

Paleoclimate Reconstruction during Pabdeh, Gurpi, Kazhdumi and Gadvan Formations (Cretaceous-Tertiary) Based on Clay Mineral Distribution

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Abstract—Paleoclimate was reconstructed by the clay mineral assemblages of shale units of Pabdeh (Paleocene- Oligocene), Gurpi (Upper Cretaceous), Kazhdumi (Albian-Cenomanian) and Gadvan (Aptian-Neocomian) formations in the Bangestan anticline. To compare with clay minerals assemblages in these formations, selected samples also taken from available formations in drilled wells in Ahvaz, Marun, Karanj, and Parsi oil fields. Collected samples prepared using standard clay mineral methodology. They were treated as normal, glycolated and heated oriented glass slides. Their identification was made on X-Ray diffractographs. Illite % varies from 8 to 36. Illite quantity increased from Pabdeh to Gurpi Formation. This may be due to dominant dry climate. Kaolinite is in range of 12-49%. Its variation style in different formations could be a marker of climate changes from wet to dry which is supported by the lithological changes. Chlorite (4-28%) can also be detected in those samples without any kaolinite. Mixed layer minerals as the mixture of illite-chlorite and illite-vermiculite-montmorillonite are varied from 6 to 36%, decreased during Kazhdumi deposition from the base to the top. This result may be according to decreasing of illite leaching process. Vermiculite was also determined in very less quantity and found in those units without kaolinite. Montmorillonite varies from 8 to 43%, and its presence is due to terrestrial depositional condition. Stratigraphical documents is also supported this idea that clay mineral distribution is a function of the climate changes. It seems, thus, the present results can be indicated a possible procedure for ancient climate changes evaluation.

Keywords—Clay Minerals, Paleoclimate, XRD, oriented slide

I. INTRODUCTION

CLAY minerals are an important group of minerals because they are among the most common products of chemical weathering, and thus are the main constituents of the fine-grained sedimentary rocks called mudrocks (including mudstones, claystones, and shales). In fact, clay minerals make up about 40% of the minerals in sedimentary rocks. In addition, clay minerals are the main constituent of soils. Understanding of clay minerals is also important from an engineering point of view, as some minerals expand significantly when exposed to water.

Clay minerals are commonly interested for industrial [1]-[4] and medical purposes due to chemical and physical properties [4]. Their application is numerous in literature which may be expressed as follows: diagenetic transformation and initiate of metamorphism [5]-[8]; Paleosalinity and clay minerals [9];

geothermometer and organic maturity indicator [10]-[12]; source rock and paleo-environment of sedimentary basin [13]-[18]; Provenance and stratigraphy studies [19]-[22]; the nature and source of clay minerals [23]-[30]; Petroleum source rock evaluation [12], [10], [11], [31], [10], [32], [33]; effects on net porosity, fluid and hydrocarbon saturation [34]; the relation between gamma ray and clay minerals [35]-[38]; Drilling problems [39]-[40]; impacts of sedimentary basin, provenance rock and tectonic factors [16], [13], [41]-[42] on the composition and frequency of clay minerals; the role on burial of atomic waste [43], and Paleogeography and paleo-climate [44]-[46]. The latest one has not applied yet in the Zagros region.

In the present study, shale units of different Tertiary – Cretaceous formations (Pabdeh, Gurpi, Kazhdumi and Gadvan) are investigated in view of clay mineral assemblages to reconstruct paleoclimate during their deposition in SW of Iran.

II. GEOLOGICAL DESCRIPTION

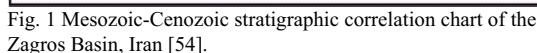
Clay mineral distribution was studied in major shale units with the age range of Tertiary (Eocene) to Lower Cretaceous (Fig.1) in different geological situation of the Zagros Range, in Dezful Embayment, SW of Iran (Fig. 2). These units are described briefly from younger to older.

Pabdeh Formation (Paleocene-Eocene) consisted predominantly marl and shale. It presents chertiferous limestone as well as phosphatic nodular and glauconitic sediments in lower contact with Gurpi Formation. These are indicating stratigraphic discontinuity by late cretaceous tectonic phase. The lower contact is discordant. The upper contact is discordant, gradational to concordant with the upper formation (Asmari). Its thickness is 798m in type locality. However, this formation has shown an excellent potential petroleum source rocks, in general, but in some cases is considered as the reservoir rock due to lateral facies changes.

Gurpi Formation thickness is 350m in type section. Its age covers Santonian to Maestrichtian. The lower contact is weak erosional discordant with Ilam-Sarvak Formation. Lithologically, it consisted of dark, grey marl, shale and limestone. The upper contact with the Pabdeh Formation is disconformable.

Kazhdumi Formation (Albian-Cenomanian) composed of 210m of dark bituminous shale in lower part and argillaceous limestone in upper part. The contact with the underlying Dariyan Formation is marked by the presence of red oxidized

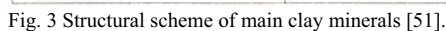
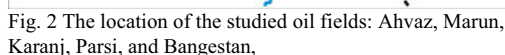
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Gadvan Formation (Late Neocomian-Aptian) forms a low weathering unit of the Khami Group. It consists of dark shale and argillaceous limestone. Gadvan Formation underlies Dariyan Formation with apparent conformity. The contact is gradational. This type of contact is also observed with the older sediments, i.e. Fahliyan Formation. Its thickness is 106m in type locality.

The samples collected from the outcrops of these formations in Tange- Maghar (Bangestan oil field), and also drilled well cuttings from Ahvaz, Marun, Parsi and Karanj oil fields (Fig. 2).

To study clay mineral assemblage, the selected samples were subjected to different processes: (a) grinding and homogenization [47]. Grind the dried sample thoroughly with the mortar and pestle. The particles should be much finer than 0.062mm to avoid fractionation of the minerals. The finer the powder the greater the opportunity for obtaining an adequate number of particles with random orientation and the less likely that surface roughness will reduce low-angle intensities. (b) Suspension clay fraction in distilled water column [48], and (c) mounting with spread the sample on the slide [49]-[50], [31], [48], [51]. The clay fraction can be also separated from the bulk sample by centrifugation or decantation and mounted as an oriented aggregate to clay-mineral identification. The oriented aggregate mounts force the clay mineral particles, usually plate-shaped phyllosilicates, to lie flat, allowing the



operator to direct the incident X-ray beam down the z axis of the minerals and to record the diagnostic basal diffractions. Oriented clay mounts treatments of each sample are including air drying, glycolation with ethylene glycol, heating to 550°C. Each oriented glass slide subjected to X-ray diffraction in XR diffractometer (model PW-1840). Clay minerals determination was carried out by their individual peaks [52], [49]. To calculate semi-quantity values, the method proposed by [53] was used.

Clay minerals are used extensively in different scientific aspects. The latest application is in paleoclimate determination. Based on structural and chemical compositions (Fig. 3), the clay minerals susceptibility varies. Clay mineral assemblages identified in selected locations of Dezful Embayment are kaolinite, illite, montmorillonite, chlorite and mixed layer. Each of these is formed under different environmental and chemical conditions, so help us to use them to interpret depositional/climate condition.

The given data in Table I presents the clay types and their distribution in area understudy. Based on these data, Kaolinite covered a range of 12-49%. The presence of kaolinite in Kazhdumi and its absence in Pabdeh-Gurpi and Gadvan formations is interesting. It can be interpreted to be the result of climate changes/depositional condition (shallow water) or

erosional rate and the composition of the initial provenance rocks. Field investigation supports the idea of the first suggestion in reason of Gurpi base conglomerate. Therefore, it is inferred dry climate during Gurpi deposition. Kaolinite is formed by weathering or hydrothermal alteration of

TABLE I
XRD RESULTS OF SELECTED SAMPLES FROM PABDEH, GURPI, KAZHDUMI, AND GADVAN FORMATIONS.

Sample	Kaolinite %	Illite %	Chlorite %	Montmorillonite %	Mixed Layer%
<i>Bangestan oil field (out crop samples)</i>					
Upper Pabdeh	----	22.4	28.6	32.7	16.3
Lower Pabdeh	----	25.5	25.6	23.3	25.6
Lower Pabdeh	----	20.3	20.3	43.5	15.9
Lower Pabdeh	----	27.5	20	27.5	25
Upper Gurpi	----	28.1	26.6	25	20.3
Upper Kazhdumi	27.6	24.2	13.8	17.2	17.2
Middle Kazhdumi	42.7	12.8	13.7	21.4	9.4
Middle Kazhdumi	34.4	15.6	15.6	18.8	15.6
Lower Kazhdumi	31.1	20.7	17.2	10.3	20.7
Lower Kazhdumi	49.2	15.9	----	17.5	17.4
Base of Dariyan	81.6	8.2	4	8.2	6
Gadvan	----	28.1	18.8	21.9	31.2
<i>Karanj oil field, Well#12</i>					
Lower Asmari	16.7	26.7	10	26.7	20
Asmari-Pabdeh	42.9	20.8	9	16.9	10.4
Base of Pabdeh	----	29.6	18.5	22.2	29.6
Tower Gurpi	----	32	24	20	24
Middle Gurpi	----	31.8	18.2	22.7	27.3
Base of Sarvak	33	23	9.6	19.2	15.2
<i>Parsi oil field, Well#35</i>					
Lower Asmari	18.9	21.6	8.1	24.3	27.1
Base of Asmari	12.5	20.8	12.5	29.2	25
Upper Pabdeh	20.8	31.9	9.7	20.8	16.7
Middle Pabdeh	----	28.6	25.2	22.9	20
Lower Pabdeh	----	36.5	21.2	23.1	19.2
Base of Pabdeh	----	28.6	23.8	28.6	19
Top of Gurpi	----	35.3	17.7	23.5	23.5
Middle Gurpi	----	25	25	18.8	31.2
Middle Kazhdumi	12.9	25.8	9.7	21.5	30.1
Lower Kazhdumi	17.3	24.1	----	24.1	20.7
<i>Ahvaz oil field, Well#228, #227</i>					
Asmari -Pabdeh	----	31.7	24.4	24.4	19.5
Asmari-Pabdeh	56.3	16.9	----	12.7	14.1
Upper Pabdeh	----	33.4	17.6	23.5	25.5
Middle Pabdeh	----	20.5	25.6	25.6	28.2
Lower Pabdeh	----	26.8	17.1	29.3	26.8
Top of Gurpi	----	28.9	21.1	28.9	21.1
Upper Gurpi	----	25.4	23.7	25.4	25.5
Middle Gurpi	----	28.1	15.7	20.2	36
<i>Marun oil field, Well#291</i>					
Base of Asmari	16.7	25	12.5	29.2	16.6
Base of Asmari	25.7	28.6	11.4	17.1	17.2
Upper Pabdeh	----	36.4	24.3	24.2	15.1
Upper Pabdeh	----	29.7	21.6	21.6	27.1
Base of Pabdeh	----	35.3	20.6	26.5	17.6

aluminosilicate minerals. Thus, rocks rich in feldspar commonly weather to kaolinite. In order to form, ions like Na, K, Ca, Mg, and Fe must first be leached away by the weathering or alteration process. This leaching is favored by acidic conditions (low pH). Granitic rocks, because they are rich in feldspar, are a common source for kaolinite. Kaolinite, because it does not absorb water, does not expand when it comes in contact with water. Thus, kaolinite is the preferred type of clay for the ceramic industry. With looking data given in table I, it is cleared the presence of kaolinite in the base of Asmari denotes a lithological marker to distinguish the stratigraphic boundary. Also, it will be supported the idea of depositional environment.

Illite percentage ranges from 8 to 36%. It seems its value increased in Gurpi. This subject can be due to conversion of kaolinite and montmorillonite [2] or involvement of mixed layer to generate more illite. Illite is essentially a group name for non-expanding, clay-sized, dioctahedral, micaceous

minerals. It is structurally similar to muscovite in that its basic unit is a layer composed of two inward-pointing silica tetragonal sheets with a central octahedral sheet. However, illite has on average slightly more Si, Mg, Fe, and water and slightly less tetrahedral Al and interlayer K than muscovite. The weaker interlayer forces caused by fewer interlayer cations in illite also allow for more variability in the manner of stacking. Glauconite is the green iron-rich member of this group. Illites, which are the dominant clay minerals in argillaceous rocks, form by the weathering of silicates (primarily feldspar), through the alteration of other clay minerals, and during the degradation of muscovite. Formation of illite is generally favored by alkaline conditions and by high concentrations of Al and K. Glauconite forms authigenically in marine environments and occurs primarily in pelletal form.

Members of the illite group are characterized by intense 10 Å (001) and a 3.3 Å (003) peaks that remain unaltered by ethylene glycol or glycerol solvation, and heating to 550°C. Glauconite can be differentiated from illite by a 1.5- to 1.52 Å (060) peak (illite's (060) peak occurs at 1.50 Å), and by the presence of only a very weak 5 Å (002) peak. The Illite clays have a structure (Fig. 2) similar to that of Muscovite, but it is typically deficient in alkalies, with less Al substitution for Si. Because of possible charge imbalance, Ca and Mg can also sometimes substitute for K. The K, Ca, or Mg interlayer cations prevent the entrance of H₂O into the structure. Thus, the illite clays are non-expanding clays.

Montmorillonite with 15-39% range is second main clay component. Its presence marked terrestrial-non marine environment. Smectites commonly result from the weathering of basic rocks. Smectite formation is favored by level to gently sloping terrains that are poorly drained, mildly alkaline (such as in marine environments), and have the high Si and Mg potentials. Other factors that favor the formation of smectites include the availability of Ca and the paucity of K. Poor drainage is necessary because otherwise water can leach away ions (e.g. Mg) released in the alteration reactions. Smectites are used in industry as filler, carrier, and absorbent. They yield X-ray diffraction patterns characterized by basal reflections that vary with humidity, exposure to certain organic molecules, heat treatment, and exchangeable cations. When saturated with ethylene glycol, the (001) reflection of most smectites will swell to about 17 angstroms (about 17.8 angstroms with glycerol); when heated to 400 C, the (001) reflection will collapse to about 10 angstroms (the exact amount of collapse is often related to the exchange cations present and to the smectite itself). Individual smectites can sometimes be differentiated by their higher-order peaks or by cation saturation. For example, dioctahedral smectites have (060) reflections at 1.50-1.52Å, whereas trioctahedral smectites have (060) reflections at 1.53-1.54 Å, and Li saturation can be used to differentiate some montmorillonites from beidellite component in drilling fluids.

The most important aspect of the smectite group is the ability for H₂O molecules to be absorbed between the T-O-T sheets (tetrahedral-octahedral-tetrahedral), causing the volume of the minerals to increase when they come in contact with water. Thus, the smectites are expanding clays. The most common smectite is montmorillonite which is characterized of

dry region.

Chlorite is formed in alkaline condition and found in where the environment is relatively reduction and is without turbulent. Low presence of this clay can be related to release of Mg^{2+} , Fe^{2+} , Ca^{2+} , Si^{4+} , and Na^{+} during montmorillonite transformation to illite. This process indicates the involvement of these elements in calcite and dolomite formation [55]. Chlorite is more common in higher latitudes where chemical weathering is reduced. Chlorite% varies up to 28. Chlorite absence in some shale units was affected by climate changes. Illite and Chlorite are frequent in marine sediments [22] but montmorillonite in terrestrial region [8]. Kaolinite is concentrated at the mouths of tropical rivers because it is produced mainly in tropical soils. Chlorite indicates 4 to 28%. It is identified in those samples which are not containing any kaolinite traces. Chlorite along with illite quantities increases from Pabdeh toward Gurpi formations.

Mixed-layer clay minerals are materials in which different kinds of clay layers alternate with each other. The mixing or interstratification in vertical stacking can be regular (ordered), segregated regular, or random. Commonly described mixed-layer clays include: illite-vermiculite, illite-smectite, chlorite-vermiculite (corrensite), chlorite-smectite, and kaolinite-smectite. Mixed-layer clays can form by weathering involving the removal or uptake of cations (e.g. K), hydrothermal alteration, or removal of hydroxide interlayers, and, in some cases, may represent an intermediate stage in the formation of swelling minerals from non-swelling minerals or visa versa. Regularly interstratified structures are readily identified by their (001) basal reflection, which corresponds to the sum of the spacing of the individual components, and subsequent peaks of higher integral orders. Thus, regularly interstratified illite-smectite, when glycolated, would be characterized by a (001) diffraction peak at about 27 angstroms, corresponding to the sum of the spacing of illite (10 angstroms) and smectite (17 angstroms). Conversely, randomly interstratified structures have non-integral peaks at positions intermediate between the peaks from the individual mineral layers. Randomly interstratified illite-chlorite would be therefore characterized by a (001) basal diffraction peak between 10 and 14 angstroms. In selected samples, Mixed Layer occurs as the mixture of illite-chlorite and illite-vermiculite-montmorillonite. Its abundance changes between 6 to 36% and appears to be higher in Kazhdumi base relative to Kazhdumi top, Gurpi and Pabdeh formations. However, its greater quantity in Pabdeh than Gurpi can be due to more leaching of illite. Vermiculite is also determined in a few samples of Pabdeh and Kazhdumi with low quantity. It almost occurred as a constituent of mixed layer.

Finally, the mean value of each clay mineral type in different stratigraphic units of selected oil fields will be revealed the following general trends (from the West to the East):

Ahvaz oil field:

Asmari-Pabdeh: Kaol.>Illi.>Mont.>M.L.>Chl.
Pabdeh: Illi.>M.L.>Mont.>Chl.
Gurpi: Illi. =M.L.>Mont. >Chl.

Marun oil field:

Base Asmari: Illi.> Mont.> Kaol.>M.L.>Chl.
Pabdeh: Illi.>Mont.>Chl.>M.L.

Karanj oil field:

Asmari-Pabdeh: Kaol.>Illi.>Mont.>M.L.>Chl.
Pabdeh: Illi.=M.L.>Mont.>Chl.
Gurpi: Illi. >M.L.>Mont. >Chl.
Base Sarvak: Kaol.>Illi.>Mont.>M.L.>Chl.

Parsi oil field:

Base Asmari: Mont.>M.L.>Illi.>Kao.>Chl.
Pabdeh: Illi.> Mont.>Chl.>M.L.
Gurpi: Illi. >M.L.>Mont. =Chl.
Kazhdumi: Illi. =M.L.>Mont. >Kaol.>Chl.

Bangestan oil field:

Pabdeh: Mont.>Illi.>Chl.>M.L.
Gurpi: Illi.>Chl.>Mont.>M.L.
Kazhdumi: Kaol.>Illi.>Mont.>M.L.>Chl.
Gadvan: M.L.>Illi.>Mont.>Chl.

It seems the appearance of these clays is not due to diagenetic effects. However, diagenesis is possible to impact on mixed layer abundances with increasing age. Consequently, the lack of kaolinite in Pabdeh-Gurpi and Gadvan formations is not related to diagenetic transformation. Therefore, these clay types mostly derived from the source and so the climate effects are to be dominant.

V. CONCLUSIONS

The present study revealed that clay mineral distribution in different locations of the Zagros Range indicated individual trends. Illite semi-quantity percentage was increased from Pabdeh to Gurpi formations due to kaolinite-montmorillonite degradation or most probably dry and terrestrial climate dominant. Kaolinite presence in Kazhdumi Formation can be indicating climate regime changes from wet to dry than other formations. Mixed layer occurred as the mixture of illite-chlorite and illite-vermiculite-montmorillonite. It decreases from the base of Kazhdumi to the base of Sarvak Formation which is may be affected by leaching of illite. Chlorite and vermiculite are detected in minor amounts in some samples. Montmorillonite is the third major detected clay mineral and it's presence is the result of non-marine/terrestrial condition. Therefore, clay mineral assemblage in this part of the world is owing to climate-depositional condition. It seems diagenetic processes are lesser important. Thus, climate factor must be considered as possible factor in monitoring observed clay types in questionable area.

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