

Mineralogy and Geochemistry of the Guenfouda Clay Deposit, Jerada Province, Northeastern Morocco

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Abstract

The Guenfouda clay deposit is located at about 36km to the southwest of Oujda city and 6km to the south of Guenfouda village. It belongs to the Jerada Province of the northeastern Morocco and hosted within the Upper Visean calc-alkaline dacite lava interbedded within a schisto-volcanic complex. This deposit is mined for more than 15 years and the product being mainly used for refractories and industrial ceramics.

This clay deposit is funnel or trough-like in form, narrowing downwards and display a E–W trend, which follows the major dextral strike-slip fault that passes through the south of the deposit. Based on mineral assemblages, four lateral alteration zones were defined from the north to south parts of the deposit: the Illite zone, the Pyrophyllite-illite zone, the Pyrophyllite zone and the Quartz zone.

The presence of high-temperature minerals such as pyrophyllite, diaspore, the alteration zonation pattern and the chemical characteristics are diagnostic of hypogene origin. However, the variation diagrams, Zr vs TiO₂ and P₂O₅ vs SO₃ as well as the values of the chemical Index of Weathering (CIW) and the Alteration Index (AI) revealed a mixed

type. It seems that the genesis of Guenfouda clay deposit was first controlled by the east-west strike-slip faults, which brought ascending hydrothermal solutions that led to clay formation and finally, the weathering processes have continued and extended the argillization.

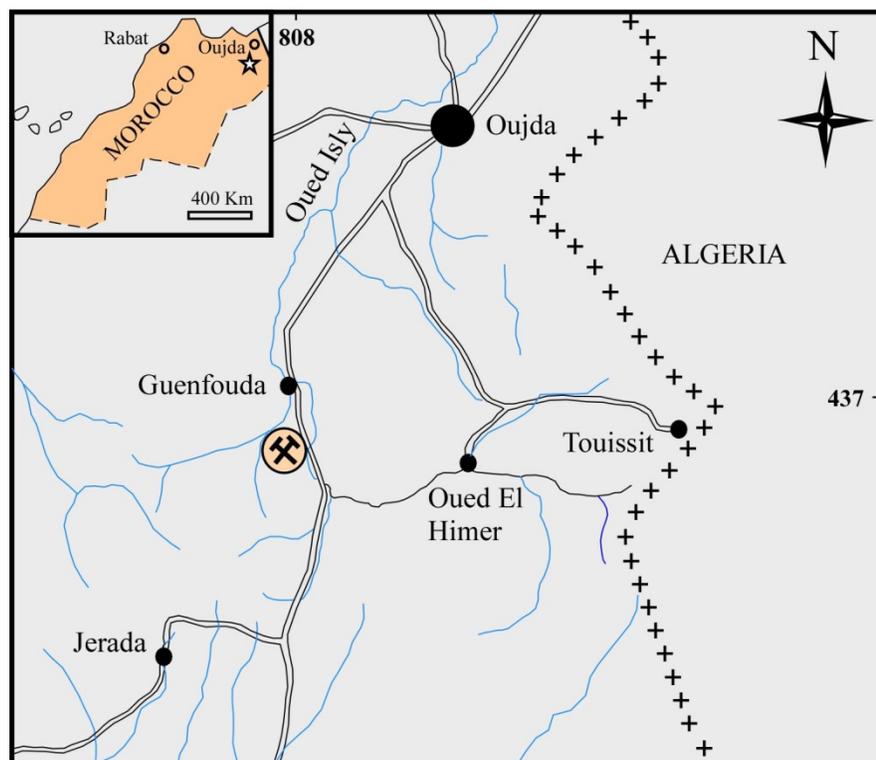
Keywords: hydrothermal alteration, mineral zoning, weathering, Guenfouda, Northeastern Morocco.

1. Introduction

The Guenfouda clay deposit is located on the northern side of the Jerada basin, approximately 36 km southwest of Oujda city and 6 km to the south of Guenfouda village (Fig. 1). It is the unique known fossil hydrothermal clay deposit in northeastern of Morocco and is mined since 2002 by the “Société Marocaine d’Exploitation et de Commercialisation Minière” (S. M. E. C. M) and is currently exploited in open pit and Quarry highwall. The core drilling data indicate that the thickness of clay zone varies from 14 m to 90 m (Hilali and Jeannette, 1981). The total clays reserve in the Guenfouda mine is approximately 2, 2 million tons with current annual production of 24 000 m³ (2000 m³/month) (Hilali and Jeannette, 1981). The major part of the extracted materials is mainly used as raw material in the manufacture of refractories and industrial ceramics.

About this deposit, as it is a mine of regional economic importance in Morocco, it was studied by other authors (Hilali and Jeannette, 1981; Bakkari, 1994), but as yet there have been no detailed mineralogical and geochemical investigations. Thus, this paper focuses on the study in detail the geology, mineralogy and geochemistry, as well as the genesis of this clay deposit developed within the Upper Visean calc-alkaline dacitic lavas flows. Such understanding may provide useful information to guide future exploration of new hydrothermal clay deposits throughout Morocco.

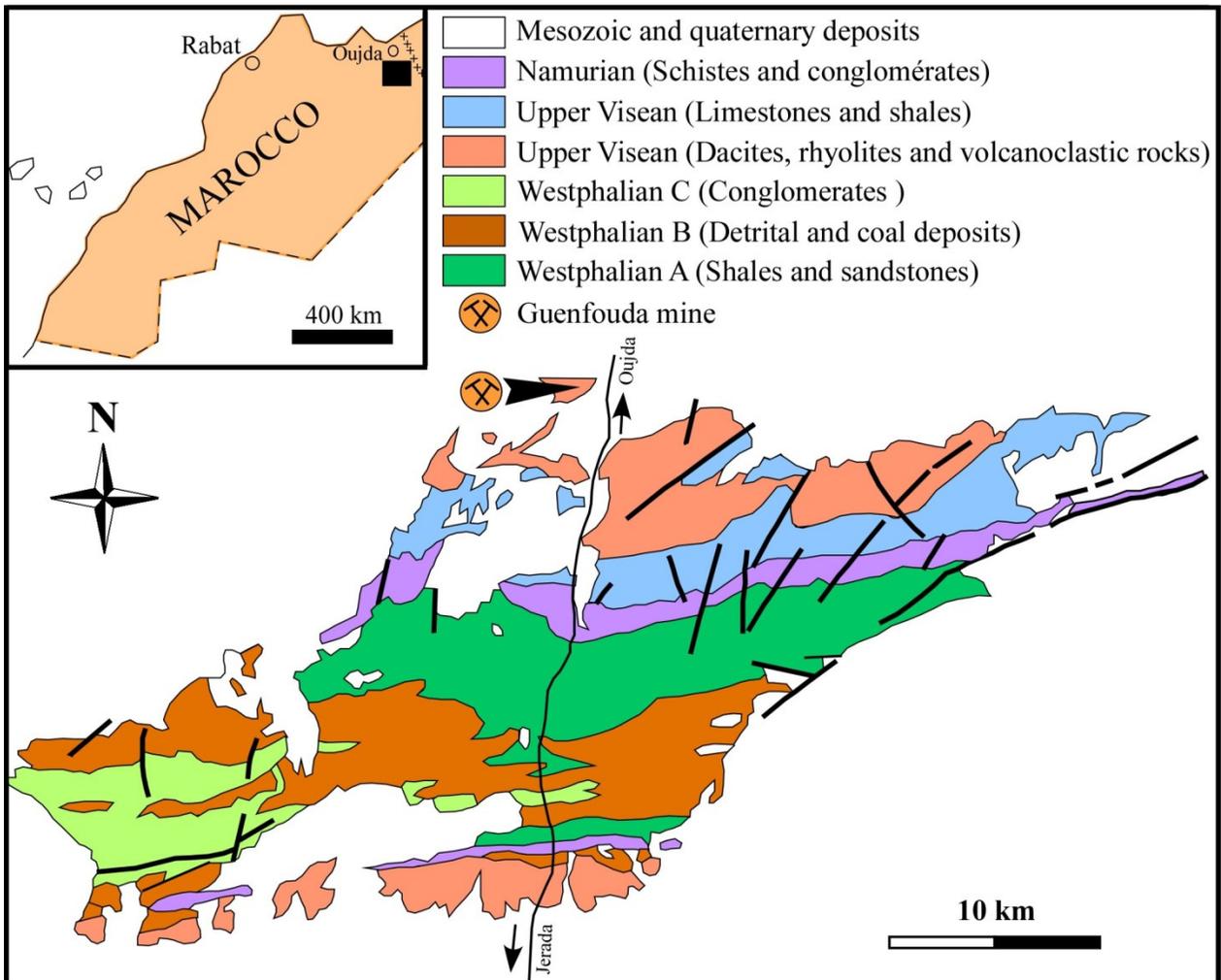
Figure 1: Location map of Guenfouda clay deposit



2. Geological Framework

The regional geology of the study area has been described in detail by Lucas, 1942; Huvelin, 1970; Owodenko, 1976; Kharbouch, 1982, 1994; Desteucq, 1982; Hoepffner, 1987; Chalot-Prat, 1990 and Berkhli et al., 1991. Succintly, the Jerada basin is characterized by paleozoic volcano-metamorphic basement that extend from Visean to Westphalien in which the Upper visean lie unconformably on a chaotic formation that could be assigned a Upper Visean age (Fig. 2) (Huvelin, 1970; Valin, 1979; Hoepffner, 1987; Torbi, 1988). The Upper Visean volcanic rocks at the studied area have been studied by different workers (Kharbouch, 1982, 1994; Kharbouch et al., 1985; Jaillard, 1986) and consist of massive dacitic, andesitic flows and ignimbritic tuffs witch evolve to rhyolites flows and rhyolitic tuffs at the top of the serie. These volcanic and volcanoclastic formations are well exposed at Koudiat El Hamri and Glib en Naam localities, situated to the Est of the study area. This Upper Visean volcanic activity is accompanied by a plutonic and hypovolcanic magmatism giving rise to granite, diorite and granodiorite intrusions (Huvelin, 1983; Chegham, 1985). These Paleozoic basement rocks are unconformably surmounted by triasic and liasic cover formations.

Figure 2: Geological sketch map of Jerada basin (after Valin and Rakkus, 1979)

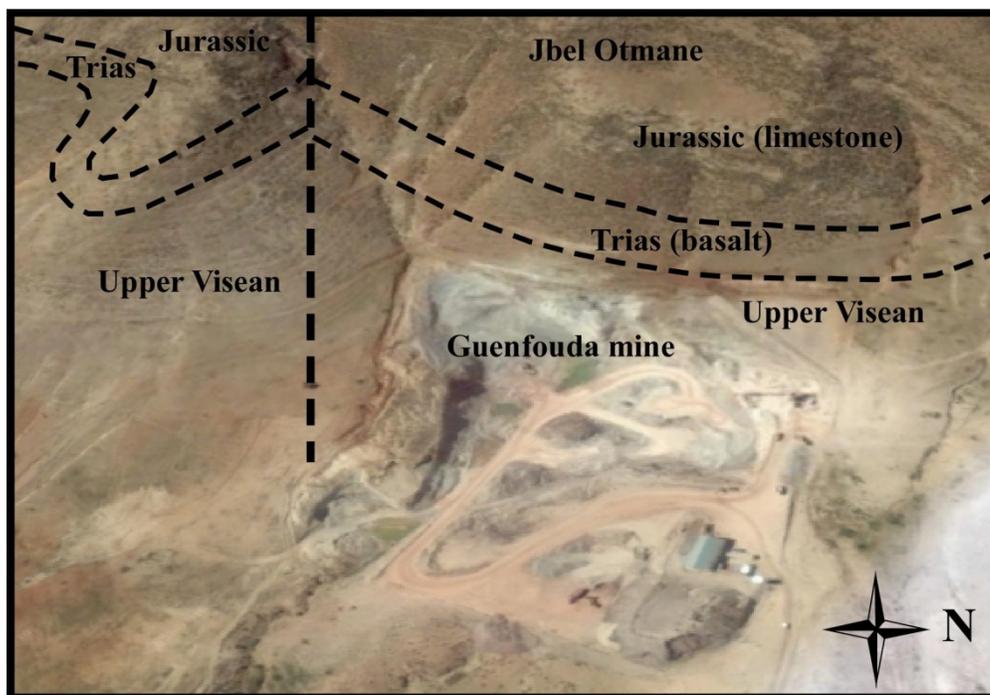


The studied area have undergone the combined effects of the Hercynian (Hoepffner, 1987, Torbi, 1988) and Alpine (Tabyaoui, 2000) orogenies. They give rise to a variety of tectonic structures including folds and associated NE-SW, NW-SE, ENE-WSW to E-W and N-S fractures and strike faults (Tabyaoui, 2000). Within this tectonic regime, it has been found that the sub-equatorial strike

faults have structured the region into horsts and grabens and served as routes of calc-alkaline volcanism and later to hydrothermal fluids (Torbi, 1996).

The Guenfouda clay deposit is exposed on the eastern flank of Jbel Otman (Fig. 3), funnel or trough-like in form and narrowing downwards. It follows a E-W trend controlled by the dextral strike-slip fault that passes through the south of the deposit. According to field investigation, the deposit is about 600 m in length, 300 m in width and drilling data indicate that the thickness of clay zones ranges from 14 to 90 m. In the field the clay deposit exhibits a clear lateral zonation shown on section in Figure 4 and has been actively exploited to supply raw materials to refractories since 2002.

Figure 3: General view of the Guenfouda mine



The Guenfouda mine is petrographically divided into the following four alteration zones in increasing order of alteration: illite alteration zone, pyrophyllite-illite alteration zone, pyrophyllite alteration zone and quartz alteration zone (Fig. 4).

3. Méthodes

Representative rock samples were collected from the host volcanic rocks and different alteration zones along the carry. The petrography of thin sections has been studied using a polarizing microscope.

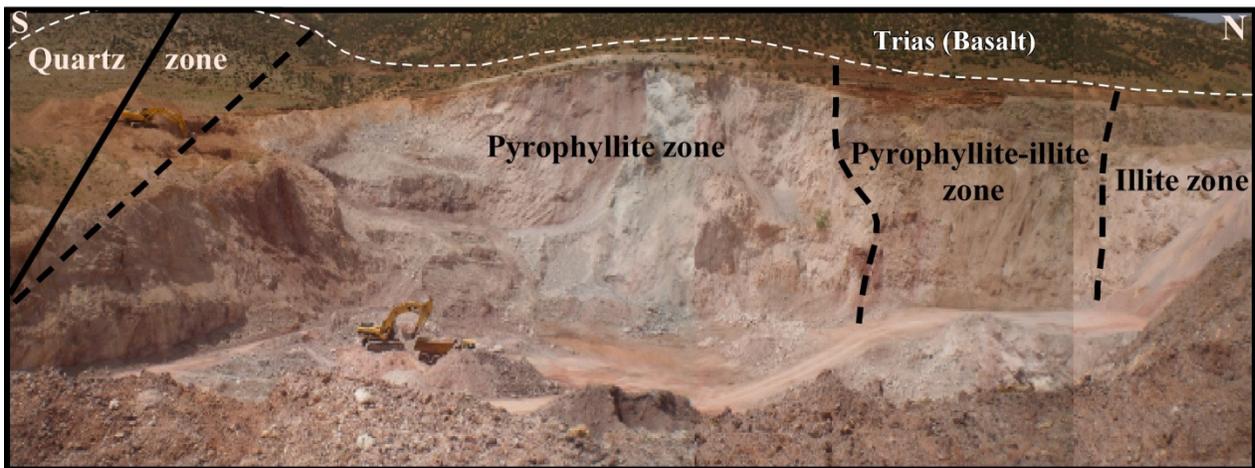
The mineralogical analyses of the representative samples were carried out by X-ray diffraction (XRD). The X-ray diffraction patterns were obtained with a Bruker D8-Avance Eco 1Kw diffractometer (Copper $K\alpha$ radiance, $\alpha = 1.548 \text{ \AA}$, $V = 40 \text{ Kv}$, $I = 25 \text{ mA}$) with LynxeyeXe energy dispersive (one dimensional coupled $2\theta/\theta$ detector with 3.28) in the laboratory of “Argiles, Géochimie et Environnements sédimentaires (AGEs)” at the University of Liège, Belgium. The analyses were carried out on the non-oriented powder with grinded particles $< 250\mu\text{m}$ (bulk material) and the oriented powder $< 2\mu\text{m}$ (clay fraction) according to Moore and Reynolds (1989). Eva software was used for the mineral phase analysis. The semi-quantitative relative abundance of minerals was estimated using the height of a diagnostic peak multiplied by a corrective factor (Cook and al., 1975; Boski and al., 1998) in combination with 100% approach (the term 100% approach connotes that the sum of all phase

quantities identified in a sample is 100% (Kahle et al., 2002) and an estimated uncertainty of +5% - 10% (Biscaye, 1965).

Five selected samples were analyzed for bulk-rock chemical compositions. Major elements were determined by X-ray fluorescence spectroscopy (XRF) using a Spectrometer à Fluorescence X de type « Axion », with dispersion of wave length= 1kW. The concentrations of trace elements were determined by inductively coupled plasma mass spectroscopy (ICP-MS). These chemical analyses were carried out in the Bureau Veritas Mineral Laboratories (Canada).

Representative clay-rich bulk samples were prepared for SEM-EDX analyses and were examined using a JEOL JSM- 5600LV scanning electron microscope (SEM) coupled with an energy dispersive spectrometer (EDS) (Bruker AXS Microanalysis) at Cadi Ayyad University.

Figure 4: General view of the Guenfouda clay quarry with different alteration zones



4. Results

4.1. Petrography

Tin sections investigations show that Guenfouda clay deposit was developed on the dacitic rocks and displays variable mineral assemblages expressed in a clear lateral zonation. From the parent rock southward, four different alteration zones were recognized: (1) illite zone, (2) pyrophyllite-illite zone, (3) pyrophyllite zone and (4) quartz zone. Distribution of alteration zones and mineral assemblages of each zone are described in detail below.

The parent rock is a nearly fresh (or less-altered) dacite that is yellowish on less altered surfaces and pinkish when highly altered. Under the microscope, it consists of porphyritic texture with coarses to medium-grained phenocrysts immersed in a microcrystalline and felsitic matrix (Fig. 6A). Plagioclase phenocrysts (>1cm) are totally altered to sericite. The anhedral to subhedral phenocrysts comprise the quartz (0.5 à 1cm) showing enbayments and alkali feldspath. They are accompanied by squelettal altered amphiboles and anhedral to subhedral iron oxides. The groundmass is dark and contains plagioclase microlaths, quartz and feldspar fragments. The accessory minerals include traces of fine-grained magnetite and prismatic zircon. Quartz-filled vacuoles within the dacite are further evidence of the silicification of the dacite rocks.

4.1.1. Illite Zone

The illite zone has a very limited distribution and defines a zone approximately 15 m wide in the north of the deposit. The rocks of this zone are yellowish (Fig. 5A) and the original textures and minerals are not preserved (Fig. 6B, 6C). Plagioclase crystals are altered, mainly to sericite and illite. Epidote

pseudomorphically replaces the amphibole, sometimes with chlorite or sphene. Saccharoidal quartz is found as patches in the groundmass. Additional accessory phases in this zone are magnetite forming angular grains or irregularly shaped patches.

4.1.2. Pyrophyllite-Illite Zone

The rocks of this zone are typically several meters wide, gray to red in color and characterized by the nearly complete destruction of preexisting texture and minerals. The mineral assemblage is composed of pyrophyllite with variable amounts of illite, kaolinite, quartz, K-feldspar, and traces of magnetite and oxidized pyrite (Fig. 6D). Silicification as small patches was also found in this alteration zone.

4.1.3. Pyrophyllite Zone

The pyrophyllite zone constitutes the largest alteration zone in the Guenfouda clay body, 30 to 40 m in width, and distributes mainly in the southern part of the study area. This zone is generally composed of light-colored fragile argillaceous rocks with hard silicified parts (Fig. 5B). This alteration zone shows complete textural and mineralogical destruction of precursor lithologies. The mineral assemblage consists mainly of pyrophyllite with subordinate kaolinite, illite, zunyite (Fig. 5C), topaz, quartz, K-Feldspar, magnetite, goethite and oxidized pyrites (Fig. 5D, 6E). Diaspore and dickite are noted in this zone of the Guenfouda clay deposit by Hilali and Jeannette (1981). These minerals were not observed during this study but are inferred to be part of the pyrophyllite alteration zone on the basis of descriptions given by these workers.

4.1.4. Quartz Zone

The quartz zone occurs as a band 20 to 30 m thick and occupies the south part of the clay deposit (Fig. 4). It is elongated along the strike of the E-W steeply dipping fault which seems to dip vertically and related to hydrothermal channel ways. The rocks of this zone are hard, compact and can be readily identified in hand specimen due to their siliceous appearance and the white to whitish gray color.

In the quartz zone, alteration is pervasive and largely destroys original volcanic textures. It consists of both residual, acid leached, vuggy porous rocks as well as hydrothermally silicified rocks (Fig. 5E). In addition to abundant silica, the rocks of this zone contain traces of clay minerals (Fig. 6F) and locally native sulphur (pyrite). Goethite is a common alteration material in this zone and occurs as blebs and veinlets that locally completely obscure primary textural and mineralogical relationships. This zone would be mainly formed of excess silica derived from the pyrophyllite alteration zone. Many stockworks of quartz veins (Fig. 5F) are observed in many parts of the body and in the surrounding rocks.

Figure 5: A. a close-up view of the illite zone with massive and yellowish rocks; B. a close-up view of white colored pyrophyllite zone with silicified patches; C. a close-up view of zunyite minerals; D. close-up view of oxidized pyrite; E. a close-up view of vuggy silica; F. a stockwork of quartz veins.

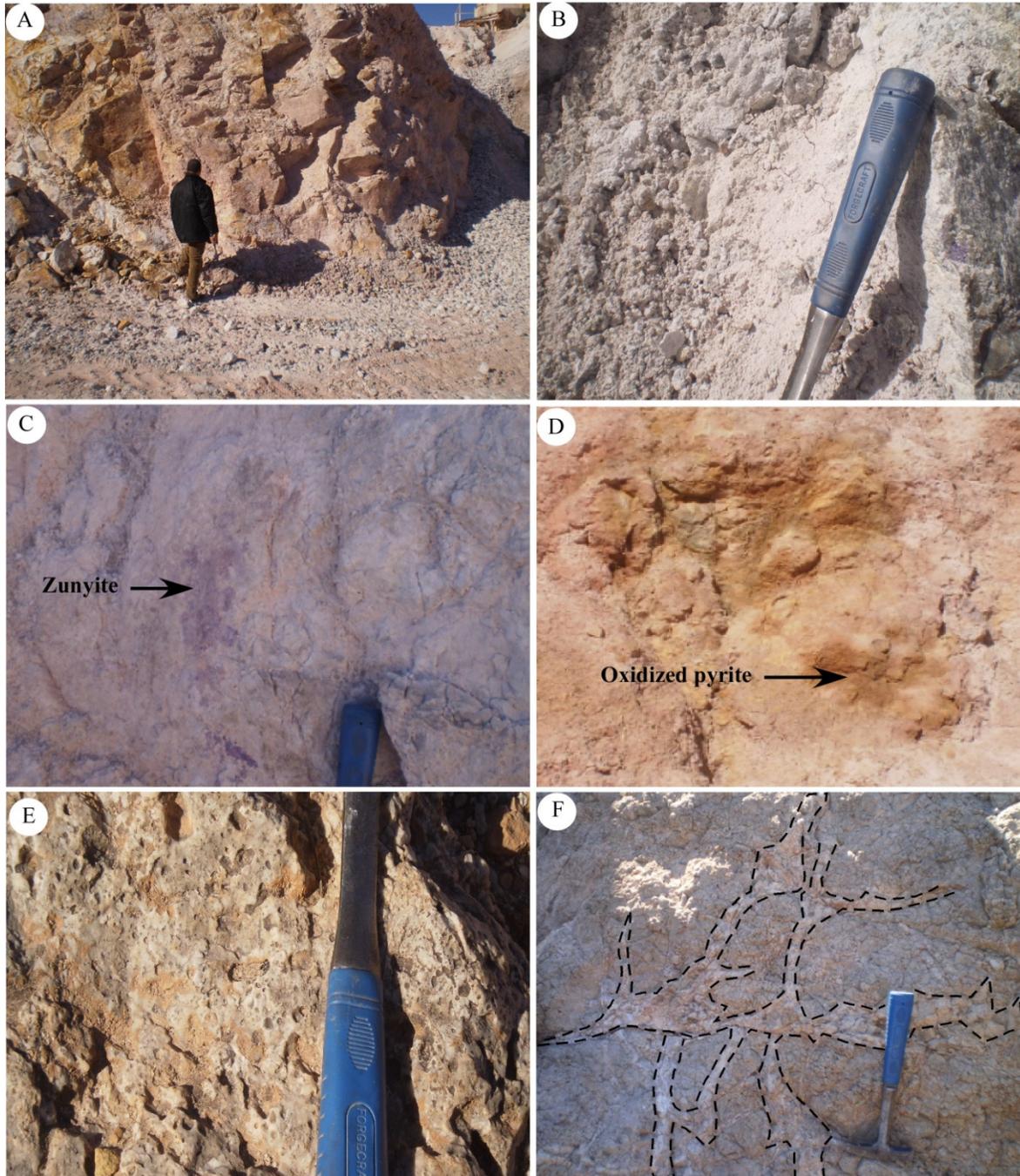
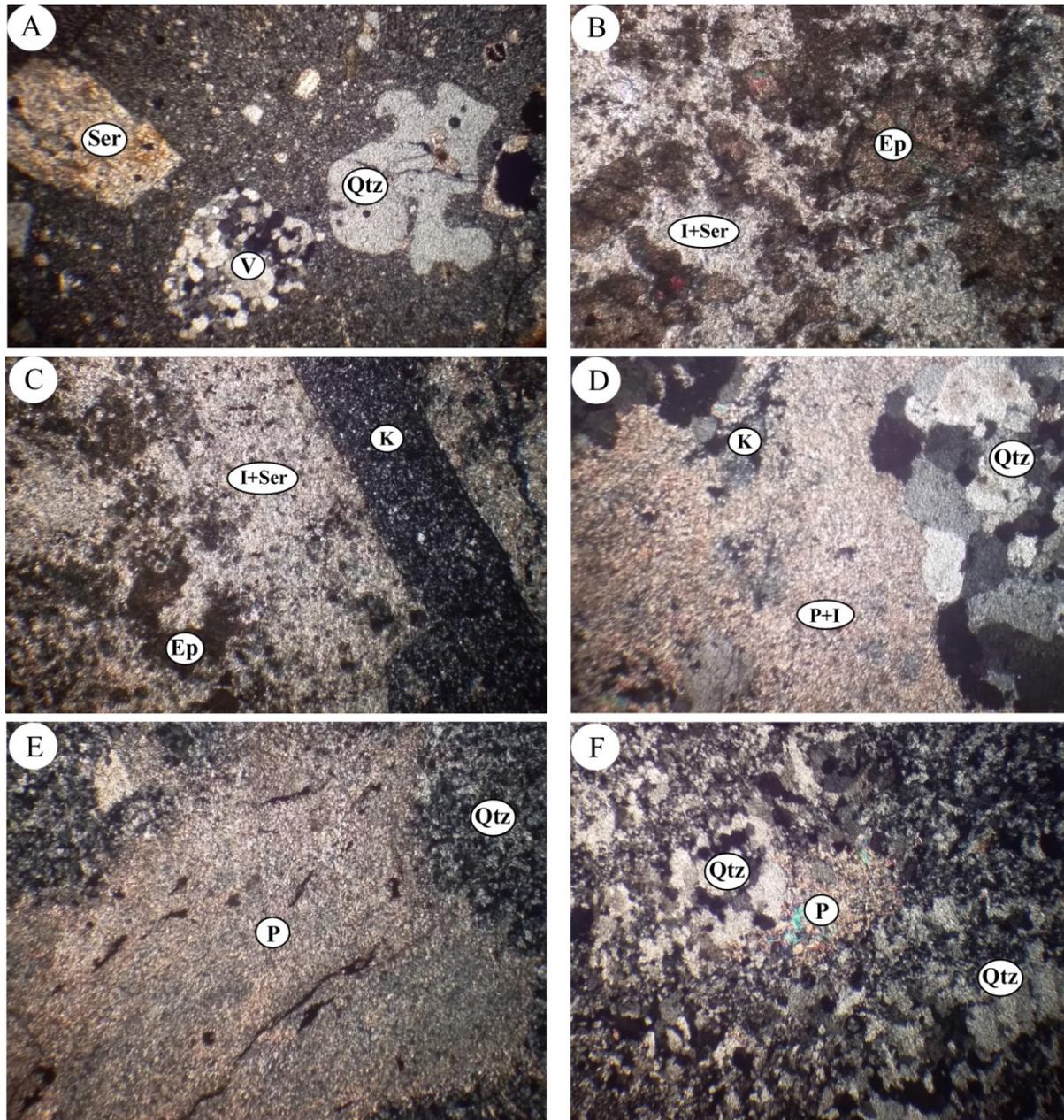


Figure 6: Photomicrographs illustrating the textures and minerals of fresh and altered rocks from the Guenfouda clay deposit. A. view of dacite (host rock) with quartz, vacuole and sericited feldspar; B. Illite zone with epidote and sericite; C. Illite zone with epidote, sericite and kaolinite vein; D. Pyrophyllite-illite zone with silicified patches; E. Pyrophyllite zone with quartz patches; F. view of quartz zone with traces of clay minerals (Qtz= quartz; Ser= sericite; I= illite; Ep= epidote; K= kaolinite and P= pyrophyllite).



4.2. X-Ray Diffraction Data

The X-ray diffraction powder patterns of the Guenfouda alteration zones are illustrated in Fig. 7. The illite alteration zone is mainly composed of clay minerals, feldspar, magnetite, hematite, goethite and quartz. In the pyrophyllite-illite alteration zone clay minerals, feldspar, goethite, magnetite, quartz and hematite can be identified. The characteristic minerals of the pyrophyllite zone are clay minerals, goethite, quartz and traces of feldspar and magnetite can be identified. The diffraction pattern of the quartz zone shows a predominance of quartz and traces of k-feldspar and goethite.

The X-ray diffraction patterns of oriented clay mineral analyses of the alteration zones are illustrated in Fig. 8. The illite alteration zone contains mostly illite as main clay mineral and scarce kaolinite can be identified. In the pyrophyllite-illite zone, these two minerals are the exclusive clay minerals. The pyrophyllite zone contains mostly pyrophyllite as the principal clay mineral, while kaolinite and illite are only observed as accessory minerals. Locally, the pyrophyllite alteration zone also contains topaz and zunyite.

Figure 7: XRD patterns of selected clay samples from the Guenfouda clay deposit (Abbreviations IZ= Illite zone, PIZ= Pyrophyllite-Illite zone, PZ= Pyrophyllite zone, QZ= Quartz zone, I= illite, Py= pyrophyllite, K= kaolinite, Q= quartz, KF= K- feldspar, Pl= Plagioclase, AT= Total clay, Go= goethite, Mg= magnetite, He= Hematite, Ha= Halite)

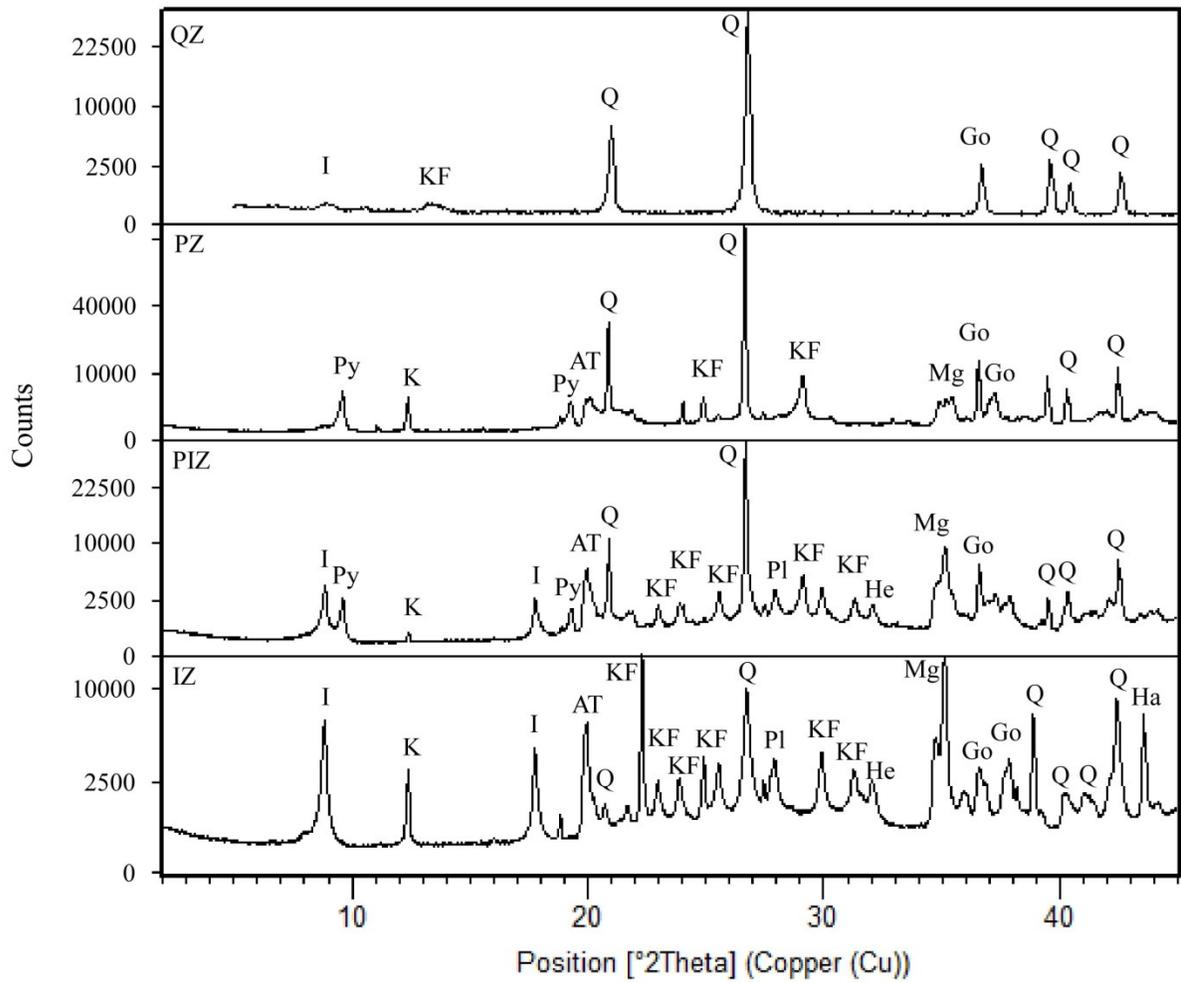
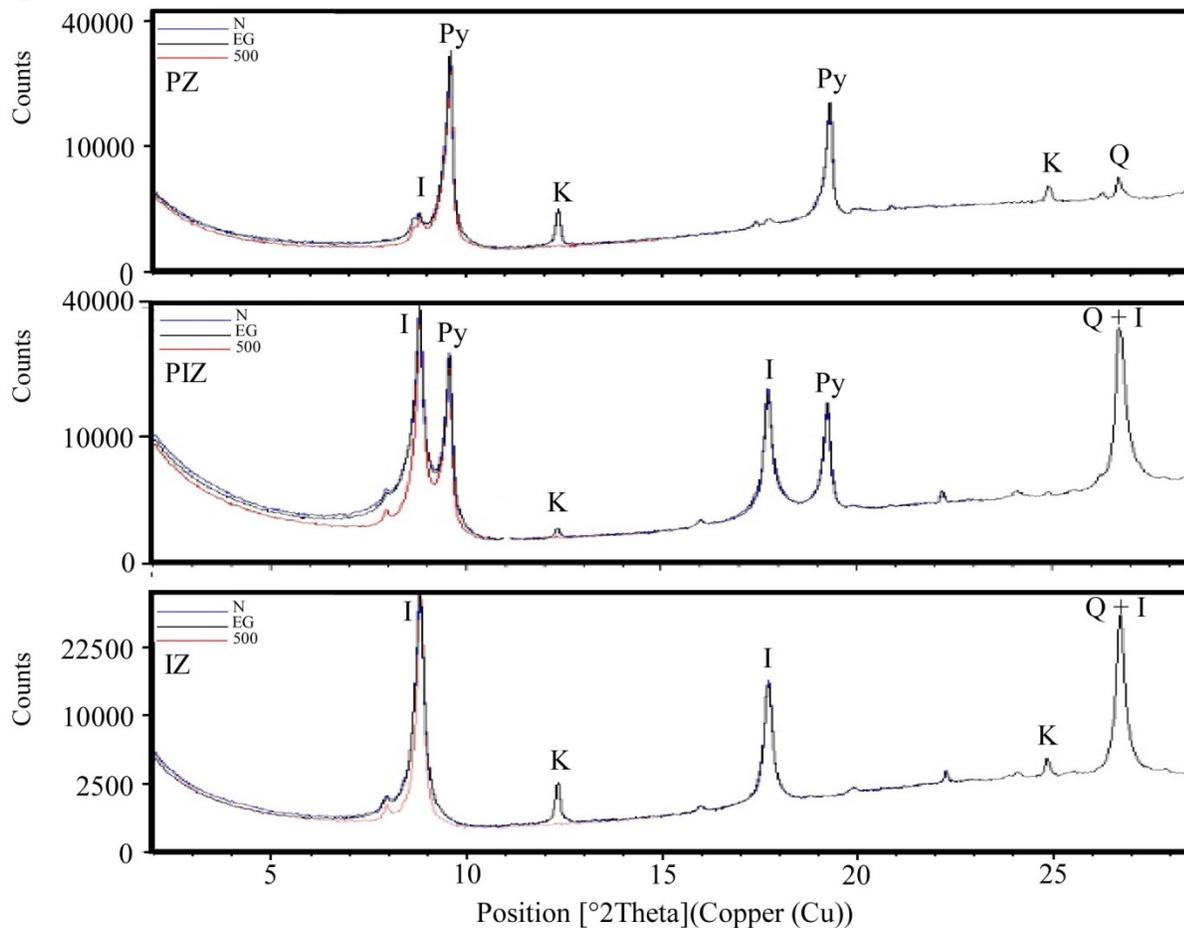


Figure 8: X-ray diffraction patterns of oriented aggregate in each alteration zone of Guenfouda clay deposit. (IZ= Illite zone, PIZ= Pyrophyllite-illite zone, PZ= Pyrophyllite zone, I = Illite, Py= Pyrophyllite, K = kaolinite, Q = Quartz).



4.3. Geochemistry

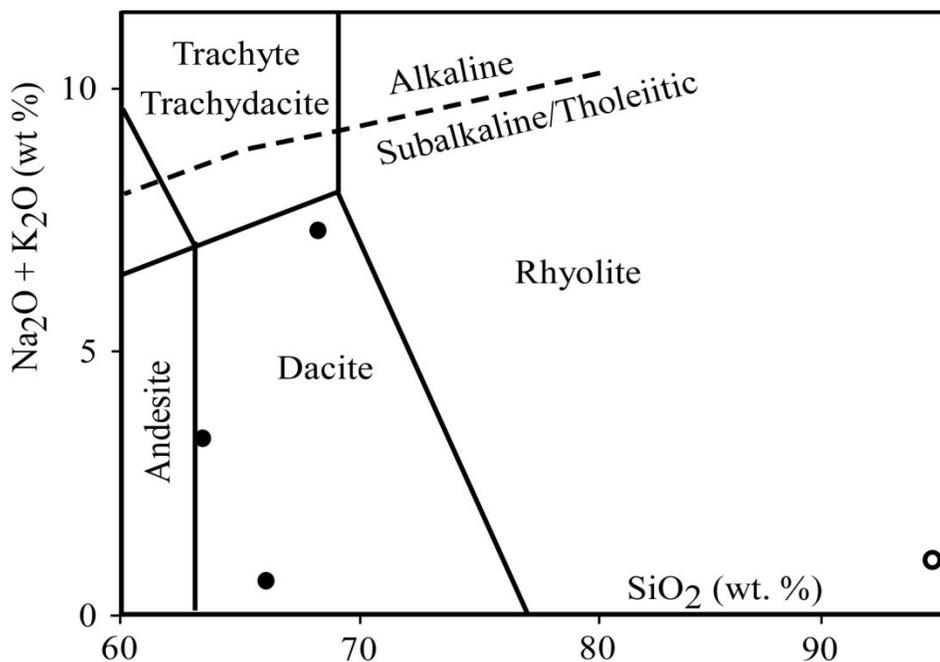
4.3.1. Major Elements

The results of representative chemical analyses of host and altered rocks are listed in Table 1. The rocks of Guenfouda clay deposit are hydrothermally altered as manifested by loss on ignition (LOI) values higher than 3% (Table 1). According to the TAS binary diagram (total silica vs alkali content) of Le Bas et al. (1986), the fresh, partially and highly altered samples plot mainly in the dacite field (Fig. 9). The marked compositional variations are shown according to the alteration zone (Fig. 10). Particularly, the concentration of SiO₂ and Al₂O₃ are exceedingly enriched in the quartz and pyrophyllite zones, respectively. The other major elements such as Fe₂O₃, TiO₂, Na₂O, K₂O and MgO are generally depleted in most of the alteration zones. Hydrothermal alteration which caused the loss of these oxides is the result of the acid dissolution of all the primary rock forming minerals except quartz (Stroffregen, 1987; Hedenquist et al, 1994).

Table 1: Major and trace elements concentrations of fresh, partially and highly altered volcanic rocks of the study area (HR: host rock, IZ: illite zone, PIZ: pyrophyllite-illite zone, PZ: pyrophyllite zone and QZ: quartz zone).

	HR	IZ	PIZ	PZ	QZ
SiO ₂	68.70	63.40	62.80	41.00	95.00
Al ₂ O ₃	14.30	23.10	24.30	46.30	2.86
MgO	1.62	0.26	0.63	1.28	0.48
Fe ₂ O ₃	4.40	3.66	3.73	3.50	0.10
CaO	2.50	0.07	0.08	0.14	0.15
Na ₂ O	4.25	0.52	0.53	0.18	0.18
K ₂ O	3.11	2.12	2.55	1.11	0.20
TiO ₂	0.47	0.15	0.21	0.70	0.23
P ₂ O ₅	0.10	0.11	0.07	0.03	0.06
SO ₃	0.15	0.25	0.24	0.06	0.06
LOI	1.39	3.74	3.31	4.61	0.60
Total	100.74	99.92	98.47	98.94	99.92
A. I	39.27	44.40	81.10	88.65	82.06
CIW	55.35	96.78	91.57	98.78	81.91
Rb	91.00	135.50	97.90	7.00	1.00
Sr	154.00	59.00	15.00	422	3.00
Cs	1.36	4.10	3.00	1.43	0.44
Ba	459.00	326.00	165.00	25.00	14.00
Sc	17.40	1.80	2.10	3.20	0.50
V	ND	11.00	9.00	16.00	0.80
Cr	3.00	3.00	2.00	3.00	0.90
Co	8.70	0.30	0.19	0.17	0.18
Ni	4.00	0.20	0.20	0.20	0.09
Zr	175	53.2	83.3	108.7	15.20
Y	23.00	0.40	1.50	3.00	0.90
Nb	13.60	2.21	0.72	1.43	0.44
Hf	3.00	1.57	2.41	3.00	0.43
Th	10.60	0.40	0.80	12.10	0.30
Ta	0.85	59.00	15.00	422.00	3.00
U	2.25	0.40	0.60	1.00	0.20

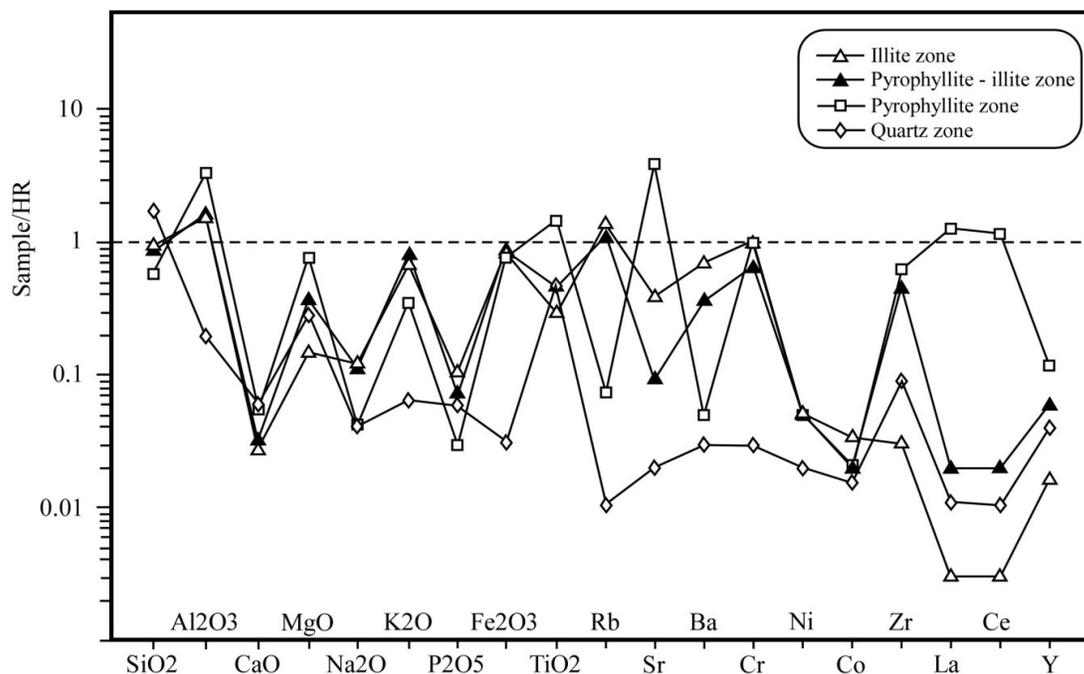
Figure 9: Classification of the volcanic rocks from the Guenfouda mine in the TAS diagram (Le Bas et al., 1986)



4.3.2. Trace Elements

In terms of trace element behavior (Table. 1), Fig. 10 shows a simplified graphical method to evaluate chemical mobility during alteration. All alteration zones have generally low contents of Ba, Ni, Cr, Co, Zr, and Y which have been depleted and moved out by the fluids.

Figure 10: The multi-element pattern of Guenfouda clay deposit, normalized with the less altered rock (HR)



Strontium and rubidium show opposite behaviors (Fig. 10). Content of Sr in the pyrophyllite-illite zone is 15 ppm which is significantly lower than in the parent rock (154 ppm). Its behavior is linked to that of calcium – they are both depleted and become mobile during the alteration of plagioclase. High increasing of Sr concentration (422 ppm) is seen in the pyrophyllite zone. It is almost totally depleted from the quartz zone where it reaches barely 3 ppm.

Rubidium behaves differently of Sr (Fig. 10). Its concentration increases in the illite zone (135 ppm) and decreases in pyrophyllite-illite zone (98 ppm) and especially in pyrophyllite zone (7 ppm). It is almost totally depleted from the quartz zone (1 ppm).

The Rb/Sr ratio is 0.59 in parent rocks; it increases up to 2.29 in the illite alteration zone, having highest values in the pyrophyllite-illite zone (6.52) and then strongly decreases in the pyrophyllite alteration zone (0.01).

REE concentrations obtained for the Guenfouda clay deposit (Table 2) reveal distinct differences in the REE distribution between the different alteration zones. The chondrite-normalized REE patterns (McDonough and Sun, 1989) of different alteration zones are shown in Fig. 11. The host rock pattern (Fig. 11) is characteristic for island-arc subduction-related magmas (Pearce, 1982; Kharbouch, 1994). It shows a smooth, light REE-enriched pattern ($(La/Yb)_N$ of 9.91) with no Eu and Ce anomalies, which are characteristic of residual or meteoric deposits (Cravero et al., 2001). However, the REE pattern of the pyrophyllite alteration zone shows slight enrichment of LREE over HREE, expressed as the chondrite-normalized ratio $(La/Yb)_N$ of 35.84 which is upper than that of the unaltered rocks (9.91).

Table 2: Rare earth elements (ppm) compositions of fresh, partially and highly altered volcanic rocks of the study area (HR: host rock, IZ: illite zone, PIZ: pyrophyllite-illite zone, PZ: pyrophyllite zone and QZ: quartz zone)

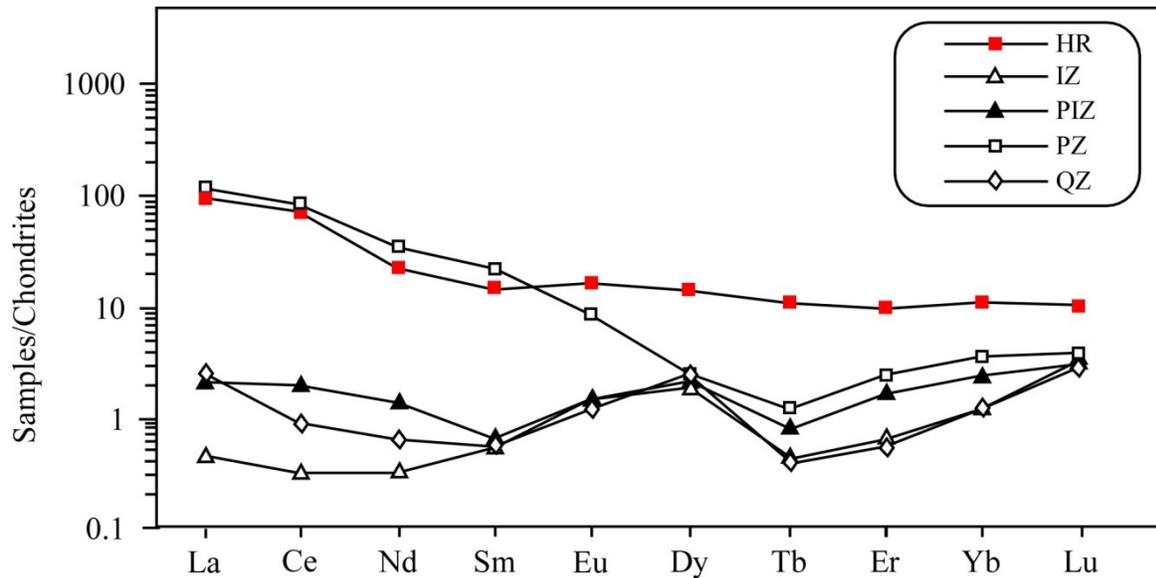
	HR	IZ	PIZ	PZ	QZ
La	23.5	0.09	0.50	29.9	0.30
Ce	45.20	0.13	1.23	52.33	0.57
Nd	17.10	0.10	0.70	16.60	0.30
Sm	3.16	0.08	0.10	2.40	0.08
Eu	0.99	0.07	0.09	0.50	0.07
Tb	0.58	0.07	0.08	0.09	0.09
Dy	2.70	0.08	0.20	0.30	0.10
Er	1.60	0.10	0.30	0.40	0.09
Yb	1.70	0.20	0.40	0.60	0.20
Lu	0.25	0.09	0.08	0.10	0.08
Σ REE	97.12	2.44	14.23	103.58	2.24
Σ LREE	90.03	0.57	8.12	101.82	1.41
Σ HREE	7.09	1.87	16.11	1.76	0.83
La/Yb	13.82	0.45	1.25	49.83	1.50
$(La/Yb)_N$	9.91	0.32	0.89	35.84	1.07
$(La/Sm)_N$	4.80	0.73	2.23	8.04	2.42
$(Tb/Yb)_N$	1.55	1.59	0.08	0.68	2.05
$(La/Lu)_N$	10.07	0.10	0.66	32.10	0.40

On the other hand, the illite, pyrophyllite - illite and quartz alteration zones are characterized by very low REE (1.01 – 3.68 ppm) (Tabl. 2), with $(La/Yb)_N$ ratios (0.31 - 1.07) far lower than those of the host rocks.

The $(La/Lu)_N$ ratios of the Guenfouda clay deposit range from 0.1 to 32.10 (Table 2). This variation is, apparently, connected with greater absorption of Lu relative to La under acidic environment (Fulignati et al. 1999). Similarly, $(La/Lu)_N$ ratios in the pyrophyllite alteration zone greater than 1 ($(La/Lu)_N = 32.6$) unveil that alteration processes were the result of fluids of low pH and

low concentrations of carbonate species, or hydroxyl and halogens (Bau 1991; Bau & Moller 1992; Kadir & Erkoyun 2013).

Figure 11: Chondrite-normalized REE distribution patterns (values from McDonough and Sun, 1989) of fresh, partially and highly altered volcanic rocks of the study area (HR: host rock, IZ: illite zone, PIZ: pyrophyllite-illite zone, PZ: pyrophyllite zone and QZ: quartz zone).



4.3.3. Alteration Indices

Chemical alteration and weathering indices are commonly used for characterizing and quantitatively estimate the weathering state of the rocks. In our study, two chemical weathering indices were calculated using major element oxides chemistry that gives the mass percentage of oxides based on the arithmetic equations according to the relationships:

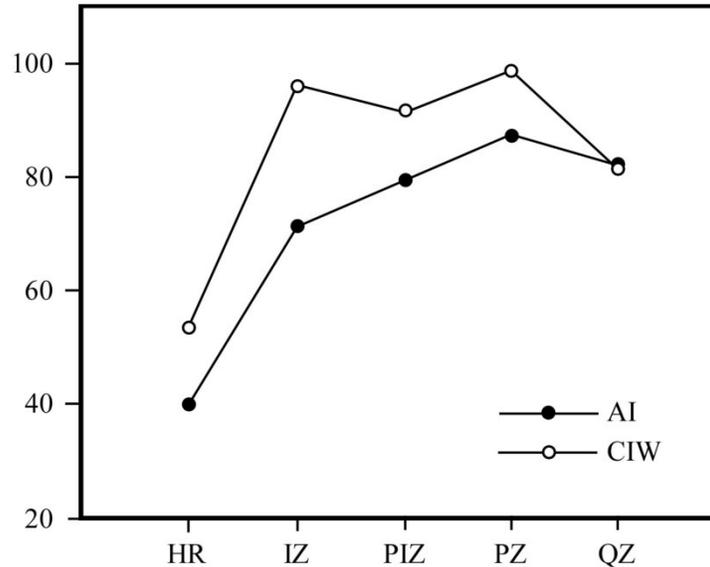
- Weathering indice (Harnois, 1988):

$$CIW = [Al_2O_3 / (Al_2O_3 + CaO + Na_2O)] \times 100$$
- Hydrothermal alteration indice (Ishikawa and al., 1976):

$$AI = (MgO + K_2O) / (MgO + K_2O + CaO + Na_2O) \times 100$$

The results show that AI and CIW indices values increase from the weakly altered host rock towards the pyrophyllite alteration zone (Fig. 12) and indicate that the both processes have combined efforts in Guenfouda clay deposit genesis.

Figure 12: Variation of the Chemical Index of Weathering (CIW) (Harnois, 1988) and the Alteration Index (AI) (Ishikawa, 1976) of the rocks in each alteration zone of Guenfouda clay deposit. (HR= Host rock, IZ= Illite zone, PIZ= Pyrophyllite-illite zone, PZ= Pyrophyllite zone, QZ= Quartz zone)



4.4. SEM/EDX Analysis

SEM images of the Guenfouda clay samples and the corresponding EDX spectra of the illite alteration zone are shown in Fig. 13. The SEM image (Fig. 13A) shows that the illite consists of crumbled plates with undefined outlines that develop on the K-feldspar. The EDX pattern (Fig. 13B) shows the elemental composition of typical illite where Al, Si and K are the main constituents.

In the pyrophyllite alteration zone the pyrophyllite shows large flat crystals, some book-like structures and also fibrous forms in lower proportions in the SEM examination (Fig. 14). Analysis by energy dispersive X-rays show a proportion of silicon and aluminum corresponding to a typical pyrophyllite mineral (Fig. 14).

Figure 13A: SEM microphotograph of illites (I) composed of numerous crystals developed on K-feldspar mineral (KF)

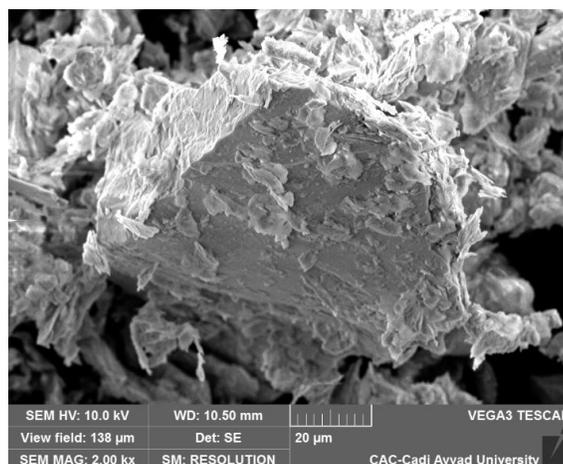


Figure 13B: SEM-EDX of illite (scale marker 10 μ m).

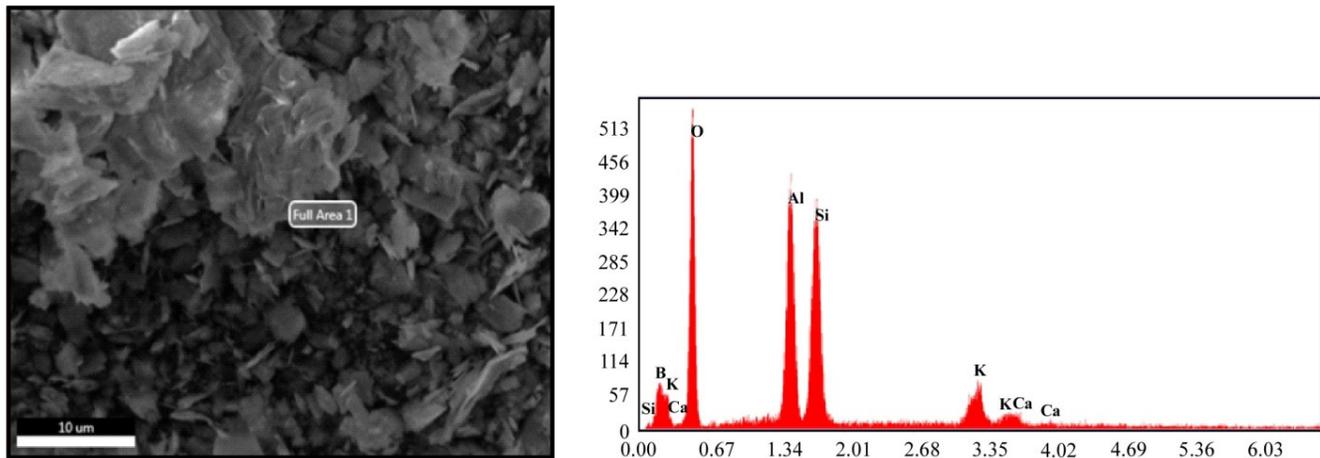
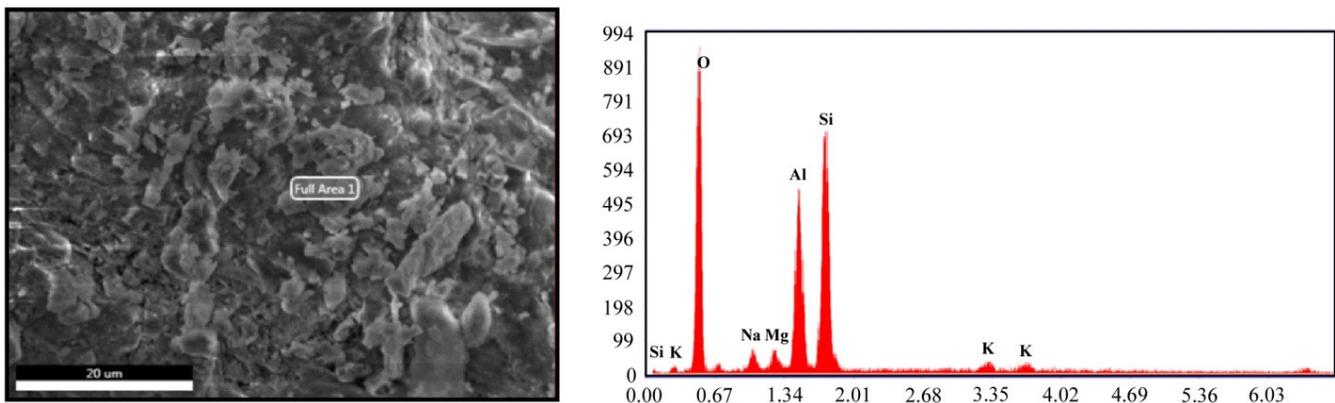


Figure 14: SEM-EDX of pyrophyllite (scale marker 20 μ m)



5. Discussion

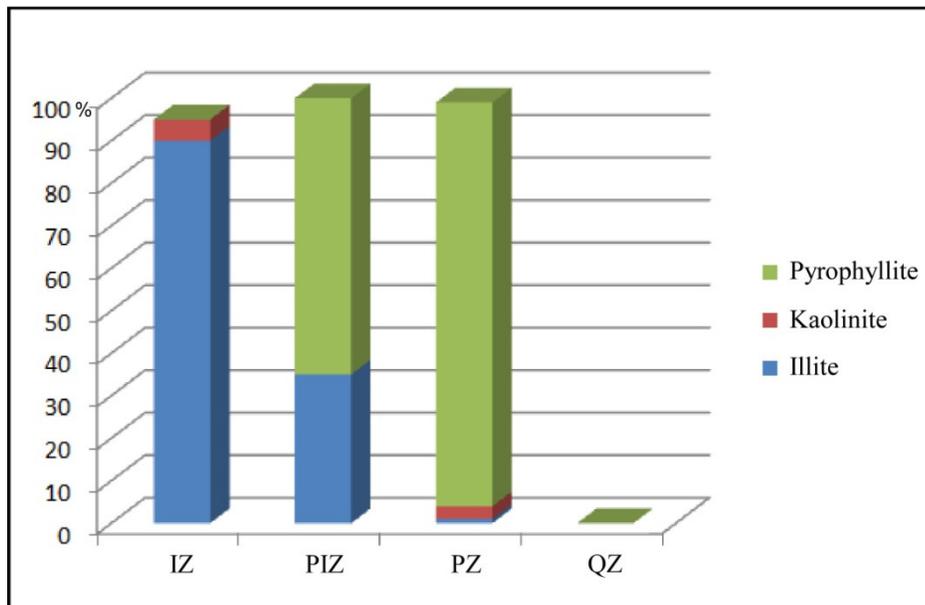
The Guenfouda clay deposit is developed within the Upper Visean dacitic lavas flows and under the control of an east-west strike-slip fault. The distribution of alteration mineral assemblages in this area reveal a clear lateral zonation which evolved, with decreasing alteration degree, from quartz zone in the south part through pyrophyllite and pyrophyllite – illite zones to illite zone in the north periphery of the deposit.

The genesis of these various zones depends not only on the temperature and composition of the hydrothermal fluids but also on the distance of the rock from the fault or the channel of the ascending hydrothermal fluids. So, the quartz zone which coincides with the fault zone is characterized mainly by vuggy silica and interpreted to be the result of extreme acid magmatic fluids (Stoffregen, 1987). Its formation needs the fluids of at least pH < 2 and a temperature of ~300°C (Stoffregen, 1987) to leach all the minerals from the volcanic hosts except quartz. According to Bogie and Lawless (1999) and Proffett (2003), the silicification can occur over a wide range of temperatures, from 300° to 360°C, where pyrophyllite is stable.

As reported in Fig. 15, the mineralogical study of the fine fraction showed that clay minerals cortège changes laterally with increasing distance from the fault zone that coincides with the quartz zone. The pyrophyllite alteration zone is identified by the presence of pyrophyllite, diaspore and dickite. Kaolinite, illite, zunyite, topaz and pyrite occur in minor amounts. This type of paragenesis has also been reported in others active geothermal systems e. g. Southern Negros (Reyes, 1984), Otake

(Hayashi, 1973), Matsukawa (Sumi, 1968) and Thames-Tapu area (Merchant, 1978). Rye et al. (1992) consider the presence of zunyite and pyrophyllite minerals as characteristic of acid sulphate alteration that took place in magmatic hydrothermal environments. According to Hsu (1985), the formation of zunyite necessitates both F and Cl and yet higher F activities destabilize it. Based on isotopic and microthermometric data, Watanabe and al. (1997) reported formation temperatures of 260 to 350°C for an assemblage of zunyite + topaz + diaspore + pyrophyllite in the Kobui area of Hokkaido (Japan).

Figure 15: Distribution histogram of clay minerals in the different alteration zones of the Guenfouda clay deposit



The geochemical data of fresh and altered rocks samples clearly indicate that the contents of SiO_2 and Al_2O_3 are exceedingly enriched in the quartz and pyrophyllite zones, respectively. Al_2O_3 is considered to be more easily dissolved in the extremely acidic solutions ($\text{pH} < 4$), whereas SiO_2 is relatively insoluble (Inoue, 1993). The addition of Silica to the hydrothermal solutions causes alteration of feldspar to clay. This type of alteration by extremely acidic solutions has also been reported in many hydrothermal systems related to sulfur deposits (Inoue, 1993). The other major elements such as CaO, MgO, Na₂O and K₂O are generally depleted in most of the alteration zones. Such removal may point to feldspar alteration and is connected to the high-temperature acid solution potential to leach most rock-forming elements which are formed mineral assemblages in the parent rock. Decomposition of ferromagnesian minerals caused the extraction of Mg, Mn from the system (Arslan et al. 2006).

The trace elements of Guenfouda alteration zones are partially depleted or enriched relative to the host rock and exhibit similar patterns, suggesting that they all originated from same source rock. Compared to the parent rocks, the trace elements are partially depleted in all zones, except, Sr which is enriched in the pyrophyllite zone and Rb in the illite alteration zone. The enrichment of strontium is a characteristic feature of the advanced argillic alteration in volcanic rocks (Hikov, 2002). Such strontium behavior has been reported in other hydrothermal deposits as well (Pirajno, 1995; Huston & Kamprad, 2000; Karakaya & Karakaya, 2001). Rb, in contrary to Sr, concentrates in illite zone and decreases in the pyrophyllite zone. Similarly, Rb/Sr ratio increase 4 to 11 times in the illite and pyrophyllite - illite alteration zones respectively. The highest value (6.52) is found in pyrophyllite – illite zone while in pyrophyllite zone Rb/Sr values are very low (0, 01). This anomalously low Rb/Sr value is characteristic of advanced argillic alteration zones and has been reported in many advanced argillic alteration systems (Hikov, 2004).

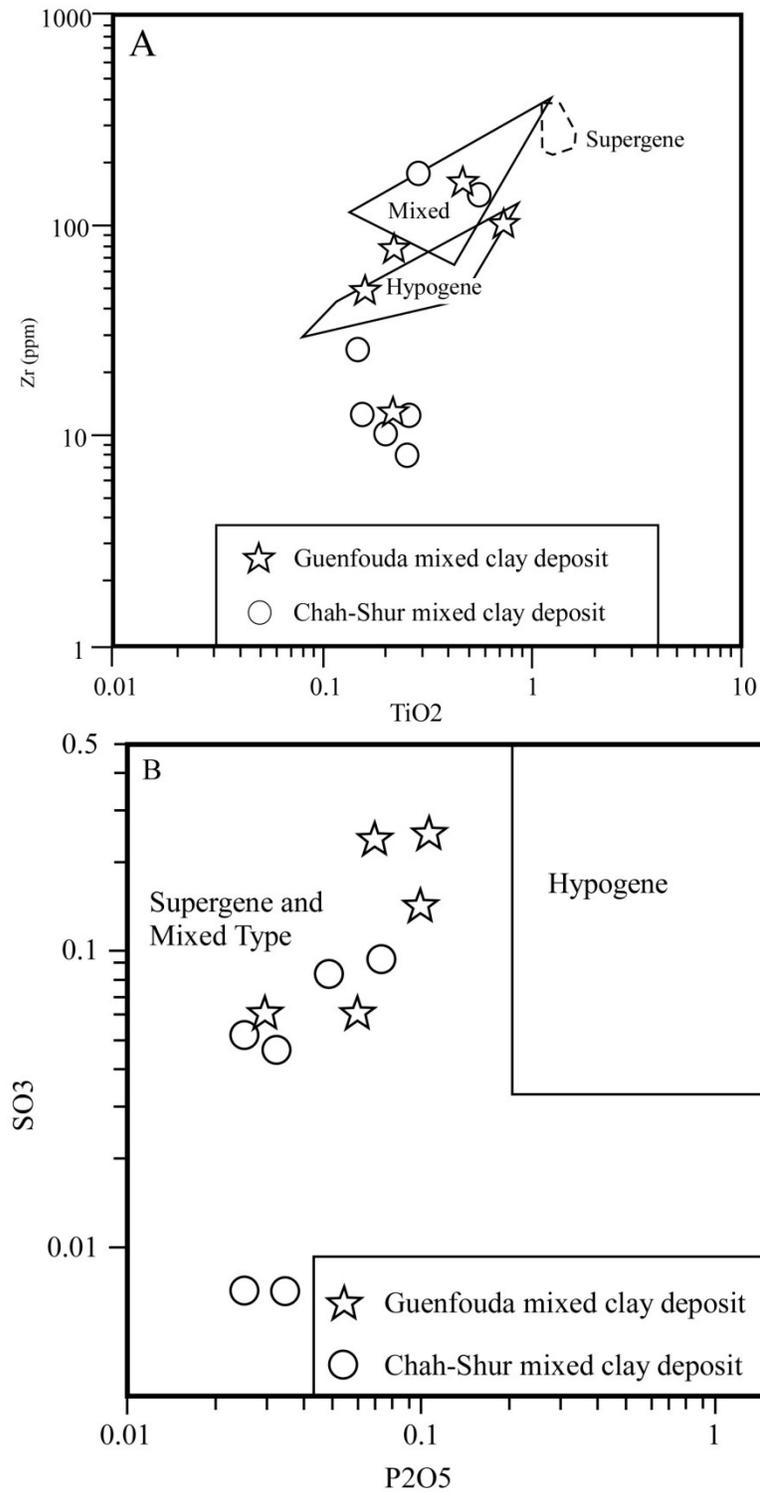
When the Guenfouda traces elements are plotted in the graphical style of Dill et al. (1997, 2000), for the distinction between hypogenic and supergenic origin, it has been found that some of the relationships are not as clear as in their work, except for SO₃ vs. P₂O₃ and Zr vs TiO₂ diagrams. The last two plots (Fig. 16) point towards a mixed origin for the Guenfouda clay deposit. The same origin has been reported in the Chah-Shur clay deposit, Southeast of Isfahan (Iran) (Khodami and Shervedani, 2018).

The REE pattern of the pyrophyllite alteration zone shows slight enrichment of LREE in relation to the host rocks with a strong depletion of MREE and HREE (Fig. 11). The enrichment of LREE over HREE, expressed as the chondrite-normalized ratio (La/Yb)_{ch} of 35.84 in the altered samples, and is higher than that of the unaltered rocks (9.91). Such behavior has been described in other high-sulphidation and porphyry copper systems (Arribas et al. 1995; Fulignati et al. 1999; Khashgerel et al. 2008; Parsapoor et al. 2009; Georgieva et al. 2012) and considered as characteristic for advanced argillic alteration and high-sulphidation style epithermal environment. The leaching of MREE and HREE and comparatively inert behaviour of LREE is connected with the high activity of F⁻, low pH of the fluids, high water/rock ratios, and their ability to form stable complexes in these conditions (Schneider et al., 1988; Fulignati et al., 1999). Furthermore, the La/Lu ratio > 1 implies that argillization occurred in low pH waters with low concentrations of hydroxyl or carbonate species and halogens (Bau 1991; Bau & Moller 1992).

The REE in the quartz, illite and pyrophyllite – illite alteration zones are strongly depleted. This depletion has been observed in other ore deposits like OK Tedi (Van Dongen et al. 2010). Such REE mobility during hydrothermal and supergene alteration was noted by Palacios et al. (1986), Torres-Alvarado et al. (2007) and Van Dongen et al. (2010). It could be explained by the extremely low pH environment (Fulignati et al., 1999) and high activity of Cl⁻ and F⁻ in the hydrothermal solutions (Michard, 1989; Wood, 1990; Lottermoser, 1992; Lewis and al., 1997). High concentrations of F and/or Cl in the studied deposit are registered by the presence of F⁻ and Cl⁻ bearing minerals such as zunyite and/or topaz.

For the distinction between hypogene and supergene origin of the studied deposit, the mineral assemblage, the alteration zonation pattern, the enrichment of LREE relative to HREE, particularly in the pyrophyllite zone and the strong enrichment of Al and Sr are the most important features confirming the hypogene origin of the Guenfouda clay deposit. However, the distribution of the studied samples in the Zr vs. TiO₂ and SO₃ vs. P₂O₅ diagrams (Fig. 16) and the chemical indexes indicate a mixed type. The last was first controlled by the east-west strike-slip faults, which brought ascending hydrothermal solutions that led to clay formation, and finally, the weathering processes have continued and extended the argillization.

Figure 16: Binary diagrams discriminating hypogene versus supergene genesis of clay deposits (after Dill et al., 1997 and 2000). A: Zr vs. TiO₂, B: SO₃ vs. P₂O₅



Conclusions

Alteration geology, mineralogy, geochemistry and alteration indexes studies of the Guenfouda clay deposit reveals following findings:

- 1) The Guenfouda clay deposit had been created from the decomposition of the Upper Visean calc-alkaline dacite. It is funnel or trough-like in form, narrowing downwards and follows a E-W trend controlled by a dextral strike-slip fault. The last have channeled the regional volcanic and hydrothermal activities.
- 2) The alteration minerals distribution exhibit a marked lateral zoning and shows a decreasing alteration degree from south to north: Quartz zone → Pyrophyllite zone → Pyrophyllite - illite zone → Illite zone. Such zonation has developed from the progressive cooling and neutralization of hot acidic magmatic fluid with the host rocks.
- 3) The main clay minerals in this deposit consist of illite and pyrophyllite. Kaolinite, dickite, zunyite, diasporite and topaz are present in small variable proportions. The accessory minerals are magnetite, hematite, goethite and pyrite. The pyrophyllite + dickite + diasporite + topaz + zunyite association testifies an acid hydrothermal solution with a temperature estimated between 270 and 350°C.
- 4) Most major and trace elements were mobilized from the original rocks by argillization and silicification processes. The leaching of MREE and HREE in the pyrophyllite zone and the strong depletion of all REEs in the quartz, pyrophyllite-illite and illite alteration zone is connected with the high activity of F⁻, Cl⁻, low pH of the fluids and their ability to form stable complexes in these conditions.
- 5) According to mineralogical and geochemical data, the genesis of Guenfouda clay deposit can be considered as mixed type formed firstly by hydrothermal alteration which generated the clay deposit and subsequently the area was subject to weathering process.

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