Knox Group Storage Capacity Report

SECARB Phase III Work Product 1.6.b

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Executive Summary

This report assesses the carbon dioxide (CO_2) storage capacity for the Knox Group and the Stones River Group in the Mississippi Black Warrior Basin. The results of this evaluation are complimentary to the Geologic Survey of Alabama (GSA) evaluation of potential CO_2 storage reservoirs in the Alabama Black Warrior Basin. The Stones River Group directly overlies the Knox Group and it contains documented porous zones that may be promising for CO_2 sequestration. The Cambrian-Ordovician interval is a thick sequence of carbonates that occurs in multiple geologic settings in the Southeast Regional Carbon Sequestration Partnership (SECARB). The Knox and Stones River Groups could likely only serve as a CO_2 storage reservoir in the southern region of its occurrence, within the Black Warrior Basin. Recorded high porosity zones in the Stones River Group, are likely discontinuous and inconsistent horizons; making it difficult to determine the potential CO_2 storage capacity. Increased data coverage of the Knox and Stones River Groups and a detailed study on injectable zones in these formations would provide a clearer picture on their potential for CO_2 storage.

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1.0 Introduction

This report assesses the carbon dioxide (CO_2) storage capacity for the Knox Group and the Stones River Group in the Mississippi Black Warrior Basin. The results of this evaluation are complimentary to the Geologic Survey of Alabama (GSA) evaluation of potential CO_2 storage reservoirs in the Alabama Black Warrior Basin. The Stones River Group directly overlies the Knox Group and it contains documented porous zones that may be promising for CO_2 sequestration. Due to the presence of porous zones and because of its proximity to the Knox, it is included in this assessment in order to expand the potential capacity for CO_2 storage.

The Cambrian-Ordovician interval is a thick sequence of carbonates that occurs in multiple geologic settings in the Southeast Regional Carbon Sequestration Partnership (SECARB) region, including the Appalachian Fold and Thrust Belt, Nashville Dome and Black Warrior Basin in the states of Alabama, Georgia, Mississippi, Virginia and Tennessee (**Figure 1**). The Knox serves as a major freshwater source in the Nashville Dome area of Tennessee (**Brahana and Bradley, 1985**) and is frequently shallower than the DOE recommended depth cutoff for safe CO_2 storage of 800 meters (2,600 feet). These parameters exclude it as a potential storage reservoir in central Tennessee. Further, thrust faults that occur across the structurally complex Appalachian Fold and Thrust Belt cause the Knox to frequently outcrop along northeast-southwest striking belts and have fractured the caprock and reservoir, compromising its integrity as a potential CO_2 storage reservoir in this structural province. The Knox and Stones River Groups could likely only serve as a CO_2 storage reservoir in the southern region of its occurrence, within the Black Warrior Basin. A recent study by the Geological Survey of Alabama assessed 10 potential CO_2 storage reservoirs, ranging from the Late Cambrian to the early Pennsylvanian, in the Alabama portion of the Black Warrior Basin (**McIntyre et al., 2012**). The Knox and Stones River Groups have large volumes making them attractive targets for potential storage, however, their generally low permeability and porosity may limit their actual use as injection reservoirs.

GENERALIZED PALEOZOIC STRATIGRAPHIC SECTION

Mississippi Black Warrior basin

Era	System	Series	Group	Formation
Paleozoic	Permian (absent)			
	Pennsylvanian			Pottsville
	Mississippian	Chesterian		Parkwood-Pennington
				Pride Mountain
	Devonian		Harriman	Devonian
	Silurian		Niagaran	
	Ordovician		Stones River	Stones River ls
				Stones River dolo
			Knox	Knox ls
				Knox dolo
	Cambrian			Copper Ridge dolo
				Conasauga ls
				Rome
				Shady dolo
				Weisner
Precambrian				

Figure 1: Stratigraphic Column (from Champlin and Moody, 2001)

2.0 Study Methodology

Our approach to calculate the CO_2 storage capacity of the Knox and Stones River saline reservoir follows the capacity assessment methodology set forth by the Department of Energy's Regional Carbon Sequestration Partnerships Capacity Estimation Subgroup. The DOE methodology provides a volumetric estimate for useable CO_2 storage capacity based on geographical area (A), gross formation thickness (h), total porosity (ϕ) and CO_2 density (ρ_{CO2}). A storage coefficient (E) is used to represent the fraction of the total pore volume that would be filled by CO_2. The efficiency factor (E) incorporates a series of variables that limit the ability of injected CO_2 to occupy 100% of the pore space in a given formation, such as geologic heterogeneity, gravity or buoyancy effects, and limited sweep efficiency. The simplified DOE CO_2 storage capacity (G_{CO2}) equation for calculating effective CO_2 storage within a particular saline formation is as follows:

$$G_{CO2} = A_t * h_g * \phi_{tot} * \rho_{CO2} * E_{saline}$$

The terms used in this equation are discussed in Table **1** below:

Table 1: Key Reservoir Parameters Used to Assess CO_2 Storage Capacity		
Parameters	Units	Description
G_{CO2}	**M**	**Usable CO_2 storage capacity (M, is mass in metric tons).**
A_t	L^2	**Geographical area that defines the basin or region being assessed for CO_2 storage (L is length).**
h_g	**L**	**Gross thickness of saline formation for which CO_2 storage is assessed within the basin or region defined by A_t.**
ϕ_{tot}	**fraction**	**Average porosity of entire saline formation over thickness h_g.**
ρ	M/L^3	**Density of CO_2 at pressure and temperature representative of storage conditions.**
E_{saline}	L^3/L^3	**CO_2 storage efficiency factor that reflects the fraction of the total pore volume that is filled by CO_2.**

When applied at a regional or basin level, the CO_2 storage efficiency coefficient (E_{saline}) incorporates inefficiencies in displacement, including volumetric displacement (E_v) and microscopic displacement (E_d) as discussed in **Table 2** below. In addition, the CO_2 storage efficiency coefficient (E_{saline}) also incorporates the following three limitations on accessibility related to geologic heterogeneity, as presented in **Table 2**.

Table 2: Geologic Components of Regional CO_2 Storage Efficiency Coefficient

Term	Symbol	P10/P90 Values by Lithology for Clastics	Description
Net to Total Area	EA_n/A_t	0.2/0.8	Fraction of total basin or region area that has a suitable formation present.
Net to Gross Thickness	Eh_n/h_g	0.21/0.76*	Fraction of total geologic unit that meets minimum porosity and permeability requirements for injection.
Effective to Total Porosity	$E\phi_\varepsilon/\phi_{\tau o \tau}$	0.64/0.77*	Fraction of total porosity that is effective, i.e., interconnected.
Displacement terms used to define the pore volume immediately surrounding a single well CO_2 injector			
Volumetric displacement efficiency	E_v	0.16/0.39	Combined fraction of immediate volume surrounding an injection well that can be contacted by CO_2 and fraction of net thickness that is contacted by CO_2 as a consequence of the density difference between CO_2 and *in situ* water.
Microscopic displacement efficiency	E_d	0.35/0.76	Fraction of pore space unavailable due to immobile *in situ* fluids

For this assessment, regional log data and published structural maps (**Manning and Statler, 1975; Kidd, 1976; Henderson, 1991; McIntyre et al., 2012**) were used to identify formation top elevations and generate structure and thickness (isopach) maps. The porosity for the Knox and Stones River Groups was determined from regional porosity log data and published values collected for the Knox and Stones River intervals. For this assessment the net-to-total area EAn/At, net-to-gross thickness Ehh/hg, and net-to-total porosity Eϕe/ϕtot terms (**Table 2**) are used due to the lack of data for this area. Efficiency factors used for the capacity estimates are taken from the U.S. DOE methodology update (**2011**) and are listed in **Table 3**.

Table 3: Saline Formation Efficiency Factors for Displacement Terms Only (Clastics)

Lithology	P_{90}	P_{10}
Clastics	5.4%	0.51%

2.1 Geologic Setting

The Knox and Stones River intervals were deposited as part of a huge carbonate platform that covered the North American craton from Canada to the southwestern U.S. and is the age-equivalent to the Arbuckle Group in Arkansas, Kansas and Oklahoma, and the Ellenburger Group in Texas and southeast New Mexico (**Raymond, 1991; Bowersox et al., 2011**). The Stones River and Knox sequence represents a period of maximum sea level transgression, deposited in a shallow marine shelf environment (**Raymond, 1991**). It is composed of a thick sequence of limestone and dolomite of upper Cambrian and lower Ordovician age (**Figure 1)**. The post-Knox unconformity overlies the Knox Group and it marks a period of sub-areal exposure of the upper portion of the Knox sequence. Sub-areal exposure resulted in erosion of the upper Knox and created solutional features such as the development of vuggy porosity and solution cavities (**Brahana and Bradley, 1985; Welch, 2002**). These zones represent the highest porosity zones in the Knox. Most of the freshwater production from the Knox Group, outside of Black Warrior Basin, comes from the Upper Knox.

This report focuses on the Black Warrior Basin where the Knox Group occurs deep enough and over a large enough area to warrant consideration for CO_2 storage (**Figure 2**). Located in the north-central Alabama and Mississippi it is bound by the Nashville dome to the north, the Appalachian orogenic belt to the east and southeast and the Ouachita orogenic belt to the southwest (**Figure 2**). The Black Warrior Basin is a foreland basin that contains Paleozoic, Mesozoic, and Cenozoic sedimentary sequences ranging in thickness from about 7,000 ft along the north basin margin to about 31,000 ft in the depocenter, located in eastern Mississippi (**Ryder, 1995**). This sequence is blanketed by Tertiary and Cretaceous rocks of the Gulf Coastal Plain and the Mississippi Embayment.

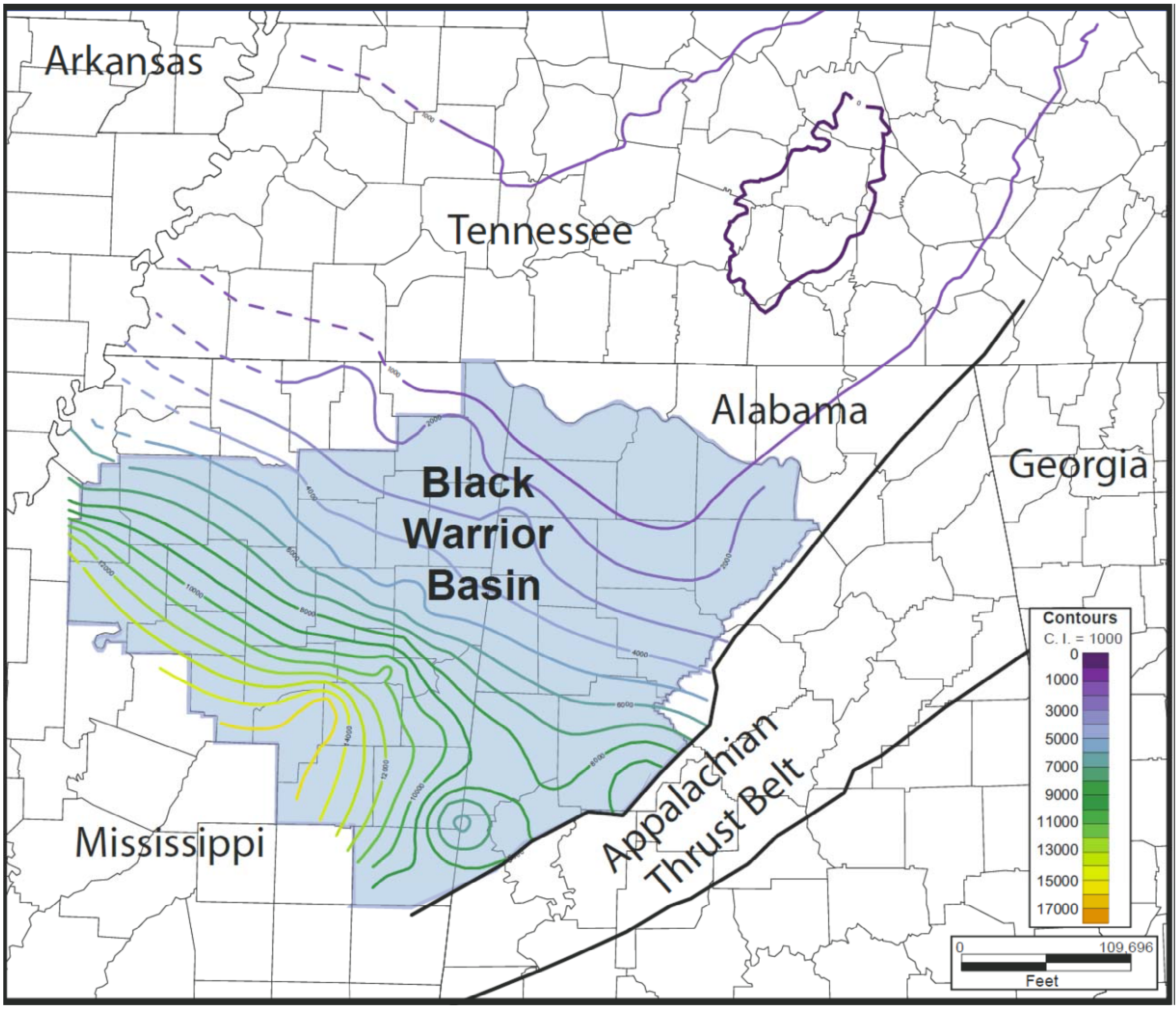

Figure 2: Structure of the Knox Limestone and the Tectonic Setting of the Black Warrior Basin. Modified from Thomas (1988), Ryder (1994), and Popov et al (2001)

2.2 Structural Setting

The Black Warrior Basin is a triangular shaped foreland basin located in northwest Alabama and northeast Mississippi (**Kidd, 1976**). The Basin is bounded to the north by the Nashville Dome and Ozark uplift and to the east by the Valley and Ridge province (Appalachian Fold and Thrust Belt). The Knox Group outcrops in north-Central Alabama, occurs in the subsurface in north-western Alabama and northern Mississippi and is buried under Mesozoic and Cenozoic sediments of the Central Coastal Plain in the central and western Portions of the Basin (**Raymond, 1991**).

Structurally, the strata of Black Warrior Basin dip in the southwestern direction and are locally broken by a system of northwest-trending hinge line normal faults (**Raymond, 1991**). In south-central Mississippi, normal faults, apparently of Early Pennsylvanian age, have placed Mississippian rocks in fault contact with Lower Ordovician and Cambrian rocks (**Hatch and Pawlewicz, 2007**). These faults are characterized by large down-to-the-basin faults and smaller up-to-the-basin complementary faults (**Welch, 2002**). It is this structural pattern that is responsible for a limited number of Knox structural hydrocarbon traps in the Black Warrior Basin, including the Maben Field in Mississippi. In Alabama, the southeastern portion of the Black Warrior Basin is overprinted by folds of the Appalachian orogenic belt. Kidd (**1975**) noted that the dip of the Knox increases from 25 to 30 feet per mile in the northern part of the Black Warrior Basin, to greater than 100 feet per mile in west-central Alabama.

Thomas (1988) outlined the geotectonic history of the Black Warrior Basin into six stages which are given below:

1. Late Precambrian–Early Cambrian rifting, with associated deposition of coarse clastic sediments.
2. Middle Cambrian–Mississippian passive continental margin, with deposition of shallow-water carbonates. This includes the Knox and Stones River Groups.

3. Late Mississippian (Chesterian) continental collision, with deposition of marine deltaic sediments and several major regressive-transgressive cycles. This includes regional confining units.

4. Early-Late Pennsylvanian maximum basin subsidence associated with the Appalachian-Ouachita orogeny and deposition of basin-fill sediments; development of barrier bars, followed by progradation of thick clastic wedges from source areas along the south margin of the basin and deposition of coal-forming materials.

5. Latest Pennsylvanian–early Mesozoic uplift, resulting in Permian-Cretaceous erosion and non-deposition.

6. Mesozoic rifting, resulting in the basin becoming down-warped to the southwest and eventually being covered by transgressive marine sediments of the Mississippi embayment (**Mancini et al., 1983**).

A structure map of the elevation of the top of the Knox Group is shown in **Figure 2**. Across the Nashville Dome region, including the Western Highland Rim, Central Basin, Eastern Highland Rim and Cumberland Plateau provinces the Knox Group occurs entirely in the subsurface. Depth to the top of the Knox Group ranges from about 350 feet below ground surface in the Central Basin to more than 2,000 feet in West Tennessee and more than 3,000 feet in the Cumberland Plateau of east Central Tennessee (**Bradley, 1986**).

The upper depth limit for the storage of CO_2 utilized in this assessment is 800 meters (2,592 feet) below the ground surface. We consider the Knox in the subsurface of Tennessee to be a low-grade prospect due to the limited area that the group occupies at depths greater than 800 meters, and the proximity to underground sources of drinking water (USDW; see **Hydrogeology Section**) found in the Knox Group.

3.0 Lithology

3.1 Knox Group

In the Black Warrior Basin the three formations of the Knox Group are identified: the Copper Ridge Dolomite, the Knox Dolostone, and the Knox Limestone (**Figure 1**). A description of Knox Formation lithology is summarized below (**Henderson, 1991**):

The Upper Cambrian Copper Ridge Dolomite is the lowermost unit in the Knox Group and is composed of a grayish-tan to dark brown, fine to coarsely crystalline dolomite with variable amounts of chert (**Henderson, 1991**). Red and yellow zones likely represent periods of subaerial exposure with subsequent oxidation and weathering. A high porosity brecciated zone has been encountered in this unit and is probably the result of karstification. The previously mentioned Karst terranes likely developed during the periods of subaerial exposure.

The Knox Dolostone (Lower Ordovician) is located above the Copper Ridge Dolomite and is a uniform sequence of cherty and sandy dolostone. The unit ranges from 650 to 1,906 feet, thickening to the northwest and north. The dolostone is light to dark gray or light to dark tan with an occasional dark greenish-gray color. This unit contains varying amounts of chert, with the majority of the chert occurring in the lower half of the unit. As in the Copper Ridge Dolomite, the Knox Dolostone contains several subaerial exposure zones of red and yellow mottling. These zones are also attributed to karstification of the dolomite that resulted in brecciation and locally increased porosity. The presence of rounded quartz sand grains is a notable feature in the Knox Dolostone. Some of the grains are frosted, potentially implying an eolian origin for these grains, however another interpretation (**Walker, 1957**) suggests the frosted quartz grains resulted from the process of carbonate replacement of quartz.

The Knox Limestone is the uppermost unit in the Knox Formation. In Mississippi this unit ranges from 490 to 2,657 feet in thickness and thickens to the southeast. The lithology of the Knox Limestone varies from light colored, micritic to very finely crystalline to darker colored, fossiliferous, very fine to finely crystalline limestone. As in the lower units of the Knox Formation, the Knox Limestone contains zones of high porosity due to karstification.

3.2 Stones River Group

In Alabama and parts of Mississippi the Stones River Dolostone overlies the Knox Group. This unit is truncated or missing in the northernmost part of Mississippi, is thickest in the north and thins to the east-southeast. Where present, it ranges in thickness from 289 to 1,535 feet. It is a fairly homogenous light grayish-tan with some occasional darker tan and light greenish-gray fine to finely crystalline dolostone with lesser fine to medium crystalline dolostone in the upper part of the section. Thin beds of green shale make up a minor portion of the lower section with argillaceous materials increasing toward the middle of the unit. Minor sand grains are also present locally and increase toward the base of the section.

A zone of porosity in the Stone River Dolostone, informally called the “Snow Zone”, is the only Cambro-Ordovician unit that has produced hydrocarbons in the Black Warrior Basin. This zone is interpreted to represent a widespread regression of the early Middle Ordovician seas, which lead to subaerial exposure of the carbonate terrane resulting in karstification.

Overlying the Stones River Dolostone, the Middle Ordovician Stones River Limestone is the youngest Ordovician unit in the subsurface of Mississippi. It is made up of a light gray or light to dark tan, micritic to finely crystalline limestone. Thin beds of shale occur in the upper part of the unit. The contact between the Stones River Limestone and the overlying Silurian sequence is an extensive unconformity. The unit is truncated or absent in a broad area of northern Mississippi. Where the Stones River

Limestone is present it ranges from 214 to 680 feet and thickens to the north and southeast.

Stratigraphy above the Know and Stone River Groups

In Alabama, the upper Ordovician Sequatchie Formation overlies the Stones River Limestone in Alabama (**McIntyre et al., 2012**) (**Figure 1**). Where present, the Sequatchie Formation is composed of interbedded shale, limestone and dolostone and ranges in thickness from ~230 to 520 feet (**McIntyre et al., 2012**). Overlying the Sequatchie Formation is the Red Mountain Formation (lower Silurian) described as a sequence of off-shore silty shale; inner shelf fine-grained sandstone; tidal channel medium- and coarse-grained sandstone and conglomerate, and shoreface sandstone, siltstone, and shale; inner and outer shelf limestone, dolomite, and shale and argillaceous, dolomitic, cherty limestone (**Chowns, 2006**). In the eastern part of the basin the Red Mountain Formation is dominantly a clastic facies, which grades into a carbonate dominated succession to the west and north-west (**McIntyre et al., 2012**).

An undifferentiated Silurian succession composed of limestone, dolomite and mudstone (**Kidd, 1975**) overlies the Red Mountain Formation. Thin siliceous units and siliceous limestone or dolomite are also present within this interval. The Devonian undifferentiated unconformably overlies the upper Silurian, and is composed of a northeast-thinning wedge of limestone and chert (**Kidd, 1975; Thomas, 1988; Pashin et al., 2011**). The black organic-rich Chattanooga shale sits disconformably above the undifferentiated Devonian. The Chattanooga shale is thin in the Black Warrior Basin and near its depositional limit in the eastern portion of the basin; it is likely present only in the Alabama part of the Black Warrior Basin (**Ryder, 1995**).

The upper Ordovician and Silurian sections, described above as the Sequatchie and Red Mountain Formations, are often 'undifferentiated' in the Black Warrior basin in Mississippi. In the western and northwestern portions of the Black Warrior Basin the upper Ordovician is not present. Missing sections are due, in part, to the Ordovician unconformity. The intervals that are present, however, have not been delineated or described as separate units because of the lack of data. There are no type localities (for transitional facies) because the units are not exposed at the surface, and exploration of the Paleozoic rocks in Mississippi has been limited.

The lower Mississippian is composed of the Fort Payne Chert and Tuscumbia Limestone interval. In Mississippi the lower Mississippian section is described as a cherty limestone. In a study by the Geologic Survey of Alabama the Fort Payne Chert is described as a dark brownish-gray siliceous micrite and bluish-gray nodular chert (**McIntyre et al., 2012**). The Tuscumbia Limestone is a light gray skeletal calcarentie with chert nodules and some caliche zones and is in gradational contact with the Fort Payne Chert (**Thomas, 1972**). The units are ~450 ft in the northeastern part of the basin and thin considerably to the southwest (~25 ft) (**McIntyre et al., 2012**). In Mississippi the two units are generally undifferentiated.

A regressive clastic facies overlies the lower Mississippian units. At the base of this sequence is the Floyd Shale, a clay-shale unit, followed by the Parkwood Formation, an interbedded sandstone and clay shale. Above this is the Pottsville Formation, a basal quartz-pebble conglomerate overlain by a sequence of cyclical carbonaceous shale, sandstone and coal beds.

Oil and Gas Exploration

Albeit limited, Knox and Stones River production in the SECARB region occurs predominantly within the Appalachian Fold and Thrust Belt region. Enhanced porosity has been discovered associated with thrust sheets. For example the Swan Creek oilfield located in northeastern Tennessee has reported porosities of 4-18%. The Swan Creek field is located within a subthrust feature beneath the Clinchport thrust sheet (**Champlin and Moody, 2011**). In the Warrior Basin, Knox and Stones River oil and gas production has been limited. The only significant Cambro-Ordovician (Knox and Stones River) production in the Black Warrior Basin has occurred in the Maben Field located in

Oktibbeha County on the southwestern flank of the Black Warrior Basin northeast Mississippi. The field produces from the karsted porosity of the Upper Knox; however the presence of horst block faults within the oilfield is thought to have created brecciated porosity which has contributed to the reservoir's volume. As of September 2009 the Maben Field had produced 58 BCF of natural gas (**Vision Exploration, LLC website**).

Hydrogeology

The upper Knox aquifer (upper 200 to 300 feet of the Knox Group) is used as a source of drinking water in the Central Basin and western Highland Rim regions of Tennessee (**Brahana and Bradley, 1986**) where it contains water having total dissolved-solids concentrations less than 10,000 mg/L. Nearly all of the groundwater in the Knox aquifer in the Central Basin occurs in thin (1 foot thick) zones containing networks of small tubular voids (**Newcome and Smith, 1962; Brahana and Bradley, 1986**). These zones represent secondary porosity and permeability in rocks that otherwise have very low primary porosity and permeability (**Brahana and Bradley, 1986**). Recharge to the Knox aquifer in the Central Basin and Western Highlands Rim regions of the Nashville Dome of Central Tennessee is likely due to vertical infiltration of meteoric waters through the Stones River Group carbonates (**Brahana and Bradley, 1986)**. For this reason, despite the fact that much of the lower Knox Group lies beneath the 800 meter depth cutoff in Tennessee, we do not consider any of the Knox as a promising CO_2 storage zone in the Nashville Dome area.

In the Alabama Black Warrior Basin the major sources of drinking water occur in Mississippian age and younger sediments. These strata are separated from the Knox Group by dense Stones River Group carbonates and Devonian shales including the Chattanooga Shale (**Miller, 1990**). Overlying Mesozoic sediments present the major groundwater source in northern Mississippi including the Black Warrior Basin (**Renken, 1989**). Dense Stones River carbonates and Devonian shale should act as a regional CO_2 confining unit in the Black Warrior Basin so we consider the Knox a prospective CO_2 storage reservoir in this region. Knox Group characterization efforts by the Midwest

Regional Carbon Sequestration Partnership (MRCSP) in northern Kentucky and southern Ohio have shown that porous Knox intervals (both vuggy and fracture zones) commonly alternate with dense impervious dolomite zones. As such, strata within the Knox may act as both as storage and confining zones (**Drahovzal et al, 2004**).

Reservoir Properties

The Knox Group generally consists of low porosity (less than 10%) and low permeability carbonates (**Bradley, 1986**). Within the Black Warrior Basin the Cambro-Ordovician is poorly understood. Porosity types for the Knox Group in the Black Warrior Basin likely are varied and include primary and brecciated (proximal to faults) carbonate porosity, and cavernous and karsted porosity. Brecciated porosity occurs along and proximal to fault planes. As discussed above, the cavernous and karsted porosity occurs primarily in the upper Knox Group as a result of a regional sea level low-stand and sub-areal exposure at the end of the Lower Ordovician (**Vision Exploration, LLC website**).

Within the Knox USDW region of central Tennessee, the aquifer has been noted to have higher porosity in the lower Knox than the middle Knox **(Brahana and Bradley, 1986**). Further evidence of porous zones capable of conducting fluids occurring in lower Knox (Copper Ridge Formation) occurs in the form of limited natural gas production from test wells and waste disposal well injection in northern Kentucky (**Greb and Solis, 2010**). Knox group characterization efforts by the MRCSP partnership, including analysis of core, log and injection from stratigraphic test wells and waste disposal and gas storage wells in northern Kentucky and Ohio, suggest that the lower Knox (Copper Ridge Formation) and Upper Knox (Beekmantown Formation) contain significant porosity and permeability (both fracture and vuggy porosity) and may serve as a backup storage reservoirs to the Mount Simon (**Drahovzal et al, 2004**). This storage capacity is evidenced as use by the AEP Mountaineer site, which used the Copper Ridge and Rose Run formations as storage targets. It is unknown if deep Knox porosity occurs in the Black Warrior Basin. For this assessment we assume that enhanced porosity only occurs at the top of the Knox group and is associated with sub-aerial exposure in the late Ordovician to early Silurian.

Averaged brine injectivity data for the Knox Group from multiple disposal wells in Alabama indicate favorable injectivity into the Knox Group (**Table 4**). However, when the logs were assessed there was no clear indication of which zones were favorable for injection because no high permeability zones were evident from the log curves (**Pashin, personal communication**).

Table 4: Brine Injectivity

Unit	Max Rate (bbl/d)	Max Pressure (psig)	Injectivity (bbl/d/psig)
Knox	3,350-10,800	995-1,750	3.4-6.2

** (modified from Clark and Pashin, 2012)*

The Kentucky Geological Survey, leading the Kentucky Consortium for Carbon Storage, drilled a CO_2 injection test well in 2009 in Hancock County in northwestern Kentucky to test the potential for Cambro-Ordovician carbonates for CO_2 storage. The project identified a 3,737 foot interval of the Knox occurring from a depth of 3,660 feet to 7,397 feet. An assessment of the Knox reservoir properties showed an average Knox porosity of 6.5% and an average permeability of 0.17 md. However, vuggy zones showed an average porosity of 13.5% (**Bowersox et al., 2011**). A small open hole (bottom of casing was at the top of the Knox) CO_2 injection test over the entire Knox interval (323 tons) was conducted. The test results showed CO_2 injection occurring over the interval of 3,660 to 5,750 feet.

Reported porosity and permeability values for the Knox and Stones River Groups in Alabama are rare. **Sternbach (1984)** reports porosity and permeability values of 0.8-6.6% and 0.1 md, respectively, from Copper Ridge (lower Knox) Appalachian shallow core samples (**Raymond, 1991**). **Welch (2002)** reports that the Upper Knox in the Black Warrior Basin is composed of 400 ft of dolomite at the top followed by about 2,500 feet of dolomitic limestone. The Lower Knox is composed of about 3,000 feet of predominantly dolomite. He reports limestone porosity values of less than 5% of primary intercrystalline porosity. However, karst zones have enhanced porosity values. Average Knox porosity and permeability values from the Plant Gorgas project, in Walker county Alabama, were reported as 1.7% and 0.0018md for the Chepultepec Dolomite, and 2.7% and 0.0031md (gas) for the Copper Ridge Dolomite (**Clark and Pashin, 2012**). A core study of the upper Knox Formation in the Maben Field, Mississippi reported matrix porosities of 5-9% and matrix permeabilities at the 1 md range. However, the authors reported a ubiquitous fracture system, possibly associated with fault growth, alongside the tight matrix fabric (**Gale et al., 2008**).

As with the Knox Group the Stones River has not been studied extensively resulting in a limited dataset. Available data indicate that porous zones in the Stones River have low porosity. Reported porosity values from the Plant Gorgas project in Alabama had values ranging from 3 to 11% with most of the porosities between 3-4% (**McIntyre et al., 2012**). As previously mentioned in the 'Lithology' section the "Snow Zone", in the Maben Field, is a producing, relatively, high porosity zone in the Stones River Dolostone (oil and gas) in Mississippi (**Henderson, 1991**). Henderson (1991) also noted that secondary dolomitization of the overlying Stones River limestone could prove to be an attractive reservoir objective for oil and gas if the black shales from the same unit were favorable source rocks. The dolomitization in the limestone could also be a favorable horizon for carbon storage.

As previously noted the Knox Group has limited available porosity data, especially in the Black Warrior Basin. An average porosity of 5% was reported for the Stones River Group and 5.5% for the Knox Group in the Geological Alabama Survey study (**McIntyre et al., 2012**). Based on these averages a value of 5% was chosen for the combined Knox and the Stones River Groups for this report.

The Knox group covers the largest area at sufficient depths of the potential reservoirs/sinks and is fairly thick; however, log porosity data is too scarce to make an informed judgment about reservoir quality. The Stones River Group has an average porosity of 5% with a range of 3% to 11%. Good reservoir quality is patchy and scarce as most of the porosity zones are marginal quality and are laterally discontinuous. Most of the Ordovician undifferentiated has below or marginal reservoir porosity, but scarce isolated wells have moderate to high porosity. In general, porous zones in the Ordovician undifferentiated are laterally discontinuous. For these reasons, despite having a large area at sufficient depths for potential reservoirs/sinks, it is questionable whether these strata can be considered to be attractive reservoirs for potential CO_2 storage (**McIntyre et al., 2012**).

In the GSA's assessment of the Knox and Stones River Groups in Alabama net porous thickness values were estimated with data collected primarily from geophysical well logs, core analyses, and fluid analyses in the databases of the Geological Survey of Alabama and the State Oil and Gas Board of Alabama. This allowed for a more detailed assessment of the reservoir capacities for the Knox and Stones River Groups (**McIntyre et al., 2012**). Further, for each well used in the GSA study, several types of well logs were available. Formation tops were determined and correlated from available resistivity, neutron-density, self-potential, natural gamma, and PEF curves, and porosity and net porous thickness was determined using resistivity and neutron-density curves, and micrologs.

For this study limited log data combined with poor quality logs and no available core data dictated that a gross thickness be used for the Knox and Stones River Groups as they occur in Mississippi. There was simply not enough available data to determine a net porous thickness for the Knox and Stones River Groups (both map and average) in Mississippi.

4.0 Knox Formation Reservoir Properties and Capacity Estimates

Estimating potential CO_2 storage capacity for the basal sandstone first requires estimating the total reservoir pore volume using a standard volumetric approach, then calculating the theoretical volume of CO_2 that can be stored in 100 percent of the available pore space, and finally, using CO_2 storage efficiency factors to generate low- and high-confidence storage capacity estimates. The following approach was used to estimate the CO_2 storage capacity for the Knox Formation.

Total Pore Volume = $A_t * h_g * \phi_{tot}$

Where:

- **A_t** is the reservoir area
- **h_g** is the gross reservoir thickness
- **ϕ_{tot}** is the total porosity of the gross interval (including shales)

$$Total\ Storage\ Capacity\ (Mass) = \sum_{i=1}^{n} (A_i * h_i) * \emptyset_{ave} * (\rho_{scf} / Bg_{CO2}) * P_{xx}$$

Where

- n is the total number of map elements i
- A_i is the surface area of map element i based on the structure map
- h_i is the average depth of map element i based on the isopach map
- ϕ_{ave} average total formation porosity
- ρ_{scf} CO_2 density at standard temperature (^{o} F) and pressure (PSI) conditions
- Bg_{CO2} Formation volume factor (describe how calculated below)
- P_{xx} Formation efficiency factors from Table 3.

To calculate the area and thickness for each saline reservoir, structure and isopach maps were created in the *Petra* geologic mapping and analysis software (**IHS Inc**). Structure and thickness maps were developed by picking the formation tops using well logs acquired for this study, using “formation tops” data provided in the Information Handling Services (IHS) Energy database of U.S. oil and gas wells, and by using existing structure and isopach maps found in publication that focused on the Cambrian-Ordovician sequence of the Knox and Stones River Groups Formation and the immediately overlying units. The total area for the reservoir was determined to be 8,807,390 (acres) using the Petra Map Module. Next, the thickness of the Knox to the top of the Stones River Group, at is occurs below 2,600 ft., was determined by generating an isopach map of that interval. The top depth of the Stones River Group was deemed the cut-off unit for storing CO_2 (see **Figures 3 and 4**). When the maps were generated using the Petra software they are discretized into grid elements, therefore, the total volume was calculated in Petra by multiplying the discretized isopach map (thickness) of the Stones River Group, representing the potential sequestration interval, by the discretized areal extent (area) of the Stones River Group.

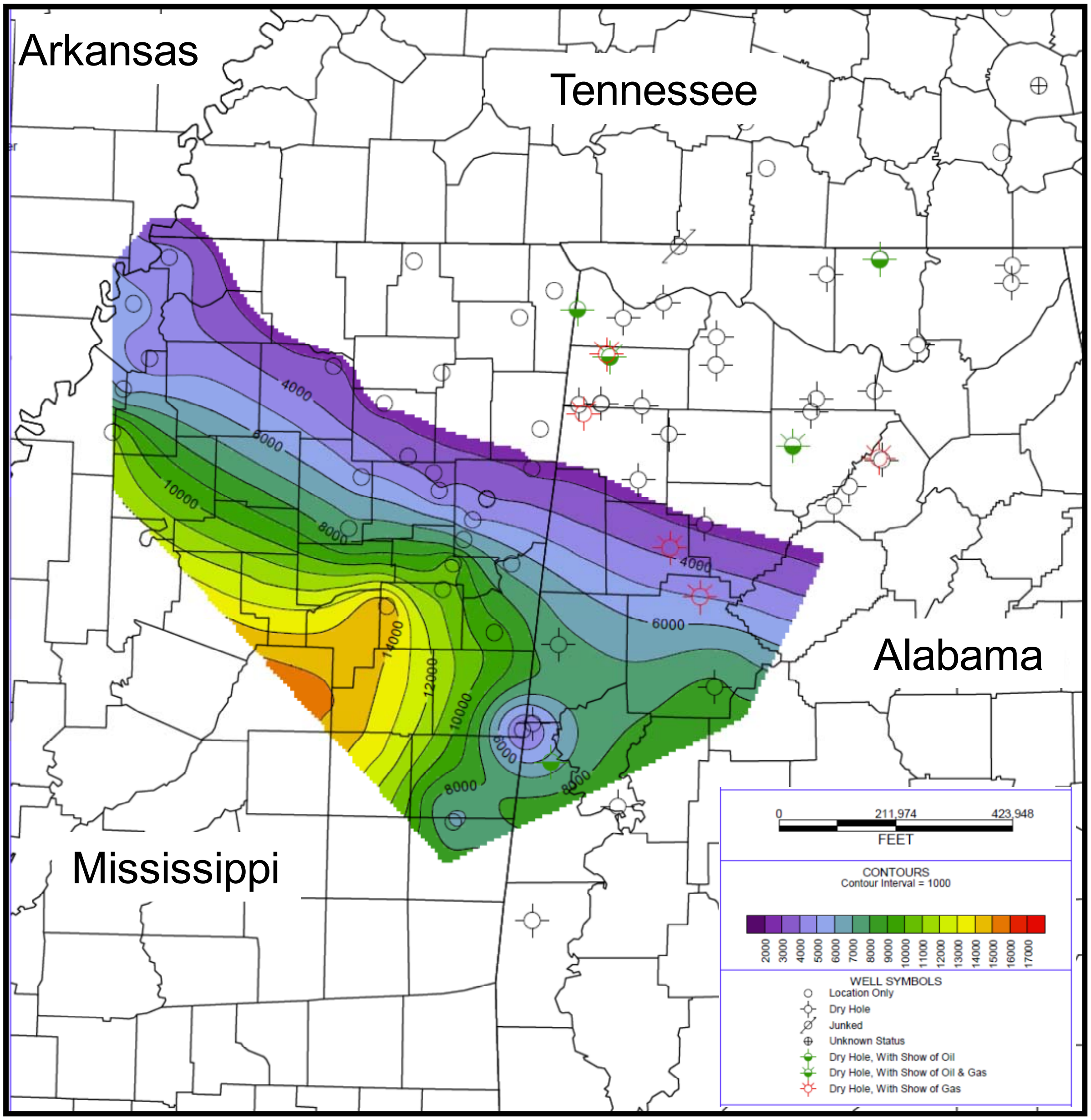

Figure 3:Structure Map on the top of the Stones River Limestone (below 2,600 ft)

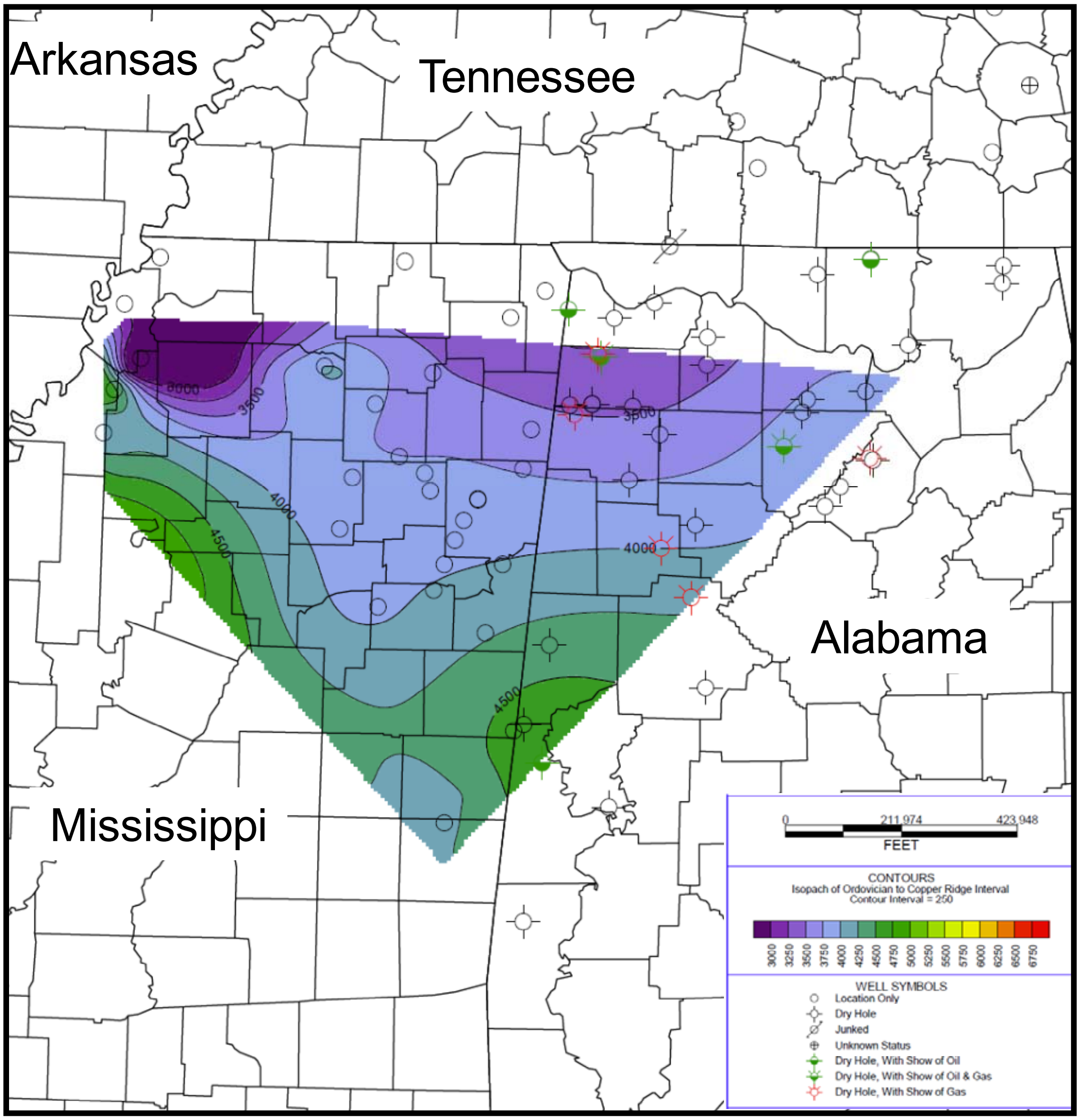

Figure 4: Isopach Map of the combined Stones River and Knox Groups

Theoretical Maximum CO_2 Storage Capacity

Theoretical maximum CO_2 storage volume assumes that 100% of the reservoir pore volume is occupied by CO_2. Theoretical maximum storage is calculated by applying an appropriate CO_2 formation volume factors based on the reservoir's estimated average native pressure and temperature conditions. The CO_2 formation volume factor (Bg_{CO2}) was calculated assuming normal temperature and pressure gradients. The temperature gradient used in this study is 1.5 °F per 100 feet plus 65 °F (ambient surface temperature) and the pressure gradient is 0.43 psi per foot.

The reservoir characteristics for the Stones River and Knox Groups are listed below (**Table 5**). The porosity data was collected from literature assessments of the Cambrian-Ordovician interval in Alabama and Mississippi (**Thomas, 1972; Thomas, 1988; Henderson, 1991; Ryder, 1995; Chowns, 2006; McIntyre et al., 2012**). Once the maps were created, grid-to-grid calculations were run in Petra to generate the low (**Figure 5**) and high (**Figures 6**) capacity maps. Effective storage capacities were applied to the DOE/NETL storage efficiency factors to the theoretical maximums and are shown in **Table 6**.

Table 5: Reservoir Characteristics of the Knox Formation

Stones River and Knox Formation	Total Area (Acres)	Porosity (%)	Average Pore Volume (Sq Ft)	Bg_{CO2} (res cf/scf)	Average CO_2 Capacity (MegaTonnes) (E=100%)
	8,807,390	5%	75,540,666,963,960	0.00270	1,473,637

Table 6: CO_2 Storage Capacity Results (mega tonnes)

	Megatonnes per Square Mile	
Combined Stones River and Knox Formation	High Estimate P(90%)	Low Estimate P(10%)
Porosity: 5%	79,576	7,516

The combined Knox – Stones River Groups are not deemed to be attractive reservoirs for carbon storage. Although, the interval is thick and aerially extensive the lack of extensive reservoir data, the overall low porosity values and the difficulty in determining high porosity zones from logs results in a poorly understood reservoir with highly uncertain injectability. High porosity zones, such as the ‘Snow Zone’ in the Stones River Group, are likely discontinuous and inconsistent horizons; making it difficult to determine the potential CO_2 storage capacity. Increased data coverage of the Knox and Stones River Groups and a detailed study on injectable zones in these formations would provide a clearer picture on their potential for CO_2 storage.

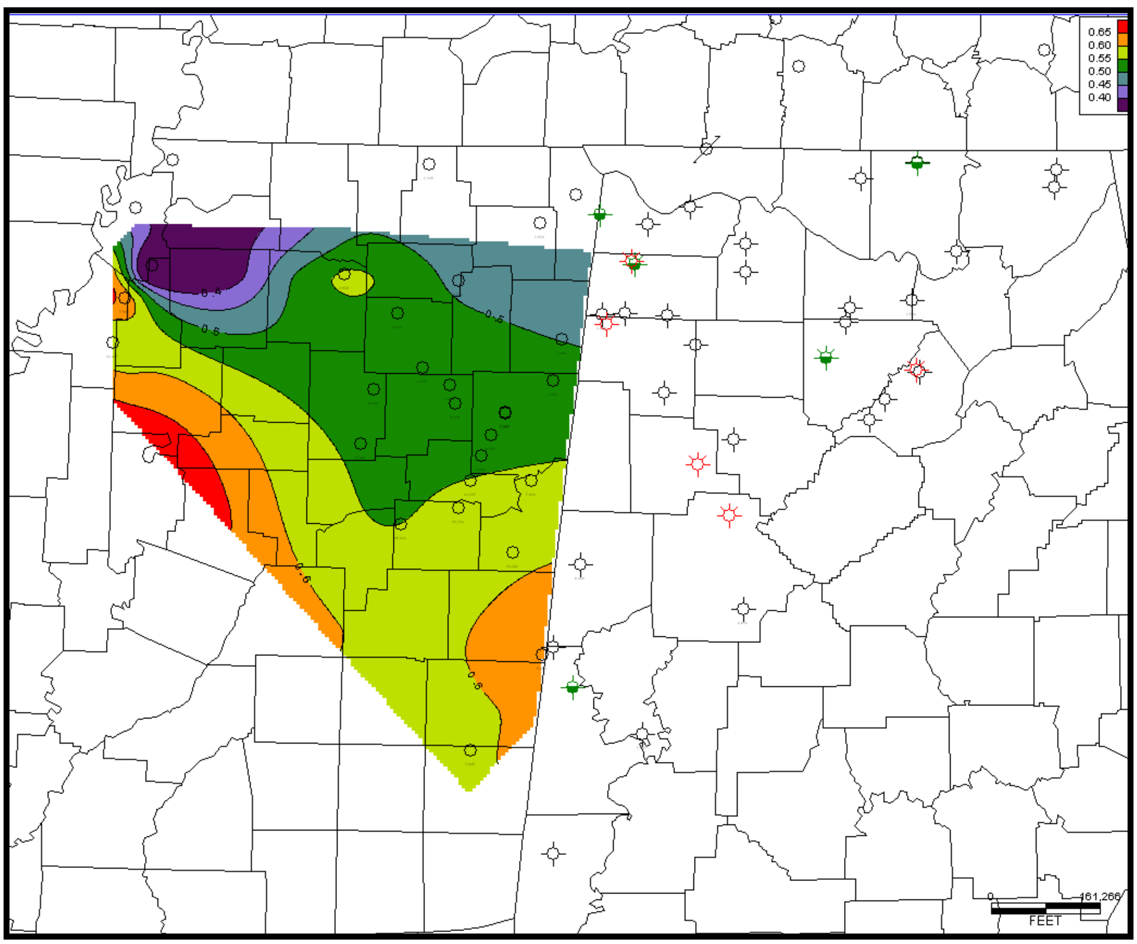

Figure 5: Capacity Map (0.51%) of the Cambro-Ordovician, Copper Ridge Dolomite to the Stones River Limestone, of the Black Warrior Basin in Mississippi, units are in mega-tonnes

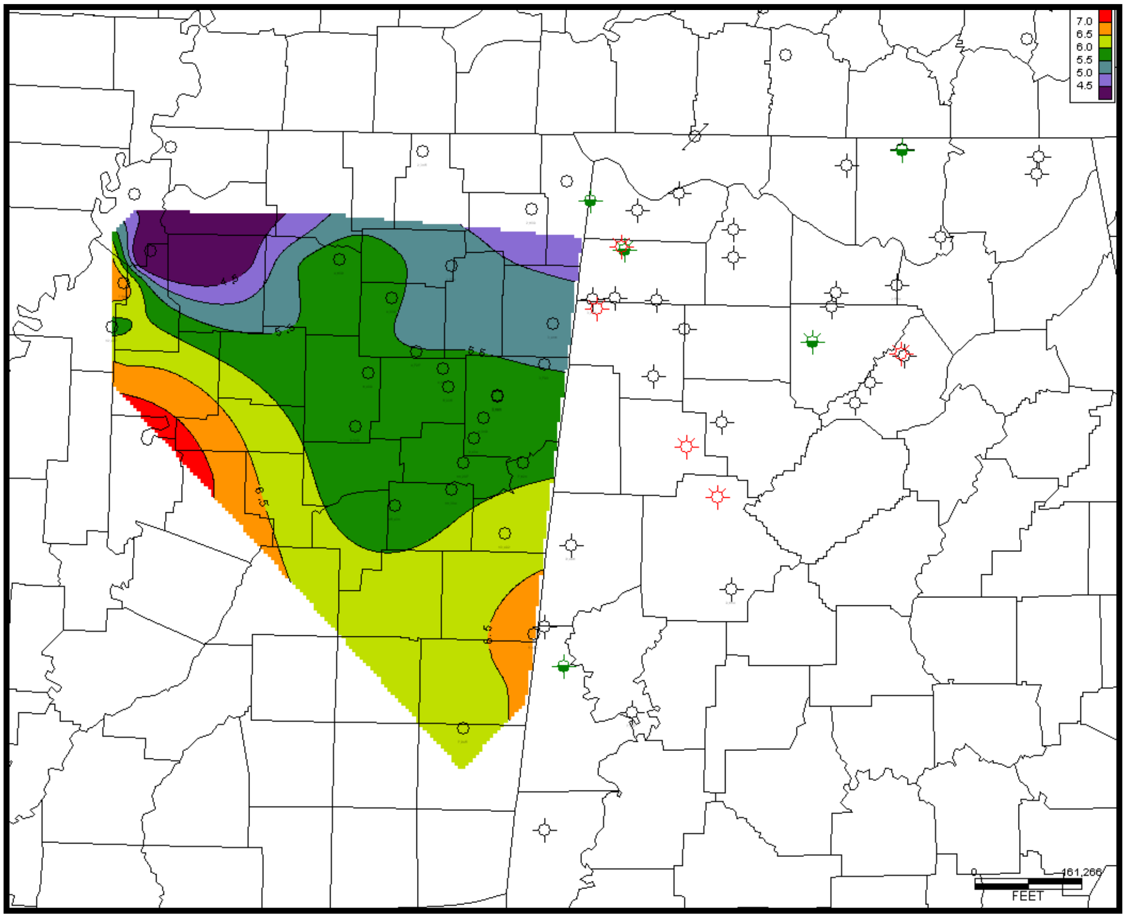

Figure 6: Capacity Map (5.4%) of the Cambro-Ordovician, Copper Ridge Dolomite to the Stones River Limestone, of the Black Warrior Basin in Mississippi, units are in mega-tonnes

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