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Mineralogical and Geochemical Constraints of Jurassic Fossil Hydrothermal Alteration Associated with an Calc-Alkaline Volcano-Sedimentary Complex in Sanandaj-Sirjan Zone, Southwest of Iran

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Abstract: The Jurassic volcano - sedimentary complex in the Zagros Mountains within the central part of the Sanandaj- Sirjan structural zone is composed of volcanics (basalts andesitic basalts and andesites), subvolcanics (dolerites and microdiorites), volcanoclastics (tuffs, lapilli tuffs, agglomerates, pyroclastic and hyaloclastic breccia and tuffites). The igneous rocks with calc-alkaline to tholeiitic affinity were erupted in a subduction environment. The volcano sedimentary complex has been affected by hydrothermal alteration. Hydrothermal minerals have replaced primary rock components (selective pervasive) or have occurred as vein and vesicle fillings (non pervasive). There are three alteration zones in the study area including, propylitic (chloritic), sericitic and intermediate argillic based on variate amounts of the chlorite, epidote, clinozoisite, calcite and illite. In spite of plagioclases, primary clinopyroxenes and amphiboles are wholly or partially preserved. The propylitic (chlorite) zone is enriched in Y and HREE especially Ho, Er, Tm and Tb relative to fresh rocks and altered rocks in another alteration zones. The intermediate argillic zone is enriched in V relative to fresh rocks and altered rocks in another alteration zones and depleted in Au relative to fresh rocks.

Key words: Jurassic, volcanism, hydrothermal alteration, REE, trace elements

INTRODUCTION

The Jurassic volcano-sedimentary complex in the north of Shahrekord southwest Iran is a part of the Sanandaj-Sirjan structural zone in the Zagros Mountains. This zone is a narrow band lying between the towns of Sirjan and Esfandagheh in the southeast and Urumieh and Sanandaj in northwest (Mohajjel and Fergusson, 2000). The volcanic belts in this area is an island arc that contribute to a linear magmatism with an age of early Jurassic with calc-alkaline affinity that have emplaced on Hercynian basements in southern margin of Eurasia (Kazmin, 1986; Alavi, 1994). These belts have formed in a subduction tectonomagmatic regime that have occurred in Neo-Tethys oceanic crust (Osman *et al.*, 2004; Ghasemi and Talbot, 2006).

The study area is located between 50° 45' 11" E to 50° 57' 28" E and 32° 27' 32" N to 32° 27' 37" N (Fig. 1). The rocks exposed in this region are predominantly volcanic and volcanoclastic rocks erupted into host graywakes, slates and black shales crosscut by some dykes. This complex has been subjected by low (propylitic) to moderate (intermediate argillic) hydrothermal alteration.

The rocks in this area are pervaded by chlorite and calcite giving them greenish color. In addition, veins of

epidote, calcite and quartz are common throughout the complex. Vesicles in basalts are filled by chlorite-epidote-clinozoisite-calcite- quartz assemblages too. The objective of the present research is introduction a low to medium paleothermal gradient that caused a regional alteration associated with hydrothermal veins and vesicles filled by secondary mineral assemblages. In addition this study present a key index to recognition and discrimination of fossil hydrothermal alteration zones based on the behavior of trace and rare earth elements during fluid-rock interaction.

MATERIALS AND METHODS

The lithological units in this study were mapped using aerial and satellite photos after field investigations. A total of 200 petrographic thin sections were prepared and analysed using an Olympus polarizing microscope. The twenty- one whole rock samples were chemically analysed for major, minor, rare and rare earth elements by induced coupled plasma and mass spectrometry (ICP-MS) in Acme Laboratory in Vancouver, Canada. Primary and secondary minerals were chemically analysed on polished thin sections using a Cameca SX50 at the University of Oklahoma Norman, (USA), equipped with 5 asynchronous wavelength dispersive spectrometers and a PGT

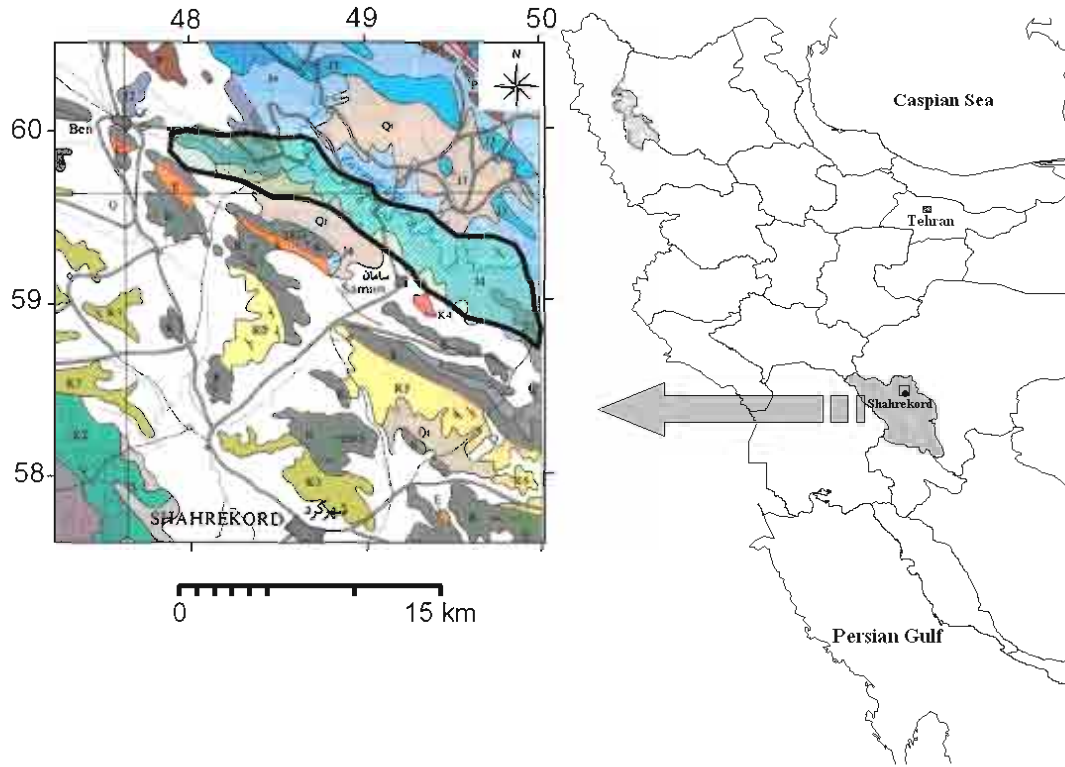


Fig. 1: Geological map of the study area (enclosed by black curve) in Chaharmahal and Bakhtiary province in southwest of Iran. (P: Permian limestones, J2, J3, J4: Jurassic Volcanics and sediments of, K, K2, K3, K5: Cretaceous limestones, E: Eocene Conglomerate, Q and Qt: Recent terraces and alluvium) (from Geological map of Shahrekord quaderangle in 1:250000 scale by Zahedi (1972)

PRISM2000 energy dispersive X-ray detector. The analytical conditions were 20 kV acceleration, 20 nA sample current, 3 μm spot size (EMPA). The major and alteration mineral assemblages were studied through petrography, X-ray diffraction (XRD). XRD analyses were performed at Mashhad Binalood Laboratory using Stoe-Stodip diffractometer with $\text{CuK}\alpha$ radiation at 40 kV and 40 nA, Ni filter and a divergence slit of 1° . Samples for ICP-MS analyses were prepared as alkaline melts by using lithium borate as a flux and the major elements measured by ICP- Emission spectroscopy. Geochronological analysis were performed by $^{40}\text{Ar}/^{39}\text{Ar}$ method in the College of Oceanic and Atmospheric Sciences of Oregon State University. To analyse of data we used of Minpet 2002 petrological and SAS statistical softwares.

RESULTS

Geological setting: According to Kazmin (1986), there have occurred various types of volcanism in different geological periods in the Zagros Mountains. He

emphasized that the magmatism with pronounced calc-alkaline character is ascribed to Jurassic. The black shales, slates and sandstones of lower Jurassic age have been metamorphosed in the vicinity of the volcanic complex. On the geological map of Shahrekord quadrangle (Zahedi, 1992), the lithostratigraphic units J2 and J4 studied here is composed of green tuffs and andesitic rocks. These units are divided into eight sub-units or members (Fig. 2). Based on $^{40}\text{Ar}/^{39}\text{Ar}$ dating of amphiboles, the hornblende andesites have an age of 148.19 ± 0.89 Ma to 169.91 ± 0.88 Ma corresponding to middle to upper Jurassic (Callovian to Tithonian stages). These rocks underlies Cretaceous limestones with a distinct nonconformity (Emami *et al.*, 2006) on which no traces of metamorphism or deformation is observed. Basalts are the predominant volcanic rocks of the study area. Small volumes of other rock types such as basaltic andesites and andesites are commonly present. The overall textures are porphyritic to seriate and microlitic with glassy and microcrystalline groundmass. Phenocrysts consist of plagioclase ($\text{An}_{17}\text{Ab}_{77}\text{Or}_{15}$) to

$An_{20}Ab_{79.4}Or_{0.4}$ in hornblende andesites and $An_{1.7}Ab_{97.8}Or_{0.5}$ to $An_{20.2}Ab_{79.4}Or_{0.4}$ in pyroxene andesites andesitic basalts), clinopyroxene including augite and diopside ($En_{43.32}Fs_{56.68}Wo_{0.47}$ to $En_{44.2}Fs_{55.8}Wo_{0.47}$) amphiboles including magnesihastingsite $Si_{4.102}Al_{1.9}O_{22}$ ($Ca_{1.77}Na_{0.40}K_{0.183}(Mg_{3.048}Fe^{2+}_{0.432}Al_{0.242}Fe^{3+}_{0.790}Mn_{0.019})$) and magnesi hornblende $Si_{4.337}Al_{1.443}O_{22}$ ($Ca_{1.97}Na_{0.423}K_{0.145}$) ($Mg_{2.313}Fe_{1.115}Al_{0.13}Fe_{0.13}Fe^{3+}_{0.948}$

$Mn_{0.077}$) up to 1 cm length, magnetite, ilmenite and pyrite (secondary) as opaques. The pyroclastic flows are 10-50 m thick and composed of tuffs, lapilli tuffs, crystal tuffs, glass and breccia with basaltic to andesitic basaltic compositions containing the same mineralogy as the lava flows. The volcanic rocks erupted in a subduction related volcanic arc (Table 1, Fig. 3), with a pronounced calc-alkaline to tholeiitic character (Emami *et al.*, 2006).

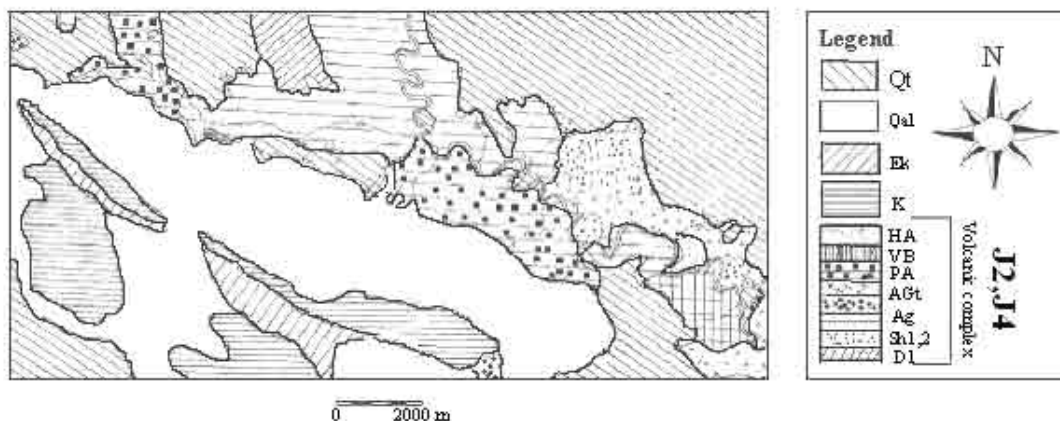


Fig. 2 Geological map of area. Qt = Quaternary terraces, Qal= alluvium, Ek= conglomerate of Kashkan formation (Paleocene), k: Cretaceous limestones, HA: Hornblende Andesites, VB: Volcanic Breccia, PA: Basalts and pyroxene andesites, Act: Andesitic and basaltic crystal tuff, Ag: Andesitic glass, Sh1,2: Shale, slate, sandstone, D1: Dolomitic limestone

Table 1: ICP-MS analyses of volcanic rocks

Sample No.	14-1	74-6	20-3	14-2	14-9	19-5	28-2	33-4	55-4	23-1	23-2
Rock	A	A	B	B	B	B	BA	BA	B	B	B
Zone	F	F	F	Ser	Ser	Ser	Ser	Ser	Ser	Int. Arg	Int. Arg
SiO ₂ (wt%)	58.44	57.37	47.38	47.77	49.08	47.49	55.00	54.02	44.34	47.82	49.15
TiO ₂	0.48	0.61	0.62	0.68	0.84	0.69	0.70	0.54	0.82	0.75	0.74
Al ₂ O ₃	15.60	17.00	15.51	15.25	18.25	15.27	16.47	15.83	17.78	17.18	18.67
Fe ₂ O ₃ (t)	11.45	6.73	16.09	14.03	8.62	13.87	7.09	7.72	9.21	6.59	8.13
Cr ₂ O ₃	0.007	0.006	0.047	0.058	0.024	0.056	0.027	0.047	0.061	0.028	0.002
MgO	2.81	3.13	7.22	8.14	4.33	8.43	6.16	6.45	10.68	4.49	4.16
CaO	2.85	5.24	7.58	7.94	7.99	7.95	6.68	6.08	9.61	10.17	6.32
MnO	0.13	0.12	0.20	0.19	0.12	0.18	0.12	0.13	0.15	0.13	0.11
Na ₂ O	3.39	7.24	2.70	2.97	1.61	2.88	2.85	2.74	1.47	4.09	4.82
K ₂ O	4.06	0.66	1.24	0.84	2.79	0.92	1.51	0.69	1.08	1.23	1.14
P ₂ O ₅	0.21	0.23	0.31	0.22	0.24	0.23	0.21	0.10	0.24	0.25	0.20
LOI	0.60	1.60	1.00	2.00	5.90	2.10	3.00	5.50	4.50	7.10	6.40
Sum	100.03	99.93	99.92	100.12	99.80	100.09	99.82	99.85	99.96	99.83	99.85
Sc (ppm)	13.00	20.00	33.00	35.00	32.00	35.00	26.00	33.00	41.00	33.00	26.00
Hf	2.00	2.20	1.20	1.10	1.90	1.40	1.30	1.40	1.60	1.50	1.10
Nb	2.70	4.10	2.80	2.30	3.10	2.50	2.30	2.90	3.60	3.20	2.40
Sr	121.50	301.70	326.20	255.80	480.10	268.10	359.60	323.80	383.00	264.00	281.40
Ta	0.20	0.30	0.10	0.20	0.20	0.10	0.10	0.20	0.20	0.20	0.20
Th	5.80	8.30	4.30	3.00	1.30	3.50	4.30	2.00	0.20	5.60	4.30
Zr	58.20	78.90	40.10	38.30	57.30	38.40	38.60	44.50	48.60	44.90	39.20
Y	15.60	17.50	17.40	18.40	21.20	18.30	18.00	14.80	21.70	19.80	18.40
La	12.30	18.20	14.70	9.80	6.80	9.80	10.30	7.70	16.00	14.80	8.80
Ce	24.80	40.00	31.00	21.60	16.40	23.40	23.70	13.80	35.90	34.50	21.70
Pr	2.95	4.92	3.80	2.85	2.27	2.93	3.03	1.87	4.68	4.56	2.99
Nd	12.00	19.80	16.70	13.30	11.40	14.10	13.70	8.20	21.00	19.70	14.40
Sm	2.30	4.09	3.20	3.10	2.98	3.00	3.22	1.93	4.39	4.27	3.51
Eu	0.79	1.31	0.92	0.98	0.94	1.05	0.78	0.59	1.21	0.99	0.82
Gd	2.38	3.28	2.94	3.33	3.29	3.37	3.04	2.11	3.81	3.43	3.17
Tb	0.37	0.54	0.45	0.44	0.39	0.43	0.53	0.42	0.63	0.59	0.54

Table 1: Continued

Sample No.	14-1	74-6	20-3	14-2	14-9	19-5	28-2	33-4	55-4	23-1	23-2
Dy	2.39	2.84	3.19	3.25	3.06	2.95	2.91	2.08	3.29	3.08	2.88
Ho	0.52	0.56	0.65	0.61	0.73	0.68	0.57	0.49	0.67	0.61	0.57
Er	1.55	1.73	1.86	1.98	2.01	1.85	1.72	1.45	2.04	1.92	1.80
Tm	0.29	0.29	0.31	0.28	0.34	0.32	0.28	0.24	0.34	0.30	0.27
Yb	1.53	1.87	1.62	1.64	2.01	1.82	1.71	1.42	2.01	1.91	1.70
Lu	0.27	0.32	0.29	0.30	0.32	0.28	0.27	0.23	0.33	0.31	0.26
Au	2.40	5.40	16.80	2.90	<0.50	<0.50	0.50	2.20	0.80	1.30	1.90
V	104.00	153.00	244.00	244.00	281.00	250.00	229.00	198.00	272.00	221.00	252.00
		28-1	29-1	64-1	22-8	22-9	18-1	48-6	56-1	56-2	22-2
Rock		B	B	BA	B	B	BA	D	D	D	D
Zone		Int. Arg	Int. Arg	Int. Arg	Ch	Ch	Ch	Ch	Ch	Ch	Ch
SiO ₂ (wt%)		48.87	48.12	52.60	44.01	47.69	53.53	46.85	47.14	46.54	44.52
TiO ₂		0.80	0.70	0.75	0.93	0.72	0.49	2.55	2.92	2.86	3.96
Al ₂ O ₃		18.19	16.53	17.13	16.20	18.44	14.53	16.08	13.99	14.92	13.87
Fe ₂ O ₃ (t)		8.63	9.12	8.15	16.84	8.24	6.31	13.11	14.56	13.62	15.88
Cr ₂ O ₃		0.027	0.053	8.15	0.039	0.035	0.022	0.008	0.012	0.005	0.006
MgO		7.47	8.40	5.58	6.23	6.24	4.71	4.97	4.99	3.44	4.80
CaO		6.57	8.56	8.04	10.24	9.60	11.00	8.10	9.32	8.19	8.74
MnO		0.13	0.16	0.12	0.15	0.10	0.14	0.21	0.24	0.23	0.26
Na ₂ O		2.59	3.00	2.49	1.84	1.79	2.96	3.90	3.77	4.16	3.81
K ₂ O		2.10	1.22	1.78	1.72	3.00	0.26	0.60	0.25	1.38	0.22
P ₂ O ₅		0.20	0.19	0.26	0.37	0.34	0.15	0.53	0.45	1.18	1.08
LOI		0.20	3.90	2.90	1.40	3.70	5.90	2.90	2.30	3.20	2.80
Sum		99.89	99.98	99.81	99.98	99.90	100.01	99.81	99.95	99.73	99.96
Sc (ppm)		31.00	37.00	36.00	40.00	30.00	21.00	32.00	33.00	23.00	34.00
Hf		1.50	1.30	1.40	2.40	1.60	1.50	5.30	5.40	5.60	5.50
Nb		3.20	2.30	2.50	4.60	3.60	1.70	11.80	9.60	19.80	20.90
Sr		371.00	377.10	366.50	326.20	453.80	162.00	300.30	355.50	377.70	242.40
Ta		0.20	0.10	0.10	0.30	0.20	0.10	0.80	0.60	1.40	1.50
Th		4.10	4.50	6.20	4.60	4.90	1.80	1.70	1.50	2.40	5.90
Zr		50.10	38.20	44.30	64.00	52.60	48.60	206.80	216.90	213.70	233.10
Y		22.50	18.90	19.30	26.50	22.30	18.80	48.10	50.90	46.00	53.60
La		12.70	12.40	15.70	17.20	18.20	5.30	16.30	13.80	25.70	22.50
Ce		29.50	29.20	37.50	37.60	38.90	12.40	39.90	35.50	59.90	55.20
Pr		3.79	3.84	4.94	4.86	5.07	1.84	5.82	5.27	8.63	8.14
Nd		17.10	17.30	21.10	21.00	22.40	9.00	26.70	25.70	40.50	39.80
Sm		4.17	3.90	4.65	5.00	4.54	2.12	6.76	7.05	9.12	9.37
Eu		1.10	0.97	1.13	1.83	1.16	0.62	2.28	2.24	3.66	3.05
Gd		3.96	3.40	3.72	4.55	3.95	2.60	7.84	8.18	9.68	10.24
Tb		0.66	0.58	0.62	0.75	0.64	0.49	1.47	1.51	1.61	1.76
Dy		3.43	2.96	3.07	3.97	3.27	2.80	7.64	7.95	8.44	9.17
Ho		0.72	0.60	0.65	0.86	0.68	0.61	1.53	1.69	1.56	1.79
Er		2.11	1.73	0.65	2.68	1.99	1.89	4.56	4.87	4.23	4.88
Tm		0.36	0.30	0.29	0.46	0.35	0.35	0.73	0.76	0.67	0.78
Yb		2.25	1.76	1.80	2.26	2.07	2.07	4.22	4.43	3.64	4.37
Lu		0.37	0.29	0.29	0.43	0.34	0.35	0.64	0.68	0.57	0.66
Au		2.60	<0.50	2.10	9.80	0.80	2.10	2.60	1.50	2.30	1.10
V		292.00	245.00	260.00	287.00	259.00	147.00	272.00	338.00	116.00	302.00

BA: Basaltic Andesite, B: Basalt, A: Andesite, Ch : Chloritic zone, Ser: Sericitic zone, Int. Arg: intermediate argillic zone, F: Fresh

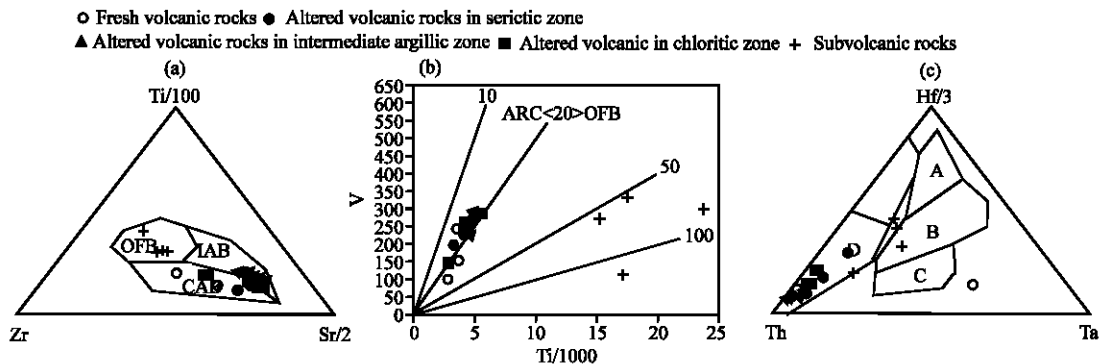


Fig. 3: Geotectonical discrimination diagrams. on the basin of (a) Ti/100-Zr-Sr/2 (Pearce and Cann, 1973). CAB: Calc-alkaline basalts. IAB: island arc basalts. (b) V-Ti/1000 (Shervais, 1982).ARC district: Island arc basalts and (c) Th-Hf/3-Ta (Wood, 1980). D district: destructive plate- margin basalts and differentiates

ALTERATION

The volcanic rocks have affected by low to medium hydrothermal alteration. In addition, hydrothermal fluids have injected via veins and veinlets into these rocks subsequent to their consolidation. A detailed mineralogical study of each of the alteration styles and zones will be undertaken below:

Alteration styles: The style of alteration, takes into account the intensity of hydrothermal alteration.

Terms, such as weak, moderate, strong, extensive, pervasive, non pervasive, are well known and frequently used (Pirajno, 1992). The alteration styles in the study area are:

- Selective pervasive alteration that is an alteration style where recrystallization of secondary minerals

occurs without destroying the rock texture. In the studied samples, plagioclases in volcanic rocks are altered to calcite, actinolite and prehnite (saussuritization).

In primary clinopyroxenes (augite and diopside) and amphiboles remain fresh (Figs. 4a, b) or partially have altered to chlorites, tremolite and actinolite. On the basis of the most common secondary minerals and XRD analyses, three alteration zones are recognized.

Propylitic or chlorite zone: This kind of alteration developed by the increase of H_2O , CO_2 and locally SO_4^{2-} without H^+ metasomatism (Pirajno, 1992). The volcanic and volcanoclastic rocks in the north towards the center of the studied area have affected by this alteration type (Fig. 4c, d). This zone is identified by the index minerals including chlorite, epidote, calcite, sericite and pyrite in thin sections. If chlorite becomes the principal secondary mineral, the term of chlorite zone should be employed.

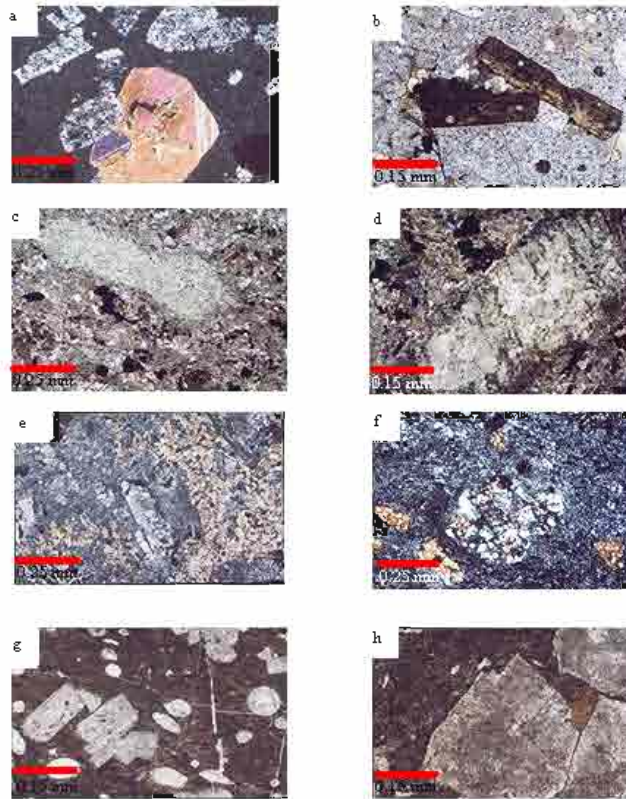


Fig. 4: Photomicrographs showing selective pervasive alteration: (a) fresh pyroxene and altered plagioclase in pyroxene Andesite (XPL× 4), (b) fresh amphibole and completely altered plagioclase in groundmass in hornblende Andesite (XPL×10), (c) distribution of chlorite in altered basalt of chloritic zone (XPL×4), (d) altered dolerite in chloritic zone (XPL×10), (e) altered andesitic basalt in sericitic zone (XPL×4), (f) altered basalt in sericitic zone (XPL×4), (g) altered vesicular basalt in intermediate argillie zone (PPL×4) and (h) altered andesitic basalt in intermediate argillie zone (XPL×10). (XPL: Cross polarized light, PPL: Plan polarized light)

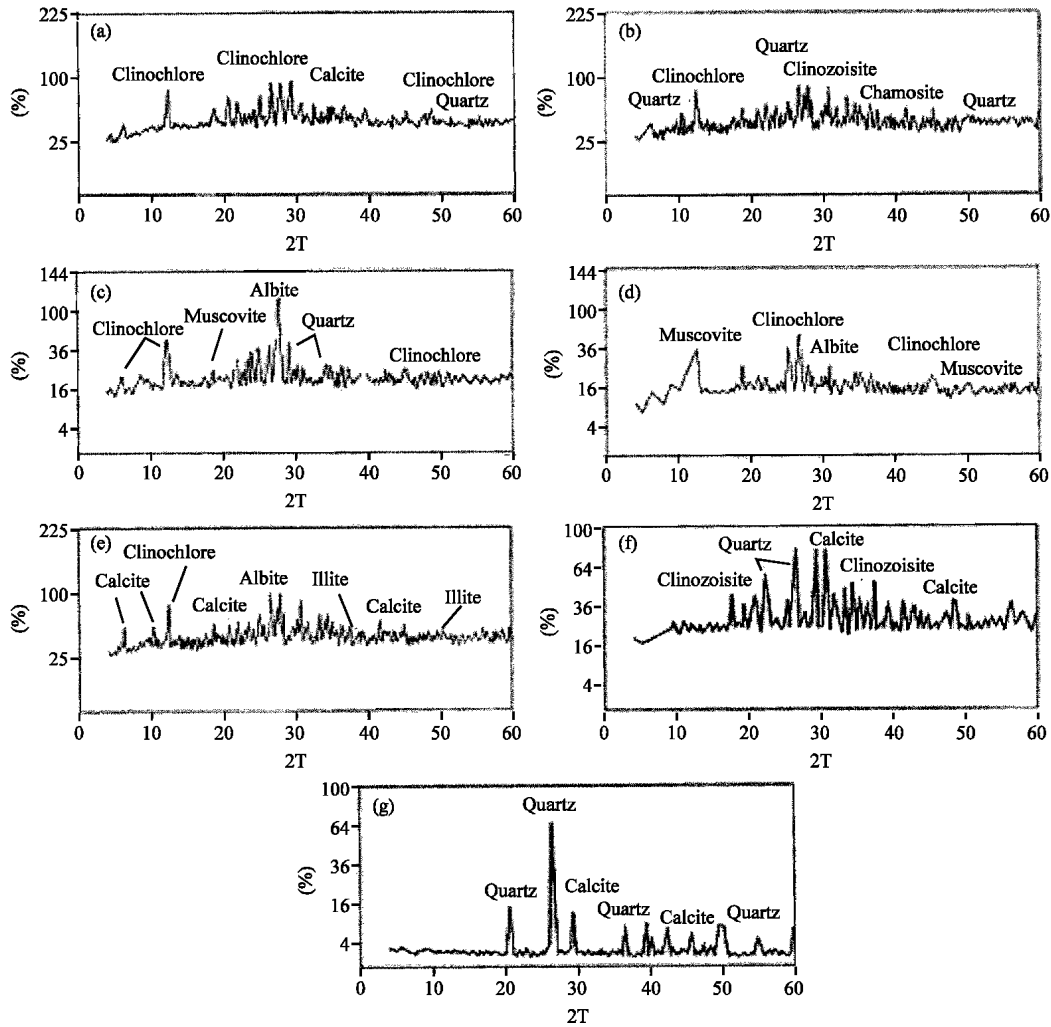


Fig. 5: X-ray diffractograms of the studied samples (a) and (b) chlorite zone, (c) and (d) sericite zone, (e) intermediate argillic zone, (f) and (g) veins

This alteration type have overmarked the other types in almost all of the studied volcanic rocks. In brief clinocllore, picnochllore, quartz and calcite are the main secondary minerals in this alteration zone (Fig. 5).

Sericite zone: The assemblage quartz-sericite-pyrite minerals occurs in the central part of the chlorite zone, where andesitic basalts and pyroclastic rocks are predominant, conduct us to sericitic zone. Secondary minerals associated with this assemblage are quartz, calcite, muscovite, clinizoisite, pyrite and apatite which were determined by thin sections study (Fig. 4e, f). Some large cubic crystals of pyrite associated with the pyroclastic units are also found in field observations. This form of alteration is due to decomposition of feldspars alteration to quartz, muscovite and pyrite in the presence of the H^+ , OH^- , K^+ , SO_4^{2-} .

Intermediate argillic zone: Several white lenses of altered volcanic and pyroclastic rocks exposed in the eastern margin of the complex, have been altered to illite, calcite, quartz, epidote, picnochllore. Here, plagioclase phenocrysts and matrix materials have altered to brown clay minerals with brown color under plane polarize light in thin sections (Figs. 4g, h). Since the primary textures and mafic minerals are preserved and no alunite is observed, the alteration assemblage is limited to intermediate argillic. - Non - pervasive alteration occurs as veins or vesicle fills are also described. In this type of alteration, only apart of the rock volume have been affected by the hydrothermal fluids (Fig. 5).

Veins alteration: Veins cutting volcanic and pyroclastic rocks are common throughout the study area. They are usually less than 30 cm in width and are composed of calcite, quartz, epidote and clinozoisite (Fig. 5).

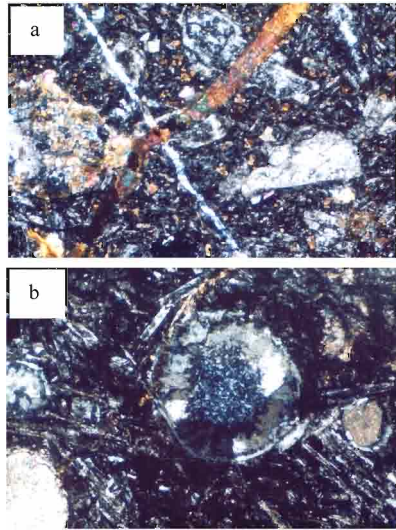


Fig. 6: photomicrographs showing non-pervasive alteration, (a) Vein alteration (XPL× 4). The epidote vein with northeast - southwest direction was deposited after the quartz vein trending Northwest-Southeast. (b) Vesicles infilled alteration minerals as chlorite, calcsite, epidote, quartz (XPL×10)

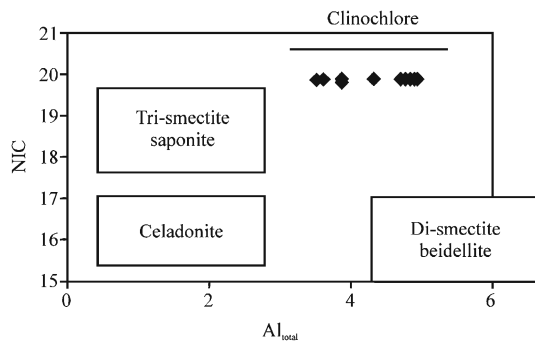


Fig. 7: Plot of non-interlayer cation totals (NIC = Si+Ti+Al_{total}+Fe+Mg+Mn) versus Al_{total} in chlorites. All cation values are calculated based 28 oxygens (after Large *et al.*, 2001)

Quartz veins are older than the others veins (Fig. 6a). Quartz veins have widths of 1 to 10 cm are elongated from West-east (in field) around the veins. This means that the temperature of veins was lower than 200°C (Fuentes *et al.*, 2004).

Vesicles infilling alteration: Vesicles in basalts are 1-5 mm in diameter and filled by chlorite, epidote, calcite and quartz (Fig. 6b).

Table 2: Representative results of microprobe analysis of chlorites from Northwest of Shahrekord area

Samples	(A)	(B)	(C)
Zone	Chlorite	Sericite	Intermediate argillic
Rock type	Ba	B	B
SiO ₂	27.93	31.43	30.65
TiO ₂	0.01	0.01	0.01
Al ₂ O ₃	19.77	15.80	16.48
FeO (t)	22.14	18.28	18.80
MnO	0.43	0.25	0.26
MgO	18.09	21.70	21.10
CaO	0.07	0.107	0.12
Na ₂ O	0.00	0.00	0.00
K ₂ O	0.04	0.02	0.02
Total	88.48	85.59	87.44
No. of oxygens	28.00	28.00	28.00
NIC	19.90	19.76	19.80
Al _{total}	4.81	3.75	3.94

BA: Basaltic Andesite, B: Basalt

Table 3: Representative microprobe analyses of epidotes from Northwest of Shahrekord area

Samples	(A)	(B)	(C)
Zone	Chlorite	Sericite	Intermediate argillic
Rock type	Ba	B	A
SiO ₂	37.32	38.18	37.78
TiO ₂	0.06	0.04	0.02
Al ₂ O ₃	21.31	25.85	23.88
FeO	14.74	8.87	11.50
MnO	0.09	0.10	0.04
MgO	0.01	0.01	0.00
CaO	22.46	23.15	23.16
Na ₂ O	0.00	0.00	0.00
K ₂ O	0.00	0.00	0.00
Total	95.99	96.20	96.38
No. of oxygens	12.50	12.50	12.50

BA: Basaltic Andesite, B: Basalt. Numbers in the brackets show the number of analysis, A: Andesite

Chemical composition of the secondary minerals

Chlorites: Chlorites partially replace plagioclase and clinopyroxene, the groundmass/matrix and fill vesicles in the volcanic and pyroclastic rocks. The color of chlorites in polarized light in amygdals varies from blue in volcanic and pyroclastic rocks to red and green in subvolcanic rocks (Fig. 4c, d, 6b). Representative microprobe analyses of chlorites in three alteration zones, recalculated on the basis of 28 oxygens, are shown in Table 2 and plotted in Fig. 7 in terms of noninterlayer cations (NIC = Si+Ti+Al_{total}+Fe+Mg+Mn) vs. Al_{total} content (Large *et al.*, 2001). The NIC values range from 19.76 to 19.90 indicated that the phyllosilicates in the mafic rocks of three alteration zones are located in clinochlore area. A legal conclusion is that all of the rocks have altered by a single alteration event.

Epidotes /clinozoisites: Epidote, associated with chlorite and calcite, appears as partial or total replacement of plagioclases (Fig. 4f).

Representative microprobe analyses of epidote from three alteration zones (Table 3) show that clinozoisite is

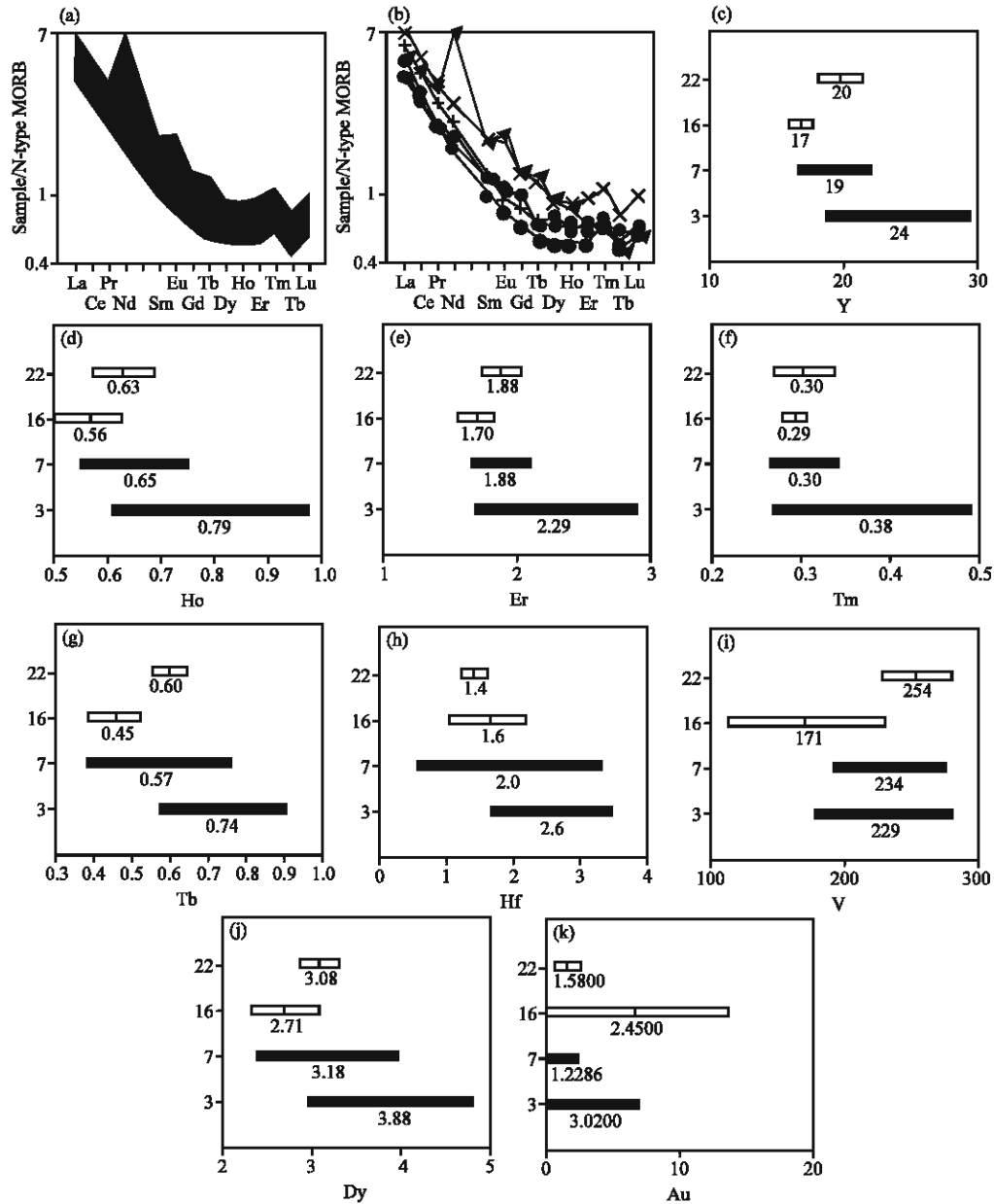


Fig. 8: Geochemical behavior of REE and some trace elements in volcanic rocks of Shahrekord area, (a) REE cumulative pattern of analysed samples normalised to MORB (b) REE Spider diagram of analysed samples normalised to MORB. (c, d, e, f, g) REE enrichment in altered basalts in chlorite zone in comparison to fresh and altered basalts in another zones (h, I, j, k) Some trace and REE enrichment in altered basalts of intermediate argillic hydrothermal zone in comparison to fresh and altered basalts in another zones. (grey: intermediate argillic zone, dark green: fresh rocks, red: sericite zone and light green: chlorite zone, Y axes are elemental frequency in ppm)

the main mineral of epidote group in the samples of all altered zones. The calculated formula are $\text{CaFeAl}_2\text{Si}_3\text{O}_{12}(\text{OH})$, $\text{Ca}_2\text{Fe}_{0.6}\text{Al}_{2.4}\text{Si}_3\text{O}_{12}(\text{OH})$ and $\text{Ca}_2\text{Fe}_{0.7}\text{Al}_{2.3}\text{Si}_3\text{O}_{12}(\text{OH})$, in chlorite, sericite and intermediate argillic zones, respectively.

Albites: Feldspars in the fresh volcanic and pyroclastic rocks are mainly oligoclase- andesine (in andesites) and anorthite (in basalts). In chlorite zone, albitization has pervasively occurred in association with chloritization. The lack of clear compositional gradients between

Table 4: Representative results of microprobe analyses of plagioclases from Northwest of Shahrekord area

Sample	22-8	74-5	12-11	26-3
Rock type	B	A	B	A
SiO ₂	44.35	62.92	67.43	69.26
TiO ₂	0.01	0.00	0.00	0.01
Al ₂ O ₃	23.53	22.09	20.96	20.05
FeO(t)	1.46	0.76	0.11	0.03
MnO	0.03	0.04	0.00	0.00
MgO	0.00	0.01	0.01	0.01
CaO	26.31	4.23	1.14	0.40
Na ₂ O	0.07	9.21	10.91	11.59
K ₂ O	0.01	0.08	0.11	0.10
Total	95.77	99.34	100.67	101.45
No. of oxygens	8.00	8.00	8.00	8.00
An	99.50	20.10	5.40	1.80
Ab	0.50	79.40	93.90	97.60
Or	0.00	0.50	0.60	0.60

B: Basalt, A: Andesite

igneous plagioclase (oligoclase and anorthite) and secondary feldspar (albite) suggests that secondary feldspars formed by dissolution precipitation reactions (Larsson *et al.*, 2002). The compositions of secondary Na-feldspar span a range between 5 to 10% An. Representative microprobe analyses of fresh and albitized plagioclases in chloritic zone are shown in Table 4.

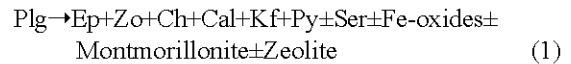
Rare earth elements variations in altered rocks: The REE behavior of altered and unaltered rocks investigated by ICP-MS analyses results (Table 1). The Spider diagrams for fresh and altered rocks, in comparison to N-MORB, show an REE enrichment specially in rock samples of the chloritic zone. Their similarity models to N-MORB reflect a cogenetic magmatism (Fig. 8a, b). The behavior of rare earth elements in altered to fresh basalts is shown in Fig. 7.

DISCUSSION

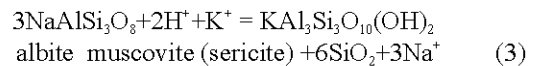
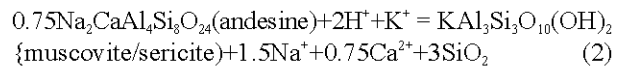
Alteration zones: There have distinguished three selective pervasive and two non pervasive form of hydrothermal alteration at the basis of mineralogical and geochemical constraints in this research. The pervasive alteration zones include propylitic (chloritic), sericitic and intermediate argillic while non pervasive alterations are veins and vesicles fillings.

Some minerals as clinozoisite, chlorite, quartz, secondary albite and calcite are the index secondary minerals that are present in the chloritic alteration zone as described in Eq. 1. This alteration is a kind of propylitic alteration that is characterized by the addition of H₂O, CO₂ and locally SO₄²⁻, with no appreciable of H⁺ metasomatism (Pirajno, 1992). The typical minerals are epidote, chlorite, carbonates, albite and pyrite. Sericite, Fe-oxides, montmorillonite and zeolite may locally be common. The observed intense albitization associated with chloritization or carbonitization in this area prefer to

consider separately, reserving propylitization for weaker H⁺-metasomatic effects (Hemley and Jones, 1964). Outward propylitic alteration grades into unaltered rocks. The similarity of chlorites compositions in all of the studied samples from this zone show that their physico-chemical alteration conditions are the same. The volcanic and pyroclastic rocks of the study area are affected by this alteration via the following mechanism.



Accumulation of Q+Ser+Py±Kf±Cal±Ru±Anh±Ap is indicative of sericitic zone. The assemblage of quartz-sericitic- pyrite-chlorite specially in crystal tuffs and pyroclastic breccia is characteristic of the sericite zone of the study area. The formation of sericite, can be expressed by the following equations (Pirajno, 1992).



In hydrothermally altered oceanic crust, mixed layer chlorite-smectite progressively grades into true chlorite with progressively more recrystallisation as more aluminium dissolves from plagioclase (Alt *et al.*, 1986; Alt, 1995).

The occurrence of illite in basalts in center of area mark the meet of intermediate argillic zone. This alteration inwardly grades into sericitic zones, whereas outwardly it merges into propylitic (chlorite) zone. This form of alteration is due to H⁺ metasomatism (acidic leaching) at temperatures of 100 to 300°C and is defined by the presence of illite, chlorite, kaolin group clays and minor sericite, while K-feldspar is absent in thin sections and XRD diffractograms. The absence of montmorillonite and alunite in studied samples show that the volume of acidic fluids were not enough to make advanced argillic alteration.

The studied rocks display similar altered mineral assemblages in amygdals and veins within each zone. Calcite, quartz, epidote and clinozoisite are common hydrothermal minerals infillings vesicles and amygdals, vein or veinlets and pervasive alteration zones. This suggest that these alteration assemblages formed during the same alteration episode.

Temperature estimates: The alteration zones develop in various temperatures and under various chemical factors (Burnham and Ohmoto, 1980; Guilbert and Park, 1985). The

evaluation of temperature of alteration processes can be made by comparison with formation temperatures of secondary minerals measured in active geothermal systems (Reyes, 1990). The presence of prehnite in some of the vesicles indicates that the temperatures should vary between 200 and 280°C according to Frey *et al.* (1991) or in the range of 240-300°C on the basis of observations of Philippine geothermal systems (Reyes, 1990). While the appearance of epidote suggests that the temperatures should be higher than 200°C (Chao *et al.*, 1986; Reyes, 1990) or even 250°C (Bird *et al.*, 1984; Liou *et al.*, 1985). The occurrence of chlorite with nearly ideal NIC totals to those of clinocllore indicates temperatures of 245 to 265°C based on Icelandic data (Schiffman and Fridleifsson, 1991). For calculating of chlorite temperature in the study area rocks, we used of modified the Cathelineau and Nivea equation (De Caritat Patrice, 1993) as:

$$T = 106Al^{IV}_c + 18(Al^{IV}_c = Al^{IV} + 0.7(Fe/[Fe + Mg]))$$

The calculated temperatures for three chlorite (pichnochlorite to clinocllore) are 226 to 288°C. Thus, the temperature of primary hydrothermal fluid likely ranges between 226 to 288°C. Furthermore, epidot-quartz hydrothermal veins had a temperature of about 250 to 300°C (Paradis *et al.*, 1993) and have penetrated after volcanics and pyroclastics emplacement and their pervasive alteration.

Alteration system and chemical controls: Field investigations as mineralogical characterization show an Mesothermal system in the study area formed at low to moderate temperatures and pressures, from dominantly magmatic hydrothermal fluids which are weakly saline (<1 to roughly 5 wt. (%) NaCl equivalent) (Browne and Ellis, 1970; Mehmet and Gevrek, 2000). The low-chlorinity fluids had the highest cobalt, nickel, aluminium, iron and chromium and the high-chlorinity fluids had the highest zinc, cadmium, manganese and lead (Jones *et al.*, 2005; Wheeler *et al.*, 2001). Hydrothermal mineral phases that develop in these systems are a function of temperature, pressure, rock type, nature of the circulating fluids (such as pH, activities of CO₂, H₂S) and water/rock ratios. Following Hedenquist and Browne (1989) and Haas *et al.* (1995), we consider the hydrothermal alteration in terms of the interaction of Alkaline fluids (pH>8) with minor chloride and a temperature about 250 to 300°C that is estimated between 200°C in intermediate argillic zone to 250-300 in propylitic (chloritic) zone.

A summary of alteration types and related hydrothermal minerals associated with their temperatures in epithermal and mesothermal systems are shown in Table 5.

Table 5: Hydrothermal alteration assemblages in epithermal and mesothermal systems related to near- neutral, chloride-rich hydrothermal fluids (after Hedenquist and Lindqvist, 1985)

Alteration type	Mineral assemblage (+key minerals±accessories)	Inferred temperature (°C)
Argillic	Smectite or interlayered Illite±Smectite±Sulfides± Zeolites±Quartz ±Calcite	<200
Sericitic	Sericite±Quartz±Sulfides±Oxides	>220
Propylitic	Epidote±Chlorite±Illite±Sulphides	>250
Inner propylitic	Epidote±Actinolite±Chlorite±Illite	>300
Potassic	Adularia+Biotite+Magnetite Epidote±Chlorite±Muscovite	>320

Geochemical variations in the alteration zones: The behavior of REE and trace elements in chlorite and sericite and intermediate argillic zones of the study area demonstrate that some of these elements were mobile under some physico-chemical conditions. Buchl and Gier (2002) showed that some elements as REE, Zr and Ti are mobile in some conditions. Terakado and Fujitani (1998) and Cuney and Regis (1995) studied the REE behavior in hydrothermal alteration of Jabiluca, Italy and concluded that these elements behave selectively. Fulignati *et al.* (1999) emphasized the high mobility of REE in acidic fluids and demonstrated that LREE are immobile while HREE are depleted in advanced argillic zone. In other word, the maximum of depletion has occurred in silicic and intermediate argillic and the minimum of depletion, belong to sericitic and propylitic zones. Patino *et al.* (2003) stressed on REE depletion in high weathered basalts in Hawaii islands. Alt and Teagle (2003) presented a depletion and enrichment pattern for different elements in hydrothermal alteration of mid oceanic ridges. For example: they showed the enrichment of U, Th, Ba, Cs, Rb, K and H₂O and weak depletion of Ni and Mg. In the study area, distribution of REE in the volcanic rocks of the three main alteration zones (Chlorite, sericite and intermediate argillic zones) show that only some elements as Hf, U, V, Y, Gd, Tb, Dy, Ho, Er, Tm, Lu and Au could mobile by hydrothermal fluids. The statistical calculation by SAS software show some important key notes as given:

- Fresh rocks are different from altered rocks in sericite and chlorite zones in U.
- Altered rocks in chlorite zone are enriched in Y, Ho, Er, Tm, Tb relative to fresh and altered rocks in another zones.
- Altered rocks in intermediate argillic zone are enriched in Hf and Dy relative to altered rocks in chlorite zone and enriched in Au relative to fresh rocks and altered rocks in sericite zone.

CONCLUSION

The volcano-sedimentary complex in north of Shahrekord in Sanandaj-Sirjan structural zone in South

West of Iran (with calc-alkaline affinity) have emplaced into lower Jurassic detrital rocks. As illustrated by discrimination diagrams, all the representative samples of the volcanic rocks lie in calc-alkaline to tholeiitic field and have erupted in a subduction environment. Approximately, all of the rock units have been affected by low to moderate hydrothermal alteration in an Mesothermal system. Based on the mineral assemblages as well as geochemical criteria, three alteration zones are distinguished: Chlorite zone comprising clinozoisite, clinocllore, pichnocllore and quartz; Sericitic zone consisting of quartz, muscovite, picnocllore, calcite and pyrite and intermediate argillic zone composing of illite, calcite, quartz and clinocllore minerals. On the base of formation conditions of the secondary phases that have achieved in active geothermal systems, the temperature of hydrothermal system varies from 200°C in intermediate argillic zone to 226-288 in chloritic (propylite) zone. The nature of hydrothermal fluids was alkaline to slightly acidic and SO_4^{2-} enriched. Besides, the precipitation of pyrite, calcite and picnocllore show that SO_4^{2-} , carbonate and chloride show that SO_4^{2-} , carbonate and chloride complexes were present in the fluids. The variation histograms of trace elements and REE using in this study, characterized the fossil chloritic alteration zone by the great content of Y and HREE especially Ho, Er, Tm and Tb relative to fresh rocks and altered rocks in another alteration and intermediate argillic zone by the enrichment in V relative to fresh rocks and altered rocks in another alteration zones and depleted in Au relative to fresh rocks. This can be regarded as an useful key index to determine the alteration zones in fossil alteration systems where field observations as well as mineralogical constraints are insufficient to work.

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