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Evaluation of Shale Source Rocks and Clay Mineral Diagenesis in the Permian Basin, USA: Inferences on Basin Thermal Maturity and Source Rock Potential

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Abstract: The use of mineral diagenetic indices and organic matter maturity is useful for reconstructing the evolution of sedimentary basins and critical assessments for potential source rocks for petroleum exploration. In this study, the relationship of clay mineral diagenesis and organic matter thermal indices (Rock-Eval Tmax) and calculated vitrinite reflectance (%R_o) were used to constrain the maximum burial depths and temperatures of three distinct intervals within the northern Permian Basin, USA. X-ray diffraction of clay fractions (<2 µm) consists of illite, chlorite, and illite-smectite intermediates. Primary clay mineral diagenetic changes progressively increase in ordering from R0 to R1 I-S between 2359.5 and 2485.9 m and the appearance of chlorite at 2338.7 m. Rock-Eval pyrolysis data show 0 to 14 wt% TOC, HI values of 40 to 520 mgHC/g TOC, and S2 values of 0 to 62 mg HC/g, with primarily type II kerogen with calculated %R_o within the early to peak oil maturation window. Evaluation of the potential for oil generation is relatively good throughout the Tonya 401 and JP Chilton wells. Organic maturation indices (Tmax, %R_o) and peak burial temperatures correlate well with clay mineral diagenesis (R0–R1 I-S), indicating that maximum burial depths and temperatures were between 2.5 and 4 km and <100 °C and 140 °C, respectively. Additionally, the use of clay mineral-derived temperatures provides insight into discrepancies between several calculated %R_o equations and thus should be further investigated for use in the Permian Basin. Accordingly, these findings show that clay mineral diagenesis, combined with other paleothermal proxies, can considerably improve the understanding of the complex burial history of the Permian Basin in the context of the evolution of the southern margin of Laurentia.

Keywords: shale diagenesis; thermal maturity; clay minerals; source rocks; Permian Basin

1. Introduction

Fine-grained organic-rich sedimentary rocks when subjected to sufficient heating and pressure are capable of becoming petroleum source rocks and/or important reservoirs for unconventional hydrocarbon production [1–3]. Unconventional reservoir production potential is highly dependent on a variety of physical and chemical properties that are controlled by depositional environment and post-depositional diagenetic history [4–9]. Post-depositional thermal histories are likely the biggest factor in transforming both inorganic components (i.e., minerals), which in turn affect rocks' physical nature [10–13], and organic matter by maturation into hydrocarbon [14–18]. Therefore, an

understanding of both the mineral and organic matter histories during burial and subsequent thermal progression are key to comprehending the potential for unconventional hydrocarbon exploration, and provide important insight to the geologic evolution of sedimentary basins [11,19–21].

Thermal history reconstruction, especially within a hydrocarbon producing basin, is typically assessed by means of Rock-Eval pyrolysis, which produces data related to the quality and quantity of organic matter. The temperature index (Tmax) obtained from Rock-Eval pyrolysis is widely used as a maturity index due to its correlation with the increase of organic matter maturation [14]. However, Tmax must be cautiously considered as a thermal maturity indicator due to factors, such as (i) small amount of organic matter in the sample, (ii) deterioration of organic matter, and (iii) varying types of organic matter at the maximum of their thermal maturity [22–26]. Vitrinite reflectance (%R_o) observations through organic petrography, especially in shale, has become the standard evaluation tool for thermal maturity [27–31]. Vitrinite reflectance is useful due to its systematic increase with increased organic matter maturation and burial depths as well as preferred arrangements in structure due to overlying stress from load pressure [27]. However, %R_o interpretations can be time consuming, relying heavily on the experience of the organic petrographer [29]. Calculated vitrinite reflectance conversion values using Rock-Eval pyrolysis data have been theoretically developed for several source rocks within a number of sedimentary basins [23,30] and can be further adjusted with the incorporation of mineral maturation indices [31].

Alterations of clay mineral assemblages, in particular mixed-layer illite-smectite (I-S) ratios and illite or chlorite crystallinity indices, have also been used to determine the maximum burial depths and interpret thermal evolution in sedimentary basins [11–14,20,21,24,32–36]. The smectite to illite ratio in mixed-layer I-S as well as the ordering of mixed-layers are both variables that are susceptible to the temperature increase with depth and are controlled by the illitization process [12,37,38]. These diagenetic changes coincide with temperatures at which organic matter starts to generate liquid hydrocarbons [11,33,37]; therefore, understanding the mineralogy and presence of I-S mixed-layered phases can be used as a geothermal indicator of potential source rocks and maximum burial temperatures.

The ability to constrain different maturation techniques at times in which only some data are available or when techniques must be modified (calculated %R_o by Rock-Eval pyrolysis [30,31]) can prove helpful during the development of unconventional shale reservoirs. The Wolfcamp, and to a lesser extent Barnett, unconventional shale plays within the Midland Basin, a small sub-basin of the Permian Basin, are some of the largest producing shale plays in the world [39]. The development of these plays has led to sizeable amounts of research employing various analytical approaches, such as vitrinite reflectance, palynofacies, total organic carbon (TOC) variability, and Rock-Eval pyrolysis, to evaluate the types of organic matter presence and source rock potential (e.g., [28,40–42]). However, the assessment of clay mineral presence, particularly the mixed-layered I-S phases, and diagenesis has been severely generalized in most mineralogical studies and limited to just few reports on the specifics of clay mineral phases [43,44]. Due to potential variability of maturation indices dealing with organic materials, the importance of using inorganic maturation indices as an indicator for thermal history becomes essential to better understand maturation processes for the construction of diagenetic models [19–21,23–25]. This study aimed to (1) determine the mineralogy and diagenesis of clay minerals within the northern Midland Basin, (2) determine the relationship between clay mineral thermal indices and organic matter maturation parameters (Tmax and calculated %R_o), and (3) extrapolate northern Midland Basin data throughout the basin to better refine thermal history regimes.

2. Geological Background

2.1. Paleogeography and Tectonics

The area of Permian Basin (Figure 1) was located along the southern margin of Laurentia where a series of sedimentary basins developed throughout the Paleozoic [45,46]. The ancestral Tobosa Basin, a

low-relief marine depression [47,48], covered much of southern craton during the Early Paleozoic. The basin was fairly inactive tectonically until the Late Mississippian when weak crustal extension and subsidence began to deepen the basin [49]. During the Pennsylvanian, the collision of Laurentia and Gondwana led to the development of the Marathon-Ouachita fold-thrust belt, creating the modern foredeep Permian Basin [50–52]. Deformation continued along high-angle fault structures through the Pennsylvanian, establishing three distinct sub-basins, the Midland (the focus of this study), Delaware, and Val Verde Basins [49,50,53]. The Midland Basin actively started to assemble during the Middle Pennsylvanian, with several pulses of subsidence through the Early Triassic [45,50,54]. Following this period, the Midland Basin would remain virtually inactive throughout the Mesozoic, until Laramide tectonics lifted and tilted the basin asymmetrically from west to east to its present-day depths [49].

Figure 1. Geographic location of the Greater Permian Basin region with associated subsurface basins. The cored samples are denoted by the red stars within the northern Midland Basin.

2.2. Deposition and Stratigraphy

Passive margin secessions dominated the ancestral Tobosa Basin during the Early Paleozoic, alternating between thick accumulations of shelf carbonates, basinal shales, and nearshore clastics [54]. Late Mississippian transgressions in the region deposited fine-grained, dark gray and brown, organic-rich sediments of the Barnett formation (Figure 2; [55]). This section is unconformably overlain by Pennsylvanian age Atoka and Bend formations and marks the fall of relative sea-level ending the Kaskaskia megasequence [54,55]. At the beginning of the Pennsylvanian, regional structures started to shift, creating uplifts within and around the basin, altering sedimentary regimens and constructing environments conducive to clastic deposition along the northwest margin and progressively more sediment starved towards the center and southern margins [56,57]. As time progressed through the Pennsylvanian, tectonic activity, rapid subsidence, and intense glacio-eustatic sea-level deviations controlled the widespread deposition of cyclothems, creating sequences of Strawn and Canyon formation shelf carbonates with time-equivalent detrital limestones and basinal clastic turbidity deposits (Figure 2, [54,57–61]). Upper Pennsylvanian Wolfcamp D/Cline formation is commonly gray to black organic-rich marine shales with increased carbonated detritus near the margins of the basin (Figure 2) [57]. In the Early Permian, continued subsidence accompanied by deltaic progradation from

the north and east supplied clastic sediment from the Ouachita fold-thrust belt [58] through incised valleys and troughs along the Eastern Shelf, giving rise to the Wolfcamp formation (Figure 2) [61–63]. Sediment conduits captured carbonate detritus and debris from exposed platform shelves, creating a series of mass flows, turbidite, and basin-floor submarine facies fanning throughout the basin [61,64–66]. As sea water receded, the basin began to fill with additional clastics and prograding carbonate margins until the Late Permian when thick accumulations of evaporite deposits covered the area [54,57]. Previously, several subsidence curves were constructed [50,67], depicting steady rates throughout the Paleozoic until the Middle to Late Pennsylvanian, in which rates dramatically increased during the Permian. These previous models suggest that Wolfcampian-aged rocks within the eastern Midland Basin (Figure 3) reached depths of approximately 2–2.5 km at the end of the Permian. Subtle uplifts and erosional events during the Mesozoic allowed the exhumation and non-deposition of sediments [54]. Finally, during the Cretaceous, marine sediments covered the entire Midland Basin, once again burying Pennsylvanian and Permian source rocks within the Western Interior seaway, until uplift from Laramide events positioned them to current depths [54,67–69].

System	Epoch/Series/Stage	Midland Basin	General Stratigraphy	
Permian	Leonardian	Upper Leonard		
		Upper Spraberry		
		Middle Spraberry		
		Lower Spraberry		
		Middle Leonard		
		Dean		
	Lower Leonard (Wolfcamp A)			
	Wolfcampian	 Wolfcamp B		
Wolfcamp C				
Pennsylvanian	 Virgilian	Wolfcamp D/Cline		
	Missourian	Canyon		
	Desmoinesian	Strawn		
	Atokan	Atoka/Bend		
Mississippian	Chesterian	 Barnett		
	Meramecian	Mississippian		
	Osagean			
	Kiderhookian			
Devonian	Famennian	Woodford		

Figure 2. Stratigraphic nomenclature used within the Midland Basin. Core intervals are noted by the black columns. General lithologies and stratigraphy are modified after Ewing (2016) [54] and Hamlin and Baumgardner, (2012) [65]. Ash bed intervals are modified after Leslie et al. (2019) [70].

Figure 3. Subsidence curve for the eastern part of the Midland Basin after Yang and Dorobek, 1995 [54], Ewing, 1993 [67], and Heij and Elmore, 2020 [71].

3. Materials and Methods

3.1. Sample Materials

Samples listed in Table 1, were selected from three cores located within the Midland Basin from depths ranging between 2322 and 3400 m (7620–11,200 ft.) with a focus on three primarily fine-grained siliciclastics units of Mississippian, Pennsylvanian, and Permian age. Tonya 401 and Tonya 901 cores are located in eastern Midland Basin, with the JP Chilton core located in western Midland Basin (Figure 4). Cores were described using petrological techniques and nomenclature schemes developed by Lazar et al., 2015 [72]. Representative samples were then chosen for X-ray diffraction (XRD), clay mineral modeling, and Rock-Eval pyrolysis analyses.

Table 1. List of analyzed drill core samples from multiple wells within the Midland Basin.

Sample	Lease	County	Location	Depth m (ft)	Lithofacies	Applied Methods
T901-7620	Tonya 901	Borden	NE MB	2323 (7620)	Black siliceous shale	XRD, CL, CM, REP
T901-7627	Tonya 901	Borden	NE MB	2324 (7627)	Brown calcareous shale	OP, XRD, CL, CM
T901-7641	Tonya 901	Borden	NE MB	2329 (7641)	Brown calcareous shale	OP, XRD, REP
T901-7645	Tonya 901	Borden	NE MB	2330 (7645)	Brown calcareous shale	REP
T901-7649	Tonya 901	Borden	NE MB	2330 (7649)	Brown calcareous shale	OP, REP
T901-7650	Tonya 901	Borden	NE MB	2330 (7650)	Brown dolomite	OP, XRD
T901-7657	Tonya 901	Borden	NE MB	2333 (7657)	Brown calcareous shale	OP, XRD, CL, CM
T901-7665	Tonya 901	Borden	NE MB	2336 (7665)	Brown mudstone	XRD, CL, CM
T901-7669	Tonya 901	Borden	NE MB	2337 (7669)	Brown dolomitic shale	OP, XRD, CL, CM
T901-7673	Tonya 901	Borden	NE MB	2339 (7673)	Black siliceous shale	XRD, CL, CM, REP
T901-7690	Tonya 901	Borden	NE MB	2343 (7690)	Black siliceous shale	OP, XRD
T901-7700	Tonya 901	Borden	NE MB	2133 (7000)	Brown calcareous shale	OP, XRD
T901-7718	Tonya 901	Borden	NE MB	2352 (7718)	Black siliceous shale	OP, XRD, CL, CM, REP
T901-7741	Tonya 901	Borden	NE MB	2359 (7741)	Black shale	XRD, CL, CM
T901-8156	Tonya 901	Borden	NE MB	2486 (8156)	Black shale	OP, XRD, CL, CM, REP
T901-8167	Tonya 901	Borden	NE MB	2489 (8167)	Black shale	OP, XRD, CL, CM, REP
T901-8175	Tonya 901	Borden	NE MB	2492 (8175)	Black shale	XRD, CL, CM, REP
T901-8187	Tonya 901	Borden	NE MB	2495 (8187)	Brown dolomite	OP, XRD
T901-8197	Tonya 901	Borden	NE MB	2498 (8197)	Black shale	OP, XRD, CL, CM
T901-8217	Tonya 901	Borden	NE MB	2505 (8217)	Black shale	OP, XRD, CL, CM, REP
T901-8236	Tonya 901	Borden	NE MB	2510 (8236)	Black shale	XRD, REP
T901-8252	Tonya 901	Borden	NE MB	2515 (8252)	Black shale	CL, CM
T901-8256	Tonya 901	Borden	NE MB	2516 (8256)	Black shale	CL, CM
T901-8275	Tonya 901	Borden	NE MB	2522 (8275)	Brown limestone	OP, XRD, REP
T901-8289	Tonya 901	Borden	NE MB	2526 (8289)	Brown dolomitic shale	OP, XRD, REP
T901-8306	Tonya 901	Borden	NE MB	2532 (8306)	Brown siltstone	OP, XRD, REP
T901-8239	Tonya 901	Borden	NE MB	2511 (8239)	Black shale	XRD
T901-8357	Tonya 901	Borden	NE MB	2547 (8357)	Black shale	OP, XRD, REP
T401-9004	Tonya 401	Borden	NE MB	2744 (9004)	Dark grey mudstone	OP, CL, CM, REP
T401-9005	Tonya 401	Borden	NE MB	2744 (9005)	Green claystone	OP, XRD
T401-9008	Tonya 401	Borden	NE MB	2745 (9008)	Dark grey limestone	XRD
T401-9015	Tonya 401	Borden	NE MB	2748 (9015)	Dark green siltstone	OP, XRD, CL, CM, REP
T401-9016	Tonya 401	Borden	NE MB	2748 (9016)	Dark green siltstone	XRD
T401-9017	Tonya 401	Borden	NE MB	2748 (9017)	Dark green siltstone	OP, XRD
T401-9026	Tonya 401	Borden	NE MB	2751 (9026)	Black limestone	OP, XRD
T401-9027	Tonya 401	Borden	NE MB	2751 (9027)	Black mudstone	OP, XRD, CL, CM, REP
T401-9028	Tonya 401	Borden	NE MB	2751 (9028)	Black mudstone	XRD
T401-9029	Tonya 401	Borden	NE MB	2752 (2029)	Grey mudstone	XRD
T401-9030	Tonya 401	Borden	NE MB	2752 (9030)]	Black-grey shale	OP, XRD
T401-9031	Tonya 401	Borden	NE MB	2752 (9031)	Black shale	OP, XRD, REP
T401-9032	Tonya 401	Borden	NE MB	2752 (9032)	Black-grey shale	XRD
T401-9033	Tonya 401	Borden	NE MB	2752 (9033)	Black shale	OP
T401-9034	Tonya 401	Borden	NE MB	2753 (9034)	Black-grey shale	OP, XRD, REP
T401-9035	Tonya 401	Borden	NE MB	2753 (9035)	Black limestone	XRD
JP11091	JP Chilton #1	Gaines	NW MB	3381 (11091)	Black shale	CL, CM, REP
JP11107	JP Chilton #1	Gaines	NW MB	3385 (11107)	Black shale	CL, CM, REP
JP11118	JP Chilton #1	Gaines	NW MB	3389 (11118)	Black shale	CL, CM, REP
JP11135	JP Chilton #1	Gaines	NW MB	3394 (11135)	Black shale	CL, CM, REP

Abbreviations: NE—Northeast; NW—Northwest; MB—Midland Basin; OP—Optical petrography; XRD—whole rock x-ray diffraction; CL—clay fraction (<2 µm) X-ray diffraction; CM—clay mineral modeling; REP—Rock-Eval pyrolysis.

Figure 4. Stratigraphic column of the Tonya 401, Tonya 901, and JP Chilton cores used for this study. Core intervals are exaggerated to depict grain size and lithologies associated to the sampling interval. Vertical scale 1 in. = 76.2 m (250 ft.). Refer to Figure 1 for well locations within the northern Midland Basin.

3.2. X-Ray Diffraction

Sample preparation for XRD analyses initially included material powdering in an agate mortar prior to whole-rock measurements. To prevent possible mixing of coarse detrital phases with authigenic

clays, the samples were not powdered but gently disaggregated. The clay fraction was separated from the crushed material by centrifugation, which involved the addition of Na-metaphosphate to disperse the clays. Further disaggregation was accomplished in an ultrasonic bath. To ensure a uniform cation exchange, clay fractions separated by centrifugation were saturated by Mg using a solution of 10 mL of 4 M MgCl_2 . Suspensions were washed and centrifuged with distilled water at least three times to minimize the free-ion content. The oriented mounts were prepared by pipetting a suspension on glass slides, which were left to dry at 50 °C prior to their utilization. The measurements were undertaken in air-dried (AD) conditions and after ethylene-glycol (EG) saturation using a Bruker D8 Advance diffractometer installed at the Geoscience Clay Laboratory of Texas Tech University (Lubbock, TX, USA). This instrument features a horizontal goniometer axis and synchronized rotation of both the X-ray source and the detector arms. Measurement parameters consisted of a step scan in the Bragg-Brentano geometry using $\text{CuK}\alpha$ radiation (40 kV and 40 mA). Sample mounts were scanned at a counting time of 1.8 s per $0.02^\circ 2\theta$, from 3 to $70^\circ 2\theta$ and from 3 to $30^\circ 2\theta$ for the whole rock and the clay fraction, respectively. The mineral phases were identified using the PDF4+ database.

3.3. Interpretation and Modeling of XRD Patterns

X-ray diffraction patterns of clay minerals were examined using methods described by Moore and Reynolds, 1997 [73] and Środoń, 2006 [74]. For chlorite-mineral interpretation, the recommendations of Lagaly et al., 2006 [75] and Meunier, 2007 [76] were followed. To characterize the mixed-layer clay XRD, clay fraction patterns were modeled using Sybilla[®] software based on the formalism of Drits and Sakharov, 1976 [77]. The modeling included a trial-and-error procedure that provided optimal clay-mineral structural and probability parameters to obtain the best fit between experimental and calculated patterns and of the intensities of the $00l$ reflections for each of the clay phases present. For mixed-layer minerals, the number, nature, and stacking sequence of different compositional layers were taken as modifiable values. Experimental spectra were produced using two discrete phases (illite and chlorite) along with a series of low-ordered (R0) illite-smectite (I-S; I-SS; I-SSS), high-ordered (R1 and R3) I-S phases, and chlorite-smectite-smectite (C-SS) following the procedures in Uzarowicz et al., 2012 [78] and Zaroni et al., 2016 [36]. The second S in disordered illite-smectite (R0 I-SS) denotes a multiple type of smectite component differing from the preceding one in terms of charge and, therefore, in terms of d spacing. In other words, expandable layers in R0 I-S are bi-hydrated and in R0 I-SS they are mono- and bi-hydrated (e.g., [79,80]). Modeling parameters of mixed-layer minerals consisted of (1) the extent of the preferred orientation of particles on the mounted X-ray slides (σ^*), (2) coherent scattering domain sizes (CSDS) expressed in number of layers, and (3) the amounts of illite component in mixed-layer phases, Table 2. Quantification of whole-rock diffractograms (Table A1) is based on the reference intensity ratio (RIR), which considers the ratio between an internal standard (i.e., corundum) and minerals of interest [81]. Conversely, the abundances of clay minerals were reported from clay fraction diffractograms as relative values from modeled samples (Table A2).

Table 2. Rock-Eval pyrolysis data from analyzed samples from the Midland basin.

Sample	Depth (m)	TOC (wt%)	HI (mg HC/g TOC)	OI (mg CO ₂ /g TOC)	Tmax (°C)	S1 (mg HC/g)	S2 (mg HC/g)	S3	S2/S3	Production Index S1/(S1 + S2)	Calculated %R _o *	Calculated %R _o ^	Estimate Peak Burial Temperature (°C) **	Estimate Peak Burial Temperature (°C) ^^
T901-7620	2323	0.71	336.07	43.15	438	0.32	2.38	0.31	7.79	0.12	0.71	1.07	123	137
T901-7641	2329	0.86	350.04	40.23	440	0.47	3.00	0.35	8.70	0.14	0.75	1.11	125	139
T901-7645	2330	3.40	406.36	8.97	438	1.66	13.83	0.31	45.29	0.11	0.71	1.07	123	137
T901-7649	2331	3.73	518.21	6.86	434	5.39	19.32	0.26	75.50	0.22	0.64	0.98	119	134
T901-7673	2339	5.85	437.15	6.22	436	2.72	25.57	0.36	70.28	0.10	0.68	1.02	121	136
T901-7718	2352	2.17	297.76	12.70	439	0.78	6.45	0.28	23.45	0.11	0.73	1.09	124	138
T901-8156	2486	3.91	306.92	9.03	439	1.69	12.01	0.35	33.97	0.12	0.73	1.09	124	138
T901-8167	2489	3.69	264.55	6.65	442	1.26	9.75	0.25	39.77	0.11	0.77	1.15	126	140
T901-8175	2492	9.16	375.14	3.85	439	3.34	34.36	0.35	97.39	0.09	0.72	1.09	124	138
T901-8217	2505	3.51	311.30	9.49	442	1.25	10.92	0.33	32.81	0.10	0.77	1.15	126	140
T901-8236	2510	3.01	300.43	3.91	441	2.35	18.06	0.23	76.93	0.12	0.76	1.13	125	139
T901-8275	2522	2.22	265.95	21.13	438	1.22	5.91	0.47	12.58	0.17	0.71	1.07	123	137
T901-8289	2526	1.22	319.83	28.90	438	0.91	3.89	0.35	11.07	0.19	0.71	1.07	123	137
T901-8306	2532	9.56	316.79	3.78	441	4.56	30.29	0.36	83.90	0.13	0.75	1.13	125	139
T901-8357	2547	3.23	327.18	12.98	438	1.87	10.57	0.42	25.20	0.15	0.72	1.07	124	137
T401-9004	2744	0.22	133.95	108.59	347	0.08	0.30	0.24	1.23	0.21				
T401-9015	2748	0.15	294.84	108.23	347	0.10	0.45	0.17	2.72	0.18				
T401-9027	2751	0.96	82.82	87.09	428	0.23	0.79	0.84	0.95	0.23	0.55	0.91	114	132
T401-9031	2753	7.69	183.12	4.43	440	1.48	14.09	0.34	41.38	0.10	0.75	1.18	125	141
T401-9034 *	2754	0.86	40.65	15.10	441	0.14	0.35	0.13	2.69	0.29	0.76	1.22	125	142
JP11091	3381	13.57	457.39	5.20	440	5.62	62.08	0.71	87.89	0.08	0.75	1.11	125	139
JP11107	3385	3.62	336.14	7.76	441	1.25	12.16	0.28	43.89	0.09	0.77	1.13	126	139
JP11118	3389	1.92	137.01	24.22	442	0.45	2.63	0.46	5.66	0.15	0.78	1.15	126	140
JP11135	3394	3.70	216.00	6.00	441	0.71	8.00	0.22	35.99	0.08	0.76	1.13	126	139

Abbreviations: TOC—total organic carbon; HI—hydrogen index; OI—oxygen index; Tmax—temperature at which maximum amount of S2 hydrocarbons are generated; S1—amount of free hydrocarbons released at 200 °C; S2—hydrocarbon generated by pyrolytic degradation of kerogen; S3—carbon dioxide generated by pyrolytic degradation; S2/S3 = generative types of hydrocarbon (<3 = gas, 3–5 = gas and oil, <5 = oil) (Peters, 1986); Production Index = oil window index (0.1–0.4) (Peters, 1986); Calculated %R_o * from Tmax = (0.0165 × Tmax) – 6.5143 (Jarvie et al., 2018); Calculated %R_o ^ from Tmax = (0.022 × Tmax) – 8.57 (Lewan and Pawlewicz, 2017); Estimate Peak Burial Temperature (°C) ** using %R_o * = (LOG(%R_o *) + 1.68)/0.0124 (Baludikay et al., 2018); Estimate Peak Burial Temperature (°C) ^^ using %R_o ^ = (LOG(%R_o ^) + 1.68)/0.0124 (Baludikay et al., 2018). Sample T401-9034 data was obtained by Weatherford Laboratories.

3.4. Rock-Eval pyrolysis

All samples were analyzed at the Institute of Earth Sciences of the University of Lausanne (Switzerland) except T401-9034, which was analyzed by Weatherford Laboratories (Houston, TX, USA). Samples were homogenized using a mortar grinder for Rock-Eval analyses performed using a Rock-Eval 6 pyrolyzer (Vinci Technologies) on aliquots of 55 to 70 mg in Incoloy crucibles. Analytical procedures closely followed detailed instructions provided by Ordonez et al., 2019 [82] and primarily include the following: TOC (wt%), the total content of organic matter in the rock; S1 (mg HC/g rock), free hydrocarbons contained in the organic matter; S2 (mg HC/g rock), the amount of hydrocarbons formed by the rock; S3 (mg CO₂/g rock), CO₂ pyrolyzed; and Tmax (°C), the temperature when the S2 peak is recorded. Additionally, source rock parameters, such as HI (mgHC/g TOC), OI (mg CO₂/g TOC), and PI (S1/S1 + S2), were calculated, to evaluate the type of kerogen and the hydrocarbon generation and expulsion potential [13,83]. Traditionally, vitrinite reflectance (%R_o) is used to infer the maturation of hydrocarbon by means of organic petrography; however, this technique may be time consuming and is dependent on the presence of vitrinite itself [29]. Furthermore, additional maturation indices, such as Rock-Eval (Tmax, HI) and clay mineral maturation, may be used in case of a paucity of %R_o data. Since petrographical %R_o data was not available during this study, calculated %R_o values were determined by Tmax obtained from Rock-Eval pyrolysis using developed formalism [43,84] from data collected in the adjacent Fort Worth Basin, USA. Subsequently, the calculated %R_o was employed to determine peak burial temperatures [85].

4. Results

4.1. Lithofacies

The Tonya 401 and 901 cores located in the northeastern Midland Basin are geographically separated by approximately 1.5 km (1 mi) with no evidence of displacement; therefore, the two were combined to create a single stratigraphic section represented by three distinct intervals: the upper (2323–2359 (7620–7741 ft.)), middle (2486–2547 m (8156–8357 ft.)), and lower (2744–2754 m (9003–9041 ft.)) sampling intervals (Figure 4). The upper sampling interval lithofacies are mostly interbedded black siliceous shales and black calcareous shales with occasional limestone and dolomitic intervals. The middle sampling interval lithofacies are predominantly black shales with very thin interbedded limestone and dolomite. These two sections represent the Wolfcamp formation of Permian (upper section) and Pennsylvanian (middle section) ages (Figure 5). In the lowest section, the lithofacies are more variable and consist of grey-black siliceous shale, grey to black calcareous shale, green-grey siltstone, and massive grey limestone, which represent the Barnett formation of Mississippian age. The JP Chilton core interval (3381–3394 m (10,091–11,135 ft.)) (Figure 4) is mostly calcareous-rich shales at the top of the interval with more silica-rich shale at the bottom that overlie massive grey grainstone carbonates (Figure 5). This core interval is part of the Wolfcamp formation within the northwestern Midland Basin.

Figure 5. Lithofacies within the Tonya 901 (A,B), Tonya 401 (C), and JP Chilton (D,E) cores. (A) Interbedded Si-rich and Ca-rich shale. (B) Si-rich black shale. (C) Green-grey siltstone and claystone. (D) Ca-rich shale. (E). Si-rich shale.

4.2. XRD Mineralogy

4.2.1. Whole-Rock Fraction

Whole-rock XRD diffractograms within the Tonya sampling intervals indicate primary phases of quartz, calcite, albite, and clay minerals, with minor phases consisting of pyrite, dolomite, microcline, analcime, and lesser amounts of Fe sulfide and gypsum. Mineral phases and their relative abundances are summarized in Figure 6 with detailed amounts found within Appendix A. Primary phases' presence corresponds well with lithofacies and appear to be mostly controlled by the depositional environment. Hence, the content of quartz and mica are abundant in Si-rich shale facies whereas calcite within Ca-rich facies is largely controlled by the amount of fossiliferous and limestone clasts debris. The minor phase of analcime is primarily found in upper and middle cores of the combined Tonya well (2322.6–2505.4 m (7620–8236 ft.)) with little presence in the lower sampling interval or the JP Chilton core. Reference intensity ratio (RIR) quantification showed that Wolfcamp formation samples average 40% quartz, 18.5% carbonate, and 26% clay minerals, depending on the prevalence of detrital carbonate, whilst Barnett formation samples average 37% quartz, 20% carbonate, and 23% clay minerals. Whole-rock diffractograms of the JP Chilton core show similar phases to those of the Tonya cores with the occurrence of quartz, calcite, dolomite, K-feldspar, clay, and pyrite and no presence of analcime. RIR quantification displays higher abundances of calcite in the upper portion of the core and dissipating near the bottom of the sampling interval.

Figure 6. RIR quantifications of representative whole rock samples from the study interval. Phases were combined into four major groups. QFPA = quartz, feldspars, pyrite, apatite; carbonates = calcite and dolomite; clay = mica and clinocllore; other = remaining minor phases, see Appendix A.

4.2.2. Clay Fraction

Clay minerals present within the sample interval account for illite, various mixed-interlayered illite-smectite (R0 I-S, R0 I-SS, R0 I-SSS, R1 I-S, and R3 I-S), chlorite, and mixed-layer chlorite-smectite (R0 C-SS). Clay mineral abundances are given in Appendix B. Discrete illite was identified predominantly by the 10- and 5-Å peaks corresponding to the 001 and 002 reflections (Figure 7) ranging from 0% to 41.3%. Interstratified mixed-layer phases are recognized by using the criteria of Reynolds and Hower, 1970 [86] featuring the broad diffraction peak near 17 Å appearing in glycolated samples as well as additional broadening of peaks near 10 Å. Once identified, pattern fitting and deconvolution of original experimental spectra (Appendix C) indicated the presence of multiple disordered mixed layered phases (R0 I-S, I-SS, and I-SSS) (Figure 7) throughout the study interval. The disordered mixed layer phases primarily occur within the upper sampling interval of the Tonya core (2322.6–2485.9 m (7620–8156 ft.)) (Figure 8). Additionally, the illite components of R0 I-S and R0 I-SS ranged from 5% to 25% and 10% to 38%, respectively. Furthermore, ordered mixed layered phases of R1 I-S (Figures 7 and 8) were recognized by reflections near 11.1 and 13.3 Å. These two reflection points indicate a

long-range ordering of the second-ordered superstructure unit cell of three 10 Å illite layers and one 17 Å smectite layer [73]. R1 I-S phases mostly occur within the middle sampling interval of the Tonya core (2485.9–2516.4 m (8156–8256 ft.)) and throughout the JP Chilton core (3380.5–3393.9 m (11,091–11,135 ft.)). The illite abundance within the R1 I-S phases range from 75–95%. Long-ordered R3 I-S phases were observed solely within the lower Tonya interval (2744.4–2753.3 m (9004–9033 ft.)). This phase contains 92–99% illite within the R3 I-S phase. Discrete chlorite was identified by peaks at 14.1, 7.1, and 4.5 Å, Figure 7. Discrete chlorite begins to appear at 2339 m (7673 ft.) and ranges from 0.9–5.5%. This phase is most abundant in lower Wolfcamp samples from depths of 2339–3393 m (7673–8256 ft.). Furthermore, mixed-layer C-SS phases were observed primarily within the lower Wolfcamp samples in the Tonya core and lower most samples in the JP Chilton core (Appendix C) and sporadically reached abundances up to 17%.

Figure 7. Deconvolution of XRD patterns of clay fraction for four representative samples. (A-T401-7673, B-T401-8197, C-T401-8252, and D-JP Chilton-11118). The experimental XRD pattern is blue with the modeled fit being orange, with phases of illite (grey), chlorite (green), R0 I-S (yellow), R1 I-S (pink), R3 I-S (red), and R0 I-SS (dark blue).

Figure 8. Mineral composition of clay fraction analyzed samples from representative samples. Si-rich Sh = silica rich shale; Ca-rich Sh = calcium rich shale, Perm = Permian; Penn = Pennsylvanian, Miss = Mississippian.

4.3. Rock-Eval Pyrolysis

TOC values from all samples range between <1 wt% and 13.57 wt% throughout the study interval. The middle sampling interval within the Tonya 901 core from 2486–2547 m produced the most consistent TOC values, averaging 4.39 wt% (Table 2). S1 values are mostly consistent, ranging from near 0.50 to 3.34 mgHC/gTOC, except in Tonya 401 samples, where values are extremely low, whereas S2 values range from 0.30–62.08 mgHC/gTOC and correlate well with TOC amounts. HI amounts typically range from 137 to 518, with most samples falling within 200 to 400 mgHC/gTOC except for two samples: T401-9027 and T401-9034. OI values mostly range from 3.78–28.90 mgHC/gTOC, with five samples over 40.23 up to 108.59 mgHC/gTOC. Kerogen types consist primarily of Type II [87–89]. Tmax values range from 434 to 442 °C, with two samples (T401-9004 and T401-9015) at 347 °C. These low Tmax values are possibly due to the very low abundance of organic matter (<0.22 wt%) within the samples and disallowing the expulsion of free hydrocarbons or cracking, thus reducing the S2 peak for which Tmax is dependent [18,90]. Calculated vitrinite reflectance (%R_o) using the Jarvie et al. [84] equation range 0.55–0.78 (Table 2). The Tmax and %R_o values suggest that sediments were exposed to temperatures near the beginning of the oil window ([20] and references therein). The %R_o values when using the Lewan and Pawlewicz [43] equation are slightly higher ranging from 0.91–1.22, indicating later maturation (Table 2).

5. Discussion

5.1. Clay Mineral Evolution

The conversion of smectite to illite through a series of mixed-layered I-S is a common diagenetic transformation within sedimentary basins, whereby the conversion dynamics and component ordering are primarily controlled by the increase in temperature, but other factors, such as reservoir characteristics, K availability, or starting composition of smectite, may also affect the conversion process [12,36,91–93]. Therefore, illite-smectite composition and ordering can be utilized as a relative geothermometer to indicate the maximum burial temperatures within a sedimentary basin [11,12,33,94,95]. Within the upper Tonya 401 core (2322.6–2359.5 m (7620–7741 ft.)), the primarily clay component is random ordered (R0) I-S and I-SS (Figure 7). Of these, the illite constituent of R0 I-S averages 90% (Appendix C). This suggests that analyzed lithofacies within this interval were likely exposed to temperatures near 100 °C based on the paleogeothermometer calibration of Środoń (1999) [12] using the proportion of smectite in I-S (Appendix C). However, with no evident appearance of R1 I-S phases within this upper Tonya 901 sections (2322.6–2359.5 m (7620–7741 ft.)), maximum temperatures likely did not surpass 100–110 °C [12,33,96]. Using a geothermal gradient of 40 °C/km for the Permian Basin [71], the maximum burial depths of this interval were less than 2.5 km and have been and still are at least moderately exposed to mesogenesis [11,12,33,97,98].

Mixed layered R1 I-S phases were observed beginning at 2485.9 m (8156 ft.) and appear throughout the middle sampling interval of the Tonya 901 (2485.9–2156.4 m (8156–8252 ft.)) core as well as the entire JP Chilton core (3381–3394 m (11,091–11,135 ft.)). The presence of R1 I-S phases implies that facies were exposed to higher paleogeothermal temperatures near or above 100–110 °C and further mesogenesis [96]. The increased ordering within the two cores can be attributed to a temperature increase to depth within the JP Chilton core and increased residence time (duration of heating) in the Tonya. As mentioned before, for the normal geothermal gradient of 40 °C/km [71], the depth for conversion of R0 to R1 (100–110 °C, [96]) should surpass 3 km below the surface. Furthermore, the lack of higher-ordered I-S in the deeper JP Chilton core suggests that both the Tonya and JP Chilton facies within the R1 I-S interval were subjected to the same maximum burial depths, and present-day depths (Tonya, 2485.9 m; JP Chilton, 3380.5 m) of core facies reflect asymmetrical deepening of the Midland basin toward the west and uplifting along the Bend arch to the east [54,67].

Additionally, I-S phases identified in the Tonya 401 facies beginning at 2744.4 m (9004 ft.) have increased illite in I-S, and significantly less smectite (Appendix C) proposes that these facies were exposed to paleotemperatures likely above 130 °C and depths greater than 4 km based on models by Hower (1981) [83] and Środoń and Eberl, 1987 [99]. These approximations appear to relate well to the calculated %R₀ from T_{max} using the Jarvie (2018) [84] equation (Table 2), which estimates sediments were exposed to maximum temperatures of near 120 °C [85] and possible burial depths of 3 km (40 °C/km). However, when applying the Lewan and Pawlewicz [43] equation for calculated %R₀ to data from this study, increases in both calculated %R₀ (0.85–1.15) and maximum burial temperatures (129–140 °C) (Table 2) were seen. This increase may better correlate with the inferred increase in burial temperatures from clay diagenesis from the Tonya 401 facies but appears to overestimate paleotemperatures for the Tonya 901 and JP Chilton facies. The differences in clay mineral and organic maturation indices may be attributed to various factors. First, the Tonya 401 facies are of Mississippian age and have been exposed to long-term burial and heating regimes since at least Morrowan (Early Bashkirian) time [56], allowing illitization of I-S to steadily increase over approximately 320 Ma. Secondly, the calculations used for the %R₀ data presented here (Table 2) were developed from datasets within the Fort Worth basin (Texas, USA) [43,84,100] and have not been calibrated with optical organic petrography data from the Midland basin and thus should be treated as approximations until the direct measurement of %R₀ can be conducted.

Likewise to illitization, the chloritization of smectite through a series of mixed-layered chlorite-smectite (C-S) to chlorite occurs in sedimentary basins in response to time, temperature, fluid to

rock ratio, the nature of the initial material, and transformation mechanisms; however, these processes are more complex and limited than those of illitization [34,101]. The widely accepted mechanism of chlorite formation in clastic sediments proposes a continuous increase in the percentage of chlorite layers within the parental smectite material as the burial depth or temperature increases [34]. The temperature of chlorite conversion is unclear; however, studies have suggested that the transformation takes place within eogenetic temperatures beginning near 40 °C and ending approximately at 120 °C [34,102–104]. Within the Tonya core, mixed-layer C-SS first appear at 2359.5 m (7741 ft.), with 41% of chlorite in C-SS (Appendix B), which indicates that at this depth the rocks commenced to diagenetically alter. As depth increased, the chlorite percentage grew to 64% at 2491.7 m (8175 ft.) and stayed consistent at 60–65% throughout the remainder of the study interval (see Appendix B). These data show that with burial, temperature increased, providing a diagenetic environment for more chlorite layers to be added to C-SS but did not reach a maximum temperature to convert all smectitic layers. While the huge difference (50%) in the chlorite content of C-S within just 160 m of the core is hard to explain relying on the present-day prevailing geothermal gradient in the Permian Basin of 40 °C/km [71], it is more likely that such an abrupt increase is due to hydrothermal activity or the presence of volcanoclastic component in the Wolfcamp formation [34,70].

Multiple studies have identified the occurrence of volcanic ash and pyroclastic deposits within the upper Wolfcamp formation in both the Midland [70] and Delaware [105] basins, along with the observation of analcime, a zeolite formed by the reaction of volcanic ash with saline water [106] within the 2323–2540 m interval reported here. This suggests that the chlorite-rich mixed-layer chlorite-smectite, which emerges at 2329 m, reflects possible the presence and rapid alteration of volcanoclastic material [34,36], which we relate to the volcanic arc environment that came into being through the collision of Laurentia and Gondwana [107,108]. A proposed source area of volcanic material for the Permian Wolfcamp formation is the Sonoran volcanic arc along the southwestern margin of Laurentia [70]. Additionally, arc-related environments associated with the convergence of Laurentia and Gondwana directly south of the Midland basin may propose a more proximal source volcanic material during the Late Pennsylvanian to Early Permian (e.g., [109–112]). In addition to C-S, discrete chlorite has also been reported in the upper Wolfcamp formation and is likely detrital in nature due to the mineral being relatively slow to undergo weathering and alteration during relatively short transport [113]. Detrital chlorite is generally transported from the continents into the oceans as a part of metamorphic or hydrothermally altered igneous lithic fragments, which essentially break down to fine-grained marine sediment [114,115]. Discrete chlorite phases reported here were possibly derived from metamorphic environments to the south of the Midland basin along the southern Laurentian and northern Gondwanan collisions zones during the formation of Pangea at the beginning of the Pennsylvanian [116].

5.2. Source Rock Potential

The capability of source rocks to generate a significant amount of hydrocarbons and become productive unconventional reservoirs is commonly assessed in terms of organic matter quantity, quality, and maturity, e.g., [18,117]. These parameters are mostly related to the depositional environment where the organic matter forms, as well as, the diagenetic processes experienced by the rock. Variation of these parameters can considerably control the properties of an unconventional reservoir and influence heterogenic organic-lean intervals alternating with organic-rich intervals [44,118,119]. The total organic content (TOC) within the Tonya study interval (2323–2754 m) averages 3.31 wt% (n = 20) (Table 2); however, the highest TOC values appear to be within the Ca-rich shales (4.01 wt%, n = 4) versus the Si-rich shales (3.39 wt%, n = 13) (Figure 9). These are contrasting results from Baumgardner and Hamlin [119] who reported higher TOC values in Si-rich mudrocks (3.0 wt%) and lower TOC values in Ca-rich mudrocks (2.0 wt%) of Wolfcamp and Leonardian age rocks. These comparisons, however, should be investigated further due to the complexity of depositional systems within the Midland basin affecting the lateral variation in debris flows as well as the local depositional conditions affecting

bottom water anoxia for the preservation of organic matter [18]. Along with TOC, S2 (hydrocarbon potential index) and production index (PI) may be used to determine if source rocks have the potential to generate and expel hydrocarbons [117]. First, S2 results are not shown to be dependent on lithofacies but overall increase within the younger Pennsylvanian – Permian sediments within the Tonya 901 and JP Chilton cores (Figure 9). Second, the PI values show that facies within Pennsylvanian-Permian Tonya 401 interval (Figure 9) have the best potential to expulse hydrocarbons falling within ranges of suggested by Peters and Cassa [117].

Figure 9. Pseudo-van Krevelen diagram modified from Espitalié et al., 1986 [87].

Kerogen types are useful in source rock assessment to determine which type of hydrocarbons are likely to form during thermal maturation [18,109,111] based on hydrogen and oxygen indices obtained from pyrolysis [26,117]. Pseudo-van Krevelen diagram results (Figure 10) shows that kerogen types are primarily type II and are oil prone upon reaching thermal maturation. Moreover, the kerogen types do not appear to be lithofacies dependent. The use of hydrogen and oxygen indices can also be used to infer changes in temperature with depth [120]. The evolution from more abundant HI within the Tonya 901 (Permian) core to lower concentrations of HI in the Tonya 401 (Mississippian) core shows a clear picture of increasing temperature with depth and time, thus indicating more mature facies (Figure 11). Furthermore, the variation in HI is likely a result of a temperature increase than a change in the depositional environment [120]. Furthermore, Tmax values stay rather consistent throughout the stratigraphic interval uniformly, further indicating early to middle oil conditions and maturation due to loss of HI (Figure 12).

Figure 10. Source rock evaluation indices sorted by depth and lithofacies modified from Peters and Cassa (1994) [117] and Peters (1998) [90]. (A,B) Display of S2 yields increasing with TOC wt. % and indicate good potential for Permian and Pennsylvanian age sediments regardless of lithofacies. (C,D) Production index versus TOC wt% plots show that samples have generally good potential for oil generation (0.10–0.30) with moderate to good potential for sizeable expulsion (TOC > 3%) despite of lithofacies and depth.

Figure 11. Organic matter types with arrows indicating the progression of maturation modified from Taylor et al., 1998 [120].

Figure 12. Cross plot diagram of HI versus Tmax modified from Espitalié et al., 1986 [88]. Tmax does not vary through the stratigraphic section and indicates primarily early to middle oil window conditions.

Tmax from Rock-Eval pyrolysis along with OM petrography have been used to develop empirical formulas for calculating %R_o for when more sufficient data is unavailable [30,43,85]. Additionally, peak burial temperature equations have also been established using %R_o [85] to provide useful tools for insights into the thermal evolution and source rock generation potential of different lithofacies and sedimentary basins for oil and gas exploration [20,24]. Jarvie, 2018 [84] developed an equation for calculated %R_o (calculated %R_o = (0.0165 × Tmax) – 6.5143) using Rock-Eval pyrolysis data sets from the Barnett Formation (Fort Worth Basin, USA) for rocks within the 430–485 °C Tmax window. When this equation is applied to samples from this study, calculated %R_o ranges from 0.55–0.78 within Tonya cores and 0.74–0.78 in the JP Chilton core (Table 2, Figure 13), again suggesting early to peak oil window maturations [117]. As mentioned before, however, when the Lewan and Pawlewicz [43] equation was applied, calculated %R_o values were higher (0.85–1.15) (Table 2, Figure 13). However, when clay mineral indices are applied in addition to calculated %R_o, the calculated %R_o from Jarvie [84] appear to fit well with the R₀ to R₁ I-S maturation index (100–110 °C) of early oil window maturation within the Tonya 901 and JP Chilton cores. Further, the increase in illite component in R₁ I-S does suggest more heating to Tonya 901 facies, thus the higher %R_o values using the Lewan and Pawlewicz [43] equation may reflect more correlatable thermal indices.

The discrepancies in the calculated %R_o formulas used here further indicated the importance of a secondary maturation index to check common organic matter maturation indices [13,20,21,33,97]. Organic matter maturation begins earlier due to increased temperatures than silicate minerals. Additionally, relationships of Tmax and clay mineral evolution are not clearly defined [121] and the interaction between kerogen and mixed-layer I-S phases can differ significantly due to reaction kinetics [13,122]. Furthermore, the importance of the pyrolysis program especially in shale lithologies has been shown to affect the quality of data [18,123]. Carvajal-Ortiz and Gentzis (2018) [123] showed that contrasting Rock-Eval methods yielded significantly different in data when being applied to shale lithologies. Therefore, calculated %R_o values determined from pyrolysis data should be further verified. Finally, it should be noted that the equations stated before have been applied to rocks within the Midland Basin [43,85] but have not been verified due to the scarcity of optical organic petrography within the basin [23,30].

Figure 13. Maturation index data from three cores spanning the study interval. Progressive ordering of I-S corresponds well with an increase of temperature proxies with depth. Calculated $\%R_o$ after Jarvie (2018) (calculated $\%R_o = (0.0165 \times T_{max}) - 6.5143$) (green dots) and after Lewan and Pawlewicz (2017) (calculated $\%R_o = (0.022 \times T_{max}) - 8.57$) (red dots). Calculated peak burial temperature (T ($^{\circ}\text{C}$) = $(\ln(v\%R_o) + 1.68) / 0.0124$) after Barker and Pawlewicz (1994) [80].

5.3. Correlation of Inorganic and Organic Indices

The use of Rock-Eval pyrolysis data, vitrinite reflectance ($\%R_o$), and illite-smectite mineralogy have been widely used to determine thermal maturation and evolution in sedimentary basins [13,20,24,30,33,43,96,97]. The percentage of illite in I-S typically increases with increased $\%R_o$ and T_{max} and decreases with decreased HI during burial and increased temperatures (Figure 13). Moreover, the changes from R0 to R1 I-S occurring near 100 $^{\circ}\text{C}$ –110 $^{\circ}\text{C}$, 0.5–0.65 $\%R_o$, and T_{max} of 430 $^{\circ}\text{C}$ –435 $^{\circ}\text{C}$ coincide closely with the onset of catagenesis and onset of the oil generation window [11–13,33,96,97,117]. Within the Tonya 901 cores, the thermal transition temperature is represented well between the upper (Permian) and lower (Pennsylvanian) cores, with the disappearance of R0 and appearance of R1 representing the transition from eogenesis to mesogenesis and temperatures of at least 100 $^{\circ}\text{C}$ under normal geothermal conditions [1,24]. The steady increase in the illite component in I-S also indicates a rise in temperatures. Organic data from Tonya 901 cores show a trend of increasing temperature by the loss of HI from the upper (Permian) to lower (Pennsylvanian) facies. T_{max} values throughout the cores display a very faint increase and are likely suppressed due to the overall increase in maturation depicted by the loss of HI and subsequent loss of expelled hydrocarbons before pyrolysis, especially in the Mississippian aged Tonya 401 samples. Accordingly, calculated $\%R_o$ values should also be suppressed due to the lower T_{max} values from which they are derived. Therefore, $\%R_o$ values calculated from Jarvie (2018) [84] are likely lower than actual $\%R_o$ and calculated $\%R_o$ from Lewan and Pawlewicz (2017) [43] may be abundantly higher. The transition of R0 to R1 I-S near 100 $^{\circ}\text{C}$ suggests $\%R_o$ values of near 1.0 for which uncorrected calculated $\%R_o$ Lewan and Pawlewicz [43] are closest to clay mineral maturation but should be taken only as approximation until further OM petrography is conducted and equations are calibrated for samples from the Midland basin.

6. Conclusions

Three cores from the northern Midland Basin spanning from the Late Mississippian to Early Permian were sampled to acquire the whole-rock and fine-grain ($<2 \mu\text{m}$) mineral assemblages along with geochemical organic characteristics to better understand the robust diagenetic and thermal evolution of the Permian Basin. Petrological and XRD measurements of whole-rock fractions showed varied lithofacies of Si-rich and Ca-rich shale with thin intervals of limestone and dolomite. Clay mineral assemblages consist of discrete phases of illite and chlorite throughout the study interval. XRD pattern modeling of fine-grain fractions displays complex mixed-layered illite-smectite (I-S), I-SS, and

I-SSS, with progressive ordering from R0 to R1, with accompanied chlorite-smectite-smectite (C-SS). Geochemical analysis of organic matter through Rock-Eval pyrolysis showed primarily TOC-rich sediments of mainly type II kerogens with limited type III. Calculated %R_o appears to be appropriate when applying the Jarvie [79] equation based on the transition and appearance of R0 to R1 I-S. However, this calculation appears to be inadequate when applied to older-age sediments due to the appearance of long-range ordered I-S. However, when applying the Lewan and Pawlewicz [41] equation, the calculated %R_o values are higher and appear to correspond closer to observed clay mineral indices, which suggests further investigation into these calculations for use in the Permian Basin. Using I-S, T_{max}, calculated %R_o, and HI maturation indices, sediments were exposed to sufficient heating for early maturation of hydrocarbons and possibly higher temperatures within the oldest age sediments. Progressive ordering of I-S also implies that lithofacies experienced transformation through eogenesis to mesogenesis conditions and maximum burial paleotemperatures ranging from < 100 °C to near 140 °C and maximum burial depths from 2.5–4 km. This study shows the importance of using two dependent maturation indices (organic and mineral) when investigating the modifications of fine-grained source rocks. In future work, measured %R_o along with kerogen type identification should be conducted in order to fully understand the nature of organic matter diagenesis. Furthermore, these findings show that clay mineral diagenesis can be applied and be of practical use to better understand regional subbasins within the larger Permian Basin and reconstruct the complex burial history in context to the geotectonic evolution of the southern margin of Laurentia.

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Conflicts of Interest: The authors declare no conflict of interest.

Appendix A

Table A1. Relative mineral abundances determined by RIR of analyzed samples from the Midland Basin.

Sample	Depth (m)	Lithofacies	Qtz	Cal	Dol	Feldspar	Py	Mca	Chl	Gyp	Jar	Flu
T401-7620	2322.6	Si-rich Sh	51.4	10.6	2.4	4.7	7.6	16.5	3.5	0.0	0.0	0.0
T401-7627	2324.7	Ca-rich Sh	23.1	53.3	4.4	1.7	6.9	10.5	0.0	0.0	0.0	0.0
T401-7641	2328.9	Ca-rich Sh	29.1	56.0	1.7	2.3	2.5	6.7	0.0	0.0	0.0	0.0
T401-7650	2331.7	Limestone	4.8	94.0	0.0	0.5	0.0	0.0	0.0	0.0	0.0	0.0
T401-7657	2333.9	Limestone	3.2	91.4	0.5	0.8	1.3	2.8	0.0	0.0	0.0	0.0
T401-7665	2336.3	Si-rich Sh	40.3	9.0	3.5	4.9	9.7	25.2	0.0	0.0	0.0	0.0
T401-7669	2337.5	Dolomite	6.6	10.4	50.6	2.5	6.0	19.5	0.0	0.0	0.0	0.0
T401-7673	2338.7	Si-rich Sh	50.2	4.0	2.5	5.3	8.2	17.7	6.2	0.0	0.0	0.0
T401-7690	2343.9	Si-rich Sh	61.2	1.9	3.7	3.9	5.4	18.4	2.9	0.0	0.0	0.0
T401-7700	2346.9	Limestone	12.0	65.9	6.6	2.9	3.1	9.1	0.0	0.0	0.0	0.0
T401-7718	2352.4	Si-rich Sh	44.3	1.2	2.9	5.4	7.7	26.6	7.1	0.0	0.0	0.0
T401-7741	2359.5	Si-rich Sh	44.3	5.5	2.5	5.6	8.8	19.4	9.0	0.0	0.0	0.0
T401-8156	2485.9	Si-rich Sh	42.3	11.5	3.3	5.1	7.3	17.9	8.4	0.0	0.0	0.0
T401-8167	2489.3	Si-rich Sh	41.3	0.0	2.1	5.3	6.1	30.4	10.2	0.0	0.0	0.0
T401-8175	2491.7	Si-rich Sh	37.3	0.0	2.3	5.2	9.7	26.8	8.8	0.0	0.0	0.0
T401-8187	2495.3	Dolomite	3.6	7.7	73.9	2.3	0.0	12.6	0.0	0.0	0.0	0.0
T401-8197	2498.4	Si-rich Sh	45.2	7.6	3.1	6.0	6.9	22.4	8.8	0.0	0.0	0.0
T401-8217	2504.5	Si-rich Sh	34.0	6.3	5.3	4.8	7.9	28.0	8.9	0.0	0.0	0.0
T401-8236	2510.3	Si-rich Sh	34.9	10.2	3.3	5.8	9.2	24.4	8.6	0.0	0.0	0.0
T401-8275	2522.2	Ca-rich Sh	32.7	39.8	2.4	2.5	9.7	12.9	0.0	0.0	0.0	0.0
T401-8289	2526.4	Dolomite	12.8	11.6	35.8	3.4	7.2	20.9	8.2	0.0	0.0	0.0
T401-8306	2449.3	Ca-rich Sh	39.5	22.6	2.9	5.5	5.1	17.3	7.1	0.0	0.0	0.0
T401-8329	2538.6	Ca-rich Sh	28.1	25.5	3.2	3.8	6.4	22.1	9.0	0.0	0.0	0.0
T401-8357	2547.2	Si-rich Sh	34.3	13.4	3.9	5.5	7.8	25.3	9.6	0.0	0.0	0.0
T901-9005	2745.6	Si-rich Sh	53.6	6.4	0.0	8.1	2.5	19.3	0.0	0.0	0.0	10.1
T901-9008	2746.5	Limestone	0.5	99.1	0.0	0.0	0.3	0.0	0.0	0.0	0.0	0.0
T901-9015	2748.7	Si-rich Sh	57.0	0.0	0.0	13.5	2.8	26.8	0.0	0.0	0.0	0.0
T901-9016	2749.0	Ca-rich Sh	18.5	48.8	0.0	6.3	1.6	24.8	0.0	0.0	0.0	0.0
T901-9017	2749.3	Si-rich Sh	49.3	0.0	0.0	14.2	3.5	33.1	0.0	0.0	0.0	0.0
T901-9026	2752.0	Limestone	22.1	52.6	0.0	5.5	4.5	11.3	4.0	0.0	0.0	0.0
T901-9027	2752.3	Limestone	22.5	64.0	0.0	1.9	3.1	6.1	0.4	0.0	0.0	0.0
T901-9028	2752.6	Si-rich Sh	43.8	18.2	0.0	7.5	6.6	21.6	2.2	0.0	0.0	0.0

Table A1. *Cont.*

Sample	Depth (m)	Lithofacies	Qtz	Cal	Dol	Feldspar	Py	Mca	Chl	Gyp	Jar	Flu
T901-9029	2752.9	Limestone	32.8	48.1	0.0	4.6	3.6	9.3	1.7	0.0	0.0	0.0
T901-9030	2753.2	Si-rich Sh	42.6	0.0	2.3	5.4	14.5	23.9	0.0	3.7	3.7	0.0
T901-9031	2753.6	Si-rich Sh	33.4	0.0	0.0	10.0	14.4	27.3	0.0	9.8	5.1	0.0
T901-9032	2753.9	Si-rich Sh	36.3	0.0	0.0	13.4	4.3	34.1	0.0	6.3	5.6	0.0
T901-9034	2754.5	Si-rich Sh	38.9	0.0	0.0	9.7	12.7	27.9	0.0	10.9	0.0	0.0
T901-9035	2754.8	Limestone	9.6	86.4	0.0	0.0	0.4	2.6	0.5	0.0	0.0	0.0
JP-11091	3380.5	Ca-rich Sh	37.4	22.7	10.3	14.9	2.5	8.7	3.4	0.0	0.0	0.0
JP-11135	3393.9	Si-rich Sh	15.0	0.7	3.5	20.4	8.7	48.3	3.5	0.0	0.0	0.0

Abbreviations: Qtz = quartz; Cal = calcite; Dol = dolomite; Alb = albite; Mic = microcline; Py = pyrite; Mca = mica-group mineral; Chl = chlorite; Anl = analcime; Gyp = gypsum; Jar = Jarosite; Flu = fluoroapatite. Mineral abbreviations after Whitney and Evans (2010); Si-rich Sh = silica rich shale; Ca-rich Sh = calcite rich shale.

Appendix B

Table A2. Relative clay mineral abundances determined by Sybilla modeling of analyzed samples from the Midland Basin.

Sample	Depth (m)	Lithofacies	Ill	R0 I-S	R0 I-SS	R0 I-SSS	R1 I-S	R3 I-S	Chl	R0 C-SS
T401-7620	2322.6	Si-rich Sh	7.3	31.9	19.0	41.7	0.0	0.0	0.0	0.0
T401-7627	2324.7	Ca-rich Sh	7.5	82.5	0.0	10.0	0.0	0.0	0.0	0.0
T401-7657	2333.9	Limestone	3.6	27.8	68.6	0.0	0.0	0.0	0.0	0.0
T401-7665	2336.3	Si-rich Sh	2.8	53.3	43.9	0.0	0.0	0.0	0.0	0.0
T401-7669	2337.5	Dolomite	4.0	56.4	39.6	0.0	0.0	0.0	0.0	0.0
T401-7673	2338.7	Si-rich Sh	20.3	40.4	37.9	0.0	0.0	0.0	1.4	0.0
T401-7718	2352.4	Si-rich Sh	15.4	82.1	0.0	0.0	0.0	0.0	2.5	0.0
T401-7741	2359.5	Si-rich Sh	7.9	55.7	28.9	0.0	0.0	0.0	2.8	4.7
T401-8156	2485.9	Si-rich Sh	24.8	0.0	25.8	0.0	45.2	0.0	0.9	3.4
T401-8167	2489.3	Si-rich Sh	32.5	0.0	0.0	0.0	62.8	0.0	1.5	3.3
T401-8175	2491.7	Si-rich Sh	19.8	0.0	10.0	0.0	65.7	0.0	1.2	3.3
T401-8197	2498.4	Si-rich Sh	21.9	0.0	0.0	0.0	73.9	0.0	3.4	0.9
T401-8217	2504.5	Si-rich Sh	19.8	0.0	0.0	0.0	75.9	0.0	2.6	1.7
T401-8252	2515.2	Si-rich Sh	16.0	0.0	0.0	0.0	79.9	0.0	4.1	0.0
T401-8256	2516.4	Si-rich Sh	21.4	0.0	0.0	0.0	73.8	0.0	4.8	0.0

Table A2. Cont.

Sample	Depth (m)	Lithofacies	Ill	R0 I-S	R0 I-SS	R0 I-SSS	R1 I-S	R3 I-S	Chl	R0 C-SS
T901-9004	2744.4	Si-rich Sh	7.3	0.0	50.7	0.0	0.0	21.4	3.2	17.4
T901-9005	2744.7	Si-rich Sh	2.6	0.0	0.0	0.0	48.0	38.4	0.0	11.0
T901-9015	2747.8	Si-rich Sh	41.3	0.0	16.9	0.0	0.0	41.8	0.0	0.0
T901-9027	2751.4	Ca-rich Sh	2.6	0.0	0.0	0.0	0.0	92.4	2.3	2.6
T901-9033	2753.3	Si-rich Sh	0.0	0.0	69.7	0.0	0.0	30.3	0.0	0.0
JP-11091	3380.5	Ca-rich Sh	16.7	37.5	0.0	0.0	40.7	0.0	5.0	0.0
JP-11107	3385.4	Ca-rich Sh	18.8	18.7	0.0	0.0	57.0	0.0	5.5	0.0
JP-11118	3388.8	Si-rich Sh	27.1	0.0	0.0	0.0	63.8	0.0	2.7	6.4
JP-11135	3393.9	Si-rich Sh	8.4	0.0	30.5	0.0	58.3	0.0	1.1	1.7

Abbreviations: Ill—illite; I-S, I-SS, and I-SSS—mixed-layered illite-smectite, illite-smectite-smectite, illite-smectite-smectite-smectite; Chl—chlorite; C-SS—chlorite-smectite-smectite; R—Reichweit (measure of order); Mineral abbreviations after Kretz (1983) and Whitney and Evans (2010).

Appendix C

Table A3. Sybilla[®] parameters of main phyllosilicates and mixed-layered phases used for XRD spectra modelling of representative clay fraction samples.

Phase/Mixed-layer Phase	Sample	σ^*	CSDS	Ill (%)	Ch (%)	Fe ^{IV}	ICC
Illite/Muscovite	T401-7620	12.00	21.67	-	-	1.52	1.50
	T401-7627	19.94	27.91	-	-	1.04	1.50
	T401-7657	12.00	27.91	-	-	0.50	1.50
	T401-7665	12.00	28.30	-	-	0.50	1.50
	T401-7669	7.46	18.16	-	-	1.00	1.50
	T401-7673	12.00	20.00	-	-	0.50	1.00
	T401-7718	12.00	20.11	-	-	0.52	1.50
	T401-7741	12.00	24.79	-	-	2.00	1.81
	T401-8156	12.00	18.55	-	-	0.52	1.50
	T401-8167	12.00	16.60	-	-	0.24	1.50
	T401-8175	12.00	19.72	-	-	0.44	1.56
	T401-8197	12.00	20.00	-	-	0.50	1.50
	T401-8217	12.00	20.00	-	-	0.50	1.50
	T401-8252	12.00	18.55	-	-	0.72	1.50

Table A3. Cont.

Phase/Mixed-layer Phase	Sample	σ^*	CSDS	Ill (%)	Ch (%)	Fe ^{IV}	ICC
R0 I-S	T401-8256	12.00	20.00	-	-	0.08	1.50
	T901-9004	12.00	18.16	-	-	0.52	1.50
	T901-9005	12.00	29.08	-	-	0.52	1.50
	T901-9015	12.00	4.51	-	-	0.20	1.50
	T901-9027	12.00	22.06	-	-	1.84	1.50
	JP-11091	12.00	20.00	-	-	0.50	1.50
	JP-11107	12.00	20.00	-	-	0.50	1.50
	JP-11118	12.00	13.87	-	-	0.08	1.50
	JP-11135	12.00	20.00	-	-	0.28	1.50
	T401-7620	12.00	16.08	90.00	-	1.96	1.50
	T401-7627	12.00	16.66	87.00	-	2.20	1.50
	T401-7657	12.14	22.17	90.00	-	2.68	1.50
	T401-7665	13.70–15.26	6.80–19.85	87.00–94.00	-	0.76–2.00	1.50
	T401-7669	16.04	7.09	94.00	-	2.12	1.50
	T401-7673	12.00	5.35	95.00	-	3.00	1.50
	T401-7718	12.00	6.22	90.00	-	2.00	1.50
	T401-7741	12.00	23.62	86.00	-	2.88	1.50
	JP-11091	12.00	6.22	89.00	-	1.56	0.96
	JP-11107	12.00	11.44	90.00	-	0.50	1.00
R0 I-SS	T401-7620	12.00	7.38	82.00	-	0.84	1.50
	T401-7627	54.26	10.86	72.00	-	0.50	1.50
	T401-7657	12.00	8.25–12.02	73.00–90.00	-	0.64–1.16	1.50
	T401-7665	13.70–16.04	6.22–20.43	80.00–81.00	-	0.52–2.52	1.50
	T401-7669	12.00–16.82	15.50–15.79	65.00–84.00	-	0.50	1.50
	T401-7673	12.00	6.22	70.00	-	0.50	1.50
	T401-7741	12.00	12.02	80.00	-	0.50	1.50
	T401-8156	9.02	6.22	80.00	-	1.60	1.50
	T401-8175	12.00	3.32	62.00	-	0.50	1.50
	T901-9004	12.00	4.77	83.00	-	3.08	1.50
	T901-9015	15.26	14.05	10.00	-	1.00	1.50
	T901-9033	12.00	24.20	75.00	-	0.84	1.50
	JP-11135	12.00	8.25	69.00	-	3.00	1.51

Table A3. Cont.

Phase/Mixed-layer Phase	Sample	σ^*	CSDS	Ill (%)	Ch (%)	Fe ^{IV}	ICC
R0 I-SSS	T401-7620	12.00	4.48	87.00	-	0.50	1.50
	T401-7627	12.00	1.29–2.74	11.00–53.00	-	0.50	1.50
R1 I-S	T401-8156	10.58	5.64	95.00	-	1.88	1.50
	T401-8167	10.58	4.77	95.00	-	1.88	1.51
	T401-8175	12.00	5.64	90.00	-	1.20	1.50
	T401-8197	12.00	5.93	89.00	-	1.88	1.50
	T401-8217	12.00	6.51	87.00	-	2.00	1.50
	T401-8252	12.00	5.64	84.00	-	1.52	1.50
	T401-8256	12.00	5.64	90.00	-	2.56	1.50
	T401-9005	12.00	4.19	88.00	-	0.52	1.50
	JP-11091	12.00	13.18	75.00	-	1.80	1.50
	JP-11107	12.00	3.61	90.00	-	2.72	1.29
Chlorite	JP-11118	12.00	11.15	77.00	-	3.80	1.50
	JP-11135	12.00	7.09	93.00	-	1.88	1.50
	T401-7673	12.00	20.00	-	-	1.80	1.00
	T401-7718	12.00	14.65	-	-	1.72	1.00
	T401-7741	12.00	15.04	-	-	1.00	1.08
	T401-8156	12.00	27.13	-	-	1.96	1.98
	T401-8167	12.00	22.06	-	-	1.44	1.02
	T401-8175	12.00	20.00	-	-	2.20	1.00
	T401-8197	12.00	15.43	-	-	2.00	1.98
	T401-8217	12.00	17.38	-	-	2.00	1.00
	T401-8252	12.00	13.87	-	-	2.00	1.00
	T401-8252	12.00	13.87	-	-	2.08	1.80
	T901-9004	12.00	17.77	-	-	2.32	1.14
	T901-9027	12.00	11.53	-	-	3.00	1.02
	JP-11091	12.00	11.92	-	-	2.08	1.00
	JP-11107	12.00	13.09	-	-	1.96	1.00
	JP-11118	12.00	14.26	-	-	1.84	1.98

Table A3. Cont.

Phase/Mixed-layer Phase	Sample	σ^*	CSDS	Ill (%)	Ch (%)	Fe ^{IV}	ICC
R0 Di C-SS	T401-7741	12.00	10.86	-	59.00	0.50	1.00
	T401-8197	12.00	5.64	-	37.00	0.50	1.00
	T401-8217	12.00	5.64	-	38.00	0.50	1.00
	T901-9005	12.00	8.54	-	25.00	3.32	2.04
	JP-11118	12.00	13.18	-	76.00	1.44	2.04
R0 Tri C-SS	T401-8156	12.00	19.27	-	83.00	2.80	4.56
	T401-8167	12.00	9.99	-	81.00	2.88	4.92
	T401-8175	12.00	3.90	-	36.00	2.00	1.00
	T901-9004	12.00	5.35	-	68.00	1.36	1.98
	T901-9027	12.00	3.03	-	50.00	0.50	1.00
	JP-11135	12.00	6.51	-	85.00	1.76	1.02

Abbreviations: σ^* —orientation of particles on the mounted X-ray slide; CSDS—coherent scattering domain sizes expressed in layers; Ill (%), Chl (%)—illite component, and chlorite component in the respective mixed-layered minerals (in %); I-S, I-SS, I-SSS, Di-SS, Di C-SS, and Tri C-SS—mixed-layered illite-smectite, illite-smectite-smectite, illite-smectite-smectite-smectite, dioctahedral smectite, dioctahedral chlorite-smectite-smectite, and trioctahedral chlorite-smectite-smectite; R—Reichweit (measure of order); Fe^{VI}—octahedral Fe in illite (I), and chlorite (C); ICC—interlayer cation content in illite (Ill) and chlorite (Chl).

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