

3.3. Origin and History of Bitumen in Geodes of the New Albany Shale

by

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Introduction

The organic carbon richness of the Devonian New Albany Shale and its stratigraphic position relative to potential reservoirs are critical characteristics that establish its role as a major source rock for hydrocarbons in the Illinois Basin (Barrows and Cluff, 1984; Hatch et al., 1991; Lewan et al., 2002). Its importance as a petroleum source rock has prompted diverse studies of the New Albany Shale (see Lazar and Schieber, this guidebook). Geochemical studies, in particular, have primarily addressed questions regarding the type and abundance of the organic matter in the New Albany Shale (e.g., Frost, 1980; Barrows and Cluff, 1984; Cluff, 1993; Comer et al., 2000; Lazar and Schieber, 2003). Fewer studies have investigated the maturity of the organic matter or the biodegradation of its derived oils (e.g., Barrows and Cluff, 1984; Hatch et al., 1991; Lewan et al., 2002). The occurrence of bitumen in vertical, sub-vertical, or horizontal veins is considered strong evidence for hydrocarbon migration and has been the subject of studies in various basins of the world (e.g., Al-Aasm et al., 1992; Evans, 1995; Jochum et al., 1995; Parnell and Carey, 1995; Parnell et al., 2000; Haggan and Parnell, 2000). Bitumen-rich geodes associated with quartz-calcareous veins have been found in exposures of the New Albany Shale in various parts of Kentucky (see Road log and stop description, this guidebook). To our knowledge, there are no published studies of bitumen in geodes from the New Albany Shale. We have investigated the molecular organic geochemistry of such bitumens to determine their possible origin and formation history. We have also analyzed extracts of a shale sample and two basinal oils to assess the character of regional correlations of bitumen, oils, and organic matter in the New Albany Shale.

Sample Description

Bitumen-rich geodes associated with quartz-dolomite veins occur within the Trousdale/Blocher Member of the New Albany Shale exposed in a roadcut located south of Junction City in central Kentucky (Stop 3, Fig. 2.1, this guidebook). In this outcrop, the Trousdale/Blocher black shale is approximately 2 m thick. Seventeen vertical to sub-vertical veins, filled with quartz and dolomite occur in the Trousdale/Blocher Shale along the roadcut. The veins have been contorted and telescoped because of continued compaction of the surrounding shale after vein emplacement (Fig. 2.3.4., this guidebook). The veins are 0.18 to 1.47 m in decompressed length and are generally oriented in NW-SE direction. Centimeter-scale sub-spherical geodes, filled with calcite and quartz, and rich in bitumen, occur along or adjacent to these veins. We investigated the molecular organic geochemistry of the bitumen from four geodes, A through D. Geodes A, C, and D were open, whereas geode B appeared closed, without fissures or cracks. All the geodes contained black solid bitumen that can impart a brown tint to interior calcite crystals (Fig. 3.3.1). The bitumen had a petroliferous odor.

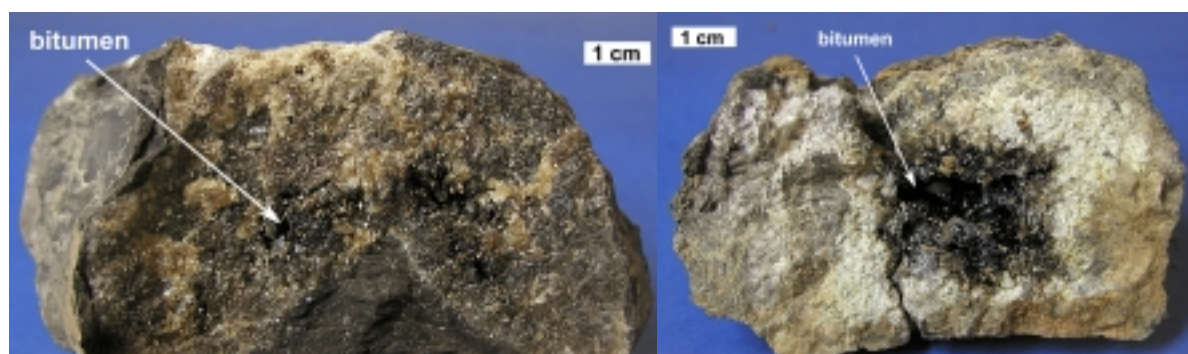


Figure 3.3.1: *Left:* Freshly broken bitumen-rich geode B. *Right:* Bitumen-rich geode A.

A shale sample (B shale) was collected adjacent to geode B after removing weathered surface material. Two oil samples were obtained from the Plummer Field, Greene County, Indiana (Plummer Field is located approximately 250 km northwest of the Junction City outcrop) and are named after their wells, namely, Page-Anderson #7 Oil and Plummer-E Oil. These oils are produced from the Salem Limestone at ~210 m depth, and the Middle Devonian Jeffersonville Limestone at ~514 m depth, respectively. The New Albany Shale is considered to be the source rock of both oils (Tom Partin and John Rupp, pers. commun., 2004).

Analytical Methods

The exterior surfaces of the geode and of the shale samples were cleaned with CH_2Cl_2 . Geode samples were extracted ultrasonically ($\text{CH}_3\text{OH}:\text{CH}_2\text{Cl}_2$ 1:2; 3x15min); the shale sample was extracted using an accelerated solvent extractor (Dionex ASE 200). Asphaltene were removed from all extracts and oil samples. Deasphalted extracts were separated by column chromatography (6-ml-volume columns) with 5 percent deactivated silica gel into saturated hydrocarbons, aromatic hydrocarbons, and nitrogen-sulfur-oxygen organic compounds (NSO) by successive elution (hexane, toluene, and methanol).

Gas chromatography of saturated and aromatic hydrocarbon fractions was performed using an Agilent Technologies 6890N gas chromatograph (GC) with a HP-5 capillary column (30m x 0.32mm). The GC oven was programmed from 60 to 320°C at 4°C/min and held isothermally for 50 minutes at 320°C; helium was used as carrier gas.

Aromatic and saturated fractions were analyzed by gas chromatography-mass spectrometry (GC-MS) using a Finnigan TSQ700 coupled to a HP5890 GC. The GC was equipped with a Varian Factor Four (VF-1ms) capillary column (50 m x 0.32 mm) programmed from 60 to 320°C at 4°C/min, and held isothermally at 320°C for 20 minutes. Helium was used as carrier gas. The transfer line was set at 320°C and the mass spectrometer scanned from m/z 50-650 in 1.2s. Compounds were identified from mass chromatograms of diagnostic ions and their mass spectra by comparison with published literature (e.g., Peters and Moldowan, 1993; Killips and Killips, 1993). Biomarker ratios were calculated from GC-MS responses.

Results

Various geochemical ratios have been calculated to assess the origin and fate of the bitumen associated with geodes within the Trousdale/Blocher Member of the New Albany Shale in Kentucky. To explore the source of the bitumen and the nature of the correlation with the Trousdale/Blocher Shale and the oil samples, *n*-alkane distribution patterns, the pristane/phytane (Pr/Ph) ratio, and the $\text{C}_{27}/(\text{C}_{27}+\text{C}_{29})$ sterane ratio were compared (Fig. 3.3.2; Table 3.3.1). The carbon preference index (CPI), the C_{29} sterane ratios (20S/(20S+20R) and $\beta\beta/(\beta\beta+\alpha\alpha)$), the triaromatic steroid ratio (TAI/(TAI+TAII)), the methylphenanthrene index (MPI-1), and vitrinite reflectance (R_o) were computed to assess the maturity of the organic matter with respect to the oil generation window (Table 3.3.1). Vitrinite reflectance was measured on a whole-rock (B shale) polished pellet mount and an average R_o value of 0.53 percent was obtained from 24 measurements. The distribution pattern of *n*-alkanes and two isoprenoid/*n*-alkane ratios (Pr/*n*- C_{17} and Ph/*n*- C_{18}) were examined to evaluate the level of biodegradation (Fig. 3.3.2; Table 3.3.1).

Discussion

Source considerations

The source of organic matter is a major control on the compositions of source rocks and oils. *N*-alkane distribution patterns, values of computed Pr/Ph, $\text{C}_{27}/(\text{C}_{27}+\text{C}_{29})$ sterane, Pr/*n*- C_{17} , and Ph/*n*- C_{18} ratios, as well as polished pellets were examined to address the question of the origin and depositional history of the bitumen. Distinct distribution patterns of saturated hydrocarbons are presented in Figure 3.3.2. The *n*-alkane distributions of all bitumens are characterized by a high abundance of pristane and phytane and by a smooth distribution of *n*-alkanes with low odd-carbon predominance in mid-chain *n*-alkanes and a relatively small abundance of high-molecular-weight *n*-alkanes (Fig. 3.3.2; Table 3.3.1). The *n*-alkane distribution of the B shale extract is characterized by a high abundance of pristane and phytane. It also shows a smooth distribution of *n*-alkanes with low odd-carbon predominance in mid-chain *n*-alkanes and a relative increase in the abundance of high-molecular-weight *n*-alkanes (Fig. 3.3.2; Table 3.3.1).

In contrast to the bitumens, the two oils are characterized by a relatively lower abundance of pristane and phytane (Fig. 3.3.2). The oils are also characterized by *n*-alkanes with low odd-carbon predominance in mid-chain *n*-alkanes and the highest abundance of high-molecular-weight *n*-alkanes (Fig. 3.3.2; Table 3.3.1). In addition, the $n\text{-C}_{12}$ to $n\text{-C}_{14}$ *n*-alkanes of the Plumer-E Oil show a more pronounced decrease compared to the $n\text{-C}_{12}$ to $n\text{-C}_{14}$ *n*-alkanes in the Page-Anderson #7 Oil (Fig. 3.3.2). This decrease could be the result of the preparatory procedures used (rotary evaporation and/or nitrogen blowing; Ahmed and George, 2004) or of storage losses.

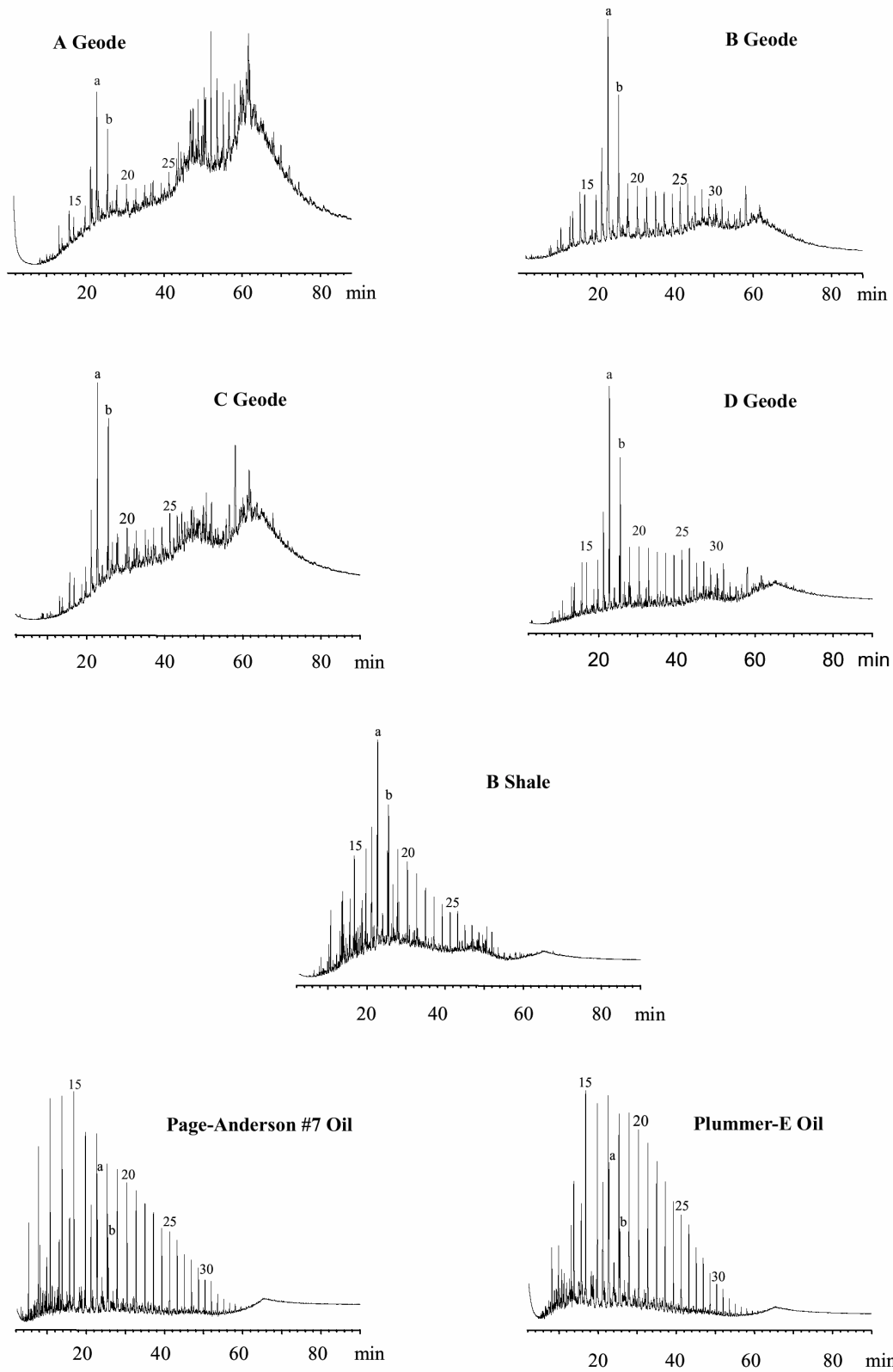


Figure 3.3.2: Gas-chromatograph traces showing the saturated hydrocarbon distributions of bitumen present in the geodes, shale, and oils. Numbers represent *n*-alkanes, *a* represents pristane, and *b* represents phytane.

Table 3.3.1: Summary of calculated geochemical ratios.

Sample	Pr/Ph	C ₂₇ / (C ₂₇ +C ₂₉)	MC-CPI	20S/ (20S+20R)	ββ/ (ββ+αα)	TAI/ (TAI+TAII)	MPI-1	R ₀ %	Pr/n-C ₁₇	Ph/n-C ₁₈
Geode										
A	1.49	0.32	1.28	0.43	0.39	0.05	0.66	0.8	8.20	4.83
B	1.38	0.34	0.92	0.42	0.38	0.05	0.75	0.85	11.89	5.70
C	1.27	0.37	1.00	0.33	0.36	0.12	1.2	1.12	9.15	7.06
D	1.38	0.28	1.06	0.35	0.31	0.11	0.91	0.95	4.98	3.71
Shale										
B	1.43	0.37	1.05	0.40	0.31	0.21	0.65	0.79	2.33	1.80
Oils										
Page-Anderson #7	1.74	n.d.	1.12	0.50	0.57	n.d.	n.d.	n.d.	0.76	0.50
Plummer-E	2.01	n.d.	1.06	0.42	0.65	n.d.	n.d.	n.d.	1.06	0.58

Notes:

$C_{27}/(C_{27}+C_{29}) = C_{27}/(C_{27}+C_{29})$ sterane.

MC-CPI = $\frac{1}{2} \{ [(C_{15}+C_{17}+C_{19})/(C_{14}+C_{16}+C_{18})] + [(C_{15}+C_{17}+C_{19})/(C_{16}+C_{18}+C_{20})] \}$; Guthrie and Pratt (1995).

20S/(20S+20R) = $5\alpha(H), 14\alpha, 17\alpha$ 20S / [$5\alpha(H), 14\alpha, 17\alpha$ 20S + $5\alpha(H), 14\alpha, 17\alpha$ 20R] sterane (C₂₉); Mackenzie et al. (1980).

$\beta\beta/(\beta\beta+\alpha\alpha) = 14\beta(H), 17\beta(H)$ sterane / [$14\beta(H), 17\beta(H)$ sterane + $14\alpha(H), 17\alpha(H)$ sterane] (C₂₉); Mackenzie et al. (1980).

TAI/(TAI+TAII) = short chain triaromatic steroids / (short chain + long chain triaromatic steroids). TAI = C₂₀ + C₂₁; TAII = C₂₆ + C₂₇ + C₂₈ (S and R isomers); Mackenzie and McKenzie (1983).

MPI-1 = $1.5 \times [(2\text{-MP} + 3\text{-MP}) / (P + 1\text{-MP} + 9\text{-MP})]$. MP = methylphenanthrene; P = phenanthrene; Radke et al. (1986).

R₀ = (0.6 × MPI-1) + 0.4; Radke et al. (1986).

Pr/n-C₁₇ = Pristane/n-heptadecane ratio; Shanmugam (1985).

Ph/n-C₁₈ = Phytane/n-octadecane ratio; Shanmugam (1985).

n.d. = not determined

The distribution of *n*-alkanes in the Page-Anderson #7 and Plumer-E oils resembles the distribution of Sangamon County Oil from central Illinois, of New Albany Shale extract from Franklin Co., southern Illinois (Bethke et al., 1991, their Fig. 26-3), and of New Albany rock extract representative for 21 shale samples collected from cores in Indiana, Illinois, and Iowa (Hatch et al., 1991, their Fig. 24-8 H). The similarity between *n*-alkanes distributions of the two oil samples we examined and that of published oil and shale samples suggest that the New Albany Shale is the source rock of the Page-Anderson #7 and Plumer-E oils.

The values of the Pr/Ph ratio and of the C₂₇/(C₂₇+C₂₉) sterane ratio of the bitumen from the four geodes fall in a narrow range (Table 3.3.1) suggesting a common source for the bitumen. The B shale is characterized by ratios similar to those obtained for the bitumen samples. The similarity of the Pr/Ph ratio raises the possibility of a common source for the bitumens and the B shale. In contrast, the Pr/Ph ratio of the two oils is higher (Table 3.3.1). Although the Pr/Ph ratio reflects the nature of the contributing organic matter, this ratio should be used with caution (Peters and Moldowan, 1993) because some of the pristane and phytane might be derived from sources other than phytol during diagenesis (e.g., ten Haven et al., 1987).

The isoprenoid/*n*-alkane ratios (Pr/n-C₁₇ and Ph/n-C₁₈) have also been used to indicate source of organic matter (e.g., Chou and Dickerson, 1985; Shanmugam, 1985). A plot of Pr/n-C₁₇ versus Ph/n-C₁₈ suggests different sources, more terrestrial and somewhat different for the four bitumens, and more mixed, marine and terrestrial, for the B shale organic matter and the oils (Fig. 3.3.3).

Maceral characterization revealed that amorphinite is the dominant organic component in the B shale, and that together with alginite represents more than 90% of the organic matter in the sample. The organic matter of the black Trousdale/Blocher Shale had a mixed source of both marine and terrestrial inputs (Mastalerz, pers. commun., 2004). The marine algae inputs have been expected because of the observation of abundant *Tasmanites* in thin sections (Fig. 2.3.5, this guidebook). Terrestrial input in the Trousdale/Blocher Shale, possibly derived from bacterial

degradation of higher plant material, has been also expected taking into consideration the location of the outcrop on the Cincinnati Arch, presumably a shallower water or even exposed region during the Late Givetian to Early Frasnian. Our preliminary results suggest that the organic matter in the bitumen and the B shale came from different sources. Future investigations of polished pellets containing bitumen and analyses of specific biomarkers used as indicators of biological input (Peters and Moldowan, 1993, their Table 3.1.3 a and b) will assist in the clarification of the source of the bitumen and its relationship to the B shale.

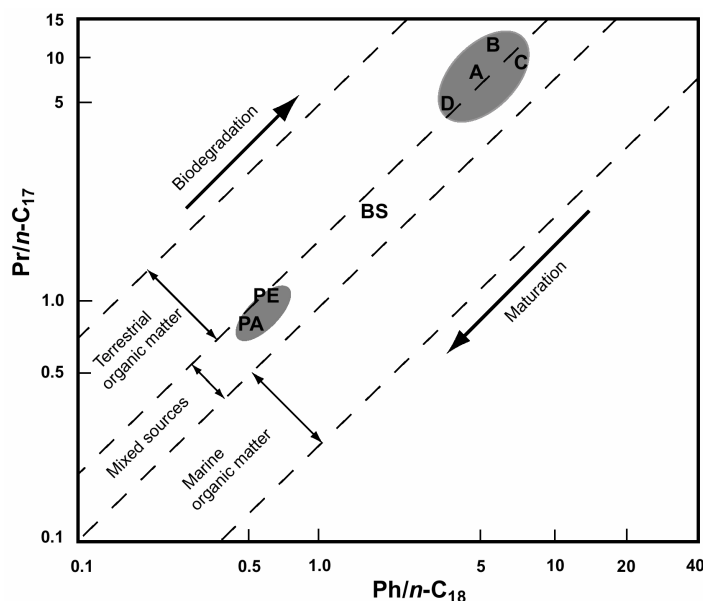


Figure 3.3.3: Plot of $Pr/n-C_{17}$ versus $Ph/n-C_{18}$ showing relative source, maturation, and biodegradation of the bitumen from geodes A to D, the B shale organic matter (BS), and Page-Anderson #7 (PA) and Plummer-E (PE) oils (modified after Shanmugam, 1985).

Maturity considerations

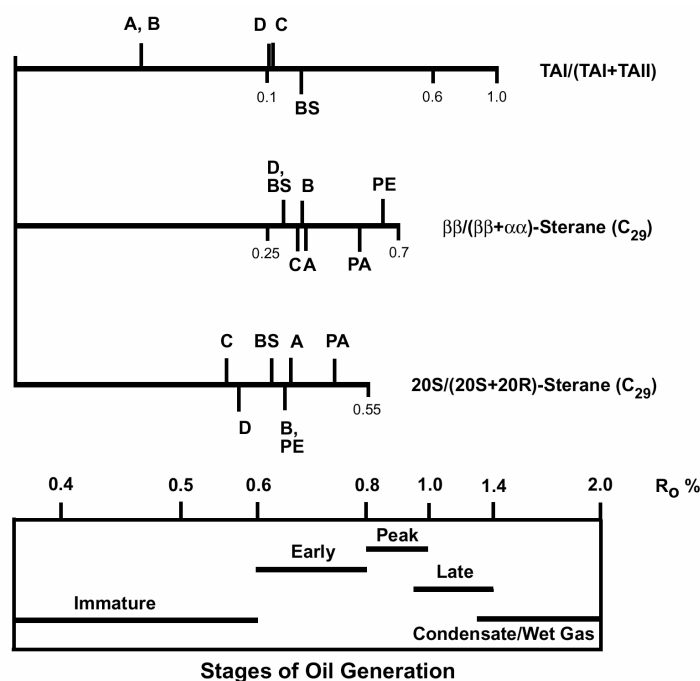
Maturation is the process of chemical change in sedimentary organic matter that is induced by burial (increasing temperature and pressure) over geologic time (Tissot and Welte, 1984). In general terms, organic matter can be described as immature, mature, or postmature depending on its relation to the oil generation window

(Tissot and Welte, 1984). Assessment of the level of thermal maturity of bitumen and oils assists in oil-source correlation studies. Six maturity parameters, the MC-CPI, $20S/(20S+20R)$, $\beta\beta/(\beta\beta+\alpha\alpha)$, $TAI/(TAI+TAII)$, MPI-1, and R_o , have been calculated to assess organic matter maturity (Table 3.3.1). The carbon preference index (CPI), the ratio of the relative abundance of odd versus even carbon number n -alkanes, decreases with increasing maturity (Peters and Moldowan, 1993). CPI values significantly above (odd preference) or below (even preference) 1.0 indicate that an oil or extract is thermally immature, whereas values of 1.0 suggest but do not prove that an oil or extract is thermally mature (Peters and Moldowan, 1993). The $20S/(20S+20R)$ and $\beta\beta/(\beta\beta+\alpha\alpha)$ C_{29} sterane ratios are thought to increase from 0 to approximately 0.55 ($20S/(20S+20R)$) and from 0 to about 0.70 ($\beta\beta/(\beta\beta+\alpha\alpha)$) during thermal maturation (Fig. 3.3.4) (Seifert and Moldowan, 1986). The triaromatic steroid ratio ($TAI/(TAI+TAII)$) increases up to 0.1 at the end of the immature stage and up to 1.0 at the end of the oil window (Fig. 3.3.4) (Peters and Moldowan, 1993). The methylphenanthrene index (MPI-1) values bracket the end of the immature stage (0.5) and the end of the oil window (1.6) (Killops and Killops, 1993). Vitrinite reflectance (R_o) is a commonly used maturation parameter which is based on the change in the reflectance of polished vitrinite particles with increasing time and temperature. R_o values range from 0 to 0.6 percent for the immature stage of oil generation, and from 0.6 to 1.4 percent for the mature stage of oil generation (Fig. 3.3.4) (Peters and Moldowan, 1993).

The values of the $20S/(20S+20R)$, $\beta\beta/(\beta\beta+\alpha\alpha)$, and $TAI/(TAI+TAII)$ ratios of the geode bitumens are broadly similar (Table 3.3.1) and indicate that the bitumens are immature-very early mature (Fig. 3.3.4). In contrast, the MPI-1 and R_o values suggest an early to peak mature stage (Fig. 3.3.4; Table 3.3.1). The C_{29} sterane and the triaromatic steroid ratios are considered to be independent of the source of organic matter input and, therefore, sensitive and effective for inferences of higher levels of maturity, whereas the MPI-1 and the calculated R_o can be adversely affected by the source of organic matter input (Peters and Moldowan, 1993). Assuming there are subtle differences in the source of organic matter input for the four bitumens, the $20S/(20S+20R)$, $\beta\beta/(\beta\beta+\alpha\alpha)$, and $TAI/(TAI+TAII)$ ratios are considered to be more accurate maturity indicators, implying that the geode bitumens reached an immature to very early mature stage.

Calculated maturity parameters from the B shale indicate that it reached an early mature stage (Fig. 3.3.4; Table 3.3.1). In contrast, the vitrinite reflectance measurements suggest an immature stage ($R_o = 0.53\%$; Mastalerz, pers. commun., 2004). Similarly, fully transparent to pale yellow conodonts and yellow *Tasmanites* indicate that both the conodont alteration index (CAI) and thermal alteration index (TAI) have a value of one, indicative of immature source rocks (Taylor et al., 1998). Although geochemical maturity indices such as those presented in Table 3.3.1 are

considered to provide, for lower maturity rocks, a more accurate assessment of thermal maturity than vitrinite reflectance (Peters and Moldowan, 1993), the observations from three different petrography-based indices makes one wonder whether the organic matter of the B shale did in fact reach the early mature stage.



The values of the $20S/(20S+20R)$ and $\beta\beta/(\beta\beta+\alpha\alpha)$ ratios obtained here indicate, as expected, the highest level of thermal maturity for the two oil samples (Fig. 3.3.4; Table 3.3.1).

Figure 3.3.4: Ranges of maturity of bitumen from geodes **A** to **D**, the B shale organic matter (**BS**), and Page-Anderson #7 (**PA**) and Plummer-E (**PE**) oils as indicated by vitrinite reflectance (R_0), and the $20S/(20S+20R)$, $\beta\beta/(\beta\beta+\alpha\alpha)$, and $TAI/(TAI+TAII)$ ratios (modified after Peters and Moldowan, 1993).

Biodegradation considerations

Degradation of petroleum by bacteria is commonly referred to as biodegradation. Peters and Moldowan (1993) proposed a scale, similar

to that of Volkman et al. (1983a, b), for assessing the extent to which an oil has been biodegraded based on the relative abundances of various hydrocarbon classes. On the Peters and Moldowan (1993) biodegradation scale, *n*-alkanes are easiest to be biodegraded (light biodegradation, levels 1 to 3), followed by isoprenoids (moderate, levels 4 to 5), steranes (heavy, levels 6 to 7), hopanes (very heavy, levels 8 to 9), aromatic steroids, and porphyrins (severe, level 10). The isoprenoid/*n*-alkane ratios ($Pr/n-C_{17}$ and $Ph/n-C_{18}$) have been used to indicate maturation and biodegradation (e.g., Chou and Dickerson, 1985; Shanmugam, 1985). Both ratios decrease with maturation because of the increasing prevalence of *n*-alkanes, and increase with biodegradation because of the loss of *n*-alkanes (Peters and Moldowan, 1993; Hunt, 1996).

Relative to the B shale the bitumens are biodegraded. The distribution patterns of *n*-alkanes indicate a sequence of decreasing biodegradation from bitumen A to C to B to D (levels 3 to 2 on the biodegradation scale of Peters and Moldowan, 1993) (Fig. 3.3.2; Table 3.3.1). The bitumen from the A and C geodes is characterized by a marked decrease in *n*-alkanes between *n*- C_{14} and *n*- C_{27} , and by the presence of an unresolved complex mixture that displays a “hump” that rises above the baseline of the GC trace that we interpret to be the result of biodegradation (Fig. 3.3.2; Table 3.3.1). The two oils show minimal biodegradation (the *n*-alkanes are more abundant than pristane and phytane) (Fig. 3.3.2; Table 3.3.1). A plot of $Pr/n-C_{17}$ versus $Ph/n-C_{18}$ illustrates also that, relative to the B shale organic matter, the bitumens have been biodegraded (Fig. 3.3.3). It is to be expected that bitumen present in open geodes will undergo biodegradation. The bitumen from the B geode, however, appears to have the highest level of biodegradation (Fig. 3.3.3). This is surprising since the B geode was found closed, with no visible fissures or cracks detected when it was collected. The fact that biodegradation also affected the bitumen from geode B suggests that this geode could have had micro-fissures that allowed microbes to enter the geode and attack the hydrocarbons. Alternatively, the bitumen might have been under microbial attack sometime before the geode closed.

Concluding remarks

To summarize, it appears that the bitumens might have had a different source of organic matter than the Trousdale/Blocher Shale. Also, the bitumens and the two oils experienced different levels of biodegradation. These bitumens have been collected from geodes associated with vertical to subvertical veins present in the shale. Several studies have attributed comparable vein development in other successions to fluid overpressuring (Marshall, 1982; Stoneley, 1983; Al-Aasm et al., 1993; Parnell et al., 1994; Parnell and Carey, 1995). Quartz-calcareous veins that occur in the Trousdale/Blocher Member of the New Albany Shale could possibly be related to the movement of

overpressured fluids underneath the Devonian shale seal. Preliminary investigations allow the suggestion that the bitumen and the shale organic matter might not share the same origin. If this is correct, then the Trousdale/Blocher Shale could have been hydro-fractured during oil generation from older, Ordovician or Silurian strata, and Ordovician/Silurian bitumen could have migrated along open fractures and then trapped in hollow geodes. However, further sedimentologic and geochemical analyses are required to firmly establish the source of the bitumen, the timing of veins and geodes, and its relationship to the shale organic matter.

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