

Mineralogy And Geochemical Characteristics Of The Propylitic Alteration In The Mejdar Area, Ardabil, NW Iran

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Abstract— Mejdar area consists of volcanic rocks, mainly andesite and basaltic andesite, volcanoclastic fall and flow deposits. Propylitic alteration, associated with native copper mineralization is major alteration in this area. The goal of this study is focused on mineralogy and distribution of major and trace elements in propylitic alteration zone. Chlorite, epidote, carbonates, zeolites and some clay minerals are the major minerals in the altered zone. Elements such as Ca and Sr were leached out of the system whereas elements such as Mg, Na, Rb, Si, Fe, Cu and LOI were added. Elements such as K, Mn, Ti, Al, Zr, U, Th, Nb, Ta, Ga, Sc, Mo and V reminded without change. Mineralogical and geochemical studies indicate alteration occurred at below 300°C and nearly neutral to slightly alkaline pH.

Keywords— Mejdar; alteration; propylitic; mineralogy; geochemistry

I. INTRODUCTION

Alteration of volcanic rocks in hydrothermal environments is a well-known process which has been studied in detail in the past [1, 2, 3, 4]. The formation of altered minerals and chemical changes in the host rock depend on various factors such as the composition of the host rock, the temperature and pressure prevailing during alteration, the pressure and chemistry of the fluid phase and the thermodynamic characteristics of the geological environment [5, 6].

Alteration of volcanic rocks is accompanied by mobilization of chemical elements. The degree of mobilization depends on the conditions prevailing during alteration and on the formation mechanism (open vs. closed hydrological system, burial diagenesis, hydrothermal activity, saline-alkaline lake, percolating ground water, etc) [3]. Major and trace elements are widely used in the investigation of chemical mobilization during alteration [3, 7]. Some elements are relatively immobile during alteration and are used to infer magmatic affinities of the parent rocks [8], whilst others are relatively mobile and are leached out or are added to the altered rock during alteration [9, 10]. In order to determine chemical element mobilization during alteration, the altered rocks are compared with their unaltered equivalents.

In the present contribution the mobilization of major and trace chemical elements during propylitic alteration of volcanic rocks in the Mejdar area is examined. Mobilization of chemical elements is studied in association with the formation of authigenic minerals, in order to establish its influence on the genesis of these alteration phases.

II. GEOLOGY OF THE STUDY AREA

Mejdar area is located in the northwest of Iran in the Ardabil province. Based on classification of structural units of Iran [11], it 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) (Fig. 1). 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 [12].

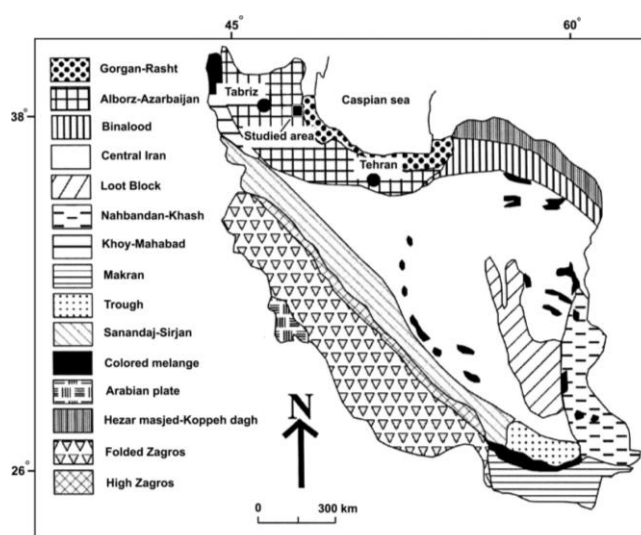


Figure 1: Major structural zones of Iran and the location of studied area in the western Alborz-Azerbaijan zone.

The geological setting of the studied area is Cenozoic volcano-tectonic zone, which contains porphyritic and megaporphyritic andesite, basaltic andesite, basalt, accompanying agglomerates and andesitic tuffs (Fig. 2).

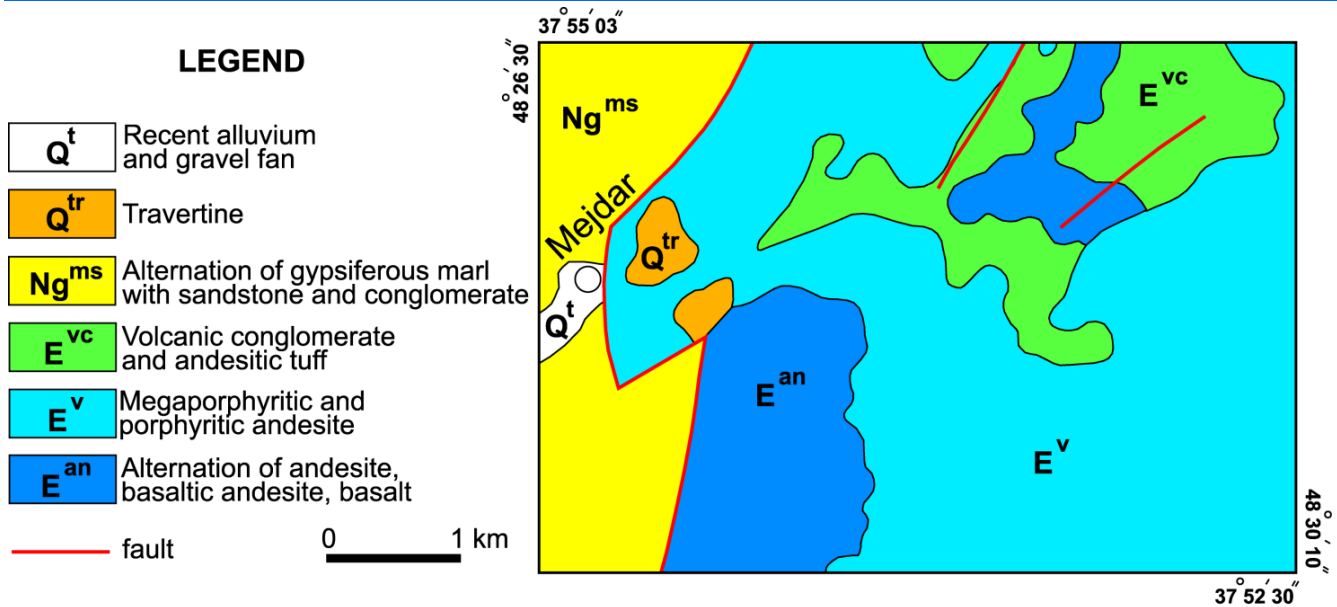


Figure 2: Geological map of the Mejdar area.

E^{an} unit that is host rock of the native copper mineralization was affected by hydrothermal alteration. Two major rock types are distinguished in the study area of alteration zone. Andesite is the most abundant type of rock with porphyritic to megaporphyritic texture. Andesite contains phenocrysts of plagioclase up to 3 cm in a microlitic

groundmass consisting of plagioclase, alkali feldspar, pyroxene, and glass (Fig. 3a,b). Basaltic andesite is the second major rock type of E^{an} unit. It contains phenocrysts of pyroxene in a groundmass of plagioclase, clinopyroxene, opaque minerals, and glass (Fig. 3c,d).

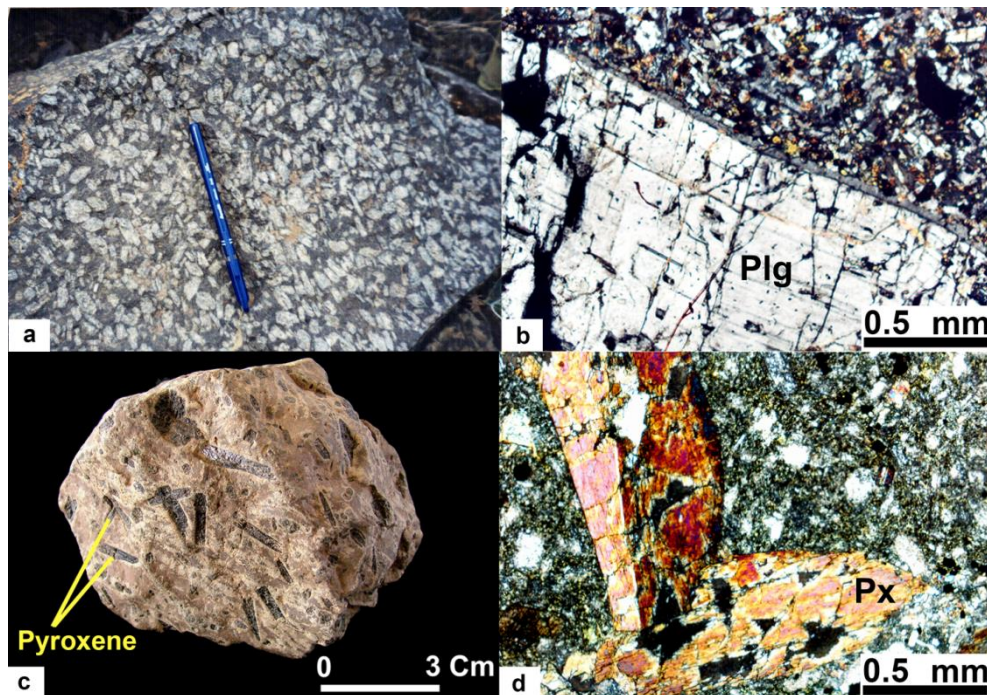


Figure 3: Photograph and microphotograph of andesite and basaltic andesite rocks from the E^{an} unit. a,b- andesite with phenocrysts of plagioclase (Plg); c,d- basaltic andesite with phenocrysts of pyroxene (Px)

III. MATERIALS AND METHODS

A large number of samples were collected from fresh and altered volcanic rocks. The petrography of selected samples was studied in thin sections using a polarizing petrographic microscope. Bulk mineral composition was determined by X-ray diffraction (XRD) using a Siemens D500 diffractometer, with Cu-

K α radiation and a graphite monochromator. Chemical analyses of major and trace elements were carried out with wavelength dispersive X-ray fluorescence spectrometry (WD-XRF) using a Siemens SRS 303 XRF spectrometer.

A considerable number of major and trace elements has been analysed, and their behavior from the non-altered to the most intensively altered rocks was followed. The geochemical analyses are combined with mineralogical studies on the common phases in the propylitic altered zone to explain which minerals may concentrate the elements of interest. The study of the distribution of trace and major elements in altered rocks will help us to better understanding of the processes that lead to the formation of this zone.

Rock alteration processes and changes of major and trace elements can be studied through geochemical Mass Balance (MB) estimation in several ways. Due to the ease of its adaptability, especially its graphical approach, the ISOCON method of mass balance is extensively used for such studies. Isocon analysis [13] is a simple and effective means of quantitatively estimating changes in mass or volume or concentrations in mass transfer. It may be accomplished graphically by plotting an altered composition against an original composition with no significant manipulation of the data. The reference frame for MB obtained by best fit regression is biased to the element scaled upward that plot away from the origin. Species that have remained immobile in the process define the isocon, which is a straight line through the origin.

IV. MINERALOGY OF PROPYLITIC ALTERATION

In hydrothermal environments, primary minerals usually tend to alter to secondary (hydrothermal alteration) minerals that are either stable or at least metastable in these environments.

Propylitic alteration is the main alteration in the study area and is widespread in the bottom levels and to the periphery of the deposit. There is a wide range of alteration degrees – from partial to whole replacement of the primary minerals. In hand specimen, propylitically altered rocks are generally pale green in color due to abundant but variable amounts of chlorite and epidote. They usually form from the decomposition of Fe-Mg-bearing minerals such as biotite, amphibole or pyroxene.

Mineral composition of altered rocks was examined in thin sections, supported by X-ray diffraction (XRD). XRD analysis shows that propylitic association consists of fluorapatite, chlorite (clinochlore), albite, carbonates (calcite, manganocalcite, ankerite), illite, montmorillonite, zeolites (clinoptilolite, stellerite) and glauconite.

Field observations show alteration of groundmass volcanic rocks to chlorite and epidote. Zeolites and carbonates formation in veins and open-spaces in the propylitic zone (fig. 4a,b). Thin section study shows alteration of mafic minerals such pyroxene and groundmass to chlorite (fig. 5a,b) and replacement of plagioclase by calcite (fig 5c). Zeolites, epidote and some calcite have filled fractures and vesicles (fig. 5d,e,f).

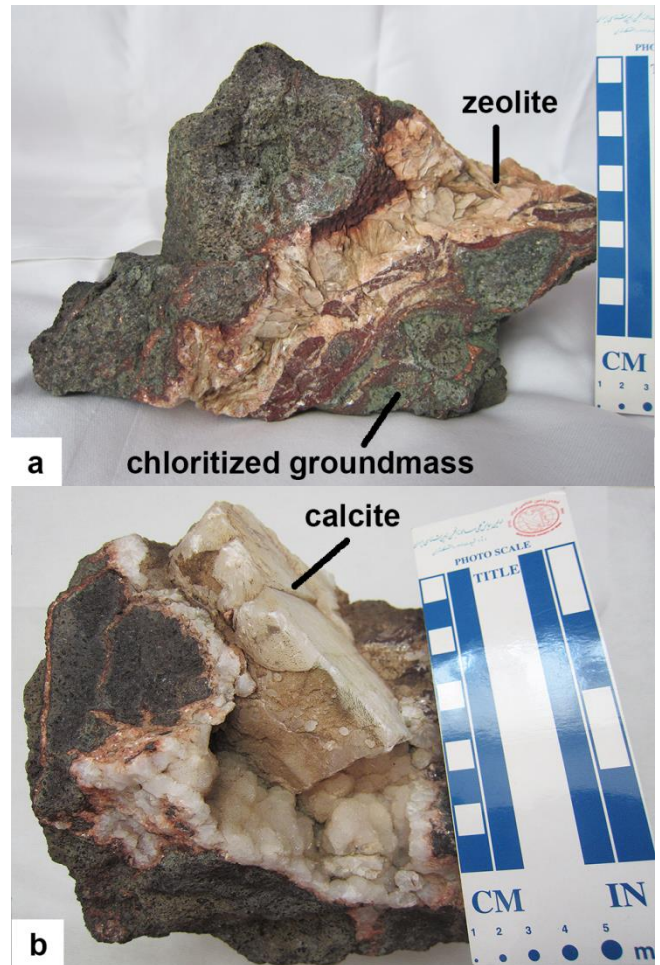


Figure 4: a) zeolite (clinoptilolite) vein in the chloritized groundmass of basaltic andesite; b) calcite formation as open-space filling.

V. GEOCHEMISTRY OF PROPYLITIC ALTERATION

Hydrothermal fluids cause hydrothermal alteration of rocks by passing hot water fluids through the rocks and changing their composition by adding or removing or redistributing components.

Native copper mineralization in the volcanic rocks of Mejdard area is accompanied by the development of propylitic hydrothermal alteration. During hydrothermal alteration significant to complete changes of mineral and chemical composition of the parent rocks took place which erases the most of their initial characteristic (textural, mineralogical, petrological and chemical).

The chemical composition of altered rocks was compared to that of an unaltered volcanic host rocks. In this part of study the technique used for calculation of mass changes is the one that was presented by the isocon method of Grant [13], allowing a direct comparison of mass transfer to composition of the protolith and to the altered rock through the ISOCON diagram. In this diagram the elemental abundances of altered and unaltered protolith are plotted on abscissa and ordinate respectively. In the isocon method all immobile elements would plot on a straight line through origin in ISOCON plot.

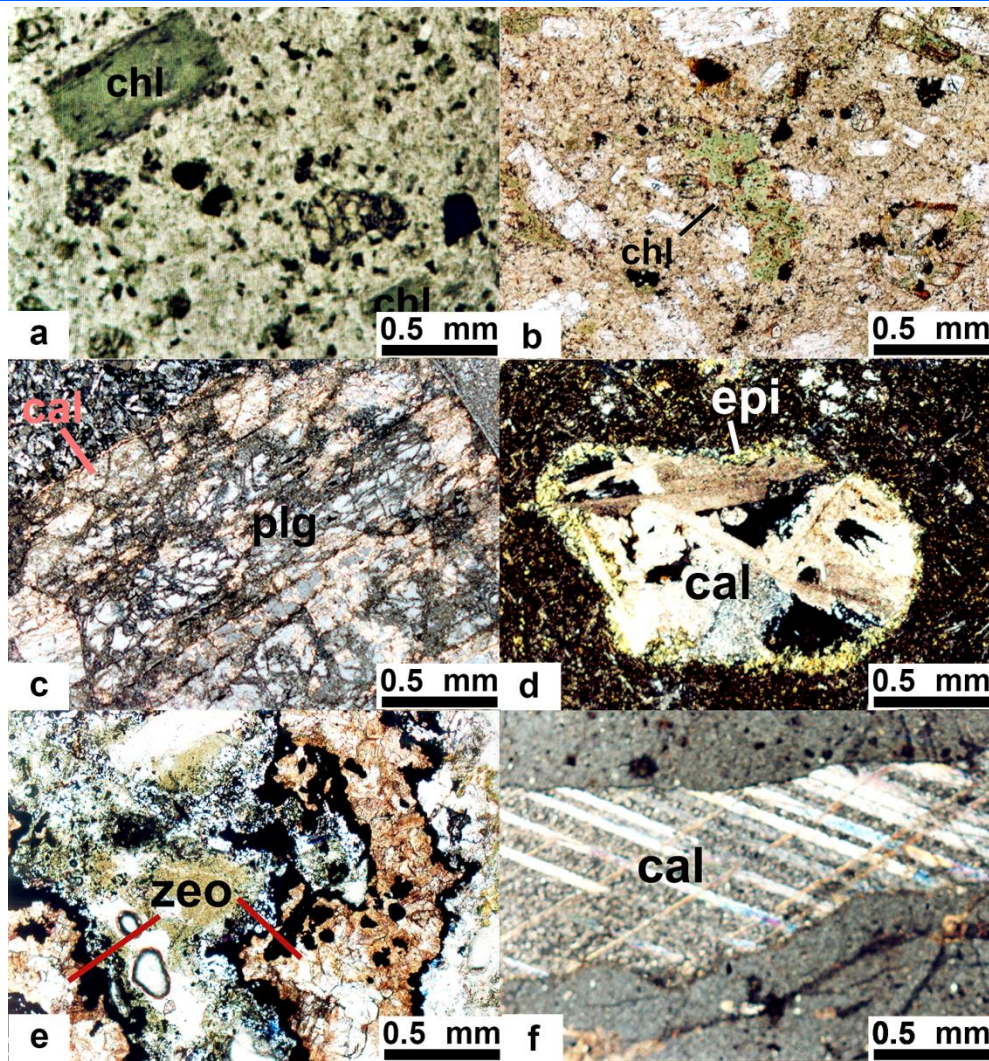


Figure 5: a) alteration of pyroxene to chlorite (PPL light); b) alteration of groundmass to chlorite (PPL light); c) alteration of plagioclase to calcite (XPL light); d) vesicle filled with calcite and epidote (XPL light); e) zeolite filling the veins (XPL light); f) calcite vein in the glassy groundmass (XPL light). chl = chlorite, plg = plagioclase, cal = calcite, epi = epidote, zeo = zeolite.

Line drawn through these elemental plots is referred to as isochemical line (line of no mass-transfer) or simply as ISOCON line. It provides an illustrative graphical solution to mass balance depicting the elements that are lost, gained or conserved depending upon its plot to the right, left or on the ISOCON line respectively. In this method Al_2O_3 is considered as immobile component and ISOCON is proposed through it. Due to its simplicity and adaptability, ISOCON method is being extensively used in diverse fields by the researchers [14].

The average chemical composition of fresh and altered rocks of the propylitic zone is given in Table 1 and the gains and losses of major and trace element for the selected samples pairs are shown graphically in figures 6 and 7.

CaO has high mobility during hydrothermal alterations. The quantity of Ca in altered rocks is low (mean 1.19%) and despite of the presence of carbonate minerals (calcite, manganocalcite, ankerite) and stellerite, Ca is leached from primarily plagioclase by hydrothermal fluids. The calcite and epidote formed by albitization of plagioclase and chloritization of mafic

in the propylitic zone could not retain all the Ca that was liberated.

MgO in propylitic rocks increases (mean 3.24%) which is higher than in unaltered rocks. Chlorite (clinocllore) as main mineral of magnesium was deposited several times during the evolution of hydrothermal system in Mejdard area.

Na_2O is accumulated in altered rocks (up to 3.5%) due to the presence of albite and some Na-clinoptilolite.

K_2O has significant amounts in Propylitic rocks and close to that of unaltered rocks due to the presence of K-feldspar.

The mean value of Mn in propylitic rocks (849 ppm) is the same as in unaltered volcanic rocks (862 ppm) but its concentration varies from 35 to 3471 ppm. This possibly is a result of redistribution of Mn during later processes and formation Mn-rich minerals such manganocalcite.

Concentration of Sr in the propylitic rocks is 206 ppm which is significantly lower than in the parent rocks. Its behavior depends on that of calcium – it is depleted and become mobile during the alteration of

Table 1: Mean values of chemical elements in hydrothermally altered volcanic and porphyritic rocks from Mejdar area

	total samples	SiO ₂ %	Al ₂ O ₃ %	Fe ₂ O ₃ %	CaO %	MgO %	Na ₂ O %	K ₂ O %
Unaltered rocks	5	59.28	14.66	5.84	5.18	2.85	2.99	3.56
Propylitic rocks	15	62.85	14.59	5.81	1.19	3.24	3.22	3.49

	total samples	U ppm	Th ppm	Nb ppm	Ta ppm	Sc ppm	Ga ppm	Mo ppm	Sr ppm	Rb ppm	Zr ppm	Ti ppm	Mn ppm	V ppm
Unaltered rocks	5	1.95	7.45	7.23	0.35	10.55	18.13	3.11	685	69	181	3464	862	112
Propylitic rocks	15	1.94	7.15	6.65	0.3	9.45	17.41	2.69	206	92	124	3518	849	145

	total samples	Cu ppm	Zn ppm	Pb ppm
Unaltered rocks	5	1014	57.1	15.3
Propylitic rocks	15	1848	91.5	27.8

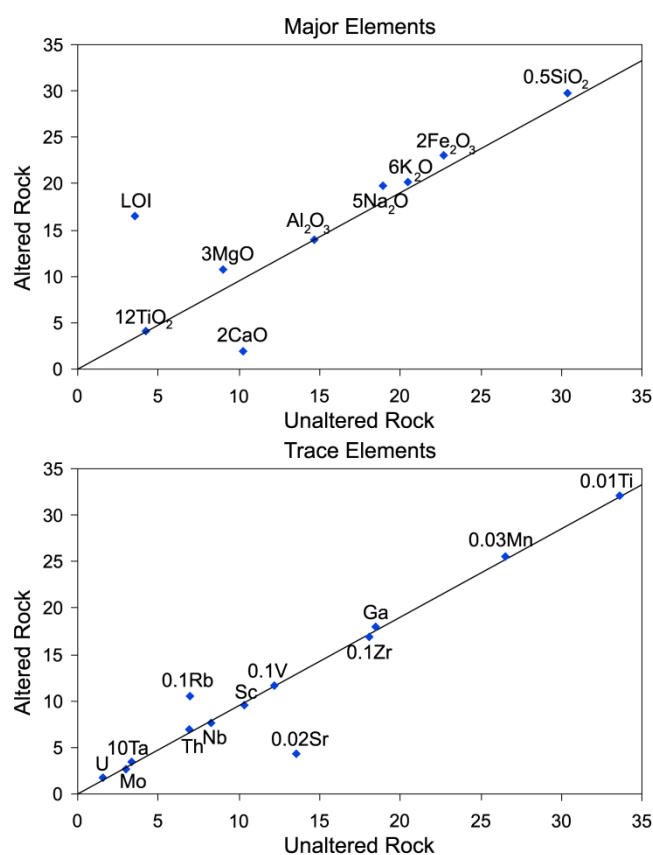


Figure 6: Isocon diagram comparing the major and trace elements of a representative sample of an altered rock from the propylitic zone with that of a representative unaltered rock

plagioclase into albite. Rb has distribution that is opposite of that of Sr. Its concentration show a minor increase in propylitic (92 ppm) rocks. Rubidium behavior depends on that of potassium in the alteration zone.

The mean values of Zr, Ti and V are constant in the alteration zone. Their behavior is defined as comparatively inert and immobile. HFS elements, such as U, Th, Nb and Ta have comparatively inert behavior in the alteration zone. To a certain extent, similar behaviors show Ga and Sc.

During the propylitic alteration there was an increase of loss of ignition (LOI) because of formation

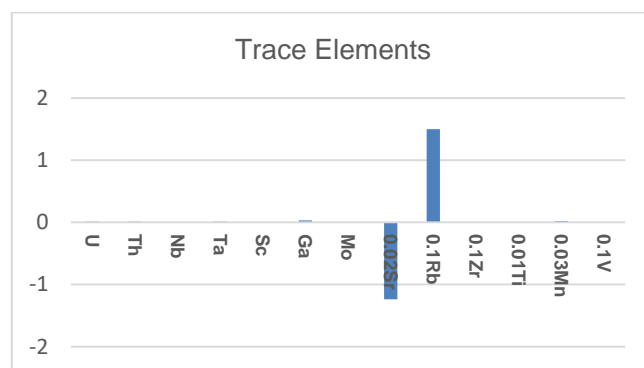
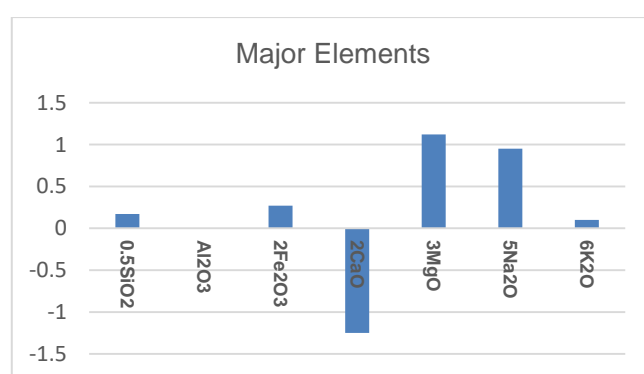


Figure 7: Gains and losses of major and trace elements for alteration propylitic versus the unaltered sample

hydrate minerals such as zeolites, chlorite, epidote and clay minerals.

The distribution of base metals such as Cu, Zn and Pb in altered rocks is not discussed here because their behavior depends on the ore-forming processes which postdate the formation of metasomatic rocks. Alteration zone is affected by ore mineralization and supergenic processes have important role for redistribution and secondary concentration of Cu. Copper values in propylitic zone rocks show a wide range and are generally in excess of background abundances.

VI. DISSCUSSION

Lithologically, Mejdar area includes a series of Eocene volcanic rocks mainly porphyritic and megaporphyritic andesite, basaltic andesite and andesitic tuffs. The volcanic rocks have suffered propylitic alteration, associated with native copper mineralization by hydrothermal fluids. Propylitic alteration is the chemical alteration of a rock caused by iron and magnesium bearing hydrothermal fluids, altering pyroxene, biotite or amphibole within the rock groundmass. It typically results in epidote-chlorite-albite alteration with minor amount of zeolite, calcite and sometimes clay minerals.

The behavior of chemical elements during alteration varies. Some are immobile and their distribution and content are not affected by alteration, but others are mobile and are leached out or are added to the altered rock. Adding elements relates to formation of new minerals in the altered zone and leaching elements relates to destroy previous minerals from altered zone.

By noticing the type of minerals and chemical changes in the altered zone, formation of alteration has been attributed to a relatively low-temperature hydrothermal system in a shallow-marine environment, with the pyroclastic rocks of the volcanic pile acting as the primary heat source. Presence of chlorite and epidote in the altered rocks indicate temperatures of 220-340°C [15]. In addition, Zeolites are widespread authigenic aluminosilicates that form during water-rock interactions below roughly 300 °C and 2 kbars [16]. Presence of carbonate minerals in the propitically altered rocks indicates high CO₂ pressure of hydrothermal fluids. Not extensive leaching of alkaline elements in the altered zone such as Na and K refers to neutral to slightly alkaline pH. Also the occurrence of clinoptilolite is favored by pH values that are close to or slightly higher than neutral (7-9) [17].

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