**Clay mineralogy and geochemistry of the Lower Pleistocene Loess in the Iranian Loess Plateau (Agh Band section) and implications for its provenance and paleoclimate change**

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**Abstract:** The clay mineralogy and geochemistry of loess is sensitive to variations in sediment source area, transport processes and weathering regime over time, and thus careful study of them can provide some insight into past climate variability. The well-known loess–paleosol sequences (Upper Pleistocene Loess (UPL)) on the Iranian Loess plateau (ILP) are generally underlain by the red deposits consisting of reddish clay to silt-sized sediments of wind-blown origin (Lower Pleistocene Loess (LPL)). Study and analyzing of this oldest brown and reddish brown loess has a specific role in paleoclimate reconstruction but no previous study of the clay mineralogical and geochemical characteristics of them has been performed to date. Therefore, total (Fet) and free iron (Fed) concentrations and Fed / Fet ratios, X-ray diffraction as well as geochemical analysis were carried out on a section near the Agh Band village in northeastern province Golestan. Geochemical analysis revealed the same provenance of all deposits in LPL and similarity of them by UPL. X-ray diffraction detected the kaolinite, smectite, chlorite, illite, vermiculite, mica-vermiculite and mica-smectite minerals in the red deposits. The results demonstrated that detrital input is the main source of kaolinite, chlorite and illite, while pedogenic formation during the early Pleistocene could be the dominant cause of smectite and vermiculite occurrences in the LPL. The presence of smectite and vermiculite is in accordance with the xeric and udic soil moisture regime in UPL, respectively. As such it can be concluded that the climate at the time of Agh Band LPL formation varied from semi-arid to sub-humid climate and wetter and more favorable conditions than the overlying late Pleistocene loess and modern soils. These results are confirmed by Al2O3/Na2O, Na2O/K2O, MgO/TiO2 and Fed/Fet ratios.

**Key words**: clay mineralogy, geochemistry, paleoclimate, Lower Pleistocene loess, Iran

**1. Introduction**

Studies of the type and the relative abundance of clay minerals and geochemical characteristics of loess can provide useful information on paleoclimate. In 2015, on the loess plateau of northern Iran a brown and reddish silt-sized deposit was discovered which dated back to 1.8 -2.4 Ma, namely Lower Pleistocene Loess (LPL). These soils are under the well-known loess–paleosol sequences that formed since late Pleistocene (Upper Pleistocene Loess (UPL)) (Frechen et al., 2009; Wang et al., 2016, 2017). Recently, field observations and grain size analysis carried out by Wang et al. (2016), Taheri et al. (2017) and Wang et al. (2017) have demonstrated that these reddish sequences are comprised of alternations of brownish-red (7.5 YR 3/6) paleosols and reddish-yellow (10 YR 6/6) loess layers. The loess horizons are moderately developed and consist of small carbonate nodules (<2 cm diameter). In comparison, the paleosols are strongly developed and contain large (up to ~20 cm diameter) carbonate concretions and are commonly underlain by carbonate-rich horizons or petrocalcic horizons. Moreover, fine-grained silts are dominant, with an average silt content of 86.5%, and in addition the average sand and clay contents are 2.6% and 10.9%, respectively. Generally, five types of B horizon are recognized in LPL, namely Bt, Btk, Bw, Bkk and Bkkm. These horizons generally have a relatively weak to strong angular or sub-angular blocky structure. Strongly prismatic structures are present in the most developed horizons and these horizons contain few to common clay skins and/or dark iron-manganese coatings. Finally, based on grain-size analysis they concluded that the red deposits are wind-blown in origin, thus extending eolian deposits in the Iranian Loess Plateau (ILP) down to the early Pleistocene. Because these loess-red sequences are the oldest eolian sediments which have been recognized in ILP, this extension provides a good opportunity to reconstruct and understand the long term climate history of this area by using uniform proxy records.

Various proxy records such as grain size (e.g. Ding et al., 1992; Vandenberghe et al., 1997, 2004; Chen et al., 1997, Wang et al., 2017), chemical weathering indexes (e.g. Liu T. S. et al., 1995; Chen et al., 1999; Hao et al., 2010, Taheri et al., 2017), micromorphology (e.g. Gunal and Ransom, 2006; Kühn et al., 2006; Khormali and Ajami, 2011; Khormali et al., 2012, Taheri et al., 2017), and magnetic susceptibility (e.g. Chen et al., 1997, 1999; Vandenberghe et al., 2004; Xie et al., 2016, Wang et al., 2016, Lauer et al., 2017) have been used for examining climate changes recorded in eolian deposits.

Clay minerals that are phyllosilicates, dominantly destruct and form during chemical weathering processes (Chamley, 1989; Gylesjö and Arnold, 2006). The nature of clay mineral accumulation (mineral composition of the clay fraction, <2 μm grain-size) is primarily a function of weathering regime (precipitation and temperature) over time (Nesbitt et al. 1997; Fürsich et al. 2005; Kovács et al. 2013). Consequently, clay mineralogy is regarded to be a powerful tool for interpreting weathering conditions and paleoclimate (Chamley 1989; Ruffell et al. 2002; Sheldon and Tabor 2009, Kovács et al. 2013).

Geochemical characteristics of deposited sediments provide information about their origins and paleoclimate, thus this approach has become a valuable method in eolian provenance research and has been effectively used in study on atmospheric dust sources, deposition processes and reconstruction of past climate (Nakai et al., 1993; Zhang et al., 1993; Liu et al., 1994; Sun, 2002; Nakano et al., 2004; Rao et al., 2006; Qingyu et al., 2008). Although in the weathering process of parent materials and subsequent transport, deposition and soil formation, the geochemistry compositions of certain elements change and the absolute content of some elements (for example Zr, Al, Fe, Mg) and the ratio of some elements such as Ti/Zr, Ti/Al, Nb/Zr do not significantly change and are mainly controlled by the provenance area (Rollinson, 1993). Therefore the amount/ratios of these kind of immobile elements are relevant to tracing sediment source (Taylor and McLennan, 1985; Shao et al., 1998 Chen et al., 2001; Sun, 2002; Qingyu et al., 2008).

Based on the above mentioned remarks and due to having no previous systematic study of the clay mineralogical, geochemical and free and total iron of the LPL, the objectives of the present study are: (1) to find out the variation of clay mineralogical composition in LPL; 2) to study the provenance of LPL and UPL; and (3) to reconstruct the paleoclimate using iron content, clay mineralogical and geochemical (Al2O3/Na2O, Na2O/K2O, MgO/TiO2) characteristics.

2. **Geographical setting**

The study area is a section exposed in a Cenozoic limestone quarry situated near the village of Agh Band in eastern Golestan province, northern Iran (latitude 37.688889° N and longitude 55.158333° E). The top part of the sequence is at 223 m a.s.l. Hence, it is located >200 m above the recent sea level of the Caspian Sea (-26 m). The sequence underlies an UPL sequence and covers the Pliocene limestone of the Akchagyl Formation (Fig. 1). The overlying loess is up to > 60 m thick and subdivided by several paleosols (Lauer et al., 2017) and the Akchagyl Formation is mainly consisted of marl, mudstone and limestones with thicknesses ranging from 3 m to more than 100 m in the Kopet Dagh sedimentary basin (Forte and Cowgill, 2013). The present-day climate of the study area is semi-arid, with a mean annual temperature of about 17°C and with mean annual precipitation of about 300 mm, with more than 85% falling during the boreal winter months. The temperature regime is thermic and the soil moisture regime is xeric border to aridic (SWRI-Soil and Water Research Institute of Iran, 2000; Soil Survey Staff, 2014).

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Fig. 1, Table 1

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**3. Materials and methods**

**3.1. Sampling**

In two field campaigns in autumn 2014 and spring 2015, the morphological characteristics of the Agh Band LPL, a section of around 20 m thickness, were recorded (the section which is studied by Lauer et al. (2017) is located in another place). According to field observations, the sequence has been subdivided into 24 units, designated [continuous](dict://key.25D62D261B9B6943BE86B7DCF8F9D255/continuous)ly as U1-U24 from the top of limestone to the bottom of the UPL (Fig. 1) (Table 1) (Taheri et al., 2017). From each unit, representative bulk samples for laboratory analysis and additional undisturbed samples for micromorphological analysis were taken. One sample was taken from the UPL as well.

**3.2. Laboratory analyses**

**3.2.1. Clay mineralogical analyses**

Prior to clay mineralogical analysis, all of twenty-four representative samples were oven-dried at 105°C. The removal of chemical cementing agents and separation of the clay fractions were done based on methodology outlined by Kittrick and Hope (1963) and Jackson (1975). Samples were grounded and treated with 1N sodium acetate buffered at pH 5 and continued until no effervescence was observed with 1N HCl to remove carbonates. The reaction was performed in a water bath at 80°C. Organic matter was then oxidized by treating the carbonate-free paleosols with 30% H2O2, and digestion in a water bath. Free iron oxides were removed from samples by the citrate dithionate method of Mehra and Jackson (1960). The iron-free samples were centrifuged at 750 rpm for 5.4 minutes and the clay separates were removed by centrifuge and studied by a Philips PW-1830 X-ray diffractometer using Cu Kα radiation, a step size of 0.02° and a time per step of 1 second.

Due to having the same concentration of clay suspensions and giving the reliable comparisons between relative peak intensities, two drops of the prepared suspension were used on each glass slide. X-ray diffractograms were obtained from Mg-saturated soil clays both before and after ethylene glycol treatment. K saturated samples were studied by X-ray diffraction after drying at room temperature and after being heated at 550°C for 4 hrs. The semi-quantitative percentages of the clay minerals were estimated based on Johns et al. (1954), from the relative X-ray peak areas of the glycol-treated samples. XRD patterns were analyzed using Highscore Plus software version 3.0.5 (2012).

**3.2.2. Geochemical analysis**

Twenty-four representative samples from the red-colored strata and one sample from the overlying Upper Pleistocene Loess succession were selected for geochemical analysis. The air-dried samples were firstly treated with 1 mol/l acetic acid (HAc) for about 12 hrs to remove the secondary carbonate content that mostly formed during pedogenic processes without significantly affecting the silicates or iron oxides. After rinsing, the samples were oven-dried at 100 °C for 12 hrs. The concentrations of major and trace elements/oxides (Ba, Co, Hf, Nb, Pb, Sr, Th, Y, Zr, Fe2O3, SiO2, Al2O3, CaO, Na2O, K2O, MgO, MnO) were determined using a PANalytical PW2403/00 X-ray fluorescence spectrometer in the Key Laboratory of Western China`s Environmental systems, Lanzhou University, China.

**3.2.3. Total and free iron measurements**

The free Fe2O3 (Fed) of the 24 samples from LPL and one sample from UPL were determined by the citrate-bicarbonate-dithionite (CBD) method (Mehra and Jackson, 1960) and total Fe2O3 (Fet) measured with PANalytical PW2403/00 X-ray fluorescence spectrometer in the Key Laboratory of Western China`s Environmental systems, Lanzhou University, China.

**4. Results and discussion**

**4.1. Geochemical evidence of LPL and UPL provenance**

The chemically immobile major (e.g. Al and Ti), and trace elements (e.g. Zr and Nb) have great potential for determining the provenance of clastic sediments (Taylor and McLennan, 1985; Bhatia and Crook, 1986; Qingyu et al., 2008; Sheldon and Tabor, 2009, Tazikeh et al., 2017), due to the fact that they maintain invariant ratios during post-depositional chemical weathering. Sun (2002), Guan et al. (2008) and Muhs et al. (2008) successfully used this method in the provenance identification of eolian deposits in various regions. Therefore the ratios of Ti/Zr, Ti/Al and Nb/Zr of the LPL and UPL were analyzed and shown as a function of depth in Fig. 2. In summary, based on each of these measures and because the amount and ratio of these elements are distinctly similar and consistent in all of the LPL units and in the UPL, it can be inferred that not only is the provenance of all deposits in the LPL the same, but that the LPL shares a similar source to the UPL.

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Fig. 2

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**4.2. Clay mineralogy**

The clay mineral compositions of the Agh Band section were determined for the <2 μm size fraction. In general, the major components are mica, kaolinite, chlorite, vermiculite, smectite, mica-vermiculite and mica-smectite which are plotted and listed in Fig. 3 as a function of depth. Peak points acquired from the X-ray diffraction of the clay fraction in the Agh Band LPL show the following variation: mica (43–73 %), vermiculite (0–18 %), kaolinite (6–15 %), chlorite (0–26 %), smectite (0–13 %), mica-vermiculite (0–8 %) and mica-smectite (0–7 %).

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Fig. 3

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The average weight percentages of clay minerals in the entire section are mica (52 %), vermiculite (8.5 %), chlorite (15 %), kaolinite (10.5 %) and smectite (8 %) and minor amounts of mica-vermiculite and mica-smectite (around 3 %).

Mica (peak at ~1.0 nm persists in all treatment and second and third order reflections of the 1.0 nm peak at 0.50 and 0.330 nm, respectively), kaolinite (presence of 001 and 002 XRD peaks at 0.72 and about 0.357 nm, respectively and loss of the basal XRD peaks when heated to 550°C) and chlorite (except in some well-developed paleosols) constitutes the main part of all studied units in Agh Band section (Fig. 4). Chlorite is found in all samples (except U18 to U24), since the reflection at 1.4 nm remains stable after saturation with K+ and heating to 550°C (Fig. 4). Chlorite and mica are two commonly observed clay minerals occurring mainly in areas where soil formation is limited (Fanning et al., 1989; Wilson, 1999). Their abundance in the soils is largely due to their presence in parent materials. However, there is some evidence that mica can form pedogenically from K fixation in pre-existing smectites under hot and dry soil conditions (Mahjoory, 1975) and kaolinite may form under intense weathering in warm and moist environments, and is common in areas with tropical or subtropical climates (Dixon and Weed 1989; White and Blum 1995). Mica, kaolinite and chlorite constitute the main part of all studied parent material of UPL (Amini Jahromi et al., 2008; Khormali and Ghorbani, 2009; Khormali and Kehl, 2011), so their presence in LPL are likely mainly of detrital origin. Also, based on the micromorphological studies on the Agh Band red sequence by Taheri et al. (2017), the annual precipitation during the formation of the reddish colored moderately-developed and well-developed paleosols in the LPL in northern Iran is estimated around 450 mm to 650 mm, respectively. Therefore, these conditions are not warm and humid tropical and subtropical climates to form kaolinite pedogenically and the detrital origin of this clay mineral is most possible.

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Fig. 4

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The peaks resulting from the X-ray diffractions of the Agh Band section confirm the presence of smectite in all units except in U13, U14 (a diffraction peak at 1.7 nm in the Mg-saturated and ethylene glycol solvation) (Fig. 4). Two main sources of smectite have been recognized in soils: detrital origin or inheritance and pedogenic formation through neoformation or transformation of 2:1 minerals (Borchardt, 1989; Aoudjit et al., 1995; Khormali and Abtahi, 2003). Accordingly, on the one side, based on previous research on UPL the amount of smectite in parent material of these eolian sediments is very low or was not detected in several studies (Amini Jahromi et al., 2008; Khormali and Ghorbani, 2009; Khormali and Kehl, 2011). On the other side, increasing available soil moisture (based on Taheri et al., 2017) and consequently a relative leaching environment, in the well-drained soils, may provide favorable conditions for the formation of smectite through mineral transformation. Because in the calcareous environment, with high Mg2+ and high Si4+ mobility, K+ release from chlorite and mica minerals. Therefore, the presence of this mineral in almost all units suggests a transformed origin of this mineral. Neoformation of smectite in UPL was also reported by Amini Jahromi et al., (2008), Khormali and Ghorbani (2009) and Khormali and Kehl (2011).

Another mineral in the LPL is vermiculite which appears in all paleosols of Agh Band section and some loess units (U4, U10, U16) named as Bkk(m) and could be leached from upper paleosols. The presence of vermiculite is confirmed by the [appearance](dict://key.25D62D261B9B6943BE86B7DCF8F9D255/appearance) of 1.4 nm peak which collapses to 1.0 nm following K saturation as seen by the sharp increase in the intensity of 1.0 nm peak (Fig. 4). Vermiculite is a fast-forming and unstable intermediate mineral which is derived initially from mica and can be transformed to other minerals, depending on the environment (Wilson, 1999; Velde and Meunier, 2008). Based on Boettinger and Southard (1995), moisture availability for chemical weathering and dampened temperature fluctuations provide favorable conditions for vermiculite stability, which may explain the vermiculite contents in paleosols. Since paleosols represent humid and warm climate.

The broad peaks observed from 1 to 1.4 nm in K treatment (Fig. 4) shifting to 1 nm following heating up to 550°C corresponds to the presence of interstratified 2:1 minerals (mica-vermiculite and mica-smectite), which give a sharp and intense 1 nm peak in K 550° C treatment (Moore and Reynolds, 1997).

**4.3. Paleoclimate based on clay mineralogy**

As discussed above, except mica-vermiculite and mica-smectite which is detected in minor amount, smectite and vermiculite are the two main pedogenically formed clay minerals in the units of LPL. Based on Khormali and Kehl (2011) and Khormali and Ghergherechi (2012) who studied the clay mineralogical properties of soil horizons in loess derived soils along a climate gradient with xeric and udic soil moisture regimes (SMR) and thermic and mesic SMRs in ILP of Northeastern Iran, smectite and vermiculite can be formed in soils with the xeric and udic SMR, respectively. Therefore, it can be concluded that loess of Agh Band sequence which has smectite in its components formed under xeric SMR and paleosols with high amounts of vermiculite formed under higher precipitation e.g. udic SMR. Also, no pedogenic existence of these two kinds of clay minerals confirmed the presence of an aridic SMR that is seen in the UPL. This is in line with the findings of Taheri et al. (2017) who concluded that the climate at the time of Agh Band LPL formation varied from semi-arid to sub-humid climate and wetter and more favorable conditions than the overlying late Pleistocene loess and modern soils.

The loss of the 1.4 nm peak after saturation with K+ and heating to 550°C and increasing the intensity of 1.0 nm in K treatment, which means weathering of chlorite to vermiculite in well developed units (based on morphological observations and micromorphological analysis (taheri et al., 2017)) such as U18 to U24 (Fig. 4) also confirms this conclusion. Chadwick et al. (2003) and Velde and Meunier (2008) revealed that chlorite can be relatively unstable and easily change under intense precipitation.

In another study, Khormali et al. (2012) demonstrated the presence of calcium carbonate and clay pedofeatures were common in the modern soils in humid and subhumid climates of the ILP. Therefore, according to our micromorphological observations that reveal the formation of clay coatings and carbonate pedofeatures as two basic pedogenic processes in the soils studied (Fig. 5), it can be concluded that the red sequence was formed under a humid to sub-humid climate (Taheri et al., 2017).

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Fig. 5

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**4.4. Paleoclimate based on geochemistry**

Weathering strongly affects major-element geochemistry of deposits, thus many semi-quantitative and quantitative tools has been developed to examine past weathering processes and pedogenesis, and to reconstruct paleoclimatic conditions at the time of loess and paleosol formation (Harnois, 1988; Jeong et al., 2008; Bokhorst et al., 2009; Vagra et al., 2011). According to this, simple ratios of chemical element composition such as Al2O3/Na2O, Na2O/K2O, MgO/TiO2 have been used successfully for the reconstruction of paleoclimate conditions (Yang et al., 2006; Jeong et al., 2008; Bokhorst et al., 2009; Vagra et al., 2011).

Based on Nesbitt et al., (1980); Nesbitt and Young, (1989, 1996); Chen, (1996); Ji et al., (2000); Nyakairu and Koeberl, (2000); Young and Nesbitt, (2001); Tao et al., (2006) and Varga et al., (2011) in reaction to considerable chemical weathering and rainfall, the values of Na2O/K2O reduces as a result of rapid loss of Ca2+ and Na+, and the amount of Al2O3 /Na2O increases from the relative enrichment of Al2O3, and vice versa. In this study due to the fact that most units have a higher content of K2O than Na2O, thus K2O/Na2O was preferred to Na2O/K2O to obtain the >1 values. Finally, based on the variations of these two indices in the Agh Band section and their high values in LPL compared to the UPL (Fig. 2), it can be deduced that wetter climate was predominant during deposition of LPL (comparing to the UPL).

Furthermore, the LPL samples (with 6.4 mean values) have lower values of MgO/TiO2 ratio than UPL samples (with 9.26 mean values) (Fig. 2). This is in agreement with the findings of Gallet et al., (1996) and Varga et al., (2011) in study of loess-paleosol sequences and report that the amount of this ratio in paleosols is less than in loess layers. Mahmudi (2012) studied the geochemical characteristics of the UPL, therefore, those data is used for more evidences.

**4.5. Paleoclimate based on total and free iron**

The existence of Fe as an element depends on the minerals inherited from the parent materials of soil, while its amount and the proportions of its various forms depend on the degree of weathering and evolution of the soil (Ziyaee et al., 2012). Fe forms can be used as indicators for understanding pedogenic processes and the degree of weathering. Therefore, in this study, the amount of total (Fet) and free (Fed) Fe2O3 of Agh Band sequence were measured and their depth distributions are shown in Fig. 2. In general Fed proportions in LPL vary from 0.77% to 1.09% and Fet ranges between 6.04–7.79%. The amount of Fed and Fe2O3 ratio clearly shows higher values in the well-developed units such as Bt and Btk. In general, the alternations of the loess and paleosol horizons are distinctly shown by the amount free iron and comparing between UPL and LPL, the quantities of both forms of Fe were smaller in UPL. This is in line with the finding of Shiling and Zhongli (2001), Ding et al., (2001) and Ziyaee et al., (2012) who state that the percentage of pedogenic Fe increases by stronger and more effective weathering processes. Moreover, the abundance of iron oxides in the micromorphological observations (Fig. 5) (Taheri et al., 2017) point to a high weathering status in these units and generally in LPL.

**5. Conclusions**

1- The variations in clay mineral composition of Agh Band section especially in the amount of vermiculite, smectite and chlorite indicate temporal and spatial changes in mineral evolution and the strength of the climate. The increase or decrease in pedogenic processes, strongly controlled vermiculite, smectite and chlorite evolution. In general, the paleosols contain more vermiculite and smectite, together with less chlorite than in the loess.

2- This study shows remarkable similarity in ratios of relatively immobile major and trace elements, indicating similarity in the provenance of all LPL units and UPL.

3- The higher quantities of free Fe2O3 and the ratio of Fed to Fet concentrations in LPL (comparing to the UPL) and also in well-developed units of LPL reveal high weathering status in these units and generally in LPL. Therefore, the amount of both forms of Fe appear to be a good proxy as a whole in paleoclimate reconstruction.

4- The reconstruction of the paleoclimate, based on analysis of Al2O3/Na2O, Na2O/K2O, MgO/TiO2 ratios, Fed, Fet, and their ratios as well as the clay mineralogy of Agh Band section demonstrated the prevalence of wetter climate during deposition of LPL (comparing to the UPL).

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