Characteristics Of Supergene Alteration In The Binamar Area, Ardabil, NW Iran

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Abstract— **Binamar area located in the northwest of Iran in the Alborz-Azerbaijan structural zone and completely is covered by a series of Eocene volcanic rocks, including mainly porphyritic and megaporphyritic andesite, basaltic andesite, basalt, and accompanying agglomerates and andesitic tuffs. The volcanic rocks partially have suffered supergene alteration associated with secondary oxide copper mineralization, including malachite, azurite, brochantite, and native copper. Clay minerals, including kaolinite, illite and montmorillonite, iron oxide and some quartz are the major components in the supergene altered zone. Based on the field observations and by noticing the type of minerals in the study zone, it is supposed that acid surface water, derived from oxidation reactions with sulfide minerals, has caused supergene alteration within the volcanic rocks.**

Keywords — mineralogy; supergene alteration; clay; volcanic rocks; Binamar; Iran

I. INTRODUCTION

Weathering and erosion are the Earth's primary natural mechanisms for redistributing mass on its surface, and these processes are driven by natural agents such as climate, animals, plants and surface and ground waters. When rocks that were formed at high temperatures and high pressures are exposed at the Earth's surface (average $T_{atm} \sim 15°C$; $P_{atm} \sim 1$ bar; and $pO_2 \sim 0.2$ bar), their equilibrium is disturbed. This causes their mineral constituents to react and undergo transformations so as to adjust to the new lower temperatures, pressures, and higher oxygen concentrations and moisture conditions. Supergene minerals form on the Earth's surface. Supergene mineralization is controlled by the parent rock composition, geomorphological environment, and climatic conditions.

In the traditional view, supergene alterations are the products of reactions between hypogene sulfide minerals and descending, acidic meteoric waters with other preexisting silicate minerals and rocks. These processes take place at or near the ground surface in subaerial environments and change compositions of host rocks and primary minerals [1]. Supergene processes, irrespective of their natural or anthropogenic origin, lead to the formation of oxygen-bearing minerals from the polar to the tropical climatic zones. All such minerals form in the *Critical Zone* — the contact zone where the atmosphere, biosphere, pedosphere, and hydrosphere interact and operate together on the rocks [2]. In the present contribution the mineralogy and interactions leading to the formation of supergene alteration of volcanic rocks in the Binamar area are examined.

II. GEOLOGY OF THE SUDY AREA

Binamar area is located in the northwest of Iran in the Ardabil province. Based on classification of structural units of Iran [3], Binamar area is situated in the western Alborz-Azerbaijan zone (Fig. 1), which is part of the Alpine-Himalayan fold belt. Studied area situated in the Tarom-Hashtjin metallogenic province (THMP). Structurally, THMP is located in merge between western Alborz Magmatic Belt and Sanandaj-Sirjan Zone and have several mineralizations of epithermal-porphyry and other type of hydrothermal ore deposits [4, 5].
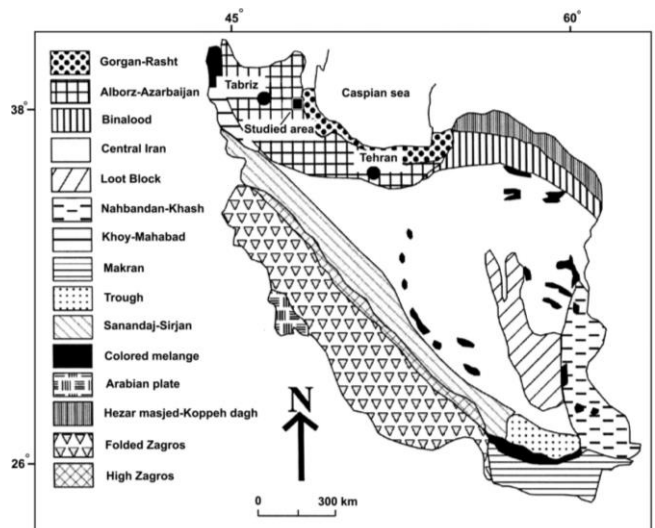

Figure 1: Major structural zones of Iran and the location of studied area in the western Alborz-Azerbaijan zone.

The geological setting of the studied area is Cenozoic volcano-tectonic zone, which contains Eocene porphyritic and megaporphyritic andesite, basaltic andesite, basalt, accompanying agglomerates and andesitic tuffs [6]. Andesite is the most abundant rock type among others. The common texture in this rock is porphyritic with cryptocrystalline to microlitic

matrix. Feldspars (plagioclase) are the most common constituent as both phenocryst and groundmass rock-forming mineral. Basaltic andesite and basalt comprise less than 10% of all volcanic rocks. These rocks consist of ferromagnesian minerals such as pyroxene with some plagioclase in a cryptocrystalline to glassy matrix (Fig. 2).
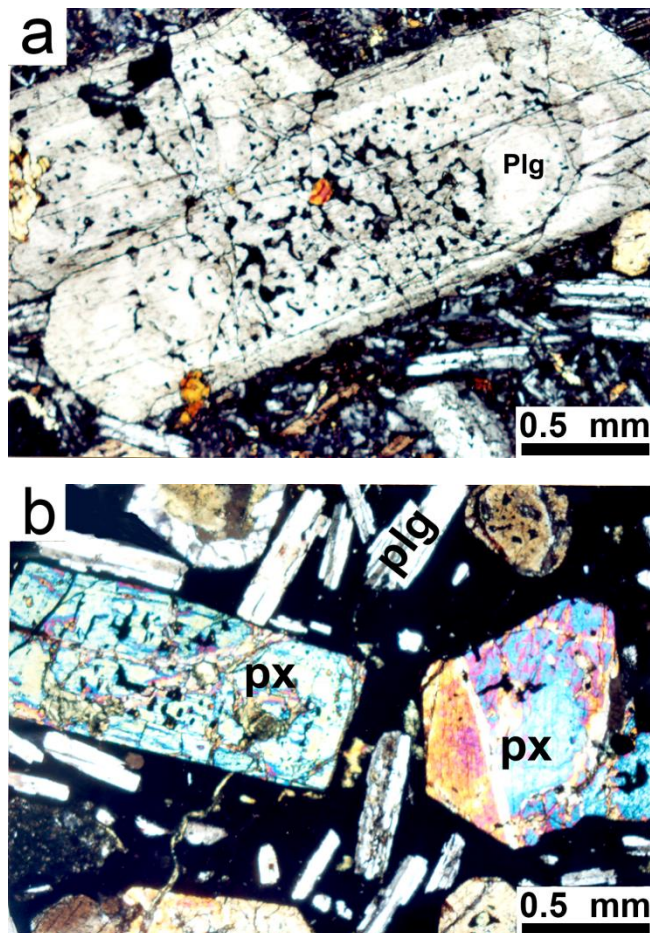

Figure 2: a) phenocryst of plagioclase (plg) in the microlitic matrix including plagioclase and glass in the XPL light. b) phenocrysts of pyroxene (px) with some plagioclase (plg) in the glassy matrix (black) in the XPL light.

III. MATERIALS AND METHODS

A large number of samples were collected from fresh and altered volcanic rocks. The petrography was studied in thin sections using a polarizing microscope. Bulk mineral composition was determined by X-ray diffraction (XRD) using a Siemens D500 diffractometer, with Cu-Ka radiation and a graphite monochromator. Chemical analyses of whole rock were carried out with wavelength dispersive X-ray fluorescence (WD-XRF) using a Siemens SRS 303 XRF spectrometer. Conclusion obtained from the combination of field observations and analytical results.

IV. SUPERGENE ALTERATION

As described above supergene process is the alteration of rock-forming minerals by interaction with acidic meteoric waters. The formation of supergene alteration involves dissolution of rock material, transport of soluble elements, and precipitation of new minerals. Circulating ground waters are the principal agents responsible for the oxidation of minerals in the supergene zone. Generation of acid waters is the most important factor to form and develop supergene alteration. The mineralogy of the host rock plays a very significant geochemical role in the development of the mineral assemblages occurring in the supergene zone. This is because host rock silicates and oxides, comprising the volumetrically dominant minerals in the weathering environment, offer exchangeable cations and thus are capable of consuming hydrogen ions via hydrolysis. The greater the quantity of reactive silicates and oxides such as feldspars, mafic minerals, and carbonates, the greater the ability of a wall rock to neutralize acid, sulfate-bearing solutions. This buffering capacity is limited in rock that has already been subjected to phyllic, argillic, and advanced argillic alteration, because phyllosilicates and clays characteristic of these assemblages have only limited capacity to exchange cations for H^+.

The supergene processes in the mineralized area due to the action of meteoric waters containing dissolved sulfate, oxygen and carbon dioxide of atmospheric origin. During these processes the mobility of the various elements is a function of the solubility of their sulfates or hydrogen carbonates, the pH of the migrating solutions, and the Eh of the environment, manifested principally by the presence of free oxygen. In addition, in most copper ore deposits, the stepwise hydrolysis and oxidation of primary pyrite-bearing assemblages leads to a decrease in the pH of descending groundwater and the liberation of oxidized sulfur as SO_4^{2-} anions [6]. In the supergene zone, alumino-silicate minerals are replaced by clays and amorphous silica in the gossan. The mature stage of gossan development is represented by an assemblage of Fe oxides, quartz (or amorphous silica), clay minerals, sulfates, and carbonates overlying the supergene blanket.

V. DISSCUSION

Supergene alteration in the study area was minor and mainly is composed of hematite, quartz and clay minerals, including kaolinite, illite and montmorillonite. Type of clay minerals is detected by XRD analysis (Fig. 3). Alteration restricted at the surface to a thin blanket near copper oxide mineralization. Copper minerals are mainly secondary, including native copper along with copper sulfate (brochantite) and carbonates (malachite and azurite) [6]. The absence of primary copper sulfides (e.g., chalcopyrite and bornite) at the surface of area suggests that most of them were oxidized to secondary supergene copper minerals. Oxidation of primary sulfides such as pyrite (1) and chalcopyrite (2) leads to a decrease in the pH of meteoric waters and the liberation of oxidized sulfur as SO_4^{2-} anions. Addition of carbon dioxide of atmospheric origin or dissolution of carbonate

minerals and rocks may generate HCO_3^- (3). Presence of copper carbonates indicates the generation of bicarbonate anions.

$$2FeS_2 + 2H_2O + 7O_2 \rightarrow 2Fe^{2+} + 4SO_4^{2-} + 4H^+ \qquad (1)$$

$$2CuFeS_2 + 8.5O_2 + 2H_2O \rightarrow Fe_2O_3 + 2Cu^{2+} + 4SO_4^{2-} + 4H^+ \qquad (2)$$

$$H_2O + CO_2 \rightarrow H^+ + HCO_3^- \qquad (3)$$

13 – 0398 brochantite   05 – 0490 quartz
06 – 0221 kaolinite   41 – 1390 malachite

20 – 0572 albite   05 – 0490 quartz
41 – 1483 augite   07 – 0051 montmorillonite

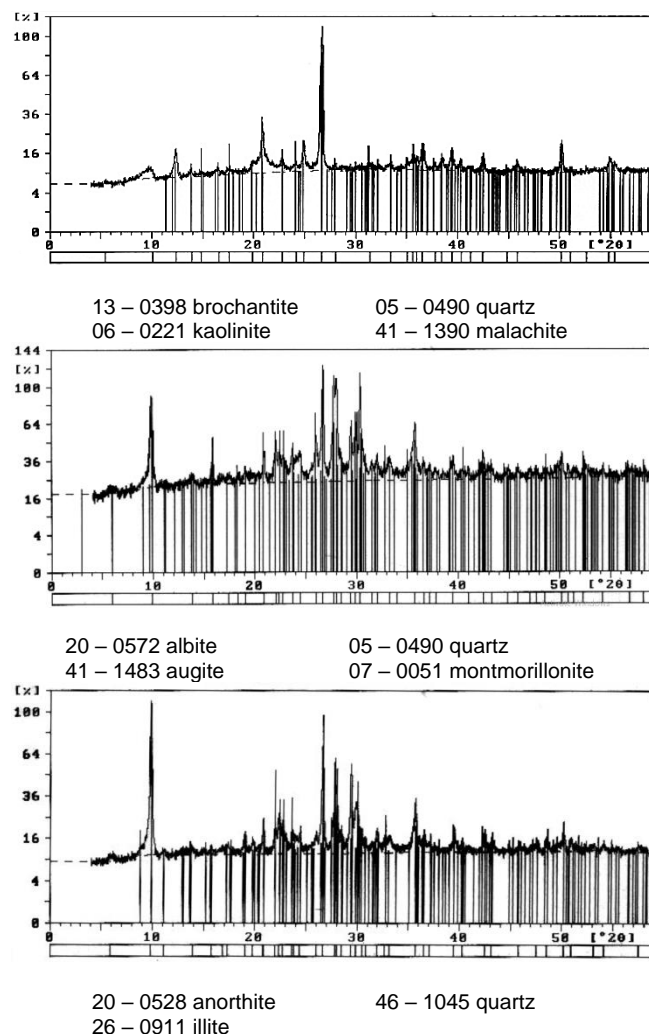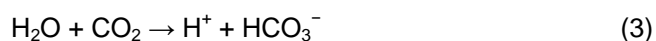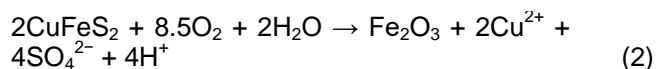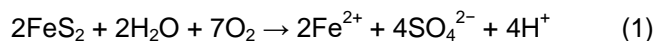20 – 0528 anorthite   46 – 1045 quartz
26 – 0911 illite

Figure 3: XRD powder pattern of altered rocks from supergene oxide zone

The element content of the natural waters and precipitates depends on many factors, including the availability of the elements in deposits or rocks, the degree of oxidation necessary to release the metals from the deposits, and the pH and Eh. The influence of the pH on the mobility of the various elements is obvious, the more acid the waters the greater the metal content. The decomposition of iron disulfides (mainly pyrite) produces acidic meteoric fluids. Pyrite is more susceptible to weathering than the other common sulfide minerals and thereby helps speed up the process of supergene alteration. The dissolved oxygen, carbon dioxide and sulfate in the meteoric waters attack minerals and release the iron, calcium,

magnesium sodium and potassium mainly as soluble hydrogen carbonates and sulfates. Chemical composition of fresh and altered volcanic rocks of the supergene zone is given in Table 1.

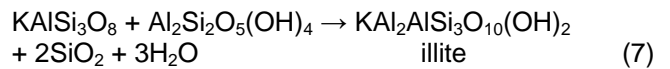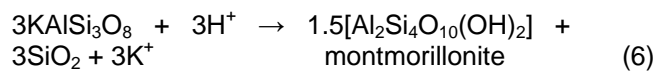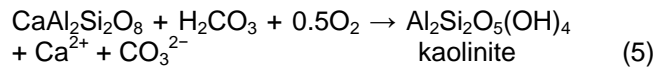Table1: mean value of major oxides of fresh and altered rocks

Oxide (%)	fresh	altered
SiO_2	61.24	57.39
Al_2O_3	13.94	17.81
Fe_2O_3	5.68	10.12
CaO	5.43	1.68
MgO	3.25	1.24
Na_2O	2.79	0.7
K_2O	3.66	0.9
MnO	0.21	0.06
LOI	2.84	9.39

The supergene waters near the surface effect an oxidation of the hypogene minerals and remove various soluble components. Comparison of chemical composition of fresh and altered volcanic rocks shows that the contents of Fe, Al and LOI have increased and contents of Mn, Si, Ca, Mg, Na and K have decreased. As mentioned above, oxidation of pyrite yields soluble ferrous sulfate and sulfuric acid as final products. Other ferrous minerals such as pyroxenes and amphiboles are also susceptible to oxidation and producing ferrous onions. These reactions occur particularly when the water is slightly acidic. In solution the Fe and Mn chemistry are markedly affected by the oxidation-reduction potential (Eh) of the environment because these elements have two possible oxidation states (Fe^{2+} and Fe^{3+}, Mn^{2+} and Mn^{4+}). A study of the redox potentials of the half reactions for iron and manganese indicates that ferrous iron will be oxidized to the ferric state by atmospheric oxygen in both an acid and alkaline environment; the reaction will, however, proceed with greatest facility in alkaline solutions. As regards manganese, however, the potential developed by the oxygen couple is not sufficiently powerful to oxidize Mn^{2+} to MnO_2, in acid solutions but is adequate in an alkaline environment. In the oxidized zones a separation of manganese and iron may take place in some veins because of the difference in the oxidation potentials of the two elements. At the lower pH (circa 4.5) the manganese is more mobile because it remains largely in the soluble Mn^{2+} state whereas the ferrous iron is nearly all oxidized and precipitated as ferric iron. This process is accompanied by capping, the precipitation of iron oxyhydroxides such as hematite (4) and limonite at the surface of supergene zone (Fig. 4a).

$$2Fe^{2+} + 0.5O_2 + 2H_2O \rightarrow Fe_2O_3 + 4H^+ \qquad (4)$$

The sulfuric acid derived from the oxidation of sulfide minerals such as pyrite and chalcopyrite would reacts immediately with any available rock-forming minerals and removes soluble elements. Feldspars, which are the most abundant mineral in the rocks of the study area, are one of the main groups of rock-

forming minerals. Chemically, the feldspars are silicates of aluminium, containing sodium ($NaAlSi_3O_8$), potassium ($KAlSi_3O_8$), calcium ($CaAl_2Si_2O_8$), or combinations of these elements. Sodium, potassium and calcium are not markedly affected by the Eh because of their single oxidation state in nature. Their mobility is essentially dependent on the pH of the solution (H^+ concentration), the concentration of H_2CO_3, CO_2^-, and $HCO3^-$ or the concentration of SO_4^{2-}. Consequently each is highly mobile under both oxidizing and reducing conditions. They exhibit depletion in the altered zone. In the oxidized zone, Na, K and Ca are released from feldspars. During supergene alteration, primary alumosilicate minerals of rocks (e.g. feldspars) are hydrolysed and altered to clay minerals (5-7) (Fig. 4b, c). The formation of illite appears to be a result of the dissolution of K-feldspar that serves as a potassium source to convert kaolinite to illite [8].

$$CaAl_2Si_2O_8 + H_2CO_3 + 0.5O_2 \rightarrow Al_2Si_2O_5(OH)_4 + Ca^{2+} + CO_3^{2-} \qquad \text{kaolinite} \qquad (5)$$

$$3KAlSi_3O_8 + 3H^+ \rightarrow 1.5[Al_2Si_4O_{10}(OH)_2] + 3SiO_2 + 3K^+ \qquad \text{montmorillonite} \qquad (6)$$

$$KAlSi_3O_8 + Al_2Si_2O_5(OH)_4 \rightarrow KAl_2AlSi_3O_{10}(OH)_2 + 2SiO_2 + 3H_2O \qquad \text{illite} \qquad (7)$$

During oxidation silica may be released either as soluble alkali silicates or as dissolved silica probably in the form of monosilicic acid, $Si(OH)_4$ [9]. By increasing the content of $Si(OH)_4$ in the circulating groundwater, it becomes supersaturated with respect to Si and some dissolved silica can precipitate as secondary quartz (8) especially in the cavities of the volcanic rocks (Fig. 4d).

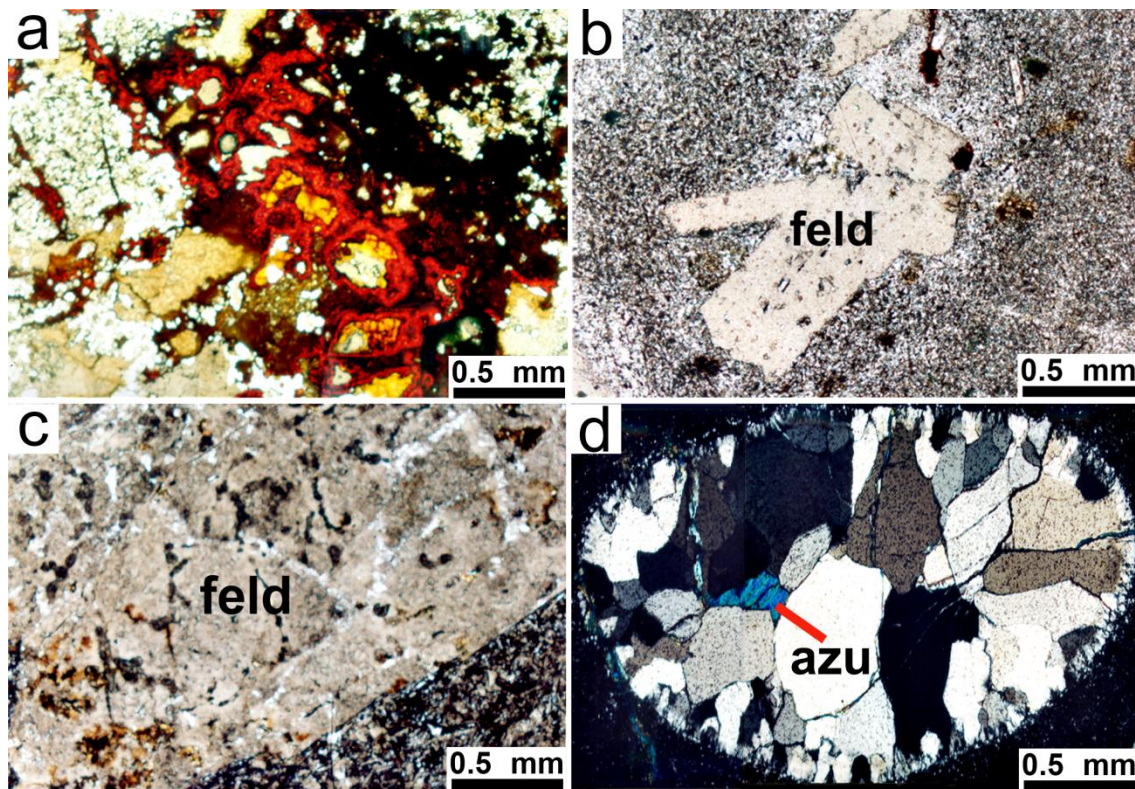$$Si(OH)_4 \rightarrow SiO_2\downarrow + 2H_2O \qquad (8)$$

Figure 4: thin sections of supergene altered rocks: a) hematite (red); b and c) phenocrysts of feldspars (feld) altered to clay minerals; d) cavity of volcanic rock filled with quartz and some azurite (azu).

Aluminum probably enters solution mainly as the soluble sulfate or as the complex alkali sulfates. Alumina follows three main courses during oxidation processes: 1. large amounts of alumina are bound in the secondary clay minerals that occur in parts of the oxidized zones. These minerals probably result mainly by hydrolysis of aluminum salts due to changes in acidity, followed by interactions with K, Na, Mg Fe, SiO_2, etc. 2. Some alumina is coprecipitated with hydrous ferric oxide between pH 5-2.5 largely as $Al(OH)_3$ as a result of the hydrolysis of aluminum sulphate either by dilution or by neutralization of the acidic solutions (9):

$$Al_2(SO_4)_3 + 6H_2O \rightarrow 2Al(OH)_3 + 3H_2SO_4 \qquad (9)$$
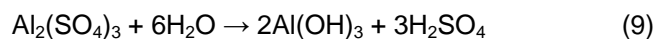
During supergene alteration there was an increase of loss of ignition (LOI). It is because of formation hydrate minerals such as kaolinite, montmorillonite and illite.

VI. CONCLUSION

The volcanic rocks, mainly andesite and basaltic andesite, have suffered supergene alteration. This alteration is associated with copper mineralization. Supergene section in the Binamar area is characterized by gossan and acidic alteration of silicate rocks and minerals. The weathering reactions that were discussed so far involved the transformation of one mineral to another mineral and the release of some ions in solution. Acid meteoric water is derived from oxidation of primary sulfide minerals or dissolution of carbon dioxide attack silicate minerals. Acid waters during this process release Fe, Mn, Si, Na, K, Ca and Mg from sulfides, feldspars and ferromagnesian minerals (e.g. pyroxene). In the supergene altered zone the main enrichments are Fe, Al and LOI and main depletions are Si, Na, K, Mg, Ca and Mn. Much of the iron may be fixed as insoluble oxides such as hematite in the oxidized zones, whereas the other elements may migrate downward in the solutions. By leaching of alkali and alkaline metals from feldspars they are converted to clay minerals such as montmorillonite and kaolinite. Some potassium is precipitated in the clay minerals such as illite.

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