# Geochemistry of Hydrothermal Alteration Zone, Sabalan, Iran

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#### **ABSTRACT**

Sabalan geothermal prospect is situated in the Azerbaijan Plateau, part of the Alpine-Himalayan orogenic belt. MT survey established the existence of a significant zone of associated low resistivity at depth. Exposed at the surface in the Moiel valley are altered Pleistocene volcanics. The wells have altered Peliocene to Pleistocene volcanics, terrace deposits and a Pleistocene trackydacite dome. Sabalan geothermal system has been cooling since the alteration mineral formed. Comparision of formation and alteration temperatures of the wells was done by plotting the downhole temperature logs and the inferred alteration temperatures of different mineral encountered in the wells. There are complex alteration patterns produced by hydrothermal events associated with the monzonite and the two phase of dyke intrusion. The main emphasis of this paper is to elucidate the nature of chemical transport in hydrothermal alteration by correlating the bulk composition of rock samples with their petrographical characteristics and results of ICP-MS analysis. We will show that it possible to assess the amount of chemical dilution that has taken place. This allows the deduction of the primary concentration of the immobile elements in the altered rocks, and by correlating these with the relatively fresh volcanic, also using the isocon method for determining mass transport. Four alteration zones including phyllic, argilic, propillitic and calcitic identified. The results demonstrate notable differences in the REE behavior in the different alteration zones. Accordingly, comparision with the fresh rocks, in the phyllic alteration, LREEs are enriched, but HREE except Yb which enriched, unchanged. In the argilic and propylitic alteration zones, all REEs are depleted. The main objective of this study of wells is to gain subsurface geoscientific information on geology and geochemistry, behaviour of Rare Earth Elements (REEs) in hydrothermal alteration zones. In this field maximum temperature is 240°C at 3197m in 7 wells. The distribution and abundance of the hydrothermal minerals were obtained from petrographic and XRD analysis of the drill cutting samples taken after every 2 m.

#### 1. INTRODUCTION

The Sabalan geothermal prospect, situated in the Azerbaijan-Alborz zone, part of Alpine-Himalayan orogenic belt, is a very large trachy-andesitic stratovolcano in the province of Ardebil in northwest Iran. The wells (NWS-6D, NWS-7D, NWS-10D) are in the Moil valley, which on satellite imagery can be seen to be a major structural zone. Warm and hot springs with neutral Cl-SO4, acid Cl-SO<sub>4</sub> and acid SO<sub>4</sub> chemistries are found within the valley. An MT survey established the existence of a significant zone of associated low shallow magma chamber beneath the mountain is also indicated by the rock chemistry and Ar-Ar and K-Ar dating (Bogie et al., 2000). The rocks typically found in the field include andesitic lava flows, flow breccias, lahars, and a variety of pyroclastic rocks ranging from tuffaceous breccias to massive lapilli and crystal tuff. Heat is considered to be provided by an intrusive complex at depth that is mainly identified from gravity surveys (Kusumah et al., in prep), although only High Ni contents are indicative of a thick crust and are consistent with crustal thickening through underthrusting, but the Ce/Yb ratios are too high for the melts to be derived from typical sialic crust (Gill, 1981). However, such chemistry is consistent with the melts being formed by crustal thickening forcing mantle wedge material, previously metasomatised during prior subduction, below its phlogopite stability depth. Breakdown of the phlogopite initiates partial melting of the metasomatised mantle wedge to produce a LILelement enriched melt (Muller and Groves, 1995). The previously metasomatised mantle wedge material was produced during pre-Pliocene subduction. Ratios of FeO\*/MgO and Na<sub>2</sub>O/K<sub>2</sub>O in the volcanic rocks of Mt. Sabalan remain the same with increasing silica content. Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, FeO\*, MgO and CaO, however decrease with increasing SiO<sub>2</sub> content. All these features are consistent with the fractional crystallisation of hornblende. K-Ar dating (TBCE, 1978) of the analysed rocks indicate that they become more silicic with decreasing age, with dates ranging from 2.9 to 1.3 Ma. A small dome of trachydacite in the Moil Valley has been dated at 0.9 Ma by Ar-Ar dating. These dates are consistent with the presence of a large, young, comparatively shallow magma chamber beneath Mt. Sabalan. Minor amounts of intrusives in the form of dykes have been found in the wells. Igneous activity began in the Eocene with the accumulation of potassic alkalic volcanics upon a sequence of Mesozoic and Paleozoic sediments. They were intruded and thermally metamorphosed by an Early Miocene monzonitic batholiths, elongate in a NW-SE direction and exposed on the western ridge of Mt. Sabalan. Significant uplift and erosion of the batholith followed and a sequence of Late Miocene nonmarine sediments, were deposited to the SW and SE of the batholiths (Bogie et al., 2000).

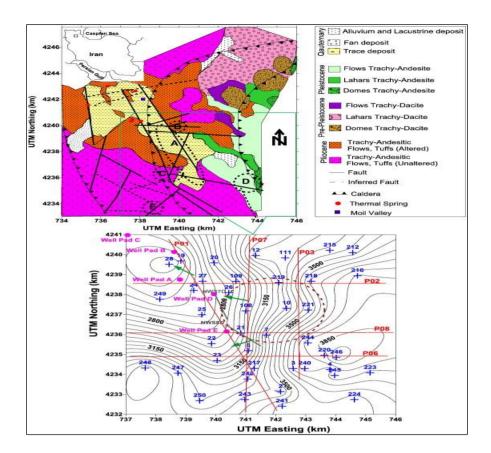


Figure 1: stratigraphy units and location map of geothermal wells and pads

### 2. GEOLOGICAL SETTING

Four major units have been identified within the Meshkin- Shahr prospect that wells (NWS-6D, NWS-7D and NWS-10D) conducted, Figure 2:

# 2.1 Stratigraphy

#### Pleistocene Volcanics

This unit is named Pleistocene Volcanics representing eruption products related to Pleistocene volcanism in Sabalan area (SKM, 2005) based on presence of trachyandesite as the dominant rock type together with juvenile crystals of biotite, hornblende, and feldspars. The lithic clasts of trachyandesitic breccias are dominated by two types of clinopyroxene-bearing porphyritic trachyandesites with green hornblende or with reddish-brown oxyhornblende and biotite as characteristic phenocrysts together with zoned and twinned feldspars. The vesicular, glass-rich matrix shows parallel orientation of plagioclase microlites indicative of its lava flow origin. Subordinate clasts are crystal vitric tuff, dacite, and rare reworked fragments of subhedral epidote-bearing altered trachyte, microdiorite and altered porphyritic andesite.

# Late Tertiary Volcanics (Valhazir Formation)

This formation consists of Pliocene pre-caldera trachyandesitic lava flows, tuffs and pyroclastic breccias witha stratigraphic thickness of at least 2000 m. They are the oldest volcanic rocks mapped in this area, and form the lowermost slopes and ridges of the volcanic complex. They are interpreted to predate the development of the caldera. The lavas occupy the highest stratigraphic and topographic positions and occur as short, thick flows, intercalated with the enclosing tuffs and breccias. They are more fractured and are more affected by faulting than the younger units. The lavas contain phenocrysts of plagioclase, sanidine, hornblende, biotite and augite in a groundmass rich in plagioclase laths, fine mafics, opaques (magnetite) and glass (where unaltered or not devitrified). Accessory titanite and zircon grains are rare, whereas apatite grains are widespread. The pyroclastics are fine grained tuffs, rich in feldspar and subordinate mafic crystal fragments. All are at least moderately altered, which means primary textures minerals are difficult to recognise, but in general, these rocks contain the same minerals in the same proportions as the coeruptive lavas.

# Early Tertiary Volcanics

This includes Quaternary alluvium, fans and terrace deposits and thin airfall ash interlayered with thick lahar and debrisflows. In part these have been subsequently reworked by fluvial processes to create crudely stratified, terraced deposits up to 150 m thick. In other areas, these terraced deposits form only a thin veneer (less than 10 m) over the volcanics. The clasts (ash, crystal and lithic fragments, and blocks of lava) within the terrace deposits are derived from all three (post-,syn- and pre-) volcanic units. Fan deposits, large enough to be mapped as discrete rock types, occur in the area, one at the head of the Moil valley and the other in a smaller valley south of Dizu. These thin deposits are debris/mass flows comprised of volcanic boulders, located on steep slopes at close to their angle of repose. The fan deposit south of Dizu appears to be a little older than the one at the head of the main valley, as it is less steep

and more vegetated. A number of areas are covered by thin (up to 10-20 m), elongate, flat-lying lacustrine deposits of sand and pebble sized volcanogenic clasts, which occur in topographic depressions developed by faulting and/or volcanism. These appear to have been created where streams and rivers have built up alluvial deposits and then been choked off, resulting in the formation of a shallow lake. The largest examples are the extensive flats on the Toas plateau and the large plain at Hoshan Medan in the north. Within the blind-drilled portion of well NWS-7D, a core was cut at 2180-2181 m (Core 4) identified as an epidote-garnet hornfels. Intense thermal metamorphism has obscured primary features of the original rock; however, faint relict texture suggests that parent rock is more likely a tuff breccia. The hornfelsic rock is now composed of clusters of reddish brown melanite to green andradite garnet varieties and epidote in a granoblastic matrix of interlocking quartz, feldspar, and clinopyroxene. The finely crystalline portion of the hornfels is possibly the tuffaceous matrix of original rock; while clusters of garnet and epidote are suspected to be original phenocrysts in trachyandesitic or andesitic clasts. The original porphyritic character is clearly discernible in the bottom portion of Core 4 where the granoblastic texture is less pronounced compared to top and middle portions of the core. Phenocrysts are replaced or pseudomorphed by subhedral to euhedral epidote or clusters of epidote and clinozoisite with occasional brown garnet, clinopyroxene, and calcite. Variations in the contact metamorphic fabric along Core 4 suggest that only a minor dike or an apophyse of a larger plutonic body has intruded at this depth causing partial contact metamorphism of volcanic units. This metamorphosed volcanic unit represented by Core 4 is proposed to be termed Early Tertiary Volcanics to include Eocene Volcanics (Epa) that were intruded by Miocene monzonite (SKM, 2005). Because of blind drilling, the bottom of the Early Tertiary Volcanics in well NWS-7D cannot be determined with certainty. However, the occurrence of hornfelsic sandstone at 2082 m (+550 m RL) in nearby well NWS-1 (SKM, 2005) suggests onset of the underlying Paleozoic Metamorphics. Thus, the bottom of Early Tertiary Volcanics is tentatively set at ~2360 m.

#### Paleozoic Metamorphics

The two deepest cores (Core 5 and 6) in well NWS-7D are clinopyroxene-garnet-calcite hornfels likely derived from carbonate sedimentary rocks based on observed texture and mineralogy. They are interpreted to be correlative to Paleozoic Metamorphics earlier identified in well NWS-1 as metamorphosed sandstone (SKM, 2005). In well NWS-7D, both Core 5 (2480-2481 m) and Core 6 (2700-2705 m) are composed of granoblastic mosaic of grossular garnet, calcite, clinopyroxene and feldspar. Vesuvianite occurs as columnar aggregates or polygonal crystals in Core 5; while green hornblende and brown biotite are interstitial in calcite in Core 6. The contact metamorphic suite is commonly corroded and retrogrades to lower temperature hydrothermal alteration minerals. The coring depths in well NWS-7D were unable to intersect the intrusive rocks. However, the contact metamorphic hornfels attests to their presence either within the unsampled sections or in the well vicinity. In well NWS-1, a plutonic monzonite body, believed to be Miocene in age (SKM, 2005) and contact metamorphic biotite hornfels were intersected from +1609 m RL till -567 mRL (TD). Older and younger dikes called Old Diorite Porphyry and Young Diorite Porphyry, respectively, intrude the Miocene monzonite. Biotite hornblende micro-monzodiorite porphyry, on the other hand, was intersected in well NWS-6D (Core 3) and correlated with the Old Diorite Porphyry.

### 3. HYDROTHERMAL ALTERATION

To investigate the effects of hydrothermal alteration on the chemistry of volcanic rocks, we analysed the whole rock chemical composition (major and trace elements, including rare-earth elements – REEs) of drill well core and cutting samples from the Sabalan geothermal field. This highly hydrothermally-altered sample allowed us to study, for the first time, the mineralogical and chemical effects imposed by hydrothermal alteration on the mm scale in this geothermal system. Seven core samples from the three wells were sent by Renewable Energies Organization to EDC Petrology laboratory. The samples are all either volcanic rocks which have been gradually buried by accumulation of younger volcanics, or intrusive rocks. The age of the accumulated sequence is progressively older and more altered as it is more deeply buried. Mineralogically, hydrothermal alteration in the samples is mainly represented by argillitization of primary plagioclase, as well as banded chlorite and quartz, with significant amounts of epidote and hematite. The "altered" part of the sample contains intensely altered remnants of the fresh rock, which show intense silicification, hematization, and dissolution boundaries Rocks. Most major and trace elements were mobilized from the original rock. Major element composition reflects the silicification, chloritization, and epidotization processes taking place in the geothermal system. The rare-earth elements La and Ce, as well as Yb and Lu were probably partially re-deposited during alteration. The positive anomaly of Eu may suggest that Eu is being concentrated in hydrothermal epidote after its release from plagioclase to the geothermal fluid. The high-field strength elements such as Zr, Ti, and P, show as well significant hydrothermal alteration-related decrease in the highly-altered rocks. The geothermal fluid responsible for this hydrothermal alteration was probably oxidizing, of high temperature (>250° C), and enriched in REE and other trace elements. (Torres-Alvarado, 2007). Therefore, contrasts in the degree of alteration within intrusive rocks and their surrounding extrusive host rocks should be expected and may depend on factors other than differences in permeability and porosity. The rock samples are acidic to intermediate, ranging from ryolite to tracky andesite. The main primary components in trackyandesite are relatively K-feldspar, Na plagioclase, and opaques (magnetite-ilmenite).

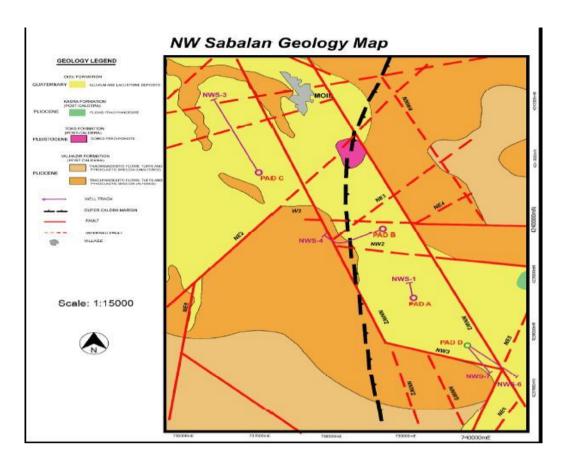


Figure 2: Part of Geological Map 1:20000, Moiel Village and tectonic and stratigraphic units

### 4. SUBSURFACE GEOLOGY

Megascopic and petrographic examinations of the cores and cuttings indicate that the rocks at depth mainly comprise of repetitive sequences of coarse pyroclastics and tuffs of rhiolitic to andesite compositions, except NWS-7, which intersected a microdiorite porphyry dyke at the bottom at around 1609 m TVD (true vertical depth). The dyke is characterized by a porphyritic texture with traces of plagioclase, hornblende. The subsurface rocks and the nature of their deposition based on borehole images of the three wells examined imply that they have come from one distinct eruptive centers.

### 4.1 Subsurface Hydrothermal Alteration

The study of hydrothermal alteration in geothermal areas can provide useful information on the processes of interaction between geothermal fluids and the host rock (Browne, 1978; Browne et al., 1992; Reyes, 1990). The alteration minerals in the three wells can be classified into two suites based on the chemistry of the altering fluids: neutral pH and acid. The neutral-pH fluid alteration suite is grouped into zones based on the occurrence and distribution of alteration minerals with depth. The zones defined include: smectite zone, transition zone, illite - smectite zone (argilic). Similarly, the occurrences of acid fluid alteration minerals with depth are classified into: kaolinite zone, kaolinite + calcite + cristobalite / quartz + pyrite zone propillitic and calcic zone. The distribution of these alteration zones in the subsurface is illustrated in Figure 3.

The hydrothermal alteration processes are distinguished here in (1) Na-Mg-Ca-metasomatism or propylitic alteration at the periphery of the system occurring due to descending meteoric waters. Subsequently the deep circulating geothermal water may experience (2) H-metasomatism or argillic alteration in the so called primary neutralization zone due to the attack of strong acids like HCl, H<sub>2</sub>SO<sub>4</sub>, and HF from the degassing magma body like HCl, H<sub>2</sub>SO<sub>4</sub>, and HF from the degassing magma body. Cutting samples will be collected at 3 m intervals, they will be washed and placed in cloth sample bags, clearly marked with depth, time and date of collection. Cores will be cut at the discretion of the site geologist, petrologic analysis. Five cores were taken from NWS-6D, and one core sample each from NWS-7D and NWS-10D. A total of 120 core and cutting samples were examined. These were prepared for thin section microscopy, X-ray diffraction and ICP-MS analysis. The main emphasis of this paper is to elucidate the nature of chemical transport in hydrothermal alteration by correlating the bulk composition of rock samples with their petrographical characteristics, we will show that it is possible to assess the amount of chemical dilution that has taken place. This allows the deduction of the primary concentration of the immobile elements in the altered rocks, and by correlating these with the relatively fresh volcanic rocks equivalents, we assess the chemical change that has taken place during the hydrothermal alteration. Furthermore, using the "isocon" method (Grant, 1986) for determining mass transport, we also evaluated chemical enrichment-immobility-depletion of various chemical components within individual samples.

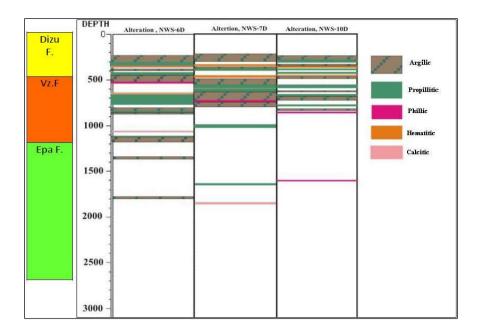


Figure 3: Columns of Stratigraphy and types of hydrothermal alteration zones in NWS-6D, NWS-7D and NWS-10D

#### 5. GEOCHEMISTRY

The main emphasis of this paper is to elucidate the nature of chemical transport in hydrothermal alteration by correlating the bulk composition of rock samples with their petrographical characteristics. We will show that it is possible to assess the amount of chemical dilution that has taken place. This allows the deduction of the primary concentration of the immobile elements in the altered rocks, and by correlating these with the relatively fresh volcanic rocks equivalents, we assess the chemical change that has taken place during the hydrothermal alteration. Furthermore, using the "isocon" method (Grant, 1986) for determining mass transport, we also evaluate the chemical enrichment-immobility-depletion of various chemical components within individual samples.

Geothermal fluid discharged by injection wells, which have been core drilled to depths as much as 2700 m at Pad D, Meshkin-shahr, has altered Paleocene to Pleistocene, silicic, mainly tracky andesite volcanic rocks, tufts and breccias. Measured temperatures (max. ~250 indicate epithermal to mesothermal conditions in buried fault fissures, the locus of both the hydrothermal fluid and most intense alteration. The stability of hydrothermal minerals is controlled by the temperature and chemical composition of the geothermal fluid ascending along the fault fissures. Description of the compositional changes resulting from alteration within the hydrothermal alteration zones will involve only the calculated mass-change data. Trace- and major-element behaviour may be discerned from a statistical analysis of the mass-balanced data. Statistical analysis of selected mass-balanced data helps to reveal elemental associations that are indicative of mineralogy and processes occurring in the alteration zone. Hydrothermal alteration zones have been investigated by X-ray diffraction, mineralogical—petrographical techniques, the cores and the cuttings from the wells were studied using a polarizing microscope on thin sections and geochemical analysis. Examination of cores and cuttings from three wells, obtained from a depth of about 230-1800 m, show that the hydrothermal minerals occurring in the rock include: K-feldspar, albite, chlorite, epidote alunite, kaolinite, smectite, illite, and opaque minerals. These alteration mineral assemblages indicate that there are geothermal fluids, which have temperatures of 150–250C in the reservoir. The distribution of the hydrothermal minerals shows changes in the chemical composition of the hydrothermal fluid, which are probably due not only to interaction with host rock.

### 5.1 Propylitic Alteration (Na-Mg-Ca-metasomatism)

This alteration expanded in the middle depth of three wells, that approved by petrographic studying and nature of fluid. Propylite is an old term used to describe altered volcanic rocks. Propylitic alteration, especially occurring in zones of descending meteoric waters in the hydrothermal system (or seawater in geothermal fields like Iceland) as stated by Giggenbach (1988), is characterized by the addition of H<sub>2</sub>O and CO<sub>2</sub>, and locally S, but without appreciable H-metasomatism. The meteoric water entering the hydrothermal system at the periphery (recharge zone) is heated and undergoes Na-Mg-Ca-metasomatism. Potassium minerals, like the K-feldspar microcline (K-Al-Si<sub>3</sub>O<sub>8</sub>), are preferentially destroyed on contact with descending solutions leading to the formation of assemblages containing albite (Na-Al-Si<sub>3</sub>O<sub>8</sub>), chlorite ((Mg,Fe,Al)<sub>6</sub>(Al,Si)<sub>4</sub>O<sub>10</sub>(OH)<sub>8</sub>), and epidote (Ca<sub>2</sub>FeAl<sub>2</sub>Si<sub>3</sub> O<sub>12</sub> (OH)). It can be said that downward flow and increasing temperatures favor assemblages containing minerals more soluble at low temperatures, XRD analysis indicate that in propillitic alteration zone this minerals can be exist: epidote, chlorite, calcite, albite. On the basis of evaluation of propyllitic alteration in tracky-andesitic rocks K2O 'SiO2'LOI, Cu are enriched and MgO 'Fe<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, Na<sub>2</sub>O, Cr, Ni, Mn, V, Cs, Sr, Ca, Ga, Zr, Hf, Ce, La, Eu, Sm, Tb and CaO depleted Al<sub>2</sub>O<sub>3</sub>, MnO, P<sub>2</sub>O<sub>5</sub>, U, Ta, Th, CaO and Hf have pattern of immobile.

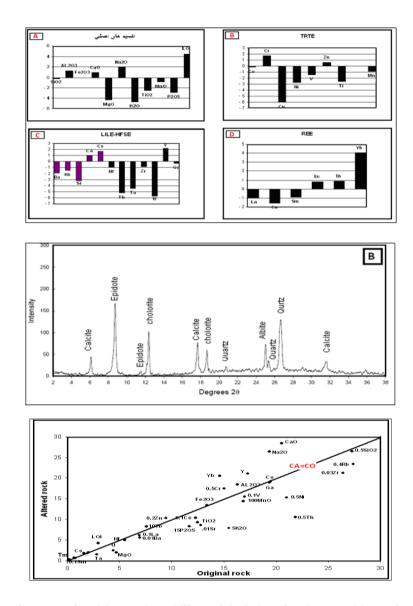


Figure 4: Isocon plot and percent of enrichment, immobility and depletion of major, transition and rare earth of elements in evolution of propillitic alteration zone in trackyandesite rock

### 5.2 Argillic Alteration (H-Metasomatism)

Argillic alteration occurred in whole surface, spacially in Moiel valley, and in the top zones (300-700 m) in three wells. Argillic alteration is characterized by the formation of clay minerals due to intense H-metasomatism, also called acid leaching. As stated above, H-metasomatism may occur within the hydrothermal system in two different cases, either deep in the reservoir within the primary neutralization zone or adjacent to the main upflow region within the secondary neutralization zone. Argillic alteration may be subdivided on the basis of the composition of the geological formations undergoing H-metasomatism, specifically rocks: 1-dominated by feldspars, 2- with a prevailing mafic composition, or 3- rich in calcium, like carbonates.

The results of XRD analysis indicate that in argilic alteration zone smektite, illite and caolinite and quartz evaluated, argilic zone extended. X-ray diffraction signatures are stronger for illit- smectite and kaolinit indicating temperature ranges between 140-200°C. Magnetite and is abundant in this zone suggesting predominantly oxidation process.

Within hydrothermal reservoirs, the circulating geothermal water may absorb strong acids like HCl, H<sub>2</sub>SO<sub>4</sub>, and HF from the deep magmatic to hydrothermal transition zone. This is a reaction most likely to occur but impossible to observe directly. The absorption of magmatic vapor into the deeply circulating fluid leads to initial rock dissolution. The vapor composition can be estimated of high temperature gases released from basaltic (Giggenbach and Le Guern, 1976) or andesitic magmas (Giggenbach, 1987). The results of Isocon method indicate that in argilic alteration zone SiO<sub>2</sub> & H<sub>2</sub>O enriched and Alkalin element (Na, K) have depleted pattern.

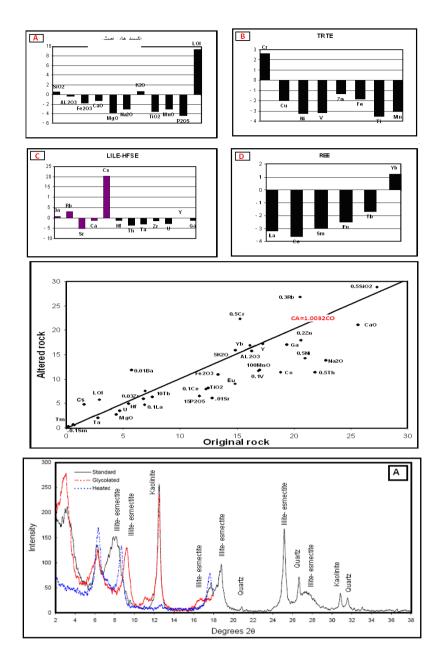


Figure 5: Isocon plot and percent of enrichment, immobility and depletion of major, transition and rare earth of elements in evolution of Argilic alteration zone in trackyandesite rocks.

# 5.3 H-Metasomatism in Ca-Rich Environments

Hydrogen ion metasomatism of carbonates is mainly described for the dissolution of calcite and the production of carbon dioxide resulting in the formation of carbonic acid  $(H_2CO_3)$ , in well NWS-7D.

$$CaCO_3 + 2 H^+ - Ca^{2+} + CO^2 + H_2O + Ca^{2+} + H_2CO_3$$

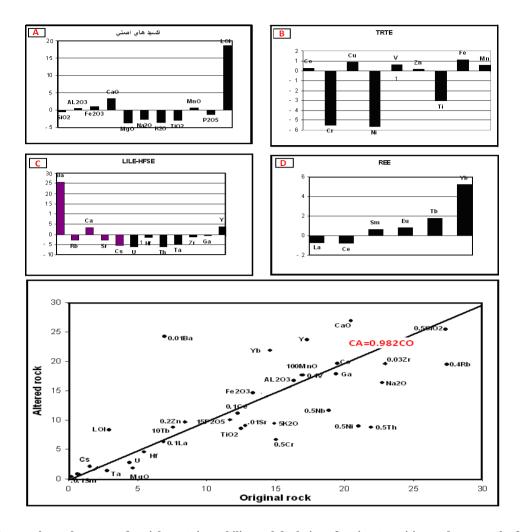


Figure 6: Isocon plot and percent of enrichment, immobility and depletion of major, transition and rare earth of elements in evolution of Calcitic alteration zone in trackyandesite rocks.

### **5.4 Phyllic Alteration (H-K Metasomatism)**

The regions of K-metasomatism and H-metasomatism are superimposed and combined under the term of phyllic or sericitic alteration. This is one of the most common types of hydrothermal alteration, present not only in Archean volcanogenic but also in recent epithermal systems, responsible for massive sulfide and gold-quartz deposits. A typical mineral assemblage for phyllic alteration zones consists of quartz, sericite, and pyrite accompanied by minerals like K-feldspar, kaolinite, calcite, biotite, rutile (TiO<sub>2</sub>), apatite (Ca<sub>5</sub>(PO4)<sub>3</sub>(OH,F,Cl)), and anhydrite. Phyllic alteration spreads into the potassic type by increasing amounts of K-feldspars and into the argillic type by increasing amounts of clay-minerals (Figure 6, Pirajno 1992). Giggenbach (1984) stated, excepting fluid and mineral compositions resulting from recrystallization of the parent rock, that a fully equilibrated system corresponds to K-feldspar / K-layer silicate coexistence. For different temperatures, theoretical CO<sub>2</sub> fugacities may be evaluated. For temperatures up to 200°C this is done taking the reaction between laumontite (CaAl<sub>2</sub>Si<sub>4</sub>O<sub>12</sub>. 4H<sub>2</sub>O), microcline, carbon dioxide, calcite (CaCO<sub>3</sub>), muscovite (KAl<sub>3</sub>Si<sub>3</sub>O<sub>10</sub>(OH)<sub>2</sub>), and silica. XRD signatures are stronger for quartz-sericite and pyrite suggesting, the formation temperatures could be above 180°C. The results of Isocon method In phyllic alteration zone indicate that K<sub>2</sub>O, Si<sub>2</sub>O and LOI have enriched pattern and MnO Fe<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, Na<sub>2</sub>O, MgO, CaO, P<sub>2</sub>O<sub>5</sub> have depleted pattern.

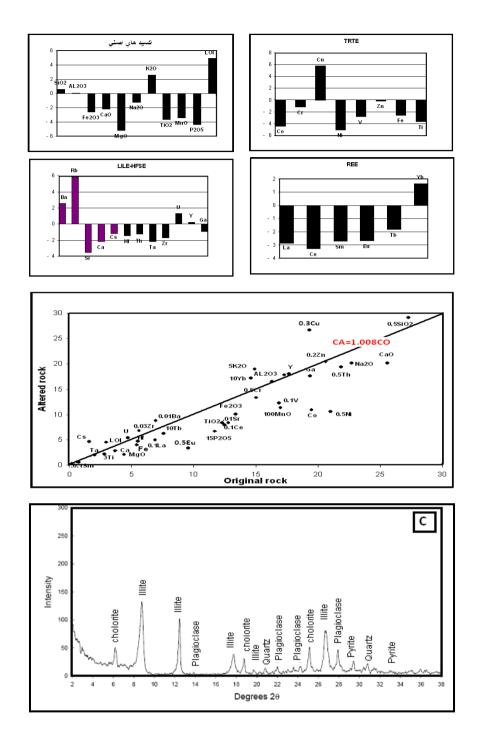


Figure 7: Isocon plot and percent of enrichment, immobility and depletion of major ,transition and rare earth of elements in evolution of Phyllic alteration zone in trackyandesite rock.

# 6. ALTERATION MINERALIZATION

Hydrothermal alteration zones have been investigated by X-ray diffraction, mineralogical-petrographical techniques, and geochemical analysis. Examination of cores and cuttings from three wells, obtained from a depth of about 814–1020 m, show that the hydrothermal minerals occuring in the rock include: K-feldspar, albite, chlorite, alunite, kaolinite, smectite, illite, and opaque minerals. In the studied area, silicified, smectite, illite, alunite, and opal zones have been recognized. These alteration mineral assemblages indicate that there are geothermal fluids, which have temperatures of 150–228°C in the reservoir. The distribution of the hydrothermal minerals shows changes in the chemical composition of the hydrothermal fluid, which are probably due not only to interaction with host rock, but also to dilution of the Na–K–Cl-rich hydrothermal fluid of the deep reservoir by cold water at shallow levels. Geochemical analyses of the solid and liquid phases indicate that the hydrothermal fluids of the geothermal system are in equilibrium with alteration products. The distribution of the hydrothermal minerals in this wells follows the temperature distribution in the wells. The mineral association (quartz, chlorite, pyrite and epidote) is often indicative of zones of boiling and good permeability (Atieno, 2011).

Clay minerals in the wells occur from the top to the bottom of the wells. The types of clay minerals encountered in the well include smectite, kaolinite, chlorite and illite. Smectite and kaolinite were notably common in the shallow zones, whereas chlorite and illite

are common at depth. The smectite zone extends from <100m to  $\sim$  1100 m depth where the clay mineral changes to chlorite and illite., smectite. Figure 7- The mineral (Kaolinite) replaces potassium-feldspar. Kaolinite is associated with low temperatures and acid alteration near the surface. The distribution of the hydrothermal minerals in this wells also follows the formation temperature distribution, the mineralization pattern shows five distinct zones that are due to differences in temperature (Table 1). The top zone which is the unaltered zone (0-200 m) has no alteration related to geothermal activity, suggesting the temperatures were < 50 °C. (Atieno, 2011). Smectite is the lowest grade mineral alteration zone.

The presence of smectite between 85 m and 300 m indicate the formation fluid is acidic and alteration temperature of less than 150°C. However, the measured downhole temperature are in the range of 40-50oC with increasing depth. The first appearance of chlorite at ~303 m indicates the alteration temperature is not less than 200oC, but the measured downhole temperature ~60oC. Therefore above ~ 1000 metres the formation temperature is far much lower than the alteration temperature indicating there was cooling in the upper parts of the well. Epidote which is indicative of temperature above 240oC occurs in the zone below ~ 957 m while the measured temperature is ~ 230oC. This indicates that the well was heating up. Therefore below 1050 m the formation temperature and the alteration temperature tend to move to equilibrium and reaches equilibrium below ~1250 m indicating there is no cooling but heating in this zone (Figure 9). Alteration minerals can be used to infer subsurface formation temperatures and also reconstruct the thermal history of a geo-thermal field. In this study, minerals such as epidote and actinolite are identified, they infer tem-peratures of >220°C and 250°C respectively and are markers for an upflow zone in the system (Zarei et al., 2017).

Similarly to permeability, the identified alteration minerals within the vapor-dominated reservoir cannot indicate current temperatures, but since there are measured temperatures available, the mineralogy deduced temperatures can be used to establish any changes with time. The following temperature ranges were used for the temperature stability of the minerals: smectite + cristobalite (<100°C); smectite + quartz (100° - 180°C); illite-smectite mixed layer (180° -220° C); illite (>240° C); kaolinite (<260°C); pyrophyllite (> 260°C (Reyes, 1990; Kingston Morrison Ltd. 1997). Table 1.

Table 1: Alteration mineral geothermometers and predicted temperatures in Well NWS10D based on megascopic analyses of rock cuttings.

epth-mRKB	Depth-mRKB	Alteration Mineral	Predicted
mMD (OWT)	mMD (ST)	Geo-thermometers	Temperature (°C)
14-84	-	Smectite + Trydimite	<100
?	?	Chlorite + Sphene	~120
303-665	-	Smectite + Vermiculite + Chlorite + Illite/Smectite	~120 - 150
686-785	712 - 954	Quartz + Illite/Smectite	~150 -180
788-797		Chlorite + Illite/Smectite	~180
800-833		Chlorite + Illite/Smectite + Quartz	~150 - 180
836-975		Quartz + Illite/Smectite	~150 - 180
1007-1070	957 - 1023	Illite/Smectite + (incipient to anhedral) Epidote	~180 - 200
	1027 - 1038	Quartz + Illite/Smectite + rare incipient Epidote (?)	~180
1073-1100	1041 - 1065	Illite/Smectite + (incipient and anhedral) Epidote	~200 - 220

a b

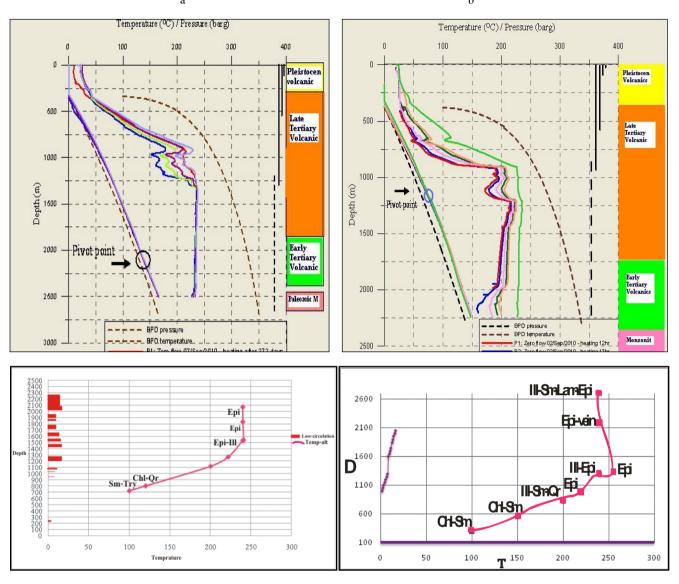


Figure 8: Comparison of formation and alteration temperatures of the well was done by plotting the downhole temperature and the inferred alteration temperatures of different minerals encountered in the well (a:NWS-6D,b: NWS-7D)

The measured temperatures in the wells are now cooler than those indicated by the mineralogy. This is consistent with an early, more magmatic-related stage of the system's development associated with the presence of intrusive rocks. (Abrenica et al., 2010)

#### 7. CONCLUSION

- -Based on available samples studied, the rock units in well NWS-7D have been hydrothermally altered by neutral-pH fluids resulting to the main alteration suite of chlorite + smectite/ illite + epidote + calcite + quartz + pyrite + anhydrite. This pervasive neutral-pH alteration assemblage is interpreted to be produced by the current hydrothermal system in Northwest Sabalan. Except for rare acid alteration, no significant amount of relict hydrothermal alteration minerals are observed among the rock samples analyzed in well NWS-7D. No intrusive was encountered in the wells (NWS-6 and NWS-10).
- -The neutral-pH alteration minerals in well NWS-7D exhibited a progradational trend with depth; with subsurface temperatures progressing from ~150-180°C at 550 m to ~200-220°C at 960 m. The hottest portion of the well possibly lies between 1316 m (Core 2) and 2180 m (Core 4) where neutral brine with temperature of ~240-250°C is likely flowing as indicated by occurrence of euhedral epidote and clinozoisite.
- -In order to illustrate mass changes of element quantitatively, isocon plots have been applied and illustrate that Al, Ti and Ga were relatively immobile during alteration and the mass was essentially conserved during alteration.
- -The characteristics of some subsurface alteration minerals (epidote) within the vapor dominated reservoir indicate disequilibrium with the present conditions.
- -Sabalan geothermal system has been cooling since the alteration minerals formed. The exploration wells seems to be more suitable for a reinjection well than the other wells.

In this paper we investigated hydrothermal alteration mineral assemblages and relationship between depth and minerals as a function of position in the geothermal system.

- -Trachytes and trackyandesite are reservoir rocks.
- -Hydrothermal alteration mineralogy indicates temperatures of more than 220°C below 1000 which is consistent with measured temperatures.
- -There is a complex alteration pattern produced by hydrothermal events associated with the monzonite and the two phases of dyke intrusion
- Illite-rich zones around faults that are the main drilling targets in the wells represent the current alteration.
- The rocks typically found in the field include andesitic lava flows, flow breccias, lahars, and a variety of pyroclastic rocks ranging from tuffaceous breccias to massive lapilli and crystal tuff.
- The behaviour of REEs in the hydrothermal alteration zones of the rocks is mainly controlled by pH, availability of complexing ions in the fluid as well as the presence of secondary phases as host REE minerals.

In the deeper parts of the well, hydrothermal alteration intensity ranged from high to extensive, and the minerals observed include, calcite, epidote, clays (chlorite, Illite), quartz, sulphides and actinolite. First

-The presence of zeolites indicate low formation temperature of <110°C. Colder waters could be dominant in this zone. Pyrite is common both in boiling and permeable zones. Abundance of pyrite indicates high activity of sulphur, good permeability and past or present boiling regimes (Lagat, 1998).

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