

TABLE OF CONTENTS

Geochemical Services).

INTRODUCTION TO FIELD GUIDE

October, 2008

Field Trip Participants and Interested Parties:

Oklahoma Geological Survey Open File Report 2-2008, Oklahoma Gas Shales Field Trip, is a recent and up-to-date compilation of observations and data about gamma-ray well log response, lithology (or lithofacies), and organic petrology from Woodford Shale exposures located in the Arbuckle Mountains and Criner Hills of Oklahoma.

Pages 6-26 are reprinted from the *Oklahoma Geological Survey Special Publication 93-3* by Cardott and Chaplin entitled *"Guidebook for Selected Stops in the Western Arbuckle Mountains, Southern Oklahoma".* Publication 93-3 provides a general context for the regional geological setting of the Arbuckle Mountains and the Woodford Shale.

New Woodford Shale data and discussions are provided on pages 29-82 of the field guide. These pages include data about spectral gamma-ray response relative to shale lithofacies, stratigraphy, and organic petrology of the Woodford Shale for each of the field-trip stops. The stratigraphic discussions in the field guide focus on variations in the internal stratigraphy of the Woodford based on the distribution and volume of 1) potassium, uranium, and thorium gammaray response, and 2) total organic carbon content (TOC). Stratigraphic relationships of spectral gamma-ray response and TOC to the underlying Hunton Group limestone are also addressed during the trip.

Some observations about lithologic controls on fracture occurrences in the Woodford are highlighted at two of the field-trip stops.

Lastly, the appendix contains some geochemical data for the solid bitumen occurrences from the Woodford Shale collected at the McAlister Cemetery Quarry. The data collection and reporting was conducted by Tim Ruble of Humble Geochemical Services, Humble, Texas.

Please have a safe and successful field trip!

Stan Paxton, USGS-Oklahoma Water Science Center, Oklahoma City *Brian Cardott,* Oklahoma Geological Survey, Norman

FIELD TRIP STOPS

Map 1. Generalized geologic map of Arbuckle Mountains showing location of field trip **stops 1A, 1B, and 2. Stop 3 is not shown on this map. Modifi ed from Johnson and others (1984, OGS Special Publication 84-1, fi gure 4, p. 5).**

Map 2. Location of (A) Henry House Falls Quarry (stop 2), and (B) McAlister Cemetery Quarry (stop 3). Modified from Kirkland and others (1992, OGS Circular 93, figure 1, p. **39).**

NOTES

NOTES

EXAMPLE OVERVIEW OF ARBUCKLE MOUNTAINS
GEOLOGY AND WOODFORD SHALE GEOLOGY AND WOODFORD SHALE

The following overview is from Oklahoma Geological Survey Special Publication 93-3 by Cardott and Chaplin.

Oklahoma Geological Survey 1993

Special Publication 93-3

Guidebook for Selected Stops in the Western Arbuckle Mountains, Southern Oklahoma

Brian J. Cardott and James R. Chaplin

Guidebook for Selected Stops in the Western Arbuckle Mountains. **Southern Oklahoma**

BRIAN J. CARDOTT AND JAMES R. CHAPLIN

GENERAL GEOLOGIC SETTING

Portions of the following sections are adapted from Ham (1969) and Ham and others (1973).

The Arbuckle Mountains are located just north of the Texas/Oklahoma border in south-central Oklahoma (Fig. 1). The Arbuckle Mountains region offers some of the best exposures of lower Paleozoic rocks in the North American Midcontinent. The Paleozoic outcrops (Cambrian–Pennsylvanian) along Interstate 35 (formerly U.S. Highway 77) have become classic geologic exposures in that they are exceptional in their thickness, lateral continuity, and excellent exposure. Reference to the Arbuckle outcrops as the Arbuckle Mountains is somewhat misleading since ~80% of the province consists of gently rolling plains. Only in the western part of the province is reference to the Arbuckle outcrops as "mountains" perhaps warranted; there the Arbuckle anticline attains an altitude of 1,377 ft (420 m), the highest elevation in the Arbuckle Mountains, with a total relief of 607 ft (185 m).

The Arbuckle Mountain geologic province consists of \sim 1,000 mi² of outcrop composed of a huge inlier of folded and faulted Precambrian rocks and ~30,000 ft (9,200 m) of fossiliferous Paleozoic sedimentary rocks ranging in age from Cambrian through Late Pennsylvanian. The sedimentary rocks are composed mostly

of carbonates that constitute the best outcrops and greatest area of exposure of this marine sequence in all of the Midcontinent and perhaps the world. The sedimentary-rock column within the southern Oklahoma aulacogen (SOA) is about seven times thicker than coeval rocks on the adjacent craton. The Arbuckle Mountains are covered on the east, north, and west by gently westward-dipping Pennsylvanian and Permian strata, and on the south by gently southward-dipping Lower Cretaceous sediments of the Gulf Coastal Plain province (Fig. 1).

GENERAL GEOLOGY

The oldest rocks in the Arbuckle Mountain region are igneous rocks exposed in the core of the Tishomingo anticline (Fig. 2), which are dated to be \sim 1.35 b.y. old. The 150 mi² exposure of Precambrian granites in the eastern Arbuckle Mountains is the largest and best outcrop of such rocks in the central United States between the Llano region of Texas and the Black Hills of South Dakota. In some parts of southern Oklahoma (e.g., Arbuckle anticline). the basement rocks are unique in that they are exposed around the margin of a profound aulacogen, and are composed of igneous flows and intrusives of Cambrian (525 m.y. old), rather than Precambrian age.

Figure 1. Geologic provinces map of Oklahoma (from Ham and others, 1990). The shaded area is illustrated in detail in Figure 2.

Figure 2. Index map of Arbuckle Mountains showing principal structural features (from Ham and others, 1990). Location of this area is shown (shaded) in Figure 1.

Pre-Devonian sedimentary rocks of the Arbuckle Mountains primarily comprise a thick (11,000-ft) [3,400-m]) sequence of cyclic platform carbonates interbedded with minor clastics of the Gondwana passive margin (Fig. 3). Because of late Paleozoic structuring of the Gondwana margin, present-day exposures occur in updip shelfal positions and lack internal stratal geometries across depositional strike. The pre-Devonian rocks are dominantly limestones in the aulacogen and dolomites upon the craton.

The younger rocks of the lower Paleozoic carbonate sequence in southern Oklahoma are those of the Hunton Group of Late Ordovician, Silurian, and Early Devonian age. The Hunton Group has an average thickness of about 100-350 ft (30-110 m) at most localities in the Arbuckle Mountains. The group is much thinner than older sequences, in part because of the numerous unconformities within and at the top of the sequence. The thickness of the Hunton Group is related more closely to the position of isolated cratonic basins and to the effectiveness of the several unconformities, than to the localization within a through-going trough. Depositional patterns of Silurian and Devonian strata differ from those of older and younger sequences of the southern Oklahoma aulacogen. Neither the Hunton Group nor the overlying Woodford Shale are appreciably thicker in most parts of the aulacogen than upon the craton (Ham, 1969).

Late Paleozoic strata (Woodford Shale, Sycamore Formation, Delaware Creek Shale, Goddard Formation, Springer Formation), of Late Devonian-Mississippian age, are dominated by dark shales deposited in a deeper-water anoxic environmental setting. The dark-shale succession is $6,000$ ft $(1,800 \text{ m})$ thick in the southern Oklahoma aulacogen; slightly more than $5,500$ ft $(1,700 \text{ m})$ is Mississippian. On the craton, coeval Mississippian dark shales are ~ 650 ft (200) m) thick. The dark shales are commonly interbedded with poorly fossiliferous, silty limestones. Some of the impure limestones are thick and massive.

Southern Oklahoma was again the site of abnormally thick sedimentation during the Pennsylvanian. The southern Oklahoma aulacogen received locally as much as 15,000-17,000 ft (4,600-5,200 m) of shales, sandstones, and generally thin limestones. Equivalent beds upon the craton are $\sim 3,000$ ft (900 m) thick and consist of shales, sandstones, and a much greater relative thickness of limestones as compared to the SOA. Rocks of Pennsylvanian age crop out around most of the Arbuckle Mountains. Pre-Desmoinesian Pennsylvanian rocks within and adjoining the Arbuckle Mountains generally are non-conglomeratic; however, Desmoinesian and younger Pennsylvanian rocks are conglomerate-bearing and record the beginning and close of mountain-building in the Arbuckle Mountains (Fritz and others, 1993).

	SYSTEM/SERIES	ANADARKO BASIN. SW OKLAHOMA			ARBUCKLE MOUNTAINS, ARDMORE BASIN			ARKOMA BASIN, NE OKLAHOMA				OUACHITA MOUNTAINS
QUATERNARY		Alluvium		and			Terrace					Deposits
TERTIARY		Ogallala Formation										
CRETACEOUS			Dakota Group									
	JURASSIC	Morrison Formation										
TRIASSIC		Dockum Group										
PERMIAN			Elk City Sandstone									
	Ochoan	Doxey Shale										
	Guadalupian	Cloud Chief Formation Whitehorse Group										
		El Reno Group										
	Leonardian	Hennessey Shale Garber Sandstone Wellington Formation		Garber Sandstone Wellington Formation								
		Chase Group Council Grove Group Admire Group							Chase Group			
	Wolfcampian			Pontotoc Group		Pontotoc Group		Council Grove Admire Group				
PENNSYLVANIAN			Wabaunsee Group						Waubunsee			
	Virgilian	("Granite Wash" eroded from Wichita Mts.) Shawnee Group Douglas Group		Ada Formation Vamoosa Formation			Ada Fm. Vamoosa		Shawnee Douglas			
			Ochelata Group					Hilltop Fm.	Ochelata Group			
	Missourian		Skiatook Group		Hoxbar Group				Skiatook Group			
	Desmoinesian		Marmaton Group		Deese Group				Marmaton Group Cabaniss Group			
		Conglomerate Cherokee Group					Krebs Group					
	Atokan		Atoka Group		Dornick Hills				Atoka Formation			Atoka Formation
	Morrowan		Morrow Group			Group		Wapanucka		McCully		Johns Valley Shale
			$\overline{?}$ Springer Formation			Springer Formation ?		Union Valley	Sausbee			Jackfork Group
MISSISSIPPIAN	Chesterian					Goddard Formation			Pitkin Limestone Fayetteville Shale Hindsville Formation			Stanley Group
			Chester Group			Delaware Creek Shale	Shale					
	Meramecian	"Meramec Lime"					"Caney"	Moorefield Formation				
	Osagean	Miss. Lime "Osage Lime"				Sycamore Limestone		Boone Group St. Joe Group				
	Kinderhookian											
DEVONIAN	Upper	Woodford Shale		Woodford Shale		Chattanooga Shale Sylamore Sandstone						
		Misener Sandstone										
	Middle											Arkansas Novaculite
	Lower							Sallisaw Fm.				
			Haragan Fm.	Hunton Group	Frisco Formation Haragan-Bois d'Arc Formation Henryhouse Formation		Frisco Fm.					
SILURIAN		Hunton Group	Henryhouse Fm.								Pinetop Chert	
	Upper					Clarita Formation		Quarry Mtn. Fm. Tenkiller Fm. Blackgum Fm.				
	Lower Upper		Chimneyhill		Chimneyhill Subgroup	Cochrane						
			Subgroup			Formation					Missouri Mountain Shale	
						UIII Keel Formation	2222 Pettit Oolite					Blaylock Sandstone Polk Creek
ORDOVICIAN		Sylvan Shale		Sylvan Shale			Sylvan Shale					Shale
		Viola Group		Viola Group		Viola Group					Bigfork Chert	
		Simpson Group		Group		Bromide Formation		Fite Formation				
						Tulip Creek Formation McLish Formation	Tyner Formation					Womble Shale
	Middle			Simpson	Oil Creek Formation Joins Formation		Burgen Sandstone					
												Blakely Sandstone
					West Spring Creek Formation Kindblade Formation Cool Creek Formation McKenzie Hill Formation							Mazarn Shale
	Lower	Arbuckle Group		Group						Arbuckle		Crystal Mountain
				Arbuckle Butterly Dolomite		Group					Sandstone	
CAMBRIAN		Timbered Hills Group				Signal Mountain Formation Royer Dolomite						Collier Shale
	Upper			Fort Sill Limestone								
				T. H. Honey Creek Limestone Group			Timbered Hills Group					
					Reagan Sandstone							
	Middle	Granite, Rhyolite, and Gabbro		Rhyolite								
	Lower											
PRECAMBRIAN		Granite, Rhyolite, and Metasediments		Granite and			Granite and					
						Gneiss	Rhyolite					

Figure 3. Generalized correlation of rock units in Oklahoma (from Johnson and Cardott, 1992b). Height of boxes is not related to thickness of rock units.

SOUTHERN OKLAHOMA AULACOGEN **TECTONIC SETTING**

Portions of the following section are adapted from Brown and Grayson (1985) and Tapp (1991).

Southern Oklahoma contains the most accessible, best exposed, and best understood aulacogen in the United States. The southern Oklahoma aulacogen (SOA) is the deepest sedimentary trough in North America, filled to a thickness of at least 45,000 ft $(13,700 \text{ m})$ (Ham, 1969). The SOA trends N 60° W from southeastern Oklahoma ~250 mi (400 km) into the Texas Panhandle. Aulacogens preserve the igneous and sedimentary rocks that record the opening and closure of ocean basins. Rocks in the aulacogen are usually preserved without metamorphism, and thus they contain invaluable information about the evolution of continents. Nickolai Shatsky (1946) first defined the term "aulacogen" as a long-lived, faultbounded trough in an otherwise stable platform that intersects a deformed belt or a continental margin at a high angle. Shatsky (1946) described the Dnieper-Donets basin of the Russian platform and the Arbuckle–Wichita system as type aulacogens. An aulacogen contains an abnormally thick, usually undeformed, section of continental and marine sediments. According to Shatsky (1947), aulacogens are distinct geotectonic features with complex evolutionary histories that are genetically related to geosynclines but are not easily explained by geosynclinal theory. Milanovsky (1981, p. 213) redefined the term "aulacogen" as "linear graben-like depressions of ancient platforms" and allowed for later inversions and cover of the structure.

Ham and others (1964) named this feature (SOA) the "southern Oklahoma geosyncline" and stated that the Arbuckle-Wichita trend evolved through three separate geosynclinal stages to reach its final configuration. According to Ham and others (1973), 17,000 ft (5,200 m) of Upper Cambrian through Mississippian sediment accumulated in the SOA. The combination of continued subsidence and periodic orogenic activity led to a further accumulation of $13,000 \text{ ft}$ (4,000 m) of mostly terrigenous clastic sediment during the Pennsylvanian. This combined total of 30,000 ft (9,100 m) of sediment was folded and faulted during the deformation stage of the aulacogen to become the presentday Arbuckle Mountains.

The tectonic significance of the SOA was first recognized by Hoffman and others (1974) who presented evidence for the evolution of an aulacogen using the Athapuscow aulacogen and the SOA as examples. The evolution of an aulacogen is divided into three stages: (1) rifting, followed by (2) subsidence and infilling of the rift, and finally, (3) deformation of the rocks in the ancient rift.

The SOA apparently developed during Late Proterozoic-Early Cambrian rifting of the southern continental margin. This margin appears to be related to the Grenville suture formed when the Llano terrane

was accreted to North America. The SOA is representative, as well as the best exposed, of a series of penecontemporaneous rifts along the southern and eastern margins of the North American plate. The only likely exposed boundary of the rift is the Washita Valley fault zone in the Arbuckle Mountains (Fig. 2): this structure juxtaposes Precambrian granite and the equivalent of the Carlton Rhyolite.

Pronounced Pennsylvanian structural inversion, at least in part, resulted in the formation of a series of linear uplifts, notably the Wichita, Arbuckle, and Criner uplifts (Fig. 4). The inversion lifted the igneous basal sections of this rift (SOA) to shallow crustal levels and exposed parts of it in the Wichita Mountains (Fig. 1). Contemporary basins filled with syntectonic sediments abut these uplifts. As much as $39,000$ ft $(11,900 \text{ m})$ of strata are preserved in the deep Anadarko basin, \sim 29,500 ft (9,000 m) in the Ardmore basin, and \sim 26,000 ft (7,900 m) in the southern parts of the Arkoma and Marietta basins (Fig. 1).

Deformation Stage of Southern Oklahoma **Aulacogen Orogenic Conglomerates**

Portions of the following section are adapted from Ham (1954,1968) and Brown and Grayson (1985).

The deformation stage of the SOA is evidenced by several orogenic conglomerates in the Arbuckle Mountain region (Table 1). These conglomerates are primarily Pennsylvanian in age; however, orogenic activity in this region began as early as Late Mississippian (Chesterian) time, as recorded by cherty conglomeratic limestones (Springer Formation) deposited in the Criner Hills region (Fig. 4). Several pulses of uplift indicated in the Pennsylvanian sediments suggest that the segments of southern Oklahoma were uplifted at different times.

Late Mississippian (Chesterian)

The initial orogenic stage of the SOA began in Late Mississippian to Early Pennsylvanian time and exposed a land mass along the Wichita Mountains-Criner Hills chain. Syntectonic cherty conglomeratic limestones within Late Mississippian sediments (Springer Formation) suggest that this activity began in the Chesterian. A syncline developed where the Ardmore basin and Arbuckle anticline are presently located.

Pennsylvanian (Morrowan and Atokan)

This synclinal basin accumulated sediments of the Dornick Hills Group, including syntectonic conglomerates of the Joliff (Morrowan) and Bostwick (Atokan) units (Table 1). The source area for these sediments is believed to have been the Criner Hills which underwent uplift separating the southeastern portion of the SOA into the Ardmore and Marietta basins. At the same time, uplift of the Hunton and Tishomingo anticlines occurred. A syncline developed between them during Atokan time and collected sediments now preserved in the Mill Creek syncline (Fig. 2).

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SOA Tectonic Setting

SOA Tectonic Setting

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Pennsylvanian (Early Atokan)

The main Wichita orogeny took place in early Atokan time and was marked by a period of strong folding and uplift along the Amarillo-Wichita-Criner trend. This uplift exposed Cambrian igneous basement along the mountain chain, and lifted the Criner Hills 10,000-15,000 ft (3,000-4,600 m) structurally higher than the Ardmore basin.

Pennsylvanian (Early Desmoinesian)

Uplift continued in the Wichita system and the initial uplift of the Arbuckle area probably occurred during Desmoinesian time. Sediments shed from the Hunton and Tishomingo landmass were preserved as the Franks Conglomerate (Deese Group) in the Franks graben and in the Mill Creek syncline. The Ardmore basin continued to receive sediments shed from the Criner Hills area. However, chert pebbles preserved in the Devil's Kitchen and Rocky Point Conglomerates (Deese Group) near Lake Murray may have been sourced from folding and thrusting along the Ouachita front.

Pennsylvanian (Late Desmoinesian-Early Missourian)

In late Desmoinesian and early Missourian time, sediments shed from uplift of the Hunton anticline were preserved as the Warren Ranch Conglomerate (Deese Group) in the Arbuckle Mountain region. Pebbles and cobbles in the Warren Ranch Conglomerate record cannibalism of the uppermost Arbuckle Group through the Hunton Group.

Pennsylvanian (Late Missourian-Early Virgilian)

In late Missourian and early Virgilian time, the major Arbuckle orogeny began. During this period of deformation, the folds of the Wichita system were rejuvenated, the Hunton and Tishomingo anticlines underwent further uplift and faulting, and the basin between these two structural systems was compressed, folded, and faulted to become the Ardmore basin and Arbuckle anticline.

Pennsylvanian (Middle Virgilian)

Sediments shed from this uplift include the syntectonic Collings Ranch Conglomerate (middle Virgilian) which is preserved along the northern part of the Arbuckle anticline region (stop 1). The Collings Ranch Conglomerate consists of clasts primarily sourced from the middle and upper Arbuckle Group. The Late Pennsylvanian Arbuckle orogeny appears to have been the last mountain-building pulse in the SOA. The Collings Ranch Conglomerate was folded and faulted during the final stages of deformation along the Arbuckle anticline.

Pennsylvanian (Late Virgilian)

The post-tectonic Vanoss Conglomerate (late Virgilian), preserved in the Mill Creek syncline (stop 7), is the chief depositional product of the Arbuckle orogeny and marks the termination of major deformation in the Arbuckle Mountain region. The Vanoss Conglomerate is generally undeformed except for some minor folding, which suggests that only minor, if any, deformation of the Arbuckle Mountain region occurred after late Virgilian time. As evidenced by arkose in the Vanoss Formation and by the presence of granite. feldspar, and vein quartz from Precambrian granites in the Vanoss Conglomerate, the first unroofing of the Precambrian granite in the Arbuckle Mountains occurred only after the highest uplift and deepest erosion of the Arbuckle Mountains in Late Pennsylvanian time.

ARBUCKLE MOUNTAINS TECTONIC SETTING

Portions of the following section are adapted from Ham (1969), Ham and others (1973), Wickham (1978), Brown and Grayson (1985), and Tapp (1988).

The structural styles of the Arbuckle Mountain region of southern Oklahoma have developed as a result of the late Paleozoic Wichita, Ouachita, and Arbuckle orogenies. The location and trends of many of these structures, however, were predetermined by the initial rifting in the late Precambrian and Early Cambrian during the development of the southern Oklahoma aulacogen (Table 1). The Arbuckle Mountains show a variety of structural styles and intensity. Changes in deformation style and intensity may be related, in part, to competency contrasts of the deforming medium. Interpretation of the surface structures has generated significant controversy. Deformation in the region has been related to: (1) wrench tectonics, (2) thrust tectonics, or (3) distinct phases of both.

Structural uplifts in the Arbuckle Mountains region consist of three prominent anticlines of differing deformation, separated from each other by high-angle faults that strike approximately N 60° W. These anticlines are the Hunton and Tishomingo, both on the platform, and the Arbuckle anticline in the aulacogen.

The Hunton anticline, composed of gently deformed lower Paleozoic carbonates, is separated from the Tishomingo anticline by the Sulphur fault, Mill Creek fault, and Reagan fault (Fig. 2). The style of deformation in this area is consistent with a wrench fault model.

The Arbuckle anticline, the principal part of the Arbuckle Mountains to be visited on this trip, is the most intensely deformed part of the mountains. Structurally, it is a faulted anticline, overturned to the north. This asymmetric, extremely complex, structure is bounded on its northern flank by the Washita Valley fault zone and on its south flank by the Ardmore basin (Figs. 1,2). Results of the tectonic activity of the Arbuckle orogeny, including karstification and collapse, can best be observed on the structurally more complex northern flank. The stratigraphy along the southern flank of the Arbuckle anticline controls the topography in that area. Carbonates, particularly cyclic shallowing-upward sequences of the upper Arbuckle Group, form prominent hogback ridges (referred to as tombstone topography); shales form valleys, and sandstones form smaller hogbacks.

The Arbuckle anticline and its associated minor folds have been interpreted as forming in two major events: (1) the first formed the main anticline and its secondary folds in the middle Virgilian, and (2) the second event formed the Dougherty anticline in the late Virgilian (Ham, 1969). The Arbuckle anticline is within the range of axial orientation proposed for a primary fold in a left-lateral wrench system (Tapp, 1988).

The northern flank of the Arbuckle anticline is bounded by the Washita Valley fault zone. The exposed length of the fault zone is 35 mi (56 km). It extends for another 50 mi (80 km) to the southeast beneath the Cretaceous cover. Some evidence suggests that the Washita Valley fault zone may link up with the Meers fault in the Wichita Mountains to the northwest (Fig. 4). Deformation in the vicinity of the Washita Valley fault zone in the uniform and competent Arbuckle Group is restricted to a narrow zone of shear, folding, and fractures at the edge of the open Arbuckle and Sycamore Creek anticlines. However, deformation in the overlying interlayered sandstones, shales, and carbonates of the Simpson Group and younger rocks is in a broader zone of folding and thrusting north of the fault.

Ham (1969) proposed that the Washita Valley

fault zone marks the northern limit of the Cambrian rift valley. The fault zone is thought to be a rejuvenated northeastern edge to the aulacogen; it separates the Arbuckle Mountains into a western block, in which the basement is the Cambrian Colbert (Carlton) Rhyolite, and an eastern block floored by the Tishomingo and associated Precambrian granites. The fault zone probably represents the only likely exposed margin to the Precambrian rift system. The present Washita Valley fault zone was reactivated during the Pennsylvanian and may have been rejuvenated during the Quaternary (Cox and Van Arsdale. 1988).

Many different interpretations of the Washita Valley fault zone have been published. The most popular is that it is a horizontal, left-lateral strike-slip (wrench) fault. Estimates for the amount of left-slip range from 3 mi (5 km), based on stratigraphic offsets (Ham. 1956: Cox and Van Arsdale, 1988), to 40 mi (64 km), based on the offset of the erosional edge of the basal Oil Creek Formation in the Simpson Group (Tanner, 1967). Carter (1979) estimated 20 mi (32 km) of left-slip based on the offset of Hunton isopachs. An alternative interpretation for the fault zone, based on subsurface evidence, has been proposed by Brown (1984), who interpreted the southwest-dipping Washita Valley fault zone to be an imbricate of the Arbuckle thrust. The asymmetric Arbuckle anticline was uplifted and its northeast flank was overturned along the Arbuckle thrust. Brown (1984) has demonstrated that apparent left-lateral offset, cited by proponents of wrench fault tectonics, can be completely accounted for by the development of reverse dip-slip movement on the Arbuckle thrust. Accordingly, Brown suggests that the fault zone is subordinate to the Arbuckle thrust and that the entire zone is a left oblique-slip reverse fault having a dip-slip component of 8 mi (13 km) and a strike-slip component of $3 \text{ mi} (5 \text{ km})$.

Figure 5. Generalized geologic map of the western Arbuckle Mountains showing location of seven field-trip stops (adapted from Johnson and others, 1984). Cross section is shown in Figure 6. $\mathbb{O} =$ Field trip stops. H = Henry House Falls quarry (Kirkland and others, 1992); T = Woodford Shale type locality (Taff, 1902); U = palynologic investigation of Woodford Shale by Urban (1960); V = palynologic investigation of Woodford Shale by Von Almen (1970); W = approximate location of Williams asphaltite prospect (possibly under water; Hutchison, 1911).

STOP₁

Collings Ranch Conglomerate

Location

Stop 1 is a scenic turnout from the southbound lanes of Interstate 35, ~2.0 mi (3.2 km) south of U.S. Highway 77 (exit 51). Detailed location: Located ~0.5 mi (0.8 km) north of milepost 49 on Figure 8 (Pcr) at the SE14SE14NW14 sec. 31, T. 1 S., R. 2 E. on the Turner Falls Quadrangle map (7.5' series), Murray County. Marker No. 29 (Fay, 1989; Station No. 2604 $+50$ ft) is 70 ft (21 m) north of a fault in the Washita Valley fault zone; the Washita Valley fault zone separates the Arbuckle anticline and Tishomingo anticline (Fig. 2).

CAUTION: Please do not walk on the roadway. If we cross the southbound lanes of I-35, please do this in groups of five.

Significance

- The first, thickest, and coarsest orogenic product following Pennsylvanian folding.
- Next to the last synorogenic conglomerate deposited during the deformation of the southern Oklahoma aulacogen.

Figure 8 (this and facing page). Geologic map and profile of Arbuckle Mountains along Interstate 35 (from Fay, 1988). A is to the south; C is to the north. Circled numbers 44-51 are mileposts.

- $\text{Qal} = \text{Quaternary}$ alluvium
- Pcr = Pennsylvanian Collings Ranch Conglomerate
- Mg = Mississippian Goddard Formation
- Mdc = Mississippian Delaware Creek Shale
- $Ms = Mississippian Sycamore Limestone$
- $Dw = Devonian-Mississippian Woodford Shale$
- Dsh = Ordovician-Devonian Hunton Group
- $Os = Ordovician Sylvan Shale$
- Ov = Ordovician Viola Group
- Obr = Ordovician Bromide Formation
- Otc = Ordovician Tulip Creek Formation
- Om = Ordovician McLish Formation
- Ooc = Ordovician Oil Creek Formation
- = Ordovician Joins Formation Oi
- Owsc = Ordovician West Spring Creek Formation
- = Ordovician Kindblade Formation Ok
- Occ = Ordovician Cool Creek Formation
- TOmh = Ordovician McKenzie Hill Formation
- $Obu = Ordovician Butterly Dolomite$
- Csm = Cambrian Signal Mountain Formation
- Cro = Cambrian Royer Dolomite
- = Cambrian Fort Sill Limestone Cfs
- Chc = Cambrian Honey Creek Limestone
- Cre = Cambrian Reagan Sandstone
- Cc = Cambrian Colbert Rhyolite

Figure 8. Continued.

STOP₃

Woodford Shale

Location

Stop 3 (Fig. 18) is a road-cut exposure along the west side of the southbound lanes of Interstate 35. ~ 0.5 mi (0.8 km) south of stop 2. Detailed location: Located 650 ft (198 m) north of milepost 44 on Figure 8 (Dw) at the SE1/4NW1/4SE1/4 sec. 25, T. 2 S., R. 1 E. on the Springer Quadrangle map (7.5' series), Carter County. Marker No. 2 (Fay, 1989; Station No. 2329 + 70 ft) is 9 ft (3 m) below the top of the Woodford Shale.

CAUTION: Pull off the road to the far right. Stay on the west side of the road, away from traffic. Large groups should seek permission from the Oklahoma Highway Department.

Significance

- Records a major regional anoxic event.
- Woodford Shale as major hydrocarbon source rock.
- May prove to be a significant reservoir rock in the Anadarko basin.
- Oldest rock in the Arbuckle Mountains that contains vitrinite.
- Sample collecting locality of early hydrous pyrolysis experiments.

Description

The Upper Devonian-Lower Mississippian Woodford Shale (Fig. 3) occurs in Oklahoma, Texas, and New Mexico (Conant and Swanson, 1961). It was named Woodford Chert by Taff (1902) for outcrops north of the town of Woodford, ~8 mi (13 km) west of stop 3 (Morgan, 1924; Gould, 1925; Jordan, 1957). The type locality is at sec. 34, T. 2 S., R. 1 W. (T on $Fig. 5)$.

Hass and Huddle (1965) determined a Late Devonian (Frasnian) age for most of the formation and based the Early Mississippian (Kinderhookian) age of the uppermost portion on conodonts. They indicated that conodonts were not abundant in the samples they collected from Carter, Murray, Pittsburg, and Pontotoc Counties in Oklahoma. New radiolarian and conodont faunas recovered from the upper part of the Woodford Shale indicate a considerably higher chronostratigraphic position (Osagean–Meramecian) for the top of this unit than previously assigned (Schwartzapfel, 1990; Schwartzapfel and Holdsworth, 1991). Age-equivalent rocks of the Woodford Shale in Oklahoma include, in part or in entirety, the Woodford Shale of New Mexico and Texas; the Chattanooga Shale in the Eastern Interior of the United States: the New Albany, Ohio, and Sunbury Shales of the central United States; the Arkansas Novaculite in southeastern Oklahoma and Arkansas; the Antrim Shale in the Michigan basin; the Bakken Formation in the Williston basin; the Kettle Point Formation of Ontario; and the Pilot Shale of Utah (Conant and Swanson, 1961).

Stop 3 (Fig. 18) is on the south flank of the Arbuckle anticline (Figs. 2,8). The strike of the Woodford Shale is N 60° W and the dip is 44° SW (Fay, 1989).

The Woodford Shale is a marine, carbonaceous and siliceous, fissile to blocky, dark-gray to black shale containing chert, subordinate amounts of greengreenish-gray shales, phosphate nodules, and pyrite.

Figure 18. Exposure of Woodford Shale along west side of southbound lanes of Interstate 35 at stop 3.

Figure 19. (A) Paleogeography and facies distribution in the Late Devonian. (B) Northwest-southeast cross section through the Woodford depositional basin showing the relationship of facies to relative water depth (from Kirkland and others, 1992).

It marks a transition from predominantly carbonate deposition in the early Paleozoic to primarily clastic deposition in the late Paleozoic (Ham and others, 1973). Figure 19 illustrates paleogeography and facies distribution in the Late Devonian. Black shale was deposited below storm wave base over most of Oklahoma. A chert facies occurs within the Woodford. primarily in southern and southeastern Oklahoma. A major unconformity at the base of the Woodford Shale is the result of uplift and erosion during the late Early to Middle Devonian (Maxwell, 1959). Brown to green shale occurs at the base of the Woodford Shale at stop 3 (Barrick and Klapper, 1990). The upper contact with the Sycamore Limestone is gradational.

The Woodford Shale attains a maximum thickness of >700 ft (213 m) in the southern Oklahoma aulacogen (Amsden, 1975) (Fig. 20). The shales of the southwest flank of the Arbuckle Mountains are part of a thick basin sequence, nearly four times as thick as the equivalent cratonic succession on the northeastern flank. Fay (1989) reported the thickness of the Woodford Shale at stop 3 to be 290 ft (88 m). The upper 102 ft (31 m) and lower 51 ft (15 m) is exposed; the middle 137 ft (42 m) is covered. Figure 21 is a measured section of stop 3 (Ellis and Westergaard,

1985). Roberts and Mitterer (1992) indicated that the upper 72 ft (22 m) of the Woodford Shale at stop 3 contains black to blackish-brown laminated shales, $0.04-11$ in. $(0.1-29$ cm) thick, and black to blackishbrown cherts, $0.2-13$ in. $(0.5-32$ cm) thick.

Hester and others (1990) subdivided the Woodford Shale in northwestern Oklahoma into three informal stratigraphic units based on log-derived characteristics. Higher total organic carbon content of the middle member was the physical basis for the subdivision. Urban (1960) recognized three depositional facies in the Woodford Shale based on microfossil content of an outcrop \sim 3 mi (5 km) east of stop 6 (sec. 3, T. 2 S., R. 3 E.; U on Fig. 5). The upper and lower facies indicate a nearshore-marine environment, whereas the middle facies indicate a more open-marine environment. Von Almen (1970) identified three depositional facies composed of marine transgressive and regressive cycles, based on palynomorphs identified from 55 outcrop and core chip samples from south-central Oklahoma. The zones were not correlative across the region. The primary outcrop in the Arbuckle Mountains used by Von Almen (1970) was along Hickory Creek (sec. 27, T. 2 S., R. 1 W.; V on Fig. 5), ~1 mi (2 km) north of the type locality.

Figure 20. Thickness and dominant lithologies of the Woodford-Chattanooga Shale (from Johnson and others, 1988).

Microfossils recognized in the Woodford Shale include miospores, acritarchs, algae (Tasmanites, Quisquilites, Foerstia), scolecodonts, conodonts, radiolarians, and sponge spicules (Cooper, 1931a,b; Urban, 1960; Wilson and Urban, 1963, 1971; Hass and Huddle, 1965; Wilson and Skvarla, 1967; Von Almen, 1970; Orth and others, 1988; Barrick and Klapper, 1990; Over, 1990; Schwartzapfel, 1990; Schwartzapfel and Holdsworth, 1991; Kirkland and others, 1992; Siy, 1993).

Macrofauna reported in rare occurrences from the Woodford Shale include brachiopods (Lingula, Productella, Spirifer, Strophomena), arthropods (crustacean), gastropods, and cephalopods (Probleoceras, Mooreoceras) (Girty, 1909; Reeds, 1927; Roth, 1929; Cooper, 1932; Green, 1972; Kirkland and others, 1992).

The progymnosperm Archaeopteris (organ genus Callixylon) and the gymnosperm Cordaitales (form genus Dadoxylon) are the most common vascular flora observed in the Woodford Shale, especially in the lower portion (Reeds, 1927; Arnold, 1934, 1947; Wilson, 1958; Huffman and Starke, 1960; Von Almen, 1970; Kirkland and others, 1992). Silicified Callixylon logs are in the basal Woodford Shale at the Henry House Falls (HHF) quarry, ~5 mi (8 km) west of stop 3 (H on Fig. 5; secs. 30 and 31, T. 2 S., R. 1 E.); measured section in Hass and Huddle (1965) and Kirkland and others (1992).

The Woodford Shale at stop 3 was deposited in the southern Oklahoma aulacogen; the Washita Valley fault is the craton/aulacogen bounding fault zone (Fig. 4). The black, organic-rich composition of the shale (organic carbon concentrations as much as 25) wt%) and the occurrence of phosphate nodules and chert suggest that the upper part of the Woodford, at least, was deposited in relatively deep water (200– 500 ft [60-150 m]) (Tucker, 1991; Kirkland and others, 1992) near the oxygen-minimum zone (Heckel and Witzke, 1979; Spesshardt and Barrick, 1986; Siy, 1993). Kirkland and others (1992) argued against an upwelling model and preferred a thermocline model for anaerobic conditions. Based on an abundance of radiolarians (siliceous microfossils), Roberts and Mitterer (1992) concluded that the chert was of primary origin. Radiolarians and sponge spicules were also a major source of silica for the shale (Kirkland and others, 1992). Siy (1993) described the inorganic petrography and geochemistry of the Woodford Shale in the Arbuckle Mountains and indicated that the nodules are 14.97–38.4 wt% P_2O_5 , classified as phosphorites.

O'Brien and Slatt (1990) described the whole-rock mineral composition (wt%) of a Woodford Shale sample from Carter County as containing 63% quartz, 3% plagioclase feldspar, 10% calcite, 6% dolomite, 5% pyrite, and 14% total layer silicates. Kirkland and others (1992) reported the mineral composition of several

Figure 21. Measured section of the Bois d'Arc, Woodford, and Sycamore Formations at stop 3 (modified from Ellis and Westergaard, 1985).

Woodford Shale samples from the HHF quarry as haying 55-87% quartz, 0-7% K-feldspar, 0-3% dolomite, 0–1% apatite, 0–1% pyrite, 8–34% illite, and 3–7% kaolin. The percentage of chert increases toward the top of the formation, and the lower portion contains black fissile shale (Siy, 1993). Kirkland and others (1992) described the occurrence and origin of phosphate nodules, pyrite concretions, and calcite concretions in the Woodford Shale in southern Oklahoma.

Orth and others (1988) described the geochemistry of the Woodford Shale from the Hass G section (SE1/4 SW1/4 sec. 35, T. 3 N., R. 6 E., Pontotoc County, Oklahoma) and reported that Ir (0.25 ppb), Pt, Au, V, Ni, U, and all measured chalcophiles (Cu, Zn, As, Se, Mo, Ag, Sb, and Hg) are highly enriched in the top 1 m of the Woodford Shale at that locality.

Cardott (1992) provided an extensive bibliography of the Woodford Shale of Oklahoma through 1991. Additional research papers are in Johnson and Cardott $(1992a)$.

Hydrocarbon Source Rock

Organic geochemistry studies suggest that the Woodford Shale is an important hydrocarbon source rock in Oklahoma (Comer and Hinch, 1987; Cardott, 1989). Comer and Hinch (1987) and Comer (1992) reported that 70–85% of the oil produced in central and southern Oklahoma was generated by the Woodford Shale. Based on gas chromatography and biomarker analysis, Zemmels and Walters (1987) and Zemmels and others (1987) concluded that the Woodford Shale was the source of oils produced from the Arbuckle Group, Simpson Group, Bois d'Arc Formation, Woodford Shale, and Deese Group in the vicinity of the Arbuckle Mountains (Fig. 3). Wavrek (1992) attributed 55% of oil sample types in Ardmore-basin and Marietta-basin reservoirs to the Woodford Shale $(Fig. 16, oil type C).$

Kerogen Type: Based on bulk geochemical composition, the organic matter in the Woodford Shale is classified as type II (oil-prone) kerogen (Johnson and Cardott, 1992b; type IID kerogen of Hunt and others, 1991). Lewan (1983) and TSOP (1989) indicated that >90% by volume of the organic matter at stop 3 is amorphous kerogen. G. E. Michael, C. L. Thompson-Rizer, and R. A. Woods (1993, personal communication) reported the visual kerogen composition of the Woodford Shale at stop 3 to be 80% amorphous type A (fluorescing, oil prone) (Thompson and Dembicki, 1986), 15% herbaceous (includes Tasmanites and acritarchs), and 5% solid bitumen; fluorescence intensity from the herbaceous kerogen was strong, and fluorescence intensity from the amorphous kerogen was weak. Thompson-Rizer and others (1988) reported the results from a sample exchange study that included a Woodford Shale sample from the Arbuckle Mountains, Carter County. They concluded that more work is needed to obtain consensus on quantitative fluorescence values of dispersed organic matter in sedimentary rocks.

Tables 2 and 3 summarize the organic geochemistry of the Woodford Shale for stop 3. Total organic carbon (TOC) contents from \sim 2 to 14 wt% indicate very good hydrocarbon source potential. Concentrated zones contain as much as 25 wt% TOC. Roberts and Mitterer (1992, p. 333) indicated that "lower organic carbon content of the cherts is inferred to be due to sedimentary dilution of organic matter during periods of high siliceous productivity rather than to differences in type of organic matter." The atomic H/C content is 1.14–1.24; the atomic O/C content is 0.07-0.08. The ratios were used by Horsfield (1989) and Comer (1992) to classify the organic matter in the Woodford Shale as type II kerogen. The hydrogen index, ranging from 377 to 763 mgHC/g OC, suggests oil-prone potential. The oxygen index is 18–35 $mgCO₂/g$ OC. Figure 22 is a Van Krevelen-type diagram of the hydrogen and oxygen indices showing the type II kerogen at stop 3 (G. E. Michael, C. L. Thompson, and R. A. Woods, 1993, personal communication). The kerogen-type indicator value of $~18$ suggests that the kerogen is oil prone. The production index of 0.02 indicates that the sample is immature.

Figure 22. Van Krevelen-type diagram of Rock-Eval pyrolysis data showing the kerogen type of the Woodford Shale at stop 3 (m) and stop 6 (m) . Data is in Table 2.

a Data from G. E. Michael, C. L. Thompson-Rizer, and R. A. Woods (1993, personal communication); parameter explanation after Peters and Moldowan (1993).

bWeathered float block from the quarry floor.

^cTotal organic carbon content. TOC = [0.82(S₁+S₂)+S₄]/10. Considered to have hydrocarbon source potential if >0.5 wt%.

^dS₁ (mgHC/gROCK). The amount of free (extractable) bitumen in a sample.

^eS₂ (mgHC/gROCK). The amount of hydrocarbons released during pyrolysis.

 fS_3 (mgCo₂/gROCK). The amount of carbon dioxide released during pyrolysis.

g S₄ (mgC/gROCK). The amount of residual carbon released during the final, high-temperature stage of pyrolysis.

hHydrogen index (mgHC/gOC). HI = (S₂/TOC). In general, gas-prone if <200 and mainly oil-prone if >300.

ⁱOxygen index (mgCO₂/gOC). OI = 100 (S₃/TOC).

^jKerogen-type indicator. Gas-prone if <5, oil-prone if >10, and mixed if between 5 and 10.

^k Production index. Pl = S₁/(S₁+S₂). In general, immature if <0.1, in oil window if between 0.1 and 0.4, and in gas window if >0.4. Higher Pl values may indicate contamination and/or oil stain.

¹The temperature at the apex of the S₂ peak. In general, a T_{max} range of 435-470°C corresponds to the oil window.

Figure 23. Photomicrograph of low-reflecting bitumen (on left; 0.36% R_o) and vitrinite (0.52% R_o) from Woodford Shale type locality (T on Fig. 5; reflected white light, oil immersion, 200x, field width is 140 μ).

 \ddotsc

a Total organic carbon content (see Table 2).

^bHydrogen/carbon atomic ratio. ([% H/1.008]/[% C/12.011]).

"Oxygen/carbon atomic ratio. ([% O/15.999]/[% C/12.011]).

^dHydrogen index (see Table 2).

^eOxygen index (see Table 2).

^fThe temperature at the apex of the S_2 peak (see Table 2).

gVitrinite reflectance (oil immersion). In general, values <0.4% are immature, 0.4-0.6% are marginally mature, 0.6-1.3% are early to middle mature ("oil window"), 1.3-2.0% are late mature, and >2.0% are postmature with respect to the generation of liquid hydrocarbons.

The T_{max} of 413–435° C indicates that the samples are marginally mature (vitrinite reflectance equivalent of 0.5–0.7%). An additional Woodford Shale sample from stop 3 contains 5,823 ppm extractable organic matter (EOM) (by Soxhlet extraction using 2:1 toluene-isopropanol) (Jane Weber, unpublished data).

Vitrinite Reflectance: The Woodford Shale is the oldest rock in the Arbuckle Mountains that contains vitrinite (Wilson, 1958; Ham and others, 1973) and was deposited prior to the Middle to Late Pennsylvanian Arbuckle orogeny. Therefore, the Woodford Shale has less high-gray (recycled) vitrinite than younger rocks and records the thermal history of the Arbuckle orogeny.

Cardott and others (1990) indicated that the Woodford Shale in the Arbuckle Mountains is immature to marginally mature with respect to the generation of oil based on mean random (nonpolarized light, stationary stage, kerogen concentrate) vitrinite reflectance values of 0.35-0.77% and a weighted average of 0.54%. The reported vitrinite reflectance values of the Woodford Shale at stop 3 range from 0.3 to 0.52% (Table 3). The wide range in values is attributed to the occurrence of low-reflecting (0.25-0.47%) vitrinite-like bitumen, overlapping the vitrinite reflectance range. Jacob (1985,1989) developed a regression equation that related bitumen reflectance to vitrinite reflectance and indicated that bitumen has a reflectance lower than vitrinite when both are <1.0%. In reflected light, the bitumen in the Woodford Shale at stop 3 can have granular or nongranular texture, can be weakly fluorescing to nonfluorescing, often is translucent, and has internal reflections from pyrite. Lewan (1987) concluded that petroleum-filled fractures in the Woodford Shale at stop 3 contained exogenous oil rather than indigenous bitumen. Excluding bitumen reflectance values, the mean random (whole rock) vitrinite reflectance of the Woodford Shale at stop 3 is 0.50% (79 measurements with 0.43–0.66%) reflectance range), which suggests that the sample is marginally mature.

Vitrinite reflectance values of Woodford Shale samples from the continuous outcrop belt to the west of stop 3 are similar to the value at stop 3. The Woodford Shale at the type locality (T on Fig. 5; sec. 34, T. 2 S., R. 1 W ., ~8 mi [13 km] west of stop 3) contains abundant bitumen (1.72% EOM by Soxhlet extraction using dichloromethane) and has a mean random (whole rock) vitrinite reflectance of 0.49% (70 measurements with $0.40-0.62\%$ reflectance range) (Fig. 23). Bitumen (tar) balls are found in the Woodford Shale at the McAlester quarry in the Criner Hills (sec. 36, T. 5 S., R. 1 E.; Kirkland and others, 1992) and at the type locality.

The Woodford Shale at the Henry House Falls (HHF) quarry (H on Fig. 5) has a mean random vitrinite reflectance of 0.50% (48 measurements with $0.43-0.64\%$ reflectance range). Comer (1992, sample $OK23$ reported 0.65% R_0 at the HHF quarry. Kirkland and others (1992) described the geology and organic geochemistry of the Woodford Shale at the HHF quarry.

Hydrous Pyrolysis: Lewan (1983,1985,1987,1992) used Woodford Shale samples from this exposure for hydrous pyrolysis experiments. Hydrous pyrolysis involves isothermally heating aliquots of crushed rock in contact with liquid water at temperatures ranging 300–360°C for 72 hours. Geochemical analysis of expelled oil-like pyrolysate, bitumen, and kerogen revealed that hydrous pyrolysis simulates the natural oil-generating process. Results were related to the stages, kinetics, and indices of petroleum generation.

Lewan (1983,1985) identified four stages of petroleum generation: pre-oil-generation, incipient oil-generation (bitumenization), primary oil-generation (expulsion), and post-oil-generation (gasification). Petroleum generation follows three basic reactions: (1) the thermal decomposition of kerogen to bitumen; maximum bitumen generation occurs at the end of the incipient oil-generation stage; (2) the thermal decomposition of bitumen to oil; maximum oil generation occurs at the end of the primary oil-generation stage; and (3) the thermal decomposition of oil to gas and pyrobitumen in the post-oil-generation stage.

The Woodford Shale at stop 3 was selected for hydrous pyrolysis study because it is in the pre-oil generation stage and contains amorphous type II (oil-generating) kerogen. Using kinetic parameters, Lewan (1985) showed that primary oil generation begins at a lower thermal stress for an amorphous type II kerogen with a high organic sulfur content (e.g., 9.0% normalized by mass) such as the Phosphoria Retort Shale than for an amorphous type II kerogen with a low organic sulfur content (e.g., 5.0% normalized by mass) such as the Woodford Shale. Lewan (1985, p. 128) stated: "It is conceivable that within a kerogen its carbon-sulfur

bonds may cleave more readily to generate liquid hydrocarbons than its carbon-carbon bonds."

Lewan (1983) found that the atomic H/C ratio of amorphous type II kerogen may be a good index for the stages of petroleum generation, and that vitrinite reflectance measurement may be a good index for the magnitude of thermal stress experienced by kerogen.

Weathering: Lo and Cardott (1993) found that vitrinite reflectance of a surface grab sample was as much as 0.20% lower than that of shallow (19 ft [6 m]) corehole samples of the Woodford Shale taken along Highway 77D (NE1/4 sec. 30, T. 1 S., R. 2 E.) in the Arbuckle Mountains. Some of the low vitrinite reflectance values in Cardott and others (1990) (e.g., sample no. 2, 0.35% R_o) may be attributed to weathering. Philp and others (1992) reported the effects of weathering on the geochemistry of Woodford Shale surface samples from the Arbuckle Mountains. Surface samples were divided into two groups based on changes in hydrocarbon and stable isotopic compositions. Both groups of surface samples were weathered compared to subsurface samples. Comparison of the two groups indicated that Group I samples had lower contents of n-alkanes and tricyclic terpanes, and higher contents of $C_{21}-C_{22}$ steranes and $\alpha\beta\beta$ steranes than Group II samples, which suggests more extensive weathering by biodegradation of Group I samples.

NOTES

NOTES

STOP 1A Overturned Woodford Shale exposure along northeast side of State Route 77D, west of Interstate Route 35.

Location NH NE¼ SW¼ NE¼ Section 30, Township 1 South, Range 2 East Murray County, Oklahoma. Turner Falls Quadrangle (7.5' series) Northeast side of State Route 77D.

Introduction

Two essential parameters for gas-shale prospectivity are 1) a hydrocarbon gas source, and 2) susceptibility of the shale to fracturing (a fracturable lithology). Lacking either enough organic matter to generate commercial quantities of gas (for a given thickness) or a brittle lithology (lacking conventional permeable reservoirs within a "shale" formation, such as siltstone, sandstone, or carbonate lenses), gas-shale potential is limited.

"What is a shale?" Is it based on grain size or lithology? At the formation level, the term "shale" (e.g., Woodford Shale) is used as a descriptive term for the predominant lithology of a basic lithostratigraphic unit (North American Commission on Stratigraphic Nomenclature, 2005). Based on grain size, Neuendorf and others (2005) define shale as "A laminated, indurated rock with >67% clay-sized minerals; a claystone with fissility."

Well-log analysts tend to separate shale from sandstone/limestone/dolomite in a wellbore on the basis of geophysical logs. Using a combination of logs, portions of any given stratigraphic section will be classified as "shale" even though, upon inspection in core or thin section, the lithology may be siltstone, shale, mudstone, or claystone. By definition, siltstone is dominated by silt-size particles (relative to clay) whether laminated or not. Shale, mudstone, and claystone are dominated by clay (relative to silt). Shale is laminated; mudstone and claystone are not laminated. "Mudrock" is a generic term for all silt and clay-sized lithologies regardless of lamination. Distinctive lithofacies contain different petrophysical and

geomechanical properties that influence gas production in the subsurface. Lithologies that are easily fractured, such as silica- or carbonate-rich lithologies, are essential for shale-gas production.

The Woodford Shale (Late Devonian-Early Mississippian) is an important hydrocarbon source rock in Oklahoma. The Woodford has recently become an important gas source rock and reservoir. As a gas shale, it contains both a gas source (from oil-generative Type II Kerogen) and a brittle lithology (a silica-rich lithofacies) that is susceptible to fracturing. However, the silica-rich lithology of the Woodford Shale is not detrital quartz but primarily siliceous pelagic deposition from radiolarian tests (amorphous silica) to form an ooze on the ancient seafloor that has been very locally redistributed during early diagenesis of the Woodford Shale to form quartz and chert.

There is not a publicly accessible complete section of the Woodford Shale in the Arbuckle Mountains. Stop 2 is a complete section of the Woodford Shale on private property. Stop 1A includes the lower and middle members of the Woodford Shale and one of the best exposures of the basal erosional contact of the Woodford Shale with the underlying Hunton Group. The upper Woodford Shale member and upper contact with the Sycamore Formation is present on the east side of I-35. This stop concentrates on the Woodford Shale/Hunton contact and members, lithofacies, and thermal maturity of the Woodford Shale.

Stratigraphy

Fay (1989, p. 46) described the Woodford Shale along I-35 on the north flank of the Arbuckle Anticline (Marker No. 36). The uppermost formations of the Hunton Group (Frisco and Bois d'Arc) are missing at this location.

Woodford Shale (274 ft thick) described from (1) upper contact with Sycamore Limestone to (5) lower contact with Hunton Group Haragan Formation.

- 1. Shale and siltstone, gray to greenish-gray, pyritic, glauconitic near middle, thin-bedded, platy, moderately to weakly indurated, with many 1- to 2-in. phosphatic nodules in basal 2 ft…………………….…………………....6.0 ft
- 2. Shale, dark-gray, thin-bedded, platy, weakly indurated, well-indurated where cherty, with many 1- to 3-in. beds of light-gray to tan chert and many 1- to 2-in. phosphatic nodules; partly covered in lower 10 ft; eroding into a slope………………….……….…………………….28.0 ft
- 3. Shale, dark-gray, thin-bedded, platy, weakly indurated, crinkly-bedded, alternating with 1- to 2-in. beds of gray to tan moderately to well-indurated chert, with 2- to 3-in. pyrite nodules in lower 60 ft; covered from 60 to 75 ft below top; eroding into a slope; the upper 160 ft was measured on the east side of east lane to Station 2675 + 75' and then extrapolated to west side of west lane to Station 2679 + 50' at top of the lower 67 ft………………………………………227.0 ft
- 4. Shale, greenish-gray to dark-gray, mottled lavender, cherty, thin-bedded, platy, weakly indurated……………………..………………….11.0 ft
- 5. Shale, greenish-gray to lavender, glauconitic, well-indurated, conglomeratic, with small angular pieces of tan to greenishgray arenaceous limestone; Station 2677 + 75' at unconformable contact with underlying Haragan Formation, west side, west lane………………………………….…………......2.0 ft

Woodford Shale strike N70°W, dip 78° SW (overturned)

The Woodford Shale at Stop 1A is north of the Washita Valley Fault and currently resides on the craton-side of the southern Oklahoma aulacogen. The Woodford Shale has been divided into three informal members based on micropaleontology (Urban, 1960), chemistry (Sullivan, 1985), and electric log response (Hester et al., 1990). Recently, Paxton and colleagues have identified three members in the Woodford Shale based on spectral gamma-ray (SGR) readings taken every 6 in. over a 231 ft complete section of the Woodford Shale in the southern Arbuckles. The southern Arbuckles section will be discussed during Stop 2.

An SGR profile was constructed for the State Route 77D (Stop 1A) exposure. The 77D SGR profile begins in the upper 2.5 ft of the Hunton Group (Haragan Formation) and transitions abruptly upward into about 3.5 ft of shale, siltstone, and very-fined grained greenish-gray sandstone before giving way to a siliceous and organic-rich Woodford Shale-type lithology. The upper bounding surface of the limestone, representing the Acadian Unconformity, is discolored by iron-staining and broken into large blocks that appear to honor the orientation of the regional joint sets. The surfaces of the joints in outcrop are coated with angular pieces of carbonate-cemented gravel that represent a localized carbonate-clast conglomerate associated with development of the unconformity surface.

The transitional shale (between the Hunton and Woodford) is gray, finely laminated, and likely represents a proto-Woodford Shale lithology. The lithology reflects changing conditions in the depocenter as the Woodford sea encroaches on the underlying unconformity surface. The transitional shale exhibits smooth joint faces typical of a Woodford Shale lithology. The thin intervals of siltstone and sandstone contain fragments of nodules (probably diagenetic phosphate) and internal casts of invertebrate fossils. Though not verified by xray diffraction analysis, the siltstone and veryfine grained greenish-gray sandstone appear to contain glauconite. Collectively, the siltstone and very-fine grained sandstone appear to represent a transgressive-lag surface. This surface is better preserved on the north side of the Henry House Creek shale quarry. Here

Total gamma-ray response across the contact of the Hunton Group carbonate (Haragan Formation, to the right or south) and the overlying Woodford Shale (to the left or north). The beds at this location are slightly overturned. The portion of the stratigraphic section between the green arrows is transitional section between the top Hunton unconformity and the Woodford Shale. The transitional section contains shale, siltstone, and very fine grained glauconitic sandstone.

at Stop 1A, the details of the layering in the lithologic transition between the Hunton and Woodford is slightly confounded by structural development of the Arbuckle Mountains. The structuring has resulted in some ductile flow of these transitional lithologies sandwiched between the rigid Hunton Group limestone and the siliceous Woodford Shale. The gamma-ray response across the basal contact of the Woodford with the Hunton is provided in an accompanying figure. Rotate the field quide image of the basal part of the section to help visualize the vertical gamma-ray profile through this portion of the outcrop.

The SGR data indicate that the transition between the Hunton Group and the lower basal Woodford Shale is potassium and thorium-rich. An elevated potassium and thorium signature at the base of Woodford provides reasonable evidence that some of the sediment making up for the base of the Woodford Shale was derived from a relatively proximal landmass and/ or was derived from a residuum of sediment inherited from the top of the Acadian Unconformity surface.

Significant elevated uranium in the lower part of the Woodford occurs at SGR measurement point 66. This position is indicated on the outcrop face for your inspection. Other significant uranium kicks are indicated in the accompanying graphics. In addition to point 66, these measurement points include, moving vertically up-section, measurement points 142, 200, and 230. The strong GR-response at these points confirms that the Woodford Shale was being deposited under conditions of slow sedimentation and that the chemistry of the pore-fluids internal to the Woodford were chemically-reducing (by virtue of the bound uranium). The measurement points also reflect positions in the vertical section where gamma-ray kicks in subsurface logs could be used to correlate and subdivide the Woodford stratigraphic section into packages for the purpose of mapping paleogeography. Most of the strong gamma-ray kicks in the profiles are related to the occurrence of uranium. Some of the elevated readings in gamma ray are attributable to potas-

sium and thorium. In most cases, the high gamma-ray kicks correspond to portions of the 77D Woodford Shale section that is laminated, fissile and less silica-rich than the surrounding lithofacies (as demonstrated in the accompanying photograph of position 230).

outcrop. Note the fissile, organic-rich shale (arrow). Remember that outcrop. Note the fissile, organic-rich shale (arrow). Remember that
the beds are slightly overturned (up is to the left). Location of gamma-ray measurement position 200 on the SR 77D Location of gamma-ray measurement position 200 on the SR 77D the beds are slightly overturned (up is to the left).

1000

crop. Note the measurements immediately adjacent to point 230 in the crop. Note the measurements immediately adjacent to point 230 in the relative to the siliceous or cherty beds located immediately below and relative to the siliceous or cherty beds located immediately below and chart to the right also have elevated gamma-ray response. This two-ft chart to the right also have elevated gamma-ray response. This two-ft thick portion of the outcrop exhibits a greater degree of shale fissility thick portion of the outcrop exhibits a greater degree of shale fissility above (arrows).above (arrows)

 $\frac{6}{3}$

Attempt is made to conduct a lithostratigraphic correlation of the vertical profiles from State Route 77D with the spillway at the Lake Classen YMCA Camp (see work of Aufill, 2007). The accompanying graphics are color coded to indicate the positions of correlative gamma-ray responses between the two sections. In some respects, the correlations appear straight forward, though one could debate the details and relevance of the correlation. Significantly, if the gamma-ray profile is expressed in terms of potassium and thorium only (minus the uranium signal), the ease of correlation improves greatly (see accompanying figure).

The upper informal member of the Woodford is not present at State Route 77D or at the Lake Classen Spillway location. The upper informal member, containing phosphate nodules and contact with the overlying Sycamore Limestone, is present on the east side of I-35

about one-quarter mile to the north of the State Route 77D location.

Boghead Coal Lens

Coal is defined as having less than 50% mineral matter by weight (ash) or more than 70% organic matter by volume (Schopf, 1956). There are two basic types of coal: banded (humic) coal (formed from peat in swamps) and nonbanded (sapropelic) coal, dominated by spores (cannel coal) or algae (boghead coal) formed primarily in freshwater lakes. Most commercial coals are banded (humic) coals. Boghead coals are rare in the geologic record. The macerals alginite and bituminite are the characteristic organic microscopic constituents of boghead coals (Taylor and others, 1998).

Bituminite, an amorphous liptinite maceral of autochthonous origin, is the characteristic groundmass maceral of sapropelic coals often associated with the macerals alginite and liptodetrinite (ICCP, 1975, 1993). Bituminite is formed from the degradation of algae, faunal plankton, and bacteria (Taylor and others, 1991; ICCP, 1993). Bituminite is known to occur in rocks other than coal, especially as thin layers in marine and lacustrine hydrocarbon source rocks (ICCP, 1993).

A thin (1 cm thick) boghead coal lens (OPL 1300e) was identified during petrographic examination from a grab sample from the lower member of the Woodford Shale. The exact location from which the grab sample was taken has not been determined. The marine algae that occurs in the Woodford Shale is *Tasmanites*. The organic groundmass of the boghead coal is the maceral bituminite. Bituminite

(also known as amorphous organic matter) is the predominate type of organic matter in the Woodford Shale (45-95%; Senftle, 1989; Cardott and Chaplin, 1993; Ascent Energy, 2005).

A 3-ft-thick zone in the Woodford Shale lower member above the Woodford-Hunton contact is a boghead shale containing abundant *Tasmanites* alginite and some bituminite. The boghead coal sample may have come from this interval.

Photograph of boghead coal grab sample in Woodford Shale lower member.

Photomicrograph of marine boghead coal lens in Woodford Shale showing *Tasmanites* **alginite in bituminite matrix (200X magnifi cation; refl ected white light; oil immersion; fi eld width is 320 μ).**

Photograph of boghead shale in Woodford Shale lower member above Woodford-Hunton contact.

Close-up photograph of boghead shale in Woodford Shale lower member.

Photomicrograph of vitrinite from Woodford Shale at Stop 1A (0.53% Ro; 500X magnifi cation; refl ected white light; oil immersion; fi eld width is 140 μ).

Weathering

The organic matter in coal begins to weather immediately after it is exposed to oxygen, demonstrated by changes in petrographic properties and chemical parameters. The severity of weathering depends primarily on the length of time of exposure, temperature (e.g., chemical weathering essentially stops at temperatures below freezing), and climate (arid to humid). Marchioni (1983) showed that coal weathering is present to a depth of about 3 to 10 m (10 to 33 ft) in outcrop depending on local weathering conditions.

The term **maceral** refers to microscopically recognizable organic matter. The **vitrinite** maceral group, derived from woody organic matter from vascular plants (tracheophyte; having a well-developed conductive system of xylem and phloem), is one of three maceral groups (the other two being liptinite and inertinite). Vitrinite reflectance, a thermal maturity indicator, is a measurement of the percentage of light reflected off the vitrinite maceral at 500X magnification in oil immersion.

In addition to investigating the effects of weathering on coal, Lo and Cardott (1995) studied the effects of weathering on organic matter in a shallow core of the lower member of the Woodford Shale from this exposure. It was estimated that about 20 ft of rock was removed from above this exposure during road construction. Weathering was detected by chemistry and petrography in only a surface grab sample from this exposure. The mean random vitrinite-reflectance value of the weathered surface sample was 0.35% Ro. Chemistry and petrography indicated the remaining core samples to a depth of 18 ft were not weathered. Indurated shale in the core protected vitrinite from weathering. Mean random vit-

from State Route 77D west of I-35.

rinite reflectance values from kerogen-concentrate pellets of twenty-two samples from depths of 0.25 to 18 ft ranged from 0.46% to 0.55% Ro with an average of 0.51% Ro. TOC content ranged from 4.87 to 12.60 wt%.

Thermal Maturity

Based on a master's thesis by Metcalf (1985) using kerogen concentrate pellets, Cardott and others (1990) indicated a mean random vitrinite reflectance of 0.35% and 0.42% Ro based on 50 measurements each from two samples from this location. The mean random vitrinite reflectance of all Woodford Shale outcrops from the Arbuckle Mountains ranged from 0.35% to 0.77% Ro, with an average of 0.54% Ro based on 14 to 98 measurements per sample with an average of 46 measurements. The low mean random vitrinite reflectance values of 0.35% and 0.42% Ro from this location are due to either weathering or including lower-reflecting vitrinite-like bitumen with the vitrinite reflectance values (Cardott and Chaplin, 1993, p. 29).

Urban (1960) indicated that the lower member of the Woodford Shale was deposited nearshore marine. Experience indicates that the lower member of the Woodford Shale has more vitrinite than the middle or upper members. Based on this information, grab samples of the Woodford Shale lower member were collected from this exposure for the vitrinite-reflectance analysis. The mean random vitrinite reflec**tance** of several grab samples from the lower member of the Woodford Shale is **0.53% Ro** based on 31 measurements of 0.45-0.67% Ro from whole-rock pellets (OGS Organic Petrography Laboratory [OPL] sample OPL 1300). Vitrinite reflectance values of unweathered Woodford Shale samples indicate that the Woodford Shale is marginally to early mature with respect to oil generation in the Arbuckle Mountains.

Photomicrograph of smooth-textured, vitrinite-like bitumen (0.35% Ro; 500X magnifi cation; refl ected white light; oil immersion; fi eld width is 140 μ).

Bitumen (defined as organic matter that is soluble in organic solvents) is very common in the Woodford Shale. Landis and Castano (1994) correlated smooth-textured, pre-oil bitumen reflectance to vitrinite reflectance. The mean random pre-oil bitumen reflectance of the Woodford Shale from this exposure is 0.32% Ro based on 3 measurements of smooth-textured bitumen from 0.20-0.40% Ro. Using a regression equation from Landis and Castano (1994), modified by Castano in 1995 (VRE = $[$ mean random bitumen reflectance of smooth-textured bitumen + 0.358]/1.05), the calculated vitrinite-reflectance equivalent is 0.65% Ro.

Fluorescence color of liptinite macerals (e.g., sporinite, cutinite, resinite, and alginite from spores, cuticles, resin, and algae) is a qualitative thermal maturity indicator. Fluorescence colors change from green to yellow to orange with increasing thermal maturity in the oil window. At the same thermal maturity, the fluorescent colors of the different liptinite macerals are often different (e.g., sporinite may have a yellow fluorescence in the same sample

that the fluorinite maceral has a green fluorescence; Crelling and Bensley, 1984). Loss of fluorescence (e.g., no longer measurable) occurs by the end of the oil window (equivalent to around 1.3% vitrinite reflectance) for most liptinite macerals (Taylor and others, 1998, p. 123). One of the most easily recognized types of structured liptinite macerals in the Woodford Shale is alginite (from the marine algae *Tasmanites*). The fl uorescence of *Tasmanites* alginite from this locality is green, which indicates a marginally mature to early thermal maturity. Fluorescence disappears early in Tasmanites by around 0.9-1.0% vitrinite reflectance (Taylor and others, 1998, p. 137).

Based on vitrinite reflectance, bitumen reflectance, and fluorescence of *Tasmanites* alginite, the thermal maturity of the Woodford Shale at this locality is **marginally mature to early mature** (e.g., beginning of the oil window).

STOP 1B Overturned Woodford Shale exposure along north side of State Route 77D, east of Interstate Route 35.

Location C NW¼ SE¼ NE¼ Section 30, Township 1 South, Range 2 East Murray County, Oklahoma. Turner Falls Quadrangle (7.5' series) North side of State Route 77D.

Introduction

This location, on the north side of the highway, highlights the fractures and some fault surfaces present on the lower bedding planes in the lower Woodford. This portion of the Woodford is slightly overturned, very siliceous, and was highly susceptible to fracturing during structural deformation.

Comments on Fractures and Faults

The basal surfaces of the bedding planes at this location are cut by numerous fractures, including joint sets and some faults. In some cases, the orientation and fracture spacing appears to vary with the lithology. Some of the bedding planes exhibit an undulatory surface, also related to structural deformation. Locally, fractures associated with the undulatory surfaces are also deformed, suggesting the rocks have experienced several stages of structural defor-

Photograph of contorted fractures in the overturned Woodford Shale lower member at State Route 77D.

mation. Some of the low relief folds or undulating surfaces terminate in faults. The displacement along the fault planes has resulted in the development of localized fault gouge. Some of the fault gouge appears to be hydrocarbon saturated. Many of the joints and joint

sets have common structural orientations related to the grain of the Arbuckle Mountains.

Woodford Shale at this location strikes N70ºW, dip 68ºSW (overturned).

Note even fracture spacing and orientation.

Fractures in siliceous shale.

Note orientation and spacing of fractures in siliceous shale (bottom) and chert (top).

Fractures in Woodford Shale chert beds in State Route 77D exposure. Note hammer for scale.

Fault in Woodford Shale at State Route 77D exposure.

Close-up view of fault gouge in Woodford Shale at State Route 77D exposure.

Thermal Maturity

Cardott and others (1990) indicated a mean random vitrinite reflectance of 0.53% and 0.59% Ro for this location measured from kerogen-concentrate pellets. A grab sample of well-indurated siliceous shale from this exposure indicated a mean random **vitrinite reflectance of 0.58% Ro** based on 26 measurements from 0.48-0.72% Ro from whole-rock pellets (OPL 1301). The fluorescence of abundant *Tasmanites* alginite from this locality is green. Some of the *Tasmanites* alginite in this sample

are replaced by quartz. Vitrinite reflectance and *Tasmanites* fluorescence indicates a marginally mature to early thermal maturity for the Woodford Shale from this exposure.

Vitrinite-refl ectance histogram of Woodford Shale from State Route 77D east of I-35.

Note: This field location is private property. The field site is not accessible to the general public after completion of the October 23, 2008 field trip.

Introduction

The Woodford Shale at Stop 2 is south of the Washita Valley Fault and was deposited in the southern Oklahoma aulacogen. To date, this location may represent one of the best preserved (and complete) sections of the Upper Devonian – Lower Mississippian black shale lithofacies in the world. Past work at this field site focused on exposures on the floor of the Henry House Falls Quarry, located just to the east of Henry House Creek and the north-south ranch road.

Stratigraphy

The stratigraphy and lithofacies in the quarry are well described by Kirkland and others (1992). Hass and Huddle (1965) measured the creek section and also described the conodont biostratigraphy (the classic Hass "A" biostratigraphic section). Over (1992) determined the conodont biostratigraphy from the basal part of the section along the creek. Schwartzapfel and Holdsworth (1996) described the occurrence of radiolarians in the highwall exposure located to the south of the quarry.

Krystyniak (2005) was the first to measure the gamma-ray character of the exposure along the west side of Henry House Creek. Magnetic susceptibility of the outcrop and association with gamma-ray response was evaluated by Aufill (2007).

For purposes of description, the resistant beds (siliceous and carbonate) at this locality were identified and labeled from the base of the Woodford section to the top of the outcrop using a permanent marker. In turn, the thickness of each resistant bed was measured. The thickness of each intervening fissile interval was also measured. Spectral gamma-ray readings (K, U, and Th) were collected every 15 cm (6 in.) on the outcrop face to yield about 462 sets of measurements from base to top. Samples for laboratory analyses were taken throughout the section based on the character of the gamma-ray response and the variations in lithology.

The Henry House Creek exposure is about 231 ft in vertical thickness. The unit contains three informal members (as defined by Lambert, 1993, for Kansas and northwestern Oklahoma) and up to eleven high-resolution intervals based on gamma-ray response.

The shale lithofacies are organic-rich throughout and either fissile or siliceous (chert-like). All lithofacies are finely laminated and no obvious evidence for bioturbation at this locality has been noted to date. Pyrite occurs throughout the section, though a few thin (cm-thick) intervals are enriched in pyrite, particularly in the fissile (middle) part of the section. The upper part of the section contains an abundance of spherical phosphate nodules. Most of these nodules contain porosity. Large dolomite concretions and/or beds occur at three locations in the section. The dolomite beds near the top of the section are saturated with liquid hydrocarbon. In all cases, the dolomite is very finely crystalline, nonporous, and very dense (see Krystyniak, 2005).

On the north end of the exposure, the contact of the Woodford with the underlying Hunton Group carbonates (Bois de Arc Formation at this locality) is hidden in the tributary creek bed that joins Henry House Creek from the west. The contact may be a subtle angular unconformity on the regional scale. Locally, the contact appears to be a disconformity surface because the dip on the underlying beds is not discernible. In the subsurface, the Hunton Group carbonates contain karst and organized erosional patterns on the unconformity surface that appear to be fluvial in origin. The Hunton Group carbonates produce significant volumes of oil and gas. On a continental scale, this unconformity is referred to as the Acadian Unconformity.

From base to top, the Henry House Creek outcrop contains about 940 discrete beds. Fissile beds make up about 50% of this total (466 beds). Siliceous beds constitute about 49% of the total beds (460 beds). About 1% of the beds are carbonate, mostly dolomite (12 beds). Fissile beds range from a fraction of an inch to about 5.4 ft in thickness. Siliceous beds range from about 0.125 in. to 4.75 in. in thickness. The mean thickness of the siliceous and fissile beds is 1.3 and 4.5 in. respectively. In terms of gross interval thickness, siliceous beds (which are brittle) make up a progressively greater proportion of the total stratigraphic section from gamma-ray marker E to marker G1.

The basal portion of the section at this location contains alternating intervals of fissile (85%) and siliceous shale (15%). The thickness of the lower informal member is 52 ft (15.8 meters) and extends from gamma-ray marker Sub-A to the base of gamma-ray marker C. The siliceous layers in this lower member contain radiolarians that are visible in some of the hand samples. Some of the siliceous layers contain inclusions of mudrock at the center of the siliceous beds that are a few centimeters in diameter. These mudrock occurrences, isolated within siliceous beds, appear to be portions of the original sediment that were not completely silicified. The mudrock inclusions preserved within the siliceous beds have a slight pinkish color, suggesting the lower part of the Woodford may have been deposited initially as Devonian red mud. Some of the bedding planes in this lower portion of the section also have a smooth feel to the touch that is reminiscent of kaolinite clay.

The first major gamma-ray kick at the base of the section is located about 10-15 ft above the contact with the underlying Hunton carbonates. The shale interval between the underlying Hunton carbonate and this first major gamma-ray response (A) is relatively K and Th rich according to the spectral data. This K and Th portion of the section is also the interval that appears to contain petrified wood (Callyxylon, see Arnold, 1957). The organic matter type in the lower member of the Woodford is woody-coaly according to Lambert (1993). In total, the observations for the base of the Woodford section along Henry House Creek are suggestive of a relatively rapid transgression of the sea across an erosional surface that was actively accumulating sediment from an adjacent continental land mass. The landmass was populated with plants.

The middle portion of the section is dominantly fissile (92%) with a few, poorly developed and thin siliceous beds. This informal member is 95 ft (29 meters) in thickness. This interval extends from the base of gamma-ray marker C

Vertical gamma-ray profi les for the Henry House Creek section. The major gamma-ray markers noted above will be examined along the length of the outcrop. Total organic carbon is highest at points A, 1, 2, and at G. The upper member is dominated by bedded siliceous shale that is chert (or cherty) in some cases.

up to the top of gamma-ray marker #2. Strong gamma-ray markers D, E, and marker #1 also occur in this interval. Based on resistance to erosion as exhibited by the small rapids in the stream, the silica content in the shale is beginning to increase between gamma-ray markers E and #1. Gamma-ray marker #1 and #2 contain the greatest concentrations of U in the outcrop (107 and 112 ppm U respectively). In terms of spectral-gamma ray, gamma-ray marker #1 contains a relatively large volume of K and Th in comparison to the immediately underlying units. The K and Th in gamma-ray marker #1 is similar to the abundance of K and Th present

in the interval just below gamma-ray marker A, located at the base of the outcrop. Perhaps the increase in K and Th is related to a tectonic uplift in the sediment source area or perhaps the development of a wetter climate (?) in the hinterland. In contrast, gamma-ray marker #2 displays a precipitous drop in K and Th abundance relative to underlying units.

The absence of siliceous beds in the middle member has a direct bearing on the mass wasting of the outcrop. When present, the siliceous beds tend to reinforce the integrity of the outcrop and help to hold the fissile beds in place.

In the absence of the siliceous beds, large subvertical tension fractures have developed in the outcrop face of the intervals dominated by fissile beds.

The upper portion of the Woodford at this locality (84 ft or 25.5 meters in thickness) contains siliceous beds $(55%)$, fissile beds $(44%)$, and a few dolomite layers (1%). This informal member is defined by the top of gamma-ray marker #2 up through the contact with the overlying lower Mississippian limestone and shale intervals (gamma-ray markers F, G1, and G inclusive). The occurrence and thickness of siliceous beds increases dramatically above gamma-ray marker #2. This change in lithology is one of the most dramatic in the physical appearance of the outcrop. The two strong eastern deflections in the stream drainage that occur in this reach of Henry House Creek are directly related to the abundance of siliceous beds that occur in the upper part of the Woodford Shale. The upper contact of the Woodford can be located near the top of the outcrop (coincident with a vegetation change). Well developed Sycamore Limestone is present in the creek about 150 ft to the south of the last occurrence of a Woodford Shale siliceous bed.

Three distinct beds of dense dolomite occur in the upper member. These beds increase in thickness up-section. The dolomite is finely laminated and saturated with hydrocarbon. The dolomite weathers to a characteristic dull white color. The upper most dolomite occurs just below the position in the outcrop where the phosphate nodules become most abundant.

Spherical phosphate nodules are locally abundant in the lower upper half of this informal member, just above the dolomite beds. Based on compaction of layers both in and around the phosphate nodules, growth of the nodules appears to have occurred shallow in burial. In some cases, the bedding surfaces that bound the nodule-rich intervals are curved and wavy, appearing to exhibit evidence for wave energy. On the other hand, the layering also exhibits characteristics of "pinch and swell" and

may suggest that relief on the nodules near the sediment-water interface was locally significant enough to influence sedimentation around the nodules. The phosphate nodules are not noticeably enriched in U.

The spectral character of the gamma-ray is diminished in both K and Th from marker #1 to the top of the outcrop. In contrast, the abundance of U in the upper part of the section stays relatively constant up through marker G1. The mutual relations of the spectral response may suggest that sedimentation rate remained relatively constant (as gauged by the U) while terrestrial sediment provenance (as recorded by K and Th) either changed or became more distant. A logical explanation would be that marine flooding of the craton in this interval of time may have sequestered sediment further back toward the hinterland. An alternative explanation is that the K and Th have been diluted by the addition of progressively greater volumes of silica (from radiolarians that now form a significant volume of the siliceous shale).

Range of total organic carbon (TOC) for the major gamma-ray markers at the Henry House Creek section. The TOC is highest at the base, top, and at major gamma-ray kicks #1 and #2. TOC and gamma-ray response are statistically associated but the relationship is not strong.

Frequency distributions of bulk density and total organic carbon for the fi ssile and siliceous (cherty) beds at Henry House Creek. The fissile shale has lower bulk density and higher total organic carbon relative to the siliceous or chertier beds. The lower total organic carbon in the siliceous beds is probably a consequence of dilution from radiolarian sedimentation.

Bulk Density and TOC

Lake Classen and along SR 77D. Note the high readings of potassium and thorium at the base of the section at all three loca-**Vertical gamma-ray profi les for potassium and thorium (minus uranium) from Lake Classen, SR 77D, and Henry House Creek.** Vertical gamma-ray profiles for potassium and thorium (minus uranium) from Lake Classen, SR 77D, and Henry House Creek. **Lake Classen and along SR 77D. Note the high readings of potassium and thorium at the base of the section at all three loca-**The contact with the underlying Hunton is not visible at Henry House Creek. In contrast, the Hunton contact is visible at **The contact with the underlying Hunton is not visible at Henry House Creek. In contrast, the Hunton contact is visible at tions.**

histogram of Woodford Shale from Henry House Falls Quarry.

Thermal Maturity

The mean random **vitrinite reflectance** of the Woodford Shale at the Henry House Falls Quarry is **0.51% Ro** based on 30 measurements from 0.44-0.62% Ro from whole-rock pellets (OPL 1017). The mean random smooth-textured, pre-oil bitumen reflectance is 0.35% Ro based on 19 measurements from 0.24-0.46% Ro, indicating a calculated vitrinite-reflectance equivalent of 0.67% Ro. The fluorescence of abundant *Tasmanites* alginite from this locality is green. Vitrinite reflectance, bitumen reflectance, and *Tasmanites* fluorescence indicates a **marginally mature to early thermal maturity** for the Woodford Shale from this outcrop.

STOP 3 Woodford Shale exposed in McAlister Cemetery Quarry in the Criner Hills. Location SW¼ Section 36, Township 5 South, Range 1 East Carter County, Oklahoma. Overbrook Quadrangle (7.5' series)

View to the southeast of middle (center right) and upper (left) members of the Woodford Shale.

Introduction

This quarry is a source of road aggregate for the Carter County and the City of Ardmore. The Woodford exposed in the heart of this quarry is similar in gross physical appearance to the shale exposed in the floor of the Henry House Creek Quarry. However, upon closer inspection, the details of the Woodford exposed throughout this quarry are quite different than observed along the west side of Henry House Creek.

The Woodford Shale lithofacies exposed in the McAlister Cemetery Quarry were described by Kirkland and others (1992). Schwartzapfel and Holdsworth (1996) described the radiolarian biostratigraphy for this locality. The conodont biostratigraphy is summarized in Over (2002).

Gamma-ray profi le for the quarry fl oor at McAlister Cemetery Quarry. The base of the section (as labeled in the distance) is approximately 30 ft from the contact with the underlying Hunton Group carbonates (Haragan Formation). This portion of the quarry fl oor represents the middle member of the Woodford and is dominantly fissile shale.

Stratigraphy

Kirkland and others (1992) report that a complete Woodford section is present in the quarry (365 ft or 111 meters). The Woodford Shale contact at the base of the quarry is with the underlying Hunton Group carbonates (Haragan Formation). The limestone blocks at the base of the section (southwest side of quarry) appear to be in place, though excavation has beveled out the Woodford Shale and the contact is not directly visible. The base of the Woodford at this locality appears to be dominated by fissile shale to the exclusion of siliceous shale. In contrast, the base of the Woodford along Henry House Creek has 15% siliceous shale.

Kirkland and others (1992, p. 47) reported a thin (0.5 ft thick) dolomite bed extending about 8 ft along strike near the top of the zone of phosphate nodules at the I-35 roadcut. A dolomite bed in the same stratigraphic

position also occurs at the Henry House Falls Quarry (stop 2) and McAlister Cemetery Quarry (stop 3).

Krystyniak (2005) was the first to collect spectral gamma-ray data at this location. Krystyniak's gamma-ray profile was compiled with data from the quarry floor. The character of the gamma-ray profile appears similar to the profile through the fissile middle member at Henry House Creek. Krystyniak's work does not include gamma-ray measurements from the base of the section or from the siliceous beds in the highwall. Spectral gamma-ray data collection from the lower and upper part of the Woodford at this location is in progress by Paxton and others. Work to date suggests that the strong gamma-ray double peak noted at Henry House Creek is present here in the McAlister Cemetery Quarry.

Attempt to correlate total gamma-ray response patterns in the McAlister Cemetery Quarry with the Woodford Shale profi le from Henry House Creek located about 20 miles to the north of this fi eld stop.

Attempt to correlate potassium and thorium gamma-ray response patterns in the McAlister Cemetery Quarry with the Woodford Shale profi le from Henry House Creek located about 20 miles to the north of this fi eld stop. Uranium contribution to gamma-ray response is not included in these profi les.

View to the northeast of Woodford Shale upper member containing dolomite beds, siliceous beds, and abundant phosphate nodules.

Aside from the characteristic gamma-ray signature, this quarry contains two significant features not observed in our last stop at Henry House Creek: (1) an upper member that is very siliceous with extremely abundant and well developed nodules and concretions and (2) the occurrence of bitumen concentrations along fractures.

The quarry highwall contains abundant siliceous shale, phosphate nodules, dolomite, and some chert. From a lithostratigraphic point of view, the siliceous upper unit appears to be a lateral stratigraphic equivalent to the upper member at Henry House Creek. In contrast to Henry House Creek, however, the degree of primary silicification (assumed from documented occurrence of radiolarians) and the abundance of phosphate nodules suggest that this portion of the ancient seafloor was overlain by a water column with extremely high biologic activity (high primary productivity).

Based on density of siliceous hand samples, the shale contains abundant microporosity (for housing natural gas). The phosphate nodules are also highly microporous (based on thin sections). The white coloration of this portion of the Woodford Shale is attributed to "bleaching" during the Pleistocene (according to Kirkland and others, 1992). However, their analysis also indicates that the TOC of this interval is high despite the bleaching. Consequently, the white coloration may be a by-product of oxidized hydrocarbon.

Siliceous shale in the upper member of the Woodford Shale. Nodules (arrows) at this location are very abundant and quite large.

Bitumen (degraded liquid hydrocarbon) occurs in the fracture system of the upper part of the middle member. Bitumen in this geographic vicinity has been described by Lewan (1987). According to Lewan (1987), the Woodford Shale in this location is in a pre-oil generative state. Consequently, bitumen recognized in fractures of source rock may not be related to primary migration but instead to secondary migration of hydrocarbon. In the case of secondary migration, the oil in the fractures today would have migrated into the fracture system of the shale from deeper and more thermally mature hydrocarbon source rock. Consequently, the bitumen in the fractures is a consequence of secondary migration and not primary migration. However, careful examination of the bitumen occurrence in the fractures of the Woodford in this location is suggestive of pri-

mary migration. The tapering of the fractures and the rhythmic co-occurrence of bitumen with the fractures over several vertical feet may provide direct evidence for very local primary migration of hydrocarbon. From a lithostratigraphic point of view, this hydrocarbon occurrence is about 20 ft below the strong double gamma-ray peaks (gamma-ray markers #1 and #2) observed both here and along Henry House Creek.

The McAlister Cemetery Quarry is about 20 miles from the Henry House Creek Woodford Shale exposure. Comparison of the two localities provides evidence for significant lateral facies changes in the Woodford Shale. Supporting evidences include: 1) the absence of siliceous shale at the base of the Woodford in this quarry relative to Henry House Creek

Concentric phosphate nodule in the upper Woodford. Note contortion of laminations around the nodule suggesting nodules formed before the Woodford Shale was fully compacted. Thin-section inset demonstrates that the nodules contain abundant porosity (blue dye indicating pore spaces).

and 2) the abundance of siliceous shale and phosphate nodules in the upper member of the Woodford here at McAlister Cemetery Quarry versus that observed at Henry House Creek. These data suggest that the internal properties of gas shale within predefined lithostratigraphic units can change significantly over relatively short distances. Significant changes in shale properties will have a major impact on gas shale resource assessments and exploration/production strategies.

As a point of interest, the folded portion of the upper siliceous member exposed in the highwall of the McAlister Cemetery Quarry is similar in appearance to the chert-rich Miocene Monterey Formation of coastal California (image of the Monterey and G.K. Gilbert for scale included below).

Folding and faulting of shale in the Woodford Shale, McAlister Cemetery Quarry (left). The inset photo on the right is an image
of G.K. Gilbert standing on an exposure of vertical Monterey Formation chert in coastal Califo **Folding and faulting of shale in the Woodford Shale, McAlister Cemetery Quarry (left). The inset photo on the right is an image of G.K. Gilbert standing on an exposure of vertical Monterey Formation chert in coastal California.**

Vitrinite-reflectance histogram of Woodford Shale from McAlister Cemetery Quarry

Thermal Maturity

The mean random vitrinite reflectance of the Woodford Shale from the McAlister Cemetery Quarry is **0.54% Ro** based on 41 measurements from 0.42-0.65% Ro from whole rock pellets (OPL 1302). Most of the vitrinite clasts were rounded suggesting considerable abrasion during transport. Smooth-textured bitumen re-

flectance of 0.29% Ro (based on 6 measurements from the wide range of 0.16-0.43% Ro) indicates a vitrinite reflectance equivalent of 0.62% Ro. Green fluorescence of abundant Tas*manites* alginite agrees with the **marginally mature to early thermal maturity** (e.g., beginning of the oil window).

Photomicrograph of rounded vitrinite (0.52% Ro) from Woodford Shale, McAlister Cemetery Quarry (500X magnifi cation; refl ected white light; oil immersion; fi eld width is 140 μ).

Photomicrograph of smooth-textured pre-oil solid bitumen (0.43% Ro; 500X magnifi cation; refl ected white light; oil immersion; fi eld width is 140 μ).

Photomicrograph of *Tasmanites* **alginite (200X magnifi cation; refl ected white light; oil immersion; fi eld width is 320 μ).**

Photograph of tar balls on bedding-plane surface of middle Woodford Shale.

Tar Balls

Kirkland and others (1992) described insoluble tar balls in a <10 ft thick zone about 140 ft from the base of the Woodford Shale at this location. They speculated that the tar balls represent the altered product of oil from a submarine oil seep generated by an older mature source rock and deposited during Woodford Shale sedimentation.

Solid Hydrocarbon Fracture Filling

Curiale (1986) classified solid bitumen in a genetic classification as pre-oil or post-oil solid

bitumen (also referred to as solid hydrocarbons by Landis and Castano, 1994). Pre-oil bitumen occurs as primary bitumen within a hydrocarbon source rock ("early-generation products of rich source rocks, probably extruded from their sources as a very viscous fluid, and migrated the minimum distance necessary to reach fractures and voids in the rock", Curiale, 1986, p. 576), whereas post-oil bitumen is a solid hydrocarbon formed as an alteration product of a once-liquid crude oil (formed from the nearsurface, low-temperature alteration of crude oil by biodegradation, water-washing, and devolatilization). Most oil is generated from pre-oil bitumen (Lewan, 1983, 1987). Post-

Close-up photograph of tar ball on bedding-plane surface of middle Woodford Shale.

oil solid bitumen in the Ouachita Mountains, classified as grahamite and impsonite in the generic classification of Abraham (1960), occur as fracture-filling vein deposits. Under the microscope at high magnification (500X) these deposits normally appear homogeneous with a uniform bitumen reflectance (Cardott and others, 1993).

An exposure of the middle member of the Woodford Shale at this locality contains fractures filled with a post-oil solid bitumen (OPL 1283). The bitumen-filled fractures extend a short distance $(1 cm)$ into the shale from the bedding plane.

Photograph looking northwest at exposure of bitumen-fi lled fractures in Woodford Shale middle member in McAlister Cemetery Quarry.

Close-up photograph of post-oil solid bitumen-fi lled fractures in Woodford Shale middle member in McAlister Cemetery Quarry.

Close-up photograph of Woodford Shale middle member in McAlister Cemetery Quarry showing limited depth of solid bitumen-fi lled fractures.

Photomicrograph of minerals within bitumen showing fl ow texture of a onceliquid oil (200X magni fi cation; re fl ected white light; oil immersion; field width is **320 μ).**

The bitumen is partially soluble in organic solvents and insoluble in immersion oil. Under a reflected-light microscope at high magnification (200X to 500X), the bitumen has a wide range of reflectance showing mixing of bitumen and minerals in a flow texture and bitumen balls. Bitumen reflectance ranges from 0.16-0.81% Ro. The lowest reflecting bitumen has a weak orange fluorescence in reflected blue light. The highly reflecting bitumen may be the result of alteration or weathering. As indicated in the Appendix, "the elevated oxygen content of the pyrobitumen suggests weathering may be a significant factor in its subsequent alteration and solidification." The flow texture is indicative of once-liquid oil, picking up minerals from the shale exposed along the fracture. The mineral-free bitumen balls formed when the oil was still viscous.

As described in the geochemistry report in the Appendix and based on the dissimilarity of the geochemistry of pre-oil bitumen extracted from the Woodford Shale and post-oil pyrobitumen from fractures, the fracture-filled solid hydrocarbon in this quarry is probably from a non-Woodford source and not an expulsion product of the in-situ Woodford Shale. The source and timing of this solid bitumen is different than the source and timing of the tar balls. Based on kinetics, the low thermal maturity (0.54% Ro) of the Woodford Shale in this quarry is too low to have generated the post-oil solid bitumen. Hunt (1996, p. 368) indicated that "0.6% (Ro) is generally recognized as the beginning of commercial oil accumulations." Roberts and others (2004) indicated that oil generation begins around 0.68% vitrinite reflectance from type II kerogen, the same type of organic matter in the Woodford Shale.

Photomicrograph of bitumen balls and minerals suspended in bitumen showing fl ow texture of a once-liquid oil (200X magnifica**tion; reflected white light; oil immersion; fi eld width is 320 μ).**

Photomicrograph of minerals and fractured bitumen balls showing a wide range of bitumen refl ectance (200X magnification; re**fl ected white light; oil immersion; fi eld width is 320 μ).**

NOTES

NOTES

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ACKNOWLEDGEMENTS

Marvin Abbott, USGS Oklahoma Water Science Center, was instrumental in collection of some of the Woodford spectral gammaray data. Sue Britton Crites, Oklahoma Geological Survey, is thanked for preparation of the guide.

APPENDIX

Geochemical analyses of solid bitumen and Woodford Shale, Carter County, Oklahoma, by T.E. Ruble (Humble Geochemical Services)

Dr. T.E. Ruble with Humble Geochemical Services has worked extensively with solid hydrocarbons (Ruble, 1990; Ruble and Philp, 1992, 1994; Ruble and others, 1994, 1999; Cardott and others, 1993). The Appendix contains a report by T.E. Ruble on the geochemical analyses of the solid hydrocarbon (a.k.a. solid bitumen) and Woodford Shale from the McAlister Cemetery Quarry.

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Executive Report *Geochemical Analyses of Solid Bitumen and Woodford Shale, Carter County, Oklahoma*

Prepared for University of Oklahoma

Prepared by T.E. Ruble

Project 07-5129 *Humble Geochemical Services*

July, 2008

Geochemical Analyses of Solid Bitumen and Woodford Shale, Oklahoma – University of Oklahoma Humble Geochemical Services – Weatherford Laboratories

Interpretative Summary

An investigation has been conducted to assess the geochemical characteristics and probable origin of solid hydrocarbons found as fracture-fill within the Woodford Shale from the McAlister Cemetery Quarry, Carter County, Oklahoma. Hand-picked, solid bitumen (OPL 1283b; HGS 07-5129-218270) from fractures and the associated country rock (HGS 07-5129-218563) were analyzed by a limited suite of geochemical techniques, including thermal extract gas chromatography (TE-GC), pyrolysis gas chromatography (Py-GC), and LECO® elemental analysis. The complete results of these analyses are documented in this report, along with an integrated geochemical interpretation that incorporates and utilizes previously published geochemical data (Kirkland et al., 1992) from McAlister Cemetery Quarry samples (shale, fracture-fill bitumen, tar balls).

The Woodford Shale in the McAlister Cemetery Quarry is tectonically fractured and while most of the abundant fractures are open, some are filled with quartz cement and others are filled with solid bitumen (Kirkland et al., 1992). This bitumen has a maximum solubility of 11,050 ppm and is essentially insoluble (Kirkland et al., 1992), thereby classifying it properly as a pyrobitumen according to the generic scheme of Hunt et al. (1954). To address the origin of the fracture-fill pyrobitumen, a carefully hand picked sample free of embedded shale was analyzed by TE-GC and Py-GC to examine its hydrocarbon fingerprint. For comparison, fragments of the Woodford Shale country rock associated with the pyrobitumen were also examined using the same analytical techniques.

The TE-GC fingerprint of the pyrobitumen (Fig. 1) shows relatively abundant low molecular weight aliphatic, branched, cyclic and aromatic components. The major peaks are identified by abbreviation and consist of normal alkanes such as $n-C_6$, which is the predominant peak in the gas chromatogram, and isoalkanes such as $i-C₅$. The alkane envelope is irregular with dual maxima at n-C₆ and n-C₁₁ and does not appear to extend beyond n-C₂₂. The dominance of lower molecular weight components in this pyrobitumen is somewhat unexpected. It may be attributable to entrained hydrocarbons trapped within the dominantly asphaltic pyrobitumen matrix that are volatilized and released during thermal extraction. If so, this could be circumstantial evidence to support a post-oil bitumen, as defined using the genetic classification scheme of Curiale (1986). This pyrobitumen would thus be the product of relatively recent (in geologic time) alteration of a migrated hydrocarbon charge moving through the fractured Woodford Shale. Branched and cycloalkanes make up a substantial portion (13 & 24% respectively) of the resolvable components in the TE-GC fingerprint and this is supported by independently performed solvent extract GC results (D. Kim, OU unpublished). This is somewhat unusual and differs significantly from the dominant aliphatic nature of typical Woodford Shale extracts and oils (Kirkland et al., 1992; Burruss and Hatch, 1989). Pennsylvanian aged oils have previously been reported to contain high abundances of branched and cycloalkanes (Burruss and Hatch, 1989), including very elevated methylcyclohexane (MCH), that show some similarities to the TE-GC fingerprint of this pyrobitumen. However, the comparison is not unequivocal in that Pennsylvanian oils also have relatively high abundances of C_{15+} hydrocarbons, which are not abundant in the pyrobitumen. Due to the difficulty of characterizing insoluble pyrobitumens and the lack of distinguishing biomarkers, confidence in any attempts at bitumen-oil correlation will always be limited.

For comparison purposes, the Woodford Shale source rock associated with the pyrobitumen was also examined by TE-GC (Fig. 1). The fingerprint from the shale differs notably from that of the pyrobitumen, but is very similar to a previously published saturate fraction GC trace from the Woodford Shale at this location (Kirkland et al., 1992). It shows relatively abundant aliphatic

Geochemical Analyses of Solid Bitumen and Woodford Shale, Oklahoma – University of Oklahoma 3 *Humble Geochemical Services – Weatherford Laboratories*

hydrocarbon components and lesser amounts of low molecular weight branched and cycloalkanes. The main n-alkane envelope is generally unimodal and extends from $n-C_{11}$ up to $n-C_{41}$ with a fairly strong odd-predominance. Attenuation of lower molecular weight components and the fairly elevated hump of unresolved complex mixture (UCM) are attributable to the low thermal maturity of this source rock sample, since biodegradation (which can produce similar features) is unlikely in freshly exposed shale within an active quarry. Measured vitrinite reflectance of 0.54% Ro for the Woodford Shale at this locality (B. Cardott, personal communication) confirms the interpreted maturity and places this source rock within the earliest oil window. Branched chain isoprenoids are also abundant in the source rock TE-GC fingerprint and the Pr/ n-C₁₇ & Ph/ n-C₁₈ ratios of \sim 2 are further evidence of low thermal maturity. The distribution of isoprenoid biomarkers, such as pristane and phytane, can be used to assess source rock kerogen type and depositional environment. In the Woodford Shale TE-GC trace, the Pr/Ph of 1.25 is generally indicative of an origin from low sulfur marine shale source rocks containing predominant Type II marine algal organic matter deposited under oxic to sub-oxic conditions.

The insoluble organic matter that composes the dominant portion of the McAlister Cemetery Quarry pyrobitumen has been further characterized by Py-GC (Fig. 2). Typical Py-GC traces display a series of doublet peaks consisting of n-alkanes and their corresponding (early-eluting) 1-alkenes. While these components are present in the pyrobitumen fingerprint out to $\sim n-C_{21}$, the overall pattern of the pyrogram is dominated by benzene, toluene, and other unidentified aromatic, branched and cyclic alkene/anes. This result has been independently reproduced using a slightly different flash pyrolysis GC system (D. Kim, OU unpublished) and appears to corroborate the TE-GC results showing a relatively low abundance of n-hydrocarbons. Curiale (1986) reported similar such pyrograms from insoluble uraniferous solid bitumens in southwestern Oklahoma that have apparently been altered by biodegradation and intense radiation. A model was proposed (Curiale et al., 1983) whereby crude oil, migrating from depth, is initially altered near the surface by biodegradation and oxidation. Concurrently migrating ground water is stripped of its uranium by the degraded petroleum to form nodular deposits. Irradiation from the uranium then causes further transformations to bitumen. Although no evidence of uranium enrichment is envisioned for the fracture-fill pyrobitumen within the Woodford Shale, similar near surface alteration (oxidation, biodegradation) may have occurred to transform the macromolecular structure into more of a condensed aromatic/cyclic ring dominated configuration.

The Py-GC fingerprint of the Woodford Shale source rock associated with the pyrobitumen is dominated by aliphatic n-alkene/ane doublets extending to at least n- C_{32} (Fig. 2.). This feature is typical of highly aliphatic, oil-prone kerogens at low levels of thermal maturity and is consistent with the interpreted maturity level of the Woodford Shale in the McAlister Cemetery Quarry. Low maturity expelled bitumens from the adjacent source rock that could be envisioned to have filled the fractures within the Woodford Shale would have elevated asphaltenes and should look very similar to this source rock pyrogram. The obvious dissimilarity between this fingerprint and that of the analyzed pyrobitumen provide further evidence that they are not related.

Elemental analysis of the pyrobitumen sample offers further insights into the probable origin of this material (Table 1). The results from the fracture-filled pyrobitumen are compared to published data from so called "tar balls" found in the Woodford Shale at the McAlister Cemetery Quarry location (Kirkland et al., 1992). The H/C ratio of the pyrobitumen is 0.91 and this suggests a highly condensed macromolecular structure dominated by aromatic, branched and/or cyclic components. The H/C ratio of the fracture-filled pyrobitumen is even lower than

Geochemical Analyses of Solid Bitumen and Woodford Shale, Oklahoma – University of Oklahoma 5 *Humble Geochemical Services – Weatherford Laboratories*

that of the tar balls, which Kirkland et al. (1992) have suggested are remains of a paleo submarine oil seep (possibly Ordovician Simpson source) deposited during Woodford Shale sedimentation. The possible reason for this highly condensed structure in the fracturefilled pyrobitumen may be provided by the relatively high oxygen content (9 wt%) and the elevated O/C ratio of 0.098. Jacob (1989) reports that when solid oil bitumens, or so called "migrabitumen", are altered by weathering they can be converted to "oxybitumens" in which the oxygen content can increase to as high as 13 wt.% or more. Curiale et al. (1983) also show a trendline of increasing O/C ratios (as high as 0.212) for uraniferous pyrobitumens from Oklahoma that may represent increased weathering and oxidation. The elevated oxygen content of the Woodford Shale fracture-fill pyrobitumen in comparison to that of the tar balls suggest a different origin and is consistent with a more recent (in geologic time) migration/weathering event through the immature fractured source rocks.

In summary, based on TE-GC, Py-GC and elemental compositional analyses the **fracture-fill pyrobitumen** collected from the Woodford Shale in the McAlister Cemetery Quarry appears to be **weathered post-oil solid bitumen associated with a previous oil migration event through the immature, fractured source rock**. The geochemical analyses reported herein are certainly not unequivocal, due to the generally insoluble nature of pyrobitumen. However, the molecular fingerprints from TE-GC and Py-GC show distributions of hydrocarbons, including abundant branched and cycloalkanes, that do not appear to match well with the associated Woodford Shale country rock, suggesting a different origin. Further, the measured geochemical data suggest that the Woodford Shale in this locality is early mature and has not generated and expelled significant volumes of oil. The origin and timing of the migrated oil charge is uncertain, but the elevated oxygen content of the pyrobitumen suggests weathering may be a significant factor in its subsequent alteration and solidification. Other processes like biodegradation undoubtedly contributed to the formation of the pyrobitumen and could also be partially responsible for the depletion of n-hydrocarbons in both the thermal extract and pyrolysate.

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Experimental Methods

Thermal Extract Gas Chromatography

Thermal Extract Gas Chromatography (TE-GC) may be completed on potential source rocks to examine source specific molecular distributions or on potential reservoir rocks to characterize and fingerprint liquid hydrocarbon components. Samples to be analyzed are typically rinsed to remove drilling mud contaminants and are sometimes hand picked to recover representative cuttings fragments for analyses. Approximately 10-50 mg of rock sample are placed in a metal crucible and inserted into the specially designed inlet system. The samples are thermally extracted at 300°C for 2.45 min. with a split portion of the volatile hydrocarbons trapped onto the front of the analytical column using a liquid nitrogen trapping system. Gas chromatography is performed using HP 6890 Series GC System with 50m high-resolution column. The GC is temperature programmed from 35°C (8 min. hold) to 50°C at 1.5°C/min. and then to 330°C at 8°C/min. with a final hold time of 40 min. Light hydrocarbons, isoprenoids and normal paraffins are identified when they are present in the sample. The GC method is specifically designed to separate light hydrocarbons and allows identification of higher molecular weight hydrocarbons out to C_{42} .

Pyrolysis Gas Chromatography

Pyrolysis Gas Chromatography (Py-GC) is completed by flash pyrolysis using a high resolution mode where all hydrocarbon gases are completely resolved. Samples are prepared for Py-GC analysis by extraction either of whole rocks, kerogens, asphaltenes or solid bitumens. A small amount of sample (approximately 5 mg (extracted rock) or 1-2 mg of kerogen or .1 to 1 mg of asphaltene) is loaded into a metal crucible and inserted into the specially designed inlet system. The pyrolysis process is open system, isothermal pyrolysis. The sample is pyrolyzed at 600 \degree C for 2 minutes with a split portion of the volatile hydrocarbons trapped onto the front of the analytical column using a liquid nitrogen trapping system. Gas chromatography is performed using HP 6890 Series GC System with 50m high-resolution column. The GC is temperature programmed from 35°C (5 min. hold) to 330°C at 5°C/min. with a final hold time of 30 min. A PY-GC fingerprint of the pyrolysis products is provided. Data for alkene-alkane pairs and selected aromatics are reported with retention time, height, peak area, and yield (if internal standard added).

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Weatherford Core Evaluation Services

218 Higgins Street Humble, TX 77338

Telephone: 281-540 6050 Fax: 281-540 2864

Depth: Field: Formation: Woodford Basin: Country:

Client: University of Oklahoma
Client ID: OPL 1283b
HGS ID: 07-129-218270
Type: outcrop outcrop county,State: Carter Co., OK
Type: McAlister Cemetary Quarry Clares (Passe Lease Passe)

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Telephone: 281-540 6050 Fax: 281-540 2864

Client: University of Oklahoma Client ID: OPL 1283b API: HGS ID: 07-5129-218270 County,State: Carter Co., OK Type: outcrop Lease Well: McAlister Cemetary Quarry Depth: Field: Formation: Woodford Basin: Country:

Interpretive Interpretive Interpretive Ratios Ratios Ratios by Area Pristane / Phytane 1.97 P1 P1 not available Pristane / nC17 0.88 P2 not available Phytane / nC18 1.09 P3 not available nC18 / (nC18 + nC19) 0.52 5N1 not available nC17 / (nC17 + nC27) 1.00 6N1 6N1 not available Carbon Preference Index #DIV/0! N2 N2 not available **Totals by Normalization** Normal Alkanes **36.13** Normal Alkanes **36.13** K1 Isoalkanes 30.69 | K2 not available Branched Alkanes 13.07 Cycloalkanes 23.92 Aromatics **6.26** 5N1 / 6N1 **not available** P3 / N2 not available **Halpern Ratios 1** Tr1 3.03 Tr2 9.64 Bz / nC6 0.09 $\begin{array}{ccc} \textsf{Tr3} & \textsf{3.31} & \textsf{1} & \textsf{5.31} \end{array}$ Tr4 2.70 (nC6 + nC7) / (CH + MCH) 1.85 Tr5 6.01 6.01 Isoheptane Value 0.49 Tr6 **not available** not available nC7 / MCH 0.92 Tr7 2.94 CH / MCP 0.82 Tr8 0.51 nC7 / 2-MH 3.57 C1 0.04 nC6 / 2,2-DMB 74.66 C2 0.41 Heptane Value 24.55 C3 0.18 C4 0.21 C5 0.17 **Thompson Ratios 3** *Gas Chromatography Interpretive Ratios Ring Preference Ratios* **Invariant Ratios Mango Ratios 2**

1 Halpern, H.I., 1995. APPG Bull.: v.79, p801-815

2 Mango, F.D., 1994. GCS: V.58, p.895-901

3 Thompson, K.F.M., 1983. GCA: v.47, p303-316

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218 Higgins Street Humble, TX 77338 Telephone: 281-540 6050 Fax: 281-540 2864

Depth: Field: Formation: Woodford Basin: Country:

Client: University of Oklahoma
Client ID: Outcrop - 1 Outcrop - 1
HGS ID: 07-5129-218563 County,State: Carter Co., OK
Type: 0throp 0throp Cluarry
Well: McAlister Cemetary Quarry

Humble Geochemical Services

Weatherford Core Evaluation Services

218 Higgins Street Humble, TX 77338

 $County, State: Carter Co., OK$

Telephone: 281-540 6050 Fax: 281-540 2864

Client: University of Oklahoma Client ID: Outcrop - 1 API: Type: outcrop Lease Well: McAlister Cemetary Quarry Depth: Field: Formation: Woodford Basin: Country:

Interpretive Interpretive Ratios Ratios Ratios by Area Pristane / Phytane 1.25 P1 P1 not available Pristane / nC17 **2.08** Pristane / nC17 **P2** not available Phytane / nC18 **Phytane / nC18** 1.94 P3 **P3** not available nC18 / (nC18 + nC19) 0.47 5N1 5N1 not available nC17 / (nC17 + nC27) 0.72 6N1 6N1 not available Carbon Preference Index 1.14 | N2 N2 not available **Totals by Normalization** Normal Alkanes 66.00 k1 not available Isoalkanes 26.33 k2 K2 not available Branched Alkanes 4.19 Cycloalkanes 1.53 Aromatics 6.15 6.15 6.15 5N1 / 6N1 not available P3 / N2 not available **Halpern Ratios 1** Tr1 6.54 $\textsf{Tr2} \hspace{2.5cm} \textsf{S} \hspace{1.5cm} \textsf{S} \hspace$ Tr3 10.67 | Tol / nC7 1.19 Tr4 1.07 (nC6 + nC7) / (CH + MCH) 1.38 Tr5 11.74 Isoheptane Value 2.94 Tr6 **not available not available** nC7 / MCH 1.41 Tr7 0.63 | CH / MCP 3.51 Tr8 1.42 nC7 / 2-MH 5.17 C1 0.06 nC6 / 2,2-DMB 0.79 C2 0.15 Heptane Value 21.06 $C3$ 0.17 $C4$ 0.44 C5 0.19 **Thompson Ratios 3** *Gas Chromatography Interpretive Ratios Ring Preference Ratios* **Invariant Ratios Mango Ratios 2**

1 Halpern, H.I., 1995. APPG Bull.: v.79, p801-815

2 Mango, F.D., 1994. GCS: V.58, p.895-901

3 Thompson, K.F.M., 1983. GCA: v.47, p303-316

Humble Geochemical Services *Weatherford Core Evaluation Services*

218 Higgins Street Humble, TX 77338 Telephone: 281-540 6050 Fax: 281-540 2864

Depth: Field: Formation: Woodford Basin: Country:

Client: University of Oklahoma Client ID: OPL 1283b API: HGS ID: 07-5129-218270 County,State: Carter Co., OK Type: outcrop Lease: Well: McAlister Cemetary Quarry

Humble Geochemical Services *Weatherford Core Evaluation Services*

218 Higgins Street Humble, TX 77338

Telephone: 281-540 6050 Fax: 281-540 2864

Depth: Field: Formation: Woodford Basin: Country:

Client: University of Oklahoma Client ID: Outcrop - 1 API: HGS ID: 07-5129-218563 County,State: Carter Co., OK Type: outcrop Lease: Well: McAlister Cemetary Quarry

tar ball data reported in Kirkland et al. (1992)

tar ball data reported in Kirkland et al. (1992) (Omplete analyses (Oxygen/15.994)/(Carbon/12.011) -1 = insufficent sample to complete analyses H/C = Hydrogen/(Carbon/12.011)
O/C = (Oxygen/15.9994) /(Carbon/12.011)
N/C = (Nitrogen/14.0067) /(Carbon/12.011)
S/C = (Sulfur/32.06) /(Carbon/12.011) N/C = (Nitrogen/14.0067) /(Carbon/12.011) S/C = (Sulfur/32.06) /(Carbon/12.011) H/C = Hydrogen/(Carbon/12.011)

 -1 = insufficent sample to complete analyses