Proterozoic times. The sediments together with volcanics have undergone low grade regional metamorphism. The younger plutonic intrusives mark the end of the tectonic activity and Proterozoic Era. They have facilitated the generation of hydrothermal solutions which have leached the metals from the rocks and transported to the sites of deposition i.e. structural weak zones. During the same time, N-NE trending shear zones have developed and facilitated deposition of copper sulfide-bearing hydrothermal fluids particularly along the contacts among metavolcanics, metasediments and MVC. It is indicated by the presence of malachite stains and anomalous concentrations of Cu (Table 2). Since the type and content of the metal depends on the nature of the source rock, the metals showing anomalous values for copper suggest the source as basic MV which is the dominating rock type in the area. Other base metals like lead and zinc as expected do not show high values in the area because of lack of the suitable source rocks such as felsic volcanics and thick sedimentary cover.

The absence of gossan and the presence of malachite and anomalous copper values (Table 2) with subordinate quantities of silver and gold (Dwivedi, 2003), particularly in shear zones indicate the presence of a shear zone-hosted copper sulfide mineralization. Interestingly, similar type of shear zone-controlled base metal mineralization (Zn up to 2-3%) about 100-150 m wide
with 5-6 km strike length near Abrha Atsbha about 10 km west of Negash is also reported. Ezana Mining Development PLC has obtained the license of the area and is undertaking exploration activities. Both the mineralizations are shear zone-controlled and are related to intrusive granitic plutons (Fig.1). Variation in the type of the base metal, copper in the study area (east) and zinc in Abrha Atsbha (west) is related to the source rock i.e. basic metavolcanics for Cu (dominant in Negash) and metarhyolite for Zn (dominant at Abrha Atsbha). Since shear zones being anomalous in the area and vary considerably in thickness and metal content, it needs to be studied in detail so as to quantify the metals and their economic significance. It is interesting to note that the quartz veins (of different generations?) in Negash area show N-NE trend similar to shear zones whereas at Abrha Atsbha in addition to N-NE trending quartz veins, there are E-W trending quartz veins parallel to Wukro fault. The veins trending N-NE are Zn-rich and E-W are barite rich.

Regarding tectonic setting, the rocks in the study area represent intra-oceanic arc sequences of northern Ethiopia (southern part of Arabian Nubian Shield) that have varied lithological and geochemical characteristics (Tadesse, 1999) and are consistent with the arc accretion models as suggested for Sudan, Egypt and Saudi Arabia (Alene et al., 2000). The arc related tectonic setting together with bimodal volcanism though supports VMS type base metal mineralization, a shear-controlled base metal mineralization is identified in the study area on the basis of petrographic, structural and geochemical data.

6.3 Geochemistry of Groundwater

Water hardness, one of the important parameters used to evaluate natural water quality is generally known to be influenced chemically by dissolution of calcite and dolomite. But it can also be influenced by other rocks which have significant amount of Ca and Mg-bearing soluble plagioclase feldspar and mafic minerals respectively. The proportion of Ca$^{2+}$ and Mg$^{2+}$ present in water can be used as an indicator of the geology of the aquifer. Calculated values for total hardness in 32 water samples range from 130 to 460 ppm. According to the hardness classification, the majority of the samples from MP come under hard water category (Todd, 1980). Interestingly, these values are comparable with high Pb values in MP. Geochemical affinity between Pb and hardness if any, need to be established. Ca and Mg ratios (Ca/Mg) range
from 2.88 (MV and MVC) to 0.258 (MP). The lack of Ca-plagioclase and the presence of Mg-rich chlorite in MP are related to the higher values for Mg in MP. Higher values for Ca in MV are related to epidote and plagioclase feldspar and in MVC to the plagioclase feldspar and mafic minerals-rich clasts (Figs. 5). Sodium, though is relatively high in the samples, it does not show a particular trend with reference to the rocks. Sodium absorption ratio (SAR) is another property of water that indicates sodium concentration and its possible effects on soil. The samples show significant variation in SAR values from 2-10 except two samples that are showing very high values about 20. It is known that higher amounts of sodium affects the soil by decreasing permeability and become toxic to plants (sodium poisoning). So, the soils either alkali (sodium with carbonate) or saline (sodium with chloride or sulphate) will not support proper plant growth. Hence the water is non-suitable for irrigation purpose (Fetter, 1994). According to TDS values, the water type is fresh water type and fit for domestic use.

Trace element data being limited, it is difficult to say whether the water particularly from shear zones is safe for drinking purposes. It is well known that the base metal mineralization, even low grade, can contribute trace elements Cu, Zn, Pb and others significantly to groundwater and influence their quality. The water geochemical data when compared with the water quality standard values (maximum limit) as proposed by World Health Organization (WHO, 1993) (Fe-0.3 ppm; Ni -0.02; Pb-0.01; Mn –0.5; Cu-2.0 & Zn 3.0), some of the trace elements like Ni, Pb and Fe show much higher in concentration (>10 ppm) than the permissible levels. These increased values are related to the alteration zones where the incidence of base metal and other metals are relatively higher. Among Fe, Ni and Pb, iron and nickel are related to MV and MVC; and lead to MP. Both Fe and Ni seem to be related to the primary mafic mineralogy such as olivine, pyroxenes and amphiboles (Fig.2A-D; Alene et al., 2000).The mafic and opaque minerals as mentioned above are quite susceptible to breakdown and capable of providing trace metals in significant quantities to groundwater.

Shear zones being good aquifers, have become sites for the construction of many hand dug wells. Since these zones show incidence of base metal mineralization with varying metal contents (Cu, Pb and Zn; and associated metals like Co, As, Cd, Ni, Cr etc) (Fig. 5) and whose concentrations are much higher than the normal background concentrations can cause serious long term health
problems. So, it is essential to regularly monitor water quality and water related irrigation and other activities so as to avert possible human risks.

7. CONCLUSION

- The presence of chlorite, muscovite, biotite (rare) in metavolcanics, metavolcaniclastics and phyllite and development of foliation and crenulations in phyllite and moderately developed schistosity along the intrusive contacts and shear zones indicate that the rocks in the area have experienced low grade of metamorphism in the area. Minerals like tremolite and biotite are rare and localized.
- Among the three types of rocks (MV, MVC and MP), MVC consists of volcanic derived tuff dominated matrix and clasts of lithic fragments varying in composition, size, shape and mostly randomly oriented.
- Opaques though are common in all rock types, those associated with hydrothermal veins are related to ore minerals.
- In the area the shear zones are commonly associated with green color malachite, sericite, quartz veins, moderately developed schistosity and elongated clasts. Copper anomalies together with malachite stains indicate a possible shear zone-controlled Cu mineralization where the source is related to basic metavolcanics. It is comparable with the nearby (Abrha Atsbha) shear zone-controlled Zn-mineralization where the source for Zn is related to metarhyolite.
- Groundwater geochemical data indicates that the water is safe for domestic purposes. Trace elements such as Ni, and Fe are related to MV and MVC whereas Pb values to MP. The major elements are Ca and Mg. Ca is related to plagioclase and epidote in MV and MVC, and Mg to chlorite in phyllite.
- Shear zones being mineralised and also form good targets for groundwater development, they need to be probed in detail to avoid long term human risks.

8. ACKNOWLEDGEMENTS

The study forms part of the NORAD-II funded project entitled “Qualitative and quantitative evaluation of metamorphites hosted base metal/ transition metal (Pb, Zn, Cu, Fe, Mn, Ni, Ag and Co) mineralization and its impact on groundwater and its chemistry in the area around Negash,
Hawzien and Wukro, Tigray Province, northern Ethiopia”. Authors duly acknowledge the funding provided by NORAD-II. Thanks are also due to Drs. Mulugeta Alene, Addis Ababa University, Dirk Kuester, BGM and Kurkura Kebeto, Mekelle University for reviewing the manuscript and providing critical comments.

9. REFERENCES
Abdeselam, M.G & Stern, R. J. 1996. Sutures and shear zones in the Arabian – Nubian shield. Journal of African Earth Science, 23: 289-310.
Alemu, T. 1998. Geochemistry of Neoproterozoic granitoids from the Axum area, northern Ethiopia. Journal of African Earth Science, 27:437-460.
Alene, M., Ruffini, R & Sacchi, R. 2000. Geochemistry and geotectonic setting of Neoproterozoic rocks from Northern Ethiopia (Arabian-Nubian shield). Gondwana Research, 3: 333-347.
Arkin, Y., Beyth, M., Dow, D.B., Levitte, D., Temesgen, H & Tsegaye, H. 1971. Geological map of Mekelle sheet area ND 37- 11, Tigre Province. Geol. Surv. Ethiopia Publication, Ministry of Mines, Addis Ababa.
Asrat, A., Barbey, P & Gleizes, G. 2001. The Precambrian geology of Ethiopia: a review. Africa Geoscience Review, 8 (3): 271-288.
Asrat, A. 2002. Structural (AMS), Petrological and Geochemical (Rb-Sr, Sm-Nd, U-Pb) studies of the Pan African Negash and Konso plutons (Ethiopia): Significance of mafic-felsic magma interactions to the construction of calc-alkaline plutons. Ph.D Thesis, Centre de Recherches Petrologiques & Geochimiques, UPR 2300, 54501 Vandoeuvre-les-Nancy.
Ayalew, T., Bell, K., Moore, J.M & Parih, R.R. 1990. U-Pb and Pb-Sr geochemistry of the western Ethiopian Shield. Geological Society of America Bulletin, 102: 1309-1316.
Bheemalingeswara, K & Nata Tadesse, 2006. Assessment of groundwater quality in an area of low grade metamorphites and associated sporadic base metals sulfides around Negash, Hawzen and Wukro, Tigray Province, northern Ethiopia: A preliminary study. In: K. Bheemalingeswara and Mebrahtom Gebrekirstos (Eds.), Research Review 2006, Proceeding volume-I, Mekelle University, Mekelle, 35-47 pp.
David Shelly. 1993. Igneous and metamorphic rocks under microscope. Chapman & Hall, 2-6 Boudary Row, London, 445p.
De Souza Filho, C.R & Drury, S.A. 1998. A Neoproterozoic supra-subduction terrane in northern Eritrea, NE Africa. J. Geological Society of London, 155: 551-566.

Dwivedi, S. B. 2003. Metamorphites hosted base/ transition metal of the area around Negash, Tigrai Province, Northern Ethiopia. 4th Ethiopian Geoscience and Mineral Engineering Association (EGMEA) Congress, Abstract Volume. Addis Ababa, 46-47 pp.

Edmunds, W.M & Smedley, P.L. 1996. Groundwater geochemistry and health: an overview. In: J.D. Appleton, R. Fuge and G. J.H. McCall (Eds.), Environmental geochemistry and health. Geological Society of London, special publication, 113: 91-105.

Fetter, C.W. 1994. Applied hydrogeology. Mac Millan College Publ. Company, Inc., New York.

Garland, C.R.1980. Geology of Adigrat Area. Memoir,1. Min. Mines & Energy, Ethiopia, 51 p.

Genna, A., Nehlig, P., Le Goff, E., Guerrot, C & Shanti, M. 2002. Proterozoic tectonism of the Arabian Shield. Precambrian Research, 117: 21–40.

Gerra, S. 2000. A short introduction to the geology of Ethiopia. Chron. Rech. Min., 540: 3-10.

Gichile, S. 1992. Granulites in the Precambrian basement of southern Ethiopia: geochemistry, P-T condition of metamorphism and tectonic setting. J. Afr. Earth Sci., 15 (2): 251-263.

Gilboy, C.F. 1970. The Geology of the Gariboro region of southern Ethiopia. Ph.D thesis, University of Leeds, England.

Hem, J. D. 1992. Study and interpretation of the chemical characteristics of natural water. 3rd Edition, Washington: United States Geological Survey, Water supply Paper, 2254p.

Jelene, D.A. 1996. Mineral occurrences of Ethiopia. Min. Mines & Energy, Ethiopia, 450p.

Johnson, P.R & Woldehaimanot, B. 2003. Development of the Arabian–Nubian Shield: perspectives on accretion and deformation in the northern East African Orogen and the assembly of Gondwana. In: M. Yoshida, B.E. Windley and S. Dasgupta (Eds.), Proterozoic East Gondwana: supercontinent assembly and breakup. Geol. Soc. London, special publication, 206: 289–325.

Kazmin, V. 1973. The geological map of Ethiopia, 1:2,000,000. Geol. Surv., Addis, Ethiopia.

Kazmin, V., Shiferaw, A & Balcha, T. 1978. The Ethiopian basement: stratigraphy and possible manner of evolution. Gologiche Rundschau, 67: 531-548.

Miller, J.A., Mohr, P.A & Rogers, A.S. 1967. Some new K-Ar age determinations of basement rocks from Eritrea. Bulletin of Geophysical Observatory, AAU, Ethiopia, 10:53-57.
Miller, N.R., Alene, M., Sacchi, R., Stern, R.J., Conti, A., Kroner, A & Zuppi, G. 2003. Significance of the Tambian Group (Tigrai, N. Ethiopia) for snowball earth events in the Arabian – Nubian Shield. Precambrian Research, 121: 263-283.

Mock, C., Arnaud, N.O., Cantagrel, J.M & Yirgu, G. 1999. $^{40}$Ar/$^{39}$Ar Thermochronology of the Ethiopian and Yemeni basements: reheating related to the Afar plume? Tectonophysics, 314:351-372.

Pearce, J.A, 1980. Geochemical evidence for the genesis and eruptive setting of lavas from Tethyan ophiolites. In: A. Panayiotou (Ed.), Ophiolites. Proceedings of International ophiolite symposium. Geological Survey Department, Nicosia, Cyprus, 261-277.

Rogers, A.S., Miller, J. A & Mohr, P.A. 1965. Age determinations on some Ethiopian basement rocks. Nature, 206:1021-1023.

Shackleton, R.M.1994. Review of the Late Proterozoic sutures, ophiolitic melanges and tectonics of Eastern Egypt and Northern Sudan. Geol. Rundschau, 83:537-546.

Shackleton, R.M.1996. The final collision zone between East and West Gondwana. Journal of African Earth Science, 23: 271-287.

Stern, R.J. 1994. Neoproterozoic (900–550 Ma) arc assembly and continental collision in the East African Orogen: implications for consolidation of Gondwanaland. Ann. Rev. Earth Planet Sci., 22:319–351

Stoeser, D.B & Camp, V.E. 1985. Pan-African microplate accretion of the Arabian Shield. Geol. Soc. Am. Bull., 96: 817-826.

Tadesse, T. 1996. Structure across a possible intra-oceanic suture zone in the low grade Pan-African rocks of northern Ethiopia. Journal of African Earth Science, 23: 375-381.

Tadesse, T., Hoshino, M., Suzuki, K & Iizumi, S. 2000. Sm-Nd, Rb-Sr and Th-U-Pb zircon ages of syn-and post-tectonic granitoids from the Axum area of northern Ethiopia. Journal of African Earth Science, 30: 313-327.

Tadesse, G & Allen, A. 2002. Geology and geochemistry of the Neoproterozoic Tuludimtu Orogenic belt, western Ethiopia. In: 19th Colloquium of African Geology- El Jadida, Morocco, Abstract volume, 173-174.

Tadesse T, Hoshino, M & Sawada, Y. 1999. Geochemistry of low grade metamorphic rocks from the Pan-African of the Axum area, northern Ethiopia. Precam. Res., 99: 101-124.
Teklay, M., Kröner, A., Mezger, K & Oberhansli, R. 1998. Geochemistry, Pb–Pb single zircon ages and Nd–Sr isotope composition of Precambrian rocks from southern and eastern Ethiopia: implications for crustal evolution in East Africa. J. Afr. Earth Sci., 26:207–227

Todd, D.K. 1980. Groundwater Hydrology. John Willy and Sons, Inc., New York.

Vail, J.R. 1983. Pan-Africal crustal accretion in north-east Africa. J. Afr. Earth Sci., 1: 285-294.

Vail, J.R. 1988. Tectonics and evolution of the Proterozoic basement of north-east Africa. In: S. El-Gaby and R.O. Grielng (Eds.), The Pan African Belt of Northeast Africa and adjacent areas. Friedr. Vieweg and Sohn, Braunschweig/Wiesbaden, 195-226.

WHO. 1993. Guidelines for drinking water quality Geneva.

Worku, H & Schandelmeier, H. 1996. Tectonic evolution of the Neoproterozoic Adola Belt of southern Ethiopia: evidence for a Wilson Cycle process and implications for oblique plate collision. Precambrian Research, 77:179–210.