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Mineralogical and geochemical characteristics of the Chah-Shur clay deposit, Southeast of Isfahan, Iran

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Abstract

The Chah-Shur clay deposit is located in 150 km southeast of Isfahan. Eocene igneous rocks and Quaternary deposits cover the area. Eocene volcanic rocks include andesite and tuff. The rocks belong to magmatic activities of Urumieh-Dokhtar magmatic belt. Alteration of the vitric and lithic tuff units has produced the clay deposit. Based on the petrographic studies the main minerals in tuff units are plagioclase, K-feldspar and quartz. The major phases in clay deposit are kaolinite, illite, montmorillonite, quartz, albite and orthoclase. Also, muscovite, chlorite and hematite are as minor phases. The mineralogical studies show an intermediate alteration. The clay deposits can be formed by supergene or hypogene processes; while the combination of both of them can result in the formation of mixed type clay. The geochemical data of Chah-Shur clay deposit show scattering between hypogene and supergene types. The abundance of Fe_2O_3+TiO_2 vs Cr+Nb and Zr vs TiO_2, as well as Sr+Ba vs Ce+Y+La suggest mixed and hypogene types. On the other hand, P_2O_5 and SO_3 plot shows the supergene and mixed types. The results obtained from mineralogical and geochemical studies indicate that the genesis of the Chah-Shur clay deposit can be considered mixed type.

Keywords: *Iran, Kaolinite, Chah-Shur, Mixed type Clay deposit, Urumieh-Dokhtar.*

1. Introduction

The Chah-Shur clay deposit is located in 150 km southeast of Isfahan. The studied area belongs to Urumieh-Dokhtar magmatic belt in the Central Iran structural zone (Fig 1). The belt is subduction-related magmatic arc between Iranian and Arabian plates. Urumieh-Dokhtar magmatic belt is a part of Zagros orogeny. The opening and closure of the Neo-Tethys had resulted in magmatic activities in Urumieh-Dokhtar (Alavi 1994; Mohajel et al. 2003). Peak of magmatic activities in Urumieh-Dokhtar magmatic belt began in the Eocene and continued up to Miocene and Pliocene-Quaternary (Alavi 1994; Mohajel et al. 2003; Khodami et al. 2010).

The Eocene calc-alkaline volcanic rocks consist of andesites, vitric and lithic tuffs are exposed in the Chah-Shur area. Eocene volcano-sedimentary rocks in the region are overlain by Miocene red sedimentary sequence (Fig 1) (Amidi and Nabavi 1972). Tuff units have altered to clay minerals and have produced a suitable clay resource. The clay minerals have many applications in various industries such as ceramics, rubber, papermaking, paint, plastics, china, porcelain, glass and pharmaceutical industries, building materials and oil industry. Regarding the increasing of their usage and for the discovery of more resources, it is essential to know the formation processes and the genesis of clay deposits as well as the quality analysis of them (Nyakairu et al. 2001; Benea and Gorea 2004; Njoya et al 2006). The clay deposits can be formed by the meteoric water and weathering processes in permeable zones in the type of supergene. In addition, it is made by hydrothermal alteration in the type of hypogene clay. Meanwhile, the combination of the two above-mentioned processes can be significant in the formation and the development of the clay resources, which known as mixed type (Dill et al. 1997; Dill et al. 2000; Njoya et al. 2006).

The meteoric water and the hydrothermal fluid especially near the faults, fractures and porosity in the regions with magmatic activities can produce the clay mineral with the binary or mixed genesis. Investigation of clay genesis is important, because of their association with the precious metals such as copper and gold. It is not hard to recognize the origin of clay at high temperature hydrothermal alteration, for example potasic alteration. But defining the origin of clay, while the reactions have occurred in lower temperatures such as argillic alteration is difficult. The formation of kaolinite and montmorillonite under the condition of argillic hydrothermal alteration by low-temperature fluids is similar to supergene conditions (Nyakairu et al. 2001; Njoya et al. 2006).

The mineralogical and geochemical evidences are necessary for the investigation of the clay genesis and the separation of two sources. The hydrothermal veins, fractures, magmatic activities, soil, and the remnants of the parent rock should be considered in the studies.

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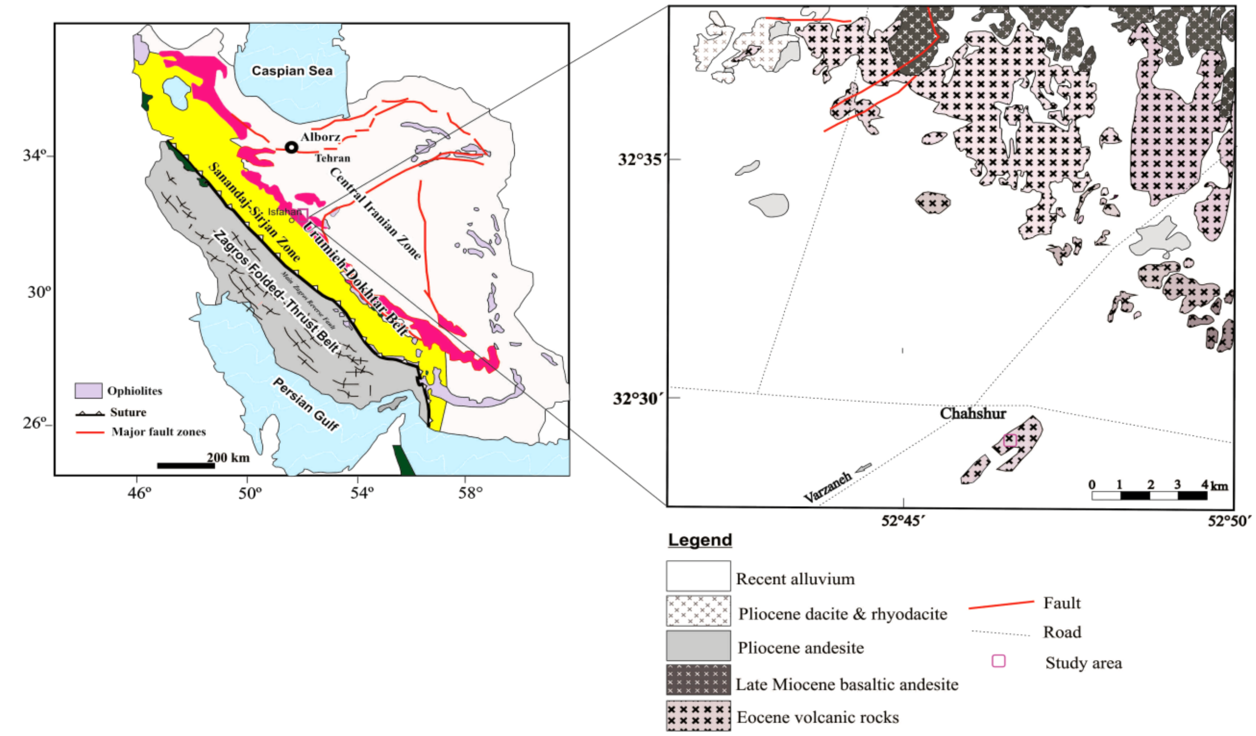

Fig 1. The geological map of the studied area (Simplified from the geological map of Naein 1:250000; Nabavi and Amidi1972), and the position of the studied area has shown with square in tectonic units of Iran (Mohajjel et al. 2003) and geological map.

The mineralogy and texture of deposit as well as geochemical characteristics are very important in identifying the source of clay. The mineralogical and geochemical data from the Chah-Shur clay deposit have been studied and discussed in this research. The results can be used for discrimination and classification of the type and source of clay deposit at regional scale.

2. Petrography

According to petrographic studies, andesite and tuff are the main groups of rocks in the area. The tuffs in the region are divided into two groups of vitric and lithic tuff with acidic composition. Quartz, K-feldspar, plagioclase, glass and lithic fragments are major constituents of them. Lithic fragments included of andesite, quartzite, dacite, and trachyte which their main minerals are K-feldspar and plagioclase (Fig 2).

The tuff units have been influenced by alteration more than the other ones. The feldspar minerals with glass matrix and the lithic components with similar mineralogy and texture have been decomposed and consequently have been altered to clay minerals. In some parts, the remnants of the parent rocks are visible among the clay deposits. The XRD analysis shows the main phases of the clay samples are quartz, kaolinite, montmorillonite and the minor phases are orthoclase, albite, muscovite, illite, chlorite, hematite, and sometimes halite (Table 1).

3. Geochemistry

The geochemistry of clay deposit and rocks has been studied, for recognizing the influence of the hydrothermal and weathering processes. The composition of altered rock and clay deposit has determined by XRF (Table 2). The SiO_2 and Al_2O_3 contents of them range from 64.39% to 74.93% and 12.15% to 22.86 % respectively. Among the other trace elements Zr (10 to 173ppm), Rb (13–128ppm), Sr (18–677ppm), Ba (189–1320ppm) show generally wide ranges of concentrations. All samples have generally low contents of Ni, Cr, Zn, Th, Y, Co and Nb. Considering the geochemical data, the amounts of Fe_2O_3, P_2O_5, TiO_2, Al_2O_3, Ni, Cr, Sr, Rb and LOI in the sample have increased by the development of alteration (Fig 3, Table 2). Al, Fe, Cr, Ni, and Ti are immobile and concentrate during the alteration processes in the deposit. Nevertheless, the alkaline elements are relatively mobile and especially the amounts of CaO, K_2O, SiO_2 and Ba in the altered samples have reduced (Fig 3, Table 2).

The study of some elements such as SO_3, P_2O_5, Zr, Cr+Nb, Ba+Sr and Ce+Y+La useful for identifying the alteration processes. The contents of SO_3 and P_2O_5 are considered as the index of the hydrothermal activities. Then, the amounts of these elements show the range of supergene and mixed type clay (Fig 4a). Because of alteration near the surface and fractures in the region,

SO_3 is released compared with hypogene conditions. In weathering process, Zr is a suitable indicator for parent rock but in hypogene conditions, it is mostly mobile (Mutakyaha et al. 2000). According to the abundance of Zr versus TiO_2 in the samples and their distribution, they plot in the range of the mixed type clay and near the hypogene clay (Fig 4b).
On the other hand, the high contents of Cr+Nb are an index of the supergene conditions of the kaolin (Dill et al. 1997; Dill et al. 2000). The samples of the Chah-Shur deposit in the diagram of Fe_2O_3+TiO_2 vs Cr+Nb are between the hypogene and the mixed type clay which is near to the hypogene clay (Fig 4c). Also the high quantities of Ba+Sr are related to the hypogene kaolin. While the amounts of Ce+Y+La from supergene deposits are higher than hypogene kaolin. Regarding the trace elements i.e. Sr+Ba against Ce+Y+La, the samples are very close to the hypogene range (Fig 5a). Moreover, in the triangular diagram of Pb, Ce+Y+La, and Ba+Sr the samples are near the Ba+Sr angle and show hypogene type (Fig 5b) (Dill et al. 1997; 2000). The enrichment of Sr and Ba in kaolin deposits could be attributed to the volcanic activity (Sayin 2007) that is supported by geological setting. The geochemical data are scattered between the field of hypogene, supergene and mixed type clay deposit.

4. Discussion

The main phases of the clay samples are quartz, kaolinite, montmorillonite (Table 1). Some samples have the remnants of K-feldspar and albite which suggest the medium degrees of alteration. Montmorillonite and albite show a moderate alteration, while kaolinite shows the advanced alteration. Probably, more concentration of Na^+ and Ca^{++} compared with K^+ and high concentrations of silica and alteration near the surface and fractures had resulted in the formation of montmorillonite (Evans 1993).
On the other hand, the higher amount of H^+, in the deeper parts, has provided a suitable condition for the formation of Kaolinite instead of montmorillonite (Pirajno 1992; Evans 1993). Both illite and Kaolinite are produced by the low temperature of argillic alteration and the intermediate weathering. Also goethite, gibbsite, smectite, vermiculite, halloisite, and illite can be formed in the supergene clay deposits (Fernández-Caliani et al. 2010). The considerable amount of phosphate, sulfide (pyrite), alunite, dickite, pyrophyllite and diaspor and lower amounts of iron oxides are common in the hydrothermal and hypogene processes (Dominguez et al. 2010; Marfil and Maiza 2012). However, supergene and weathering conditions show enrichment of iron oxides and hydroxides (Dominguez et al. 2008; Dominguez et al. 2010; Fernández-Caliani et al. 2010).

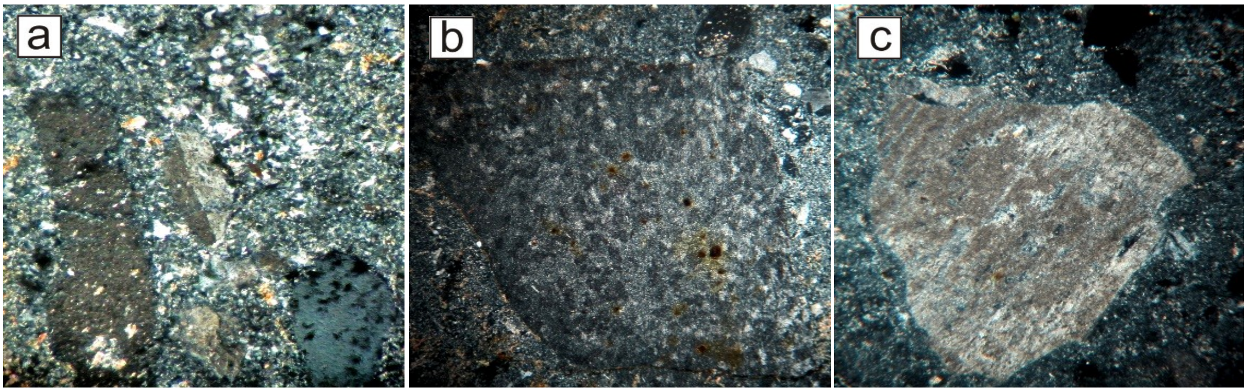

Fig 2. Photomicrographs of altered volcanic rocks a) Quartz and altered feldspar in tuff (XPL, field of view 0.97mm) b) altered matrix to clay in lithic tuff (XPL, field of view of 4.5 mm). c) Altered plagioclase phenocrystal (XPL, field of view field 4.5 mm).

Table1- Mineralogical distribution and results of XRD analysis of the altered rocks and clay deposit of the Chah-Shur (Ma: mineral phase as Major, Mi: mineral phase as Minor).

Minerals Samples	Quartz	Illite	Kaolinite	Hematite	Halite	Chlorite	Orthoclase	Albite	Muscovite	Montmorillonite
FA1	Ma						Ma	Mi		
FB2	Ma						Ma		Mi	
KA4	Ma	Ma						Mi	Ma	
KB2	Ma	Ma				Mi	Ma	Ma	Ma	Mi
KA1	Ma	Mi	Mi	Mi			Ma	Ma		Ma
KA2	Ma	Mi	Ma		Mi		Mi	Mi		Ma

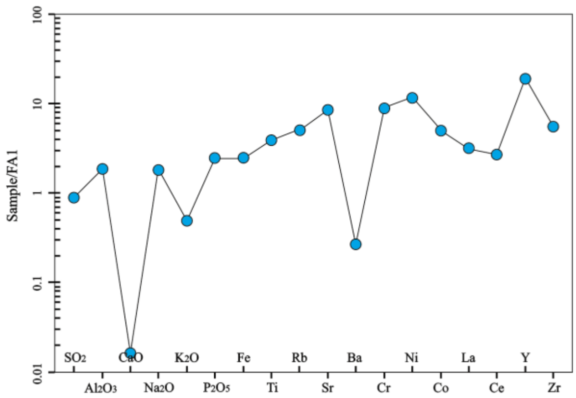

Fig 3. The multi element pattern of clay deposit (KA2), normalized with the less altered rock (FA1). The amounts of Fe_2O_3, P_2O_5, TiO_2, Al_2O_3, Ni, Cr, Sr, Rb and L.O.I. in the altered sample have increased whereas the amounts of CaO, K_2O, SiO_2, Ba, have reduced.

Table 2-Representative whole-rock major elements (wt %) and trace element (ppm) (XRF) for less altered rock (FA1), altered rocks (KA1, FB2) and clay samples (KA2, BK300, KB2, KA4) from the Chah-Shur deposit.

Sample	FA1	FB2	KA4	KB2	KA1	KA2	BK300
SiO_2	72.96	74.93	73.77	64.64	73.04	64.39	70.11
TiO_2	0.141	0.148	0.195	0.248	0.272	0.553	
Al_2O_3	12.15	13.72	15.22	18.84	15.34	22.86	15.02
$Fe_2O_3^*$	0.62	1.50	1.44	2.54	1.83	1.88	4.21
MnO	0.006	0.005	0.001	0.015	0.002	0.003	
MgO	0.01	0.14	0.36	0.85	0.30	0.65	1.54
CaO	5.54	0.16	0.18	0.13	0.20	0.09	2.34
Na_2O	0.73	0.20	1.36	1.28	3.78	1.35	1.85
K_2O	6.72	6.40	3.50	6.95	2.99	3.24	1.63
P_2O_5	0.025	0.025	0.074	0.032	0.034	0.061	
L.O.I.	0.70	1.51	2.44	3.70	1.94	4.71	4
SO_3	0.005	0.26	0.88	0.21	0.005	0.005	
Ba	716	820	350	1320	421	189	
Cl	10	280	2200	690	489	2798	
Rb	25	17	16	13	128	124	
Sr	79	18	100	48	294	677	
Zr	25	12	10	12	173	138	
Nb	9	8	5	9	4	4	
Ni	3	1	1	1	37	35	
Zn	2	5	6	7	45	86	
Cr	1	1	1	1	11	9	
Co	1	5	1	2	7	5	
La	7	4	5	7	14	22	
Ce	21	11	15	10	31	56	
Y	2	7	10	6	49	38	
Cu	21	55	300	145	21	30	
Pb	15	4	4	5	19	14	
Th	8	8	6	8	7	1	
U	6	2	4	1	1	1	
Total	99.60	98.74	98.54	99.25	99.73	99.79	100

L.O.I. = Loss on ignition; $Fe_2O_3^*$ = as Fe total

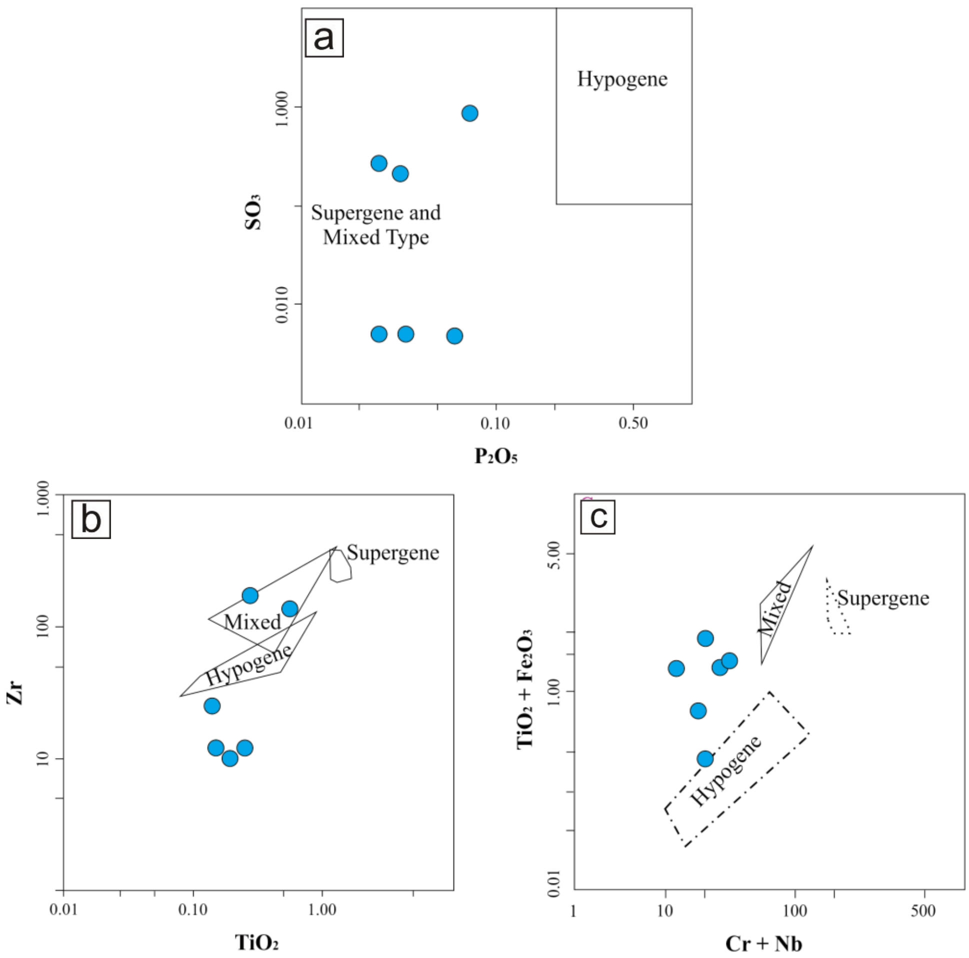

Fig 4. Discrimination diagrams between supergene, hypogene and mixed type clay deposit and the position of the samples from the studied area A) SO_3 vs P_2O_5 diagram, the samples plot in the range of supergene or mixed type clay B) Zr vs TiO_2 diagram, they plot in the range of the mixed clay and near the hypogene clay C) TiO_2+Fe_2O_3 vs Cr+Nb diagram, the samples plot between the hypogene and the mixed type clay which is near to the hypogene clay (Dill et al.1997; Dill et al.2000).

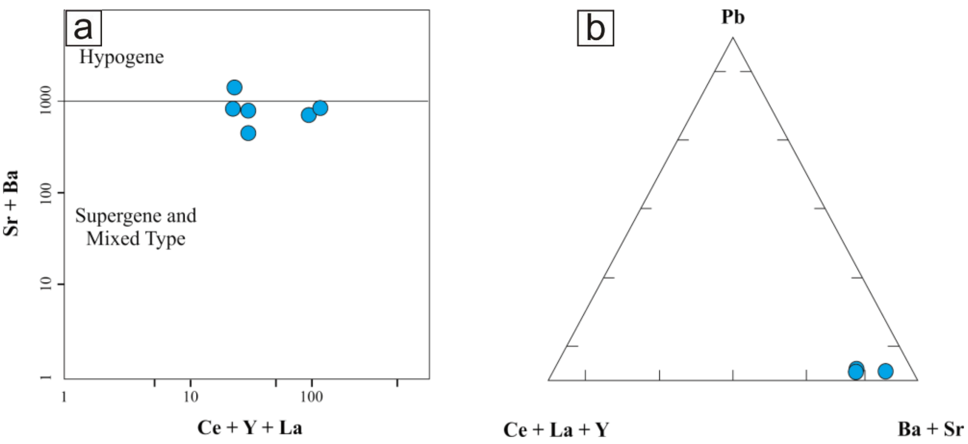

Fig 5. a) Sr+Ba vs Ce+Y+La diagram, the samples plot near the boundary between field of supergene and mixed type clay deposit and hypogene type b) Triangular diagram of Pb, Ce+Y, Ba+Sr, the samples are near the Ba+Sr angle showing hypogene type (Dill et al.1997; Dill et al.2000).

Among above minerals, Kaolinite, illite and hematite are seen in deposit (Table 1). The mineralogical characterization of the Chah-Shur deposit is not sufficient for determining the main source of clay and only suggests the mixed origin and intermediate degree of alteration. On the other hand, the mineralogy of the parent rock as well as alteration processes play significant role on the geochemistry of clay deposits. The plagioclase and K-feldspar are the main minerals in the parent rock in the Chah-Shur deposit. According to the content of sodium or calcium in plagioclase, a high degree of variation of these two elements can be seen in the final products. Generally, calcium-plagioclases are weak during hydrothermal alteration and commonly are altered to illite and calcite (Marfil and Maiza 2012). The depletion of Ca and K are related to the alteration of the plagioclase and K-feldspar, respectively (Nyakairu et al. 2001; Fernández-Caliani et al. 2010).

The lack of Na depletion in the deposit shows the intermediate alteration and less leaching of Na. On the other hand, according to petrography, the abundance of Na-plagioclase is more than the other feldspars in the Chah-Shur deposit. Some elements such as Ca, K, and Na are leached during the supergene processes and weathering and, therefore, the intensity of the weathering are determined by the amount of the above mentioned elements in the remaining materials (e.g. Nyakairu et al. 2001; Fernández-Caliani et al. 2010). When the fluids circulate between the acidic pyroclastic rocks, alkaline and alkaline earth elements are leached. SiO_2 is more mobile in the intensive alkaline conditions. But Al is an immobile element and moves only in the very acidic or very alkaline conditions. The percent of Al_2O_3 and LOI have increased by the intensity of alteration and also in alkaline situations (Dominguez et al. 2008; Ece et al. 2008; Dominguez et al. 2010). The enrichment of TiO_2 and Al_2O_3 in hydrothermal deposits shows the argillic alteration or the leaching of alkalis (Dill et al. 2000; Najoya et al. 2006).

The amounts of CaO, K_2O, SiO_2 and Ba in the Chah-Shur clay deposit have depleted, but the increase in other elements is not noticeable, showing medium degree of alteration. The investigations on the geochemistry of the weathering process indicate that Na, K, Ca are leaching whereas Al is immobile (Dill et al. 2000; Najoya et al. 2006). Chemical index of alteration CIA (CIA= $[Al_2O_3/ (Al_2O_3 + CaO + Na_2O + K_2O)] \times 100$; Nesbitt and Young, 1982) is used for the determination of the intensity of weathering that is the chemical practical index of the intensity of weathering. CIA in kaolinization parts of the region is between 67%-83%. Some researchers believe that it is 85% to 100% for residual clays (e.g. Taylor and McLennan 1985; Fernández-Caliani et al. 2010; Ghadimian and Khodami 2015). Also relatively low CIA represents the less influence of the supergene than the hypogene processes in the formation of the studied clay deposit. The enrichment of P_2O_5, Sr, Pb, V, Mo, Gd, Sb, W, V, Ba, and S occurs in the hydrothermal deposits, whereas in the weathering activities Fe_2O_3, Ce, Y, La, Rb, V, Zr, Cr, Ni and Ti would increase in the final products (Dominguez 2010). Moreover, the enrichment of Sr and Ba in kaolin deposits indicates the volcanic activities (Sayin 2007) and the amount of these elements varies with the intensity of alteration (Cravero et al. 2010). Due to the fact that Sr is concentrated in Ca-plagioclase and Ba is concentrated in K-feldspar, the proportion of these two elements in the kaolin deposit is dependent on the proportion of them in the source rock. The combination of these items is useful to determine the genesis of clay deposits (Dill et al. 1997; Dill et al. 2000). The variation diagrams show scattering between hypogene and supergene origin for the Chah-Shur deposit. Therefore, the pyroclastic rocks of the region have been altered in situ to clay deposit and then kaolinization has occurred by the hydrothermal fluids and finally has followed with the weathering processes. All evidences such as remains of K-feldspar and plagioclase and occurrence of kaolinite accompanied by illite in the deposit as well as the lack of Na depletion show an intermediate alteration.

5. Analytical methods

After gathering the basic information about the region, the rock samples were collected from the volcanic rocks and clay in the studied area. The mineralogy and textures of selected samples were investigated by microscopic studies of thin-sections and X-ray diffraction technique (XRD). The samples were selected for whole-rock major and trace element analysis too. The chemical compositions of samples were measured by X-ray fluorescence spectrometer (XRF), using the standard-pellet technique. The samples were crushed in a tungsten carbide swing mill and analyzed for major and trace elements by XRF (Philips PW2400, equipped with a Rh-tube, using fused borate glass beads) at the Binalood Kansaran laboratory, Iran.

6. Conclusion

Based on the results and the discussion presented above the following conclusions for the genesis of the Chah-Shur clay deposits might be outlined:

1) The clay deposit of the region has been produced by the alteration of the Eocene vitric and lithic tuffs with acidic composition. The feldspars and glass in matrix of the volcanic rocks have been altered to clay minerals.

2) Considering the results of XRD, the clay deposit has the main phases of quartz, kaolinite, montmorillonite, orthoclase, illite, albite and also some minor phases including chlorite and hematite. Some samples with higher percentage of alteration have more kaolinite. The minerals, which form in high temperatures of alteration, such as dickite, pyrophylite, and diaspor are not observed in the deposit, which means the lower temperature for its formation. Therefore, we suggest that

the hydrothermal fluids have combined with meteoric fluids during the alteration.

3) The amounts of Fe_2O_3, P_2O_5, TiO_2, Al_2O_3, Ni, Cr, Sr, Rb and LOI in the deposit have increased whereas CaO, K_2O, SiO_2, Ba have reduced by the development of alteration, these results as well as the lack of Na depletion show an intermediate alteration.

4) The quantity of P_2O_5, SO_3 show mixed or supergene genesis. This is probably due to the formation of clay deposit near the surface and fractures.

5) Regarding the abundance of TiO_2 and Zr and the amount of Fe_2O_3+TiO_2 versus Nb+Cr, the samples are in the range of the mixed type clay deposits and hypogene.

6) The clay deposit of the Chah-Shur in the triangular chart of Pb, Ba+Sr, and Ce+Y+La has more amounts of Ba+Sr, which show the hypogene genesis.

7) According to the results of mineralogy and geochemistry, the genesis of the Chah-Shur clay deposit can be considered as mixed type. The hydrothermal and meteoric fluids have mixed and formed kaolinite deposit. These fluids have effective role in the formation of the Chah-Shur clay deposit. Finally, the weathering processes have continued and extended the kaolinization.

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