

## The origin of the Bentonite deposits of Tashtab Mountains (Central Iran): Geological, Geochemical, and Stable Isotope evidences

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*(received: 07/07/2013 ; accepted: 26/11/2013)*

### Abstract

Bentonite deposits of economic interest are widespread in Tashtab Mountains (Khur), east of Isfahan province, Iran. Several bentonite deposits have been developed in this area as a result of Eocene volcanic alteration. These deposits are classified as Khur bentonite horizon. XRD analyses reveal that alteration products consist of Na-montmorillonite, kaolinite, quartz, calcite, and cristobalite. The studied volcanic rocks predominantly consist of andesite and basalts, which have developed in back arc basin. Field studies demonstrate that there are many active faults that have had a significant role in transporting great volumes of silicic liquids to the surface and precipitated as geode, jasperoid and silicic veins. Alteration of volcanic parent rocks to bentonite is accompanied by gains and losses of some elements. The concentration of major and trace elements displays variable reduction in analogy to the parent rock. Most of the Large Ion Lithophile Elements (LILEs) are markedly depleted; Nb, U, Cr, Ni and V. The aforementioned elements have relatively decreased, whereas Al, Ti and Zr are rather immobile. Cesium is essentially derived from hydrothermal fluids and incorporated in bentonite structure. Both argillic and silicic zones are enriched in Cs. The chondrite-normalized Rare Earth Element (REE) patterns show similar trends in the andesite-basalt as well as bentonite and silicic zone. Slight depletion of REE's, and in particular heavy REE's, is observed in the bentonite samples in comparison with the unaltered rocks. Hydrogen and oxygen stable isotope results indicate a meteoric source of fluids responsible for transformation of volcanic rocks into bentonite at a temperature of about 83°C. The hydrothermal fluids have reached the surface by fault system activity, and silicic liquids have escaped frequently in a sedimentary basin, caused probably by Miocene compressive stresses.

**Keywords:** *Bentonite, Central Iran, Hydrothermal alteration, Stable isotope, Tashtab Mountains*

### Introduction

The alteration of volcanic glass generally leads to the formation of smectites and zeolite group minerals (Hay & Guldman, 1987; Altaner and Grim, 1990; Christidis *et al.*, 1995), which in turn gives rise to the development of economic deposits of bentonites or zeolites. According to Christidis (1998), conversion of volcanic glass possibly occurs through a number of processes including weathering, burial diagenesis, hydrothermal alteration, contact metamorphism, and reactions of vapors and gases with igneous materials. The alteration process is controlled by Si activity, pH, alkalinity, the activity of alkalis, alkaline earth elements, temperature, pressure, and partial pressure of H<sub>2</sub>O (Hay, 1977; Iijima, 1980). The formation of smectites or zeolites at the expense of volcanic glass is significantly accompanied by mobility of both major and minor elements from and to the altered glass. Hence, during the initial stage of alteration, crystallization of smectite requires removal of alkalis and Si (Senkayi *et al.*, 1984). Fine-grained Si -phases are closely associated with smectite. If excess Si remains in the system, leaching of Si from the acidic rocks tends to form free opal-Cristobalite-Tridymites (opal-CT)

bentonite (Zielinski, 1982; Christidis & Scott, 1997; Christidis, 1998).

The chemistry of the parent rocks may influence the nature of the reaction products (Christidis & Dunham, 1993, 1997; Muchangos, 2005). Intermediate (dacitic-andesitic) precursors tend to form Wyoming type montmorillonite (Christidis & Dunham, 1993). Apparently, this does not seem to be always the case.

Color, among the characteristics of bentonites, is the function of parent rock and its alteration (Allo & Murray, 2004). The abundance of iron oxides and the occurrence of Fe and its oxidation state are responsible for variation in the color of many bentonite deposits (Christidis & Scott, 1997).

Bentonites are valuable to a great variety of industries including electric, ceramics, painting, pharmaceuticals, cosmetics, filtering agents, household products and in particular detergents (Murray, 2000; Allo & Murray, 2004). For many years, bentonite has been used as a binder in the feed industry and pharmaceutical preparations (Grosicki, 2008). Bentonite as a feed additive has been used successfully in poultry feeds without any harmful effects (Prvulovic *et al.*, 2008; Safaeikatouli *et al.*, 2010). Also, smectites, the

essential component of bentonites, provides other beneficial features such as absorption of fission products like  $^{137}\text{Cs}$  and  $^{90}\text{Sr}$  (Iwasaki & Onodera, 1993).

White bentonites are characterized by higher whiteness and a lack of organic materials and iron compounds (Clarke, 1985). Because of high quality, their market value is much higher than the colored bentonites. These deposits are widespread in the USA, Greece, Italy, Spain, Turkey, Argentina, the Mediterranean countries, and to some extent in Iran.

The Iranian bentonites are widespread in several regions, particularly in the Alborz Mountains as well as in central and eastern parts of the country. They are mainly associated with Cenozoic volcanic activity and are characterized by variable thickness, concordant contact with their host rocks, lack of traces of fossil, and the presence of abundant primary gypsum as the essential evaporate mineral (Hejazi & Ghorbani, 1994). These deposits, due to their lack of organic materials, can be classified as white bentonites.

The purpose of the present paper is to: 1) examine the influence of the nature of the parent rocks on smectite formation, 2) investigate mobilization and fixation of both major and trace elements, and 3) determine stable isotope ratio in the bentonite deposits from the Khur Tashtab Mountains (KTM).

### Geological Setting

Tashtab Mountain is a part of the Central Iranian micro-continent which should be regarded not so much as a stable zone, but rather as an area with a history which is stratigraphically and structurally very complex. The Central Iran microplate as a triangle lies between Paleo-Tethys in the northeast and Neotethys in the south-southwest (e.g., Aftabi & Atapour, 2000; McQuarrie et al., 2003; Atapour & Aftabi, 2007). The Central Iranian magmatic arc is an Andean-type arc formed by the subduction of the Afro-Arabian plate under an active Iranian continental margin in the Eocene–Miocene time (Berberian & Berberian, 1981).

The subduction of Tethyan oceanic plate underneath Central Iran started in the Middle to Late Triassic era (Kazmin et al., 1986; Arvin et al., 2007), followed by the subduction and arc magmatism through the Mesozoic, which is indicated by scattered Jurassic to Cretaceous intrusive rocks, mainly within the Sanandaj-Sirjan zone (Berberian & Berberian, 1981; Regards et al.,

2004), and continental-continental collisions of Arabian and Eurasia plates.

The Eocene volcanism in Central Iran started as continental arc magmatism and continued into Oligo-Miocene as back arc basalt in lower amounts. Effusive volcanic activity is less common; nonetheless, explosive volcanism appears to have played a major role. Thick, rapidly accumulated sediments, volcano-sedimentary rocks, pyroclastics, and lava flows were deposited in subsiding basins (Amidi et al., 1984). They remodeled the tectono-sedimentary framework of the Iranian territory and were accompanied by major foldings, regional uplifts, metamorphisms, and magmatisms (Amidi et al., 1984; Kazmin et al., 1986; Vincent et al., 2005).

As a result, the area is dominated by Eocene volcanic rocks ranging from alkali basalt, trachy-basalt, trachy-andesite to trachyte with minor sub-volcanic and plutonic rocks. The overall geochemical character of these rocks is calc-alkaline with all features of continental margin (Amidi et al., 1984; Tarkian et al., 1984; Hassanzadeh et al., 2005). The microplate is divided by long thrust faults into three major sub-zones: Lut, Tabas, and the Yazd block (Jung, 1984; Takin, 1972). The study area is located in the Yazd block and is surrounded by three major faults as a graben, consisting of Doruneh fault in the north, Torkmani-Ordib in the south, and Posht-e-Badam fault on the right side (Fig. 1).

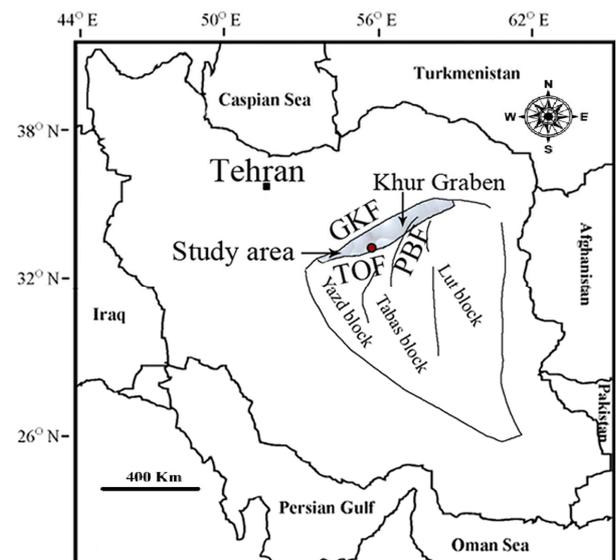


Figure 1: Geological situation of Khur Graben in Iran GKF: Great Kavir Fault, TOF: Torkmani-Ordib Fault, PBF: Posht-e-Badam Fault.

The Darreh Anjir conglomerate at the base and the Qom Formation at the top, consisting mostly of sandstone and limestone, enclosed the Eocene volcanics. The Khur volcanic association, containing shoshonite group members from basic to intermediate terms, formed during an extensive period of Eocene magmatic activity.

Khur Tashtab Mountain structurally belongs to the Central Iran zone. From a tectonic perspective, the role of block faulting seems to be more crucial than that of folding. The geological map is shown in Fig. 2.

**Materials and Methods**

Thirteen unaltered samples of parent rock, argillic zone, and silicic zone were collected. In order to minimize the weathering contamination effects, the researchers gathered the samples from both the underneath and surface of the study area.

The clay fraction (< 2 μm) was obtained according to Stokes' Law. Whole-rock mineralogy

was determined by X-Ray Diffraction (XRD), using a Bruker D8 advance powder equipped; operating at 40 kV and 40 mA, using a Ni filtered Cu Kα radiation. The clay fraction was diffractometer separated, spread on glass slides, and allowed to dry in atmospheric conditions. The slides were then saturated with ethylene glycol at 60 °C for at least 12h to ensure maximum saturation. Analytical data were obtained by X-Ray Fluorescence (XRF) for major elements (Si, Al, Ti, Fe, Mn, Mg, Ca, Na, K, P and LOI) and Inductively Coupled Plasma Mass Spectrometry (ICP-MS) for selected trace elements at the School of Earth and Environmental Science, Washington State University (WSU), USA. The stable isotope analysis was performed at the Department of Ecology and Evolutionary Biology, Cornell University, USA. Preparation method consists of carbonates' being dissolved with acetic acid while amorphous silica was removed with sodium carbonate.

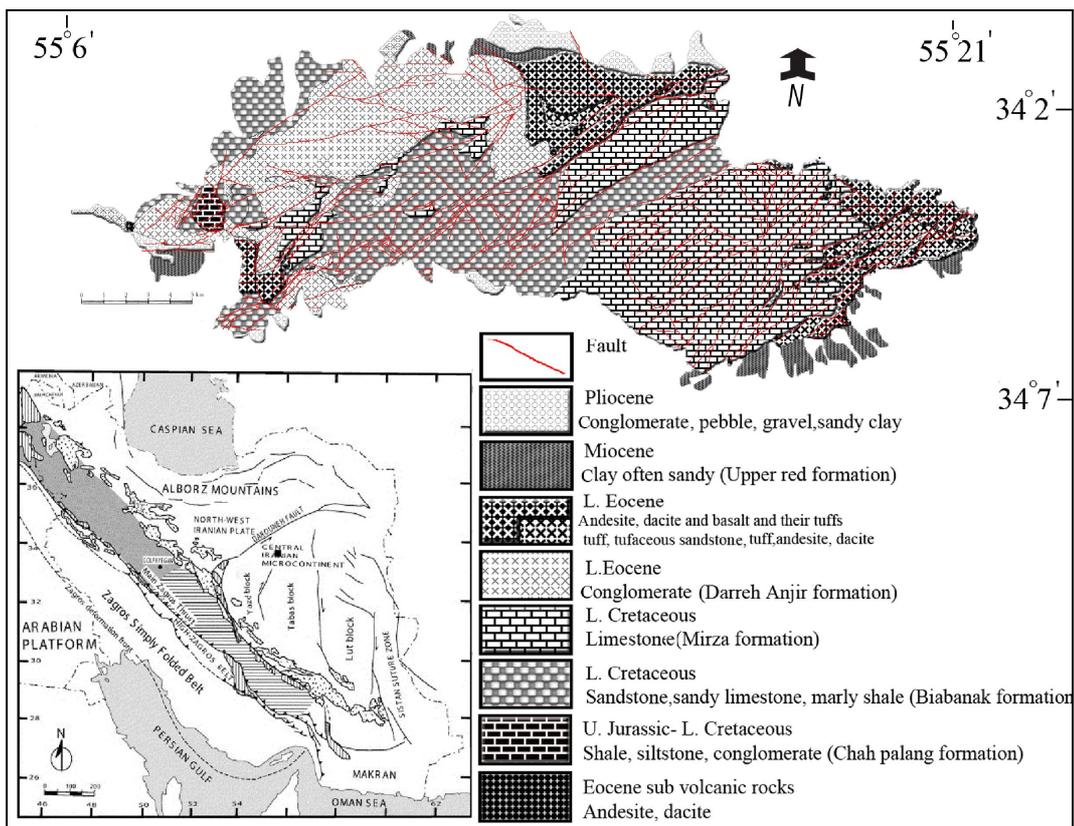


Figure 2: Geological map of Tashtab (after Technoexport, 1984)

The chemical treatments used in our study do not affect the isotopic composition of smectite (Bird *et al.*, 1992; Jioneck, 1995). The smectite samples were heated at 180°C for 8h under vacuum to

eliminate interlayer water.

**Field Observations- Petrographic Features**

In the studied area, the rocks are exposed as several

distant low lying hills, surrounded by argillic deposits developed at the expense of volcanic and to a lesser extent intrusive rocks belonging to late Cretaceous-Tertiary time. The Eocene volcanic rocks are mainly composed of andesite, andesite-basalt, and trachy andesite.

In an overall field observation, the volcanic parent rock appears as short hills surrounded by argillic zone containing bentonites in plain (Fig. 3a). Bentonite deposit formed as massive stratiform and lenses, having a thickness of several meters at several regions with gradational contacts with their host rocks. Outcrops of silicic compositions have been developed as agates, jasperoids, and siliceous veins (Fig. 3b) with the compositions of low quartz, chalcedony, also containing calcite, barite, hematite, and also low amounts of aragonite, siderite, and anhydrite (Nazari, 2004). These silica compounds have been mostly formed near the faults and fine joints, also

some agates can show the growth during fault activities. The alteration processes are reflected in the occurrence of typical paragenetic minerals such as clay minerals, zeolites and/or iron oxides as well as high concentrations of Al, Fe, Ca, K, and Na in the agates. However, the occurrence of calcite and fluorite and unexpected high concentrations of some elements such as Ge, U, and B\_ especially in agates of acidic volcanics\_ indicate that other fluids can play a role in the alteration of volcanic rocks, the mobilization and transport of SiO<sub>2</sub> and also other chemical compounds (Gotze *et al.*, 2012).

Figure 4 illustrates that calcite have been formed beside the quartz in a geode, with a serrate margin. Silica and calcite could not be formed in the same pH situation; therefore, it seems that silicic hydrothermal fluids flow outward alternatively in an alkaline aqueous basin. Calcite macles show a temperature of below 200°C in Burkhard's (1993) classification.

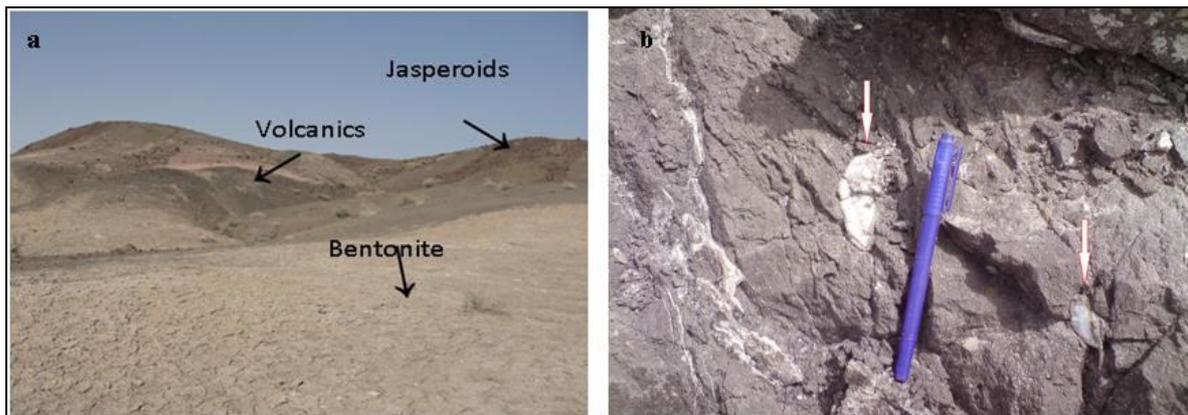


Figure3: a. A landscape of the study area and b. Agates beyond the silica vein

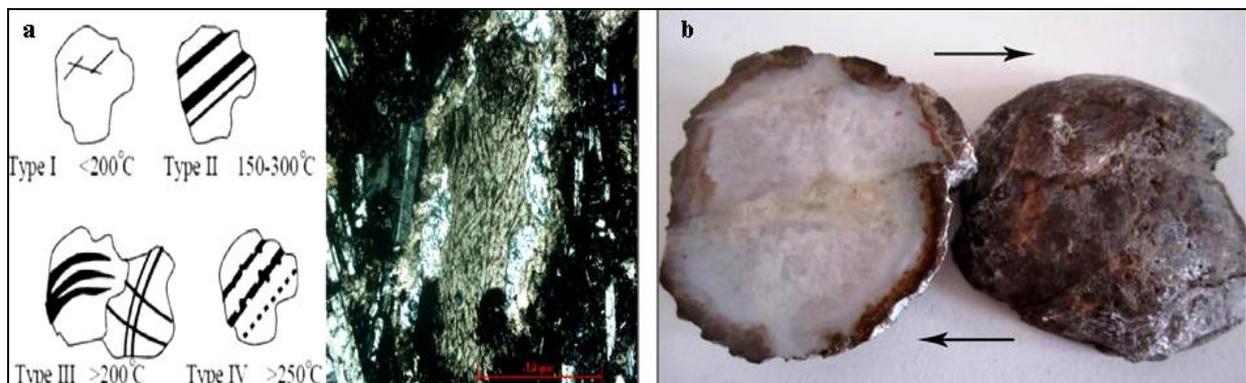


Figure 4: a. Microscopic photo of a nodule filled by quartz and calcite; Schematic illustration of the influence of temperature by calcite twinning (after Burkhard, 1993). b. Cross section of an agate growing during fault activity

The study of fluid inclusions represents all fluid inclusions formed as single-phase liquids, so the temperature of formation could not reach 100°C. It is widely accepted that temperatures of agate

formation are usually below 100°C (Moxon *et al.*, 2006). On the other hand, Gotze *et al.*, (2001) suggest that a temperature of at least 50°C is necessary for agate formation; in some cases it

could reach up to 400°C. So, we can imagine a temperature between 50 and 100°C for agates and the silicic zone.

The XRD analysis revealed that in all of the

samples, Na-smectite is the principal clay mineral phase, associated with plagioclase, kaolinite, and a silica phase which could be either quartz or opal-CT (Fig. 5).

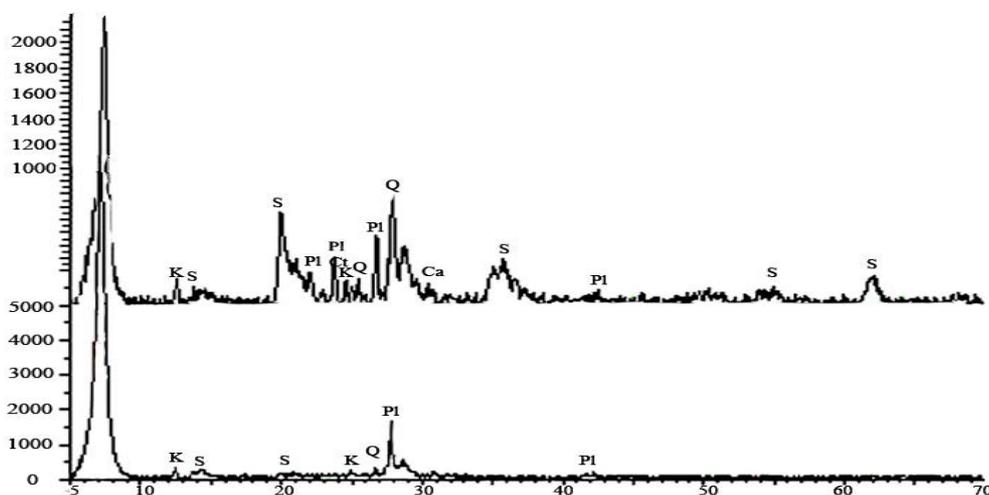


Figure 5: Representative XRD pattern of the KTM bentonites (S. Smectite, Q. Quartz, K. Kaolinite, Pl. Plagioclase, Ca. Calcite, Ct. Opal CT)

### Geochemistry

Arc volcanism across Iran is dominated by a Paleogene pulse, despite the protracted and presumably continuous subduction along the northern margin of the Neotethyan Ocean for most of Mesozoic and Cenozoic time (Verdel *et al.*, 2011). As a result, the rocks exposed in this region are basaltic, andesitic, dacitic, rhyolitic, and mainly lava and ignimbrites, with minor subvolcanic and plutonic rocks. According to Jung *et al.*, (1984), the overall geochemical character of these rocks is calc-alkaline, with all of the features of the continental margin. In order to identify the magma type and the tectonic setting in which the studied volcanic rocks were generated, the researchers applied the major and trace element chemistry of volcanic rocks to the data obtained from bentonites.

The results of the chemical analyses for the studied rocks are given in Table 1. As the analyses show, the studied magma does not have a large amount of water; thus, it could be inferred that our hydrothermal alteration does not have a magmatic source. The volcanic rocks are plotted on the discrimination diagrams proposed by Winchester and Floyd (1977) (Fig. 6). The selective use of relatively immobile elements in such diagrams ensures that errors, due to a loss of elements during alteration, are minimized. The projection of the bentonite samples on the Nb/Y against Zr/TiO<sub>2</sub>

clearly demonstrates that the bentonites were changed from andesite to andesite basalt parent rock. As the TiO<sub>2</sub> vs. Al<sub>2</sub>O<sub>3</sub> diagram (Muller & Groves 1997) represents, the KTM bentonites were derived from an arc-related basin source. While on the V vs. Ti diagram, a back-arc source is proposed as the origin of these deposits (Fig. 7 a, b).

During the process of alteration, the chemistry of the parent rock generally controls both the type and the composition of the reaction product (Iijima, 1980; Christidis & Dunham, 1993, 1997). Moreover, environmental qualifications are so operative. For example, while an intermediate volcanic rock is altered to bentonite in an alkaline situation, acidic environment leads to the formation of kaolinite instead of bentonite (Drits & Kossovskaja, 1990).

**Major Elements:** During bentonite formation from andesitic parent rock, there is a migration of alkalis and alkalies earth, while Al, Ti, and to some extent Fe are immobile. Na due to its incorporation in clay minerals is less depleted, whereas elements such as K<sub>2</sub>O, CaO, and MnO are easily released into a fluid phase. Fe and TiO<sub>2</sub> are generally fixed during bentonite formation by a structural incorporation into clay and in secondary oxides and hydroxides (Zeilinski, 1989; Christidis, 1998).

Table 1: Whole rock analyses of Khur samples containing volcanics, silicas and clay samples.

Sample	Volcanic Samples				Silica Samples				Clay Samples				
	Si3	Si4	Tb14	Tb15	Si1	Si10	Tb16	Tb17	Si7	Si8	Si13	Si14	Si16
SiO <sub>2</sub>	55.41	55.53	54.5	52.78	88.96	86.87	88.24	88.88	46.39	55.75	51.86	53.70	52.68
TiO <sub>2</sub>	0.879	0.879	0.89	0.904	0.026	0.025	0.03	0.025	0.784	0.817	1.140	0.94	0.88
Al <sub>2</sub> O <sub>3</sub>	16.46	16.51	16.12	15.40	0.86	0.68	0.82	0.91	15.57	16.73	19.50	19.40	17.43
FeO*	6.57	6.28	6.72	7.31	2.97	2.97	2.21	0.70	8.04	6.65	4.39	4.48	5.13
MnO	0.092	0.092	0.108	0.138	0.053	0.112	0.07	0.036	0.174	0.075	0.08	0.01	0.06
MgO	3.19	3.32	3.99	5.44	0.82	0.65	0.57	0.25	3.79	2.22	2.18	2.96	2.68
CaO	8.80	8.81	8.78	8.72	1.91	3.64	3.39	4.61	6.41	4.00	3.01	1.19	2.28
Na <sub>2</sub> O	2.98	2.96	2.96	2.94	0.23	0.13	0.17	0.16	2.60	2.53	2.52	2.15	2.12
K <sub>2</sub> O	3.12	3.08	2.96	2.73	0.11	0.09	0.11	0.13	1.42	1.22	1.25	0.53	1.21
P <sub>2</sub> O <sub>5</sub>	0.38	0.38	0.4	0.43	0.01	0.02	0.017	0.02	0.32	0.3	0.44	0.26	0.32
Sum(%)	97.89	97.85	97.43	96.80	95.96	95.18	95.62	95.73	85.50	90.28	86.37	85.62	84.81
LOI	2.28	2.51	2.89	3.88	3.67	3.71	3.61	3.45	13.41	9.02	12.87	14.24	14.00
SO <sub>3</sub>	0.28	0.32	0.28	0.26	0.44	0.28	0.25	0.04	0.26	0.23			
Traces	Si 3	Si 4	Tb14	Tb 15	Si 1	Si 10	Tb16	Tb 17	Si 7	Si 8	Si13	Si 14	Si 16
Rb	79.3	76.8	70.3	54.8	8.0	6.8	7.2	6.8	35.2	28.4	26.6	20.5	36.5
Sr	1012	1062	966	834	261	143	149	43	412	434	370	404	249
Ba	495	494	503	519	14	18	13.3	8	226	213	190	52	170
Th	6.10	5.94	5.86	5.54	0.18	0.19	0.26	0.40	5.89	6.31	5.04	4.92	5.53
Nb	5.85	5.73	5.0	5.08	0.53	0.48	0.48	0.42	4.99	5.60	6.50	5.77	5.56
Y	20.01	19.71	19.6	19.37	0.63	0.67	0.91	1.43	19.44	20.41	20.42	13.23	17.48
Hf	3.57	3.54	3.41	3.35	0.42	0.34	0.39	0.41	3.06	3.38	3.71	3.28	3.42
Ta	0.41	0.40	.33	0.34	0.02	0.02	0.02	0.03	0.36	0.41	0.44	0.39	0.38
Cs	2.22	2.03	2.96	4.34	7.05	5.30	4.69	1.72	5.21	3.21	3.80	8.65	15.01
U	1.62	1.61	1.51	1.46	0.95	1.41	1.01	0.67	1.56	1.45	2.10	1.25	1.67
Ni	31	33	34	38	5	3	2	0	40	37	52	49	41
Cr	89	98	114	154	7	10	9	9	167	106	133	219	115
Sc	25	25	27	30	4	4	3.5	2	26	24	21	26	17
V	214	211	218	229	80	87	59	10	195	194	252	293	203
Ga	17	18	18	18	2	2	2	2	17	18	21	22	18
Cu	80	69	63	40	107	96	73	16	50	63	32	42	59
Zn	81	84	80	75	13	13	12	12	86	87	96	118	166
Pb	13.47	13.83	13.3	12.71	2.00	1.66	3.21	5.97	12.57	12.04	11.12	11.76	17.05
Zr	132	130	128	122	36	28	29	24	119	122	130	107	120
REEs	Si 3	Si 4	Tb14	Tb 15	Si 1	Si 10	Tb16	Tb 17	Si 7	Si 8	Si13	Si 14	Si 16
La	21.17	20.81	21.12	21.40	0.67	0.82	0.847	1.02	22.96	22.26	19.67	18.82	18.43
Ce	43.36	42.66	43.56	44.68	1.41	1.58	1.73	2.21	45.54	46.22	41.79	36.58	37.81
Pr	5.52	5.45	5.58	5.77	0.16	0.18	0.20	0.27	5.64	5.80	5.47	4.36	4.83
Nd	22.36	22.09	22.79	23.92	0.64	0.72	0.78	0.98	22.44	23.21	23.09	17.17	19.84
Sm	5.08	4.98	5.15	5.38	0.14	0.16	0.17	0.20	4.82	5.08	5.29	3.72	4.50
Eu	1.43	1.43	1.47	1.53	0.03	0.04	0.05	0.07	1.36	1.45	1.48	0.97	1.22
Gd	4.52	4.49	4.58	4.73	0.13	0.17	0.16	0.18	4.20	4.58	4.76	3.30	4.00
Tb	0.68	0.69	0.69	0.70	0.02	0.02	0.02	0.03	0.64	0.70	0.72	0.49	0.60
Dy	4.05	3.87	3.91	3.86	0.10	0.12	0.13	0.18	3.70	4.02	4.13	2.74	3.49
Ho	0.77	0.77	0.77	0.77	0.02	0.02	0.03	0.04	0.73	0.80	0.81	0.53	0.68
Er	2.06	2.03	2.01	1.99	0.07	0.07	0.09	0.12	2.02	2.10	2.10	1.36	1.76
Tm	0.30	0.30	0.29	0.28	0.01	0.01	0.019	0.02	0.29	0.30	0.29	0.19	0.24
Yb	1.82	1.82	1.78	1.70	0.08	0.08	0.1	0.13	1.78	1.82	1.67	1.10	1.39
Lu	0.29	0.29	0.28		0.01	0.01	0.01	0.02	0.30	0.29	0.25	0.16	0.21

However, the behavior of these elements in the studied samples is consistent with bentonite formation (Benitoa *et al.*, 1998; Muchangus, 2006).

*Rare Earth and Other Trace Elements:* The REE pattern of samples from argillic and siliceous zones

that had been normalized to chondrite values (McDonough & Sun, 1995) were compared with the REE pattern in fresh rocks (Fig. 8). The REE pattern in bentonite and siliceous deposits are very similar to that of the unaltered rocks. Siliceous deposits have strongly lower total REE content,

whereas bentonite samples display insignificant depletion particularly with respect to HREE. This reduction could be explained in terms of high

acidity and the presence of  $F^-$ ,  $Cl^-$  and  $SO_4^{2-}$ , complexing the ions in hydrothermal system.

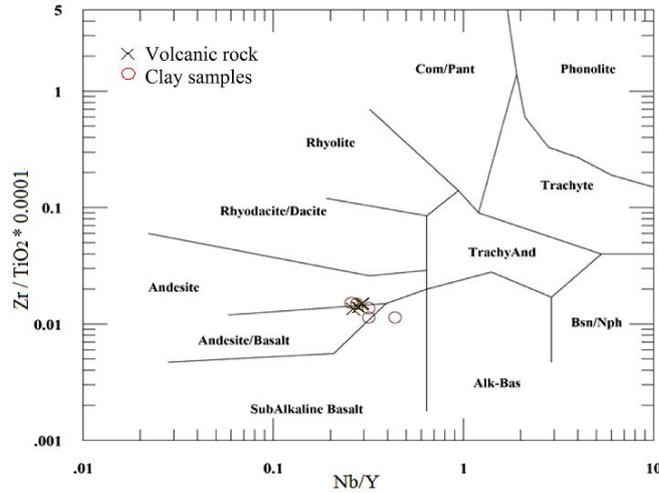


Figure 6:  $Zr/TiO_2$  vs.  $Nb/Y$  (Winchester & Floyd, 1977) classification diagram for KTM volcanic rocks

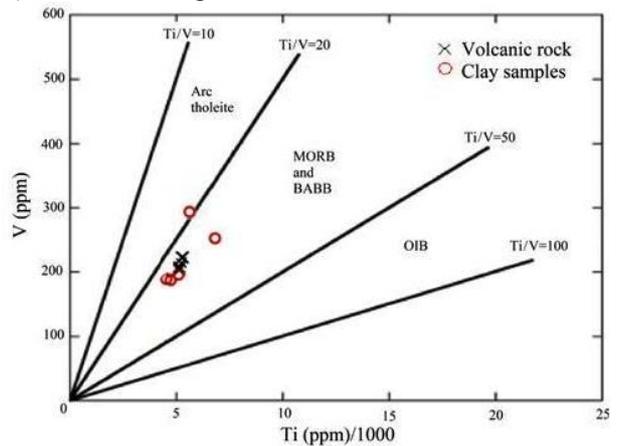
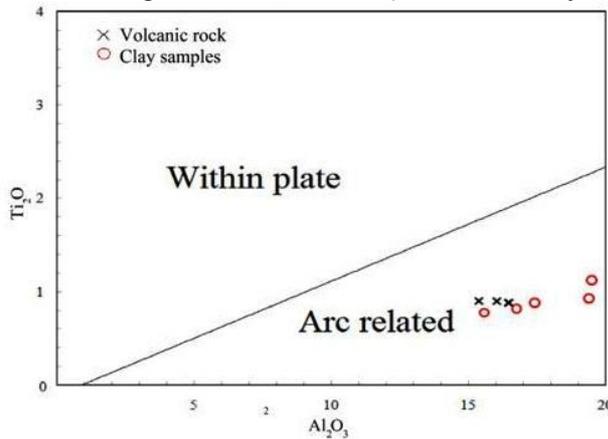


Figure 7: Tectonic setting discrimination a. after Muller and Groves (1997); b. Shervise (1982).

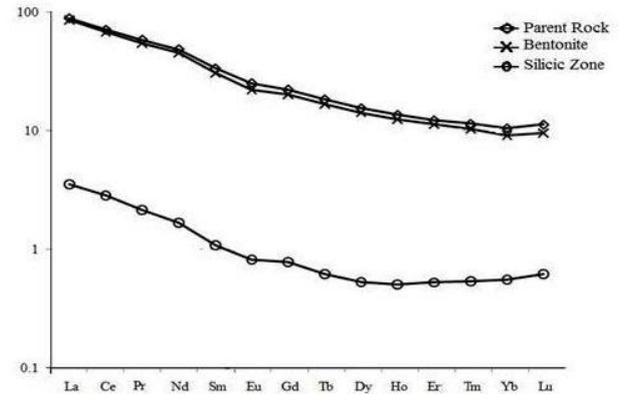
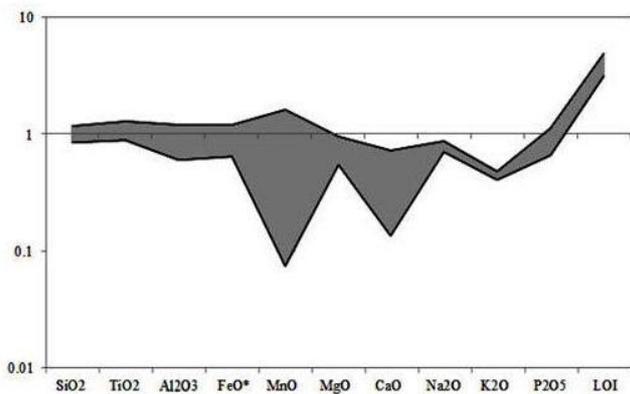


Fig. 8. a) shaded area shows major elements in clay samples normalized to parent rock, b) a comparison of REEs in volcanics, clay and silica samples.

The REE ratios were employed to demonstrate the REE fractionation among LREEs (Light REEs) expressed as  $(La/Sm)_{cn}$  and between MREEs (Middle REE) and HREEs (Heavy REE) shown as

$(Tb/Yb)_{cn}$ . Also, the  $(La/Yb)_{cn}$  ratio was calculated to investigate the enrichment of LREE over HREE in the studied alteration zones. The ratios of  $Eu/Eu^*$  are plotted on diagram. The  $Ce/Ce^*$  ratio is

relatively constant. All the values are reported in Table 2.

A notable fractionation between HREEs and LREEs occurred in the argillic zone. This could happen because of two reasons: 1) high acidity and 2) abundance of  $\text{Cl}^-$ ,  $\text{F}^-$  and  $\text{SO}_4^{2-}$ . HREEs could be removed by making complexes in hydrothermal fluids (Michard & Albarede, 1986; Wood, 1980; Lottermoser, 1992; Fulignati *et al.*, 1998), while smectite group minerals could save LREEs by adsorption.

Table 2. La/Sm, La/Yb, Tb/Yb and Eu/Eu\* ratios used in Fig. 9

Sample	la/sm	La/Yb	Tb/Yb	Eu/Eu*	Ce/Ce*
Si 3	2.691	8.338	1.703	0.915	0.983
Si 4	2.696	8.184	1.709	0.923	0.982
Tb14	2.65	8.53	1.76	0.923	0.98
Tb 15	2.570	9.047	1.868	0.929	0.986
Si 1	3.189	5.934	1.016	0.762	1.05
Si 10	3.278	7.701	1.274	0.793	0.99
Tb16	3.08	9.26	1.65	0.93	0.98
Tb 17	3.306	5.835	1.088	1.064	1.03
Si 7	3.079	9.263	1.637	0.926	0.981
Si 8	2.831	8.778	1.738	0.918	0.997
Si13	3.268	12.239	2.032	0.843	0.988
Si14	2.646	9.478	1.967	0.880	0.99
Si16	2.400	8.452	1.948	0.900	0.983

The  $(\text{Eu}/\text{Eu}^*)_{\text{cn}}$  ratio represents relatively wide values in the rocks of the siliceous zone. According to some workers (i.e., Michard & Albarede, 1986, Lottermoser, 1992), the high concentration of  $\text{Cl}^-$  in hydrothermal fluids is a good complexing agent and is probably responsible for Eu depletion. Also, Eu could move as  $\text{Eu}^{2+}$  at high temperatures or in acidic environments (Sverjensky, 1984; Bao, 1991). Negative Eu anomaly could be enhanced by dissolution of Eu-enriched minerals (Lewis *et al.*, 1997).

**Isocon Diagram:** The Isocon diagram can be applied for the direct comparison of element concentrations in altered and unaltered rock samples (Grant, 1986). For the purpose of this study, we adopted a constant value. Therefore, the isocon equation will be used.

$$C^A = (\rho^0 / \rho^a) C^0$$

$$(\Delta C_i / C_i) * 100 = (\rho^a / \rho^0) (C_i^a / C_i^0) - 1$$

The enrichment and depletion of various elements are calculated. The geometry of the

diagram is such that the elements below the straight isocon are depleted, whereas those above are enriched by the hydrothermal alteration (Fig. 10).

In the argillic zone, all trace elements except Cs are depleted. Among those, the Large Ion Lithophile Elements (LILEs) (i.e., Ba, Rb and Sr) and to some extent High Field Strength Elements (HFSEs) (Nb, Zr, Th) display strong depletion. Transitional elements (i.e., V, Ni, Cr), in particular Cu, are highly depleted. High-T alteration is required for mobility of these elements (Pokrovsky *et al.*, 2005). In the siliceous zone, strong removal of all elements has occurred. Uranium, Pb and Cu have lower amounts of depletion and Cs is enriched as in the argillic zone. Cesium generally replaces K in mineral structures and was found to be strongly enriched in the bentonite samples. Smectite has the potential to accommodate Cs. Its uptake by montmorillonite has been studied by several researchers (e.g.: Iwasaki & Onodera, 1993; Oscarson *et al.*, 1994; Coppin *et al.*, 2002; Kónya *et al.*, 2005; Giannakopoulou *et al.*, 2012). Na-montmorillonite, due to having a large interlayer space, is suitable for absorption of Cs. Apparently, octahedral negative charge, generated by the reduction or removal of  $\text{Fe}^{3+}$  ion, plays a significant role in this phenomenon (Tsutmu *et al.*, 1996). The release of  $\text{Fe}^{3+}$  and an increase in the substitution process of Al for Si in montmorillonite are associated with a negative charge in octahedral position and favor Cs absorption; however, these processes cannot be a reason for silica composition by themselves. Thus, Cs must have come from an external source, which could be hydrothermal fluids.

### Stable Isotopes

The stability of the isotope ratios of hydrogen and oxygen in clay minerals depend on the formation temperature and the isotopic composition of the water from which the clay mineral was formed (Delgado & Reyes, 1996). This implies that some information about the past environments is usually recorded in clay minerals, and in suitable cases they can be used as a paleoclimate indicator (Stern *et al.*, 1999; Chamberlain & Poage, 2000; Gilg, 2000). Thus, the simultaneous study of  $\delta\text{D}$  and  $\delta^{18}\text{O}$  is of prime importance for a better understanding of the origin of the water involved in the genesis (Savin, 1980; Sheppard *et al.*, 1969; Savin & Epstein, 1970a, Lawrance & Taylor, 1971) and the formation temperature of the clay minerals (Delgado & Reyes,

1996; Caballero & Cisneros, 2010; Nele-Muttik *et al.*, 2010). According to Sheppard and Gilg (1996), a convincing evidence for complete oxygen and hydrogen isotope exchange without

recrystallization is lacking, unless the minerals have been subjected to either thermal effects or some particular geological conditions.

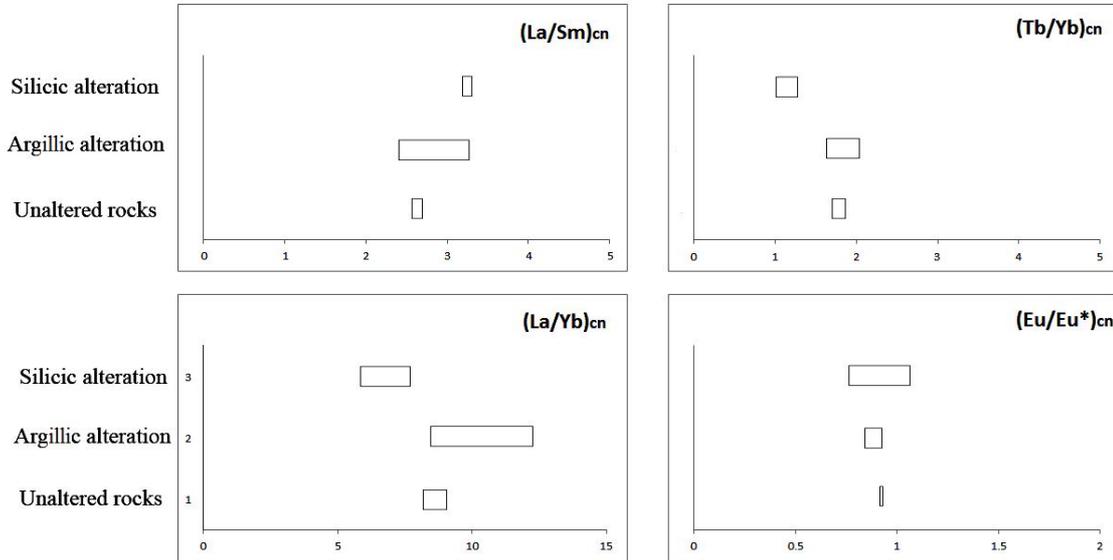


Figure 9: Fractionation of REEs in volcanics, silica and clay samples

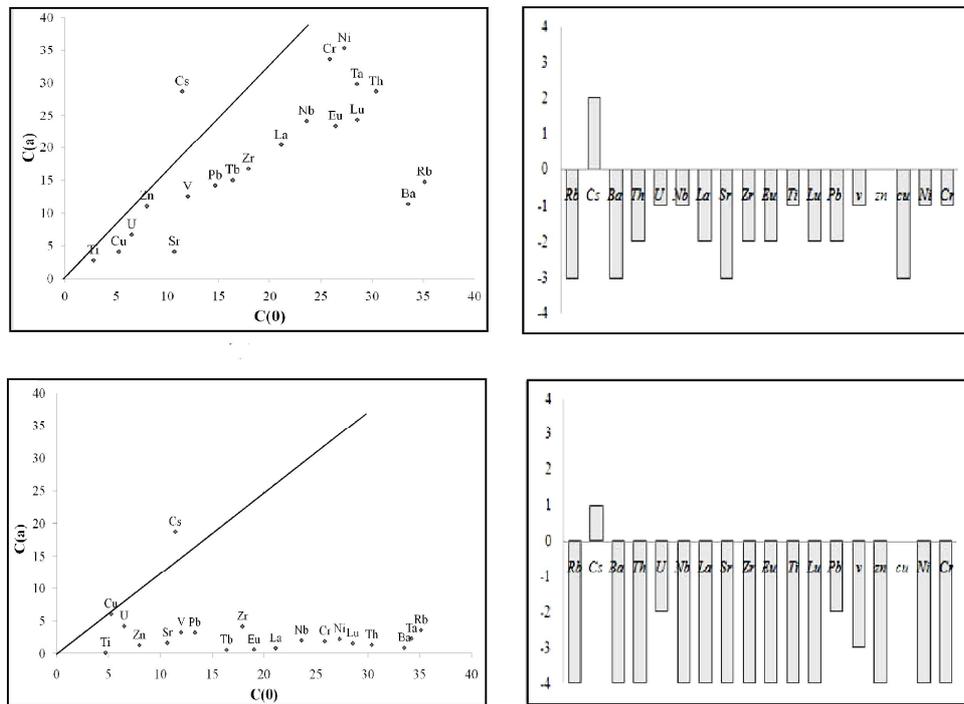


Figure 10: Representative isocron diagrams (left side) and the percentage of gains and losses (right side) focused on REE behavior in KTM altered zone: (a) silicic alteration; (b) argillic alteration. In the isocron diagrams, the component abundances of fresh rocks ( $C_{(0)}$ ) are plotted on the horizontal scale and those of equivalents ( $C_{(a)}$ ) are plotted on the vertical scale. The isocron position was determined by considering the variation of density percentage of gains and losses plotted on the histogram were calculated using the isocron equation:  $(\Delta C_i/C_i) * 100 = (\rho^a / \rho^0)(C_i^a/C_i^0) - 1$  where  $(\Delta C_i/C_i) * 100$  is the percentage variation of the *i*th element in the altered rock compared with the fresh rock.  $\rho^a$  and  $\rho^0$  are density of altered and fresh rocks. Values of +4 to +1 = a gain of more than 100 to 80, 80 to 60, 60 to 40, 40 to 20 percent. 0 means immobile elements (values in the range of +20 to -20). values -1 to -4 represent losses of elements

Therefore, the isotopic composition of clay, developed in contact with meteoric water, should be characterized by isotopic compositions plotting on subparallel lines to meteoric water line (Craig, 1961); the offset is related to their respective fractionation factor. This indicates that clay minerals are able to record some information about the past environments and can be used as a paleoclimate indicator (Stern *et al.*, 1999; Chamberlain & Poage, 2000, Gilg, 2000).

In the present study,  $\delta D$  and  $\delta^{18}O$  isotopic composition of smectite were applied to constrain the origin of hydrothermal fluids and the formation temperature of the studied bentonite deposits. The  $\delta^{18}O$  and  $\delta D$  value for 6 smectite samples are presented in Table 3. Isotopic ratios of oxygen and deuterium are normalized to SMOW standard. The  $\delta^{18}O$  value varies from -13.3 to -8.11 and  $\delta D$  ranges from -97.89 to -87.51.

Table 3: Stable isotopic analyses equilibrated for water-mineral.

Sample	$\delta^{18}O$ vs. SMOW	$\delta^2H$ vs. SMOW
TB5	-11.81	-97.89
K3	-11.01	-87.51
Si7	-8.65	-87.72
Si11	-11.78	-90.51
Si13	-13.32	-96.35
Si14	-8.11	-89.52

Minerals with oxygen atoms in different structural sites, such as tetrahedral [ $SiO_4$ ] and octahedral hydroxyl, are potentially the basis of single-mineral thermometers. Smectite group minerals contain oxygen in both positions. The opposite slopes of the isotopic fractionation of hydrogen and oxygen in the clay-water system and the well-known relationship between  $\delta^{18}O$  and  $\delta D$  in meteoric waters allow the isotopic composition of clay minerals to be used as a single-mineral geothermometer (Delgado & Reyes, 1996). Using the following formula:

$$3.54 \times 10^6 \times T^{-2} = \delta^{18}O_{Sm} - 0.125 \delta D_{Sm} + 8.95 \quad (0-150^\circ)$$

a temperature of 83°C was calculated for bentonite formation which is consistent with the temperature that we expect for silicic zone.

The Geothermometric equation based on stable isotope data was calculated for oxygen and deuterium after Sheppard and Gilg (1996):  $1000 \ln \alpha$

$$\begin{aligned} O_{(Smectite-Water)} &= +2.55 \times 10^6 \times T^{-2} - 4.04 \\ 1000 \ln \alpha D_{(Kaolinite-Water)} &= -2.2 \times 10^6 \times T^{-2} - 7.7 \end{aligned}$$

The studied samples ranged between hydrothermal clay and meteoric water in Fig. 11. It has been found that, while many clay-enriched soils lie close to the kaolinite line on the plot of  $\delta^{18}O$  against  $\delta D$ , hydrothermal clays were formed at higher temperatures plot, closer to the meteoric water line. This is due to the fact that clays that equilibrated isotopes at higher temperatures have  $\delta D$  and  $\delta^{18}O$  values approaching those of water; because the fractionation factors come closer to unity as the temperature rises (Bowen, 1994). Some contamination with meteoric water has probably happened in clay minerals, too. However, the studied samples presumably were not formed in a weathering situation.

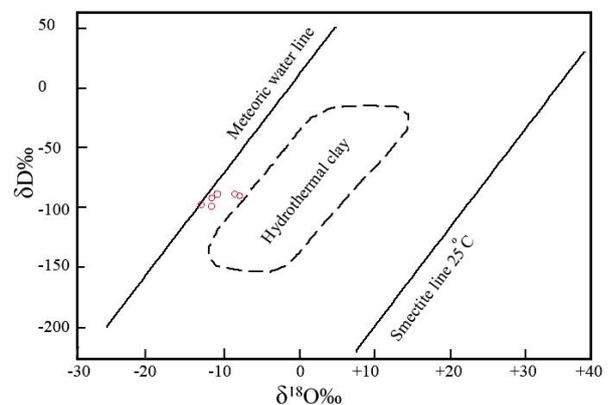


Figure 11:  $\delta^{18}O$  vs.  $\delta D$  plotted on meteoric water area (Rozanski *et al.*, 1993), smectite line (Kyser, 1987) and hydrothermal clay.

## Discussion

Since tectonic movements have played a significant role in the alteration process of the study area, we paid particular attention to the tectonic setting of KTM. Based on the isotopic evidences, hydrothermal fluids with meteoric nature were involved in bentonite formation in the Tashtab Mountain.

Eocene epoch in Central Iran was an active time in volcanism, because of Neothetys subduction. From a tectonic perspective, the role of block faulting seems to be more crucial than that of folding. The overall structure of KTM is graben, which is surrounded by three major faults including Doruneh fault in the north, Torkamani Ordib in the south, Posht-e-Badam fault on the right side, and several other minor faults and fractions. The amount of relative displacement of faults cannot be determined; however, from a geomorphological standpoint, it appears that they are normal faults with a relative displacement of at least a few tens of

meters to several kilometers. The main faults form a triangle, and based on detailed field study these faults appear to have been channels for the hydrothermal fluids migration.

The KTM volcanic rocks linked up with the thickness of Darreh Anjir conglomerate at the base and the Qom Formation at the top; mostly sandstone and limestone enclose the Eocene volcanics. These rocks underwent hydrothermal alteration, which led to the formation of widespread bentonite masses as well as siliceous deposits. The essential components of the former deposits are beidellite and Wyoming-type montmorillonite (WTM).

The studied area developed by a tension regime in the back-arc basin in the Eocene. In comparison

with the Iranian geological evidences, some relationships are obvious a shallow marine environment was formed in this graben (Abedini *et al.*, 2011), and magmas with andesite basaltic nature erupted in this basin. The pillow form of volcanics and cavities filled by calcite indicate the presence of this environment. During the Miocene, subduction ended, and a compression regime was dominant in the area. The major faults became reactive from normal to reverse faults (Hashemi, 2001). Meteoric waters moved through the fracture into the depth replaced by hot fluids from which siliceous materials were precipitated in several pulses on the surface. Thus the studied hydrothermal bentonites were likely formed as a result of tectonic movements (Fig. 12).

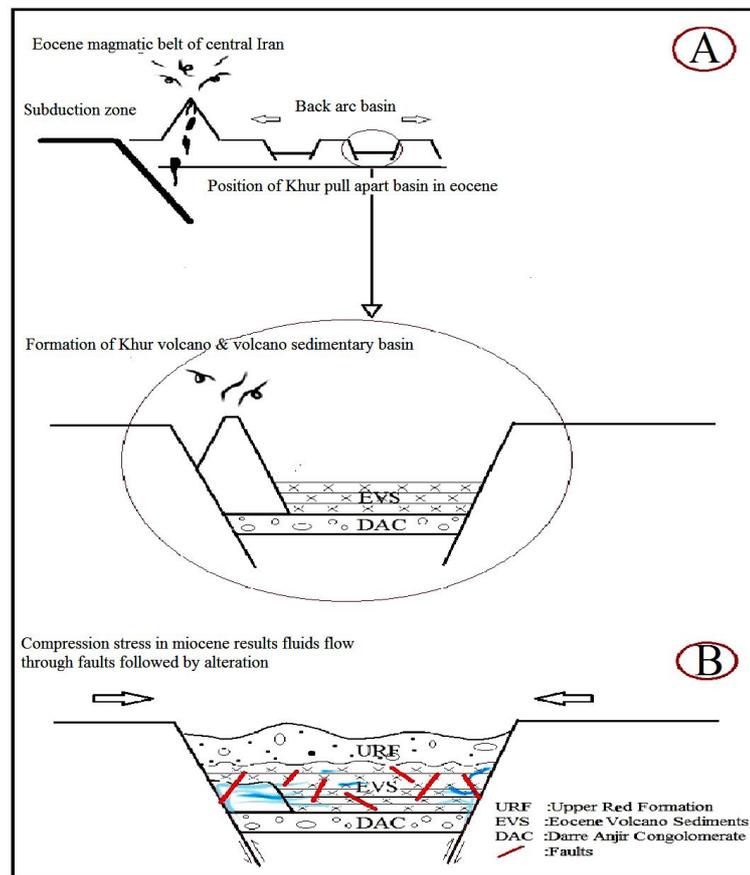


Figure 12: A schematic picture of tectonic events during a. Eocene and b. Miocene (Malek-Mahmoodi, 2010).

**Conclusions**

Bentonites in the Tashtab Mountains were formed from andesite-basaltic parent rocks, tectonically belonging to back arc basin. The studied clay minerals consist of Na-montmorillonite with a low amount of kaolinite. In addition, quartz, calcite, and crystalbite were found in the samples. Based on

the field observation, several active faults are responsible for transporting siliceous fluids to the surface and their precipitation as geode, jasperoid, and silicic veins. Microscopic observation indicates that these fluids flow outward in an alkaline aqueous basin. Hydrothermal alteration process leached most of the major and trace elements. In

argillic zone, alkaline elements were mostly leached. Aluminum and Ti are immobile elements and show lower amounts of changes. Chemical compositions of both siliceous and bentonitic samples as well as host volcanic rocks show the same trend in trace elements and support the role of these hydrothermal fluids in bentonite formation. LILEs are highly depleted and HREEs are more depleted than LREEs. Meanwhile HREEs are more depleted than LREEs. This may be due to leaching HREEs as complexes and absorbing LREEs into the clay minerals structure. Therefore, removal of

these elements gave rise to Cs enrichment. Oxygen and deuterium stable isotope studies revealed that bentonites formed in a temperature of about 83°C, and hydrothermal fluids are essentially derived from meteoric water that passed through active faults.

#### Acknowledgments

This paper stems from an M.Sc. thesis carried out by the first author. It had been supported financially by the University of Isfahan.

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