

The Role of Clay Minerals in Hydrocarbon Generation, Migration and Accumulation.

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ABSTRACT

This study focuses on the understanding of the role of clay minerals in hydrocarbon generation, migration and accumulation. Clay minerals are involved in the formation of kerogen, catalytic cracking of kerogen into petroleum, migration of crude oil, and the continued change to hydrocarbon composition in petroleum reservoirs. In kerogen formation, clay minerals act as catalysts and sorbents to immobilize organic matter through ligand exchange, hydrophobic interactions and cation bridges by the mechanisms of Maillard reactions, polyphenol theory, selective preservation and adsorptive protection. Clay minerals also serve as catalysts in acid-catalyzed cracking of kerogen into petroleum hydrocarbon through Lewis and Bronsted acid sites on the clay surfaces. The amount and type of clay mineral affect the composition of the petroleum. Bronsted acidity of clay minerals is affected by the presence and state of interlayer water, and displacement of this water is a probable driver in crude oil migration from source rocks. During crude oil migration and accumulation in reservoirs, the composition of petroleum is continually modified by interaction with clay minerals. Clay minerals remain the most difficult of all earth materials to study and characterize. Their sheet structure results in features that can only be resolved at the sub-micron scale. They are also subtly variable in chemical composition (Fe, Mg, K, Al, et cetera) and can be confused with each other and other silicates. The recent innovative analytical tools and modern analysis techniques, example., micro- and nano-X-ray Computed Tomography (XCT), QEMSCAN (Automated Mineralogy and Petrography), FIB/SEM (Focused Ion Beam/Scanning Electron Microscope), EDS (Energy-dispersive X-ray spectroscopy), etc., have the capability of quantitative and qualitative characterizing nano-pore features and mineralogy of fine grained shale rocks, which create new era of studying clay minerals for facilitating unconventional (shale) reservoir exploration. Even though there have been reports about the application of clay minerals in the oil and gas exploration, surprisingly little work has been documented.

Keyword: clay mineral, organic matter, generation, vitrinite, kerogen, montmorillonite.

INTRODUCTION Petroleum crude oil, or crude oil, is a naturally occurring oily, flammable liquid usually found in geologic formations deep beneath the surface of the earth. Crude oil consists mainly of hydrocarbons and polar organic compounds (resins, asphaltenes, etc.). The typical types of crude oil are light and heavy crude oil. Light crude oil contains more saturated hydrocarbons and less aromatic hydrocarbon, for example, naphtheno-paraffinic oil contains more than 50% saturated hydrocarbons and less than 40% paraffinic hydrocarbons, while heavy crude oil is referred to as any type of crude oil that does not flow easily. It is closely related to natural bitumen, which is distinguished by a high proportion of C15+ (Perrodon, 1983). Petroleum has played a

pivotal role in modern civilization. The past few decades have witnessed increasing exploitation and utilization of petroleum. Today petroleum is predominantly processed to provide transportation fuels and numerous petrochemicals and materials, including pharmaceuticals, solvents, fertilizers, pesticides, and plastics (Parra, 2004). Petroleum occurs naturally in sedimentary rocks and can usually be traced to primary source rocks that contain abundant clay minerals (Tannenbaum et al., 1986). Diagenetic changes in clay minerals provide clues about the burial history of sedimentary basins. In particular, the type and distribution of clay minerals in and around source rocks provide information on the depth of burial, thermal history and fluid interactions; factors significant in the formation and migration of hydrocarbons (Weaver, 1960; Pollastro, 1993). This has particular relevance to petroleum exploration and recovery. Moreover, the interrelationship of clays and petroleum raises wider scientific questions regarding the extent to which clay minerals play an active role in petroleum formation, migration, accumulation and storage. Clay minerals exist in nature mostly as nano- to micro-sized particles with high capacity for adsorption, ion exchange capability, and acid sites. Clearly, continuing investigation and greater understanding of the relationship between clay minerals and crude oil formation are increasingly of significance both technically and academically.

THE ACIDITY OF CLAY MINERALS

Clay minerals are a form of solid acid having their Brønsted and Lewis acid sites. In chemistry, a Brønsted acid is a molecule or ion that is able to lose, or “donate,” a hydrogen cation (proton, H^+). A Lewis acid is a molecule or ion which can act as an electron-pair acceptor. For layered clay minerals, the hydrated cations in the interlayer space, $-OH$ and active broken-edge $M - O^- H_2^+$ bonds on the layers are the sources of Brønsted acidity. The dehydrated cations in the interlayer space and those cations on the layer can form Lewis acidity. Clay minerals are able to donate H^+ as a Brønsted acid through dissociation of water associated with hydrated exchangeable cations, as shown in Eq. (1) (Johns, 1979).



where M is the exchangeable cation, Z is the charge, X the amount of water molecules coordinated with M, n the amount of exchangeable cations, K_1 is the ionization (dissociation) constant for the interlayersystem. From Eq. (1), it is clear that factors, which affect the dissociation of water, also affect the acidity and consequently the catalytic ability of clay minerals. The exchangeable cations (including the amount and the type) and the content of water in clay minerals are the main factors affecting the catalytic activity of Brønsted acid sites. Cation exchangeability of clay minerals correlates directly with the degree of tetrahedral substitution and accordingly the layer charge density (LCD). The diagenesis of smectite to illite/mixed layer clays occurs synchronously with hydrocarbon formation. Compared to smectite, the amount of tetrahedral substitution of Al^{3+} for Si^{4+} in illite is increased (Reynolds and Hower, 1970; Johns and Mckallip, 1989). Hence, the amount of layer charge and exchangeable ions is increased, leading to an increase of Brønsted acidity. Also, the content of water is an additional factor affecting the Brønsted acidity. At low water content, residual water molecules cause a significant increase in their dissociation and proton-donating ability, in which the dissociation constant may be of the order of 106 times higher than for normal water (Fripiant, 1970). In addition, for different types of exchangeable cations, the ability to polarize water increases in the order of $K^+ < Na^+ < Ca^{2+} < Mg^{2+}$ (Li et al., 1998). Furthermore, organic acid formed with petroleum could act to acidify clay minerals and increase their overall acidity. (Andresen et al. 1993) conducted pyrolysis of nineteen hydrocarbon source

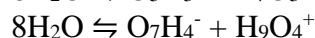
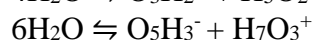
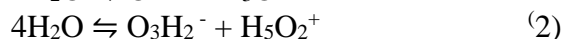
rocks and found the amount of organic acid generated through pyrolysis of kerogen yielded around 1.3 mol organic acids per mol organic carbon. Notably, the organic acid generated was effective in producing acid-activated clay minerals (Wang et al., 2006). Besides donating a proton, clay minerals may provide other possible active hydrogen species. (Chaplin 2000) proposed the model of water where the structure of water is more complicated than expected. Sub-surface water exists in the form of water clusters composed of water positive groups

(H_3O^+ , H_5O_2^+ , H_7O_3^+ , H_9O_4^+ ...)

and water negative groups

(OH^- , H_3O_2^- , H_5O_3^- , H_7O_4^- ...),

and these groups are connected by hydrogen bonding (Eq. (2)). Zhou (2005, 2010b) proposed that such a water cluster structure is more apparent among interlayer water and lattice water of clay minerals under certain geological conditions. This is due to numerous metal cations (Fe_3^+ , CO_3^+ and Ni_3^+ etc.) and electronegative anionic groups of kerogen between the layers of clay minerals. These water clusters are more active than the surrounding groundwater.



(Zhou 2005) also proposed that, when the pressure reaches a critical value with the increase of burial depth, and under the driving force of metal cations and electronegative anionic groups in the clay minerals–kerogen system, the water positive groups (H_3O^+ , H_5O_2^+ , H_7O_3^+ , H_9O_4^+ ...) may crack to give free proton flow. Moreover, two protons obtain an electron and generate hydrogen molecule H_2^+ and then hydrogen H_2 ; it is also possible that a proton gets one electron with the formation of hydrogen atom H. These reactions are a potential source of active hydrogen species for hydrocarbon generation reactions. Moreover, clay minerals can possibly act as an electron-pair acceptor. For example, the aluminum ion (Al_3^+) in zeolite can accept an electron-pair from OH groups to form AlOH_2^+ and $\text{Al}(\text{OH})_2^+$, which means that Al_3^+ exhibits Lewis acidity (Beran et al., 1981). Lewis acid sites in clay minerals come from the Al_3^+ , Fe_3^+ in octahedral coordination exposed at the edges of crystallites, which act as electron acceptors (Stackhouse et al., 2001). Al_3^+ , Fe_3^+ are commonly occurring cations within phyllosilicate clays (Zhou, 2010a). Lewis acidity also depends on the water content of clay minerals (Lewis acidity is dominant when water is largely removed), exchangeable cations and the temperature of thermal activation (Brow and Rhodes, 1997). Maximum Lewis acidity was obtained for the temperature range 250 °C to 300 °C, and after 250 °C activation, the Lewis acid strength increased as follows: Al_3^+ -exchanged clays < Fe_3^+ -exchanged clays < Ni_2^+ -exchanged clays (Brow and Rhodes, 1997). It is worth noting that Lewis acidity increases as Brønsted acidity falls due to the directly coordinated water of exchangeable cations being driven off (Brow and Rhodes, 1997). Therefore, Brønsted and Lewis acid activity in clay minerals are not independent; rather they are mutually dependent on the activity of each other.

Phenomenon of swelling in oil and gas industry

Formation damage is an undesirable operational and economic problem that can occur during the various phases of oil and gas recovery from subsurface reservoirs including drilling, production, hydraulic fracturing, and work over operations. Water-based drilling fluids are increasingly being used for oil and gas exploration, and are generally considered to be more environmentally friendly,

easy to use and cheaper than oil-based or synthetic-based drilling fluids which makes them more acceptable. Unfortunately, their use facilitates clay hydration and swelling. Problems caused shales in petroleum activities are not new. At the beginning of the 1950s, many soil mechanics experts were interested in the swelling of clays, which are important for maintaining wellbore stability during drilling, especially in water-sensitive shale and clay formations. Wellbore instability is the largest source of trouble, waste of time and over costs during drilling. In drilling industry, a phenomenon of swelling clays is frequently observed. It has an important impact on the cementing quality. Inadequate cementing is often the result of the problem of swelling clay layers, which is often encountered at holes. The phenomenon of expansion of clay into the hole significantly influences the quality of cemented pipe sections. A number of adverse phenomena, such as the deposition (sticking) of rock formation with high viscosity to the surface of pipes: preventing proper bonding of the cement or casing contacting with clay stones, is just one of many threats shortening the lifetime of the hole and exposing the company to additional costs. Clay swelling during the drilling of a subterranean well can have a tremendous adverse impact on many others drilling operations. The overall increase in bulk volume impedes the removal of cuttings from beneath the drill bit, increases friction between the drill string and the sides of the borehole, and inhibits formation of the thin filter cake that seals formations. Clay swelling can also create other drilling problems, such as loss of circulation drilling fluids (Civan et al) pointed out that fines migration and clay swelling are the primary reasons for formation damage measured as permeability impairment. (Amaefule et al). determined that poorly lithified and tightly packed formations having large quantities of authigenic, pore-filling clays sensitive to aqueous solutions, such as kaolinite, illite, smectite, chlorite, and mixes-layer clay minerals, are especially susceptible to formation. Formation damage also occurs as a result of the invasion of drilling mud, cements, and other debris during production, hydraulic fracturing, and work over operations. With the drilled depth, the percentage of mixed layers and illite increases, while that of smectite decreases. In deposits of Silurian, Ordovician and Cambrian origin, illites are the dominant structure. Also the mixed package minerals contain smectite. The stability of the borehole depends to a large extent on interactions between the drilling fluid and exposed shale formations. Interactions between the mud filtrate and the clays present in producing horizons may restrict productivity of the well if the wrong type of mud is used. All of these point out the need for knowledge of clay mineralogy.

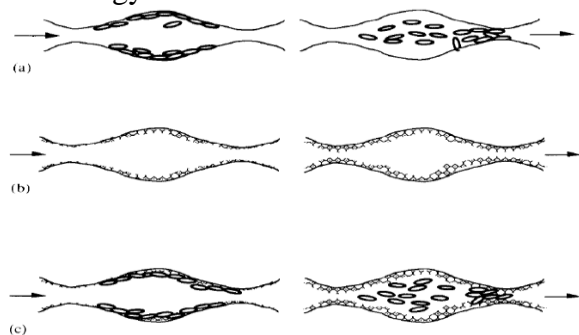


Fig. 1. Mechanisms of permeability reduction caused by clays in porous media. (a) Migration: changing ionic conditions cause the release of clays from pore walls and result in pore blockage. (b) Swelling: changing ionic conditions cause swelling of clays lining the pores and reduce cross-sectional area for flow.

(c) Swelling-induced migration: changing ionic conditions cause swelling of clays lining the pore walls and dislodge fines in the process

CLAY MINERALS IN KEROGEN FORMATION

The biogenic formation theory of crude oil formation is concerned with the geological evolution of organic matter. It involves the formation of kerogen, the decomposition of kerogen into hydrocarbon, fluid hydrocarbon migration, and hydrocarbon transformation within natural reservoirs. Kerogen is commonly defined as the insoluble macromolecular organic matter dispersed in sedimentary rocks. It is by far the most abundant form of OM which generates petroleum and natural gas (Vandenbrouck and Largeau, 2007). The role of clay minerals in the formation of kerogen has attracted particular attention. Kerogen conventionally contains two main fractions. One is the structured fraction, organic particles typical of recognizable biological affinity, for example spores and wood (vitrinite), while the majority of kerogen has no structures relatable to precursor organisms and is termed the amorphous fraction. The latter fraction is most significant in understanding the petroleum-generating properties and paleodepositional environment of the sediment (Senftle et al., 1987; Thompson-Rizer, 1993). The amorphous kerogen was once thought to be derived from the breakdown of biological macromolecules (proteins, nucleic acids, lipids, lignin and cellulose) that had escaped from complete microbial degradation and were then re-assembled in a random fashion with low molecular weight biochemicals to form kerogen. Clay minerals, acting as natural adsorbents in sedimentary systems, can adsorb and then protect amorphous, labile and dissolved organic components (e.g., amino acid and simple sugars) from complete microbial degradation. As a result, the presence of clay minerals might play a significant part in the organic matter accumulation and subsequent concentration reactions to kerogen in sedimentary rocks. The chemical change of organic matter adsorbed on clay minerals to kerogen is proposed to proceed through either a sorptive protection pathway (Salmon et al., 2000). Natural sulphurization has also been proposed to explain the formation of kerogen dispersed in sedimentary rocks. Most probably, these organic matter interactions and reactions on clay minerals are likely to occur in tandem. However, few studies have reported the role of clay minerals in the process of natural sulphurization.

ADSORPTION AND PROTECTION OF CLAY MINERALS

The adsorptive ability of smectitic clay minerals derives from the active sites on their structure, including Si–OH, Al–OH, hydrophobic surface, exchangeable cation, and isomorphic substitution (Fig. 1) (Cornejo et al., 2008). The interaction of labile organic compounds with the active sites of clay minerals occurs through ligand exchange; polyvalent cation bridges; and/or weak interactions (including hydrophobic interaction; Van der Waals forces; H-bonding). Recently, (Kleber et al. 2007) proposed a conceptual zonal model of organic compound-clay mineral interactions to interpret the self-assembly of organic molecules on the surfaces of clay minerals. In the model, OM in a sedimentary environment consists of amphiphilic molecules. The OM molecules are adsorbed onto the surfaces of clay minerals in a discrete zonal sequence that includes a contact zone, a zone of hydrophobic interaction, and a kinetic zone (Fig. 3). In the contact zone, particularly strong associations of organic compounds and clay minerals formed on the surface of a low-charge smectite, on clay minerals with a coating of hydroxylated Fe-oxide, and the uncharged siloxane surface of a hydrophobic kaolinite. On the one hand, the polar organic functional groups of amphiphiles could interact via ligand exchange with singly coordinated hydroxyls from clay minerals or Fe-oxide coating, forming stable inner-sphere complexes. On the

other hand, the certain hydrophobic organic compounds could associate with the non-charged siloxane surface of kaolinite by hydrophobic interactions. The formation of organic compounds in the contact zone gives rise to a hydrophobic zone. Hence, further adsorption and accumulation of organic molecules and fragments is possible in the outer region or kinetic zone, dependent on the input of organic sources. The adsorbed organic matter onto the surfaces of clay minerals should favor subsequent condensation reactions because it helps concentrate the reactants, thereby leading to the formation of kerogen. As illustrated by (Collins et al., 1995), the clay minerals selectively adsorb organic matter and condensation reactions between adsorbed compounds occur on the surface of clay minerals. Moreover, the resulting new chemical bonds can increase the binding of corresponding organic compounds to the surface of clay minerals. The compounds with multiple binding sites will compete with those with fewer binding sites. The resulting macromolecules will uncoil into more extended forms on the surface, displacing less strongly bound compounds. Meanwhile, the surface coverage is increased by their further reactions with other surface-bound molecules. The chain scission within a bound region of the macromolecular polymer is less likely to occur than that in unattached regions of the polymer due to entropic effects. In this way, the clay minerals play a role in the adsorption and protection of OM from complete micro biodegradation. Instead, they are conducive to the condensation of discrete organic species to yield kerogen.

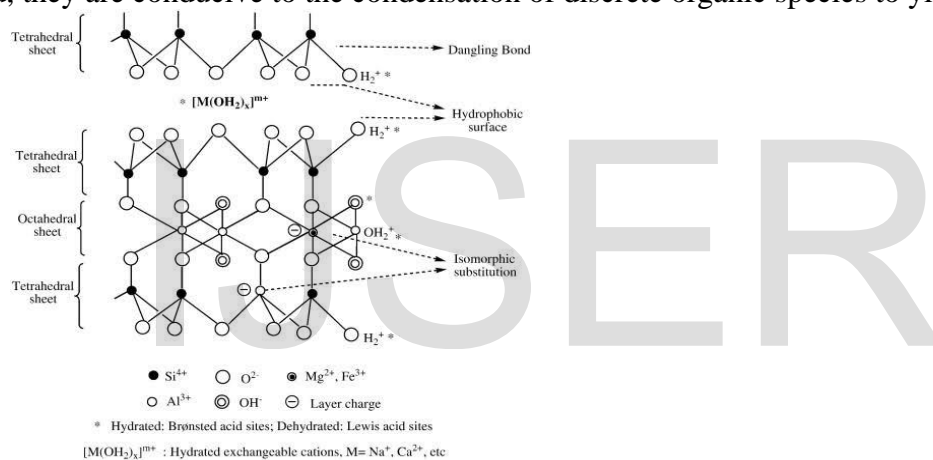


Fig. 2. Schematic drawing of adsorption sites, Brønsted and Lewis acid sites, on a smectitic clay mineral

CLAY MINERALS IN DEGRADATION–RECONDENSATION OF ORGANIC MATTER

According to the “degradation–recondensation” pathway, some biodegradation products of biopolymers (e.g. lignin, cellulose, protein) can recondense progressively, thus avoiding mineralization. The resulting insoluble geopolymer products are likely to be the precursors of kerogen. It is now well-known that proteins and carbohydrates can be broken into water-soluble amino acids and sugars by ubiquitous enzymes or microorganisms (Tuck et al., 2012). The biodegradation of phenol-containing biomolecules (e.g. lignin) also generates large amounts of water-soluble phenolic compounds (Zhou et al., 2011a). In the presence of clay minerals, catalytic recondensation reactions between degraded products occur and form kerogen. The whole process is thought to be similar, at least in part, to natural humification to form humic substances (Okabe et al., 2011), in which clay minerals have an influence on the degradation–recondensation of organic compounds. For humification and then kerogen formation, Maillard reactions and polyphenol theory of humic substance formation are proposed. There is another mechanism also proposed to explain the natural humification and generation of kerogen, for example, the oxidative

crosslinking of fatty acids and the esterification between fatty acids and phenols. The reaction of the oxidative crosslinking of fatty acids would be initiated by sunlight-mediated autoxidation. This leads to oxygen-rich humic products with aromatic structures and aliphatic chains ending with free terminal carboxyl groups (Vandenbrouck and Largeau, 2007). However, the role of clay minerals in the oxidative crosslinking of fatty acids and the esterification between fatty acids and phenols remains unclear and thus they are not discussed further in the context of this review.

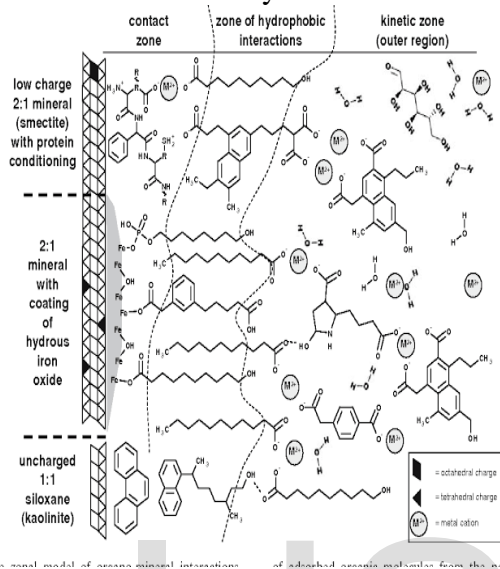


Fig. 3. The zonal model of organo-mineral interactions (Kleber et al. 2007). With kind permission from Springer Science and Business Media: Biogeochemistry, A conceptual model of organo-mineral interactions in soils: self-assembly of organic molecular fragments into zonal structures on mineral surfaces, 85, 2007, 9–24.

The Maillard reaction is viewed as a major pathway in humification and it involves the condensation reactions between reducing sugar and amino acid (Ikan et al., 1996). For example, D-glucose reacts with glycine to form amadori compound that is an intermediate product in the Maillard reaction (Mossine et al., 1994). The two proposed precursors, sugars and amino acids, are among the most abundant constitutions of terrestrial and aquatic environments (Anderson et al., 1989). For instance, lingocellulosic sources can be converted to reducing sugar catalyzed by acidic clay minerals. The first step in the Maillard reactions is the dehydration of reducing sugars to form various furfural compounds (Gonzalez and Laird, 2006). However, the hypothesis of Maillard reactions has the difficulty of explaining how reducing sugars can be dehydrated in a sedimentary aqueous system. In addition to the catalysis in the hydrolysis of cellulosic sources, clay minerals and related catalysts could also facilitate the subsequent reactions involving reducing sugars: isomerization of glucose to fructose; dehydration of glucose to 5-(hydroxymethyl)-2-furfural (HMF); dehydration of glucose to organic acid (Lourvanij and Rorrer, 1997; Zhou et al., 2011b). Recently, a study by (Gonzalez and Laird 2006) provided evidence that smectites are capable of abiotically catalyzing the dehydration of glucose to form furfural compounds, under conditions similar to those in sedimentary environments. The dehydration reaction was affected by the acidic character of the smectites and the type of exchangeable cation. The acidity of the exchangeable cation increases in the order of $\text{Fe} > \text{Na} > \text{Ca} > \text{Al}$. The yield of glucose decreased with the increasing acidity of the smectites. Further, the dehydrated glucose can react with amino acid to generate Maillard product melanoidins that consist of a mixture of fulvic acid, humic acid,

humic, and kerogen-like polymers. This proposition has been partly tested by many studies on the interaction between clay minerals and glucose and amino acid. (Arfaiolo et al. 1999) produced humic-like polymeric compounds with D-glucose and L-tyrosine as starting materials in different mineral systems: Me^+ - clay and Me^+ -quartz, (where $\text{Me}^+ = \text{Ca}^{2+}$ or Cu^{2+} or Al^{3+}); (Bosetto et al. 2002) prepared the humic-like compounds from glycine and D-glucose, on clay (K^+ , Ca^{2+} and Al^{3+} -saturated montmorillonite and kaolinite and quartz systems in the presence of the same cations); (Gonzalez and Laird 2004) made humic-like polymeric compounds with arginine and glucose in smectite and goethite systems. These results revealed that the humified C from Me^+ -clay was more complex than those from Me^+ -quartz systems. Comparatively, more complex substances formed over montmorillonite than that formed on kaolinite. In addition, for the formation of humic-like substances, cation exchange capacity (CEC) of clay minerals was more important than the type of cation (K^+ , Ca^{2+} , and Al^{3+}). Besides K^+ , Ca^{2+} and Al^{3+} , Cu^{2+} had an obvious influence on the overall amount of humified carbon. Presumably, this was because the low molecular weight compounds were retained on the surface of clay minerals through complexation with the Cu^{2+} (Arfaioli et al., 1997). These findings showed that the type of clay mineral, and the type and the amount of exchangeable cation could affect the formation and composition of kerogen in a manner similar to that shown by Maillard reactions.

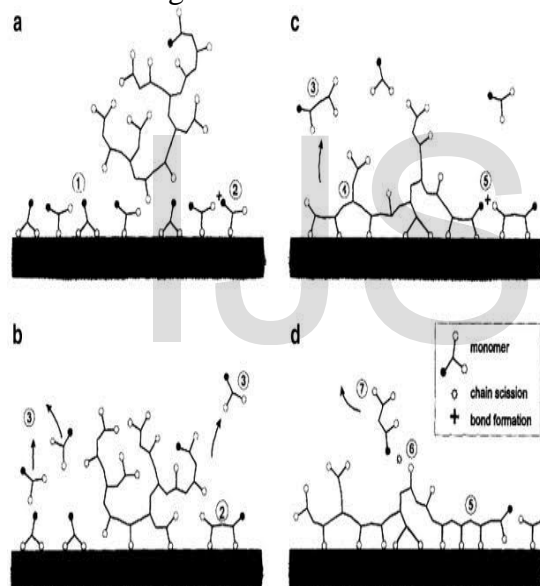


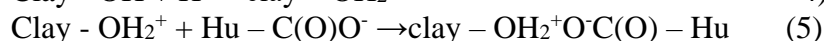
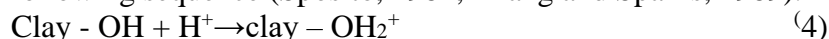
Fig. 4. Evolution of organic matter adsorbed on the surface of clay minerals. (1) and (2): OM selectively adsorbed by clay minerals; (3): weak bound compounds; (4): macromolecules; (5): other surface bound molecules; (6): unattached regions; (7): segments of chain scission (Collins et al. 1995). Reprinted from *Geochimica et Cosmochimica Acta*, 59, Collins, M.J., Bishop, A.N., and Farrimond, P., Sorption by mineral surfaces: Rebirth of the classical condensation pathway for kerogen formation? 2387–2391., Copyright (1995), with permission from Elsevier

POLYPHENOL THEORY Polyphenol theory provides an explanation for the recombination processes between degraded amino acids and phenols, or polymerization of phenolic compounds without amino acids. The phenolic compounds produced during organic matter degradation vary substantially with the organisms involved. For instance, lignin degradation by brown rot fungi gives rise primarily to low molecular weight catechol-type phenolic derivatives, including catechol (Fillee et al., 2002) and pyrogallol and hydroquinone (Martin and Haider, 1980). In these

recombination reactions, the influence of properties of clay minerals cannot be ignored. Polycondensation reactions between phenols and amino acids proceed via a nucleophilic reaction. It is well known that both Brønsted acid and Lewis acid sites are present on the surface of clay minerals. Their results suggested that the conditions on the surface of clay minerals were important factors. Recently, (Miura et al. 2009) found that the polycondensation reactions between catechol and glycine can be effectively enhanced by Lewis acids in clay minerals. The Lewis acid sites of clay minerals are dependent on the type and content of metal atoms and ions in their structure.

CLAY-HUMIC COMPLEXES FORMATION

Humic-like compounds, with certain similarity to the kerogen type substances, are adsorbed by clay minerals and subsequently lead to the formation of clay-humic complexes. (Taguchi, and Sampei, 1986) The adsorption of humic substances by ligand exchange is thought to occur in the following sequence (Spósito, 1984; Zhang and Sparks, 1989).



Where clay-OH represents the surface hydroxyl group of clay minerals, and Hu-C(O)O⁻ represents the carboxyl group of humic substances. The protonation in Eq. (4) makes the surface hydroxyl group more reactive. The carboxyl groups with the protonated hydroxyl groups may then form complexes on the surface of clay minerals as shown in Eq. (5), followed by ligand exchange (Eq. (6)). As a result, the clay-humic complex is formed and adsorbed. Experimental study by (Murphy et al. 1990) showed that desorption of the humic substances from the clay minerals was insignificant after 7 days. The results were interpreted as evidence of the formation of stable complexes between multiple carboxyl groups on the humic polyelectrolyte and surface hydroxyls on the surface of clay minerals (Murphy et al., 1990). The adsorbed humic substances exist in the form of clay-humic complexes rather than simply a mixture of clay minerals and humic substances. The existence of two distinct types of clay-associated humic substances were revealed by (Laird 2001) through modern characterization techniques such as scanning electron microscopy, Solid state ¹³C nuclear magnetic resonance spectroscopy (¹³C MAS-NMR), and energy dispersive X-ray analysis (EDX). The results suggested that one type of humic substance existed as a diffuse filamentous film covering the surfaces of the medium clay (0.02–0.2 μm) and fine clay (<0.02 μm). It had a low C/N ratio, high contents of extractable biomolecules (primarily amino acids and fatty acids). Another type of humic substance was in the form of discrete particles of much denser metal-humic complexes on the coarse clay fraction (0.2–2 μm) due to the distributions of Cu, Fe, Si and O on the clay surface. The complex had a higher C/N ratio, lower contents of extractable biomolecules with more carboxyl, O-alkyl, and alkene-aromatic regions. Examination of the structural changes of humic acid (HA) after adsorption by clay minerals through ¹³C MAS-NMR indicated that aliphatic fractions were preferentially adsorbed by clay minerals while aromatic fractions remained in solution (Laird, 2001). The adsorbed humic acid was largely insoluble, which lead to subsequent condensation reactions towards the formation of kerogen (Wang and Xing, 2005; Ghosh et al., 2009).

CLAY MINERALS IN SELECTIVE PRESERVATION OF ORGANIC MATTER

In the natural system, some insoluble biomacromolecules exhibit a high resistance to chemical and bacterial degradation. Hence, they are not likely to undergo the above-mentioned “degradation–recondensation” pathway in which biodegraded products of organic matter from living organisms recondense randomly into kerogen. Generally, these insoluble bio macromolecules are highly

aliphatic and remain almost unaffected even under drastic basic and acidic conditions at laboratory scale. Such macromolecular components also show a high resistance to attack by microbial hydrolytic enzymes. Thus, they are relatively stable during sedimentation in geological systems. In this case, possibly there is selective preservation of recalcitrant organic matter and then selective aggregation of such biomacromolecules during diagenesis to form kerogen. By such an aggregation, fecal matter from microorganisms, microorganisms and mineral particles clumps together to form larger particles that settle rapidly (McCave, 1984). Clay minerals can affect selective aggregation of recalcitrant organic matter, especially the resistant fraction of organic matter in marine and lacustrine environments, to form kerogen. In the marine system, the marine dissolved organic matter spontaneously assembles into marine macroaggregates (Chin et al., 1998). The macroaggregates are predominately composed of a saccharidic matrix with accumulated lipid refractory substances (Baldi et al., 1997). The presence of mineral particles, including clay minerals, enhances the agglomeration. However, the mechanisms between macroaggregates stabilized by clay minerals and further kerogen formation remain elusive.

THE CATALYSIS OF CLAY MINERALS IN THE CONVERSION OF KEROGEN INTO CRUDE OIL

Macromolecular kerogen is metastable. Consequently, it is susceptible to gradual decomposition into thermodynamically favored compounds of lower molecular mass within the sediment. This catagenic process is considered the most probable way to generate liquid (crude oil) and volatile (natural gas) organic alteration products (Hunt, 1996). In addition to time, temperature and the composition and structural characteristics of the source kerogen, inorganic compounds, such as water and minerals, may participate as reactants or catalysts during the catagenic process. Namely, the chemical environment around kerogen in sedimentary basins also plays an important role in the formation and compositional evolution of petroleum (Seewald, 2003). Two types of catalytic sites (Brønsted and Lewis acid sites) on clay minerals can contribute to the conversion of kerogen into crude oil. As mentioned above, Brønsted acids are H^+ proton donors; Lewis acids are electron acceptors. Owing to the presence of acid sites, clay minerals can act as natural catalysts in the catagenic process of kerogen to crude oil. Brønsted and Lewis acid sites of clay minerals are responsible for C-C bond cleavage (hydrocarbon cracking) and decarboxylation, respectively, in the process of crude oil generated from kerogen (Johns, 1979). Besides, clay minerals also can function as sorbents to selectively adsorb polar compounds (e.g. asphaltenes) on their surface and thereby have an influence on the expulsion of crude oil from source rocks.

CATALYTIC HYDROCARBON CRACKING

Clay minerals have the potential to bring about catalytic cracking of kerogen to form lighter hydrocarbons. Previously, (Tannenbaum et al. 1986) found that carbonate source rocks mainly yielded heavy oils, whereas light oils and gases were the main products from source rocks that contained expandable clays. This observation alluded to the interaction of clay minerals to adsorb kerogen and heavy oils and then catalyze them into lighter crude oil. The overall process of crude oil formation involves the initial cleavage of weak non-covalent bonds in kerogen to form a macromolecular bitumen phase, followed by cleavage of covalent bonds in bitumen (also known as asphalt, closely related to heavy oil) to form liquid oil and natural gas (Miknis et al., 1987; Lewan, 1997). Clay minerals not only crack kerogen to form hydrocarbon directly, but also interact with the bitumen phase to produce secondary hydrocarbons. It has been shown that such Brønsted acidity can catalyze the cracking of long-chain hydrocarbons into shorter chain hydrocarbons through a carbonium ion mechanism involving positively charged intermediates (Lao, 1989). A series of subsequent reactions, such as cracking, isomerization, and transformation, can convert

carbonium ions into hydrocarbons (Li et al., 1998). Under the initiation of proton activity, kerogen can form positive and negative alkane intermediates, which may contribute to the crude oil generation (Zhou, 2010b). Although clay minerals could act to transform kerogen to hydrocarbons by carbonium-ion mechanisms, compared to free-radical mechanisms, this would be expected to produce a predominance of branched hydrocarbons (Kissin, 1987). As this is not the case, it is likely the Brønsted acid-catalyzed carbonium-ion mechanism on the surface of clay minerals is not a major process. However, Lewis acid sites on clay minerals could take reactions through free-radical mechanisms. (Fan et al. 2004) investigated the catalytic effects of minerals on hydrothermolysis of heavy oil. The results showed that, when clay minerals (montmorillonite, illite, kaolinite, and chlorite) and steam coexist, saturated hydrocarbons increased to 27.8%, aromatic compounds increased to 32.2%, while resin decreased to 33.8% and asphaltene decreased to 6.2%. In this process, clay minerals can react with steam to produce more surface hydroxyl groups and their acidity becomes stronger. As a result, the hydrothermolysis of heavy oil was accelerated, and the viscosity and average molecular weight of heavy oil was reduced (Fan et al., 2004). These findings also support the proposition that the various states of water are a factor in the catalytic activity of clay minerals in hydrocarbon generation (Lewan, 1997) and refute earlier suggestions that the catalytic activity of clays was suppressed in the presence of water (Tannenbaum and Kaplan, 1985). Moreover, the composition of generated crude oil is also partly dependent on the amount of clay mineral present. (Faure et al. 2006) identified the progressive disappearance or appearance of specific compounds on pyrolysis-gas chromatography–mass spectrometry (PyGC–MS) by using the reactant of Na-smectite/humic acid mixtures containing from 10% to 100% humic acid. The results showed that, in the case of the higher clay content; n-alkanes of high molecular weight (C28–C31) disappeared whereas n-alkanes of low molecular weight (C9–C14) increased (Fig. 5). Such results were in accordance with previous findings by (Dembicki, 1992) that, at low organic matter, montmorillonite clay minerals can activate organic matter more easily. Based on these findings, therefore, it could be concluded that the type of clay mineral and the ratio of clay mineral to organic matter have a significant influence on the conversation of kerogen into crude oil. In the process of kerogen to crude oil, liquid hydrocarbons were not the only products, gas hydrocarbons were also released. Recently, (Pan et al. 2010) conducted pyrolysis experiments using crude oil alone, oil and montmorillonite, and oil and calcite. The results showed that the heating rate and the type of minerals both affected the distribution of the various products. Clay minerals favored the formation of light gaseous hydrocarbons. Furthermore, it has been shown that the major clay minerals in the biotermocatalytic transitional zone of source rock are montmorillonite, illite/montmorillonite, illite, kaolinite and chlorite. Among these minerals, montmorillonite is the major catalyst in the formation of the transitional zone gas (Lei et al., 1997). Comparatively, the thermo-degradation temperature of organic matter was lowered by 50 °C over montmorillonite (Lei et al., 1997).

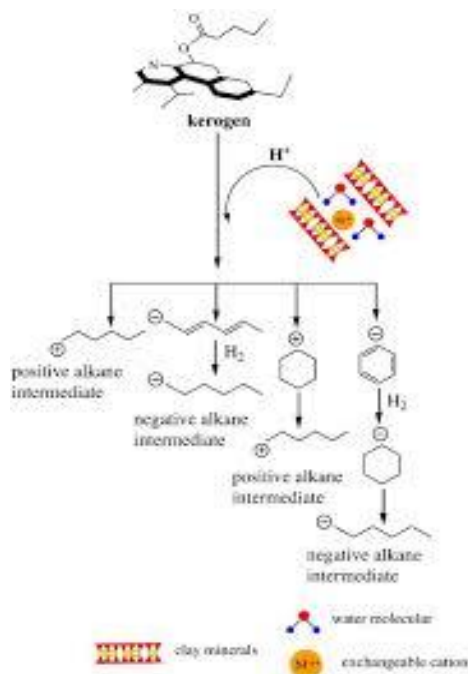
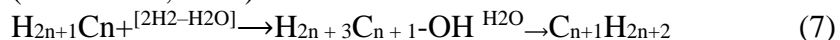


Fig. 5. The formation of positive and negative alkane intermediates deduced by proton (Modified from Zhou, 2010b).

CATALYTIC DECARBOXYLATION

One of the possible origins of petroleum was identified from the lipid materials (e.g. fatty acids), either in a free form or in a combined form in kerogen. Fatty acids and hydrocarbons, typically alkanes with general formula (C_nH_{2n+2}), have chemical and structural similarity (Shi and Xiang, 2001). Experimental study showed that fatty acids can be converted into hydrocarbons in the presence of mineral-based catalysts (Tong et al., 2010a). Lewis acid sites of clay minerals are thought to be responsible for decarboxylation reactions. Theoretical calculation (Geatches et al., 2010, 2011) by ab initio DFT computation has been used to probe the interaction between a clay catalyst and a fatty acid in a decarboxylation reaction. However, recent studies indicate that multiple transition states (CH₃-CH₂OH+CO) could exist in the process of catalytic decarboxylation of fatty acid to crude oil in the presence of clay minerals (Geatches et al., 2011). The resulting alcohol intermediates subsequently undergo further reduction to yield hydrocarbons with the simultaneous formation of CO₂. The dehydration/hydrogenation reactions of fatty acids and their esters have been shown to involve alcohol intermediates in studies of biofuel production (Senol et al., 2005) as illustrated in



Besides the multiple transition states, (Geatches et al. 2011) also determined that decarboxylation reaction in iron-bearing aluminum silicate clay environment involved the transfer of electrons. These findings are in agreement with earlier observations that in the process of transformation of kerogen into petroleum, clay minerals accepted electrons from kerogen, resulting in simultaneous reduction of Fe³⁺ to Fe²⁺ in dioctahedral smectites (Devey and Curtis, 1989; (Drits and Manceau, 2000). Consequently, the reaction facilitates the polarization of adsorbed water to yield Brønsted acid sites (Yan and Stucki, 1999). The interrelationship of Lewis and Brønsted acid sites on clay minerals is illustrated by this catalytic reaction.

The expulsion and migration of crude oil from source rocks

Crude oil generation is followed by migration from the source rocks into carrier beds and along faults until an appropriate trap is reached. Crude oil migration has been categorized as primary and secondary. The former refers to the movement of crude oil within and out of non-reservoir source rocks into more permeable rocks. Secondary migration is the movement of crude oil within permeable pathways and reservoir rocks leading to petroleum accumulations. In primary migration, crude oil and gas migrate through a three-dimensional OM (kerogen) hydrophobic network, which would not be subject to interfacial forces until the petroleum enters much larger water-filled pores in the reservoir rock. Secondary migration is made through separate-phase buoyancy-driven transport. Under hydrostatic conditions, crude oil rises in water as a continuous-phase droplet due to oil being less dense than water, and the immiscibility of the two fluids (hydrocarbon and water). As to the migration process, identification of the driving force and the form of crude oil during migration has received much attention. Gases and water were considered to account for the driving force for petroleum liquid hydrocarbon transportation. Gas hydrocarbon (e.g. methane), CO and CO₂ always form at the time of crude oil generation. The gases could be the driving force of primary migration of crude oil by the dissolution of heavy liquid components (e.g. hydrocarbons up to C₁₈, aromatic rich condensates) in gases. However, as secondary migration occurs under the hydrostatic conditions, large volumes of water are required, rather than the flow of water. Clay diagenesis occurs under burial and temperature conditions associated with crude oil migration and could provide a driving force for primary migration. Smectite–illite transformation process and the process of smectite dehydration both result in loss of water, mostly from the interlayer of smectite (Burst, 1969; Perry and Howe, 1972; Zhang et al., 2010; Cai et al., 2012). This expelled water may result in fluid overpressure (Powers, 1967) which could provide a driving force to mobilize and flush out hydrocarbons (Bruce, 1984). The smectite–illite transformation in potential source rocks is therefore a possible geochemical/mineralogical tracer for hydrocarbon formation and primary migration with application to petroleum exploration (Abid and Hesse, 2007). Although hydrocarbon and water are immiscible in secondary migration they can interact in the presence of minerals to form a crude oil–mineral (micron-sized mineral particles) water mixture described as “clay-oil flocs” or as “oil–mineral aggregates” (OMA, particles $\geq 2 \mu\text{m}$). The “clay-oil flocs” or OMA reduces the adhesion of oil to other materials and allows it to be easily removed by gentle water motion (Owens, 1999). However, these interactions of oil and minerals have been studied mostly in shoreline treatment techniques (cleanup techniques, e.g. oil removal processes) (Owens and Lee, 2003). Research has not focused on the role of “clay-oil flocs” or OMA in crude oil migration. It remains an open question therefore, as to whether crude oil in the form of “clay-oil flocs” or OMA can migrate over a long distance under a gentle driving force. The influential parameters in the OMA formation include the type of minerals, the properties of crude oil, water salinity, and the oil/mineral ratio. Three OMA types (droplet, solid and flake aggregates) have been identified on montmorillonite, quartz and kaolinite they vary with mineral type and oil concentration. In the case of montmorillonite, flake OMA was formed due to the retention ability of crude oil. In the case of quartz, droplet OMA was obtained. Kaolinite surface is more hydrophobic than quartz, and had greater tendency to form droplet OMA. By using a flocculation index, Omotoso et al. (2002) found that hydrophilic quartz and kaolinite interacted more strongly with low-viscosity oils than with high-viscosity oils, whereas calcite (an oleophilic mineral) interacted strongly with crude oils, irrespective of their viscosities. In addition, in low-viscosity oils with hydrophilic minerals (kaolin, montmorillonite), a water-continuous phase was predominant, while OMA with calcite appeared to be an oil-continuous phase. In fresh water, quartz and kaolin interacted more strongly with crude oils than montmorillonite but the

reverse was observed in seawater (Omotoso et al., 2002). At higher salinity, a higher concentration of clay minerals improved the formation of aggregates, the ratio of oil to mineral was also the primary factor in controlling OMA buoyancy (Stoffyn-Egli and Lee, 2002). While OMA will likely form in natural systems, its role during crude oil migration remains unclear. During expulsion and migration, crude oil undergoes changes in composition, which may be influenced by interaction with clay minerals. Experimental simulation on crude oil migration through montmorillonite clay by (Bonilla and Engel 1986), showed C15+ aliphatic hydrocarbon fractions (favorably composed of n-alkane components of the lower molecular weight) and the distribution of methylphenanthrene isomers of the aromatic fraction appeared to be accentuated with increasing migration distance. Clay minerals as sorbents selectively adsorbed polar compounds.

Indicator of hydrocarbon generation and expulsion

For oil and gas exploration, we need at least to confirm the exploration area has potential source that generates the oil and gas. This drives geologists to study the potential source rocks (usually organic rich shale) to understand if the organic matter in the source rock can generate hydrocarbons at a given depth in a specific geologic time and when the generated hydrocarbons reach the expulsion peak. Organic geochemistry is the main discipline for studying oil and gas generation and expulsion. However, clay mineralogy is also important for evaluation of these parameters since clay minerals and organic matters usually coexist in the sedimentary rocks and the ultrafine clay minerals are sensitive to the changes in the rocks accompanying the hydrocarbon generation and expulsion processes. Association of clay minerals and organic matter in shales is a significant factor in petroleum genesis. Many authors report the transformation of clay minerals during diagenesis is from montmorillonite to mixed-layer montmorillonite/illite to illite (Hower et al, 1976) and changes in the ordering of Illite/smectite (I/S) are particularly useful in studying the hydrocarbon generation because of the common coincidence between the temperatures for the conversion from random to ordered I/S and those for the onset of peak oil generation. The use of mixed-layer illite/smectite (I/S) as a geothermometer and indicator of thermal maturity is based on the concepts of shale diagenesis that were first described in detailed studies. The clay mineral association even can be used to evaluate the hydrocarbon generation degree, e.g., the presence of illite-smectite-to be illite demonstrates that oil generation has taken place and absence of to be illite layers shows that the rock has not been heated sufficiently to generate large amounts of oil (Drits et al., 2002). The significant changes of clay minerals during burial and their relations with diagenetic stages, temperature, organic matter maturity, hydrocarbon generation and expulsion can be summarized in (Figure 7). During early diagenesis, the maturity of source rock indicated by vitrinite reflectance (R_o) is low and low percentage of illitic beds in illite-smectite mixed layer clay minerals, e.g. $R_o = 0.5\%$ approximately corresponds to around 25% illite presence. The Clay minerals mainly experience loss of pore water and little oil is generated during this period. 25 to 50% illitic beds in illite-smectite mixed-layer clay minerals correspond to major oil generating zone ($R_o = 0.5$ to 1.0%). When more than 75% illitic layers are present in illite smectite mixed-layer clay minerals, cracking of hydrocarbons form dry gas ($R_o > 1.5\%$). This general trend can be used to predict if the source rock is able to generate hydrocarbon in an area. For example, the smectite alters to illite at temperature of 80 to 120°C , which corresponds to the oil generation peak at the same temperature range. (Figure 7) presents data from Liaodong Bay area in Bohai Bay Basin in Northeast China to this aspect showing the change in maturity of organic matter and reaction progress in the smectite to illite transformation, which indicates that the rapid increase in illite and decrease in smectite (montmorillonite) in I/S correspond to rapid oil generation. The reaction of smectite to illite in these clays also can indicate the producing high

porefluid pressures (Powers, 1967) and expulse hydrocarbons from the shales (Burst, 1959; Bruce, 1984). This can be demonstrated in (Figure 7) that the overpressure development interval corresponds to the transformation of smectite to illite and hydrocarbon generation zone (Figure 8C, D, E).

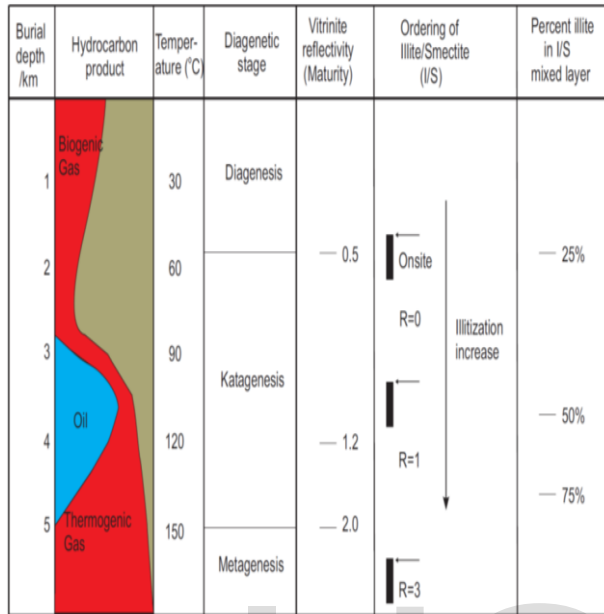


Figure 7. Generalized relationship between temperature, hydrocarbon generation, diagenesis, source rock maturity (vitrinite reflectance), changes in mixed-layer illite/smectite.

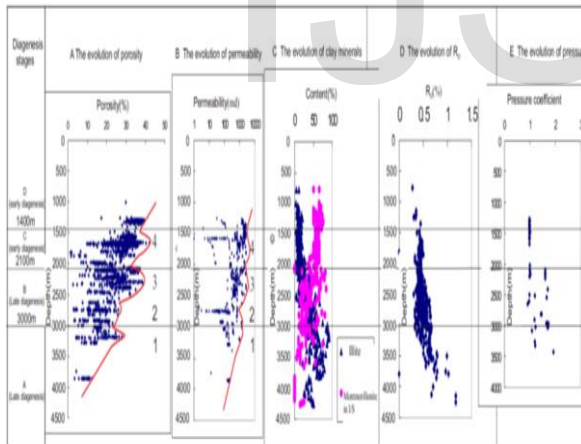


Figure 8. Five plots showing the relationships between diagenetic stages, porosity (A), permeability (B), clay minerals evolution (C), vitrinite reflectance (R_o) (D), and pressure (E) in Liaozhong depression,

INDICES FOR HYDROCARBON MIGRATION AND ACCUMULATION

It is critical to establish that hydrocarbon formation and migration occurred after the formation of the trap (anticline, etc.) that is to hold the oil. There is still very little known about the manner in which hydrocarbons formed in argillaceous source rocks migrate and accumulate in porous reservoirs. Some evidence exists, however, that the clay mineral kerogen complex plays a role in modifying hydrocarbon compositions during migration. A number of investigators (Powers, 1967;

Burst, 1969) have focused attention on the late stage dehydration which accompanies smectite to illite transformation during burial diagenesis. This firstly suggests that the replacement of kaolinite by illite or direct precipitation of illite indicates fluid flow where the chemical potential of the fluids is in disequilibrium within the reservoir sandstone. The existence of secondary illite does indicate aqueous fluid flow and thus can be used as indices of fluid movement and hence signal the possible hydrocarbon migration. Secondly, it indicates that the water release could create a flushing action responsible for the migration of petroleum hydrocarbons from the source rock through the migration paths to nearby reservoirs. Also, the water liberation can build up abnormal pressures in less permeable sediments, which can provide migration dynamic for hydrocarbons (Figure 9C, E). Abnormal Illite distribution has been used as an index to determine if certain rocks/strata/areas are a hydrocarbon migration pathway and its conducting capability (Zeng and Yu, 2006, Jiang et al., 2011). If there shows abnormal illite distribution, it indicates the hydrocarbon migration happened. The illite abnormal distribution of three wells from three different structure zones in Liaodong Bay Sub-basin of Bohai Bai Basin in Northeast China in suggests hydrocarbon migration happened in these three areas represented by three wells, but the conduiting capabilities are different in the three areas based on different abnormal magnitude of illite content. At the same depth of these three wells, illite content of well JZ25-1s-1 is the highest and the illite content of well JZ21-1-1 is the lowest, which indicates the hydrocarbon migration in the JZ25-1s-1 well area is the most active and the JZ21-1-1 area is the relatively least active area regarding to hydrocarbon migration (Figure 8). This result is consistent with current oil discoveries: The Liaoxi uplift (represented by well JZ25-1s-1) to the west of Liaodong Bay contributes to the most reserves in the Liaodong Bay sub-basin. Tan-Lu strike-slip area (represented by well JZ23-1-1) is emerging as the second largest hydrocarbon migration and accumulation area (Jiang et al., 2010, 2011). Almost no oil and gas discoveries in the rest area of Liaozhong depression (represented by well JZ21-1-1) away from strike-slip zone and Liaoxi uplift so far due to poor hydrocarbon migration pathway and poor conduiting capability. The smearing of clay minerals can also prohibit the hydrocarbons' further migration and facilitate the hydrocarbon accumulation. When the soft clays are smeared into the fault plane during movement and they will provide an effective seal. In many cases, the presence of clay types and their proportions can even indicate if there is oil and gas accumulation.

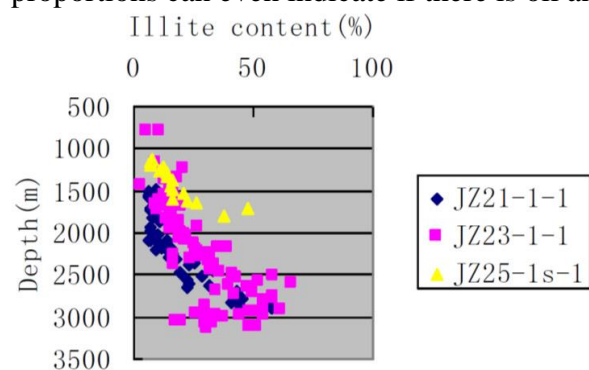
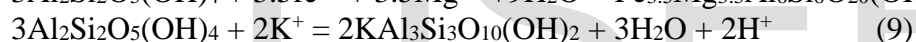
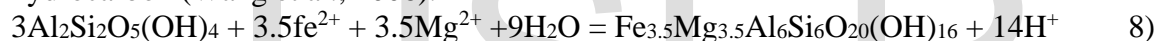


Figure 9. The illite content distribution versus depth from three wells in Liaodong Bay area, Bohai Bay Basin.

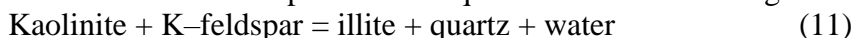
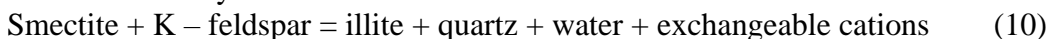
CLAY MINERALS IN HYDROCARBON ACCUMULATION

An oil reservoir is a subsurface container of hydrocarbon, in which hydrocarbons are trapped in pores and fractures by overlying rock with low permeability. Reservoirs are divided into two

main families, sandstone reservoirs (mainly siliceous) and carbonate reservoirs. About 60% of all petroleum reservoirs are sandstones; outside the Middle East, carbonate reservoirs are less common and the percentage of sandstone reservoirs is much higher (Bjørlykke and Jahren, 2010). Clay minerals in sandstone reservoirs act as adsorbents and reactants with crude oil components. Polar components of crude oil are selectively adsorbed by clays minerals which affects the rank of the crude oil. (Pan et al. 2005) separated the free oil and adsorbed oil (obtained from the clay minerals in the b_2 μm size fraction) in hydrocarbon reservoirs (from the southwestern part of the Bohai Bay Basin in Northern China). Using GC, GC–MS and elemental analyses, it was shown that the free oil was dominated by saturated hydrocarbons (61.4–87.5%) with a low content of resins and asphaltenes (6.0–22.0% in total) while the adsorbed oil was dominated by resins and asphaltenes (84.8–98.5% in total) with a low content of saturated hydrocarbons (0.6–9.5%). These were mixed with water and sealed in gold tubes to investigate the effects of reservoir minerals on the destruction of crude oil. In comparison with the system containing only crude oil+water, there was a retardation effect on crude oil cracking in the presence of illite and montmorillonite whereas there was an acceleration effect on the destruction of crude oil in the presence of calcite and quartz. Clay minerals in crude oil reservoirs also undergo diagenetic changes where kaolinite transforms to chlorite and/or illite (Johnsand Mckallip, 1989). Transformation of kaolinite to illite and chlorite in reservoirs located in Gulong Depression, northern Songliao Basin, China was associated with increased light organic compounds in the crude oil (Wang et al., 2006). Release of protons during the mineral transformations provides a possible explanation for the increased catalytic cracking of heavy hydrocarbon (Wang et al., 2006).



Diagenetic conversion of clay minerals also affects the reservoir quality by modifying porosity and permeability and altering the storage capacity. Smectite and kaolinite reactions with K-feldspar to form illite (Nadeau et al., 2002; Thyberg et al., 2010), Eq. (10) and (11) significantly reduce the permeability and porosity of reservoir rocks, which can act to preserve areas where crude oil has already accumulated



Clearly, the role of clay minerals present in crude oil reservoirs can result in various outcomes. On the one hand, clay minerals can adsorb polar and heavy components in crude oil. Consequently, the crude oil becomes light. On the other hand, clay minerals can react with crude oil. In addition, clay minerals may also undergo diagenetic changes that modify reservoir properties. All these have an effect on the hydrocarbon composition in the crude oil reservoir.

INDICATION OF TECTONICS AND SEDIMENTATION

During the evolution of petroliferous sedimentary basin, the clay minerals contained in the rocks undergo a series of changes in composition and crystal structure in response to tectonics and sedimentation. The amount and type of clay minerals are a function of the provenance of clastic minerals and of diagenetic reactions at shallow and greater depth in different tectonic and sedimentary settings. Clay minerals can be used to infer tectonic/structural regime, basin evolution history and the timing of various geologic events. This trend is probably the result of multi-stage reverse faultings resulted from the compressional tectonic movement. I/S data were also used to infer several kilometers of uplift and subsequent erosion of the section. The depositional facies appears to be an important factor controlling the abundance of clays in the sediments. Fluvial facies

generally possesses higher clay mineral abundance. Well-sorted clean aeolian sands typically have a low clay abundance (<15%).

SIGNIFICANCE OF CLAY MINERALOGY FOR RESERVOIR QUALITY PREDICTION

Porosity and permeability are the most important attributes of reservoir quality. They determine the amount of oil and gas a rock can contain and the rate at which that oil and gas can be produced. Most sandstones and carbonates contain appreciable fine-grained clay material including kaolinite, chlorite, smectite, mixed layer illite-smectite and illite. These clay minerals commonly occur as both detrital matrix and authigenic cement in reservoir sandstones. The reservoirs initially have intergranular pores that are main space for oil and gas accumulation. When the reservoirs are deposited, their primary porosity is frequently destroyed or substantially reduced during burial compaction. The clay minerals are usually assumed to be detrimental to sandstone reservoir quality because they can plug pore throats as they locate on grain surface in the form of films, plates and bridge and some clay minerals promote chemical compaction. Generally, the porosity loss is mainly caused by the diagenetic process including mechanical compaction, quartz and K-feldspar overgrowths, carbonate cementing and clay mineralization. Especially, the diagenetic clay minerals play a very important role in determining the reservoir quality. Authigenic clays from diagenesis in the sandstones studied occur as illite, illite-smectite and kaolinite. They form cements around the detrital minerals. During the period of intermediate to deep burial diagenesis, Illite and illite-smectite clays are the first cements. These early-formed clay films play an important role in reducing reservoir porosity and permeability during burial diagenesis. For example, pore-filling illite formed mainly at the expense of kaolinite. The illitic clays usually occur as pore-bridging clays to reduce the pore space and block the fluid movement by reducing permeability. For clay minerals that replaced rigid feldspar minerals are easily compacted and can be squeezed into pore throats between grains. This will also greatly influence the decrease of reservoir quality. For oil and gas exploration, we expect the occurrences of high-quality reservoirs. Even though the porosity and permeability of reservoir generally decrease with the increase of burial depth due the diagenetic processes as state above, other diagenetic processes may enhance porosity through the forming of secondary porosity including fractures, removal of cements or leaching of framework grains, preexisting cements and clay minerals, limited compaction and/or limited cementation. The dissolution of authigenic minerals that previously replaced sedimentary constituents or authigenic cements may be responsible for

CONCLUSION

The clay minerals are important compositions in source rocks and reservoir rocks that can generate and store oil and gas respectively. The presence of clay minerals strongly influences the physical and chemical properties of conventional sandstone, carbonate and unconventional shale. Regionally, the clay minerals can be used to interpret and understand such perspectives as the basin evolution on tectonics, sedimentation, burial and thermal history, to infer the sedimentary environment and to correlate strata, etc. For clay minerals in source rocks, they are important for quality evaluation of the hydrocarbon generation, expulsion and migration. Clay minerals help concentrate organic matter by adsorption and subsequently act as catalyst to generate petroleum. The transformation of montmorillonite to illite and increasing ordering of I/S can indicate the

hydrocarbon generation and expulsion events. For clay minerals in reservoir rocks, their presence has an important impact upon reservoir properties such as porosity and permeability and upon those measured physical data that are used to evaluate reservoir quality. Geologists use clay minerals information to decipher the burial diagenetic process and reveal the pore type and pore evolution. Even though they are usually considered to be detrimental to reservoir quality because they can plug pore throats and can be easily compacted, other diagenetic processes may enhance porosity through the forming of secondary porosity through providing porosity by clay dissolution, creating micropores in clays and coating of chlorite on grains to prevent quartz cementation. The recent emerging shale oil and gas exploration requires state-of-art imaging and characterization techniques to study the application of clay minerals in the exploration of this unconventional resource. The modern innovative QEMSCAN® and FIB/SEM/EDS have been playing key roles in the identification and quantitative characterization of clay minerals, which help define the best brittle reservoir interval and avoid exploration failure by choosing the compatible drilling and hydraulic fluids.

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