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RELATIONSHIP BETWEEN ILLITE/SMECTITE DIAGENESIS AND HYDROCARBON GENERATION IN LOWER CRETACEOUS MOWRY AND SKULL CREEK SHALES OF THE NORTHERN ROCKY MOUNTAIN AREA

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Abstract—The percentage of expandable layers in illite/smectite (I/S) mixed-layer clay decreases with increasing temperature and depth in a section through marine Cretaceous shales in the Champlin 1 Hartley Federal well in the Powder River basin, Wyoming. This systematic change in I/S expandability is evidence that low-expandable I/S in Cretaceous shales of the northern Rocky Mountain area reflects, at least in part, thermal alteration during burial diagenesis. In eastern Montana and western North Dakota where I/S in the Lower Cretaceous Mowry and Skull Creek source rocks is diagenetically unaltered, only trace amounts of hydrocarbons have been found in the Lower Cretaceous and other Cretaceous sandstones. Elsewhere in the northern Rocky Mountain–Great Plains region, hydrocarbons in the Lower Cretaceous Muddy Sandstone and its equivalents occur within or immediately adjacent to areas in which I/S clay in the Mowry and Skull Creek shales has been diagenetically altered during burial. Altered I/S and thermally mature organic matter, as defined by Rock-Eval pyrolysis values, coexist in these source rocks. Both may be used as maturation indicators in the search for Cretaceous-source hydrocarbons in the northern Rocky Mountain area.

Key Words—Diagenesis, Hydrocarbon, Illite/smectite, Interstratification, Maturation, Pyrolysis, Shale.

INTRODUCTION

The Lower Cretaceous Mowry and Skull Creek shales of the northern Rocky Mountain area are organic-rich and possess significant potential as petroleum source rocks (Geis, 1923; Rubey, 1928; Schrayer and Zarrella, 1963, 1968). They and their equivalents, such as the Aspen and Thermopolis Formations, are widespread throughout the northern Rocky Mountain–Great Plains region and are closely associated with hydrocarbon accumulations in Lower Cretaceous reservoirs (Forgotson and Stark, 1972).

The above shales are now recognized as the source of at least a portion of the hydrocarbons in the Jurassic Nugget Sandstone in the western overthrust belt of Wyoming and Utah (Warner, 1982), the Lower Cretaceous "J" Sandstone of the Denver-Julesburg basin (Clayton and Swetland, 1977, 1980), the Lower Cretaceous Muddy Sandstone in the Powder River basin (Momper and Williams, 1979) (Figure 1), and probably some of the other Cretaceous reservoirs such as the Dakota and Frontier formations (Figure 2). Information regarding the source rock potential and thermal maturation of the Mowry and Skull Creek shales is therefore of significance in delineating areas likely to contain commercial reserves of hydrocarbons. The present report shows that I/S expandability and organic indices yield comparable information regarding regional variations in the thermal maturation of the Mowry and Skull Creek shales.

The discovery of major new reserves in the Lower Cretaceous Muddy Sandstone of the Powder River basin in the mid-1960s prompted this regional study of the organic-rich source rocks (Mowry and Skull Creek shales and their equivalents, Figure 2) which enclose them. Several ways of measuring directly the thermal maturation of the organic matter or the sediment in which it was deposited were sought. Because the maturation of organic matter involves the loss of CO_2 and hydrocarbons relative to the inorganic fraction of the rock, thermal maturation of a source rock must ultimately produce a measurable decrease in its organic carbon content. Thus, anomalously low values of total organic carbon (TOC) of a source rock may be indicative of hydrocarbon generation, if areas of lower TOC depart from regional trends and coincide with areas, such as basins, where the source rock may have been subjected to higher temperatures. Clay minerals, such as smectite and mixed-layer illite/smectite (I/S), common components of the inorganic fraction of shales, are also sensitive indicators of thermal conditions that

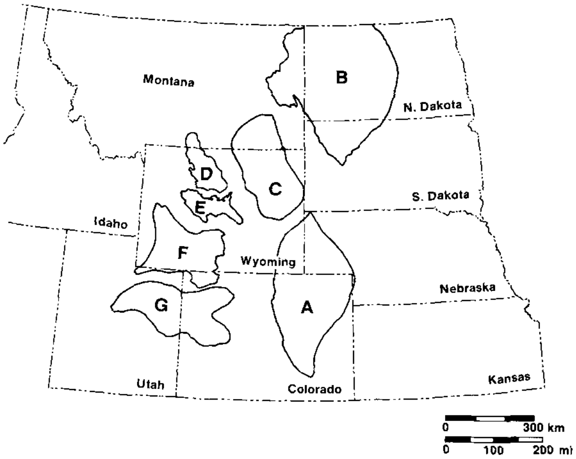

Figure 1. Index map of basins included in this study. Basin letters are keyed to stratigraphic sections in Figure 2.

can generate hydrocarbons from organic matter (see, e.g., Burst, 1969; Perry and Hower, 1972, Foscolos *et al.*, 1976). More recently Espitalie *et al.* (1977), Dembicki *et al.* (1983), and Peters *et al.* (1983) demonstrated that Rock-Eval pyrolysis (see Burtner and Warner, 1984; Tissot and Welte, 1978) is a powerful technique for determining the source rock potential and thermal maturation of the organic fraction.

All three of the above techniques have been applied in the present study of the thermal maturation of Lower Cretaceous source rocks in northern Rocky Mountain basins. Because the Rock-Eval and TOC data have been discussed at length in a separate paper (Burtner and Warner, 1984), the present paper will be primarily concerned with the clay mineral evidence for thermal maturation and how it compares with the organic data regarding thermal maturation.

REGIONAL STRATIGRAPHY AND LITHOLOGY

The Skull Creek Shale is equivalent to the Thermopolis Shale in parts of Wyoming and Montana and the Kiowa Shale in eastern Colorado. For the purposes of this regional study, the Mowry Shale is defined as that portion of the stratigraphic section between the distinctive Clay Spur bentonite at the top and the Muddy Sandstone at its base (Figure 2). It includes the Shell Creek Shale where the Shell Creek has been recognized as a separate formation. The Skull Creek and Mowry shales are typically medium to dark gray, organic-rich mudstones that were deposited during major Albian transgressions of the Western Interior Cretaceous sea (Figure 3). These organic-rich source rocks enclose the Muddy or "J" Sandstone, a major reservoir for Cretaceous oil in the Powder River and Denver-Julesburg basins (Figure 1). The regional distribution of the Muddy Sandstone is similar to that of the Mowry Shale. Both the Mowry and Skull Creek shales were deposited in a north–south trending seaway (Figure 3) that was bordered on the east by a low-lying land mass. To the west it was bounded by a tectonically active belt wherein movement took place on the Paris-Willard Trust in north-central Utah and eastern Idaho. In northern and central Idaho active volcanism was associated with the early stages of emplacement of the Idaho Batholith during Skull Creek time.

The Mowry Shale is typically a hard, dark gray, siliceous mudstone containing abundant fish scales and interbedded bentonite layers. The siliceous aspect of the Mowry has been interpreted as being the direct result of volcanic activity that accompanied the emplacement of the Idaho Batholith (Rubey,

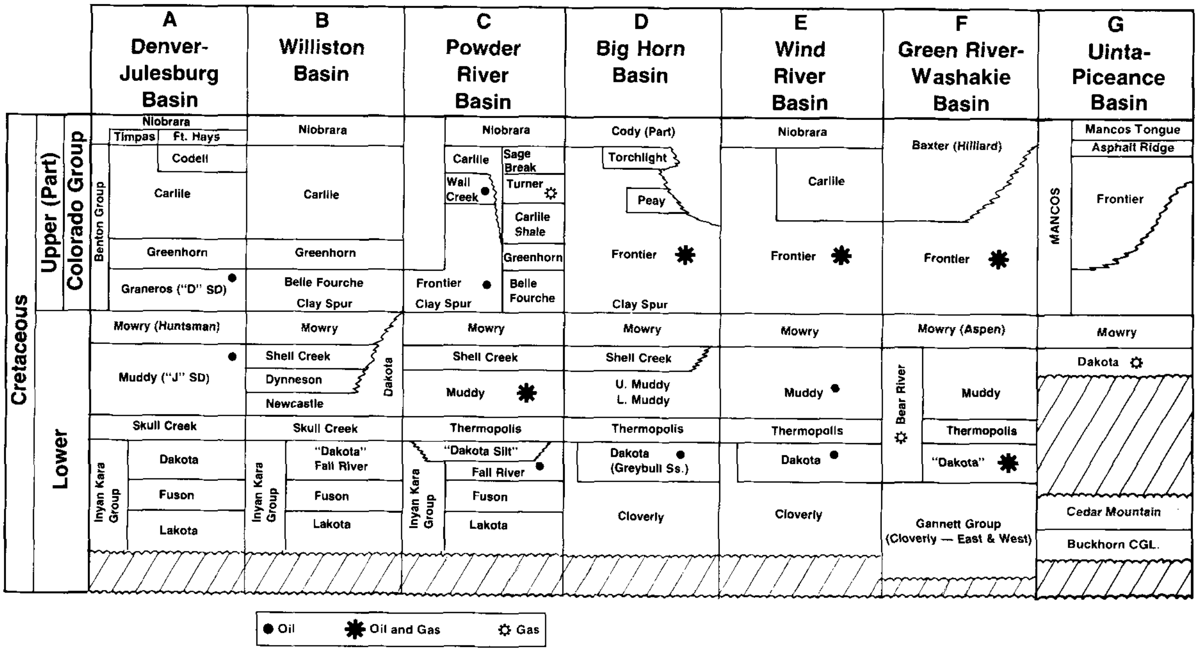

Figure 2. Stratigraphic correlation chart for Cretaceous (partial) strata in northern Rocky Mountain basins. Major producing horizons are indicated by oil and gas symbols.

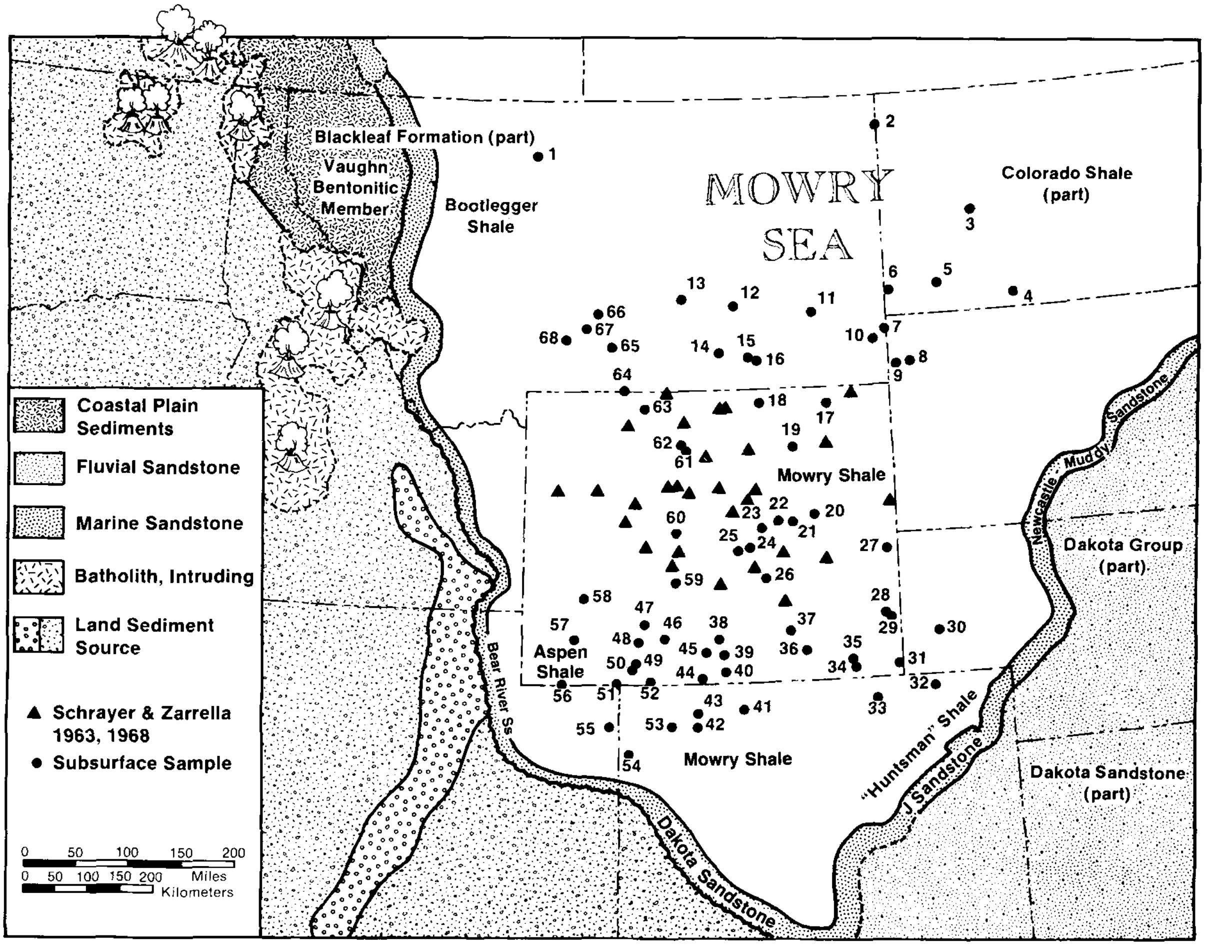

Figure 3. Index map showing Mowry Shale sample localities studied for this report. Sample locality numbers are keyed to data in Table 1. Triangles = samples used for TOC, only. Base map from McGookey *et al.* (1972).

1928). Davis (1970) and Byers and Larson (1979), however, concluded that the abundant radiolarians in the Mowry served as the immediate source of silica. Davis (1970) noted that I/S is the predominant constituent in the Mowry Shale, especially in the siliceous facies. He attributed the presence of smectite having strong basal X-ray powder diffraction reflections to the mixing of bentonitic material with normal detritus in the shales. Discrete illite was found to be widespread as a minor component. The distribution of kaolinite was noted to be inversely related to the distribution of smectite and I/S. He concluded that the distribution of clays in the Mowry suggests that "smectite-rich sediment progressively spread across the Cretaceous basin, displacing kaolinitic sediment derived from the east." The sources of the smectite and I/S clays in the Mowry were therefore probably alteration of ash from the explosive volcanism associated with emplacement of the Idaho Batholith, fine-grained sediment eroded from western highlands, such as the Paris-Willard thrust plate, and soils developed on fringing alluvial plains and deltas.

SAMPLE SELECTION, PREPARATION, AND ANALYSIS

Cuttings of Mowry Shale were selected from 68 wells scattered over a seven-state area (Figure 3 and Table 1). Where these wells penetrated the Skull Creek Shale, this shale was also sampled. Twenty-one Skull Creek Shale samples were included in the study (Table 1). Washed cuttings for a given formation were sieved to retain material greater than 32 mesh, and hand picked to exclude obvious foreign material. In the few samples in which a minor amount of sandstone was encountered, it too was excluded. An attempt was also made to exclude very light colored, very clayey cuttings which were believed to be bentonite, mainly because the I/S in a bentonite layer commonly displays less alteration than the I/S in the mudstone that encloses it (J. Hower, personal communication; Rettke, 1981). Representative shale samples were selected from each sample interval in a well and then composited by weight in proportion to the thickness of the interval they represented. The composited samples were thus similar to a channel sample taken through the whole thickness of the Mowry or Skull Creek Shale. Each composite was washed in distilled water, dried, and subdivided into fractions for clay mineral, TOC, and Rock-Eval analysis.

Additional samples were selected from the Champlin 1 Hartley Federal (CHF) well (locality 20, Figure 3), a deep well in the Powder River basin, to determine if the I/S in a vertical section through Upper and Lower Cretaceous shales in the northern Rocky Mountain area defined a typical burial diagenesis sequence. Shale cuttings were hand picked about every

65 m and prepared as discussed above, but were not composited. These samples were split for clay mineral, TOC, and Rock-Eval analysis.

The fraction for clay mineral and I/S analysis was ultrasonically disaggregated in acetic acid buffered at pH 4.5 by sodium acetate. After repeated washing with distilled water to remove the acid, the <1-μm size fraction was separated by multiple centrifuge runs, each followed by decantation of the <1-μm fraction. After drying, a small portion of this size fraction was resuspended in distilled water and placed on dry, porous Vycor slides to produce oriented clay aggregates (Burtner, 1974). Heat-treated (550°C for 30 min) and glycolated slides were examined on a Norelco X-ray powder diffractometer equipped with a graphite crystal monochromator. The samples were scanned at 1°2θ/min using CuKα radiation and a time constant of 1.0 s. The type of layer interstratification in the I/S clay and the percentage of expandable (smectite) layers were determined according to the method of Reynolds and Hower (1970) and Hower (1981a).

I/S EVIDENCE FOR THERMAL MATURATION OF THE MOWRY AND SKULL CREEK SHALES

Previous work and its implications

In a clay mineral study of cores of Lower Cretaceous Dakota Group shales in the Denver-Julesburg basin, Rettke (1981) reported that ordered, low-expandable I/S was abundant in many samples that never experienced significant heating. He noted that the wide range of expandabilities that existed within and between shales in the Dakota Group at low borehole temperatures was significantly reduced where the Dakota Group is currently above 60°C (140°F). At temperatures where the rock is currently above 90°C (194°F), only low-expandable I/S was found in Dakota Group shales. Rettke (1981) attributed the diverse expandability and ordered mixed-layering of the I/S to variability within the original, unaltered detrital clay. This variability decreased in response to increased borehole temperature which apparently caused the more highly expandable I/S to alter to low-expandable I/S.

Although similar variability in I/S expandability probably exists elsewhere in Lower Cretaceous shales of the northern Rocky Mountain area, I/S in these shales can be used as a thermal maturation indicator if at least a small fraction of it originally was highly expandable. The presence of numerous bentonite layers in the Lower Cretaceous shales indicates that a significant fraction of the clay mineral assemblage in these shales was at one time highly expandable I/S or smectite which formed from the alteration of volcanic ash. I/S of high expandability is relatively easy to detect by X-ray powder diffraction (XRD) because XRD reflections from its basal crystal planes are relatively intense. The intensity of these reflections decreases as expandability decreases until ordering begins. As a result, the high expandable I/S in a sample tends to mask the presence of I/S of lower expandability even when ordered I/S is present. In addition, the process by which drill cuttings are obtained creates an "average" sample and tends to reduce variation in bed-to-bed I/S expandability. Therefore, I/S expandability in Lower Cretaceous Skull Creek and Mowry shales is likely to be a good indicator of thermal maturation.

I/S burial diagenesis in the Champlin 1 Hartley Federal well, Powder River basin

In the absence of highly expandable I/S, low-expandable I/S in a shale may reflect provenance, diagenesis, or both. Thus, if I/S is to be used as a thermal maturation indicator, one must determine if the low-expandable I/S formed diagenetically during the current cycle of burial or whether it is wholly detrital.

I/S in the CHF well was studied for evidence of progressive thermal alteration as indicated by decreasing I/S expandability with increasing depth. Upper Cretaceous, as well as Lower Cretaceous (Mowry and Skull Creek), marine shales were included in the profile to determine if low expandability of the Mowry and Skull Creek I/S near the bottom of the profile was likely to have resulted from progressive thermal alteration of smectite layers to illite layers. Rock-Eval evidence for progressive thermal alteration of the organic fraction in the Cretaceous shales in the CHF well was reported in an earlier paper (Burtner and Warner, 1984).

The expandability of I/S in the CHF well is recorded in Table 2. Representative XRD patterns of oriented, ethylene glycol-treated samples of the <1-μm size fraction of shale cuttings from this well (Figure 4) show the presence of abundant I/S, discrete illite (mica), kaolinite, and a small amount of chlorite. The systematic change in the intensity and position of the I/S peaks between 5° and 10°2θ and 15° and 18°2θ reflect decreasing expandability and increasing order with depth. They are similar to systematic changes in diffractograms published for shales from the Gulf Coast (Perry and Hower, 1970, 1972; Hower, 1981b).

I/S burial-diagenesis profiles are typically represented by plotting the percentage of illite or smectite layers as a function of depth and noting changes in their stacking sequence (ordering). The percentage of smectite (expandable) layers in I/S from the CHF well is plotted in Figure 5 as a function of depth alongside a composite temperature profile constructed from temperature data for nearby wells. Although these sediments are not currently at their maximum depth of burial, erosion probably has not removed more than about 457 m (1500 ft) of sediment. Thus, unless the geothermal gradient was greater in the past, the sediments at any given depth were probably not more than about 14°C (25°F) hotter than they are today.

In the Powder River basin Cretaceous section, randomly interstratified I/S clay with 65–80% smectite layers begins to alter between 2499 m (8200 ft) and 2743 m (9000 ft), and within 305 m (1000 ft) it becomes ordered I/S with 20% expandable layers. This

Table 1. Illite/smectite and T_{max} data for ditch cuttings from the Mowry and Skull Creek shales.

Locality	Well	Formation	Depth (m)	Depth (ft)	I/S interstratification	% Expandable layers in I/S	T_{max} (°C)
1	Webb Resources #5-5 Meissner Ranches	Mowry	387–494	(1270–1620)	Random	90–100	423
2	Chevron #4-1 Melby	Mowry	1201–1259	(3940–4130)	Random	80–85	418
2	Chevron #4-1 Melby	Skull Creek	1277–1339	(4190–4390)	Random	80–85	—
3	Cities Service #1 Clarke	Mowry	1393–1417	(4570–4650)	Random	80–85	422
3	Cities Service #1 Clarke	Skull Creek	1439–1509	(4720–4950)	Random	≅80	—
4	Helmerich and Payne #3-1 Burlington Northern "A"	Mowry	966–991	(3170–3250)	Random	85–90	429
4	Helmerich and Payne #3-1 Burlington Northern "A"	Skull Creek	997–1067	(3270–3500)	Random	85–90	431
5	International Nuclear #1-51 Overbo	Mowry	1433–1469	(4700–4820)	—	—	430
5	International Nuclear #1-51 Overbo	Skull Creek	1481–1554	(4860–5100)	—	—	437
6	International Nuclear #1-56 Flor	Mowry	1155–1207	(3790–3960)	Random	85–90	425
6	International Nuclear #1-56 Flor	Skull Creek	1222–1298	(4010–4260)	Random	80–85	—
7	HLM 3-1 Gov't.	Mowry	1280–1322	(4200–4337)	Random	≅80	431
7	HLM 3-1 Gov't.	Skull Creek	1359–1414	(4460–4640)	Random	≅80	—
8	Murfin Drilling #1 Truman	Mowry	1036–1082	(3400–3550)	Random	90–100	427
8	Murfin Drilling #1 Truman	Skull Creek	1097–1186	(3600–3890)	Random	90–100	427
9	Amerada #2 Short Pine Hills	Mowry	954–994	(3130–3260)	Random	90–100	419
10	Placid #21-6 Goedders	Mowry	1082–1134	(3550–3720)	Random	90–100	417
10	Placid #21-6 Goedders	Skull Creek	1152–1213	(3780–3980)	Random	90–100	415
11	Chambers and Kennedy #1 Hogg	Mowry	1314–1393	(4310–4570)	Random	85–90	423
11	Chambers and Kennedy #1 Hogg	Skull Creek	1408–1460	(4620–4790)	Random	85–90	426
12	Pubco #26-1 Empire Decock	Mowry	1143–1289	(3750–4230)	Random	85–90	430
12	Pubco #26-1 Empire Decock	Skull Creek	1289–1320	(4230–4330)	Random	≅80	434
13	Amerada #1 Jones	Mowry	1530–1600	(5020–5250)	Ordered	20–25	437
14	Woods Petroleum #34-1 Crow Tribal	Mowry	1042–1128	(3420–3700)	Random	90–100	428
15	King Resources #1-6 Sandcrane-Cheyenne	Mowry	2030–2103	(6660–6900)	Ordered	≅15	435
16	King Resources #1-1 Cheyenne Federal	Mowry	2051–2121	(6730–6960)	Ordered	≅20	435
17	Leben-NCRA #1 Devel. Fed.	Mowry	1603–1664	(5260–5460)	Random	90–100	423
17	Leben-NCRA #1 Devel. Fed.	Skull Creek	1692–1725	(5550–5660)	Random	75–80	433
18	Cleary #1-23 Duncan Fed.	Mowry	2910–3039	(9580–9970)	Ordered	25–30	442
18	Cleary #1-23 Duncan Fed.	Skull Creek	3057–3075	(10,030–10,090)	—	—	441
19	Chevron #1 Ranger Fed.	Mowry	3200–3271	(10,500–10,730)	Ordered	≅20	445
19	Chevron #1 Ranger Fed.	Skull Creek	3283–3322	(10,770–10,900)	Ordered	≅20	—
20	Champlin #1 Hartley Fed.	Mowry	3844–3898	(12,610–12,790)	Ordered	≅20	441
20	Champlin #1 Hartley Fed.	Skull Creek	3917–3953	(12,850–12,970)	Ordered	≅20	442
21	Amerada #1 USA Ritchie	Mowry	2472–2624	(8110–8610)	Partial order	35–40	433
22	Champlin #1 Holbeck Fed.	Mowry	1905–1966	(6250–6450)	Partial order	≅40	433
23	Amerada #1 Horse Ranch	Mowry	905–975	(2970–3200)	Random	85–90	426
24	Union #8 West Poison Spider Unit	Mowry	4572–4642	(15,000–15,230)	Ordered	≅10	—
25	Chorney #1 Soap Creek	Mowry	2972–3042	(9750–9980)	Random	≅80	428
26	Carrl #9-1 State	Mowry	899–957	(2950–3140)	Random	90–100	429
27	Carrl #36-1 State	Mowry	530–585	(1740–1920)	Random	75–80	430
28	King Resources #1-29 Helzer	Mowry	2277–2310	(7470–7580)	Ordered	30–35	434
29	Gary #12-4 Schwab	Mowry	2170–2202	(7120–7225)	Random	85–90	430
30	Shell #1-B Brown	Mowry	1504–1535	(4935–5035)	Random	≅60	430
31	Morton and Sons #1 Rauner	Mowry	2249–2274	(7380–7460)	Random	65–70	435
32	West Central Pet. #1 Keester	Mowry	1573–1734	(5160–5690)	Ordered	≅25	437
32	West Central Pet. #1 Keester	Skull Creek	1759–1801	(5770–5910)	Partial order	35–40	433
33	Chevron UPRR #1 Jones—USA	Mowry	2396–2417	(7860–7930)	Partial order	35–40	439
33	Chevron UPRR #1 Jones—USA	Skull Creek	2441–2505	(8010–8220)	Partial order	35–40	439
34	Chevron #1 Morton King	Mowry	2548–2585	(8360–8480)	Ordered	30–35	434
35	Apache #1 Polo Ranch	Mowry	3152–3185	(10,340–10,450)	Ordered	30–35	435
36	Tenneco #1 Baille	Mowry	415–466	(1360–1530)	Ordered	20–25	428
37	Ohio #1 Diamond Ranch	Mowry	1551–1597	(5090–5240)	Random	90–100	431
38	Tenneco #1 UPRR—Bolton	Mowry	1131–1183	(3710–3880)	Ordered	≅20	441
39	Raymond #1 Gov't. Wenger	Mowry	1045–1091	(3430–3580)	Ordered	30–35	436
40	Humble #1 Battle Creek	Mowry	1850–1905	(6070–6250)	Ordered	20–25	448
41	Texaco #1 Peavy	Mowry	460–497	(1510–1630)	Ordered	15–20	437
42	Pan American #1-D USA	Mowry	924–941	(3030–3086)	—	—	442

Table 1. Continued.

Locality	Well	Formation	Depth		I/S interstratification	% Expandable layers in I/S	T_{max} (°C)
			(m)	(ft)			
43	Intex #1-16 Alpha	Mowry	2713–2740	(8900–8990)	Ordered	≅20	450
44	Phillips #8 Baggs	Mowry	4118–4151	(13,510–13,620)	Ordered	≅15	—
45	Sohio #1 Cow Creek	Mowry	2722–2771	(8930–9090)	Ordered	≅20	447
46	Texaco #15 Table Rock	Mowry	4353–4420	(14,280–14,500)	Ordered	15–20	434
47	Prenalta #14 Gov't.	Mowry	2426–2505	(7960–8220)	Ordered	≅20	447
48	Prenalta #11 State	Mowry	1372–1451	(4500–4760)	Partial order	≅40	436
49	Ashmund and Hilliard (Potter Mtn.) #3 LTD., #2 Unit	Mowry	2199–2271	(7215–7450)	Ordered	≅20	444
50	British American #1 Potter Mtn.	Mowry	2106–2173	(6910–7130)	Ordered	≅20	445
51	Mountain Fuel #14 Clay Basin	Mowry	1722–1768	(5650–5800)	Random	85–90	432
52	Texaco #1 Sugarloaf	Mowry	3786–3840	(12,420–12,600)	Ordered	≅15	440
53	Southland Royalty #1 Wyman	Mowry	1350–1399	(4430–4590)	Random	80–85	431
54	Continental #34-1 Conoco Amerada Fed.	Mowry	3395–3426	(11,140–11,240)	Ordered	≅20	—
55	Stanolind #8 USA Ashley Valley	Mowry	360–387	(1180–1270)	—	—	424
56	Phillips #5-A and #6-A Fork	Mowry	4618–4691	(15,150–15,390)	Random	≅60	437
57	Shell et al. #31-35 UPRR	Mowry	3527–3618	(11,570–11,870)	Ordered	≅20	433
58	International Nuclear #1 Gov't.—Swanson	Mowry	3298–3405	(10,820–11,170)	Ordered	≅15	441
59	Gulf #1 Trail Ridge Fed.	Mowry	274–351	(900–1150)	Random	85–90	428
60	Continental #32-6 Tribal	Mowry	3368–3466	(11,050–11,370)	Ordered	≅10	—
61	Husky #1 Torgeson	Mowry	2847–2926	(9340–9600)	Ordered	≅20	436
62	Husky #1 Gov't.	Mowry	3120–3194	(10,235–10,480)	Ordered	≅20	439
63	Tidewater #1 Atteberry	Mowry	3045–3136	(9990–10,290)	Ordered	≅15	440
64	Phillips #1 NPRR	Mowry	3380–3441	(11,090–11,290)	Ordered	≅20	440
64	Phillips #1 NPRR	Skull Creek	3447–3502	(11,310–11,490)	Partial order	35–40	443
65	Continental #1 Gov't.	Mowry	1561–1652	(5120–5420)	Partial order	35–40	—
65	Continental #1 Gov't.	Skull Creek	1652–1692	(5420–5550)	Partial order	35–40	440
66	Cities Service #1 Cremer	Mowry	1250–1335	(4100–4380)	Ordered	≅20	442
66	Cities Service #1 Cremer	Skull Creek	1341–1402	(4400–4600)	Ordered	≅20	444
67	Stanolind #1 Rapstad	Mowry	1554–1779	(5100–5835)	Ordered	≅20	—
67	Stanolind #1 Rapstad	Skull Creek	1779–1839	(5835–6035)	Ordered	≅20	—
68	Superior #22-25 Windsor	Mowry	1494–1594	(4900–5230)	Ordered	≅10	—
68	Superior #22-25 Windsor	Skull Creek	1615–1670	(5300–5480)	Ordered	≅20	460

burial diagenesis profile differs significantly from those reported by Foster and Custard (1982, 1983) and Schmidt (1973) for Tertiary strata in Louisiana near the Mississippi River delta. The latter profiles are marked by a much more gradual increase in the I/S ratio with depth.

The CHF well profile of I/S burial diagenesis is similar to those noted by Foster and Custard (1982, 1983), Bruce (1983, 1984), and Perry and Hower (1972) for Tertiary strata along the Gulf Coast of Texas. Like this Cretaceous profile, the Texas profiles are marked by abrupt changes in the rate at which smectite layers appear to be converted to illite layers. The beginning of the smectite conversion is fairly sharply defined, as is the point at which a 4:1 ratio of illite to smectite layers is reached. Foster and Custard (1982, 1983) reported that burial diagenesis profiles marked by abrupt systematic changes in the percentage of expandable layers in I/S contain a form of I/S in which the smectite layers have a low layer charge produced by divalent cation substitutions in the octahedral layer. This type of I/S is common in Tertiary strata of the Texas Gulf Coast. Profiles marked by a more gradual increase in the I/S ratio with depth contain I/S in which the smectite layers possess a higher lattice charge that is produced by substitution of Al for Si in the tetrahedral layer. Although a high geothermal gradient can also produce rapid changes in I/S expandability and a low geothermal gradient can produce more gradual changes with depth, the abrupt changes in the profile of I/S expandability in the Powder River basin suggests that the marine Cretaceous section is composed of I/S in which the smectite layers are predominantly of low charge.

An ordered I/S structure with 20% smectite layers was encountered in the CHF well at about 99°–102°C (210°–215°F) (Figure 5), but these samples may have been as much as 14°C (25°F) hotter in the past prior to uplift and erosion of late Tertiary strata, such as the Oligocene White River Formation. The Eocene Wasatch Formation is the youngest stratigraphic unit penetrated by the CHF well. Consequently, the Cretaceous marine shales in the burial diagenesis zone have been at their present or higher temperatures for about 50

Table 2. Illite/smectite, T_{max}, and PI data for marine Cretaceous shales in Champlin 1 Hartley Federal well, Powder River basin, Wyoming (locality 20).

Depth (m)	Depth (ft)	I/S interstratification	% Expandable layers	T_{max}[1]	PI[2]
2137–2155	(7010–7070)	Random	≅75	434	0.07
2195–2204	(7200–7230)	Random	≅65	434	0.07
2256–2265	(7400–7430)	Random	75–80	435	0.18
2316–2326	(7600–7630)	Random	≅75	437	0.07
2377–2387	(7800–7830)	Random	≅65	436	0.05
2438–2448	(8000–8030)	Random	75–80	435	0.06
2499–2509	(8200–8230)	Random	≅60	435	0.11
2560–2569	(8400–8430)	Random	65–70	436	0.08
2621–2630	(8600–8630)	Partial order	≅45	434	0.15
2682–2691	(8800–8830)	Random	65–75	434	0.15
2743–2752	(9000–9030)	Random	65–75	435	0.11
2807–2816	(9210–9240)	Partial order	≅45	436	0.22
2868–2874	(9410–9430)	Partial order	35–40	435	0.31
2926–2929	(9600–9610)	Partial order	≅35	437	0.23
2987–2993	(9800–9820)	Ordered	25–30	435	0.21
3048–3051	(10,000–10,010)	Ordered	≅20	437	0.23
3109–3112	(10,200–10,210)	Ordered	≅20	436	0.28
3170–3179	(10,400–10,430)	Ordered	≅20	437	0.24
3231–3240	(10,600–10,630)	Ordered	≅20	434	0.34
3292–3301	(10,800–10,830)	Ordered	≅20	436	0.41
3353–3359	(11,000–11,020)	Ordered	≅20	438	0.40
3414–3423	(11,200–11,230)	Ordered	≅20	438	0.29
3475–3484	(11,400–11,430)	Ordered	≅20	438	0.24
3536–3545	(11,600–11,630)	Ordered	≅20	439	0.29
3597–3606	(11,800–11,830)	Ordered	≅20	438	0.35
3658–3667	(12,000–12,030)	Ordered	≅20	442	0.28
3719–3728	(12,200–12,230)	Ordered	≅20	443	0.35
3780–3789	(12,400–12,430)	Ordered	≅20	441	0.34
3840–3850	(12,600–12,630)	Ordered	≅20	441	0.39
3906–3911	(12,815–12,830)	Ordered	≅20	442	0.36
3950–3956	(12,960–12,980)	Ordered	≅20	441	0.37
4003–4005	(13,135–13,140)	Ordered	≅20	439	0.45

[1] T_{max} = temperature during programed pyrolysis at which the rate of generation of S2-hydrocarbon production peaks; reflects the intensity of thermal maturation of the organic matter.

[2] PI = production index [S1/(S1 + S2)], a maturation indicator.

million years. The uncorrected temperature of 99°–102°C (210°–215°F) for the first appearance of I/S with 20% smectite layers is about the same (100°C (212°F)) as that reported by Perry (1969; figure 4.8 in Hower, 1981b) for the first appearance of a similar I/S structure in Eocene strata in the Gulf Coast. The higher value of 113°–116°C (235°–240°F) is only slightly less than the temperature (about 124°C) at which one of us (R.L.B.) noted the appearance of similar I/S in Gulf Coast Miocene and Oligocene sediments. Temperatures for these profiles were taken from surveys that were conducted three months or more after the wells had been shut in.

Although temperature is evidently a significant factor in the alteration of I/S during burial diagenesis, the role of other factors, such as time and I/S composition, is difficult to assess. Weaver (1979) reported only a general relationship between temperature and the expandability of I/S, but concluded that there was little evidence that time played a role. In contrast, McCubbin and Patton (1981) concluded that a close relationship exists between I/S expandability and the time-temperature burial history of eight Tertiary wells in the Gulf Coast. More recently Foster and Custard (1982, 1983) concluded that for I/S diagenesis profiles in which the sediments have been at their maximum depth of burial for more than a few million years, the depth of the smectite-to-illite transition is largely controlled by temperature. Bruce (1984) reported that the appearance of 20–25% expandable I/S in both the Texas and Mississippi River areas of the Gulf Coast is accompanied by the disappearance of potassium feldspar from the shale. He suggested that conversion of the remaining smectite layers was retarded by the lack of potash feldspar which served as a source of potassium.

The fact that no clear consensus exists regarding the relative importance of the factors responsible for I/S diagenesis is perhaps not surprising. Attempts to determine the significance of time and differences in I/S composition have undoubtedly been complicated by many other factors. For example, measured borehole

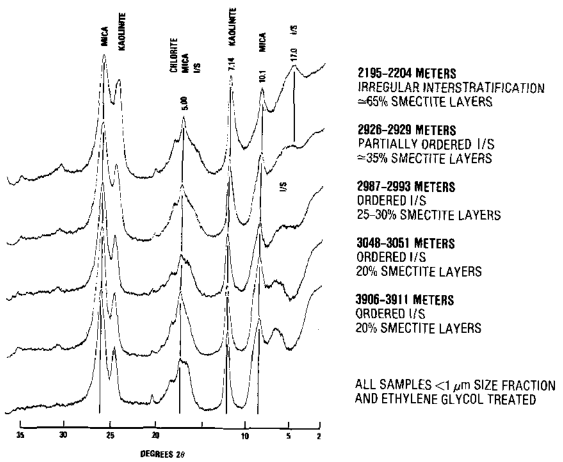

Figure 4. Representative X-ray powder diffractograms (CuKα) for the <1-μm size fraction of marine Cretaceous shales in the Champlin 1 Hartley Federal well, Powder River basin, Wyoming (locality 20).

temperatures may be several tens of degrees lower than equilibrium borehole temperatures, and corrected values, when available, may still contain significant errors. Precise geologic histories are often hard to reconstruct in detail. Problems in sampling can produce errors. Poorly lithified smectite-rich shales tend to slough and may go unrecognized in drill cuttings. Strong XRD peaks from this material tend to mask the weaker peaks of more altered I/S, thereby shifting the diagenesis profile to higher temperatures. Sample lag and sampling errors are not uncommon when working with drill cuttings. The two deepest, highly expandable (>60% expandable layers) samples plotted in Figure 5 may reflect sample lag or sampling errors. In spite of the difficulty of relating specific temperatures to specific I/S compositions and accounting for the effect of time and I/S composition, thermal alteration is clearly a major factor in determining the expandability of I/S in both Gulf Coast and Cretaceous Rocky Mountain shales.

Comparison of I/S and organic matter diagenesis in the Champlin 1 Hartley Federal well

Rock-Eval data for the same suite of samples from the CHF well were reported by Burtner and Warner (1984). Production index (PI) and T_{max} values (Table 2) of these samples are plotted alongside the I/S data in Figure 5. PI is defined as the ratio of the soluble, mobile hydrocarbons (S1) in a sample to the sum of S1 + the hydrocarbons pyrolyzed from insoluble kerogen (S2). PI is therefore a measure of the maturity and generative history of a source rock in which the hydrocarbons have been generated *in situ*. T_{max} is the Rock-Eval pyrolysis temperature (°C) at which the generation of hydrocarbons from kerogen reaches a maximum rate. It is a good measure of thermal maturity.

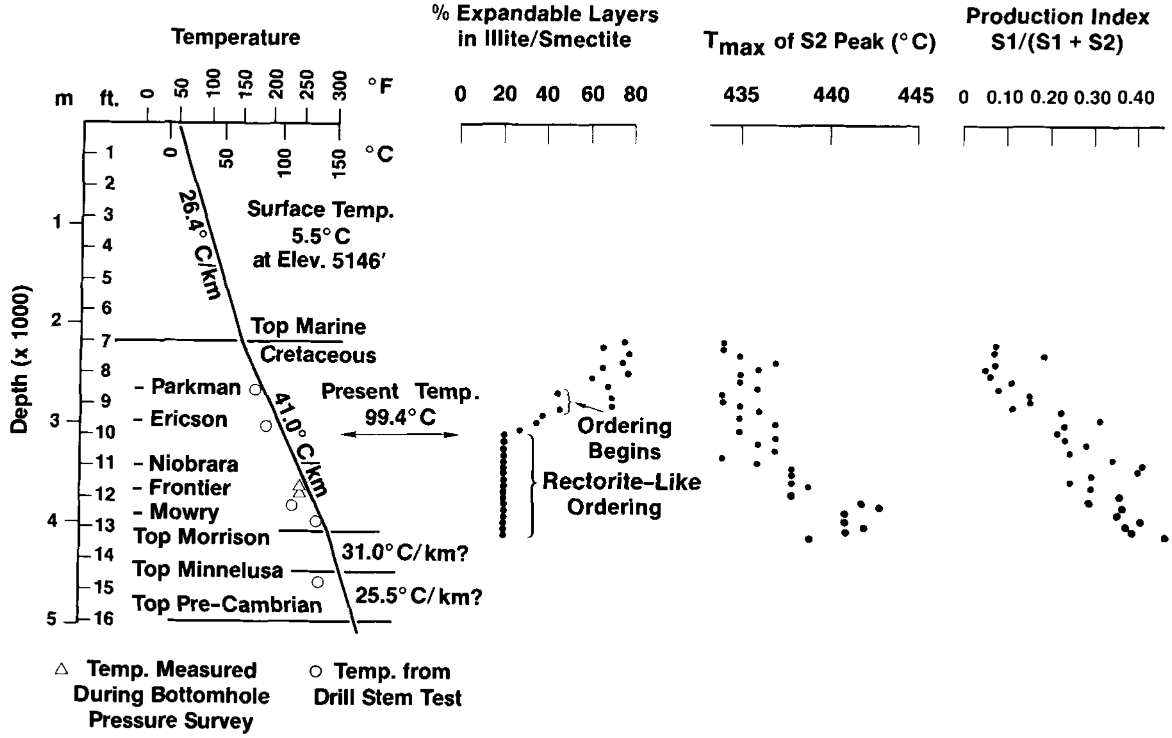

Figure 5. Profiles of I/S and organic matter diagenesis in the Champlin 1 Hartley Federal well, Powder River basin, Wyoming (locality 20).

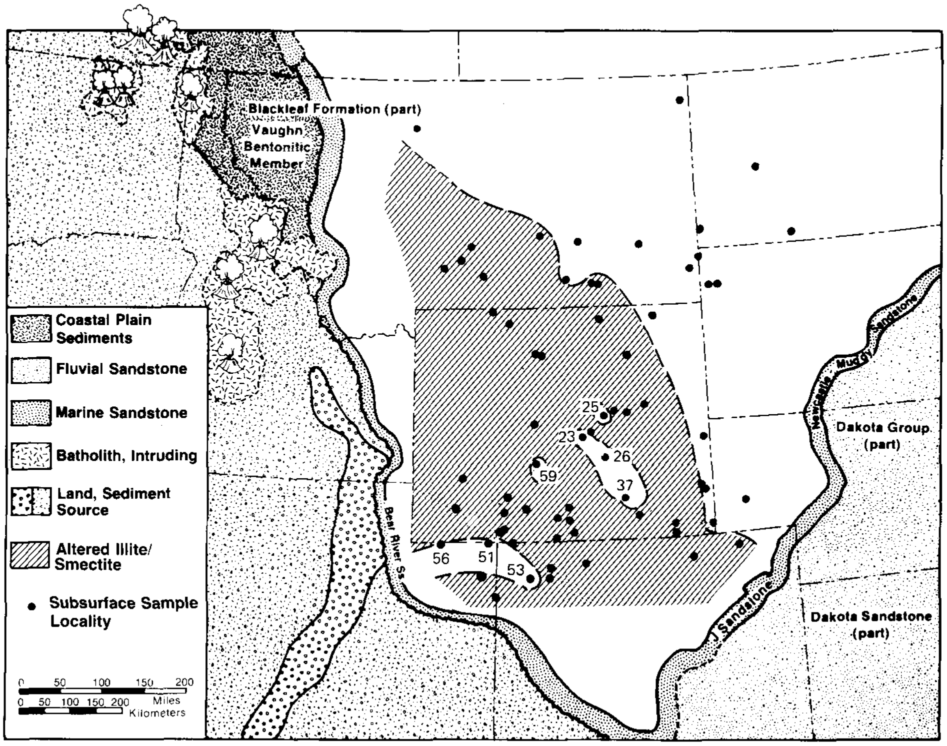

Figure 6. Distribution of altered (<65% smectite layers) and unaltered I/S in the Mowry Shale of the northern Rocky Mountain area.

T_{max} values between 435° and 460°C generally coincide with the zone of oil generation. PI values greater than 0.10 are characteristic of source rocks which have generated hydrocarbons if the PI values are accompanied by T_{max} values in excess of about 435°C.

Figure 5 shows that I/S alteration, which begins between 2438 m (8000 ft) and 2743 m (9000 ft), is accompanied by a systematic increase in PI values >0.10 and T_{max} temperatures >435°C. From the PI values, oil generation apparently began fairly abruptly between 2499 m (8200 ft) and 2621 m (8600 ft). The temperature at these depths today is about 82°–88°C (180°–190°F) and may have been about 96°–102°C (205°–215°F) in the past. Although scatter in the I/S and T_{max} data makes it difficult to relate the beginning of I/S alteration to specific organic-matter maturation values, in this stratigraphic section the illitization of smectite appears to have coincided with the generation of liquid hydrocarbons. The first occurrence of ordered, 20% expandable I/S was noted near the top of the oil generative zone. At least 1000 m of shale containing ordered I/S with 20% expandable layers are within this zone. Thus, more Cretaceous shales in the northern Rocky Mountains which contain only ordered I/S with 20% or fewer expandable layers probably have had a time-temperature history adequate to generate hydrocarbons and will have done so if the requisite organic matter was present.

The Mowry and Skull Creek shales in the CHF well are present between 3844 m (12,610 ft) and 3953 m (12,970 ft). They are currently at a temperature of about 135°C (275°F) as indicated by the composite profile of basin temperatures (Figure 5). All of the maturation criteria indicate that these source beds have been within the oil generative zone for at least 50 million years.

I/S as an indicator of regional thermal maturation for the Mowry and Skull Creek shales

I/S in the Mowry and Skull Creek shales exhibits a wide range of expandability (Table 1). The I/S types in the Gulf Coast have also been recognized in the Mowry and Skull Creek shales. The similiarity between the Powder River basin burial-diagenesis profile and the Gulf Coast profiles is evidence that the same processes were active in the shales of both areas. Rock-Eval pyrolysis data for the organic matter in the Mowry and Skull Creek shales also confirmed that these source rocks experienced widely differing degrees of thermal maturation throughout the northern Rocky Mountain area (Table 1).

All but a few of the Mowry and Skull Creek samples can be grouped into two arbitrary populations on the basis of the ordering and percentage of expandable layers in their I/S. One population contains randomly interstratified I/S with >65% expandable layers. The other contains ordered I/S with <25% expandable

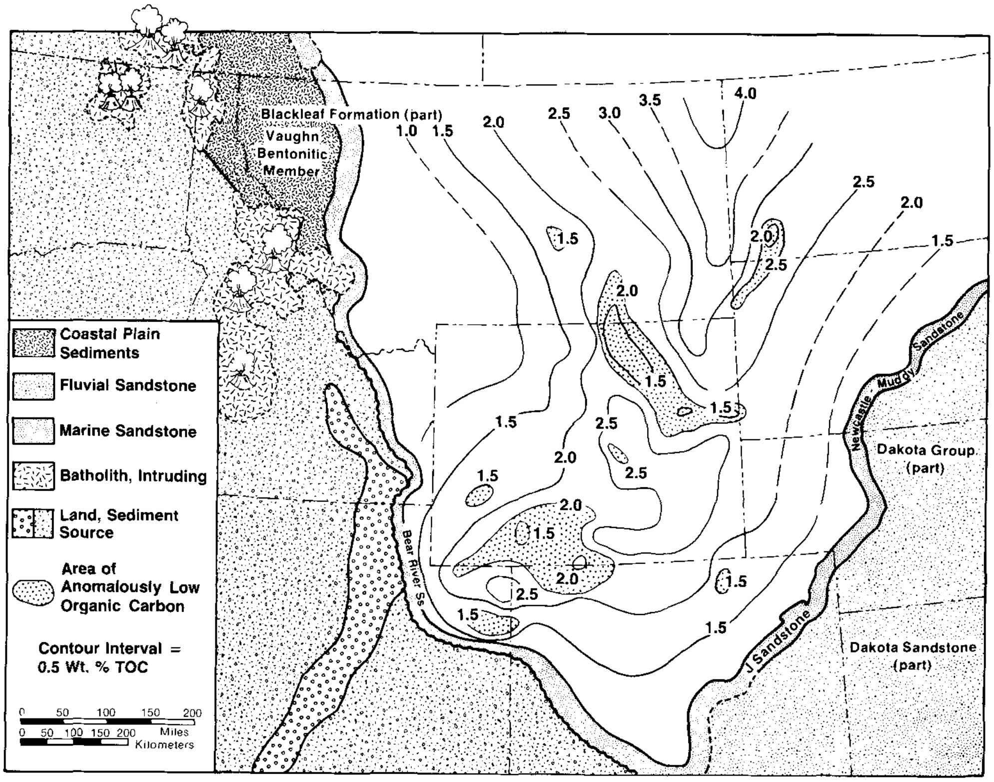

Figure 7. Regional distribution of total organic carbon (TOC) in the Mowry Shale. Note that most areas of anomalously low TOC values coincide with deeper portions of Laramide structural basins.

layers. A few samples contain I/S with 25–65% expandable layers. The I/S is transitional in nature between the two populations defined above. Using the I/S diagenesis profile in Figure 5 as a guide, it is reasonable to conclude that Mowry and Skull Creek samples containing randomly interstratified I/S with 65% or more expandable layers were subjected to little or no thermally induced alteration of the I/S clay. Figure 6 shows the distribution of altered and unaltered I/S in the Mowry Shale. Sample localities within the hachured area contain I/S with <65% expandable layers. Sample localities outside the hachured area contain I/S with >65% expandable layers.

The distribution of I/S layer types shown in Figure 6 is clearly not a function of provenance. The northwest–southeast trending line which marks the boundary between the majority of samples with >65% expandable layers and those with <65% expandable layers is oblique to the trend of the shorelines and the axis of the Mowry seaway. In addition, a few sample localities southwest of this line contain I/S having a high percentage of expandable layers. Samples from north and east of the boundary contain I/S with >65% expandable layers. They are from localities in eastern Montana, the Williston basin of western North and South Dakota and the northern portion of the Denver-Julesburg basin in which Burtner and Warner (1984) showed that the Mowry Shale is too immature to have generated hydrocarbons. All of the other samples with highly expandable I/S are from localities where the Mowry Shale was never deeply buried, such as the Casper arch (localities 23, 25, and 26), the north end of the Laramie basin (locality 37), and the south end of the Wind River basin (locality 59) or from areas in which the geothermal gradient is unusually low (localities 51, 53, and 56).

Most of the samples containing I/S with a small percentage of expandable layers are from the deeper portions of major Laramide structural basins such as the Powder River, Big Horn, Wind River, and Green River-Washakie basins. Because these structural basins formed long after the Mowry and Skull Creek shales were deposited, variations in I/S mineralogy and organic matter abundance that are related to them must reflect post-depositional alteration.

COMPARISON OF I/S AND ORGANIC THERMAL MATURATION CRITERIA FOR THE MOWRY SHALE

Regional variations in I/S and total organic carbon

Burtner and Warner (1984) showed that the original distribution of TOC in the Mowry conforms to late Albian paleogeography. TOC isopleths generally conform to the outline of the former Mowry seaway (Figure 7) and the lowest values are from locations closest to the shoreline where oxidation and benthic scavengers were most active. TOC values increase toward the center of the seaway where anoxic bottom conditions were prevalent (Byers and Larson, 1979); however, several areas of anomalously low TOC are superimposed on the regional TOC pattern. The two largest anomalies coincide with the Powder River and Green River-Washakie basins. These areas of anomalously low TOC were probably formed as a result of the generation and migration of CO_2 and hydrocarbons during thermal alteration of organic matter. These TOC anomalies lie within areas in which the I/S has experienced thermal alteration (Figure 6). The small TOC anomaly in the Williston basin, which is outside the area of altered I/S, probably does not reflect a reduction of the original TOC content as a result of hydrocarbon generation. It is based on only two samples, both of which have T_{max} values less than 435°C and, thus, are thermally immature.

Comparison of I/S and Rock-Eval thermal maturation criteria for the Mowry and Skull Creek shales

Burtner and Warner (1984) demonstrated that the Rock-Eval parameter (T_{max}) is an excellent indicator of the level of thermal maturation of organic matter in the Mowry Shale. Figure 5 shows that for Cretaceous sediments in the Powder River basin a close correlation exists between T_{max} which marks the beginning of oil generation and the depth at which smectite layers in I/S began abrupt alteration to illite. This relationship exists for the Mowry and Skull Creek shales throughout the northern Rocky Mountain area and is probably valid for most marine Cretaceous strata in that area (*vide infra*).

T_{max} values are a function of time, temperature, and, perhaps to a lesser extent, type of organic matter. The percentage of smectite layers in I/S is a function of temperature, sediment and pore fluid composition, smectite layer composition, and time. Bruce (1983, 1984) concluded from studies of I/S diagenesis profiles in the Texas Gulf Coast that time appears to be more significant in the maturation of organic matter than in the diagenesis of I/S. Because temperature plays a major role in both processes and the zone of I/S diagenesis in the CHF well coincides with the zone of oil generation, we used T_{max} instead of depth (temperature) in Figure 5 and plotted the percentage of expandable layers as a function of T_{max} (Figure 8) for the Mowry and Skull Creek shales. When plotted in this fashion, the relationship between T_{max} and percentage of expandable layers in I/S bears a striking similarity to a typical burial diagenesis profile. This similarity is further evidence that Mowry and Skull Creek samples, which contain only ordered, low-expandable I/S, have been thermally altered.

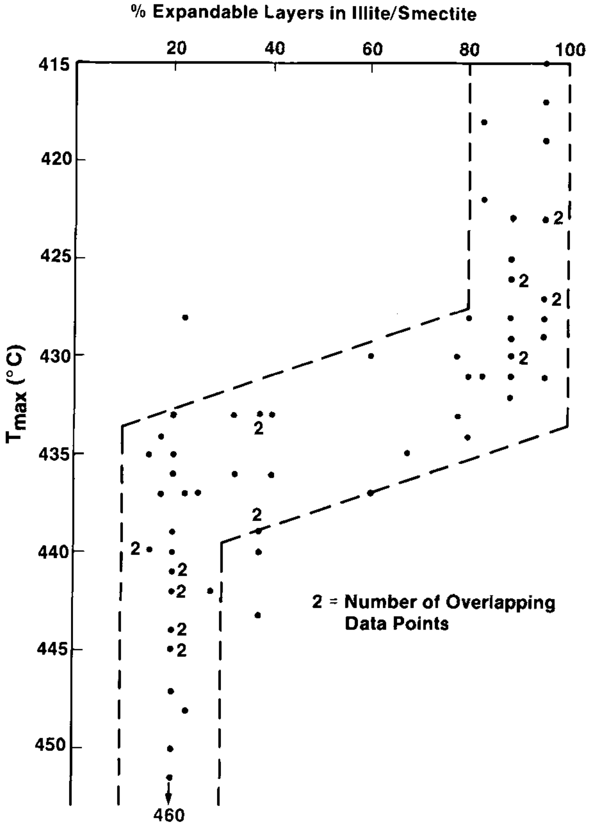

Figure 8. Percentage of expandable layers in illite/smectite plotted as a function of T_{max} (from Rock-Eval pyrolysis) for the Mowry and Skull Creek shales.

Samples containing I/S with >75% expandable layers have T_{max} values of 435°C or less. Between T_{max} values of 430° and 437°C, a wide range in the percentage of expandable layers exists, but above T_{max} values of 437°C, the samples contain only ordered, low-expandable I/S. All samples, except two (localities 30 and 36), which contain I/S with <65% expandable layers have T_{max} values of 433°C or greater. T_{max} values of about 435°C are generally accepted as marking the top of the oil-generative zone for Type II and Type III organic matter (Espitalie *et al.*, 1977), such as that in the Mowry and Skull Creek shales. Therefore, in Mowry and Skull Creek samples in which ordered, low-expandable I/S is the only I/S present, the low expandability of the I/S is a good indicator that the samples have attained the thermal maturity required to generate hydrocarbons. I/S expandability is a useful maturity indicator because some Mowry and Skull Creek samples yield very small or bimodal S2-pyrolysis peaks for which it is difficult to determine a T_{max} value. In these samples thermal maturation can be assessed from the I/S data alone.

Localities with T_{max} values of 435°C or greater are

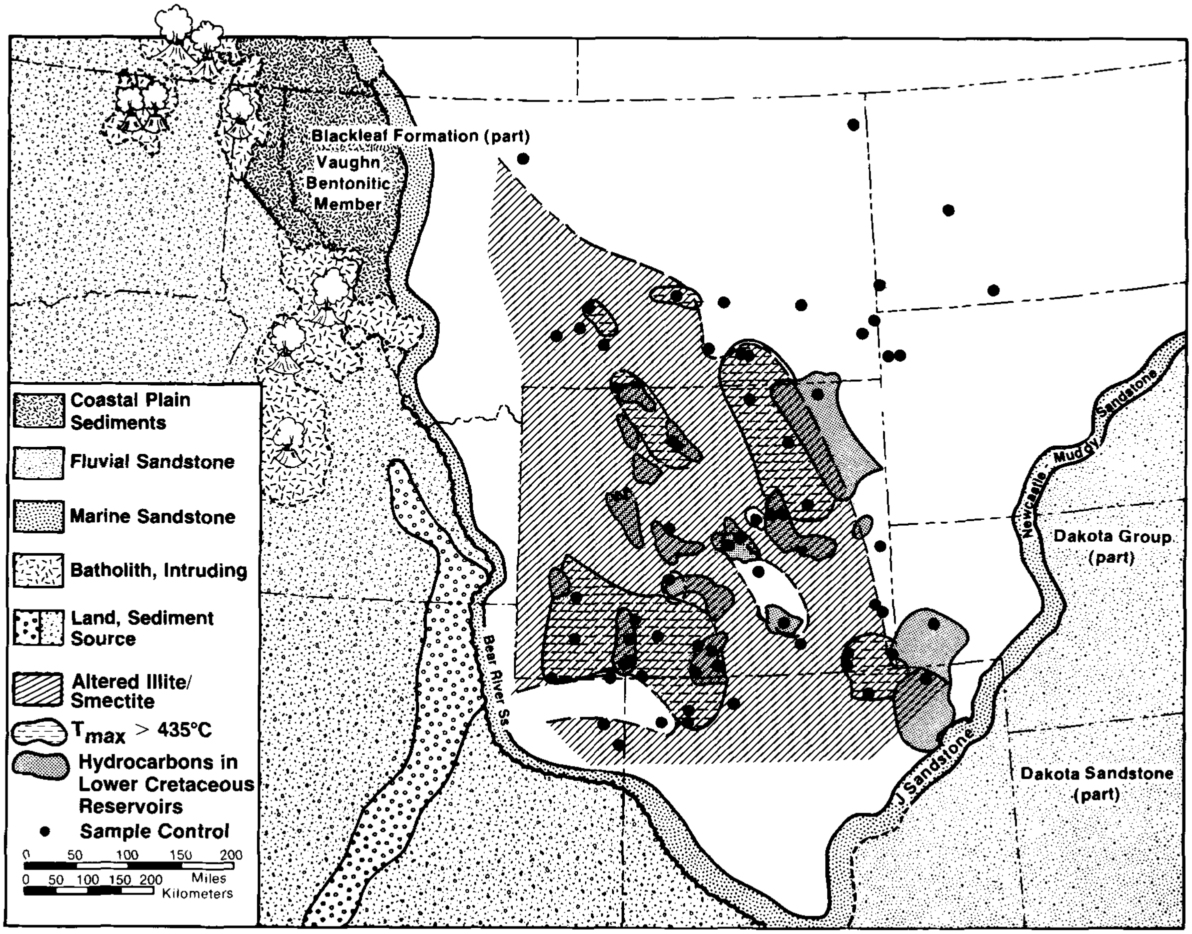

Figure 9. Regional relationship between the distribution of illite/smectite types, T_{max} values, and Cretaceous hydrocarbons in Lower Cretaceous reservoirs.

restricted to the deeper portions of Laramide structural basins and coincide in the Powder River and Green River-Washakie basins with areas of anomalously low TOC. These areas are fully contained within areas of altered I/S with <65% expandable layers (Figure 9). As can be seen in Figure 9, all Cretaceous hydrocarbons in Lower Cretaceous reservoirs, such as the Muddy and Dakota sandstones, are within or immediately adjacent to areas in which Lower Cretaceous source rocks contain altered I/S. No commercial reserves of Cretaceous hydrocarbons have been found north and east of the area of altered I/S except on the updip flanks of basins where hydrocarbons have migrated into thermally immature sediments (Forgotson and Stark, 1972). Thus, I/S alteration, reduction of TOC, and magnitude of T_{max} are all useful indicators of areas where the Lower Cretaceous source rocks have reached the thermal maturity required for the generation of hydrocarbons.

None of the three techniques alone, however, yields totally unambiguous thermal maturation data. Anomalously low TOC values may be recorded for samples in which other criteria indicate that the sediment is thermally immature (e.g., localities 5 and 9). In addition, using TOC as a hydrocarbon-generation indicator requires that TOC analyses be performed on a regional basis before areas of thermally reduced TOC can be identified. Some of the samples analyzed by Rock-Eval pyrolysis produced very small or bimodal S2 peaks, thereby making it impossible to obtain accurate T_{max} values. Moreover, reworking of older sediments can result in the presence of a significant quantity of organic matter and I/S which are both more thermally mature than the sediment in which they are now present. This condition might make it difficult to interpret thermal maturity from only a few samples. Therefore, if all three techniques are applied on a regional basis, interpretation of thermal maturation trends is likely to be less ambiguous than when only one or two techniques are applied. All three techniques are thus of exploration significance in the search for hydrocarbons in the northern Rocky Mountain area.

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John Hower taught one of us (R.L.B.) how to interpret X-ray powder diffraction patterns of mixed-layer clays, especially I/S. We are grateful to D. R. Pevear, R. C. Rettke, and L. G. Schultz for reviewing the paper and making many suggestions which improved it. We are also grateful to Chevron Oil Field Research Company and Chevron USA, Inc., for granting permission to publish it.

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