Geochemistry and genesis of Mehredjan bentonite deposit, southeast of Khoor, Isfehan province

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Abstract

Mehredjan bentonite deposit is located ~33 km southeast of Khoor in Isfehan province. It includes 15 discrete outcrops and occurs as layered and massive forms within a volcano-clastic sequence. Bentonitization process was accompanied with development of minerals such as montmorillonite, quartz, cristobalite, calcite, kaolinite, halite, albite, orthoclase, and muscovite. The collected field and laboratory data indicate that this deposit was developed by authigenic alteration of tuffs ranging in composition from trachyandesite, through andesite to basaltic andesite in a shallow marine environment. The distribution patterns of REEs normalized to chondrite in both bentonite and enclosing tuffs illustrate similar trend indicating the fractionation and enrichment of LREEs relative to HREEs and negative anomalies for Eu. Geochemical data revealed that transformation of tuffs into bentonite took place in an open system where leaching and fixation processes were two basic regulating factors in concentrating of common trace and rare earth elements. By pointing to the obtained results, factors such as differences of alteration intensity of protolith, physico-chemical conditions of alteration environment, adsorbing mechanism, structural incorporation, existing of organic matters, effects of diagenesis, carbonate complexation, ionic exchange, physical concentrations, and existing of resistant minerals played important roles in development of Mehredjan bentonite. Further geochemical considerations unveiled that relatively humid environmental conditions brought about residual concentration of elements such as Al, Nb, Zr, Hf, Sc, and Th in Mehredjan bentonite.

Keywords: *Mehredjan; Isfehan; Bentonite; Alteration; Tuffs; Residual concentration; Structural incorporation*

Introduction

Mehredjan area is located in ~33 km southeast of Khoor, Isfehan province, and extends from 55◦, 06' to 55◦, 10' east longitude and from 33◦, 34', 30" to 33◦, 37' north latitude. Eocene tuffs in this area includes the nation's largest reserves of bentonite deposits. Little geological works were done on Mehredjan bentonite. The early geological studies in the area were done by Ghorbani (1991) and Hejazi and Ghorbani (1994). Akbari (2007) investigated the geology and factors controlling the distribution of elements during bentonitization. The behavior of elements during bentonitization was presented in preliminary form in Akbari *et al*. (2007).

Recently, detailed investigations have been carried out worldwide concerning genesis and behavior of major, minor, and particularly rare earth elements on bentonite deposits by many workers (Spears *et al*., 1999; Christidis, 2001; Berkley & Baird, 2002; Pellenard *et al*., 2003; Muchangos, 2006; Foreman *et al*., 2007; Savage *et al*., 2007; Huff, 2008; Kolarikova & Hanus, 2008; Hints *et al*., 2008). The present study, however, provides considerably comprehensive data regarding mineralogy, setting, controlling factors in distribution of elements during bentonitization, minerals hosting REEs, and conceivable genesis of Mehredjan bentonite deposit.

Method of investigation

The study of bentonite ores at Mehredjan were fulfilled in two parts, (1) field and (2) laboratory. A large portion of field works were allocated to determine the various lithological units, the form of deposit and its relation to enclosing rocks, and some macroscopic characteristics of various types of bentonite ores across the profiles. About 60 samples were taken from bentonitic and enclosing rocks. Sampling from bentonitic rocks was carried out on the basis of color, density, degree of induration, and texture.

The lab works include petrographical examinations of 10 thin-polished sections, identification of minerals in 9 samples employing X-ray diffraction

(XRD) technique at Kansaran-Binalud Mining Company. Both bentonite and its enclosing rocks (12 samples) were chemically analyzed applying both XRF (for major and minor elements) and ICP-

MS (for trace and rare earth elements) techniques in Amdel company, Australia (Table 1).

Table1. Chemical compositions of bentonites and parent tuffaceous rocks from Mehredjan analyzed by XRF and ICP-MS methods.

Sample No	Tuff	Tuff	Tuff	B-1	B-2	B-3	B-4	B-5	B-6	B-7	B-8	B-9
SiO_2 (Wt%)	66.40	66.61	67.55	66.83	60.99	62.58	63.98	58.19	56.72	58.49	65.36	48.67
Al_2O_3	9.88	11.04	11.73	11.69	10.78	18.35	12.67	18.64	15.53	21.43	14.74	15.60
Fe_2O_3	2.00	1.98	1.85	2.11	1.41	2.49	2.15	3.58	4.59	2.35	2.41	4.36
CaO	8.87	4.54	3.38	3.98	8.95	0.94	5.60	2.86	2.88	0.50	0.26	9.48
Na_2O	0.08	0.06	0.09	0.21	0.22	0.26	0.17	0.49	0.51	0.16	0.20	0.22
MgO	1.42	0.82	0.89	1.87	0.98	3.06	2.12	2.40	2.06	2.26	1.77	1.37
K_2O	2.90	5.25	5.21	1.43	1.83	0.41	0.94	0.10	1.49	1.99	0.71	1.90
TiO_2	0.1	0.08	0.07	0.17	0.3	0.11	0.17	0.39	0.61	0.12	0.14	0.68
MnO	0.03	0.01	0.01	0.10	0.22	0.01	0.10	0.02	0.03	0.01	0.00	0.08
P_2O_5	0.06	0.02	0.02	0.14	0.10	0.04	0.21	0.16	0.19	0.02	0.03	0.16
Sr	0.02	0.02	0.02	0.02	0.03	0.02	0.02	0.05	0.05	0.02	0.00	0.01
L.O.I	7.84	9.40	8.74	11.40	14.23	11.58	11.8	14.06	15.14	12.56	14.26	17.5
Sum	99.6	99.83	99.56	99.95	100.04	99.85	99.93	99.94	99.8	99.91	99.88	100.03
U (ppm)	1.58	1.33	1.36	3.06	3.32	4.50	4.22	1.19	1.56	1.30	2.06	1.11
Th	4.61	5.6	5.91	5.48	5.31	6.13	5.46	5.81	6.09	5.62	5.83	5.0
Ba	161	120	129	313	379	62.2	164	220	290	55.6	88.1	96.5
Cu	22	43.8	36.2	6.1	9.9	86.2	7.3	30.6	28.5	22.4	37.8	19.1
Hf	1.7	2.0	1.9	2.1	1.6	2.4	1.7	2.9	3.9	2.7	1.9	3.0
Co	21.2	7.1	7.4	6.2	2.2	3.5	4.5	10.4	10.1	9.3	5.1	6.9
Cr	21	12	11	6	10	2	6	3	2	3	5	10
Zn	27.5	3.06	29.3	29.1	21.0	49.7	34.0	42.4	42.8	77.3	88.1	40.7
Nb	7.9	8.1	7.8	8.6	8.9	8.3	8.7	8.4	9.6	8.2	8.2	9.4
Cs	14.4	13.9	13.4	8.7	6.5	6.8	8.1	8.0	10.9	11.1	32.0	14.6
Rb	137	14.6	120	79.7	89.3	23.2	76.1	40.1	43.1	36.7	42.5	45.5
V	68	65	59	21	28	19	26	50	74	52	33	65
Y	8.5	8.26	8.9	12.7	15.9	10.2	13.1	13.59	23.2	8.18	8.45	19.7
Pb	16.4	5.1	12.5	10.5	18	8.1	18.8	10.2	14.6	20.5	5.6	28
Be	8.9	10.7	11.1	9.2	7.4	11.7	9.5	3.2	5.3	5	9.3	5.5
Sc	4	4	3	4	4	3	5	5	10	3	5	5
Zr	37	45	47	74	75	49	72	79	142	51	47	110
Ni	29	13	12	7	7	11	11	12	8	34	24	11
La (ppm)	19	14	15	15	15	13	14	19	24	13	13	17
Ce	37.2	27.4	28.9	32.4	31.0	29.6	28.9	39.9	50.2	27.9	26.9	36.5
Pr	4.6	3.63	3.71	4.01	4.06	3.79	3.71	4.90	6.31	3.68	3.54	4.92
Nd	19.5	15	15.3	17.4	17.5	15.5	16.1	20.9	28.7	15.2	14.6	22.1
Sm	3.68	3.3	3.06	3.59	3.78	3.33	3.60	3.77	6.09	3.23	2.96	4.59
Eu	0.68	0.51	0.53	0.71	0.76	0.58	0.66	0.91	1.10	0.54	0.53	1.06
Gd	2.59	2.06	2.10	2.53	2.81	2.17	2.72	2.39	4.73	2.15	1.83	3.59
Tb	0.39	0.44	0.36	0.43	0.45	0.37	0.46	0.36	0.76	0.36	0.30	0.55
Dy	2.36	3.08	2.22	2.66	2.88	2.17	2.90	2.12	4.67	2.16	1.70	3.34
Ho	0.47	0.61	0.45	0.53	0.58	0.42	0.58	0.40	0.96	0.41	0.33	0.66
Er	1.42	1.62	1.34	1.56	1.73	1.17	1.67	1.09	2.75	1.11	0.92	1.86
Tm	0.22	0.29	0.21	0.24	0.26	0.18	0.25	0.16	0.41	0.17	0.14	0.27
Yb	1.43	1.22	2.37	1.53	1.67	1.14	1.57	0.99	2.53	1.07	0.88	1.63
Lu	0.23	0.29	0.21	0.24	0.26	0.17	0.24	0.15	0.43	0.16	0.14	0.25

Discussion

Geology

The most conspicuous lithological units at Mehredjan, from oldest to the youngest, include formations such as Chahpalang (e.g., shale,

sandstone) of Jurassic, Shahkuh (limestone) of Cretaceous, Biabanak (e.g., limestone, slate) of Cretaceous, Mirza (s e.g., hale, limestone, sandstone) of Cretaceous, Darrehanjir (e.g., sandstone, conglomerate, limestone, mudstone) of

Eocene, volcano-sedimentary (e.g., tuff, mudstone, tuffaceous sandstone and tuffaceous conglomerate, dacite, andesite, basalt, trachyandesite) of Eocene, Upper-Red (e.g., claystone, sandstone, gypsiferous marl, conglomerate) of Miocene, and alluvial terraces of Quaternary ages (Fig.1). Lithostratigraphically, the bentonite ores have 15 discrete outcrops in the area (Fig.1), and occur as massive and layered bodies with various colors (e.g., green, white, yellow, cream, light green, pinkish gray, whitish gray, pink, and greenish white) principally in tuffaceous and arenaceous members and to a lesser extent in the mudstone members of

Eocene series .

Variations of strikes and dips of bentonite horizon (due to local folding and faulting), greasy touch and adhesive property of green bentonites, low induration of most bentonite ores, orderly alternate of bentonite layers with light to gray tuffaceous units, presence of dark grains of chert in yellow bentonite, conchoidal fracture surfaces in white bentonite, and the presence of diabasic dikes above bentonite layers are the noticeable morphological aspects at Mehredjan.
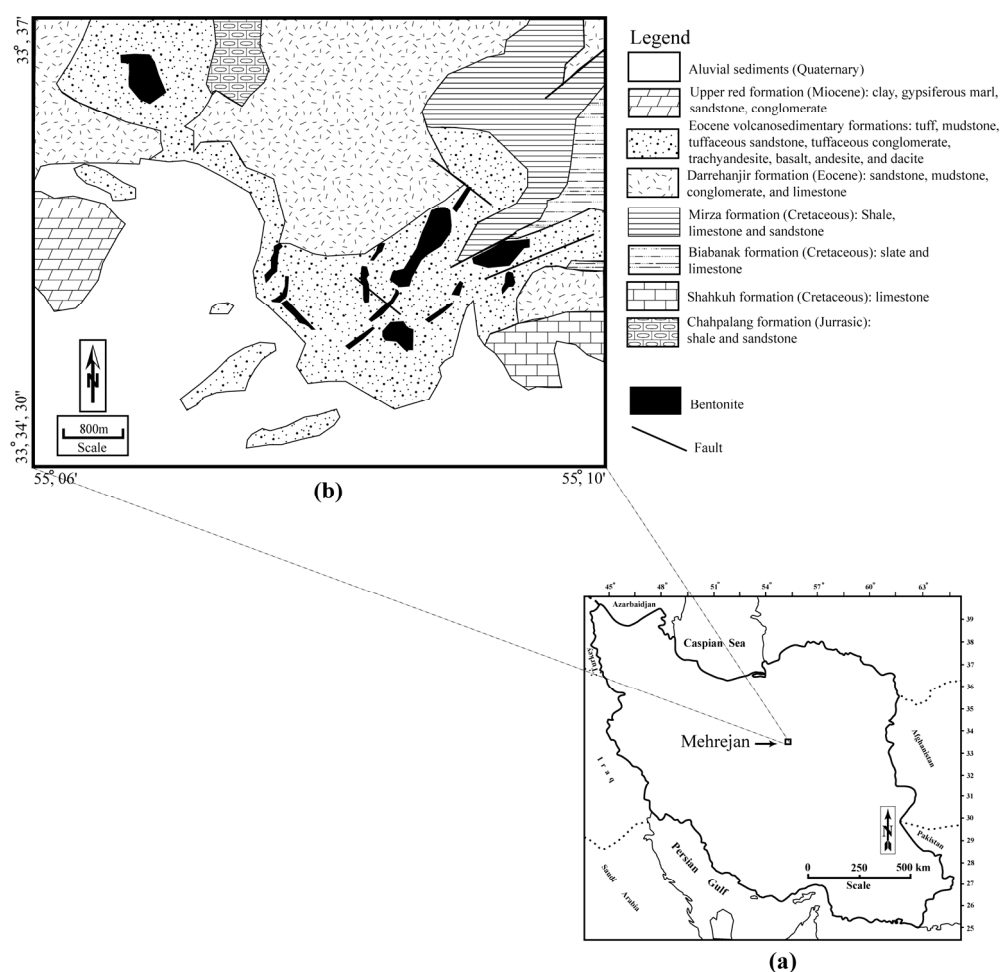

Figure 1: (a) Index map of Iran showing the location of study area. (b) A geologic map illustrating the position of bentonitic materials at Mehredjan.

Mineralogy

Petrographical examinations showed that the dominant mineral paragenesis in tuffs at Mehredjan area include plagioclase, quartz, pyroxene, muscovite, and tremolite accompanied, in some samples, by minor amounts of biotite, zeolite, chalcedony, and glass. Plagioclase occurs as

shattered fragments with polysynthetic twins (Fig.2a). Quartz is present as fine to medium-grained subhedral to euhedral phenocryst and microcryst with undulose extinction within the matrix. Muscovite occurs as fine flakes within glassy matrix (Fig.2b). Pyroxene is intensely chloritized. The XRD data, however, revealed that

Mehredjan bentonite includes minerals such as Ca-smectite (montmorllonite), quartz, albite, cristobalite, calcite, kaolinite, muscovite, halite, and orthoclase (Fig.1). Among these montmorillonite and quartz have harmonious distribution and are present in almost all types of bentonites.
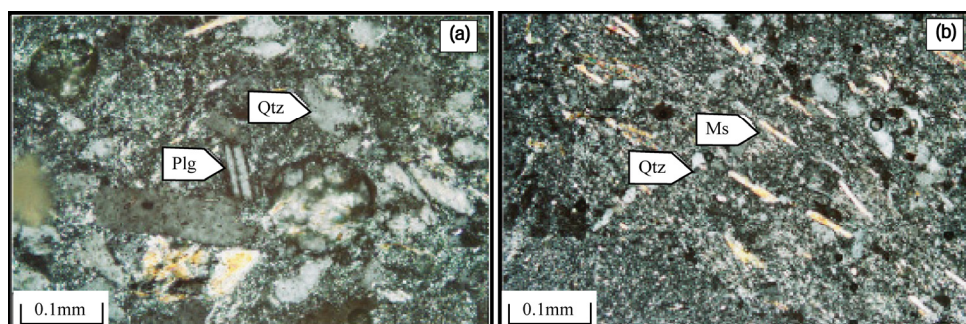

Figure 2. Photomicrographs of tuffs. (a) Quatz and Plagioclse with polysynthetic twins. (b) Fine oriented flakes of muscovite within a glassy matrix. Mus= Muscovite, and Qtz=Quartz.
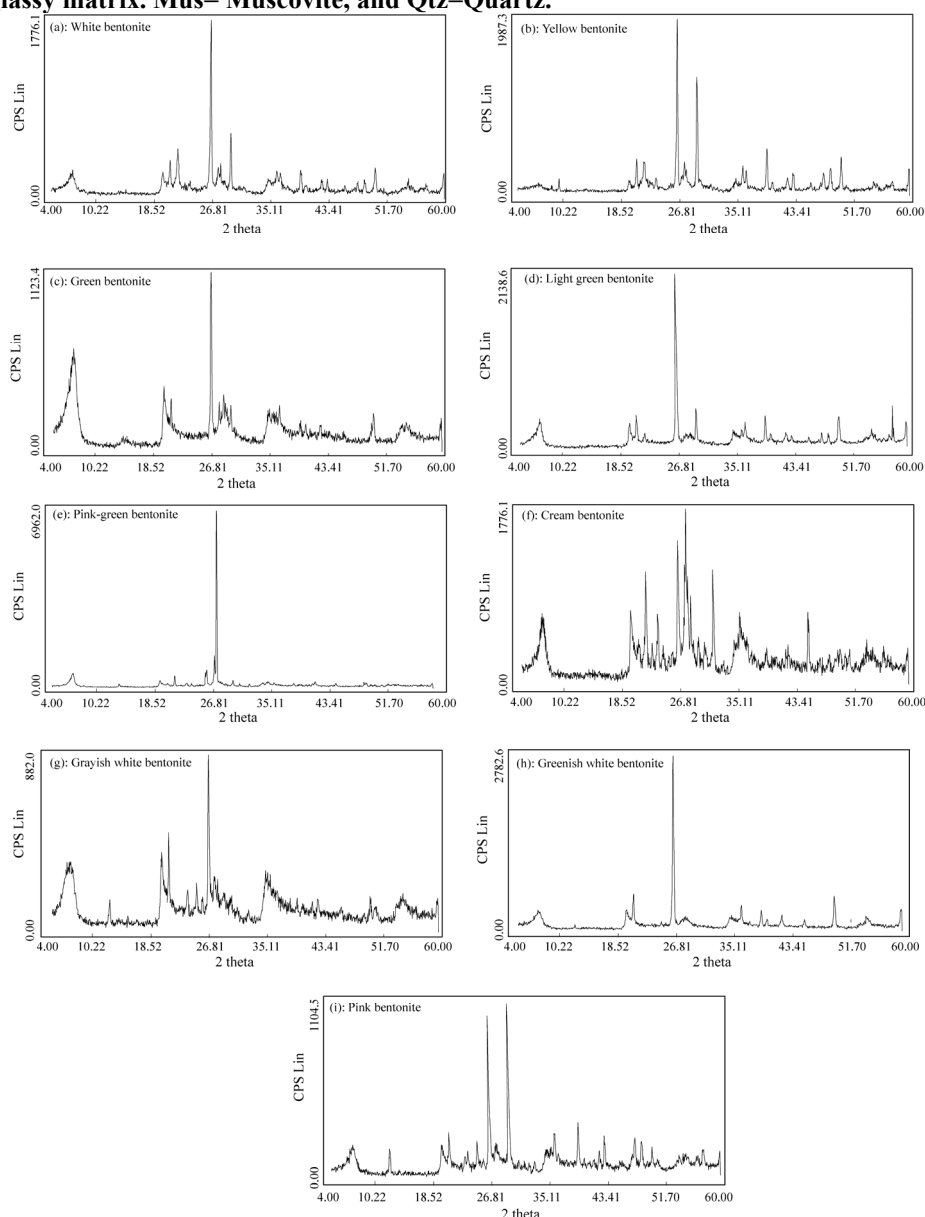

Figure 3: XRD patterns of bentonite samples: (a) White bentonite (montmorillonite, quartz, crystobalite, calcite, and albite); (b) Yellow bentonite (montmorillonite, quartz, crystobalite, calcite, albite, and muscovite); (c) Green bentonite (montmorillonite, quartz, calcite, and albite); (d) Light green bentonite (montmorillonite,

quartz, crystobalite, calcite, and albite); (e) Pink-green bentonite (montmorillonite, albite, and quartz); (f) Cream bentonite (montmorillonite, albite, quartz, and halite); (g) Grayish white bentonite (montmorillonite, quartz, kaolinite, albite, and orthoclase); (h) Greenish white bentonite (montmorillonite, quartz, and kaolinite); (i) Pink bentonite (montmorillonite, quartz, calcite, albite, and kaolinite).

Protolith, tectonic setting, and composition of the original magma

Diagrams of minor, trace, and rare earth elements which are normally used for determination of original magmas and their tectonic settings for igneous rocks can be correspondingly applied for bentonite ores (Huff & Morgan, 1990; Huff *et al.*, 1991; Spears *et al.*, 1999; Yalcin & Gumuser, 2000). Selective application of immobile elements such as Nb, Zr, Y, and Ti in these kinds of diagrams minimizes the error resulting from elemental depletion during alteration of tuffs and their conversion into bentonite. Calculation of correlation coefficients among elements and bivariate plots (Fig.4) show that there are high positive correlations among elements (R= 0.87-0.97). In better words, the elemental ratios remained almost constant during the conversion of the original materials (tuffs) into bentonite and also the elements behaved similarly. The line of alteration trend for bentonite ores depicts that the data points of the enclosing tuffs rest either on or close to this line (Fig.4).
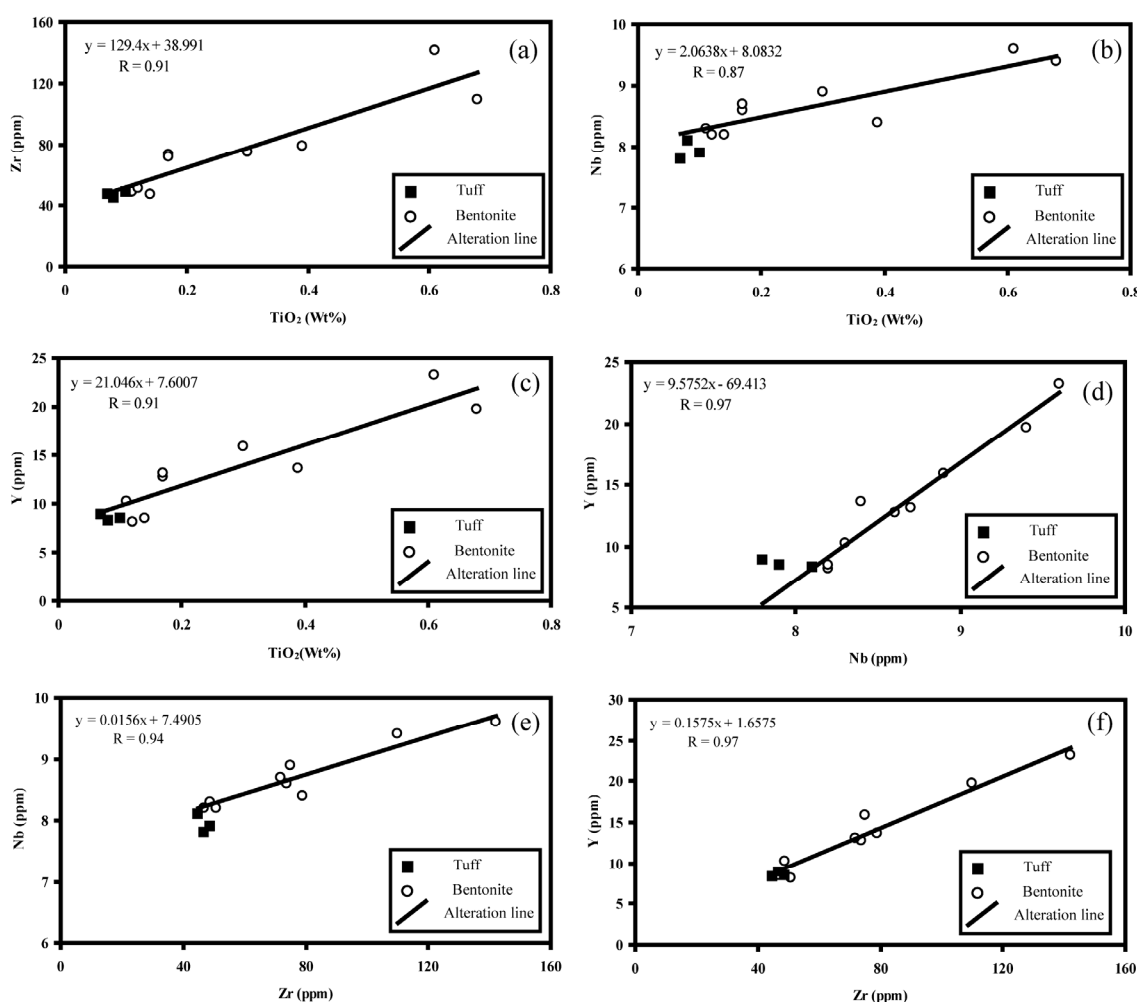

Figure 4: Diagrams featuring the positive correlations between (a) (a) Zr–TiO$_2$, (b) Nb–TiO$_2$, (c) Y-TiO$_2$, (d) Nb-Y, (e) Zr-Nb, and (f) Y-Zr for bentonite and tuff samples. The tuff data points lie on and close to the so called alteration line.

According to MacLean and Kranidiotis (1987) this type of behavioral pattern ascertains the intimate genetic relation between bentonite and tuffs (as protolith). Since the elemental ratios among Nb, Zr, Y, and Ti remain almost constant, the bivariate plot of (Zr/Ti)-(Nb/Y) (Winchester & Floyed, 1977) was

applied for determination of protolith for Mehredjan bentonite. This bivariate plot revealed that the original magma, from which the Mehredjan bentonite was derived, might have had a composition within the range of trachyandesite through andesite to basaltic andesite (Fig.5).
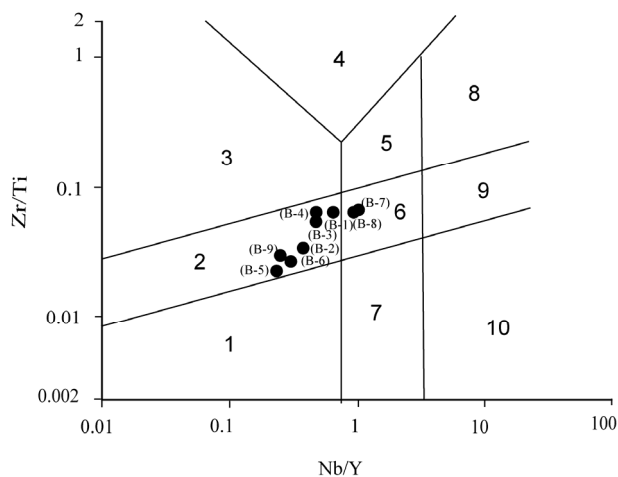

Figure 5: Representation of data points of Mehredjan bentonite on (Zr/Ti)-(Nb/Y) bivariate plot (proposed by Winchester and Floyd, 1977). Key to the numbers: 1 = basalt, 2 = andesite / basaltic andesite, 3 = rhyolite/ dacite, 4 = alkali rhyolite, 5 = trachyte, 6 = trachyandesite, 7 = alkali basalt, 8 = phonolite, 9 = tephri-phonolite, 10 = foidite.

The distribution of REEs normalized to chondrite (Boynton, 1984) in tuffs and bentonite ores shows similar patterns (Fig.6).
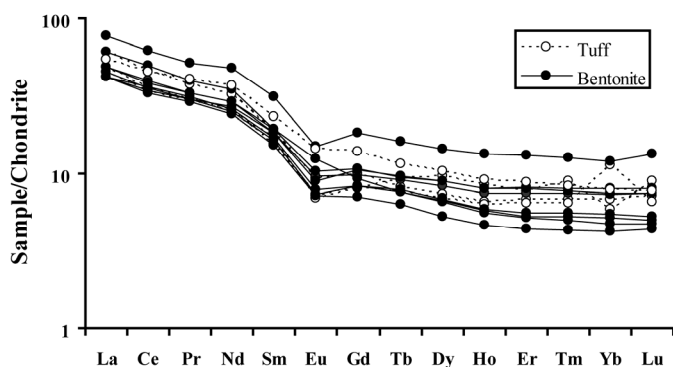

Figure 6. Chondrite-normalized concentrations of REEs in bentonites and tuffs from Mehredjan. The chondrite values are from Boynton (1984).

In both types of rocks, LREEs relative to HREEs fractionated markedly and became more enriched. These characteristics are peculiar to bentonite ores and are also reported for bentonite deposits in south England, Wales, and United Kingdom (Huff and Morgan, 1990; Huff *et al.*, 1993). The relative

enrichment of LREEs relative to HREEs coupled with negative anomaly of Eu are related to calc-alkaline magmas that erupted in plate margin subduction zones or collision environments (Spear *et al.*, 1999). Therefore, such tectonic environments can be also envisaged for original magma in Mehredjan bentonite.

Behavior of elements during bentonitization

In this study, for consideration of, attempt was made to normalize the elements in bentonite to the corresponding values in tuffs (Element$_{(bentonite)}$/Element$_{(tuff)}$). The values >1 is indicative of fixation and <1 of leaching. In general, the behaviors of three separate groups of elements were considered during bentonitization: (1) major and minor elements; (2) trace elements; and (3) rare earth elements (REEs).

Major and minor elements: By noting to the concentration variations of constituent oxides in bentonites and tuffs, elements such as Mg, Na, and Al experienced mass increase while Si and K were leached out of the system and became depleted. On the other hand, elements such as Ca, Mn, Fe, Ti, and P underwent both leaching and fixation processes during alteration of tuffs (Fig.7). The relative mass increase of Al may be due to the conversion of volcanic glasses into clay minerals (Broxton *et al.*, 1987; Altaner & Grim, 1990). The mass gain of Mg is likely owing to the development of diagenetic minerals (e.g., smectite). The enrichment of Na is probably due to either its presence in interlayer positions in montmorillonite crystal structure or its substitution for dissolved calcium (Muchangos, 2006). Depletion of K and Si can be attributed either to the alteration of feldspars and their entering into altering solutions within water-rock reaction system (Munch *et al.*, 1996). Enrichment and depletion of Ca, Mn, Fe, Ti, and P in general, may indicate the openness of the alteration system and/or probably differences in alteration intensity in tuffs (Munch *et al.*, 1996). Fe was likely fixed either in clay minerals by structural incorporation or by secondary oxides and hydroxides (Zielinski, 1982; Christidis, 1998; Muchangos, 2006). The enrichment of Ti in most samples can be due either to its entering into crystal lattice of clay minerals or to the existing of negligible amounts of heavy minerals in bentonite ores (Zielinski, 1982; Christidis, 1998). Depletion of Ca in most samples is because of its high solubility

in alteration environment. Its enrichment in some samples, however, may be due either to its emplacement in interlayer positions in crystal lattice of clays or to the formation of calcite (Vogt and Kostner, 1978; Christidis, 1998). Analogous to Na, the enrichment of Mn is likely owing either to its presence in interlayer position in montmorillonite crystal structure or to its substitution for dissolved Ca (Muchangos, 2006). Depletion of Mn in some samples, however, may be related to alteration of ferromagnesian minerals (e.g., pyroxene) within water-rock reaction system. Enrichment of P may be because of the existing negligible amounts of phosphate minerals in bentonite ores. In general, it appears that the enrichment of major and minor elements in bentonite samples was likely controlled by factors such as structural incorporation, ionic exchange, adsorption mechanism, and physical concentration in insoluble residual phases.
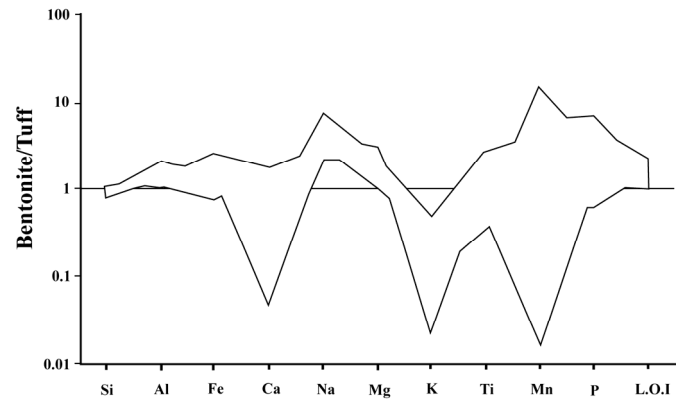

Figure 7: Major and minor element concentrations in bentonite samples normalized to that of mean value of tuffs. All bentonite samples plot in the shaded area.

Trace elements: In this study, four separate groups of trace elements were considered for their behavioral characteristics and distributions in bentonites (Fig. 8).
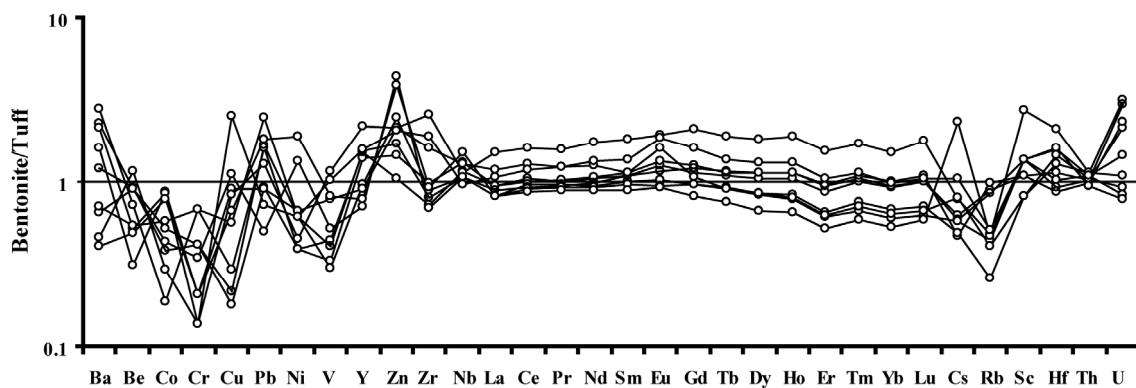

Figure 8: Relative enrichment and depletion of selected trace elements and REEs during bentonitization.

The first group belongs to elements such as Co, Ba, Rb, and Cs which chiefly suffered depletion during alteration of tuffs. Particularly, the intensity of their leaching is very analogous to that of K. The depletion of these elements was accompanied with enrichment of Zr and Nb. This is because Zr and Nb are almost immobile and were enriched in alteration products (Christidis, 1998). After breaking down of alkali-feldspars, Ba, Rb, and Cs moved out of the system. The second group elements are Zn, Pb, Sc, and U which were enriched relative to tuffs. Analogous to major elements, fixation of Zn can be attributed to structural incorporation in clay minerals (Vogt & Kostner, 1978; Muchangos, 2006). The third group of elements are Cr, V, and Be featuring inconsistent behavior during alteration.

The fourth group is related to elements such as Hf, Zr, Th, and Nb which are relatively immobile and have similar behavior with Al during bentonitization (Fig.8). The mode of distribution of these elements, in general, suggests that relatively humid environmental conditions allowed this group of elements to be concentrated in residual form.

Rare earth elements: The behavior of REEs is a function of protolith characteristics and physico-chemical conditions of alteration environment in the course of bentonitization of tuffs (Ronov *et al.*, 1967; Nesbitt, 1979; Muchangos, 2006). It can be deduced from REEs and Y values that there is a preferential enrichment of LREEs while little mobility is observed in HREEs in most samples (Figs.6, 8). This might be happened under alkaline

conditions which the stability of HREEs complexes was higher than that of LREEs. Therefore, fractionation among REEs occurred (Ronov *et al*., 1967; Muchangos, 2006) which led to preferential enrichment of LREEs. The mobility of REEs in some samples took place probably owing to complexation of leached elements. Complexes that might be active in alkaline pH conditions are carbonates (Cantrell & Byrne, 1987; Wood, 1990a, 1990b). However, complexes of chloride (Brookins, 1989; Wood, 1990a) sulfide (Brookins, 1989; Wood, 1990b) and particularly fluoride (Wood, 1990b) may be important in low pH alteration systems, but they did not seemingly play a significant role under physico-chemical conditions being prevailed during bentonitization at Mehredjan.

Host minerals for REEs

Many groups of minerals were introduced as host minerals for REEs in alteration products. The most important ones are clays (Duddy, 1980; Condie, 1991), secondary phosphates like apatite (Nyakairu et al., 2001; Kanazawa and Kamitani, 2006; Roy and Smykatz-Kloss, 2007), manganese oxides and hydroxides (Koppi *et al*., 1996), and iron oxides and hydroxides (De Carlo *et al*., 1998; Bau, 1999; Ohta & Kawabe, 2001; Pokrovsky *et al*., 2006). Normally mineral phases identified by XRD technique have abundances >4%. Therefore, there is a possibility that many mineral phases with abundances <4% in bentonite, were not identified by this technique. In this study, for determination of potential host minerals for REEs it was attempted to calculate the Spearman correlation coefficients between different elements with REEs (Table 2).

Table 2: Spearman's correlation coefficients of major, trace and rare earth elements for Mehredjan bentonites.

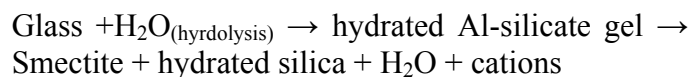|	Si	Al	Ti	Mn	Fe	P	Th	Y	Zr	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Si	1.00																						
Al	-0.52	1.00																					
Ti	-0.65	-0.16	1.00																				
Mn	0.02	-0.70	0.49	1.00																			
Fe	-0.71	0.34	0.90	-0.37	1.00																		
P	-0.28	-0.25	0.69	0.56	0.37	1.00																	
Th	0.12	0.40	-0.44	-0.71	0.12	-0.24	1.00																
Y	-0.62	-0.27	0.91	0.58	0.43	0.75	-0.30	1.00															
Zr	-0.72	-0.05	0.93	0.52	0.37	0.68	-0.32	0.92	1.00														
La	-0.60	-0.09	0.92	0.46	0.78	0.72	-0.19	0.89	0.96	1.00													
Ce	-0.60	0.03	0.79	0.38	0.81	0.63	-0.03	0.83	0.92	0.94	1.00												
Pr	-0.70	-0.02	0.85	0.44	0.84	0.61	-0.15	0.92	0.95	0.93	0.97	1.00											
Nd	-0.68	-0.08	0.91	0.52	0.83	0.71	-0.25	0.95	0.98	0.96	0.95	0.98	1.00										
Sm	-0.68	-0.18	0.90	0.61	0.76	0.74	-0.33	0.98	0.95	0.89	0.85	0.93	0.97	1.00									
Eu	-0.68	-0.08	0.91	0.52	0.76	0.71	-0.25	0.95	0.98	0.96	0.95	0.98	0.99	0.97	1.00								
Gd	-0.52	-0.37	0.81	0.72	0.70	0.75	-0.42	0.93	0.87	0.78	0.73	0.83	0.88	0.95	0.88	1.00							
Tb	-0.43	-0.34	0.65	0.66	0.64	0.74	-0.36	0.81	0.72	0.61	0.59	0.69	0.74	0.84	0.74	0.95	1.00						
Dy	-0.42	-0.33	0.60	0.65	0.58	0.69	-0.37	0.77	0.68	0.55	0.53	0.65	0.70	0.80	0.70	0.93	0.99	1.00					
Ho	-0.44	-0.35	0.62	0.66	0.56	0.65	-0.38	0.79	0.70	0.57	0.55	0.68	0.72	0.82	0.72	0.95	0.99	0.99	1.00				
Er	-0.45	-0.37	0.63	0.67	0.50	0.60	-0.38	0.80	0.72	0.58	0.57	0.70	0.73	0.83	0.73	0.95	0.98	0.98	0.99	1.00			
Tm	-0.45	-0.37	0.63	0.67	0.48	0.60	-0.38	0.80	0.72	0.58	0.57	0.70	0.73	0.83	0.73	0.95	0.98	0.98	0.99	0.99	1.00		
Yb	-0.38	-0.45	0.58	0.72	0.43	0.56	-0.37	0.78	0.68	0.55	0.53	0.67	0.70	0.82	0.70	0.93	0.95	0.95	0.97	0.98	0.98	1.00	
Lu	-0.37	-0.46	0.58	0.73	0.45	0.53	-0.36	0.78	0.69	0.57	0.56	0.69	0.71	0.81	0.71	0.93	0.93	0.94	0.96	0.98	0.98	0.99	1.00

The obtained results demonstrate that there are high internal correlations among REEs (0.53-0.99). The lack of positive correlation of Al and Si with REEs indicates that clay minerals played a poor role in
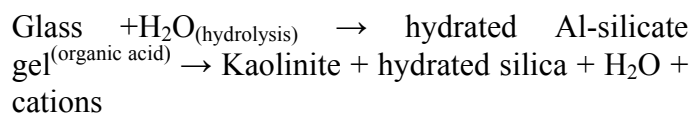
concentrating REEs in Mehredjan bentonite. On the other hand, the positive correlations of MnO (0.46-0.73), TiO_2 (0.58-0.92), Fe_2O_3 (0.43-0.84), and P_2O_5 (0.53-0.74) with REEs may attest to the important role of Ti, Mn, Fe, and phosphate-bearing minerals in fixation and concentration of lanthanides during the evolution of this deposit. Although negative correlations of Al and Si with REEs was interpreted as incapability of clay minerals in fixation of REEs, entering elements such as Mn, Ti, and Fe in crystal structures of clays might give them the capacity to fix and concentrate REEs. The positive correlations between P_2O_5 and LREEs (0.63-0.75) also indicate the efficient role of phosphate minerals like Vitusite, monazite, rhabdophane as substantial carriers for REEs in this deposit. Y features conspicuously positive correlations with REEs (0.78-0.98) that may testify to the concentration of lanthanides by Y-rich phosphate minerals like xenotime (YPO_4). The high positive correlation between HREEs with Zr (0.68-0.72) may also indicate that, in addition to above mentioned host minerals, zircon also played an crucial role in fixing of these elements.

Genesis
Three different types of origins were presented for bentonite deposits by Grim and guven (1978): (1) authigenic alteration of volcanic ashes and tuffs; (2) hydrothermal alteration of magmatic rocks; and (3) deuteric alteration of magmatic materials. Bentonites with non-magmatic origin that occurred during weathering, sedimentation, and re-transportation were also reported by Yalcin and Gumuser (2000). Some lines of evidence such as (1) the presence of a series of volcano-sedimentary rocks (andesite and pyroclastic products), (2) alternates of tuffs and lateral and vertical transitional changes of pyroclastic layers (tuff-bentonite, mudstone-tuff), (3) existing of abundant montmorillonite, and (4) the lack of interlayers of epiclastic materials conceivably indicate that the bentonite at Mehredjan genetically belongs to the first type of origin. For hydration and conversion of tuffs and ashes into smectite, an aqueous environment such as shallow marine environment is necessary. According to Bohor and Triplehorn (1993) the Mg^{2+}-bearing shallow water with weak leaching capacity can develop smectitic Alumino-silicate gels in alkaline environments. The following reaction conceivably took place at Mehredjan:

Glass $+H_2O_{(hyrdolysis)} \rightarrow$ hydrated Al-silicate gel $\rightarrow$ Smectite + hydrated silica + H_2O + cations

The presence of considerable amounts of kaolinite in some bentonite samples may testify that the formation of kaolinite was somehow related to the presence of organic matters and the following reaction probably happened (Bohor & Triplehorn, 1993).

Glass $+H_2O_{(hydrolysis)} \rightarrow$ hydrated Al-silicate gel$^{(organic\ acid)} \rightarrow$ Kaolinite + hydrated silica + H_2O + cations

The identified critobalite in some samples at Mehredjan was presumably derived from volcanic glasses. The excess Si for formation of cristobalite and quartz was assumably acquired from smectitization of volcanic ashes (Bohor & Triplehorn, 1993). However, Henderson *et al.*, (1971) from oxygen isotope studies on bentonite deposits deduced that cristobalite was derived from amorphous silica during devitrification of volcanic glasses at 25°C.

Conclusion
Alteration of Eocene tuffs at Mehredjan was favored with development of 15 outcrops of bentonitic materials. Mineralogically, Mehredjan bentonite includes minerals such as montmorillonite, quartz, cristobalite, calcite, kaolinite, halite, orthoclase, albite, and muscovite. The behavior of elements during the formation of this deposit was a function of factors such as differences in alteration intensity of protolith, alteration of feldspars and pyroxenes, alkaline pH environment, absorption mechanism, structural incorporation, existing of organic matters, diagenesis, carbonate complexation, ionic exchange, physical concentration, humid climate, and existing in resistant mineral phases. Almost all elemental variations took place in an open system during bentonitization. The obtained data indicate that Mehredjan bentonite was formed in a shallow marine environment originated from a rock ranging in composition from trachyandesite through andesite to basaltic andesite. The distribution pattern of REEs show that the origin of this deposit is related to calc-alkaline magmas evolved in a plate margin subduction or collision zones. Geochemical

investigations suggest that in addition to phosphates (e.g., vitusite, monazite, rhabdophane, and zenotime), minerals such as montmorillonite, kaolinite and zircon also acted as potential hosts for REEs in this deposit.

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