COMPARISON OF THERMAL MATURATION INDICATORS WITHIN
HYDROCARBON BEARING SEDIMENTARY ROCK

by

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Abstract

The thermal maturity of hydrocarbon-rich source rocks can be estimated by several different methods. These methods focus on a specific geochemical or mineralogical aspect contained within the rock.   Because each method has limitations, it is advisable to use several methods to better determine thermal maturation. This report summarizes two common methods used to determine thermal maturity, vitrinite reflectance and illitization. Vitrinite reflectance and illitization have both been shown to be effected by similar temperatures that are within the hydrocarbon generation window. In some previous studies these two methods give different levels of maturation when looked at in tandem. Formations such as the Woodford Shale of Oklahoma are made up almost completely of illite in the clay fraction, even at low levels of vitrinite reflectance. These are also without a clear source of potassium, which is often the limiting factor in the process of illitization. Totten et al. (2013) suggest that in place of potassium feldspars, which are a common source of K^+ for illite (but lacking in the Woodford) that the needed K^+ was provided by the organic material that was being altered under the same temperatures of the clay minerals. The Woodford contains large amounts of organic matter, This would be consistent with promoting illitization at lower thermal maturities than organic-poor shales.

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Chapter 1 - Introduction

Several previous studies have documented a correlation between diagenetic temperatures and the transformation of both organic material and that of the clay minerals found within sedimentary rock (Iacoviello et al., 2012; Guthrie, 1986). Hydrocarbon- rich reservoirs will vary in present day content due to varying organic matter types and differing thermal histories caused by geologic activates such uplifts due to faulting or increases in pressure and temperature brought about by burial depths. For this reason, relationships between different methods to determine thermal maturation are examined closely. Guthrie et al. (1986) argued that, due to the temperature dependencies of both vitrinite reflectance and illite crystallinity (Figure 1), the degree of illitization could be used to approximate stages of hydrocarbon generation in the absence of vitrinite. The sharpness ratio, based upon XRD measures of illitization, was proposed by Weaver (1960) as a way to measure the degree of metamorphism in clay-rich rocks. It is also useful for diagenetic regimes.

Research has subsequently shown that sections of the Woodford Shale found in central Oklahoma do not consistently present matching thermal maturity ranking (Kirkland et al, 1992; Alkhammali, 2015). This review integrates studies performed at Kansas State University, along with several outside researchers' publications, to show correlations and discrepancies of source rock evaluation techniques of thermal maturation, burial history, and hydrocarbon production of the Late-Devonian/ Early-Mississippian Oklahoma Woodford Shale.
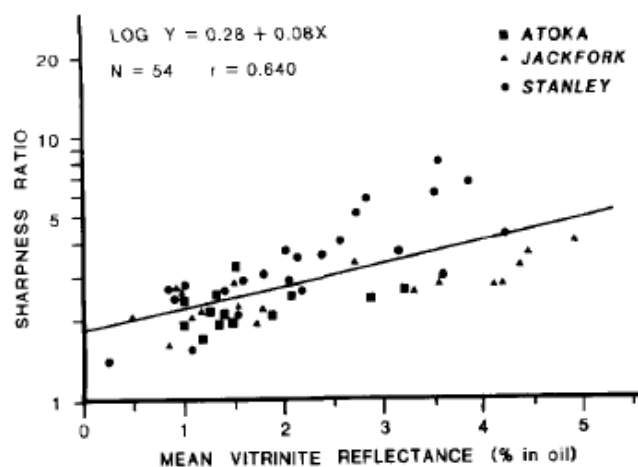

Figure 1 **– Relationship between mean vitrinite reflectance in oil (VRo) and illite sharpness ratio (Weaver, 1960) from the Stanley, Jackfork, and Atoka shales (Guthrie et al., 1986).**

Chapter 2 - Mineralogy

The term "clay" by definition refers to a naturally occurring material composed primarily of fine-grained mineral (Guggenheim and Martin, 1995). Geologists define the term "fine-grained " as particle size less than 2 μm. Clay minerals are primarily comprised of phyllosilicates, but can contain other types of minerals in this size range (Moore and Reynolds, 1989). Most clay minerals are not found in pure mineral form but in layers of mixed composition. Other minerals such as quartz can be identified in the clay fraction but are not considered clay minerals (Moore and Reynolds, 1989).

The characteristics of clay minerals (i.e. composition, structure, charge) will have a direct effect on reservoir quality and exploration interpretations (Nadeau and Bain, 1986). Even though clay minerals are very small, being measured in angstroms (Å), they can comprise ~30 to 50% of sedimentary rocks (Środoń, 1990; Melka, 2009). Because of their abundance and small size, the vast surface area available to clay minerals has the potential to have a very large impact on diagenesis.

The main structure of all clays consists of two main structures, a tetrahedral sheet and an octahedral sheet (Figure 2). A pure tetrahedral silicate sheet would have the formula Si_2O_5 (Figure 2a). Si^{4+} is the dominant cation but can be substituted for Al^{3+} and to a lesser extent Fe^{3+}. The octahedral will vary more than the tetrahedral sheet. The octahedral sheet will comprise of six oxygen ions, sometimes single bonded with hydrogen to make hydroxyl bonds. The shape leaves an open spot in the middle, called the octahedral cation site. As shown in Figure 2b, typical cations to fill these spaces are Al^{3+}, Mg^{2+}, Fe^{2+}, Fe^{3+}, and occasionally Li (Moore and Reynolds, 1989).
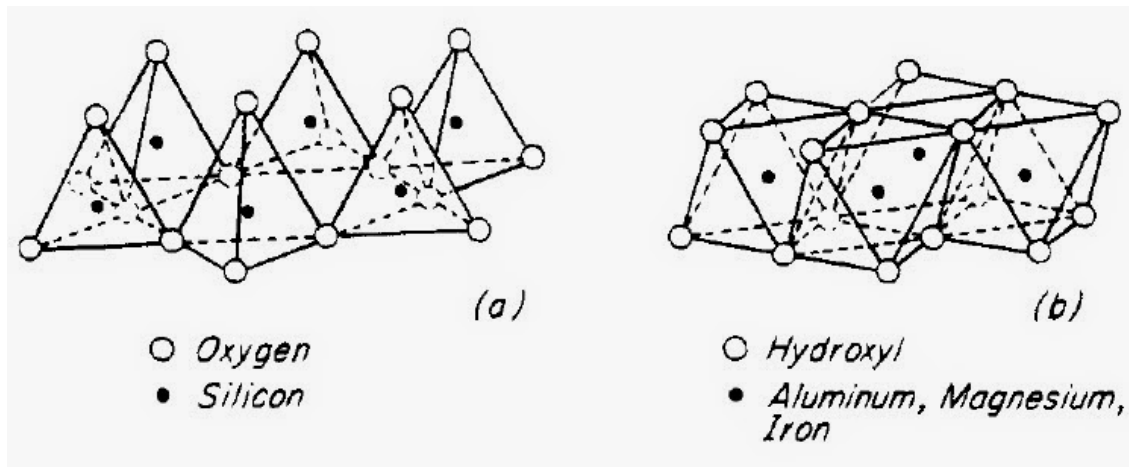
Figure 2 a) Tetrahedral Layer, b) Hydroxyl Layer

The manner in which these two types of layers fits together determines the type of clay mineral formed, the size it will be, and if it will be expandable or not. For example with a single layer of each, they will form a 1:1 layer clay mineral such as kaolinite. A clay mineral with a 2:1 layer formation will have two tetrahedral layers to either side of an octahedral layer. If Al^{3+} substitutes for Si^{4+}, the clay mineral will have developed a negative net charge (Bailey, 1988). The strength of this net charge determines the likelihood of a 2:1 clay mineral being expandable, and the extent it is able to exchange cations. These include Ca, Na, K, and H_2O. Moore and Reynolds (1989) stated that there is a linear increase in CEC with increasing layer charge. Smectite has a high CEC, therefore it will frequently expand or contract to allow for different sized cations. Illite on the other hand has a lower CEC. Once illite has formed with potassium as the dominant intralayer cation (Figure 3), it becomes more ordered and does not expand (Moore and Reynolds, 1989).

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Figure 3 – This figure is showing a comparison of non expanding clay minerals along side ones that expand. The length here is measured in nanometers. (1nm=10Å). As the size of the minerals increase, so does the Cation Exchange Capacity allowing for more miscellaneous material to pass through the interlayer spacing.

Smectite represents a group of expandable clay minerals, which includes the clay mineral montmorillonite. Smectites are the main phyllosilicate phase that forms from the weathering of bentonites and potassium bentonites. The general chemical formula is listed as:
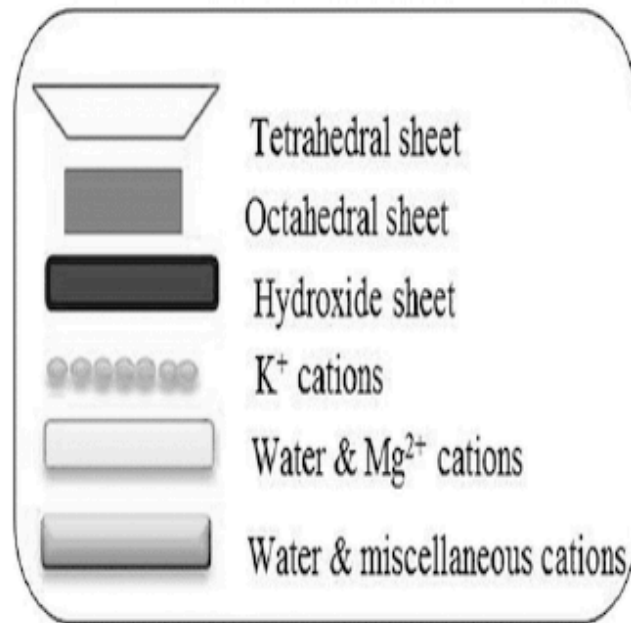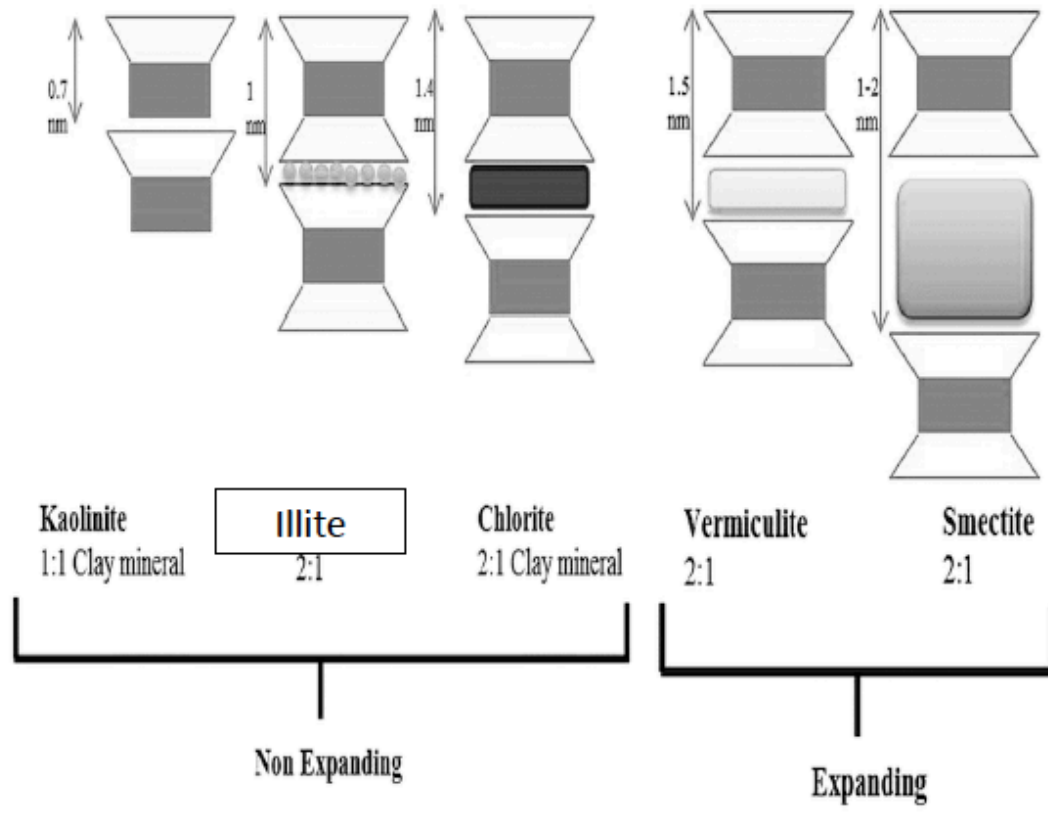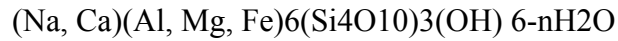
$$(Na, Ca)(Al, Mg, Fe)6(Si4O10)3(OH) 6-nH2O$$

These clays are arranged in a 2:1 di-octahedral sheet, the most abundant cation controls the interlayer spacing. Smectite interlayer spacing ranges from 10-17 Å (Ransom and Helgeson, 1994). Its weak layer charge can vary between 0.2-0.6 allowing for this expansion. This capacity allows for the movement of water in between sheets, giving smectite its plastic properties. It is one of the most basic clay minerals and the starting point for different clay-mineral transitions (Moore and Reynolds, 1989).

Illite is also a 2:1 dioctahedral clay mineral; however, it is non-expandable. Unlike smectite, illite contains a non-exchangeable monovalent cation and an exchangeable cation. The half –cell formula for illite has been documented by Nadeu and Bain (1986) as:

$$(K^+E^+)_{x+y}(Al^{3+}_{2-y}Mg^{2+}_yFe^{2+})(Si_{4-x}Al_x)O_{10}(OH)_2$$
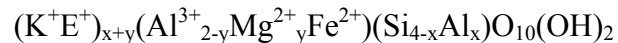
For this formula K^+ is the non-exchangeable cation and E^+ represents any exchangeable monovalent cation. K^+ is a strongly held component in illite that prevents the clay mineral from expanding and also inhibits the passage of water.

Modern muds, and shallow buried sediments, have a high percentage of smectite. More deeply buried rocks become more illite-rich. This has been reported by many authors, and is summarized by Totten et al. (2002). This diagenetic process occurs when smectite transforms into illite by forming a smectite/illite (I/S) mixed layer complex of growing illite abundances. The reaction for this process is, according to Nadeu and Bain (1986):

$$Smectite + Al^{3+} +K^+ \rightarrow Illite + Quartz + Na+ +Ca++ + H2O$$
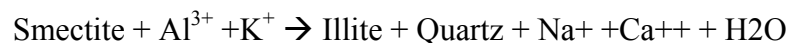
Smectite starts to incorporate K^+ as it becomes illite, with a coupled substitution of Al^{3+} for Si^{4+} within the tetrahedral sheet, and Mg^{2+} for Al^{3+} in the octahedral sheet. As burial diagenesis progresses, smectite-rich I/S becomes illite-dominated I/S as a function of time, temperature, and the concentration of K^+ in pore fluids (Pytte and Reynolds, 1989; Hower et al., 1976; Huang et al., 1993). End-member illite is the ultimate product of the process called illitization, and resembles the mica mineral muscovite. This transition is seen by XRD as a sharpening of the 10Å illite peak, which is described as an increase in illite crystallinity (Totten and Blatt, 1993).

The extent of illitization that has occurred is based on the percent of illite/smectite within the mixed layer stacking order and designated according to a "Reichweite" (R) value. When smectite is the dominant clay mineral (compared to illite) the order is considered random. As the percentage of illite found within the mixed layer clays increases, the illite layers stack in a more orderly arrangement. The stacking orders are divided into three interstratification ranges. These ranges are based on the probability that the more ordered of two mixed-layer clay minerals, in this case illite, having a 10 Å peak compared to smectites 17 Å, will be affected by the other. The Reichweite "reach back" value of R is the frequency of occurrence for any combination of illite/smectite and is calculated using the junction probabilities and compositions.

$$P_{A.B} = 1 \text{ and } P_{A.A} = 0 \quad \text{(Reynolds, 1980)}$$

The first order (R=0) is smectite dominated and can contain up to 20% illite. Short-ranged, random ordered I/S (R≥1) is comprised of approximately 50% smectite and illite. Clays

with long range ordering (R≥3) have 50%-95% illite (Lanson, 1997; Pollastro, 1993; Meuneir and Velde, 2004).
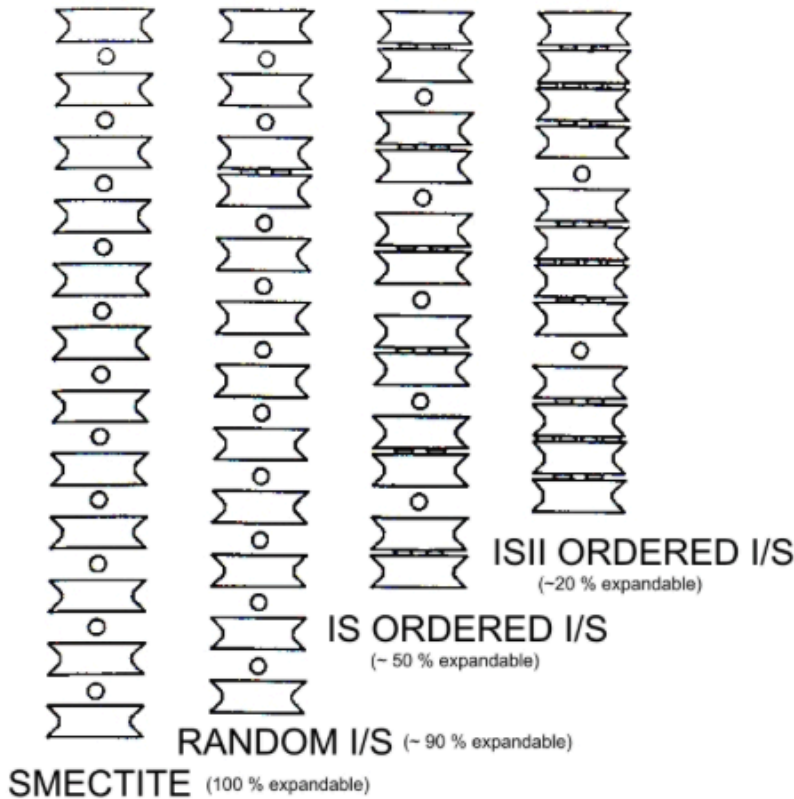
Figure 4 - Graphical representation of Illitization ordered stacking

The different ordering stages of illitization follow specific trends that correlate with burial temperature (Waples, 1980; Pollastro, 1993; Hover, 1996). The conversion of smectite to illite begins at ~50°C and continues through to ~200°C (Hoffman and Hower, 1979; Sass et al, 1987). There is a rapid increase in illite content as temperature increases and the ordering of I/S moves from R=0 to R≥1 (Figure 5). The start of this change also corresponds to the temperature at which organic matter begins to break down into hydrocarbons, i.e. ca. 60°C (Pevear, 1999) (Figure 6).
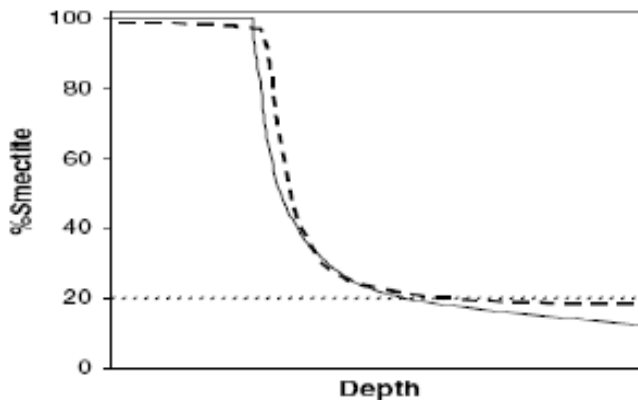
Figure 5 - The rapid conversion of smectite to illite represents R=0 to R>1. The bottom curve is R>1 to R>3 and occurs more slowly when ordering is near 80% illite (Cuadros, 2006)
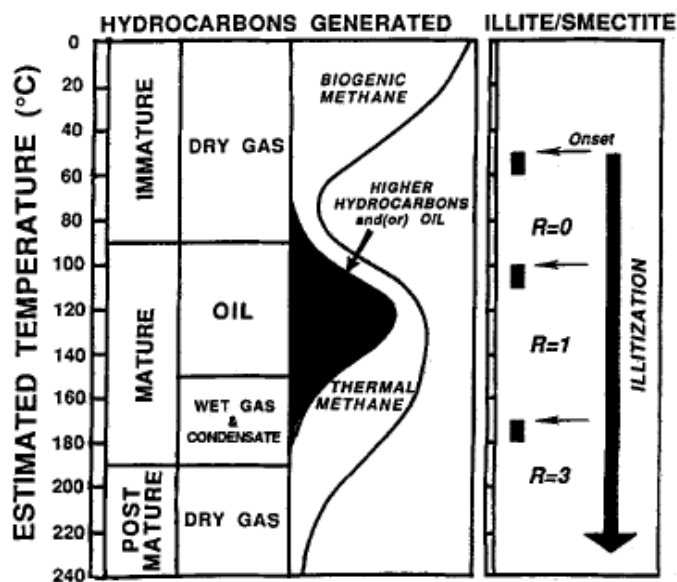
Figure 6 – This figure shows a generalization of the relationship between illitization R values, hydrocarbon generation, and temperature (Pollastro, 1993).

Since both time and temperature can affect the degree of illitization, two different models are used when looking at the extent of illitization. These are the short-life geothermal model and the long-range model (Table 1). The short-life geothermal model (Pollastro, 1993) is used for areas of deposition that are under 3 m.y. old, whereas the long-range model, otherwise known as

the Hoffman and Hower model, is used for regions of deposition that are 5 m.y. to 300 m.y in age (Pollastro, 1993). When illitization is being used as a geothermometer, these two models show that higher temperatures are needed for younger sediments to achieve the same percentage of illite as older sediments. If a heating event duration of under 3m.y. is not taken into account, the maximum temperature inferred would be incorrect compared to the indicating R value (Pollastro, 1993).

Change in I/S	Hoffman and Hower model (5-300 m.y.)	Short-life geothermal model (<3 m.y.)
Smectite-to R =0	50°-60°C	Variable
R= 0 to R=1	100°-110°C	120°-140°C
R=1 to R=3	170°-180°C	170°-180°C

Table 1 - Comparison of Hoffman and Hower's long-range illite versus a short-life younger model (Pollasro, 1993)

The timing of illitization can be determined by radiometric dating techniques. Because illite is a K-bearing phase, it can be dated using the ^{40}K-^{40}Ar or the ^{40}Ar-^{39}Ar geochronological technique (Pevear, 1999). Its utility in this regard was tested and confirmed by Alkhammali (2015) at Kansas State University. In his study, it was shown using ^{40}K-^{40}Ar dating that the start of illitization occurred after the time of deposition of the Woodford, i.e. the illite was not a depositional phase in the sediments that would become the Woodford shale. Using this type of dating and comparing it to previous models, two stages of development were seen in relation to the oil generation window. The earliest illite formed before oil generation began, whereas the second occurred during oil generation (Higley et al., 2014; Alkhammali, 2015).

Chapter 3 - Types of Hydrocarbon Producing Organic Matter

Thermal maturity of organic material is measured by the degree of coalification that the organics have undergone (McCarthy et al, 2011). With sufficient time, temperature and pressure, the organic matter contained within sediment transforms into kerogen and bitumen. Kerogen is organic matter that is insoluble in organic solvents, whereas bitumen is organic matter that is soluble in organic solvents, and results from thermal maturation of kerogen (Cardott, 1989). Kerogen can be classified into 4 types (Type I-IV) based on their respective origins. The kerogen types are identified through pyrolysis, by determining their distinctive hydrogen to oxygen ratio (Cardott, 1989).

Type I kerogen is sourced from lacustrine algae and marine algae. The organic matter comes from a low energy environment that has a major contribution from bacteria and other microorganisms. Hydrocarbons that are produced from these kinds of locations are typically oil prone, and are characterized by having high hydrogen to oxygen ratio (Zhang et al, 2013).

Type II kerogen is sourced from marine phytoplankton, zooplankton and various other microorganisms including bacteria. It can also contain limited organic matter of terrestrial origin. This type is typically generated in a moderate to deep marine environment where reducing conditions promote the preservation of organic matter. These environments limit the metazoans and bacteria that would have consumed the organic matter. Kerogens of this type can produce both oil and gas depending on the heat and maturation time (Kirkland et al. 1992).

Woody tissues from terrestrial plants, such as stems, bark, roots and leaves of vascular plants, make up Type III kerogen (Cardott, 1989). The depositional environment for this type is typically from terrestrial environments to shallow marine areas. Kerogens from this type tend to

generate dry gas with very little to no oil. Most coals are derived from Type III kerogen (Tissot et el, 1974).

Type IV is oxidized organic matter or high-gray vitrinite (Cardott, 1989). The organic matter found is residual from older sediments that have been altered by weathering or biologic oxidation such as that in swamps or soils. This kerogen type produces almost no hydrocarbons because of its very low hydrogen content, even though it is rich in carbon (Tissot et el, 1974).

Kerogen Type	Source Material	General Environment of Deposition
I	Mainly Algae	Lacustrine setting
II	Mainly plankton, some contribution from algae	Marine setting
III	Mainly higher plants	Terrestrial setting
IV	Reworked, oxidized material	Varied settings

Table 2 - Summary of source material and environmental deposition of the four kerogen types (Cardott,1989).
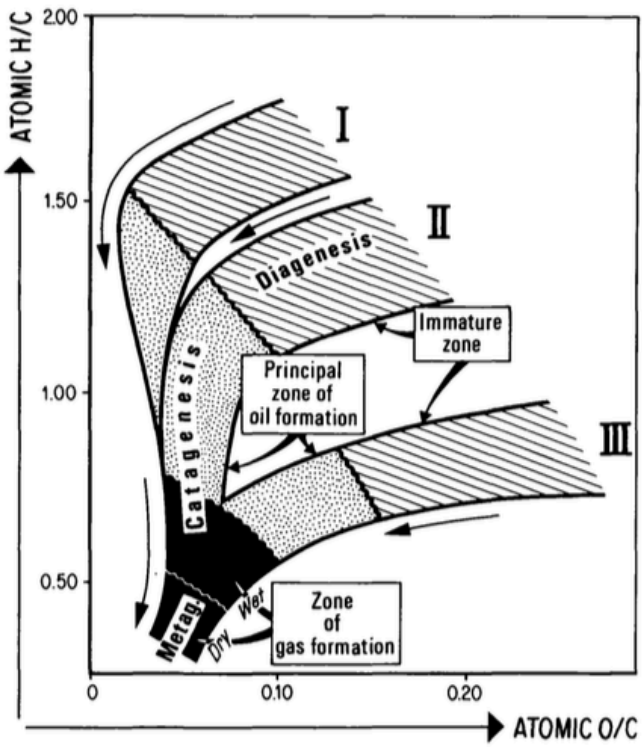
Figure 7 - Modified Van Krevelen diagram illustrating how hydrogen, oxygen and carbon content can be used to identify kerogen types and the transitions each type will go through to produce hydrocarbons (Tissot et al, 1980)

Chapter 4 - Different Measures of Thermal Maturity

Thermal history helps with understanding the processes needed to generate oil and natural gas by examining the processes and extent of organic maturation (Héroux et al. 1979). Vitrinite reflectance is the most widely used optical method and is the measure of light reflected from specific organic material found within woody plant material that first began colonizing terrestrial environments during the Silurian (McCarthy et al, 2011). Vitrinite is an organic maceral with two sub-components, collinite and telinite. Telinite represents the remains of the plant cell walls while collinite is a structureless component that remains after chemical decomposition. Vitrinite reflectance examines the collinite portion and is further divided into sections. Telocollinite is vitrinite that is free of inclusions, whereas desmocollinite contains inclusions of liptinite and other materials. Telocollinite provides the most accurate reflectance measurements, because desmocollinite tends to have higher H/C values and a lower reflectance, making maceral identification extremely important (Peters and Cassa, 1994).

The reflectivity of vitrinite increases because of the increased amount of aromatization caused by increased burial temperatures. Vitrinite contains multiple carbon ring structures that become more planar with exposure to heat. As the aromatization continues, the newly formed aromatic rings align with each other, making the internal structure more ordered, which subsequently reflects more light (Peters et al., 2006). Reflectivity (VRo) values measure only the maximum temperature reached, since this procedure is irreversible. The technique can be less reliable for very immature levels of maturation due to a lack of aromatization activation energy (Héroux et al., 1979).

A method of source rock evaluation that is less focused on any particular organic type is Rock-Eval pyrolysis. Pyrolysis involves the heating of organic matter in an oxygen-free

environment. In a chamber of inert gas filled with either helium or nitrogen, a sample is heated in intervals from 100 °C to 850 °C. Each interval is used to simulate heating that would occur in an undisturbed sedimentary basin over millions of years. Pyrolysis results are derived by the gases that are produced during heating, which are then used to determine the amount of pyrolyzable carbon (free oil and gas), the residual carbon, mineral carbon and the total organic carbon. Pyrolysis will also give the amount of hydrogen and oxygen needed to determine the Hydrogen/ Oxygen Indexes used to identify the kerogen type from Figure 4 (Staplin, 1969; Herdoux et al, 1979; Jarvie, 1991).

Illitization temperatures, as well as temperatures that effect vitrinite reflectance, have a strong correlation to oil/gas production, making illitization a commonly used and reliable geothermal gauge. Vitrinite reflectance coupled with illite crystallinity, and organic typing provided from pyrolysis, provides a more accurate understanding of diagenetic history than any singular observation (Figure 8). For example, R=0 to R≥1 stacking orders correspond to vitrinite reflectance values ranging from 0.5-0.66% which is near the beginning of the oil generation window (Pevear, 1999). The VRo, R ordering values along with identifying in-situ microfossils and the identification of types of kerogen, may be used to determine the original depositional environment, length and depth of burial, and possible types of hydrocarbons that may be produced from the sample area (Figure 8).
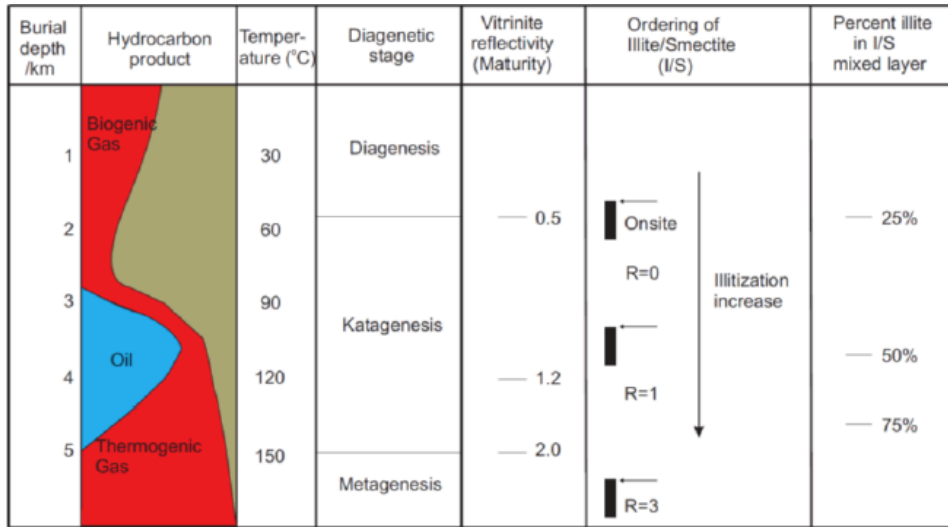
Figure 8 - Correlation between vitrinite reflectivity, illitization, temperature, and hydrocarbon production.

Chapter 5 - Factors Affecting Thermal Maturation Indicators

Thermal maturity, as determined by both illitization and vitrinite reflectance, usually is consistent despite the different methods to determine it. One should expect this, if temperature is the dominant control on these maturation indicators. These indicators do not always agree, however, prompting the question of which one is reliable. Since kinetics affects each of the thermal indicators at different rates, different indicators are only rough estimates. When looking at a particular indicator it is important to examine any factors that may cause enhanced or suppressed rates of thermal maturation.

The conversion from smectite to illite has been tested in natural environments as well as reproduced in a laboratory (Nadeau and Bain, 1986; Proust et al, 1990). Illitization is a process that has been studied in regions such as the Ouachita Mountains in North America (Guthrie et al, 1986), McMurdo Sound, Antarctica (Iacoviell et al. 2012), and the South China Sea (Jiang, 2012). In each study, the transition from smectite to illite remained consistent with previously documented temperature curves. This consistency further enforces the use of illite as a reliable geothermometer for most sedimentary rocks.
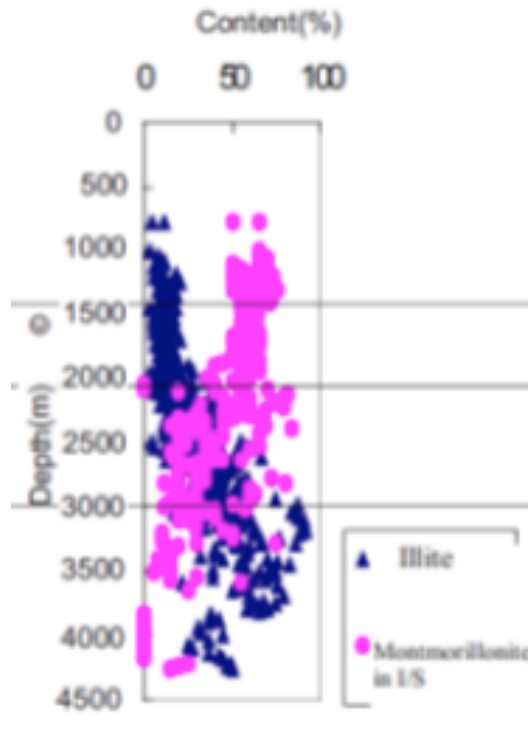
Figure 9- South China Sea Illitization (Jiang, 2012)
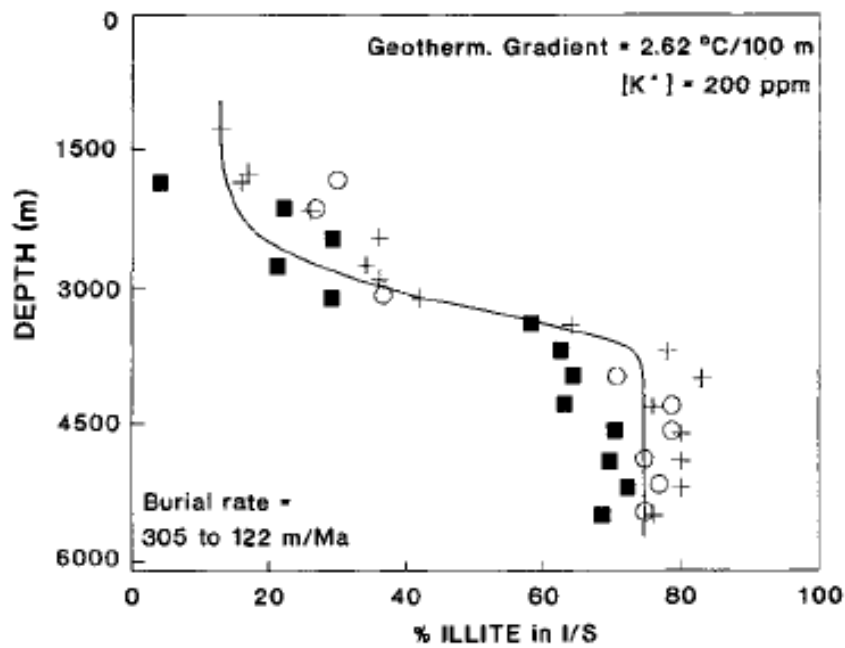
Figure 10 - Comparison of modeled and observed smectite/ illite conversion found in the Gulf Coast (Huang et al., 1993)

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The geochemical path of illitization requires a few rate-limiting constituents, in particular K and Al. Whitney and Northrop (1988) examined potassium as the main limiting factor. Their study found that when an excess of K^+ was available to smectite, not only was more illitic I/S produced, but also more random I/S of a lower R ordering value. When K^+ was withheld, the reaction dramatically changed, because some of the original smectite layers were consumed in order to form the illite. Other factors limit illitization, such as a lack of porosity, which may hold volatiles that may have otherwise been removed from the rock. High concentrations of Mg^{2+} and Na^+ can both lead to the suppression of illitization, and must be looked at in when using illitization as an indicator of paleotemperatures (Whitney and Northrop, 1988; Huang et al., 1993).
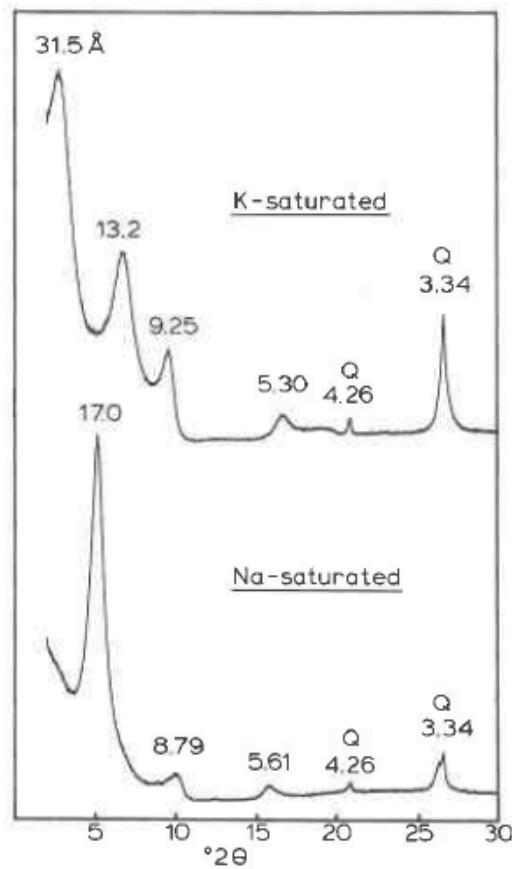
Figure 11 - X-ray diffraction patterns for K-saturated I/S showing an increase in illite above a pattern showing Na-saturated I/S with a decrease in illite (Whitney and Northrop, 1988).

Vitrinite reflectance may also yield false indications of thermal maturity (Barker, 2004; Fedor, 2002). There are several reasons why inaccurate estimates of thermal maturity might occur (Héroux et al, 1979; Fedor and Vido, 2003; Cardott, 1993; Cardott, 2013). Factors that may bring about suppressed or enhanced reflectance can be attributed to the quality, quantity, and accuracy of analysis of the samples used in vitrinite examination (Fedor and Vido´, 2003).

Vitrinite values may be inaccurate because of contamination of samples. This can be ameliorated with careful sampling strategies, by counting enough vitrinite grains in each sample, and by close scrutiny of the standard deviation of the counting statistics. Error includes such things as misidentification of non-vitrinite inclusions.   Drilling fluids can throw off reflectance readings as well if the vitrinite is impregnated with foreign material from oil-based drilling fluids. If the samples are well cuttings, there is the potential for rock from above the stratigraphic unit under consideration to fall back down the well, providing cross-contamination (Héroux et al, 1979).

Less straightforward to unravel are sources of suppression and enhancement that occur during burial.   Goodarzi et al. (1988) investigated vitrinite reflectance in different types of sedimentary rock and found carbonates presented a slightly increased VRo value compared to coal beds, which in turn were slightly higher than shales. Researchers have even found a strong suppression of vitrinite in liptinite-rich petroleum source rock (Hutton and Cook, 1980; Peters et al., 2006).

Over pressurization of sedimentary basins can also retard maturation (Carr, 1999; Law et al, 1989; Quick and Tabet, 2003). Michels et al. (1994) found a significant suppression effect on kerogens in a hydrous environment when examined using confined pyrolysis versus hydrous pyrolysis. Both pyrolysis systems had temperatures and pressures increasing from 260 – 400 °C

and 250-1300 bar pressure respectively. They found that the availability of water, the type of system (open or confined), and the type of kerogen available would respond differently to heat and pressure. Hill et al. (2009) found similar results in coal beds, although their results suggest that pressure had a secondary effect on organic maturation. Carr (1999) attributed this to the retention of volatiles that prevented the molecular reorganization associated with aromatization. These could include the amount of gelification (vitrinitization) of huminite macerals and any pressure-induced retardation that might have occurred (Cardott, 1990).

Chapter 6 - Discussion – The Woodford Shale as a Case Study

The Woodford Formation of Oklahoma is a hydrocarbon-rich source rock of Late Devonian to Early Mississippian age characterized by inter-bedded shales and cherts (Cardott and Lambert, 1985; Roberts and Mitterer, 1992). There are three distinct layers to the Woodford that Kirkland et al. (1992) identified using conodonts. Although the total organic content can range from 0.3 to 25wt%, the middle layer is the most hydrocarbon rich and has the greatest organic content (Cardott and Lambert, 1985; Kirkland et al., 1992).

The Woodford has a recorded reflectance value (Ro) trend of 0.48 to over 5% in Oklahoma (Cardott and Lambert, 1985). Cardott (1990) suggested in his study of the Woodford Shale that VRo values <1.3% may be suppressed, but he was unable to explain why, or the degree to which the values were suppressed. An example of this may be found by revisiting the research of Kirkland et al. (1992). The samples examined by Kirkland et al. (1992) all showed

immature VRo values averaging 0.42% while having no mixed layer illite/smectite content

which would suggest a thermally mature zone.

TABLE 1. — MINERAL COMPOSITION OF TYPICAL WOODFORD SAMPLES FROM X-RAY DATA
(in wt%)

Locality[a]	Quartz	K-Feldspar	Dolomite	Apatite	Pyrite	Illite	Kaolin
MC	44.0	0.0	21.9	0.0	1.4	26.1	5.1
MC	69.2	1.1	0.0	0.0	1.2	26.1	2.4
MC	49.1	2.3	4.8	0.0	1.5	35.2	7.1
MC	29.4	0.6	56.3	0.0	0.9	11.2	1.3
MC[b]	71.5	0.0	2.1[e]	0.0	0.0	9.2	15.2
MC[b]	77.0	0.0	0.0	0.2	0.0	15.4	6.9
MC[b]	96.2	0.0	0.1	0.0	0.0	1.7	2.0
HHF	55.1	6.6[d]	3.0	0:0	1.0	27.1	7.3
HHF	59.7	2.5	0.1	0.0	0.4	33.9	3.3
HHF	87.0	0.0	0.0	1.2	0.4	8.1	3.3
HHF[c]	4.6	0.0	0.0	91.8	0.0	2.0	1.2

[a] MC, McAlester Cemetery Quarry; HHF, Henry House Falls Quarry
[b] Weathered shale
[c] Phosphate nodule
[d] Includes 2.8% plagioclase
[e] Calcite

Table 3 - Results from Kirkland et al, 1992

Totten et al. (2013) demonstrated that if there were an insufficient source of potassium to

sustain the conversation of smectite to illite, illitization would be suppressed. The source of this

K^+ is typically from potassium rich feldspars (Lynch, 1997). The average Gulf of Mexico shale

would have initially needed to be composed of at least 13.4% K_2O to sustain the amount of

illitization that has occurred (Totten and Blatt, 1993). The Woodford would be have similar

potassium requirements. Kirkland et al. (1992) examined an outcropping with exposure to all

three members of the formation. From the middle layer K-feldspars were absent from weathered

samples and only averaging <1wt% in the other samples. In those samples quartz made up 29 to

96 wt% of the inorganic fraction, while illite was the dominant clay mineral in all three members of the Woodford.

Totten et al. (2013) suggested that sources of potassium other than K-feldspar may be involved in providing the necessary K^+. Their study looked at different types of materials including organic matter, clay minerals, oil, and brines and found that the potassium to rubidium ratio within the clay fraction closely matched that of the organic fractions, and were distinctly different than they would have inherited from silicate precursors, and were similar to the K/Rb of other organics (Chaudhuri et al., 2007). From these findings they concluded that a major source of K^+ ions could be the deposited organic matter and that the two events, illitization and organic matter transformation, occurred simultaneously (Totten et al., 2013). A reaction path that would support that theory might be (Freed and Peacor, 1992):

$$3.93\ K^+ + 1.57\ smectite = illite + 1.57\ Na^+ + 3.14\ Ca^{+2} + 4.28\ Mg^{+2} + 4.78\ Fe^{+3} +$$

$$24.66\ Si^{+4} + 57\ O^{-2} + 11.40\ OH^- + 15.7\ H_2O$$
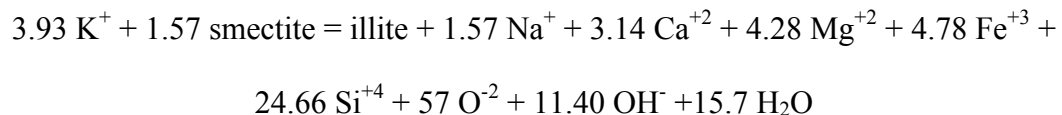
This equation does not take into account the addition of Al^{3+}, although it is also typically high in organic matter. Because 1.57 moles of smectite yields 1 mole of illite and 24 moles of silica, this reaction might also explain the cherty nature of the Woodford described by Kirkland et al. (1992).

In the area of Payne County, Oklahoma, vitrinite isoreflectance maps indicate a VRo value of 0.50% - 0.60% (Figure 13). This value would suggest that the maturity level of the shales in this region are at the very beginning of the oil generation window as seen previously in Figure 5. This would also be a value that typically correlates to a stacking order of a little greater than R=0, containing ~20% illite and nearly 80% smectite within I/S mixed layer composition. This is not observed in these samples.

The red triangle markings in Figure 13 are wells from Payne County that were examined by Alkhammali (2015). From the XRD patterns from Alkahmmali's research, it was demonstrated that the I/S clay minerals are very well ordered. He calculated that I/S mixed layer was about 90-95% illite and was well crystalline. This means that the ordering would have a value of R=3 (Moore and Reynolds, 1989).

Using the Xrd patterns from these wells (Alkhammali, 2015) Weavers sharpness ratio can be determined. An example is shown in Figure 12, measuring the height of the 10A peak and showing it in relation to the height of the peak at 10.5 A. Actual measured ratios on the XRD patterns from Alkhammali (2015) can be found in Appendix A.

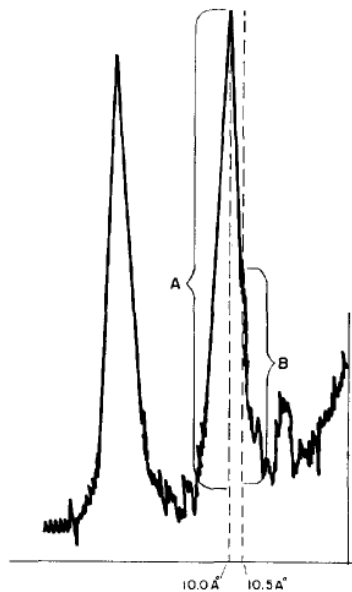Weaver (1960)   Sharpness Ratio = A/B (Figure 12)

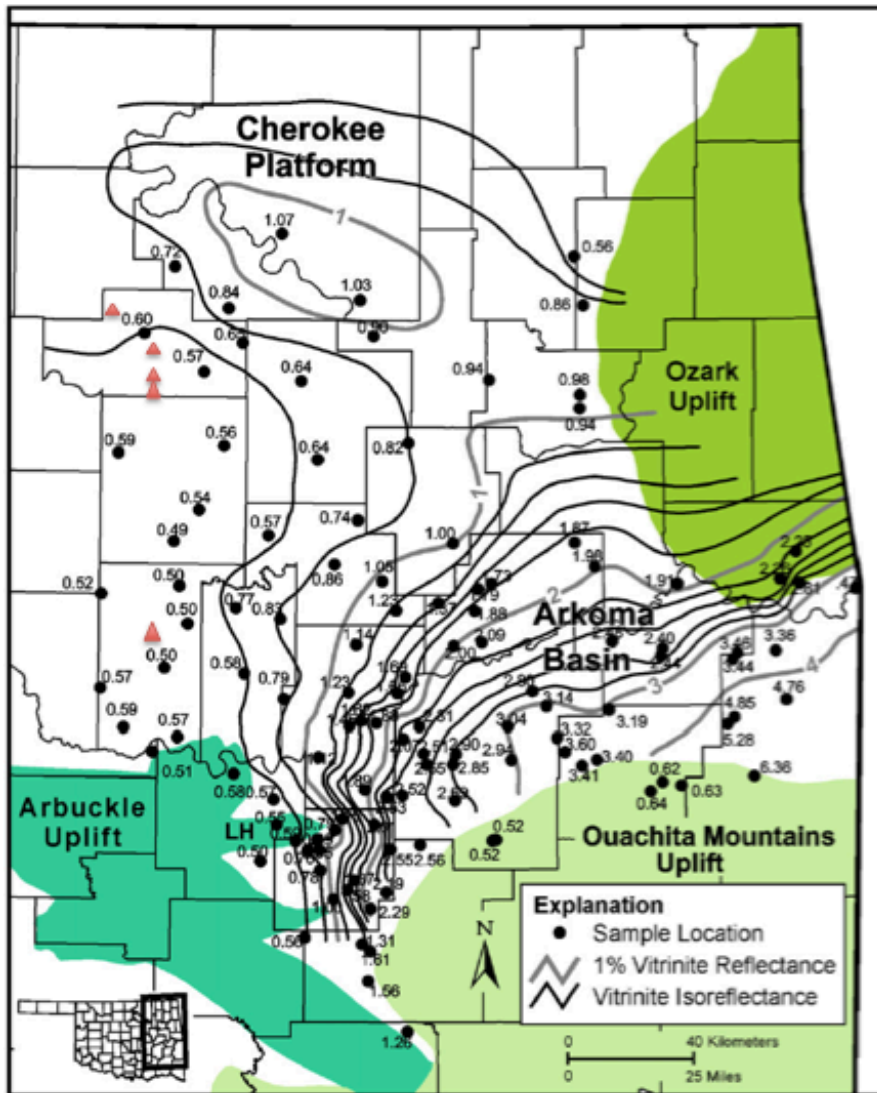**Figure 12 - Sharpness ratio measurements (Weaver, 1960)**

Figure 13 - Vitrinite isoreflectance map of the Woodford Shale of eastern Oklahoma (modified from Cardott, 2013). The triangle markers signify locations of sample wells from Alkhammali (2015).

The illite crystallinity shown by Wearvers sharpness ratio and the vitrinite relfectance values estimated from the isoreflectance map (Figure 13) are plotted in Figure 14 and compared to the trend from Guthrie et al., (1986). The shales that were examined in the study done by Guthrie et al were of comparable age (Mississippian and Pennsylvanian) as the Woodford (Late Devonian) and are from a nearby region in Oklahoma. The Woodford samples do not agree with

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the correlation between vitrinite and illitization found in Guthrie et al. (1986). The Woodford samples are almost entirely illite, even at thermally immature vitrinite reflectance values (Figure 14).

The major difference between the Woodford and the Ouachita Mountain shales studied by Guthrie et al. (1986) is the increased amount of organic matter. As stated previously, the Woodford can have a TOC of up to 25wt%, and averages almost 20%. This is much higher than average shales, which typically contain less than 1% TOC. It is likely that the increased potassium available from the organic fraction promoted the early transformation of smectite to illite at lower thermal maturity than occurs in average shales. This is consistent with previous observations of Woodford behavior by Totten et al. (2013).
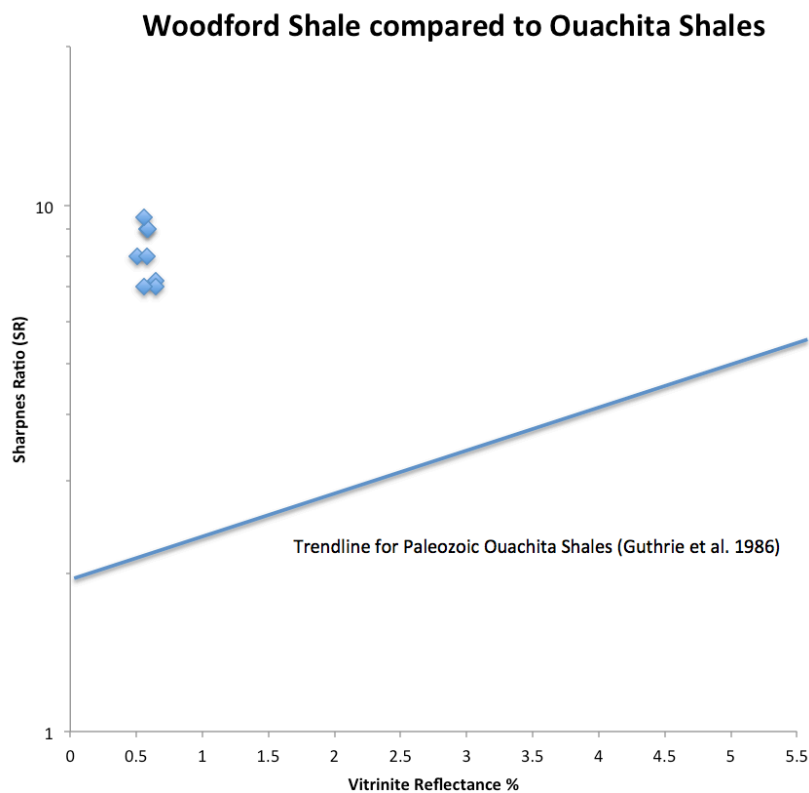

Figure 14 – Woodford Shale compared to Ouachita Shales

Chapter 7 - Conclusion

Increased subsurface temperatures during burial alters both clay minerals and organic matter. To determine the extent of these changes, geologists focus on thermal maturity indicators, such as vitrinite reflectance and illite crystallinity. Vitrinite reflectance, measured as the percentage of light reflected from multiple grains of vitrinite, are semi-quantitative; they tend to be more accurate at lower maturity levels. Illitization is used as a geothermometer by determining the extent of known clay-mineral transformations on XRD. While it is recognized that time plays a role in these transformations, it is usually assumed that a minimum time (therefore a maximum temperature) has occurred. This record of maximum diagenetic temperatures are usually in agreement with each other, and with other organic transitions such as hydrocarbon generation.

Guthrie et al. (1986) stated that, in the absence of vitrinite, illite crystallinity could be used to approximate hydrocarbon generation-preservation stages of potential source rocks. This comparison cannot be used when trying to interpret the maturity of the Woodford Shale. The Woodford has an advanced level of progression of illitization, at least in Payne County, Oklahoma, that does not correspond with observed vitrinite reflectance values or with early hydrocarbon maturation (oil window). This could be explained by the high level of organic content within the Woodford, supplying an abundance of potassium to accelerate illite formation in I/S mixed layer clay minerals at lower temperatures than observed in shales with lower organic content.

References

Alkhammali, S.A., 2015, Geochemical And Clay Mineralogical Characteristics Of The Woodford Shale, Payne County, Oklahoma, Masters Thesis, Kansas State University. 82 pp

Bailey, S.W., 1988, Structures and compositions of other trioctahedral 1:1 phyllosilicates: *in* Bailey, S.W., editor, *Hydrous Phyllosilicates (exclusive of micas),* Vol. 19 in Reviews in Mineralogy, Mineralogical Society of America, Washington, D.C., p 169-188.

Barker, C., 2004, Update On The Influence Of Extractable Organic Matter On Vitrinite Reflectance: Implications To Liquid Hydrocarbon Or Bitumen Impregnation As A Suppression Mechanism, Abstracts of the 21 Annual Meeting of the Society for Organic Petrology: 2004, Volume 21 p 83-86

Berner, E. and R. Berner, 1996, Global environment water, air, and geochemical cycles Prentice-Hall, Englewood Cliffs, NewJersey. 376 pp.

Cardott, B. J. and M. W. Lambert, 1985, Thermal maturation by vitrinite reflectance of Woodford Shale, Anadarko basin, Oklahoma, AAPG Bulletin, vol. 69, no. 11, p. 1982-1998.

Cardott, B.J. (1989) Thermal maturation of the Woodford Shale in the Anadarko basin, in K.S. Johnson, ed., Anadarko basin symposium, 1988: OGS Circular 90, p. 32-46.

Cardott, B.J., W.J. Metcalf, III, and J.L. Ahern, 1990, Thermal maturation by vitrinite reflectance of Woodford Shale near Washita Valley fault, Arbuckle Mountains, Oklahoma, *in* V.F. Nuccio and C.E. Barker, eds., Applications of thermal maturity studies to energy exploration: SEPM, Rocky Mountain Section, p. 139-146.

Cardott, B., 2013, Woodford Shale: from hydrocarbon source rock to reservoir, AAPG Education Directorate Woodford Shale Forum, Oklahoma City, Oklahoma, April 11, 2013, Power Point Presentation, http://www.searchanddiscovery.com/pdfz/documents/2013/50817cardott/ndx_cardott.pdf.html

Carr, A., 1999, A vitrinite reflectance kinetic model incorporating overpressure retardation, Marine and Petroleum Geology, vol. 16, no. 4, p. 355-377.

Chaudhuri, S., N. Clauer, and K. Semhi, 2007, Plant decay as a major control of river dissolved potassium: a first estimate, Chemical Geology, vol. 243, no. 1, p. 178-190.

Cuadros, J., 2006, Modeling of smectite illitization in burial diagenesis environments, Geochimica et Cosmochimica Acta, vol. 70, no. 16, p. 4181-4195.

Fedor, F. and M. Hamor-Vido, 2003, Statistical analysis of vitrinite reflectance data—a new approach, International journal of coal geology, vol. 56, no. 3, p. 277-294.

Freed, R. L. and D. R. Peacor, 1992, Diagenesis and the formation of authigenic illite-rich I/S crystals in Gulf Coast shales: TEM study of clay separates, Journal of Sedimentary Research, vol. 62, no. 2.

Goodarzi, F., T. Gentzis, and R. M. Bustin, 1988, Reflectance and petrology profile of a partially combusted and coked bituminous coal seam from British Columbia, Fuel, vol. 67, no. 9, p. 1218-1222.

Guggenheim, S. and R. Martin, 1995, Definition of clay and clay mineral: joint report of the AIPEA nomenclature and CMS nomenclature committees, Clays and Clay Minerals, vol. 43, no. 2, p. 255-256.

Guthrie, J. M., D. W. Houseknecht, and W. D. Johns, 1986, Relationships among vitrinite reflectance, illite crystallinity, and organic geochemistry in Carboniferous strata, Ouachita Mountains, Oklahoma and Arkansas, AAPG Bulletin, vol. 70, no. 1, p. 26-33.

Héroux, Y., A. Chagnon, and R. Bertrand, 1979, Compilation and correlation of major thermal maturation indicators, AAPG Bulletin, vol. 63, no. 12, p. 2128-2144.

Higley, D. K., T. A. Cook, and M. J. Pawlewicz, 2014, Petroleum Systems and Assessment of Undiscovered Oil and Gas in the Anadarko Basin Province, Colorado, Kansas, Oklahoma, and Texas—Woodford Shale Assessment Units, Higley, DK, compiler, Petroleum systems and assessment of undiscovered oil and gas in the Anadarko Basin Province, Colorado, Kansas, Oklahoma, and Texas—USGS Province, vol. 58.

Hoffman, J. and J. Hower, 1979, Clay mineral assemblages as low-grade metamorphic geothermometers: application to the thrust faulted disturbed belt of Montana, USA: Society of Economic Paleontologists and Mineralogists Special Publication 26: 55-79.

Hover, V. C., 1996, Relationship Between Organic Matter And authigenic Illite Smectite in Devonian Black Shales, Michigan and Illinois Basins, USA, in Crossey, L.J., Loucks, R., and Totten, M. W., eds., Siliciclastic diagenesis and fluid flow; concepts and applications: SEPM (Society for Sedimentary Geology), Special Pub. 55, p. 73-83.

Hower, J., E. V. Eslinger, M. E. Hower, and E. A. Perry, 1976, Mechanism of burial metamorphism of argillaceous sediment: 1. Mineralogical and chemical evidence, Geological Society of America Bulletin, vol. 87, no. 5, p. 725-737.

Huang, W., J. M. Longo, and D. R. Pevear, 1993, An experimentally derived kinetic model for smectite-to-illite conversion and its use as a geothermometer, Clays and Clay Minerals, vol. 41, p. 162-162.

Hutton, A. C. and A. C. Cook, 1980, Influence of alginite on the reflectance of vitrinite from Joadja, NSW, and some other coals and oil shales containing alginite, Fuel, vol. 59, no. 10, p. 711-714.

Iacoviello, F., G. Giorgetti, F. Nieto, and I. T. Memmi, 2012, Evolution with depth from detrital to authigenic smectites in sediments from AND-2A drill core (McMurdo Sound, Antarctica), Clay Minerals, vol. 47, no. 4, p. 481-498.

Jarvie, D. M., 1991, Total organic carbon (TOC) analysis, in Treatise of Petroleum Geology, Handbook of Petroleum Geology, Source and Migration Processes and Evaluation Techniques, Ed. R.K. Merrill, AAPG Press, Tulsa, Ok. p. 113-118

Jiang, S., 2012, Clay Minerals from the Perspective of Oil and Gas Exploration, Clay Minerals in Nature, Ch. 2, p. 21-38

Kirkland, D., R. Denison, D. Summers, and J. Gormly, 1992, Geology and organic geochemistry of the Woodford Shale in the Criner Hills and western Arbuckle Mountains, Oklahoma, , vol. 93, p. 38-69.

Lanson, B., 1997, Decomposition of experimental X-ray diffraction patterns (profile fitting): a convenient way to study clay minerals, Clays and Clay Minerals, vol. 45, no. 2, p. 132-146.

Law, B. E., V. Nuccio, and C. Barker, 1989, Kinky vitrinite reflectance well profiles: evidence of paleopore pressure in low-permeability, gas-bearing sequences in Rocky Mountain foreland basins, AAPG Bulletin, vol. 73, no. 8, p. 999-1010.

Lynch, F. L., 1997, Frio shale mineralogy and the stoichiometry of the smectite-to-illite reaction: the most important reaction in clastic sedimentary diagenesis, Clays and Clay Minerals, vol. 45, no. 5, p. 618-631.

McCarthy, K., K. Rojas, M. Niemann, D. Palmowski, K. Peters, and A. Stankiewicz, 2011, Basic petroleum geochemistry for source rock evaluation, Oilfield Review, vol. 23, no. 2, p. 32-43.

Melka, K, 2009, A Scheme for the Classification of Micaceous Minerals, Acta Geodyn. Geomater., Vol. 6, no. 1, p. 69-75.

Meunier, A., B. Velde, and P. Zalba, 2004, Illite K–Ar dating and crystal growth processes in diagenetic environments: a critical review, Terra Nova, vol. 16, no. 5, p. 296-304.

Michels, R., P. Landais, R.P. Philp, and B.E. Torkelson, 1994, Effects of pressure on organic matter maturation during confined pyrolysis of Woodford kerogen: Energy Fuels, v. 8, p. 741-754.

Moore, D. M. and R. C. Reynolds, 1989, X-ray Diffraction and the Identification and Analysis of Clay Minerals, Oxford university press Oxford. 332 pp

Nadeau, P. and D. Bain, 1986, Composition of some smectites and diagenetic illitic clays and implications for their origin, Clays and Clay Minerals, vol. 34, no. 4, p. 455-464.

Peters, K. S., C. Walters, and J. M. Moldowan, 2006, The Biomarker Guide: Biomarkers and isotopes in the environment and human history, Cambridge University Press, vol. 1, p. 90-91.

Peters, K. E. and M. R. Cassa, 1994, Applied source rock geochemistry, Memoirs-American Association of Petroleum Geologists, p. 93-93.

Pevear, D. R., 1999, Illite and hydrocarbon exploration, Proceedings of the National Academy of Sciences of the United States of America, vol. 96, no. 7, p. 3440-3446.

Pollastro, R. M., 1993, Considerations and applications of the illite/smectite geothermometer in hydrocarbon-bearing rocks of Miocene to Mississippian age, Clays and Clay Minerals, vol. 41, p. 119-119.

Proust, D., J. Lechelle, A. Lajudie, and A. Meunier, 1990, Hydrothermal reactivity of mixed-layer kaolinite/smectite: experimental transformation of high-charge to low-charge smectite, Clays Clay Miner, vol. 38, no. 4, p. 415-425.

Pytte, A. and R. Reynolds, 1989, The thermal transformation of smectite to illite, in Anonymous Thermal history of sedimentary basins, Springer, p. 133-140.

Quick, J. C. and D. E. Tabet, 2003, Suppressed vitrinite reflectance in the Ferron coalbed gas fairway, central Utah: possible influence of overpressure, International Journal of Coal Geology, vol. 56, no. 1, p. 49-67.

Ransom, B. and H. C. Helgeson, 1994, A chemical and thermodynamic model of aluminous dioctahedral 2: 1 layer clay minerals in diagenetic processes; regular solution representation of interlayer dehydration in smectite, American Journal of Science, vol. 294, no. 4, p. 449-484.

Reynolds Jr., R. C., 1980, Interstratified clay minerals: in Crystal Structures of Clay Minerals and Their X-ray Identification, G. W. Brindley and G. Brown, eds. Mineralogical Society, London, 249-303.

Roberts, C.T., and R.M. Mitterer, 1992, Laminated black shale-bedded chert cyclicity in the Woodford Formation, southern Oklahoma, in K.S. Johnson and B.J. Cardott, eds., Source rocks in the southern Midcontinent, 1990 symposium: OGS Circular 93, p. 330-336.

Sass, B. M., P. E. Rosenberg, and J. A. Kittrick, 1987, The stability of illite/smectite during diagenesis: An experimental study, Geochimica et Cosmochimica Acta, vol. 51, no. 8, p. 2103-2115.

Środoń, J., 1990, Illite-Smectite in the rock cycle: Lectures 6th Meet. European Clay Groups. Seville: 137-150.

Staplin, F. L., 1969, Sedimentary organic matter, organic metamorphism, and oil and gas occurrence, Bulletin of Canadian Petroleum Geology, vol. 17, no. 1, p. 47-66.

Tissot, B., B. Durand, J. Espitalie, and A. Combaz, 1974, Influence of nature and diagenesis of organic matter in formation of petroleum, AAPG Bulletin, vol. 58, no. 3, p. 499-506.

Totten, M. W., Blatt H., 1996, Sources of silica from the illite to muscovite transformation during late-stage diagenesis of shales, Siliciclastic diagenesis and fluid flow, Concepts and Applications: Society of Economic Paleontologists and Mineralogists, Special Publication No. 55, p. 85-92

Totten, M. W. and H. Blatt, 1993, Alterations in the non-clay-mineral fraction of pelitic rocks across the diagenetic to low-grade metamorphic transition, Ouachita Mountains, Oklahoma and Arkansas, Journal of Sedimentary Research, vol. 63, no. 5, p. 899-908.

Totten, M. W., M. A. Hanan, D. Knight, and J. Borges, 2002, Characteristics of mixed-layer smectite/illite density separates during burial diagenesis, American Mineralogist, vol. 87, no. 11-12, p. 1571-1579.

Totten, M.W., Ramirez-Caro, D., Chaudhuri, S., Clauer, N., Boutin, R., Riepl, G., Miesse, J. and Semhi, K., 2013, Source of Potassium for the Illitization Process in Buried Argillaceous Rocks: A Case for Evidence from the Woodford Shale, North-Central Oklahoma. GCAGS Transactions, 2013, p 449-454

Waples, D., 1980, Time and temperature in petroleum formation: Application of Lopatin's method to petroleum exploration; Am. Assoc. Pet. Geol. Bull; vol. 64, no. 6. P 499-454.

Weaver, C. E., 1960, Possible uses of clay minerals in search for oil, AAPG Bulletin, vol. 44, no. 9, p. 1505-1518.

Whitney, G. and Northrop, H. R., 1988, Experimental investigations of the smectite to illite reaction: Dual reaction mechanisms and oxygen-isotope systematics: Amer. Mineral 73, 77-90.

Zhang, T., G. Ellis, S. Ruppel, K. Milliken, M. Lewan, and X. Sun, 2013, Effect of organic matter properties, clay mineral type and thermal maturity on gas adsorption in organic-rich shale systems, Conference Paper, no.1543690 Unconventional Resources Technology Conference, Denver, Colorado, 12-14 August 2013. 6pp
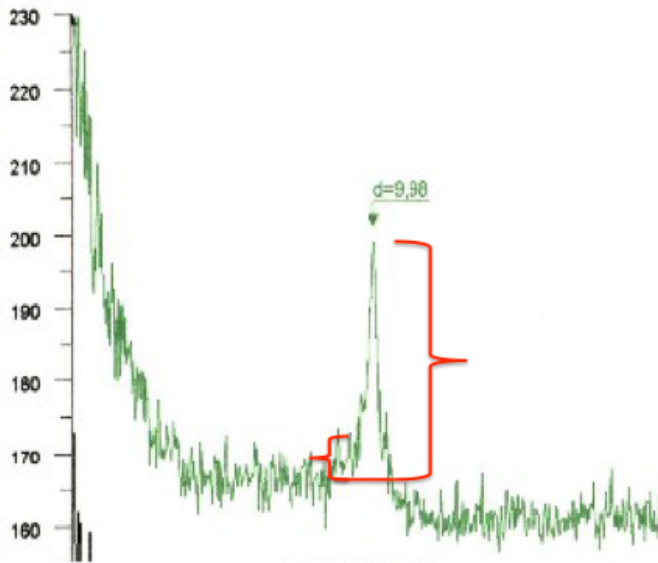
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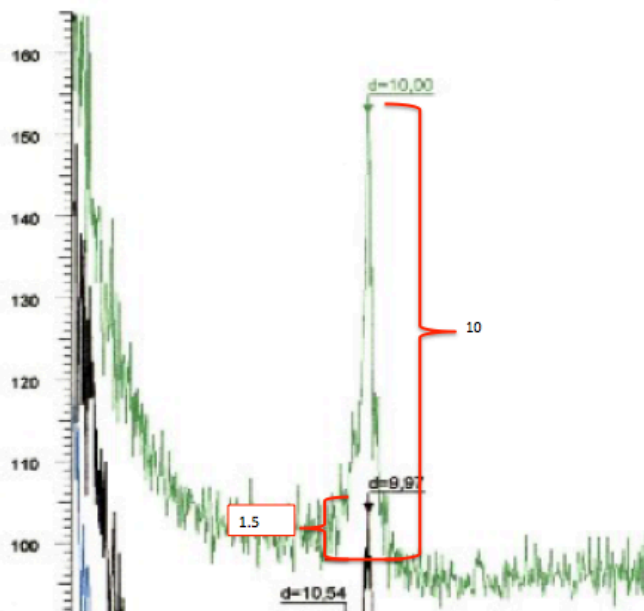
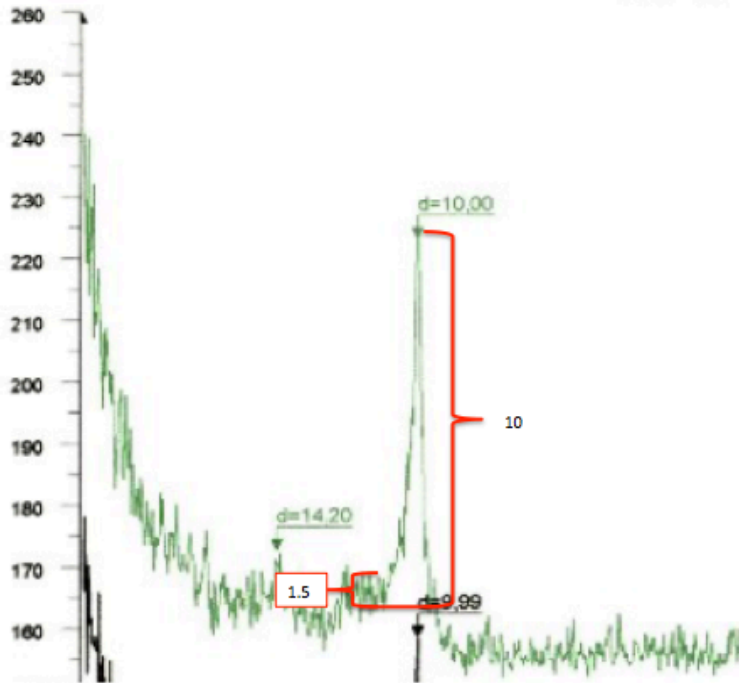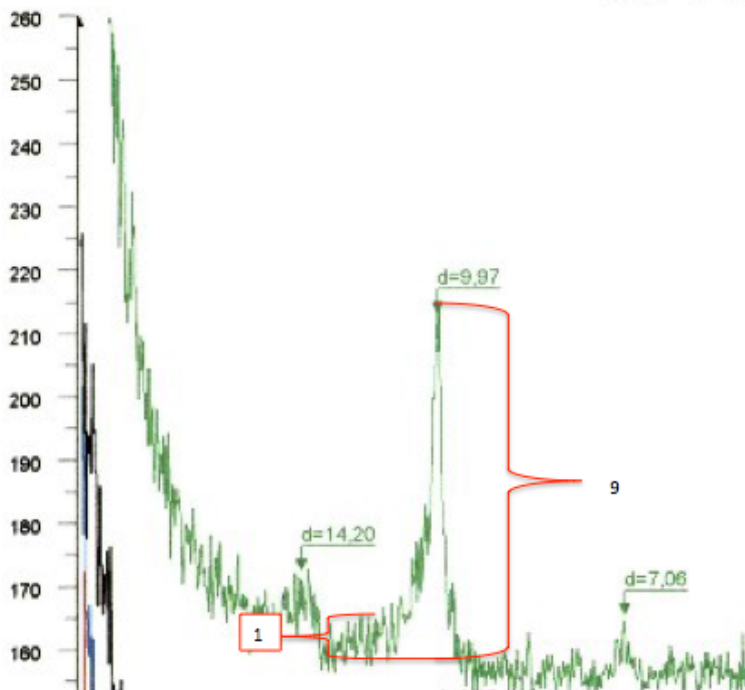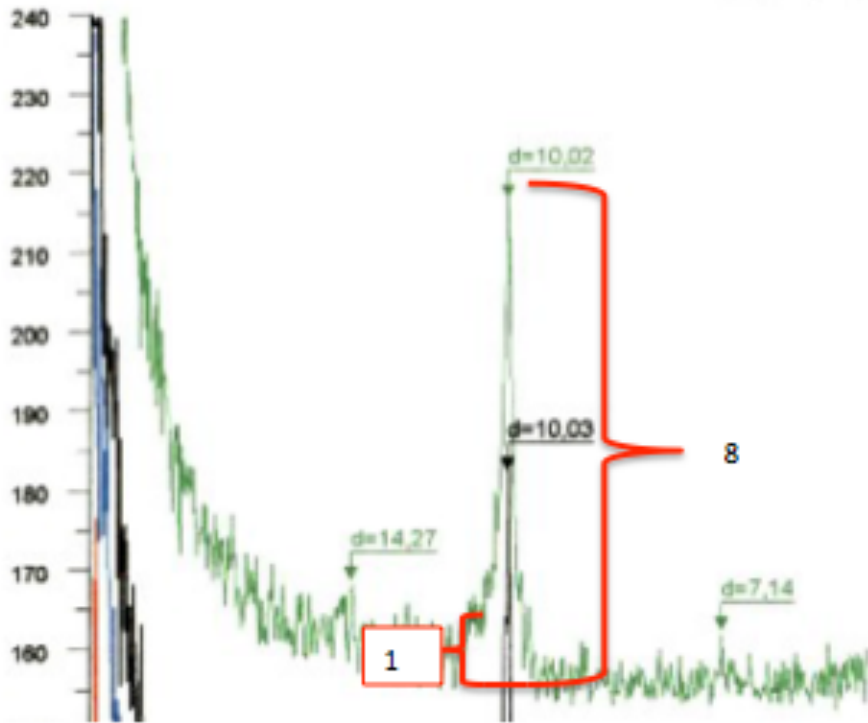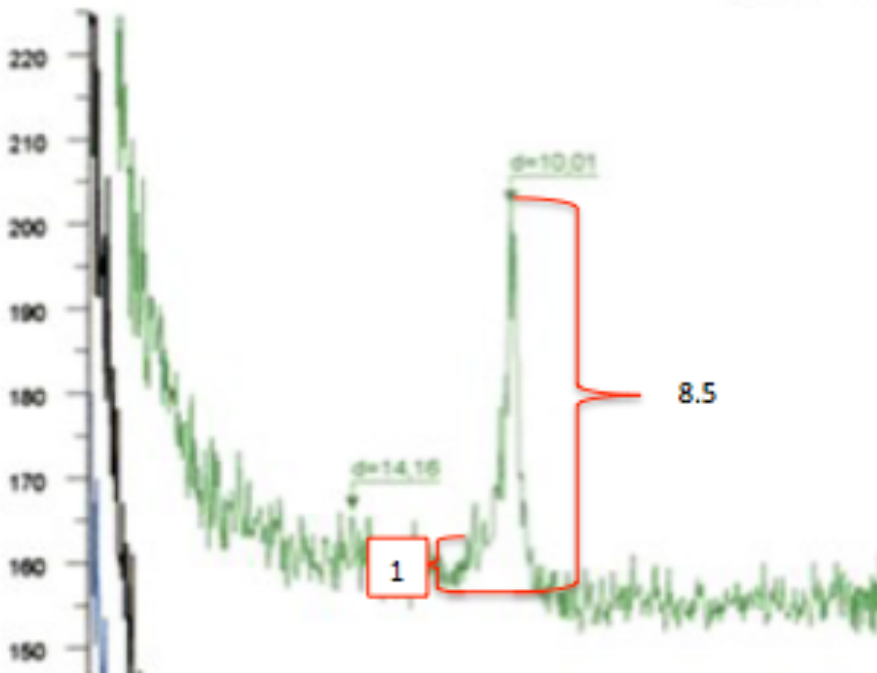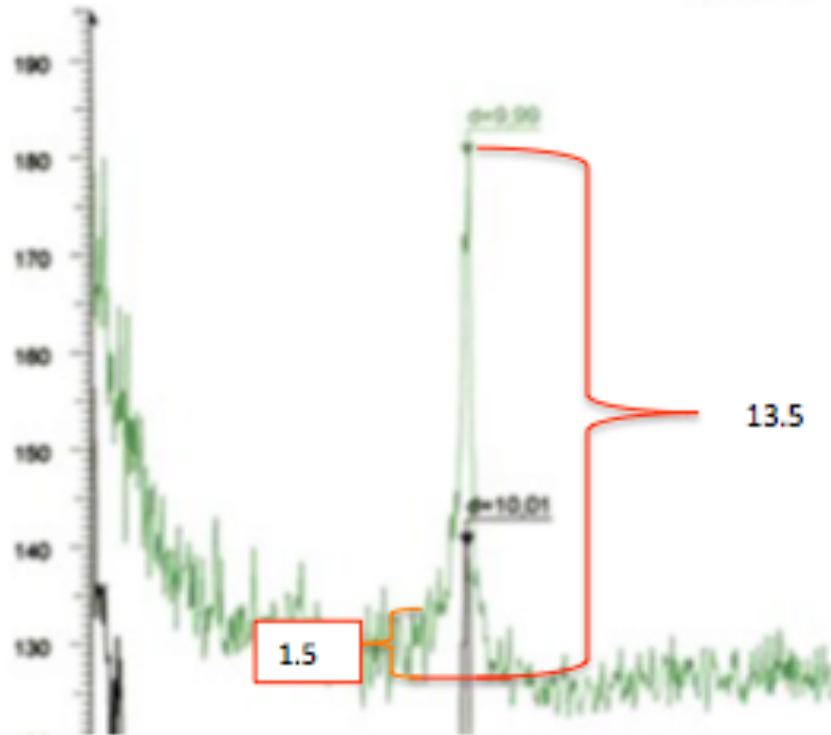# SA-14-3

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