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Mass and chemical changes of immobile elements in Yamaghan Occurrence, Zanjan Province, Iran①

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[Abstract] Using mass and chemical changes, behavior of some elements have been evaluated in the study area, Yamaghan Occurrence. The techniques using immobile elements can precisely identify altered volcanic rock precursors and measure material changes. The rocks of the study area were affected by hydrothermal alteration. Testing of some compatible-incompatible and compatible-compatible immobile pairs indicates that Al_2O_3 is the most immobile component in the study area. It means that during the three main stages of hydrothermal alteration (phyllic, intermediate argillic and propylitic) aluminum was the most immobile and titanium was slightly immobile. Increases in mass mostly result from mineralization, silicification or carbonatization as voids and other open space fillings and may have replaced the part of glassy matrix. Mass addition has diluted the immobile elements at constant rates. Mass loss is commonly due to leaching of Si, Ca and Na_2O during chloritization and sericitization. The mass loss is recognized by increased proportions of inert minerals such as chlorite and sericite. Mineralographic studies in the study area shows the existence of a supergene zone. Chalcocite and covellite are considered enriched minerals. Considering this evidence and mass change results, the enrichment of copper in the circulating fluid is suspected with occasional sulfide precipitation.

[Key words] mass and chemical changes; immobile elements; lithogeochemical; Yamaghan
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1 INTRODUCTION

Mass and chemical change techniques are used in exploration fields. The procedure utilizes elements with high degree of immobility in hydrothermal and associated interactive fluid-rock systems. These elements notably Zr, TiO_2, Y, Sc, Nb, REE and Al_2O_3 are highly immobile during the alteration of volcanic rocks owing to metamorphism, hydrothermal events and weathering[1]. Using binary plots of analyses which produce linear arrays, these elements and Al_2O_3 are shown to be with high correlation coefficients, which go through bulk composition and origin. Al_2O_3 is the most immobile, followed by Zr, Nb, TiO_2, and Y[2~4]. They yield precise identifications of precursor volcanic rock type and magmatic affinity, and quantitative estimates of mass, volume and mineralogical changes. Immobile incompatible elements (Zr, Y, Nb, REE) establish affinities, and monitor fractionation of compatible elements in tholeiitic and transitional volcanic suites. Mass change in mobile components can be determined for a homogeneous rock unit or a continuous volcanic series. Immobile element techniques produce a large number of parameters that can be illustrated on maps and diagrams, and otherwise used in exploration. Usage of these techniques brings deeper insight to the evolution of volcanic stratigraphy and the hydrothermal processes that formed the alteration zones and ore deposits. In the study area these techniques were used because this mass-based approach finds, nowadays, direct application in exploration and drilling programs. This paper is a part of comprehensive research including geology, geochemistry, petrology, petrogenesis, mineralogy, mineralography, tectonic setting, and genesis of the study area.

2 GEOLOGY AND PETROLOGY

2.1 Background

Many indications of copper are known in the volcanic rocks of Tarom area, particularly all the copper mineralization are in Tertiary volcanic and intrusive rocks. The study area is located in Tarom-E-Sofla area, in Zanjan Province of Iran in 49° 05′ 56″ longitude and 36° 34′ 30″ latitude (Fig. 1). The prospect is confined between Shomeh-Dasht Mountain in north and NE, Ghorghlur Mountain in the south and a small plain in the west[5,6]. Based on a comprehensive study of the area using different classification methods such as major, minor and trace elements, rocks of the study area mostly are alkali olivine basalts and classified as extrusive rocks belonging to potassic alkaline rocks. As no chemical or petrological evidence confirms the primary origin of productive magma so the secondary origin of magma or a metasomatically magma is proposed as productive magma in the study area. The volcanic rocks in the study area were

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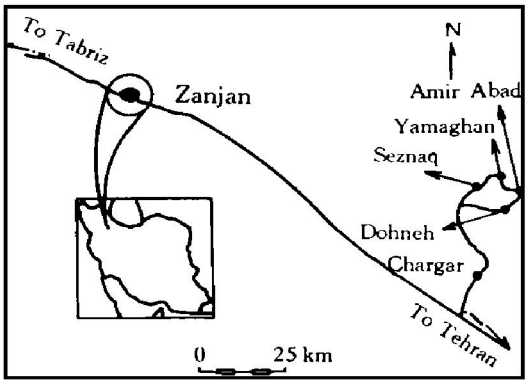

Fig. 1 Geographical location of study area (Access roads are also shown)

erupted in Tertiary.

2.2 Hydrothermal alteration

All the rocks in the study area altered to a lesser or greater extent. The alteration in the study area will be discussed in detail in another paper. By studying of mineral assemblage phyllic (sericite), prophylactic and intermediate argali zones have been distinguished and the main one is phyllic alteration. This alteration in the study area is recognized with sericite, quartz and chlorite; moscovite, quartz and sericite; sericite and quartz; and chlorite, illite and quartz assemblages. XRD studies also confirmed phyllic alteration.

3 METHODOLOGY

Immobile elements that are in hydrothermal alteration and other interactive water-rock systems are concentrated during net mass loss and diluted by net mass gain[3]. Calculation of these changes (material changes) requires different approaches when the altered rocks are derived from one, or more parent rocks (single or multiple precursors). In a single precursor system, such as the study area, residual concentration and dilution of immobile elements produce linear arrays of data on binary diagrams contain the precursor composition and extrapolate to the origin. The correlation coefficient is used as a gauge of mobility. Mass changes have been calculated from the concentration ratio of an immobile element in an altered sample and its precursor. The above methodology was used by MacLean and Kranidiotis[3]; MacLean[4] and Shrives and MacLean[7] to show that Al, Ti, Zr, Nb, Y, Yb and Lu were highly immobile in the alteration zones. Therefore the described method was adopted in this research.

3.1 Recognition of altered samples

Samples were designated as "altered" using those chemical parameters defined by Sheriver and MacLean[7]. On the other hand the least altered samples were established from mentioned procedure. As the sample number R. 31 was chosen as "least altered sample", it also was considered "precursor".

3.2 Recognition of immobile elements

Some compatible-incompatible and compatible-compatible immobile pairs were tested to choose the best immobile element as a monitor of mass change calculations. Samples of the study area produce a highly correlated alteration line using pairs of an immobile-incompatible element (HFS) such as Zr and immobile-compatible elements such as Al_2O_3 and TiO_2. The regressions produced by Al_2O_3-Zr (r = 0.9967) and TiO_2-Zr (r = 0.9943) demonstrates that Al_2O_3 and TiO_2 are immobile in the altered zones of the study area. The correlation coefficients of these pairs are listed in Table 1. The regressions produced by Al_2O_3-Zr, Al_2O_3-Yb and Al_2O_3-Ce have the highest correlation coefficients. It indicates that they are most immobile pairs in comparison to similar pairs of TiO_2. Therefore Al_2O_3 is the most immobile component as it correlates slightly better with other elements than TiO_2 does.

Table 1 Correlation coefficients for element pairs in the study area

Immobile pairs	r	Immobile pairs	r
Al_2O_3-Zr	0.9967	TiO_2-Zr	0.9943
Yb-Zr	0.9491	Al_2O_3-Yb	0.9128
TiO_2-Yb	0.8492	Ce-Zr	0.9680
Ce-Yb	0.9392	Al_2O_3-Ce	0.9475
TiO_2-Ce	0.9126	Al_2O_3-TiO_2	0.8597

$$r = \frac{n\sum xy - \sum x \sum y}{\sqrt{[n\sum x^2 - (\sum x)^2][n\sum y^2 - (\sum y)^2]}}$$

3.3 Mass change

Mass changes are based on the differences in concentration of immobile elements between an altered sample and its precursor. The immobile elements in the altered samples are normalized to their original proportions, and the contents of the mobile elements are readjusted by the same factor (Al_2O_3 fresh/Al_2O_3 altered). These reconstructed compositions (R-C) reflect the actual mass of the altered rocks. The differences between reconstructed and precursor compositions constitute the mass changes incurred during alteration. The gains and loses of components were calculated, using a starting mass of 100 grams of the least altered rock (sample No. R. 31) and the established immobility of Al_2O_3 during hydrothermal alteration. All samples were recalculated to full percentage, then compositions of samples were calculated, for this mean, the reconstructed composition (R-C) of the altered sample, calculated at the constant concentration of the monitor element (Al_2O_3), is computed for each component as

$$R\text{-}C = w\ (\text{component, altered rock}) \cdot \left| \frac{\text{I-}\ M(\text{precusor})}{\text{I-}\ M(\text{altered rock})} \right| \quad (1)$$

where w (component, altered rock) is mass fraction, %; $I-M$ is the immobile element monitor[3]. When the precursor mass is taken as 100, mass additions and subtractions are equivalent to mass fraction changes. For example, the residual amount of SiO_2 (in grams) remaining after alteration at constant Al_2O_3 is calculated as

$$m(SiO_2)/g = \left| \frac{w(SiO_2)}{w(Al_2O_3,\ \text{altered rock})} \right| \cdot w(Al_2O_3,\ \text{precursor}) \quad (2)$$

3.4 Mass change calculation

Changes in individual components are the differences between the precursor and the reconstructed compositions (R-C) given by Eqn. (3)[4,7].

Material Change= R-C- Precursor Composition (3)

Immobile elements and mass changes can be used to measure the severity of alteration. From initial inspection, samples (MIN. 24, MIN. 40 & SM. 2) seem to have been altered severely.

4 GEOCHEMICAL CHARACTERISTICS OF ELEMENTS AND THEIR BEHAVIOR DURING ALTERATION IN THE STUDY AREA

4.1 Zinc

Zinc concentration in the precursor is 60×10^{-6}. According to mass change calculations, it is entirely added to the rocks in the study area. The total addition of Zn is 5921×10^{-6} with an average of 151.8×10^{-6}. High correlation coefficient of zinc with lead ($r = 0.811$) certifies the mentioned paragenetic behavior.

4.2 Strontium

Concentration of Sr in precursor is 420×10^{-6}. Its high concentration backs to potassic characteristics of its productive magma. Sr is apparently mobilized during hydrothermal alteration in the study area and its concentration has previously been observed to decrease concomitantly with calcium. This means that Sr is mostly leached from the altered zones but it is added in carbonatization and epidotization zones along with Ca especially in samples MIN. 05, MIN. 30 and MIN. 80. Sr shows a good correlation coefficient with K_2O ($r = 0.8082$), and has acted as a very mobile element during alteration, and its behavior is the same as Ca and K. It means that Sr has participated in potassic minerals, and after decomposition of these minerals due to alteration it is leached from the system but where carbonatization, saussuritization and somehow formation of barite has occurred, it has admitted by Ca. Therefore it has participated in the structure of carbonate, saussurite and barite. Fig. 2 shows the mass changes of Sr along with CaO.

4.3 Manganese

MnO_2 concentration in the precursor is 0.15%. It is mostly added to the system with an average of 0.18%. All evidences show the wide variation in the concentration of Mn in the altered basalts and suggest that this element is mobilized during hydrothermal alteration and migrated in the circulating fluid. Referring to correlation coefficients of Mn with FeO ($r = 0.0048$), TiO_2 ($r = -0.1094$), Al_2O_3 ($r = -0.4053$), CaO ($r = 0.0017$), Ba ($r = -0.599$), it did not show any good, excusable and acceptable trends. Variable Mn concentrations, with no consistent trend during alteration, have previously been observed. Although it seems that after decomposition of its primary minerals (e. g. olivine) manganese has entered the structure of chlorites. In addition, its rapid increase along with Ca and iron in some

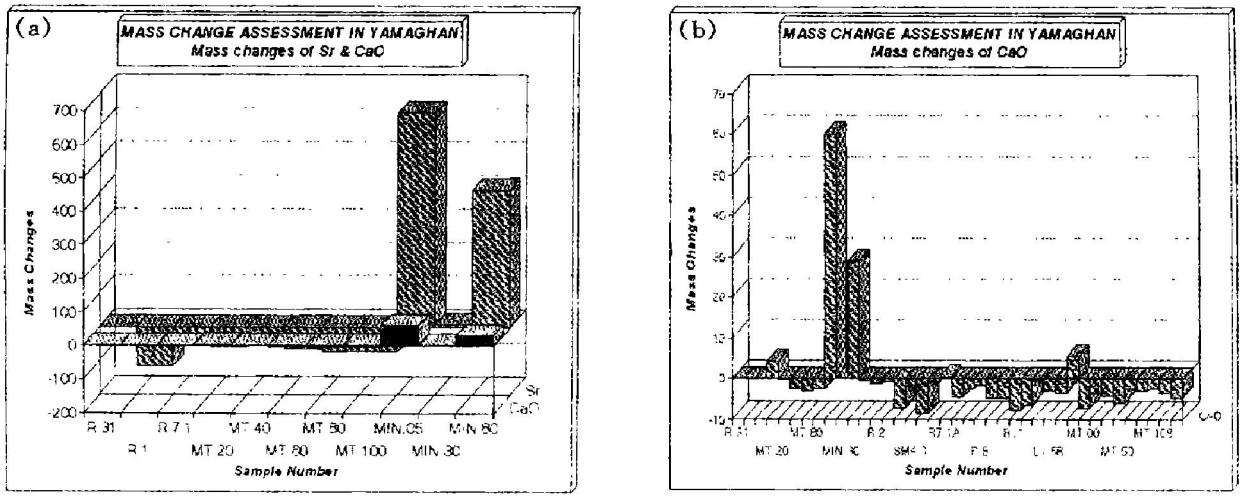

Fig. 2 Gains and losses of Sr (a) and CaO (b) from reconstructed composition
($\times 10^{-6}$ of altered rock normalized to rock precursor versus Al_2O_3)

samples such as Min. 05 and Min. 80 may be due to its replacement in the structure of Ca and iron in the carbonatization zone.

4.4 Copper

Copper concentration in the precursor is 500×10^{-6} that is three times more than that in composition of normal basic rocks. Fig. 3 illustrates the mass changes of copper in the samples of the study area. Based on mass change results, it is mostly added to system with an average of 4219×10^{-6}. Therefore all the rocks show strong enrichment in copper. Copper shows strong correlation coefficient with FeO (r = 0.951), K_2O (r = 0.897), Mg (r = 0.774), and Ag (r = 0.823). These high correlation coefficients certify emphatically the coincidence of copper mineralization with sericitic and to some extent argillic zones. Leaching of copper has carried out only in two samples and it is deciphered as leaching zones above supergene zone. In addition copper minerals in the study area were observed as sulfide, carbonate and to some extent silicate forms. The high correlation coefficient of copper with FeO and Fe_2O_3 is seen as their participation in making copper sulfides such as chalcopyrite and bornite. The reason of high correlation of copper with silver is that geochemically, copper is located along silver and gold in the same group. Silver sulfides have been detected in copper sulfides of the study area in the form of replacement. The high correlation coefficient of copper with silver (r = 0.823) certifies this paragenesis.

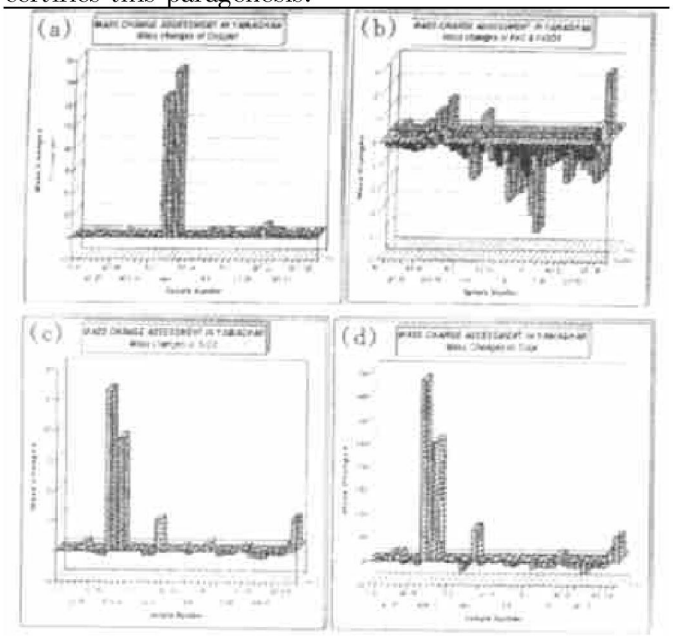

Fig. 3 Gains and losses of copper (a), FeO and Fe_2O_3 (b), Si (c) and total mass (d) from reconstructed composition ($\times 10^{-6}$) of altered rock normalized to rock precursor versus Al_2O_3

4.5 Calcium

Rocks of the study area, contain calcium in composition of their major, minor and accessory minerals such as plagioclases, augites, apatites, and moreover some secondary minerals such as carbonates and apatites. During alteration part of CaO is retained in unreacted plagioclases, pyroxenes, epidote and calcite but totally calcium along with Sr (r = 0.977) and Na depleted strongly from the system except carbonitization and epidotization zones. Mass change of calcium in the samples of the study area is shown in Fig. 2. The concentration of Ca in the precursor is 8.87% and it is depleted by an average of − 0.11%.

4.6 Barium

The only major element of comparable size is potassium, and barium appears, therefore, in biotite and potash feldspar. Because of its higher charge, barium should be captured by potassium compounds. Barite is by far the most abundant barium mineral that was detected and formed in the study area as hydrothermal veins. Barium shows a fair correlation coefficient with potassium (r = 0.8097) but, it shows commendable correlation coefficient with Mo (r = 0.868), Na_2O (r = 0.829), Cr (r = 0.6361) and L.O.I (r = − 0.671). Ba chiefly has leached during alteration but it is added somewhere and forms barite veinlets. These veinlets have formed where ground preparation has acted and prepared suitable place to precipitation of barium as barite. Dimensions of these veins vary from millimeters to more than one meter (Fig. 4).

4.7 Potassium

The precursor rock contains 2% K_2O and an average of 0.55% is added. Accordingly, during alteration, based on mass change calculations, released K_2O from decomposition of feldspars has been adsorbed to illite and did not leach from the system. K_2O added except in pure kaolinitization zones.

4.8 Phosphorus

The concentration of P_2O_5 in the precursor is 0.43%. It mostly leached but due to its abruptly high addition in two samples that are accompanied with silicification and carbonatization, the average mass change is + 0.01%.

4.9 Iron (Fe_2O_3 and FeO)

There is an average loss of 0.89% for FeO and 0.27% for Fe_2O_3. Calculation shows a total loss of 34.89% for FeO and 10.54% for Fe_2O_3, respectively. Their mass changes are shown in Fig. 3.

4.10 SiO_2

SiO_2 shows a mixed addition-depletion behavior. There has been a total addition of 527.76% and an average net addition of 13.53% SiO_2. Mass changes of SiO_2 in the study area are shown in Fig. 3. Samples showing SiO_2 losses are heavily chloritized.

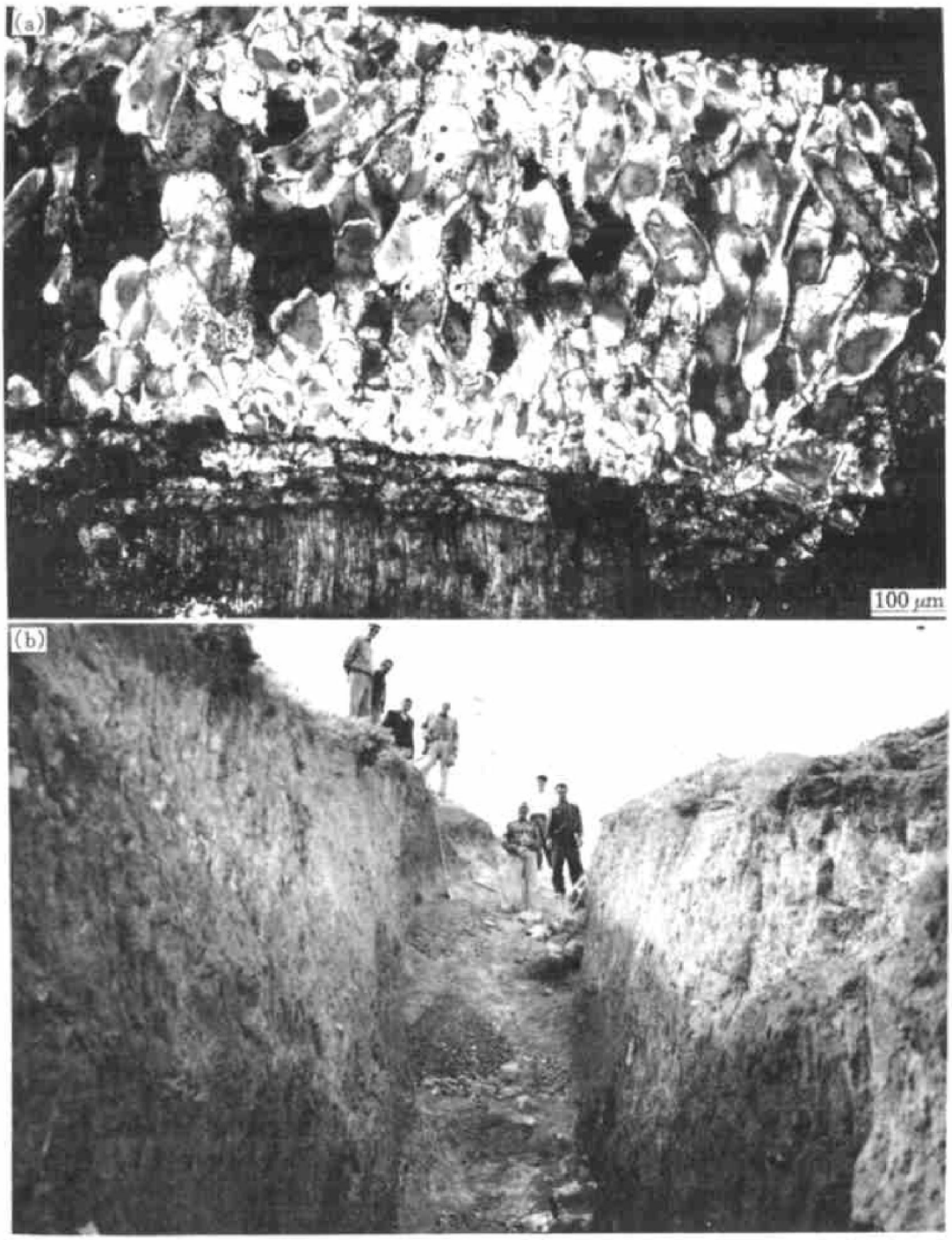

Fig. 4 Comb structure (a) showing growth of barite crystals outward from open fracture walls crossed nicols; A barite vein (b) with about 120 cm width and tens of meter length. (The photo is taken towards north (N180S), Yamaghan village)

4.11 Total mass

Total mass changes are shown in Fig. 3. Total mass obviously dominated by additions (average 16.00%). These changes are mostly a function of the addition of silica, but also reflect the constant losses of Na, Fe, Mg and large addition of CaO.

5 RESULTS AND DISCUSSION

The mass changes for the main components of the host rock (alkali olivine basalt) pose the identity of the minerals being lost, added, or reconstituted during the alteration process.

Increase in mass mostly result from mineralization, silicification or carbonatization as vesicles, voids and other open space fillings (amygdales, veinlets) and may have replaced part of the glassy matrix. In this case, the overall volume of the volcanic units generally is retained. SiO_2 and CaO were added in rather large amounts to samples indicating silicification and carbonatization coincide with addition of iron, MnO, P_2O_5, loss on ignition (LOI), Cu, Co and Al. Calcite was added only to the altered basalts, and mainly formed calcite and dolomite and to some extent epidote. Mass addition has diluted the concentration of the immobile elements at constant ratios.

Potassium and Rb behaved similarly (Rb versus K_2O, $r = 0.936$) and increased at constant ratios owing to their incorporation exclusively into illite (sericitic zone). Furthermore, Ca and Sr were added to the rock in carbonatization zone, but almost entirely removed from the samples. Sr and Ca also, participated in structure of barite. Sulfur was not analyzed, so assessing of its changes is impossible although microscopic and SEM studies certified obvious increasing of sulfur within altered zones. The addition of 13.53% SiO_2 to the alteration zone represents a net silicification of the basalts. This, in part, is the increase in modal and normative quartz that results from the breakdown of plagioclase to sericite, or to chlorite and quartz. Iron and Mg were added and incorporated into chlorite and sulfides in some mineralized samples. Furthermore, Mg has participated in formation of dolomite. The introduced K (with an average of 0.55%) produced illite. Cu, Zn, Mn, Cr and Pb were added to system in most cases, mainly in the mineralized zones. Barium shows a multiple addition-depletion behavior. It substitutes (along with Rb) for K in sericite. Ba occurs as barite, suggesting a higher oxidation state and higher concentration of Ba for the hydrothermal fluids. It shows a weak correlation coefficient with K ($r = 0.597$) and Sr ($r = 0.403$). This weak correlation coefficient with K and Sr can be deciphered as participating of Ba in two stages. In first stage, alteration of feldspars caused liberating of K, Rb, and Ba and formation of illite so that Ba along with K and Rb has participated in illite structure. In the second stage, another fluid has affected the system and along with oxidation condition, fugacity of sulfur has increased. Therefore, barium expelled from illite structure and formed the independent barite mineral. The mass additions represent net amounts of individual components which were brought into the alteration zone from an external source via hydrothermal fluids.

Mass loss is commonly due to leaching of Si, Na and Ca during chloritization and sericitization, but can involve Fe and Mg loss as well. The loss is recognized by increased proportions of inert minerals such as chlorite and sericite. Some elements like V, Cs and Na_2O did not share in structure of any secondary minerals therefore they show tendency to total removal in all samples studied. The lower net value (16.00% total) of mass change in the basalt indicates that it has experienced a lower degree of chemical alteration, but does not necessarily reflect a lower degree of mineralogical alteration; the unit initially contained large quantities of Fe and Mg which were converted to chlorite and illite, whereas these elements were less aboundant in the precursor and were added in the chlorite rich zone. Chromium, Cu, Pb, Cr and Zn markedly enriched in all of samples and such material may represent the site of later deposition (such as supergene) of the removed material. A number of elements such as V show this tendency to total removal in all samples studied. It indicates that they did not share in structure of any secondary minerals.

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