Thermal Maturity Patterns (CAI and %R_o) in Upper Ordovician and Devonian Rocks of the Appalachian Basin: A Major Revision of USGS Map I–917–E Using New Subsurface Collections

By John E. Repetski, Robert T. Ryder, David J. Weary, Anita G. Harris, and Michael H. Trippi

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Conversion Factors

Multiply	By	To obtain
inch (in)	2.54	centimeter (cm)
inch (in)	25.4	millimeter (mm)
foot (ft)	0.3048	meter (m)
mile (mi)	1.609	kilometer (km)

Temperature in degrees Celsius (°C) may be converted to degrees Fahrenheit (°F) as follows:

$$°F=(1.8\times°C)+32$$

Temperature in degrees Fahrenheit (°F) may be converted to degrees Celsius (°C) as follows:

$$°C=(°F-32)/1.8$$

Thermal Maturity Patterns (CAI and %R_o) in Upper Ordovician and Devonian Rocks of the Appalachian Basin: A Major Revision of USGS Map I–917–E Using New Subsurface Collections

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Introduction

The conodont color alteration index (CAI) introduced by Epstein and others (1977) and Harris and others (1978) is an important criterion for estimating the thermal maturity of Ordovician to Mississippian rocks in the Appalachian basin. Consequently, the CAI isograd maps of Harris and others (1978) are commonly used by geologists to characterize the thermal and burial history of the Appalachian basin and to better understand the origin and distribution of oil and gas resources in the basin. The main objectives of our report are to present new CAI isograd maps for Ordovician and Devonian rocks in the Appalachian basin and to interpret the geologic and petroleum resource implications of these maps. The CAI isograd maps presented herein complement, and in some areas replace, the CAI-based isograd maps of Harris and others (1978) for the Appalachian basin. The CAI data presented in this report were derived almost entirely from subsurface samples, whereas the CAI data used by Harris and others (1978) were derived almost entirely from outcrop samples. Because of the different sampling methods, there is little geographic overlap of the two data sets. The new data set is mostly from the Allegheny Plateau structural province and most of the data set of Harris and others (1978) is from the Valley and Ridge structural province, east of the Allegheny structural front (fig. 1).

Vitrinite reflectance (%R_o), based on dispersed vitrinite in Devonian black shale, is another important parameter for estimating the thermal maturity in pre-Pennsylvanian-age rocks of the Appalachian basin (Streib, 1981; Cole and others, 1987; Gerlach and Cercone, 1993; Rimmer and others, 1993; Curtis and Faure, 1997). This report also presents a new vitrinite reflectance (%R_o) isograd map based on dispersed vitrinite recovered from selected Devonian black shales. The Devonian black shales used for the vitrinite studies of this report also were analyzed by RockEval pyrolysis and total organic carbon (TOC) content in weight percent. Although the RockEval and TOC data are included in the report (table 1), they are not shown on the maps.

The new CAI isograd and vitrinite reflectance isograd maps cover all or parts of Kentucky, New York, Ohio, Pennsylvania, Virginia, and West Virginia (fig. 1), and the following three stratigraphic intervals: Upper Ordovician carbonate rocks, Lower and Middle Devonian carbonate rocks, and Middle and Upper Devonian black shales. These stratigraphic intervals were chosen for the following reasons: (1) they represent target reservoirs for much of the oil and gas exploration in the Appalachian basin; (2) they are stratigraphically near probable source rocks for most of the oil and gas; (3) they include geologic formations that are nearly continuous across the basin; (4) they contain abundant carbonate grainstone-packstone intervals, which give a reasonable to good probability of recovery of conodont elements from small samples of drill cuttings; and (5) the Middle and Upper Devonian black shale contains large amounts of organic matter for RockEval, TOC, and dispersed vitrinite analyses.

Thermal maturity patterns of the Upper Ordovician Trenton Limestone are of particular interest here, because they closely approximate the thermal maturity patterns in the overlying Upper Ordovician Utica Shale, which is the probable source rock for oil and gas in the Upper Cambrian Rose Run Sandstone (sandstone), Upper Cambrian and Lower Ordovician Knox Group (Dolomite), Lower and Middle Ordovician Beekmantown Group (dolomite or Dolomite), Upper Ordovician Trenton and Black River Limestones, and Lower Silurian Clinton/Medina sandstone (Cole and others, 1987; Jenden and others, 1993; Laughrey and Baldassare, 1998; Ryder and others, 1998; Ryder and Zagorski, 2003). The thermal maturity patterns of the Lower Devonian Helderberg Limestone (Group), Middle Devonian Onondaga Limestone, and Middle Devonian Marcellus Shale-Upper Devonian Rhinestreet Shale Member-Upper Devonian Ohio Shale are of interest, because they closely approximate the thermal maturity patterns in the Marcellus Shale, Upper Devonian Rhinestreet Shale Member, and Upper Devonian Huron Member of the Ohio Shale, which are the most important source rocks for oil and gas in the Appalachian basin (de Witt and Milici, 1989; Klemme and Ulmishek, 1991). The Marcellus, Rhinestreet, and Huron units are black-shale source rocks for oil and (or) gas in the Lower Devonian Oriskany Sandstone, the Upper Devonian sandstones, the Middle and Upper Devonian black shales, and the Upper Devonian-Lower Mississippian(?) Berea Sandstone (Patchen and others, 1992; Roen and Kepferle, 1993; Laughrey and Baldassare, 1998).

Methods

Approximately 425 samples of drill-hole cuttings were analyzed for CAI values specifically for this study (fig. 1; table 1). In several wells, more than one sample was collected. Of these 425 samples, about 225 samples were Ordovician carbonates and about 200 samples were Devonian carbonates. About 15 to 20 conodont collections, already on file at the U.S. Geological Survey (USGS), also were used in this study (for example, A.G. Harris, unpublished data; J.E. Repetski, unpublished data; Harris and others, 1994; Ryder and others, 1992, 1996). Between the conodont samples collected specifically for this study and the conodont samples previously collected and now residing in USGS collections, approximately 195 new Ordovician CAI control points and approximately 125 new Devonian CAI control points are available for the CAI isograd maps shown in this report (table 1). These new CAI control points (Ordovician and Devonian) do not include the sample collections from Virginia listed in table 1 because the Virginia collections have not yet been fully analyzed.

Approximately 230 samples were collected from Devonian black shales and analyzed for RockEval parameters, TOC, and reflectance of dispersed vitrinite (table 1). Another 85 to 90 vitrinite reflectance values from Devonian black shales were obtained from analyses reported by Streib (1981). The approximately 315 Devonian black shale samples, represented by our collection and the Streib (1981) collection, provide about 170 control points for the vitrinite reflectance isograd map shown in this report.

Samples for this report were collected from drill cuttings and core in the repository holdings of the State geological surveys of Kentucky, New York, Ohio, Pennsylvania, Virginia, and West Virginia (see Acknowledgments). Also, several samples were collected from wells recently drilled by the petroleum industry (see Acknowledgments). Where possible, different target intervals were sampled from the same well to establish thermal maturity gradients. In such cases, the multiple samples consisted of either a Devonian black shale-Devonian carbonate pair or a group of three or more Devonian black shale samples. The sample weights averaged about 120 grams (g), with a range of 2.1 to several hundred grams, and the sample sizes were greater than 20 mesh. Most samples were composites representing from about 100 to several hundred feet of stratigraphic section. The carbonate samples were shipped to Reston, Va., where they were processed for conodonts using the standard chemical and physical extraction procedures described by Harris and Sweet (1989). The black shale samples were sent to Humble Geochemical Services, Humble, Tex., for processing and analysis for RockEval, TOC, and vitrinite reflectance.

The conodonts recovered were compared visually with a set of conodont color standards of approximately the same age (to Period), provided by A.G. Harris, and assigned a CAI value as defined in the CAI scale of Epstein and others (1977) and Harris and others (1978). An empirical CAI value of 1+ was introduced in this study to improve the definition of isograds in Ohio and Kentucky (J.E. Repetski, unpublished data). Samples exhibiting a range in CAI values and samples with very few individual conodont elements or only a few fragments were assigned a minimum and maximum CAI value. Each CAI_{max} value was assigned to its respective map location and contoured by hand. The maximum CAI values were used for drawing the isograds in order to maintain consistency with procedures used by Harris and others (1978). The conodonts used in this study are reposited in the collections of the USGS in Reston, Va., and are curated using the USGS Cambrian-Ordovician (CO) and Silurian-Devonian (SD) fossil collection locality numbers. Summaries of the location, age, and depth of the samples, as well as their measured CAI, TOC, RockEval, and vitrinite reflectance values, are given in table 1. Also given in table 1 are notable minerals and fossils seen in the heavy fraction (specific gravity >2.87) of the picked insoluble residues. The taxonomy and age ranges of conodont elements recovered from samples in New York, Pennsylvania, and West Virginia are reported in Weary and others (2000, 2001), Repetski and others (2002, 2006), and Repetski and others (2005), respectively.

Reflectance values for dispersed vitrinite in the Devonian black shales were reported as $\%R_{o(mean)}$ (table 1). The $\%R_{o(mean)}$ values were determined from $\%R_o$ histograms that typically consist of 25 to 50 readings (table 1). Each $\%R_{o(mean)}$ value was assigned to its respective map location and contoured by hand. Where $\%R_{o(mean)}$ values were reported for multiple black shale horizons in a single well, all values were plotted on the map but only the average value was used to draw the isograds. Anomalous $\%R_{o(mean)}$ values (both high and low) are plotted on the vitrinite reflectance isograd map but were not incorporated in the isograds. Anomalous $\%R_{o(mean)}$ values are defined as those values that are considered to be extreme in comparison to adjoining groups of sample values. Also, the six $\%R_{o(mean)}$ values for the Lower Mississippian Sunbury Shale in Virginia (table 1) were disregarded as control points.

The correlation between vitrinite reflectance values and their equivalent CAI values is imperfect and needs additional refinement. Figures 2 and 3 are examples of the variability that exists between $\%R_{o(mean)}$ values and equivalent CAI values. The straight lines shown on the cross plot in figure 2 represent several examples of $\%R_{o(mean)}$ versus CAI linear correlations from the literature that are based on large sample collections. The cross plots by Bustin and others (1992) and Hulver (1997) are probably the most applicable to this study. Figure 3 is a diagram, modified from many sources (such as Dow, 1977; Hunt, 1996), that shows the estimated relation between CAI and $\%R_{o(mean)}$ values maturity indicators and associated zones of hydrocarbon generation.

All of the maps were constructed by plotting control points (wells) in ArcView over a digital base map. Latitude and longitude coordinates for each well were obtained from State geological survey well databases. The control points were then attributed with American Petroleum Institute (API) numbers, minimum and maximum CAI values, TOC and RockEval values, and mean vitrinite reflectance (%$R_{o(mean)}$) values. Data points and CAI isograd contours from Harris and others (1978) were captured and replotted by tracing and attributing the points and lines in ArcInfo. The coverages were exported to ArcView version 3.1 for ease of manipulation and graphic display.

Stratigraphy of Sampled Intervals

Most of the Ordovician carbonate samples used in this report are assigned to the Trenton Limestone and (or) the Black River Limestone (Group), although a small number of the Ordovician carbonate samples from West Virginia are assigned other stratigraphic names that include the Chazy Limestone, Beekmantown Dolomite, Utica Shale, and Reedsville Shale (fig. 4; table 1). Most Ordovician carbonate samples used in this report are considered to be of Late Ordovician age, following the geologic time scale of Gradstein and others (2004) and the International Commission on Stratigraphy (Webby, 1995; Cooper, 1999).

The majority of the Devonian carbonate samples used in this study are assigned to the Helderberg Limestone (Group), Onondaga Limestone, Columbus Limestone, or Tully Limestone. Other stratigraphic names assigned to the Devonian carbonate samples are the following: (1) the Boyle Limestone (Dolomite) in Kentucky, (2) the Genundewa Limestone Member, Lodi Limestone, Moscow Shale, Ludlowville Shale, Skaneateles Shale, Penn Yan Shale, Genesee Formation, Geneseo Shale Member of the Genesee Formation, Cherry Valley Limestone, Tichenor Limestone Member of the Moscow Formation, and Manlius Limestone in New York, (3) the Keyser Limestone, Needmore Shale, Licking Creek Limestone, New Creek Limestone, and Wildcat Valley Sandstone in Virginia, and (4) the Hamilton Group and Landes Limestone in West Virginia. The Devonian carbonate samples used in the investigation are considered to be of Early and Middle Devonian age, following the geologic time scale of Gradstein and others (2004). Devonian carbonate samples were selected in wells where carbonate rocks could be located stratigraphically with reasonable confidence and sampled in suitable quantity. Where possible, samples constitute a single carbonate lithostratigraphic unit, although most samples are composite drill cuttings from more than one unit to obtain enough material for analysis.

Most of the Devonian black shale samples used in this study are assigned to the Marcellus Shale, Rhinestreet Shale Member, Huron Member of the Ohio Shale, or Ohio Shale (fig. 4). Other stratigraphic names assigned to the Devonian black shale samples are the following: (1) the Lodi Limestone and Pipe Creek Shale Member in New York, (2) the Olentangy Shale in Ohio, and (3) the Millboro Shale, Needmore Shale, and Chattanooga Formation in Virginia. The Devonian black shale samples used in the investigation are considered to be of Middle and Late Devonian age, following the geologic time scale of Gradstein and others (2004).

Thermal Maturity of Ordovician Rocks

Distribution of Ordovician CAI_{max} Isograds

Figure 5 shows the distribution of Ordovician CAI_{max} isograds, superimposed on selected structural provinces and features in the Appalachian region. Most of these Ordovician CAI_{max} isograds are distributed across the Allegheny Plateau province, an autochthonous terrane that constitutes the majority of the Appalachian basin. This terrane is bounded on the east by several prominent structural fronts and west-verging thrust faults (for example, the Allegheny structural front and the Pine Mountain thrust fault) and on the west by several structural arches (for example, the Findlay arch). East of the Allegheny Plateau province, the Valley and Ridge province is an allochthonous terrane that is characterized by thrust faults that originated during the Alleghanian orogeny of Late Pennsylvanian and Early Permian age (Hatcher and others, 1989).

Allegheny Plateau Province

The Ordovician CAI_{max} 5 isograd in the Allegheny Plateau province defines a 20- to 35-mi (mile)-wide, northeast-trending area of very high thermal maturation that extends from Lewis County, northern West Virginia to Lycoming County, north-central Pennsylvania. Northeast of Lycoming County, the area between the CAI_{max} 5 isograds widens to about 70 mi where it is represented by a bulbous-shaped area centered in Bradford, Sullivan, Susquehanna, and Wyoming Counties, Pa. Furthermore, the CAI_{max} 5 isograd in Bradford County, Pa., extends about 10 mi into Chemung and Tioga Counties, N.Y. The CAI_{max} 5 isograd is enclosed by the CAI_{max} 4.5 isograd and together they form a northeast-trending region of high thermal maturation that extends nearly 500 mi from Braxton and Gilmer Counties, W. Va., to Schenectady County, N.Y. In southeastern and south-central New York, the area of high thermal maturation defined by the CAI_{max} 4.5 isograd is about 145 mi wide and nearly three times the width of the area of high thermal maturation in central Pennsylvania. Moreover, in Seneca County, N.Y., at the northern end of the 145-mi-wide area of high thermal maturation, the CAI_{max} 4.5 isograd changes abruptly from a west-northwest trend to north-northeast trend (fig. 5). The CAI_{max} value of 4.5 in the subsurface of Centre County, Pa., and the CAI_{max} values of 4.5 and 5 in the subsurface of Pendleton County, W. Va., are interpreted to be near the eastern edge of autochthonous rocks that underlie thrust-faulted rocks east of the Allegheny structural front.

The northeast trend of the isograds that have CAI_{max} values of 4 or less in western New York, northwestern Pennsylvania, eastern Ohio, and western West Virginia generally conforms to the trend of the CAI_{max} 4.5 and 5 isograds (fig. 5). In western New York, CAI_{max} 2.5 through 4 isograds trend northeastward for about 80 mi but then change abruptly in north-central New York to a west-northwest trend to conform with the previously noted sharp bend in the CAI_{max} 4.5 and 5 isograds. The CAI_{max} 2 isograd in western New York appears to trend consistently northeastward into Canada without any noticeable changes. In northwestern Pennsylvania, eastern Ohio, and western West Virginia, the northeast- to north-northeast-trending CAI_{max} 2 to 4 isograds are rather uniformly distributed except where they are tightly grouped in Mercer County, Pa., and where they form several conspicuous, northwestward-protruding salients in central Ohio.

In central West Virginia, the CAI_{max} 3.5 to 4 isograds wrap around the southwestern end of the area of high thermal maturation defined by the CAI_{max} 4.5 and 5 isograds. The configuration of the CAI_{max} 2 to 4 isograds in southern West Virginia is largely unknown because Ordovician rocks have not been drilled in this region. However, judging from the CAI value of 3 in subsurface rocks of Randolph County, W. Va., a narrow southwest-opening reentrant of lower CAI values may be present between the Central West Virginia arch and the Allegheny structural front (fig. 5). The CAI_{max} 4.5 and 5 isograds in the subsurface of Pendleton County, W. Va., about 25 mi east of the Randolph County locality, are interpreted to be located in autochthonous strata at the easternmost part of the reentrant.

CAI_{max} 1+ and 1.5 isograds in central Ohio trend approximately northward except where they conform to the westward-protruding salients in the CAI_{max} 2 to 3 isograds previously described in eastern Ohio (fig. 5). In northeastern Kentucky, the CAI_{max} 1+ and 1.5 isograds change abruptly to an east-northeast trend that continues into south-central Kentucky. The CAI_{max} 2 isograd in subsurface rocks of Bell County, Ky., is interpreted to be located near the southeastern limit of autochthonous Ordovician rocks in Kentucky.

Valley and Ridge Province

Ordovician CAI_{max} isograds in the allochthonous terrane of the Valley and Ridge province shown in figure 5 are derived largely from outcrop data in Harris and others (1978). These isograds trend northeastward and subparallel to the isograd trend in the adjoining autochthonous terrane (Allegheny Plateau province). In general, the level of thermal maturity of the allochthonous terrane increases northward along strike and eastward toward the Great Valley and Blue Ridge provinces. The isograds increase eastward from CAI_{max} 4.5 to 5 in eastern New York, from CAI_{max} 4 to 5 in eastern Pennsylvania, eastern West Virginia, and northwestern Virginia, and from CAI_{max} 2 to 5 in southwestern Virginia. In several localities, allochthonous rocks in the western Valley and Ridge province have CAI_{max} values that are lower than or equal to CAI_{max} values in the adjoining autochthonous terrane. For example, in Centre County, Pa., allochthonous rocks at the surface that have CAI_{max} values of 4 overlie autochthonous subsurface rocks that have a CAI_{max} value of 4.5. Similarly, in Pendleton County, W. Va., allochthonous subsurface rocks that have CAI_{max} values of 4 overlie autochthonous subsurface rocks that have CAI_{max} values of 4.5 and 5 (fig. 5). In addition, allochthonous rocks that have CAI_{max} values of 2 in the outcrop and subsurface of Lee County, Va., overlie autochthonous rocks that also have a CAI_{max} value of 2 in nearby Bell County, Ky. (fig. 5).

From this limited data set, the Ordovician CAI_{max} isograds in the Valley and Ridge province are interpreted as being detached (along frontal thrust faults) from the Ordovician CAI isograds in the Allegheny Plateau province (fig. 5). Therefore, in figure 5, the CAI_{max} isograds in the Valley and Ridge province are truncated at the structural fronts. In contrast, the CAI_{max} isograds in the Allegheny Plateau province are shown by dashed lines to continue beneath the Valley and Ridge province (fig. 5).

Distribution of Ordovician CAI_{max} Isograds with Respect to Structural Features

The area of high thermal maturation defined by the CAI_{max} 4.5 and 5 isograds in the autochthonous Ordovician rocks of the Allegheny Plateau province roughly coincides with a broad region of extended crust that includes the Rome trough (a Middle Cambrian graben) and the adjoining Central West Virginia arch, both of which involve Mesoproterozoic crystalline rocks (Kulander and Dean, 1986; Shumaker, 1996; Kulander and Ryder, 2005). Also, the northeastern extremity of the area of high thermal maturation overlaps a large part of the Scranton gravity high (fig. 5) where early Paleozoic and (or) early Mesozoic crustal extension and possibly volcanism occurred (Diment and others, 1972; Harrison and others, 2004). In northeastern, central, and southwestern Pennsylvania the area of high thermal maturation is roughly centered over the Rome trough, whereas in northern and central West Virginia the area of high thermal maturation is located slightly east of the Rome trough and is centered more over the Central West Virginia arch. Between western West Virginia and eastern Kentucky, the Rome trough is again aligned with the CAI isograds, although the values are relatively low (CAI 1+ and 1.5).

Most of the kimberlite intrusives identified in the Appalachian basin (Phipps, 1988) are located within the area of high thermal maturity and (or) the Rome trough (fig. 5). The kimberlite intrusives shown in figure 5 are located in south-central and east-central New York (Smyth, 1896; Hopkins, 1914; Basu and others, 1984), southwestern Pennsylvania (Parrish and Lavin, 1982; Bikerman and others, 1997), northern West Virginia (Watts and others, 1992), and eastern Kentucky (Basu and others, 1984). The kimberlite (titaniferous diatreme) locality of Watts and others (1992), based on stream sediment data, covers a three county area in northern West Virginia (fig. 5) that is associated with a high intensity aeromagnetic anomaly (Zietz and others, 1980). Most of these intrusives are of middle to late Mesozoic age. A younger middle Eocene group of basalt and rhyolite dikes, sills, plugs, and diatremes (fig. 5) intrudes lower Paleozoic allochthonous rocks in Highland County, Va., and Pendleton County, W. Va. (Southworth and others, 1993).

In northeastern Ohio, the axis of the northwest-bulging salient in the CAI_{max} 2, 2.5, and 3 isograds is very closely aligned with the Pittsburgh-Washington structural discontinuity and several faults such as the Akron-Suffield fault zone (fig. 5). A similar, although more subtle, relation is present in southeastern Ohio where the northwest-bulging salient in the CAI 2 isograd is partially aligned with the Cambridge structural discontinuity (arch).

Distribution of Ordovician CAI_{max} Isograds with Respect to Cambrian, Ordovician, and Silurian Oil and Gas Fields

Cambrian and Ordovician Fields

Oil and (or) gas fields in Cambrian and Ordovician reservoirs are widely distributed across the Appalachian basin. The largest field in reservoir rocks of this age is the giant Lima-Indiana oil and gas field located on or near the Findlay arch of northwestern Ohio and part of neighboring Indiana (fig. 6). Discovered in 1885, this field has produced about 500 million barrels of oil (MMBO) and 1 trillion cubic feet (TCF) of natural gas from the Ordovician Trenton Limestone (Wickstrom and others, 1992). As shown in figure 6, additional important oil and gas fields in Ohio include those in the Cambrian Knox Dolomite in central Ohio (Morrow County fields) and in the Cambrian Knox Dolomite and Rose Run sandstone and Lower Ordovician Beekmantown dolomite in east-central Ohio (for example, Baltic, Caanan, and Randolph fields). Hydrocarbon entrapment for both groups of fields in Cambrian and Lower Ordovician reservoirs is commonly controlled by the Middle Ordovician Knox unconformity (fig. 4) (Riley and others, 1993, 2002; Shafer, 1994). Between 1959 and 1995, about 38 MMBO and 35 billion cubic feet (BCF) of natural gas were produced from the Morrow County fields (Riley and others, 1996b). The ultimate size of the Baltic field, discovered in 1965, is estimated to be about 75 to 80 BCF and 3 to 5 MMBO (R.T. Ryder, unpublished data). Riley and others (2002) reported that the ultimate size of the Caanan and Randolph fields combined, discovered in 1960 and 1990, respectively, is about 21 million barrels of oil equivalent (MMBOE).

Recent gas discoveries in fault-controlled, hydrothermal dolomite reservoirs in the Ordovician Black River and Trenton Groups (Smith and others, 2003; Smith, 2006) largely in Steuben and Chemung Counties, N.Y. (fig. 6), have increased the annual gas production in New York State to a modern State record of 55.2 BCF (New York State Department of Environmental Conservation, 2005). The Black River and Trenton hydrothermal dolomite reservoirs for these gas discoveries are highly fractured and are confined to linear fault zones. Among the major fields discovered in this trend are the Glodes Corners Road field, discovered in 1986, and the adjacent Muck Farm field, discovered in 1998; Wilson Hollow field, discovered in 1999; and Quackenbush Hill fields, discovered in 2000 (fig. 6). Through 2005, about 17.4 BCF of natural gas have been produced from the Glodes Corners Road and Muck Farm fields combined, whereas about 64.8 and 35.2 BCF of natural gas have been produced from the Quackenbush Hill and Wilson Hollow fields, respectively (New York Department of Environmental Conservation, 2004, 2005). About 155 BCF of natural gas have been produced from the entire Trenton-Black River trend in New York through 2005 (New York State Department of Environmental Conservation, 2004, 2005). The Cottontree gas field in Roane County, W. Va. (fig. 6) (Avary, 2001), is similar to the New York Trenton-Black River fields except that the reservoir apparently consists of fractured limestone rather than fractured hydrothermal dolomite. Approximately 9.25 BCF of natural gas have been produced from the field since its discovery in 1999 through 2005 (West Virginia Geological and Economic Survey oil and gas production database).

The Grugan field in central Pennsylvania produces gas from fractured sandstone in the Upper Ordovician Bald Eagle Formation (Laughrey and Harper, 1996) (fig. 6). The ultimate size of this two-well field is about 8.2 BCF of natural gas. Gas produced from about 13,000 feet (ft) at the Grugan field represents the second deepest production in the Appalachian basin (fig. 6). The deepest gas well in the basin is the Exxon No. 1 McCoy in Jackson County, W. Va. (fig. 6). Completed in 1975, this well produced gas for about 6 months from a depth of 14,350 to 14,360 ft in the Middle Cambrian Conasauga Group (Oil and Gas Journal, 1975; Harris and Baranoski, 1996).

The most plausible source rock for the oil and gas fields in Cambrian and Ordovician reservoirs in Ohio, Pennsylvania, New York, and West Virginia is the Upper Ordovician Utica Shale (Cole and others, 1987; Jenden and others, 1993; Laughrey and Baldassare, 1998; Ryder and others, 1998). The Utica Shale is 150 to 300 ft thick across much of Ohio, Pennsylvania, New York, and the northern part of West Virginia (Wallace and Roen, 1989). In southeastern New York, the Utica Shale increases in thickness to as much as 800 ft (Martin, 2005; Martin and others, 2005). The Ordovician CAI_{max} isograds shown in figure 6 are good indicators for establishing regional thermal maturation patterns in the Utica Shale (which conformably overlies the Trenton), because the isograds are based on conodonts collected from the Trenton Limestone.

Most of the oil and gas fields associated with the Knox unconformity in central and eastern Ohio are located between the Ordovician CAI_{max} 1+ and 2.5 isograds (fig. 6). These isograd values signify that the Ordovician Trenton Limestone and the overlying Utica Shale source rock have reached the "window" of oil and wet gas generation and preservation (fig. 3). Following the definition of Tissot and Welte (1984), wet gas consists of less than 98 percent methane with significant amounts of ethane, propane, and heavier hydrocarbons (C_1/C_1-C_5<0.98). The close association of the oil and wet gas that constitute the petroleum in these fields (Moore and Sigler, 1987; Laughrey and Baldassare, 1998) with moderate levels of thermal maturation in the Utica Shale suggests that the petroleum was probably locally derived.

The giant Lima-Indiana field is located in an area where the Trenton Limestone and overlying proposed Utica Shale source rock (CAI_{max} 1–1+) are immature with respect to oil and gas generation (figs. 3, 6). This low level of thermal maturation for the proposed source rock in the vicinity of the Lima-Indiana field implies that the oil and gas were derived from an adjoining region of higher thermal maturation.

The fields of nonassociated gas in the Trenton-Black River dolomite reservoir in south-central New York (such as Glodes Corners Road and Muck Farm), the Trenton-Black River limestone reservoirs in west-central West Virginia (such as Cottontree), and the Ordovician Bald Eagle Formation sandstone reservoir in central Pennsylvania (Grugan field) are located between the CAI_{max} 3.5 and 5 isograds (fig. 6). These isograd values indicate a level of thermal maturation within the "window" of dry gas generation and preservation (fig. 3). Following the definition of Tissot and Welte (1984), dry gas consists of 98 percent or more of methane ($C_1/C_1\text{-}C_5 \geq 0.98$). The close association of dry gas in these fields (Jenden and others, 1993; Laughrey and Baldassare, 1998) with high levels of thermal maturation in the proposed Utica Shale source rock suggests that the gas was locally derived.

Cambrian and Ordovician oil and gas fields in eastern Kentucky were derived from several source rocks. The gas and associated oil produced in the Homer field in Elliott County, Ky. (fig. 6), were probably derived from dark-gray shale in the Middle Cambrian Conasauga Group in the Rome trough (Ryder and others, 2005). Reservoirs in the Homer field consist of Middle Cambrian sandstone (Rome Formation and Conasauga Group), Middle Ordovician sandstone (St. Peter Sandstone), and Upper Ordovician limestone (Lexington (=Trenton) Limestone). Also, nonassociated gas produced from the Conasauga Group at 14,358 ft in the Exxon No. 1 McCoy well, Jackson County, W. Va. (Harris and Baranoski, 1996), probably was derived from Cambrian source rocks in the Rome trough (Ryder and others, 1998). In addition, Cambrian source rocks in the Rome trough may be responsible for oil and associated gas in a group of small fields along the crest of the Rockcastle River uplift (such as the Raccoon Mountain field), Clay and Laurel Counties, Ky. (fig. 6), whose reservoirs consist of Knox and Trenton carbonates. Oil and gas that are produced from a variety of Ordovician carbonate reservoirs in Clinton and Cumberland Counties, south-central Kentucky (J.A. Drahovzal, written communication *in* Wickstrom, 1996), probably were derived from the Devonian Ohio Shale. At most localities in this area, these Devonian Ohio Shale source rocks rest unconformably on Ordovician rocks.

At the Rose Hill field in the Valley and Ridge province of Lee County, Va. (fig. 6), oil and gas have been produced from the Ordovician Trenton Limestone since 1946 (Bartlett, 1988). The nearby Ordovician CAI_{max} 2 isograd is consistent with the petroleum phases (oil and associated wet gas) produced in the field (figs. 3, 6). Alkane distributions in the oils from the Rose Hill field indicate that the oils were derived from an Ordovician source rock (K.O., Dennen, written commun., 2007).

Silurian Fields

Oil and gas fields in Silurian reservoirs in the Appalachian basin are dominated by the Lower Silurian regional oil and gas accumulation that extends across eastern Ohio, northwestern Pennsylvania, and western New York (Ryder and Zagorski, 2003) (fig. 7). The major reservoirs consist of the Lower Silurian Clinton sandstone in Ohio and the Lower Silurian Clinton-Medina Group sandstones in Pennsylvania and New York. Gas-saturated reservoirs appear to be nearly pervasive across the regional accumulation so that most wells drilled in the accumulation have commercial production. However, the sandstone reservoirs are "tight gas sandstones" that have a very low permeability (Dutton and others, 1993, p. 161–177) and must be stimulated by hydrologic-fracturing techniques to yield a commercial well. Ryder and Zagorski (2003) estimated that approximately 8.7 TCF of natural gas and 400 MMBO have been produced from the Clinton-Medina reservoirs. Furthermore, Milici and others (2003) considered the Clinton-Medina petroleum resource to be a continuous-type accumulation that is estimated to contain a mean of about 24 TCF of recoverable undiscovered gas.

The Lower Silurian Tuscarora Sandstone, an eastward equivalent of the Clinton-Medina sandstones, is a gas reservoir in several fields in Pennsylvania and West Virginia (fig. 7). The Devils Elbow field in central Pennsylvania and the Leadmine and Indian Creek fields in West Virginia (fig. 7) are examples of such gas fields and are characterized by low-British thermal unit natural gas with a large percentage of nitrogen or carbon dioxide (Avary, 1996). Fracture porosity is commonly required for commercial production. The largest of the Tuscarora Sandstone gas fields is the Indian Creek field (fig. 7) in Kanawha County, W. Va., with an ultimate size of about 60 BCF of gas (Avary, 1996).

The Utica Shale is the most probable source rock for the oil and gas in the Lower Silurian Clinton-Medina regional accumulation and in the Silurian Tuscarora Sandstone (Drozd and Cole, 1994; Laughrey and Baldassare, 1998; Ryder and others, 1998). Silurian shale and carbonate units associated with the Lower Silurian Clinton-Medina regional oil and gas accumulation do not appear to be adequate source rocks (Cole and others, 1987; Ryder, and others, 2007). Devonian black shale source rocks may have contributed some oil and gas to the Clinton-Medina sandstone reservoirs (Cole and others, 1987), but widespread evaporite units in the Salina Group probably minimized large-scale mixing of Ordovician- and Devonian-derived petroleum (Drozd and Cole, 1994; Ryder and others, 1998). To date, there is no evidence in the Appalachian basin for vertical leakage of Ordovician petroleum through Silurian evaporites to younger reservoirs as reported by Hatch and others (2005) in the Michigan basin. Because the Ordovician CAI_{max} isograds shown in figure 7 are based on conodonts from the Trenton Limestone (Group), the isograds are good indicators for establishing regional thermal maturation patterns in the Utica Shale.

The majority of the Lower Silurian regional oil and gas accumulation is located between the Ordovician CAI_{max} 1.5 and 2.5 isograds (fig. 7). These isograd values signify that the Ordovician Trenton Limestone and nearby rocks have reached the "window" of oil and wet gas generation and preservation (fig. 3). The close association of oil and wet gas in this accumulation (Moore and Sigler, 1987; Burruss and Ryder, 1998, 2003) with moderate levels of thermal maturation in the proposed Utica Shale source rock suggests that the petroleum was locally derived.

Nonassociated gas fields in the Tuscarora Sandstone in Pennsylvania and West Virginia are located between the Ordovician CAI_{max} 3 and 5 isograds, and thus these fields occur in the "window" of dry gas generation and preservation (figs. 3, 7). The implied high level of thermal maturation of the Utica Shale source rock beneath these fields is consistent with the produced dry gas (Moore and Sigler, 1987; Jenden and others, 1993; Laughrey and Baldassare, 1998) and suggests that the gas was locally derived.

Small gas fields in the Upper Silurian Lockport Dolomite are distributed across east-central Ohio, northwestern Pennsylvania, and western New York (fig. 7). In Ohio, the reservoir interval is called the "Newburg zone" where bioherms with thin zones of vuggy dolomite are present (Santini and Coogan, 1983; Noger and others, 1996). Small amounts of oil and traces of H_2S are associated with these "Newburg zone" gas fields (Janssens, 1975; Santini and Coogan, 1983; Noger and others, 1996). Additional oil and gas fields in Silurian reservoirs occur in eastern Kentucky where productive intervals are the Lower Silurian Keefer Sandstone (Big Six sandstone) and the Upper Silurian "Corniferous" carbonate interval that consist of the Lockport Dolomite and Salina Group (Meglen and Noger, 1996; Noger and others, 1996) (fig. 7). Oil and gas fields in the Keefer (Big Six) reservoir are trapped primarily by stratigraphic pinchouts in combination with anticlinal structures, whereas oil and gas in "Corniferous" reservoirs are trapped beneath a regional Upper Devonian unconformity (Meglen and Noger, 1996; Noger and others, 1996). From 1915 through 1970, the large Big Sinking-Irvine-Furnace oil field in Lee, Powell, and Estill Counties, Ky. (fig. 7), produced about 96 MMBO from the "Corniferous" reservoir (Miles, 1972). In west-central West Virginia, several medium-size gas fields occur in the Upper Silurian Newburg sandstone, which is a thin sandstone unit located between the Wills Creek Formation and the McKenzie Limestone (Patchen, 1996). The Rocky Fork field (fig. 7) in the Newburg sandstone reservoir in northern Kanawha County, W. Va., has an ultimate size of about 144 BCF of gas (Patchen, 1996).

The oil and gas in the Lockport Dolomite of Ohio, Pennsylvania, and New York were derived from either the Utica Shale or from presently unrecognized source rocks associated with the Silurian biohermal buildups. Although the most likely source of natural gas in the Newburg sandstone is Ordovician or Devonian black shale (Patchen, 1996), the Wills Creek Formation and McKenzie Limestone in West Virginia may be potential source rocks (Ryder, and others, 2007). Oil and gas in Silurian sandstone and carbonate reservoirs (Corniferous) in eastern Kentucky were derived from the Upper Devonian Ohio Shale that rests unconformably on many of the reservoirs (Ray, 1971).

The majority of the gas fields that produce from the Lockport Dolomite in Ohio are located between the Ordovician CAI_{max} 1+ and 2 isograds (fig. 7). These isograd values signify that the fields are within the "window" of oil and wet gas generation and preservation (fig. 3). However, the predominance of natural gas over oil in these Lockport fields is apparently inconsistent with these lower Ordovician CAI_{max} isograd values. In north-central New York, isolated gas fields in the Lockport Dolomite are associated with Ordovician CAI_{max} 4 to 4.5 isograds (fig. 7). This implied high level of thermal maturation of the Utica Shale beneath these fields is consistent with the dry gas produced from the Lockport reservoir in the Auburn field (fig. 6), which is 10 mi northeast of the West Auburn field (fig. 6) (Jenden and others, 1993). Newburg sandstone gas fields in Jackson and Kanawha Counties, west-central W. Va. (fig. 7), are associated with CAI_{max} isograds in the 2 to 3.5 range, values which are consistent with the slightly wet gas (C_1/C_1-C_5= 0.92–0.95) produced in the fields (Moore and Sigler, 1987).

Thermal Maturity of Devonian Rocks

Distribution of Devonian CAI_{max} Isograds

Allegheny Plateau Province

A group of closely spaced concentric Devonian CAI_{max} 4, 4.5, and 5 isograds define an elongate, north-northeast-trending, 225-mi-long by 40-mi-wide area of high thermal maturation that extends from Lycoming County in northeastern Pennsylvania to approximately Albany County in east-central New York (fig. 8). This area of high thermal maturation defined by the Devonian CAI_{max} isograds is coincident with the bulbous-shaped area of high thermal maturation defined by the Ordovician CAI_{max} 5 isograd (fig. 5). Additional Devonian CAI_{max} 4 and 4.5 isograds are located near the Allegheny structural front in northeastern Pennsylvania. Much smaller areas of high thermal maturation are present in West Virginia, such as in Taylor and Preston Counties, where a small, isolated area is enclosed by a CAI_{max} 4 isograd (fig. 8). Another example occurs farther south in Monroe, Raleigh, and Summers Counties, W. Va., where an arcuate, northwest-facing salient is defined by the Devonian CAI_{max} 4 isograd (fig. 8).

Isograds with Devonian CAI_{max} values of 2.5, 3, and 3.5 in central New York, western Pennsylvania, and central West Virginia generally conform to the regions of high thermal maturity described previously in the discussion of Ordovician thermal maturity patterns. In north-central New York, the CAI_{max} 2.5 and

3 isograds wrap around the northern end of the region of high thermal maturation to form a 75-mi-wide zone, across which CAI_{max} values of 3 and a small enclosed area of CAI_{max} 3.5 and 4 isograds are present (fig. 8). The Devonian CAI_{max} 2.5 and 3 isograds have an east-west trend in north-central New York, but they bend rather abruptly to a northeastern trend near eastern Ontario County, N.Y., and continue southward to the New York-Pennsylvania border (fig. 8). These Devonian CAI_{max} 2.5 and 3 isograds are tightly spaced (approximately 15 mi between them), and they closely mimic the location and shape of the previously described Ordovician CAI_{max} 4.5 isograd in south-central New York (fig. 5). Moreover, the western side of this region of high thermal maturation (CAI_{max} 4, 4.5, and 5 isograds) was first recognized by Johnsson (1986) using clay mineralogy data (illite/smectite) and apatite fission track ages obtained from the Middle Devonian Tioga bentonite bed that directly overlies the Onondaga Limestone.

Near the New York-Pennsylvania border, the 2.5 and 3 isograds change from a northeastern trend to an east-west trend; they swing nearly 100 mi west of the region of high thermal maturation and wrap sharply around its western end to produce a northwestward-protruding salient (fig. 8). In southwestern Pennsylvania, another northwestward-directed salient is defined by the CAI_{max} 2.5 and 3 isograds and possibly the CAI_{max} 3.5 isograd. Farther south in northern and southern West Virginia, the CAI_{max} 2.5, 3, and 3.5 isograds wrap tightly around areas of high thermal maturation (defined by CAI_{max} 4 isograds) to form distinct west- to northwest-bulging salients with an intervening re-entrant (fig. 8). The 2.5, 3, and 3.5 isograds that define the western side of the northern West Virginia salient are highly compressed, and the isograds have lobate-shaped extensions at the northern and southern ends of the salient (fig. 8).

The Devonian CAI_{max} 2 isograd is characterized by a relatively smooth line with minor changes in curvature where the isograd crosses western New York, northwestern Pennsylvania, eastern Ohio, western West Virginia, and eastern Kentucky. Subtle northwest-facing concave-shaped CAI_{max} 2 isograds in northwesternmost Pennsylvania and northeastern Ohio may represent the westward extension of the northwestern and southwestern Pennsylvania salients, respectively. In addition, four small areas of higher thermal maturation (enclosed by Devonian CAI_{max} 2.5 isograds) are located in a region extending from western Pennsylvania to easternmost Kentucky between the Devonian CAI_{max} 2 isograd and the prominent west-bulging salients in the Devonian CAI_{max} 2.5, 3, and 3.5 isograds. The largest of these local increases in thermal maturation is centered in Roane County, west-central West Virginia (fig. 8). Another small area of higher thermal maturation (enclosed by a CAI_{max} 2.5 isograd) is located in westernmost West Virginia and eastern Kentucky. Several miles farther westward into Kentucky, Devonian CAI_{max} 1.5 and 2 isograds are deflected sharply around the isolated CAI_{max} 2.5 isograd.

In central Ohio, a conspicuous west-protruding salient in the CAI_{max} 1+ and 1.5 isograds extends as far west as Franklin County (fig. 8). North and south of the salient in central Ohio, the CAI_{max} 1.5 isograd has a northerly trend with only minor westward deflections (fig. 8).

Valley and Ridge Province

Devonian CAI_{max} isograds in the allochthonous terrane of the Valley and Ridge province shown in figure 8 are derived largely from outcrop data in Harris and others (1978). In general, the isograds trend northeastward, subparallel to the isograds in the Allegheny Plateau province. Moreover, the isograds in the Valley and Ridge province show an eastward increase in thermal maturation toward the Great Valley and Blue Ridge provinces. For example, the isograds in central Pennsylvania increase in an easterly direction from CAI_{max} 2.5 to 4.5. At several localities, such as Giles County, Va., and south-central Pennsylvania, allochthonous rocks in the western part of the Valley and Ridge province have Devonian CAI_{max} values that are lower than or equal to Devonian CAI_{max} values in the adjoining autochthonous terrane of the Allegheny Plateau province. In the outcrop of Giles County, Va., allochthonous rocks with probable CAI_{max} values of 3.5 appear to be juxtaposed against autochthonous rocks with CAI_{max} values of 4, whereas in south-central Pennsylvania (Bedford County) allochthonous rocks with CAI_{max} values of 3 are juxtaposed against autochthonous rocks with CAI_{max} values that range from 3 to 3.5.

From this limited data set, the Devonian CAI isograds in the Valley and Ridge province are interpreted as being detached, along frontal thrust faults, from the Devonian CAI isograds in the Allegheny Plateau province (fig. 8). Therefore, in figure 8 the CAI_{max} isograds in the adjacent provinces are truncated at the structural fronts.

Distribution of Devonian $\%R_{o(mean)}$ Isograds

Most of the Devonian $\%R_{o(mean)}$ control points are located in the Allegheny Plateau province (fig. 9). Ten $\%R_{o(mean)}$ control points shown in figure 9 were not used as control points (eight in Pennsylvania, one in New York, and one in West Virginia) for the isograds because they have anomalously low values compared with adjacent control points. One control point in northwesternmost Pennsylvania and one in northern West Virginia were not used to construct the isograds because these points have anomalously high values. Also, several of the control points (Erie County, Pa.; Mason and Wetzel Counties, W. Va.) that were used to construct the Devonian $\%R_{o(mean)}$ isograds (fig. 9) are based on data reported by Streib (1981).

Allegheny Plateau Province

Devonian $\%R_{o(mean)}$ 2.5, 3, and 3.5 isograds delineate three areas with a high level of thermal maturation (fig. 9). The first area in northeastern Pennsylvania has $\%R_{o(mean)}$ 2.5, 3, and 3.5 isograds that trend northeastward into southeastern New York. The southwestern end of these isograds may bend southward to form a subtle northwest-facing salient. The second area of high thermal maturation is located in southwestern Pennsylvania where the $\%R_{o(mean)}$ 2.5 isograd forms a prominent northwest-bulging salient (fig. 9). A third well-defined area of high thermal maturation is located in southern West Virginia where 2.5 and 3 isograds form a prominent north- to northwest-bulging salient.

A region of moderate thermal maturation, marked by Devonian $\%R_{o(mean)}$ 1, 1.5, and 2 isograds, extends from central New York to southeastern Kentucky and southwestern Virginia (fig. 9). In western Pennsylvania, this group of $\%R_{o(mean)}$ 1, 1.5, and 2 isograds forms a conspicuous southeast-trending re-entrant and two accompanying northwest-bulging salients (fig. 9). Another northwest-bulging salient zone in the $\%R_{o(mean)}$ 1, 1.5, and 2 isograds is located in northwestern West Virginia and adjoining southeastern Ohio (fig. 9). In southwestern Virginia and southeastern Kentucky this group of isograds narrows to about 20 mi and occupies the western margin of the previously described north- to northwest-bulging salient formed by the $\%R_{o(mean)}$ 2.5 and 3 isograds in southern West Virginia (fig. 9).

The Devonian $\%R_{o(mean)}$ values (0.33–0.46) in central and northeastern Ohio (fig. 9) are low in comparison to analyses reported by Maynard (1981), Streib (1981), and Curtis and Faure (1997). Also, these Devonian $\%R_{o(mean)}$ values in central and northeastern Ohio are consistently lower than $\%R_o$ values in overlying Pennsylvanian coal beds (Rowan, 2006; L.F. Ruppert, written commun., 2007). Similar low $\%R_{o(mean)}$ values in comparison to $\%R_o$ values in overlying Pennsylvanian coal beds are recognized in eastern Kentucky (L.F. Ruppert, written commun., 2007). The $\%R_{o(mean)}$ values in western New York are also probably too low, but there are no nearby Pennsylvanian coal beds with which to compare them. These seemingly low $\%R_{o(mean)}$ values may be related to vitrinite suppression (Lo, 1993) caused by the high total organic content of the rocks (table 1).

Valley and Ridge Province

Devonian $\%R_{o(mean)}$ isograds in the allochthonous terrane of the Valley and Ridge province of Virginia are based on data from 14 wells (fig. 9). In most of these wells, two or more Devonian black shale intervals were sampled and measured, and the mean of the individual $\%R_{o(mean)}$ values was used to construct the isograds. For example, well P in Montgomery County, Va. (fig. 9), has six $\%R_{o(mean)}$ values for the Devonian black shale interval, but only the mean of the six values (2.51) was used to construct the isograd patterns.

The $\%R_{o(mean)}$ isograds appear to have been offset by several thrust faults in the Valley and Ridge province of Virginia, West Virginia, and Kentucky (fig. 9). Isograds have the following characteristics within each thrust sheet in the allochthonous terrane: (1) the isograds trend northeastward, roughly subparallel to those in the autochthonous terrane, (2) the isograd values increase toward the northeast, and (3) the isograd values increase eastward toward the Blue Ridge province, except within the Pine Mountain thrust sheet. Moreover, the $\%R_{o(mean)}$ isograds are commonly discordant across the juxtaposed allochthonous and autochthonous terranes. For example, the St. Clair thrust fault in southern West Virginia has juxtaposed allochthonous rocks with $\%R_{o(mean)}$ values of 1.5 to 2 against autochthonous rocks with $\%R_{o(mean)}$ values of 2.5 to 3. In contrast, the Pine Mountain thrust fault in southwestern Virginia and adjoining Kentucky has juxtaposed allochthonous rocks with $\%R_{o(mean)}$ values of 1 to 2 against autochthonous rocks with $\%R_{o(mean)}$ values of 0.5 to 1.5.

Distribution of Devonian CAI_{max} and $\%R_{o(mean)}$ Isograds with Respect to Structural Features

Similar to the Ordovician rocks, Devonian rocks have the highest levels of thermal maturation in northeastern Pennsylvania and south-central to southeastern New York (figs. 5, 8, 9). Although both the Devonian CAI_{max} and $\%R_{o(mean)}$ isograds in this area indicate high levels of thermal maturation, the isograd configurations are very different. For example, the $\%R_{o(mean)}$ isograds show no closure in this area and several of the isograds bend abruptly northward in south-central New York from an eastward trend along the Pennsylvania-New York border (fig. 9). The reasons for these differences between the Devonian CAI and $\%R_o$ isograd patterns are unknown. As previously noted, this area overlies the Scranton gravity high and the northeastern end of the Rome trough where crustal extension occurred during the early Paleozoic and possibly was renewed during the early Mesozoic. Whatever tectonic-thermal event caused the high thermal maturation, it clearly affected both the Ordovician and Devonian rocks.

The next highest levels of thermal maturation in Devonian rocks are located in four areas, each of which has a prominent west- to northwest-bulging salient in the CAI_{max} and $\%R_{o(mean)}$ isograds. Most of these prominent salients also are recognized in the Ordovician CAI_{max} isograds (fig. 5). The northernmost salient is defined by Devonian CAI_{max} 2.5 to 3 isograds and the $\%R_{o(mean)}$ 0.5 to 2 isograds that are closely aligned with the northwest-trending Tyrone-Mt. Union structural discontinuity in northwestern Pennsylvania (figs. 8, 9). The second northwest-bulging salient is located in southwestern Pennsylvania and northeastern Ohio (defined by Devonian CAI_{max} 2, 2.5, 3, and 3.5 isograds and $\%R_{o(mean)}$ 0.5 to 2.5 isograds) and is closely aligned with the Pittsburgh-Washington structural discontinuity and several faults in Ohio such as the Akron-Suffield and Highlandtown faults (figs. 8, 9). The third salient is present in northern West Virginia where it is defined by an enclosed Devonian CAI_{max} 4 isograd with adjoining tightly compressed 2.5 to 3.5 isograds and by $\%R_{o(mean)}$ 1.5 to 2 isograds (figs. 8, 9). This salient is coincident with the southeastern margin of the Rome trough, the Central West Virginia arch, and a region of probable kimberlite intrusions (figs. 8, 9). The fourth prominent west- to northwest-bulging salient, defined by the 2.5 to 4 CAI isograds (fig. 8) and the $\%R_{o(mean)}$ 2.5 to 3 isograds (fig. 9), is located in southern West Virginia and terminates against the St. Clair thrust fault at the northwestern margin of the Valley and Ridge province. Whether or not this salient is present in the Ordovician rocks underlying the thrust fault is presently unknown because Ordovician CAI data are absent in this area.

Devonian CAI_{max} isograds show a subtle alignment with structural features in the following small areas: (1) Wayne County, W. Va.; (2) Roane County, W. Va.; and (3) southeastern Ohio. In Roane and Wayne Counties, W. Va., areas enclosed by CAI_{max} 2.5 isograds are located within the Rome trough and are elongated subparallel to its flanks (fig. 8). In southeastern Ohio, the axis of the northwest-bulging salient in the CAI_{max} 1.5 isograd is partially aligned with the Cambridge structural discontinuity, as is suggested by the salient in the underlying Ordovician CAI_{max} 1.5 isograd (figs. 5, 8). The $\%R_{o(mean)}$ 1 isograd that extends the northern West Virginia salient into southeastern Ohio also is aligned with the Cambridge structural discontinuity (fig. 9).

Distribution of Devonian CAI_{max} and $\%R_{o(mean)}$ Isograds with Respect to Lower and Middle Devonian Oil and Gas Fields

Lower Devonian Oriskany Sandstone Fields

Gas fields in the Lower Devonian Oriskany Sandstone are widely distributed across the study area from central New York, through western and central Pennsylvania, through northern and central West Virginia, to southern West Virginia (figs. 10, 11). The Middle Devonian Huntersville Chert, which overlies the Oriskany Sandstone, is also a major reservoir for natural gas in southwestern Pennsylvania, western Maryland, and northern West Virginia (Flaherty, 1996). Scattered gas and local oil fields in the Oriskany Sandstone are located in eastern Ohio, northwesternmost Pennsylvania, and western New York (figs. 10, 11). Faulted anticlines, stratigraphic pinchouts, and pinchouts combined with anticlines form the majority of the traps in these accumulations (Flaherty, 1996; Harper and Patchen, 1996; Opritza, 1996; Patchen and Harper, 1996). The largest gas field in the Oriskany Sandstone is the giant Elk-Poca field in western West Virginia where westward (updip)-thinning of the reservoir and an associated loss of permeability forms the trap (figs. 10, 11). Discovered in 1933, this field has an estimated ultimate size of about 1 TCF of natural gas (Patchen and others, 1992). The largest Oriskany Sandstone gas fields in Pennsylvania are the Leidy field (Clinton and Potter Counties) and the Punxsutawny-Driftwood field in Cameron, Clearfield, and Elk Counties (figs. 10, 11). These fields were discovered in northeast-trending, faulted anticlines in 1950 and 1952, respectively, and have ultimate field sizes of 175 and 224 BCF of natural gas (Harper, 1990; Harper and Patchen, 1996). The Wayne-Dundee field (centered in Schuyler County, N.Y.) is one of the larger Oriskany Sandstone fields in New York with 11 BCF of in-place gas (Harper and Patchen, 1996), and the Cambridge field (Guernsey County, Ohio) is one of the larger Oriskany Sandstone fields in Ohio with an ultimate field size of 20 BCF (Opritza, 1996) (figs. 10, 11).

The most plausible source rocks for the Oriskany Sandstone gas fields are the Middle Devonian Marcellus Shale and the Upper Devonian Rhinestreet Shale (Patchen and others, 1992; Jenden and others, 1993; Laughrey and Baldassare, 1998). Both of these units are within the lower part of the Devonian black shale interval that for many years has been considered to be the primary source rock in the Appalachian basin (de Witt and Milici, 1989). The Marcellus Shale is 50 to 100 ft thick across most of Pennsylvania, southern New York, and northern West Virginia (de Witt and others, 1993). In eastern Ohio, however, the Marcellus Shale is generally less than 10 to 20 ft thick. The thicker, but less widespread, Rhinestreet Shale is approximately 200 to 250 ft thick in western New York and northwestern Pennsylvania and thins to between 50 and 100 ft thick in western Pennsylvania, eastern Ohio, and western West Virginia (de Witt and others, 1993).

Because the Devonian CAI isograds shown in figure 10 are based on conodonts collected from the Lower Devonian Helderberg Limestone and the Middle Devonian Onondaga Limestone, the isograds are good indicators for establishing regional thermal maturation patterns in the Marcellus Shale, which directly overlies the Onondaga Limestone. The Onondaga- and Helderberg-based Devonian CAI isograds are also good indicators for establishing regional thermal maturation patterns in the Rhinestreet Shale Member, which is located within 200 to 300 ft above the top of the Onondaga. Also, Devonian $\%R_{o(mean)}$ isograds shown in figure 11 are good indicators for establishing regional thermal maturation patterns in the Marcellus and Rhinestreet Shales, because these isograds are based on dispersed vitrinite. Most of the $\%R_{o(mean)}$ values in New York, Pennsylvania, and West Virginia are derived from the Marcellus Shale, whereas most of the $\%R_{o(mean)}$ values in Kentucky are derived from the Huron Member of the Ohio Shale. In Ohio and Virginia, the $\%R_{o(mean)}$ values are derived from several black shale units (Marcellus Shale, Rhinestreet Shale Member, and Huron Member in Ohio; Millboro Shale and Chattanooga Formation in Virginia).

The eastern belt of Oriskany Sandstone gas fields is a 100-mi-wide zone that extends from southern West Virginia, through northern and eastern West Virginia, western Maryland, and western Pennsylvania, to south-central New York. This belt of gas fields is located between Devonian CAI_{max} 2.5 to 4 isograds (fig. 10) and between Devonian $\%R_{o(mean)}$ 1.5 to 2.5 isograds (fig. 11). This belt of Oriskany fields coincides very well with the region where the Marcellus Shale is 50 to 100 ft thick (de Witt and others, 1993). Moreover, the close association of dry gas in most Oriskany fields in the eastern belt (Moore and Sigler, 1987; Jenden and others, 1993; Laughrey and Baldassare, 1998) with high levels of thermal maturation in the Marcellus Shale suggests that the gas was locally derived. Therefore, the Marcellus Shale is considered to be the primary source rock for the eastern belt of Oriskany fields. The sets of CAI_{max} and $\%R_{o(mean)}$ isograd values (figs. 10, 11) signify that the Marcellus Shale (the primary source rock for the gas) has reached the “window” of dry gas generation and preservation (fig. 3).

The western belt of Oriskany Sandstone gas fields, including the giant Elk-Poca field, extends from western West Virginia, through eastern Ohio and northwestern Pennsylvania, to western New York. This western belt is located between Devonian CAI_{max} 1.5 to 2.5 isograds (fig. 10) and between Devonian $\%R_{o(mean)}$ ≤0.5 to 1.5 isograds (fig. 11). The Marcellus Shale is relatively thin (<50 ft thick) in this area (de Witt and others, 1993), but the close association of wet gas and local oil in the western belt of Oriskany fields (Coogan and Reeve, 1985; Moore and Sigler, 1987; Patchen and others, 1992) with moderate levels of thermal maturation in the Marcellus-Rhinestreet-Ohio black shales suggests that the petroleum was locally derived. The sets of CAI_{max} and $\%R_{o(mean)}$ isograd values (figs. 10, 11) signify that the Rhinestreet Shale Member and nearby black shales have reached the "window" of oil and wet gas generation and preservation (fig. 3). Therefore, the Rhinestreet Shale and nearby shales are considered to be the primary source rock for the western belt of Oriskany fields. In eastern Ohio, however, the values of the Devonian CAI_{max} and $\%R_{o(mean)}$ isograds show conflicting levels of thermal maturation for the Devonian source rocks associated with the Oriskany fields. In this area, the Devonian CAI_{max} 1.5 isograd suggests that the Devonian black shale source rocks are in the "window" of oil and wet gas, whereas the Devonian $\%R_{o(mean)}$ 0.5 isograd suggests that the Devonian black shale source rocks are immature with respect to oil and gas generation (figs. 3, 11). As previously mentioned, most of the $\%R_{o(mean)}$ values for the Devonian black shale in Ohio are probably too low because of vitrinite suppression (Lo, 1993).

Middle and Upper Devonian Shale-Gas Fields

The USGS identified the Upper Devonian shale-gas accumulation in the Appalachian basin as a continuous gas resource where most wells drilled into the accumulation are productive or have shows (Milici and others, 2003). The Upper Devonian Rhinestreet Shale Member of the West Falls Formation and the Upper Devonian Huron Member of the Ohio Shale are the most important reservoirs in the Devonian shale-gas accumulation. The largest field is the Big Sandy field, which is located in southeastern Kentucky and adjoining southernmost West Virginia (Hunter and Young, 1953; Milici, 1993; Boswell, 1996) (figs. 10, 11). In this area, Devonian black shale is both the reservoir rock and the source rock, and commercial gas production usually depends on a combination of hydraulic fractures and natural fractures to improve the porosity and permeability of the reservoir. Boswell (1996) estimated the ultimate size of the Big Sandy field, discovered in 1921, to be about 3.4 TCF of natural gas.

Major gas production in the Devonian black shale interval (Upper Devonian black shales play of Boswell, 1996) extends northward of the Big Sandy field into southern and western West Virginia and southern Ohio. Milici and Swezey (2006) introduced the term "Greater Big Sandy field" in order to combine the area of Big Sandy shale-gas production with adjoining areas of abundant shale-gas production in southeastern Kentucky and southern West Virginia. Shale-gas production north of the Greater Big Sandy field gradually diminishes towards southern Ohio, where shale-gas production generally consists of small scattered fields (Boswell, 1996). Another zone of Upper Devonian shale-gas production is located east and north of the Upper Devonian black shales play. This additional zone of Upper Devonian shale-gas production, identified as the Upper Devonian fractured black and gray shales and siltstones play (Milici, 1996), extends from southwestern Virginia, through southern and northern West Virginia and southeastern Ohio, to western Pennsylvania and western New York. The greatest concentration of gas wells and fields in the Upper Devonian fractured black and gray shales and siltstones play is located between Ritchie County, W. Va., and eastern Washington County, Ohio (Milici, 1996). This play also includes scattered gas wells and small gas fields distributed along the Lake Erie shoreline of Ohio, Pennsylvania, and New York. In figures 10 and 11, the shale-gas production in the Upper Devonian black shales play and the Upper Devonian fractured black and gray shales and siltstones play are combined and shown as one area having major shale-gas production.

Devonian shale-gas fields in southern West Virginia and southwestern Virginia are associated with Devonian CAI_{max} values ranging from 2.5 to 3.5 (fig. 10) and with Devonian $\%R_{o(mean)}$ values ranging from 1.5 to 2 (fig. 11). These values are among the highest thermal maturation values for Devonian rocks in the Appalachian basin. Dry gas produced from Devonian shale in western McDowell County, W. Va. (Moore and Sigler, 1987), is consistent with these high isograd values. By comparison, the Big Sandy field in southeastern Kentucky and the adjoining shale-gas fields that continue northeastward, through southern and western West Virginia to southeastern Ohio, are located between Devonian CAI_{max} isograds from 1.5 to 2.5 (fig. 10) and between Devonian $\%R_{o(mean)}$ values from 0.75 to 1 (fig. 11). Although wet gas is the predominant petroleum phase in the Big Sandy field and in the adjoining fields (Moore and Sigler, 1987), oil is commonly produced with the gas in Calhoun, Pleasants, Ritchie, Wirt, and Wood Counties in northwestern West Virginia (Hohn and Timberlake, 1988) and in Monroe, Noble, and Washington Counties in southeastern Ohio (Baranoski and others, 1988) (figs. 10, 11). The presence of wet gas in the Big Sandy field and wet gas with local oil in the northern West Virginia-southeastern Ohio shale-gas fields is consistent with local derivation (figs. 3, 10, 11).

The narrow band of Devonian shale-gas fields along the Lake Erie shoreline of Ohio, Pennsylvania, and New York is associated with Devonian CAI_{max} 1.5 to 2 isograds (fig. 10) and the Devonian $\%R_{o(mean)}$ 0.5 isograd (fig. 11). Wet gas is the dominant petroleum phase along this trend (Gearheart and Grapes, 1977; Van Tyne, 1983; Moore and Sigler, 1987). On the basis of a single sample, Laughrey and Baldassare (1998) reported that shale-gas from the Lake Erie shoreline in Pennsylvania consists of wet gas of probable thermogenic origin with a composition that seems to be consistent with the nearby Devonian CAI_{max} 2 isograd (fig. 10) and the Devonian $\%R_{o(mean)}$ 0.5 to 1 isograds (fig. 11). The origin of the high nitrogen content (22.8 percent) of the shale-gas from this locality (Laughrey and Baldassare, 1998) is unknown. Most likely, the high nitrogen content is either an atmospheric contaminant or a derivative of the organic matter in the black shale source rock. In contrast to the Devonian CAI_{max} 1.5 to 2 values, $\%R_{o(mean)}$ ≤0.5 values suggest that the Devonian shales in many of the shoreline fields are immature with respect to oil and gas generation. However, most of the $\%R_{o(mean)}$ values for the Devonian black shale along Lake Erie in Ohio and Pennsylvania are probably too low because of vitrinite suppression (Lo, 1993).

Discussion and Interpretations

Geologic Controls of Observed Thermal Maturation Patterns

Burial and Thermal History

Harris and others (1978) concluded that the CAI isograd patterns in the Appalachians are a function of the regional structural trends and accompanying overburden thicknesses. Harris and others (1978) also concluded that most of the CAI isograd values in the Appalachians are largely inconsistent with present depths of burial and subsurface temperatures. In other words, either the present overburden thicknesses are too thin and (or) the present subsurface temperatures are too low to account for the CAI values measured by Harris and others (1978). The poor correlation between thermal index values (CAI and $\%R_o$) and present overburden thickness in the Appalachian basin is commonly attributed to a thick overburden of Carboniferous and Permian strata that was removed during post-Alleghanian uplift and erosion. The original thickness of this overburden may be restored by combining (1) calculated temperatures at maximum burial based on thermal maturity indices and (2) typical foreland basin geothermal gradients (20°C/km–30°C/km). For example, based on paleogeothermal gradients (from CAI and coal rank data) of 25°C/km to 40°C/km and maximum burial temperatures of 100°C to 300°C, Hulver (1997) estimated that post-Alleghanian denudation of the Appalachian basin (including the West Virginia and Pennsylvania parts of the basin) ranged from 6,500 to 32,800 ft (2–10 kilometers (km)) with increasing amounts of erosion from west to east. In comparison, based on a two-dimensional burial and thermal history model, Rowan (2006) concluded that the CAI and $\%R_o$ isograds in this report and the Pennsylvanian $\%R_o$ isograds put forth by L.F. Ruppert (written commun., 2007) are best explained by an eastward thickening wedge of Pennsylvanian and Permian rocks as thick as 10,000 ft (3 km) in central West Virginia and as thick as 12,500 ft (3.8 km) in south-central Pennsylvania. The model by Rowan (2006) used a heat flow of 52 milliWatt per square meter, which is consistent with other foreland basins (Blackwell and Richards, 2004). Among the greater estimates of former overburden thickness in the basin, Friedman and Sanders (1982) estimated a thickness of 20,300 ft (6.5 km) in Greene County, eastern New York, on the basis of a vitrinite reflectance value of 2.5 and an estimated geothermal gradient of 26°C/km (1.4°F/100 ft).

As shown in figure 5, the strong coincidence between the area enclosed by Ordovician CAI_{max} ≥4 isograds and the area enclosed by the ≥12,000 ft (3.65 km) thickness of Middle Ordovician through Permian strata (Harris and others, 1978) supports the conclusion that the observed thermal maturation patterns in this area are largely controlled by the thickness of foreland basin overburden. Thus, it follows that the area enclosed by the Ordovician CAI_{max} 4 isograd represents the approximate location of a 50- to 100-mi (80- to 160-km)-wide, northeast-trending depocenter in the Appalachian basin consisting of Middle Ordovician to Permian sedimentary rocks. Moreover, the close proximity of the 8,000-ft (2.4-km) isopach for Devonian through Permian strata (fig. 8) and the 12,000-ft (3.65-km) isopach for Middle Ordovician through Permian strata suggests that about two-thirds of the depocenter consists of Devonian through Permian deposits. The depocenter is roughly coincident with the Rome trough between northern West Virginia and central Pennsylvania suggesting that the position and configuration of the depocenter may, in part, have been controlled by the trough. The juxtaposition of this eastward-thickening, 12,000- to >20,000-ft (3.65- to 6.1-km)-thick sedimentary wedge of Middle Ordovician through Permian strata against the frontal thrust belt of the Valley and Ridge province is consistent with the frameworks of other foreland basins (Bally and Snelson, 1980).

The original Appalachian basin depocenter probably extended about 100 mi (161 km) into southeastern and south-central New York, based on the presence of Ordovician CAI_{max} 4.5 to 5 isograds (fig. 5) and Devonian CAI_{max} 2.5 to 3 isograds (fig. 8). This part of the depocenter and the accompanying high thermal imprint probably was caused by thick Upper Devonian Catskill strata and overlying Carboniferous and Permian strata that have since been removed by erosion. Accordingly, the 4,000- to 12,000-ft (1.2- to 3.65-km) thickness of the Middle Ordovician to Permian section reported for the depocenter by Harris and others (1978) greatly underestimates the thickness of the original sedimentary section. Epstein and others (1974) reported a thickness of 7,858 ft (2.4 km) for the Upper Devonian Catskill strata in eastern Pennsylvania, and Faill (1997) suggested an even greater thickness for these same strata in southeastern New York where the section is largely incomplete. Also, Friedman and Sanders (1982) estimated, from $\%R_o$ data in Tully-equivalent Middle Devonian strata in southeastern New York, that approximately 20,300 ft (6.5 km) of post-Middle Devonian overburden was present at one time in this area. Probably at least half of this estimated overburden thickness consisted of Carboniferous and Permian strata that extended northeastward from the Lackawanna syncline (figs. 5, 8) in the anthracite district of northeastern Pennsylvania (for example, see Levine, 1986; L.F. Ruppert, written commun., 2007). The western margin of the Appalachian depocenter in south-central New York is defined by the north-trending gradients in the closely spaced Ordovician and Devonian CAI_{max} isograds (figs.

5, 8) and by the coincident abrupt changes in clay mineralogy and apatite fission-track ages from Johnsson (1986).

The southern end of the Appalachian basin depocenter probably extends beyond the Ordovician CAI_{max} 4 isograd into central and southern West Virginia, between the Rome trough and the frontal thrust belt of the Valley and Ridge province, where the thickness of Middle Ordovician through Permian strata ranges from 12,000 ft (3.65 km) to as much as 16,000 ft (4.9 km) (Harris and others, 1978). Although Ordovician CAI_{max} data are absent in this area, the Ordovician CAI_{max} values should be at least as high as the Devonian CAI_{max} values of 3.5 and 4 reported in figure 8.

The Rome trough in western West Virginia and eastern Kentucky does not appear to be part of the northeast-trending Middle Ordovician to Permian Appalachian basin depocenter, because the Rome trough in this region is centered 25 to 50 mi north of the depocenter, where the Middle Ordovician through Permian rocks are only 6,000 to 10,000 ft (1.8–3 km) thick (Harris and others, 1978). The discordant trend of the Ordovician CAI_{max} 2 to 3 isograds in western West Virginia provides further evidence that overburden rocks in this part of the Rome trough had minimal control on the Ordovician CAI isograds. However, in eastern Kentucky, the abrupt change in trend of the Ordovician CAI 1+ and 1.5 isograds from north (north of the Rome trough) to west (within the trough) suggests that the Rome trough exerted a subtle influence on the Ordovician CAI isograd patterns. Perhaps a modest increase in the thickness of overburden rocks occurred in the Kentucky part of the Rome trough, although such an increase is not apparent in the isopach map of Harris and others (1978).

The strong coincidence between the area enclosed by Devonian CAI_{max} ≥2.5 and $\%R_{o(mean)}$ ≥1.5 isograds (figs. 8, 9) and the area delimited by the ≥8,000 ft (2.4 km) thickness of Devonian through Permian strata (Harris and others, 1978) delineates a northeast-trending Devonian through Permian depocenter that coincides with the Middle Ordovician through Permian depocenter. Consistent with the Middle Ordovician through Permian depocenter in southeastern and south-central New York, the 150-mi (241-km)-wide northeastern end of the Devonian through Permian depocenter (defined by the Devonian CAI_{max} 3 isograd) (fig. 8) probably was caused by a thick overburden of Upper Devonian Catskill, Carboniferous, and Permian strata. The four previously described foreland-directed salients in the Devonian CAI_{max} 3 and $\%R_{o(mean)}$ 1.5 to 2 isograds give the western margin of the Devonian through Permian depocenter a very irregular appearance (figs. 8, 9).

The prominent salient in the Devonian CAI_{max} 2.5 to 4 and Devonian $\%R_o$ 2.5 to 3 isograds that defines the southern end of the post-Silurian depocenter in southern West Virginia (figs. 8, 9) was probably caused by burial beneath a thick overburden of Mississippian and Pennsylvanian strata, as shown by isopach maps by Heck (1943) and de Witt (1975). Vitrinite reflectance ($\%R_o$) isograds derived from Pennsylvanian coal beds also show a northward-bulging salient in southern West Virginia (Cole and others, 1979; L.F. Ruppert, written commun., 2007). Surprisingly, this salient does not appear on the Devonian through Permian isopach map of Harris and others (1978). The westward-bulging salient in northern West Virginia, defined by Devonian CAI 2.5 to 4 isograds (fig. 8), also is interpreted in this study to be caused by burial beneath thick overburden. This interpretation is based on the modest salient in the 8,000 and 10,000 ft isopachs of the Devonian through Permian isopach map of Harris and others (1978) and on the prominent salient in the isopach map of Devonian rocks by de Witt and others (1975), both of which are broadly coincident with the northern West Virginia salient.

Although the Rome trough is aligned with the Devonian through Permian depocenter from central Pennsylvania to northern West Virginia, the trend of the Rome trough diverges from the proposed depocenter in northwestern West Virginia and continues into western West Virginia and eastern Kentucky where Devonian CAI isograds range from 1.5 to 2.5 and the thickness of Devonian through Permian strata ranges from about 3,000 to 6,000 ft. Thus, in the Rome trough in western West Virginia and eastern Kentucky, the thickness of the Devonian through Permian overburden rocks probably did not significantly control Devonian CAI isograd patterns. Minor exceptions occur in western West Virginia, where several small areas enclosed by Devonian CAI 2.5 isograds are confined to the Rome trough, and in eastern Kentucky where tight loops and bends in the Devonian CAI 1.5 and 2 isograds are confined to the trough (fig. 8). These subtle changes in thermal maturation may be related to modest increases in overburden thickness in the Rome trough.

Dennison (1982) proposed a keel line to represent the axis of maximum tectonic subsidence in the Appalachian basin during times of relatively low clastic input. This proposed keel line is located about 25 to 50 mi northwest of the Middle Ordovician through Permian depocenter, where the accumulation of thick clastic orogenic deposits loaded the eastern margin of the basin and caused maximum subsidence. During periods of minimal clastic sediment input, the basin depocenter shifted northwestward to become aligned with the keel line (Dennison, 1982). The results of this study suggest that Dennison's keel line is a secondary feature because it is not aligned with the highest Ordovician and Devonian CAI_{max} isograds and with the region of maximum burial (depocenter) (figs. 5, 8).

Although high heat flow (initiated during the Neoproterozoic-Early Cambrian opening of the proto-Atlantic ocean) probably continued into the Middle Cambrian when crustal extension and thinning formed the Rome trough, it does not appear to have influenced the observed CAI and $\%R_o$ isograd patterns in the Appalachian basin. Very likely, the higher heat flow that accompanied the formation of the Rome trough had greatly diminished before the accumulation and subsequent burial of the Ordovician Trenton Limestone and the Devonian Helderberg and Onondaga Limestones (intervals sampled for this study).

During the early Mesozoic, crustal extension and thinning associated with the breakup of Pangea (Manspeizer and others, 1989) introduced a later phase of high heat flow to the Appalachian region. During this period, basaltic magmas largely of

Early Jurassic age (Seidemann and others, 1984; Sutter, 1988) intruded nonmarine strata in rift basins along the eastern margin of North America. During the later Mesozoic (Jurassic and Cretaceous), basement faults farther westward in the Rome trough and adjoining crust may have been reactivated, allowing mantle-derived magmas to intrude the Appalachian basin as kimberlites (Parrish and Lavin, 1982; Basu and others, 1984; Phipps, 1988; Watts and others, 1992) (figs. 5, 8). Dennison (1982) hypothesized that these kimberlites originated during post-orogenic uplift of the Appalachian keel line and associated crustal stretching. Tectonic models introduced by Parrish and Lavin (1982) and Phipps (1988), however, attributed the origin of the kimberlites to one or more stages of basement faulting along the Rome trough. In outcrop, these kimberlites are small features with minimal alteration halos and, thus, probably were incapable of introducing high heat flow to the basin, except locally where the kimberlite bodies may have coalesced at depth. Likewise, the Eocene magmatic intrusives in eastern West Virginia and adjoining Virginia appear to have been incapable of introducing high heat flow to the basin.

Cercone and others (1996) suggested that Carboniferous coal beds and carbonaceous shale-bearing strata affected the temperature history of the Appalachian basin by acting as insulators. Consequently, strata that contain large quantities of organic matter may have created higher thermal maturation values in a given area than strata with little organic matter. Also, low-conductivity Devonian black shale beds may have contributed to the insulation process. One could further argue that the thick, high conductivity Silurian salt interval in eastern Ohio, western Pennsylvania, and western New York might have influenced thermal maturity values. Although these factors are accounted for in the burial and thermal history models by Rowan (2006), it is unclear whether they have substantially influenced thermal maturity indices in this study.

Fluid-Flow History

Although overburden thickness is considered to be the most important control on the thermal maturation patterns identified in this study, there are certain areas where the observed thermal maturation patterns cannot be explained by overburden thickness alone. For example, several of the westward-bulging salients in the Ordovician and Devonian isograds may represent migration pathways of warm to hot, basin-derived fluids. The salients in southwestern and northwestern Pennsylvania are particularly convincing candidates for a fluid-flow origin because they are not associated with an obvious overlying depocenter (de Witt and others, 1975; Harris and others, 1978). The coincidence of the southwestern Pennsylvania salient with the northwest-trending Pittsburgh-Washington lineament and the associated Akron-Suffield-Highlandtown faults suggests that these structures were preferred avenues of flow for warm to hot fluids through both Ordovician and Devonian strata (figs. 5, 8, 9). In the same approximate area, a salient-like feature delineated by $\%R_o$ isograds from Pennsylvanian coal beds has been interpreted as a fluid-flow feature (Zhang and Davis, 1993; Evans and Battles, 1999; L.F. Ruppert, written commun., 2007). Moreover, Evans and Battles (1999) suggested that the similar northward-bulging salient in Pennsylvanian vitrinite reflectance ($\%R_o$) isograds in southern West Virginia (also recognized by Cole and others, 1979; L.F. Ruppert, written commun., 2007) may indicate another area affected by fluid flow. However, as previously noted, the southern West Virginia salient is interpreted in this paper to have been caused by thick overburden. The salient in Devonian CAI_{max} and $\%R_{o(mean)}$ isograds in northwestern Pennsylvania is considered to be another example of focused fluid flow through Middle Devonian strata, because of its close alignment with the Tyrone-Mt. Union structural discontinuity (figs. 8, 9). In the vicinity of the southwestern Pennsylvania salient, fluid inclusion homogenization temperatures in calcite veins in Middle Devonian shale have a bimodal distribution and range between 63°C and 128°C (Evans, 1995).

In central and eastern Ohio, the prominent west-facing salient in the Ordovician CAI_{max} 1.5 and 2 isograds (fig. 5) and the Devonian CAI_{max} 1+ and 1.5 isograds (fig. 8) also may represent a thermal imprint left by westward-migrating warm to hot fluids. These fluids appear to have originated in southeastern Ohio and (or) near the previously described northern West Virginia salient (fig. 8). In this area of Ohio, the north-trending Cambridge structural discontinuity may have focused some of the proposed fluid flow. Hayba (2006) suggested that similar warm to hot fluids migrated as far west as the southeastern margin of the Michigan basin.

In south-central New York where hydrothermal fluids selectively dolomitized the Ordovician Trenton and Black River Group limestones along narrow, east-trending fracture zones (Smith and others, 2003; Smith, 2006), fluid flow may have, in part, controlled the thermal maturation patterns. For this region, Smith and others (2003) and Smith (2006) concluded that the fractures and hot dolomitizing fluids developed during the Ordovician Taconic orogeny, soon after deposition of the Trenton and Black River Groups. Fluid inclusion measurements indicate that the zone of dolomitization has homogenization temperatures between 110°C and 170°C, with an average of 130°C (Smith, 2006), although these temperatures seem to be unusually high for basin-derived fluids in an area of no known volcanism and limited overburden thickness during the proposed time of fluid flow.

Along the Kentucky River fault zone at the northern boundary of the Rome trough, warm fluids appear to have interacted with early Paleozoic carbonate rocks (Ramsey and Onasch, 1999; Parris and Harris, 2006). Within the fault zone, fluid inclusion temperatures from saddle dolomite in Upper Ordovician and Cambrian rocks are approximately 100°C (Parris and Harris, 2006), whereas fluid inclusion temperatures from calcite veins in Middle and Upper Ordovician limestones range from about 90°C to 125°C (Ramsey and Onasch, 1999). In the Rome trough in eastern Kentucky, these warm fluids may account for observed thermal maturation patterns such as the alignment of Ordovician CAI_{max} 1+ and 1.5 isograds (fig. 5) and the minor west-facing perturbations of the Devonian CAI_{max} 1.5 and 2 isograds (fig. 8).

The following two models have been proposed for the origin of the warm to hot migrating fluids: (1) a topography-driven flow system created by meteoric influx through high-relief orogenic uplands (Garvin, 1986) and (2) a compaction-driven flow system created by overriding thrust sheets (Oliver, 1986). The first model is favored largely because it permits sustained high levels of fluid flow over long periods of geologic time. Thrust faults in the Valley and Ridge province and Blue Ridge province may have facilitated the transfer of hot migrating fluids from the Alleghanian orogenic belt to the Appalachian basin (Dorobek, 1989; Evans and Battles, 1999; Goldhaber and others, 2003). A contrasting interpretation by Evans and Hobbs (2003), also based on fluid inclusion evidence, suggested that the majority of these warm fluids were vented to the surface before they entered the Allegheny Plateau province.

Late Carboniferous to Early Permian radiometric dates of authigenic feldspar in Cambrian carbonate strata indicate that a regional fluid-flow event occurred in the Appalachian basin during the Alleghanian orogeny (Hearn and others, 1987). This regional fluid-flow event during the Alleghanian orogeny probably is responsible for the westward-facing salients in the Ordovician and Devonian CAI_{max} and $\%R_{o(mean)}$ isograds. Also, the fluid flow that probably occurred along the Kentucky River fault zone is interpreted to be an Alleghanian event (Ramsey and Onasch, 1999). Fluid-flow events in south-central New York, however, may have been associated with the Ordovician Taconic orogeny, as suggested by Smith and others (2003) and Smith (2006).

Thermal Regime of Thrust Sheets in the Valley and Ridge Province

Harris and others (1978) showed that in several Valley and Ridge province localities, allochthonous Ordovician strata have higher CAI values than the underlying autochthonous Ordovician strata. They concluded that thrusting from the east placed thermally more mature strata over less mature strata to the west and that the isograds measured in the allochthonous thrust sheet do not necessarily characterize the isograds in the autochthonous strata. However in this study, the reverse situation appears to be most common. For example, allochthonous Ordovician rocks in the No. 1 Sponaugle well in Pendleton County, W. Va., have a CAI_{max} value (4) that is lower than CAI_{max} values (4.5–5) in underlying autochthonous Ordovician rocks (fig. 5; table 1). Moreover, allochthonous Ordovician rocks that crop out in Centre County, Pa., have lower thermal maturity values (CAI_{max}=4) than the underlying autochthonous Ordovician rocks in the No. 1 Long well (CAI_{max}=4.5) in Centre County (fig. 5; table 1). Similar thermal maturation patterns were reported by O'Hara and others (1990) in Pennsylvanian coal beds involved in the Pine Mountain thrust fault in southeastern Kentucky, where a coal bed with $\%R_{o(max)}$ values of 0.8 to 0.85 in the hanging wall (allochthonous rocks) is juxtaposed against an equivalent coal bed with $\%R_{o(max)}$ values of 0.9 in the footwall (autochthonous rocks). The only example in this report where higher maturity allochthonous strata are located above lower maturity autochthonous rocks is the Devonian part of the Pine Mountain thrust fault where the hanging wall of the thrust fault has higher Devonian $\%R_o$ values ($\%R_{o(mean)}$=1–2) than the footwall ($\%R_{o(mean)}$=0.5–1) (fig. 9).

Coalification profiles observed by England and Bustin (1986) in deep drill holes through thrust sheets in the southeastern Canadian Cordillera show examples of both increased and decreased thermal maturity in successively deeper thrust sheets. Increased thermal maturity across successively deeper thrust sheets is commonly interpreted to be the result of post-orogenic maturation where "hot" hanging wall rocks have been emplaced at a relatively high rate of thrusting so that little warming of the footwall has occurred (Furlong and Edman, 1984; England and Bustin, 1986). After emplacement, the thrust sheet cooled and the overridden footwall rocks were warmed by heat conduction (Furlong and Edman, 1984; England and Bustin, 1986). Model studies by Shi and Wang (1987) suggest that lower maturity allochthonous rocks over higher maturity autochthonous rocks also may be explained by synorogenic maturation whereby an increased duration of thrusting has caused temperature-depth profiles to remain relatively unaltered from their pre-thrusting configuration. England and Bustin (1986) also concluded that profiles showing a decrease in thermal maturity across successively deeper thrust sheets have resulted because post-orogenic heat conduction generated by the upper sheet is insufficient to overprint the pre-thrusting levels of thermal maturity in the lower sheet. One or more of these proposed mechanisms may account for the observed thermal maturity patterns in the Valley and Ridge province.

Origin of Selected Oil and Gas Fields

CAI and $\%R_o$ data presented in the investigation provide evidence for the following key elements of Appalachian basin petroleum systems: (1) the present levels of thermal maturation of Ordovician and Devonian source rocks and (2) where oil and (or) natural gas are most likely to have been generated from the Ordovician and Devonian source rocks. These data do not indicate the timing of the maturation and the generation of oil and natural gas from the source rocks. For an estimate of the timing of petroleum generation, the thermal maturation data in this investigation must be combined with selected two-dimensional burial and thermal models as shown by Rowan (2006) and Pawlewicz (*in* Ryder and others, 2005). A presentation of the results of these models is beyond the scope of the present study. The following discussion focuses on the estimated direction and distance of migration that accompanied most of the important groups of oil and gas fields in the Appalachian basin. These scenarios are cursory and only take into account a single episode of migration, rather than continuous generation and migration from the source rocks. Moreover, this approach ignores potential source rock intervals in the eastern hinterland from which petroleum may have been generated and migrated prior to Alleghanian deformation.

Cambrian and Ordovician Fields

The close proximity of the Cambrian and Ordovician oil and gas fields in central and eastern Ohio to Ordovician CAI_{max} values representative of the "window" of oil and wet gas generation and preservation (fig. 6) suggests to us that no more than 25 to 50 mi of lateral migration occurred between the proposed Utica Shale source rock and the hydrocarbon traps. Given the present 1° easterly dip of the basin, 25 mi of lateral migration is about the minimum distance required to move oil and gas updip (by buoyant forces) from the Utica Shale, through Trenton-Black River limestones, to dolomite and sandstone reservoirs beneath the Knox unconformity. All gases in the Knox unconformity fields are wet, on the basis of data from Moore and Sigler (1987) and Laughrey and Baldassare (1998), but there seems to be no consistent pattern to the degree of wetness. For example, although the gas wetness tends to increase from about C_1/C_1-C_5=0.94 in eastern Ohio to about C_1/C_1-C_5=0.89 in central Ohio (maximum wetness of 0.76 in Morrow County), there are many exceptions, such as localities in central Ohio where gases with a wetness of C_1/C_1-C_5=0.92–0.93 are adjacent to gases with a wetness of C_1/C_1-C_5=0.88–0.89. This lack of a consistent pattern in gas wetness across eastern and central Ohio suggests that the Cambrian and Ordovician gases may have experienced multiple migration histories ranging from local (<25 mi) to more distant (as much as 75 mi). Isotopic values of $\delta^{13}C_{methane}$=39.8 and -38.1, reported by Laughrey and Baldassare (1998) for gases in the Randolph and Baltic fields, respectively, in eastern Ohio suggest that these gases were locally derived from the Utica Shale (CAI_{max} values of 1.5–2) and, thus, represent the lower end of the proposed spectrum of migration distances.

In northwestern Ohio, the association of the giant Lima-Indiana field with Ordovician CAI_{max} values representing immature conditions with respect to oil and gas generation in the proposed Utica Shale source rock (fig. 6), implies at least 100 mi of petroleum migration before entrapment. Either the petroleum migrated westward from the Utica Shale source rock in the Appalachian basin (Ryder and others, 1998) or southward from the Utica Shale (or an equivalent Ordovician unit) in the Michigan basin (Drozd and Cole, 1994).

In southwestern Virginia, petroleum in the Rose Hill field (fig. 6) was derived from an Ordovician source rock (K.O. Dennen, written commun., 2007), although the question remains whether the petroleum was derived in situ from the Trenton Limestone, locally from the overlying Ordovician Reedville (Martinburg) Shale, or from the distant Ordovician Sevier Shale (Milici and others, 2006). The same question applies to petroleum in the Swan Creek field in Grainger County, Tenn., about 15 mi south of the Rose Hill field where the source rock also is Ordovician in age (K.O. Dennen, written commun., 2007).

In New York, central and northwestern Pennsylvania, and west-central West Virginia, nonassociated gas fields in the Cambrian and Ordovician reservoirs are closely associated with Ordovician CAI_{max} values (3.5–5) that represent the "window" of dry gas generation and preservation (fig. 6). All of these fields contain dry gas (Moore and Sigler, 1987; Jenden and others, 1993), and those in Ordovician reservoirs in south-central New York and central Pennsylvania may be near the limit of gas preservation. In the case of the Grugan field (Ordovician Bald Eagle Formation) in central Pennsylvania and the West Auburn field (Ordovician Queenston Formation) in central New York (fig. 6), gas probably migrated 1,000 and 1,500 ft vertically upward from the Utica Shale source rock to the reservoir. Isotope values from gases in the Grugan field (Laughrey and Baldassare, 1998), the Fayette-Waterloo field near the West Auburn field (Jenden and others, 1993), and a well that produced from the Black River Group near the Glodes Corners Road field (Jenden and others, 1993) all indicate that the gases were derived from a source rock with a $\%R_{o(mean)}$ value of ≥4. Also, all of these gases probably migrated laterally less than 25 mi from the Utica Shale source rock.

Silurian Fields

The close proximity of the Lower Silurian regional oil and gas accumulation to Ordovician CAI_{max} values representative of the "window" of oil and wet gas generation and preservation (fig. 7) suggests to us that no more than 25 mi of lateral migration occurred between the proposed Utica Shale source rock and the hydrocarbon traps. This conclusion implies that substantial amounts of oil and gas generated from the Utica Shale migrated vertically upward through at least 1,000 ft of overlying Upper Ordovician shale and argillaceous siltstone before being entrapped in the Clinton-Medina-Tuscarora sandstone reservoirs (Ryder and others, 1998; Ryder and Zagorski, 2003). All gases in the Lower Silurian regional accumulation are wet, based on many analyses (Moore and Sigler; 1987; Jenden and others, 1993; Burruss and Ryder, 1998, 2003; Laughrey and Baldassare, 1998). Moreover, unlike the Cambrian and Ordovician gases, there seems to be a consistent pattern of increasing wetness in the Lower Silurian gases from eastern Ohio to central Ohio (from C_1/C_1-C_5=0.96 in Columbiana County to C_1/C_1-C_5=0.89 in Knox County). A similar pattern of westward-increasing gas wetness in the Lower Silurian gases is noted from Butler County in western Pennsylvania (C_1/C_1-C_5=0.975) to Geauga County in northeastern Ohio (C_1/C_1-C_5=0.88). This well-defined trend of increasing gas wetness from western Pennsylvania to northeastern Ohio, over a distance of approximately 75 mi, is associated with another well-defined trend where $\delta^{13}C_{methane}$ values in Lower Silurian gases become progressively lighter toward the northwest (Burruss and Ryder, 2003). These remarkably consistent trends in gas wetness and $\delta^{13}C_{methane}$ values further support the interpretation of vertical migration from the underlying Utica Shale source rock with minimal lateral migration. Although oil is relatively abundant in the Lower Silurian regional accumulation in Ohio, it gradually diminishes northeastward so that wet gas is clearly the dominant petroleum phase in northwestern Pennsylvania and New York. This phenomenon seems to have been caused by the greater level of thermal maturation of the Utica Shale (Ordovician CAI_{max} 2.5 to 3 isograds) toward the northeast (fig. 7).

Lower Devonian Oriskany Sandstone Fields

The close proximity of the eastern belt of nonassociated dry gas fields in the Oriskany Sandstone to Devonian CAI_{max} and $\%R_{o(mean)}$ values representative of the "window" of dry gas generation and preservation (figs. 10, 11) suggests that very short-range lateral migration, probably 1 to 2 mi, occurred between the Marcellus Shale source rock and the hydrocarbon traps. Short-range lateral migration is plausible for the following reasons: (1) about 150 to 200 ft of Onondaga Limestone and (or) Huntersville Chert separate the Oriskany Sandstone from the overlying Marcellus Shale and therefore the Marcellus Shale is nearly in contact with the Oriskany Sandstone and (2) high-amplitude, faulted anticlines in the eastern belt of the Oriskany Sandstone have placed the Marcellus Shale (on the limbs of the anticlines) in a lower structural position with respect to the Oriskany Sandstone near the crest of the anticline, thus, facilitating very short-range, updip migration of gas into the reservoir. Wet gases reported near the northern and western margins of the eastern belt of the Oriskany Sandstone fields (for example, Steuben County, N.Y.; Armstrong County, Pa.; Lewis County, W. Va.) suggest that some of the gas was derived from younger Devonian black shales, such as the Rhinestreet Shale, that have a lower level of thermal maturation.

The western belt of the Oriskany Sandstone gas fields, largely controlled by stratigraphic traps, probably required greater distances of lateral migration because of the much lower dips involved. As suggested by Patchen and others (1992), some gases in the Elk-Poca field may have migrated laterally about 12 to 15 mi westward from the basal Rhinestreet Shale, through 200 to 300 ft of older intervening shales and carbonates, to the Oriskany Sandstone. In comparison, other gases in the Elk-Poca field may have migrated laterally about 4 to 6 mi westward from the Marcellus Shale and the Oriskany Sandstone.

Devonian Shale Fields

Wet shale-gas (C_1/C_1-C_5=0.72–0.82) in the Big Sandy field (Moore and Sigler, 1987) and levels of thermal maturation in the Devonian carbonates (CAI_{max}=1.5–2.5) and Devonian shales ($\%R_{o(mean)}$=0.6–1.5) are consistent with in situ hydrocarbon generation from Devonian black shale (figs. 10, 11). Similar gas wetness values (C_1/C_1-C_5=0.75–0.84) are associated with the Devonian shale-gas trend in western and northwestern West Virginia north of the Big Sandy field, including the area with associated oil. As yet, there is no satisfactory explanation as to why shale-gas is associated with oil in northwestern West Virginia and southeastern Ohio when the shale-gas is nonassociated at Big Sandy (Greater Big Sandy). At both localities, the shale-gases have similar wetness values.

In northwesternmost Pennsylvania, isotopic values from a shale-gas sample from the Huron Member of the Ohio Shale indicate that the source rock that generated the gas was in the early stages of oil generation (Laughrey and Baldassare, 1998). The Devonian $\%R_{o(mean)}$ value of 0.5 and the CAI_{max} value of 1.5 near the sample locality are consistent with this interpretation (figs. 10, 11).

In eastern Kentucky, the Devonian CAI_{max} 1+ to 2 isograds and $\%R_{o(mean)}$ 0.6 to 1 values are consistent with the common notion that oil and gas fields in the Silurian and Devonian Corniferous were derived from the overlying Devonian black shales (figs. 7, 10, 11). Similarly, in south-central Kentucky, the Devonian CAI_{max} 1+ and $\%R_{o(mean)}$ 0.5 isograds are reasonably consistent with the suggestion that oil and gas in nearby Ordovician carbonate reservoirs were derived from the overlying Devonian black shales (figs. 6, 10, 11). Again, it is rather puzzling why the Corniferous and Ordovician carbonate strata in eastern and south-central Kentucky have abundant oil that is supposedly derived from Devonian black shale, whereas the shale-gas at the nearby Big Sandy field is nonassociated.

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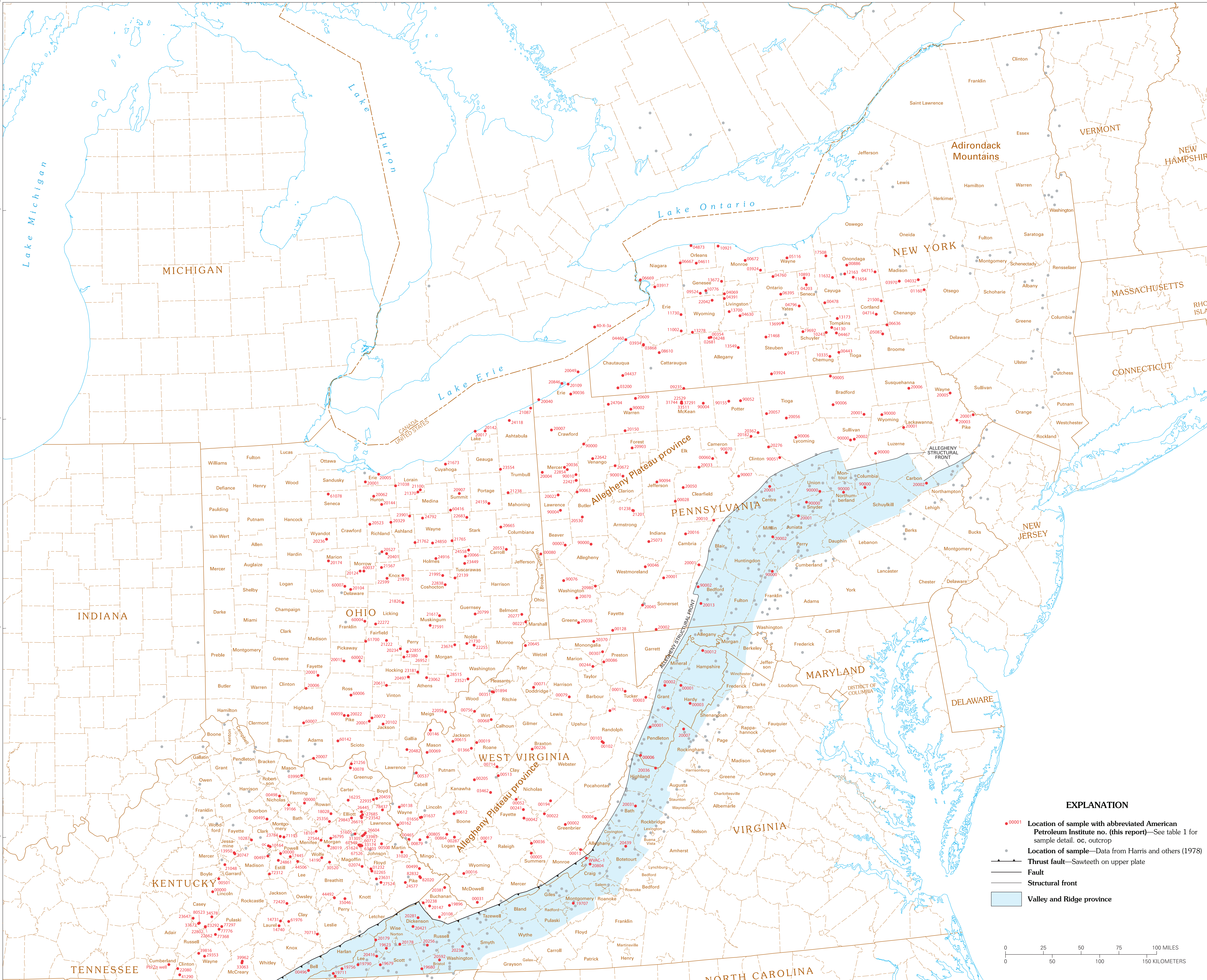

Figure 1.—Location of wells and surface locations sampled for conodonts and (or) dispersed vitrinite in this study. Also shown are the wells and surface localities sampled by Harris and others (1978).

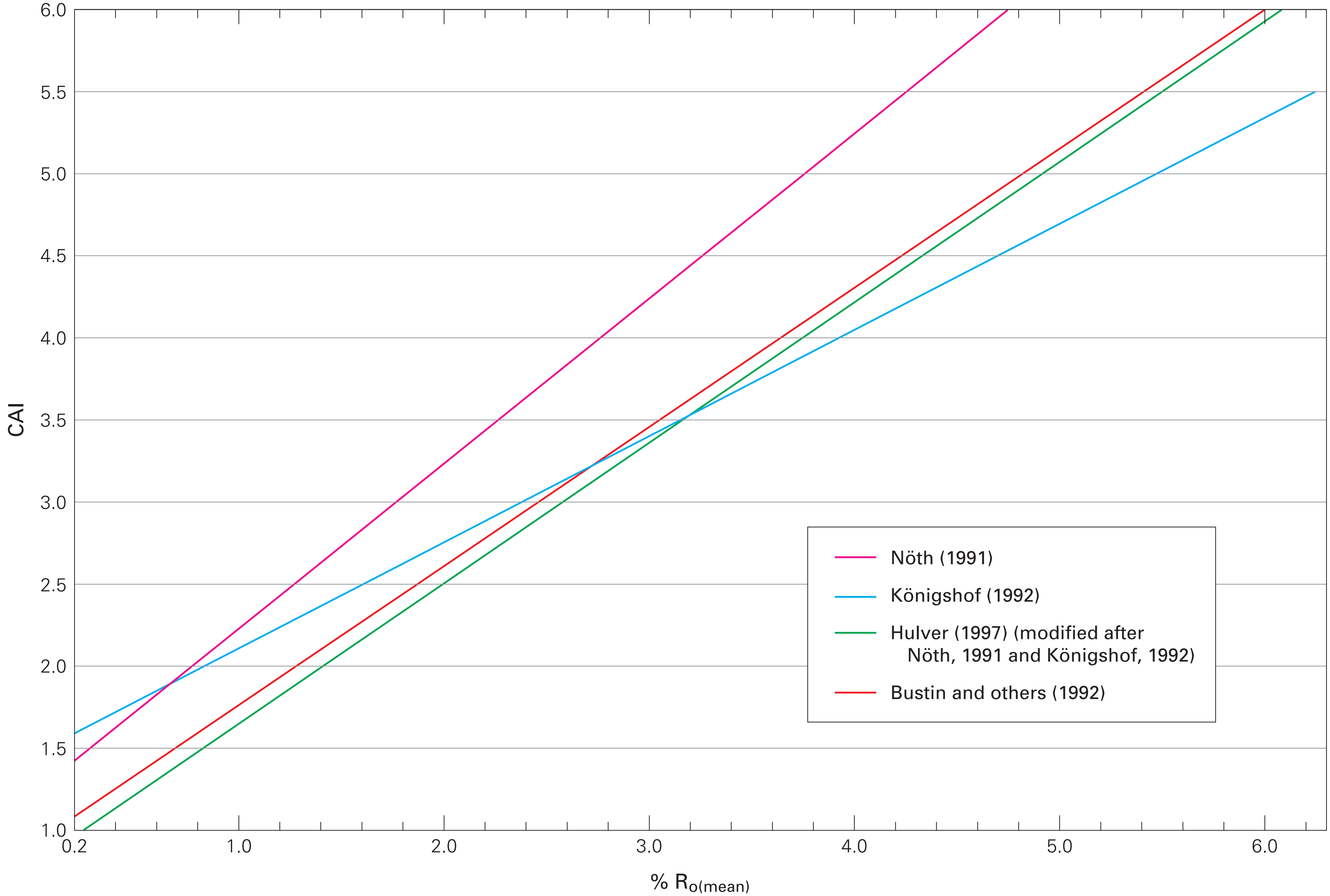

Figure 2.—Correlation plots of mean vitrinite reflectance (%$R_{o(mean)}$) and conodont color alteration index (CAI) values (after Nöth, 1991; Bustin and others, 1992; Königshof, 1992; Hulver, 1997). %$R_{o(max)}$ values reported by Nöth (1991), Königshof (1992), and Hulver (1997) were converted to %$R_{o(mean)}$ by using an equation from Zhang and Davis (1993). Data points and error bars are not shown.

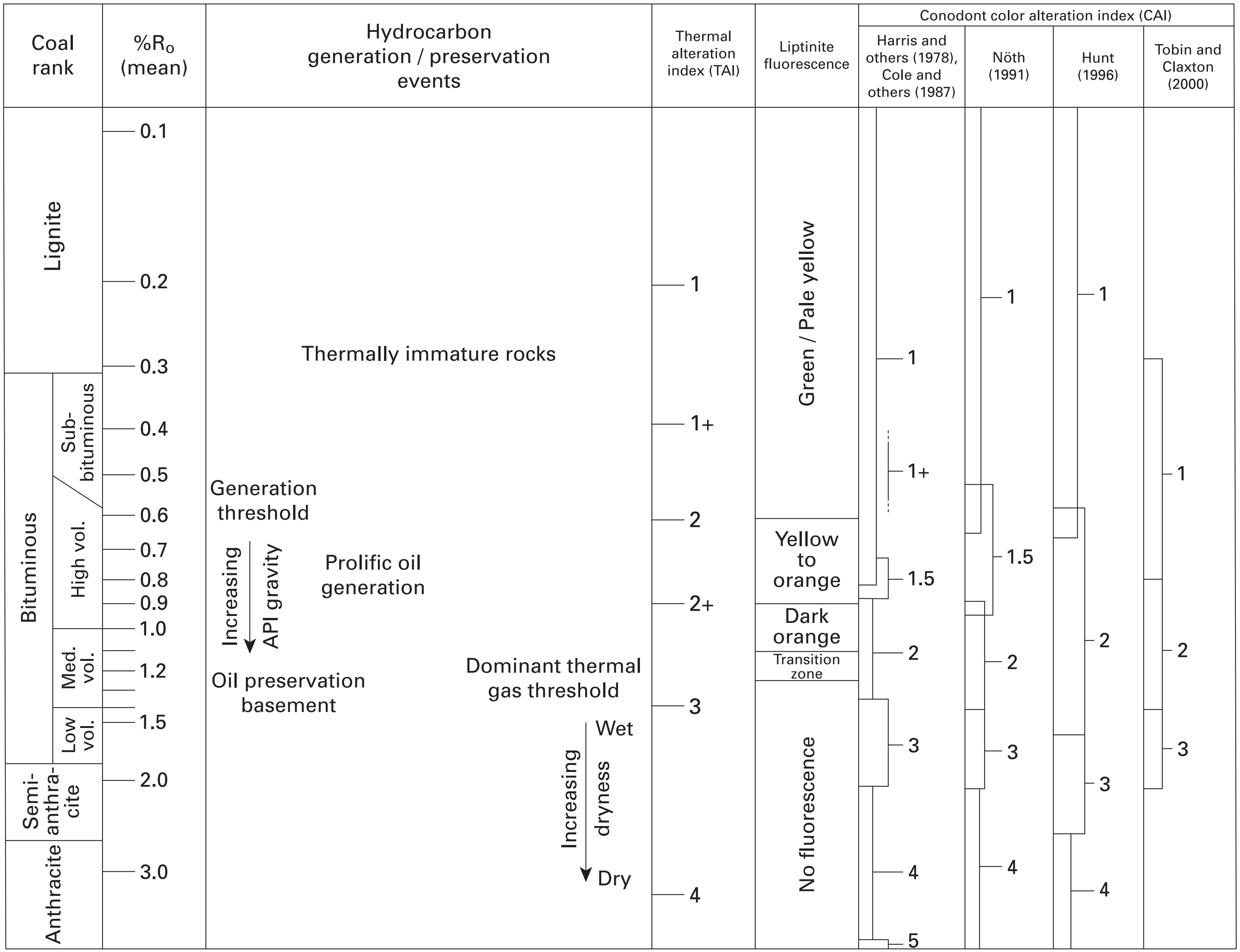

Figure 3.—Diagram that shows the relation among various thermal maturity indicators (including CAI and %R_o) and associated zones of hydrocarbon generation (modified after Stach and others, 1975; Dow, 1977; Harris and others, 1978; Cole and others, 1987; Nöth, 1991; Hunt, 1996; Tobin and Claxton, 2000). The CAI 1+ is introduced by J.E. Repetski in this report.

Figure 4.—Correlation of Paleozoic rocks in Kentucky, New York, Ohio, Pennsylvania, Virginia, and West Virginia showing intervals sampled for conodonts and dispersed vitrinite.

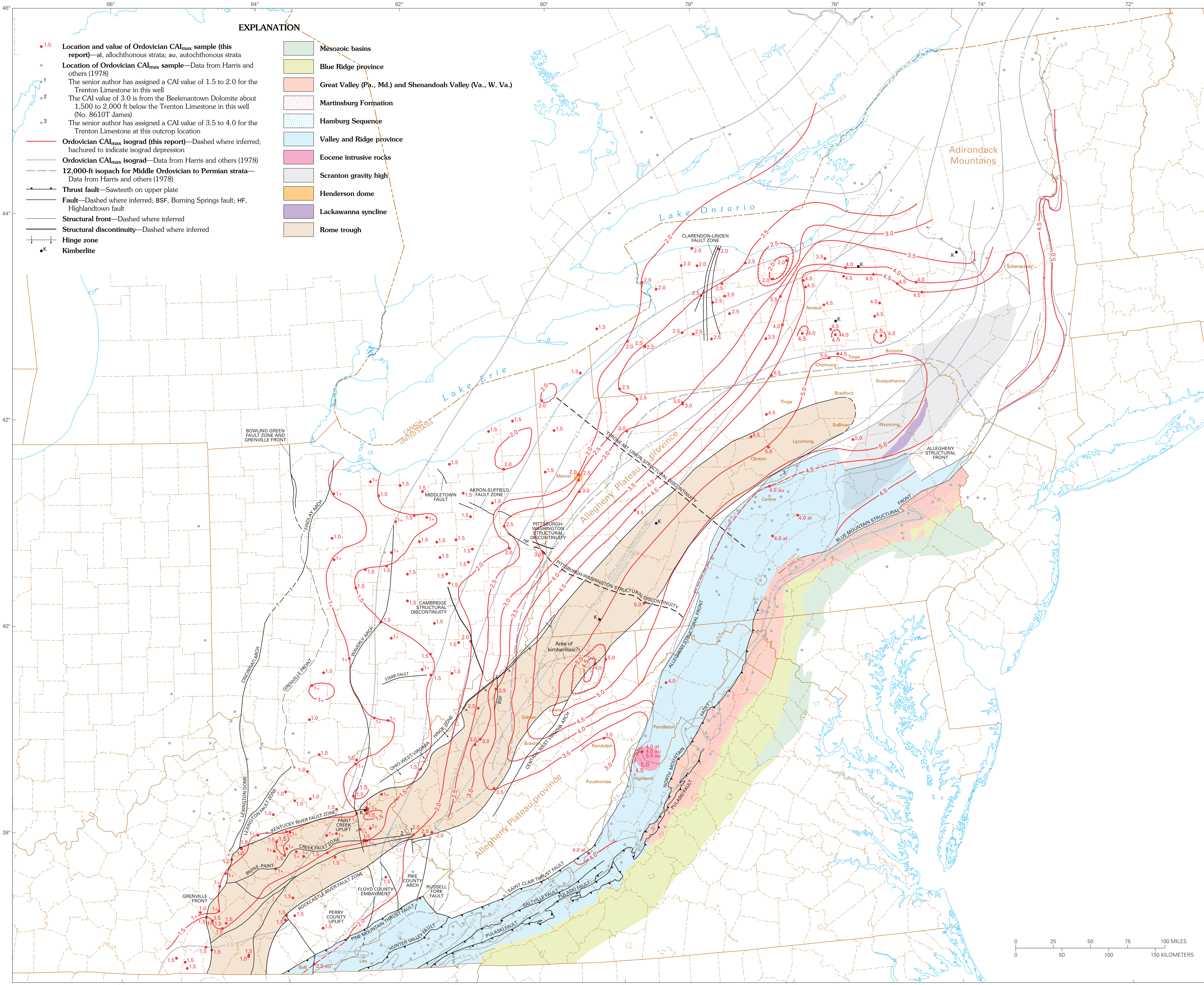

Figure 5.—Ordovician conodont color alteration index (CAI_{max}) isograds superimposed on selected structural features and provinces.

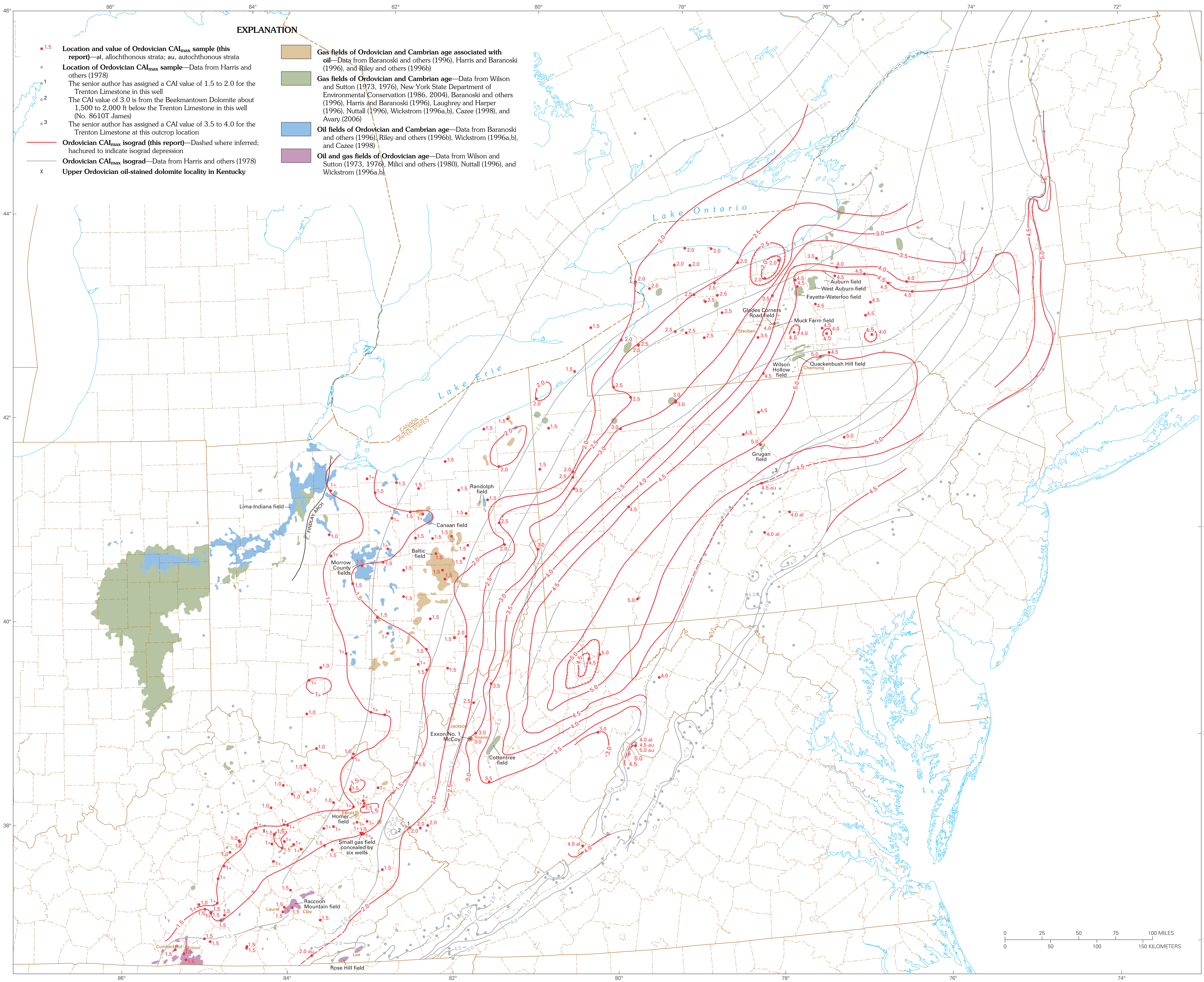

Figure 6.—Ordovician conodont color alteration index (CAI_{max}) isograds superimposed on oil and gas fields in Cambrian and Ordovician reservoirs.

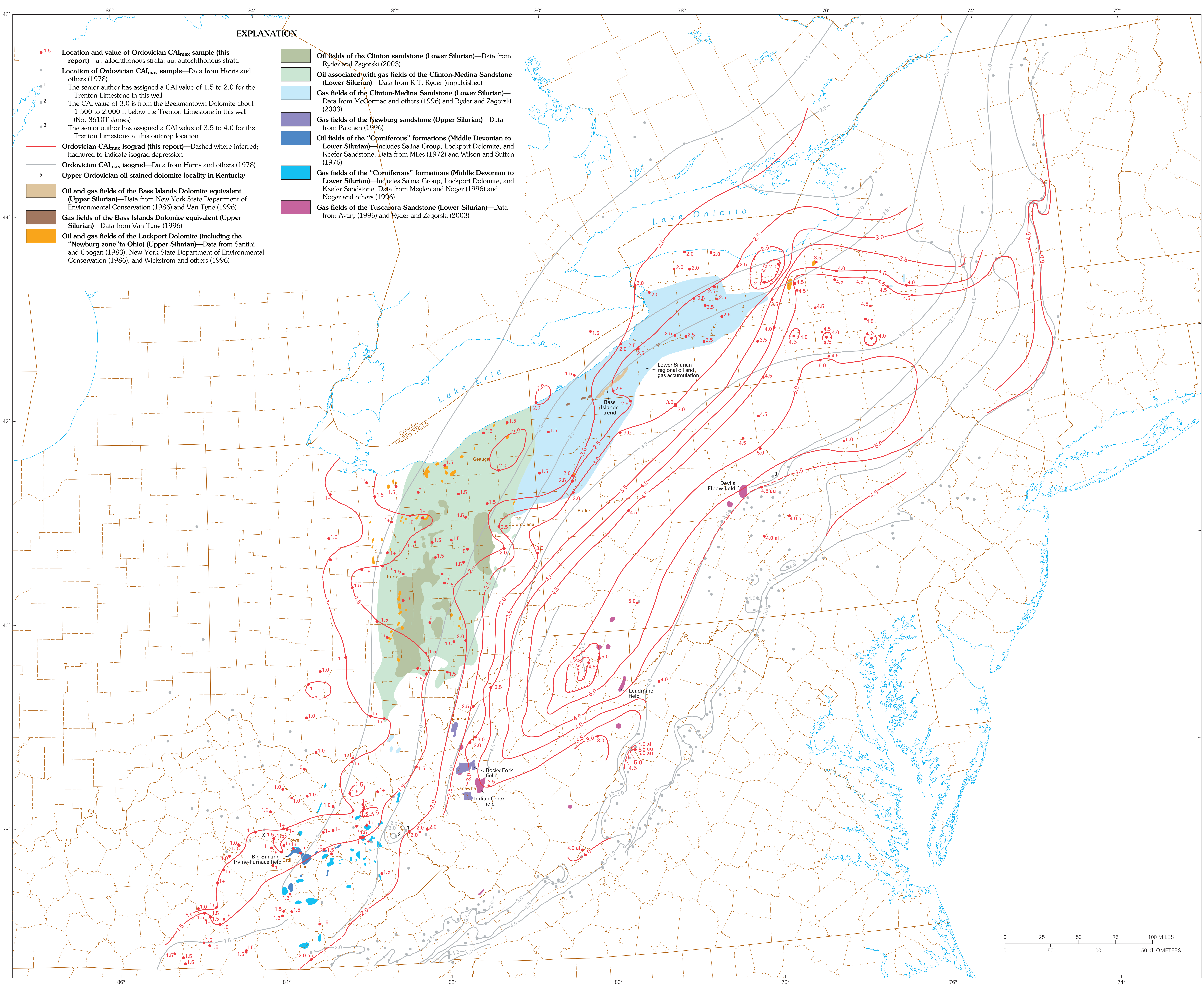

Figure 7.—Ordovician conodont color alteration index (CAI_{max}) isograds superimposed on oil and gas fields in Silurian reservoirs.

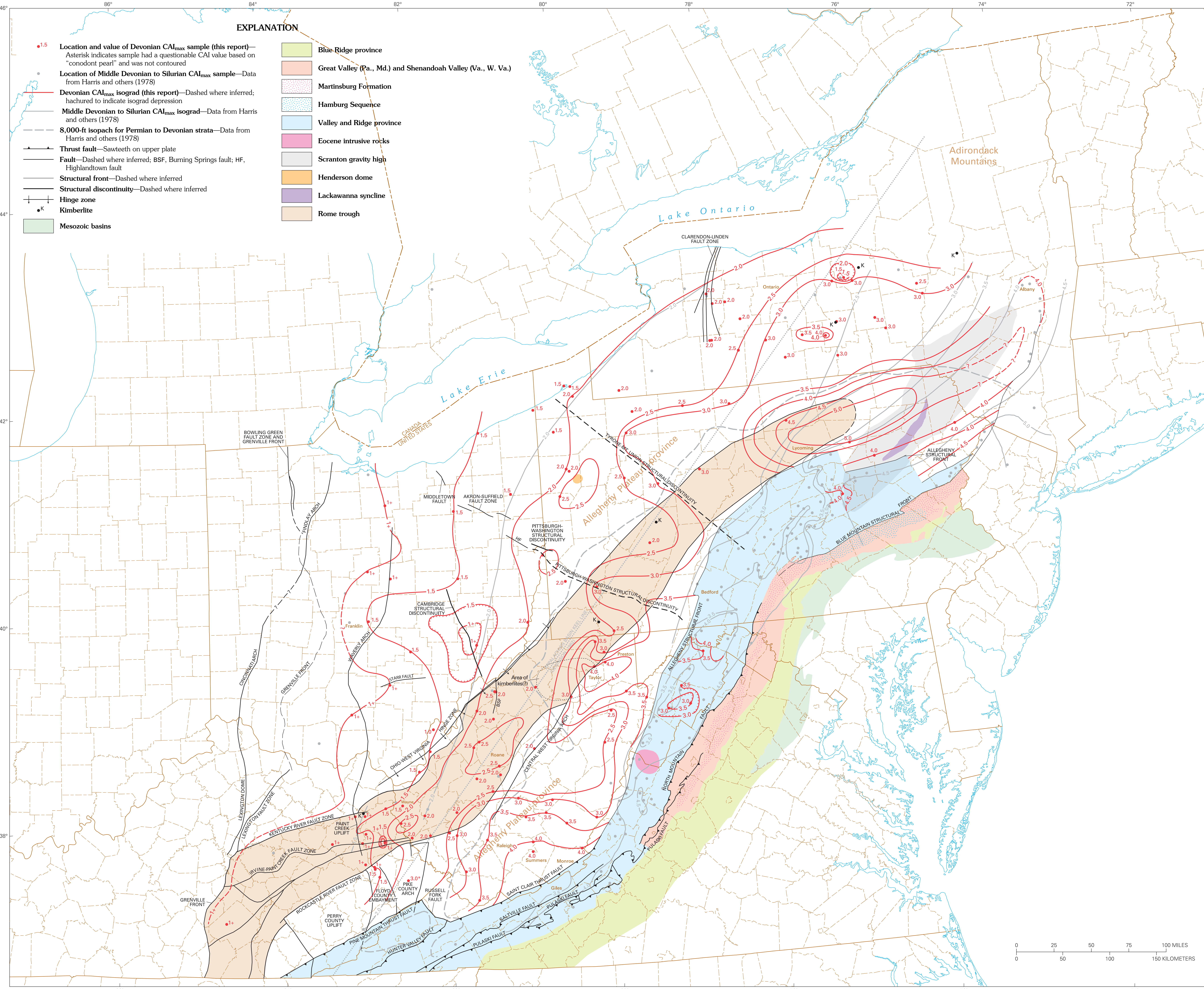

Figure 8.—Devonian conodont color alteration index (CAI_{max}) isograds superimposed on selected structural features and provinces.

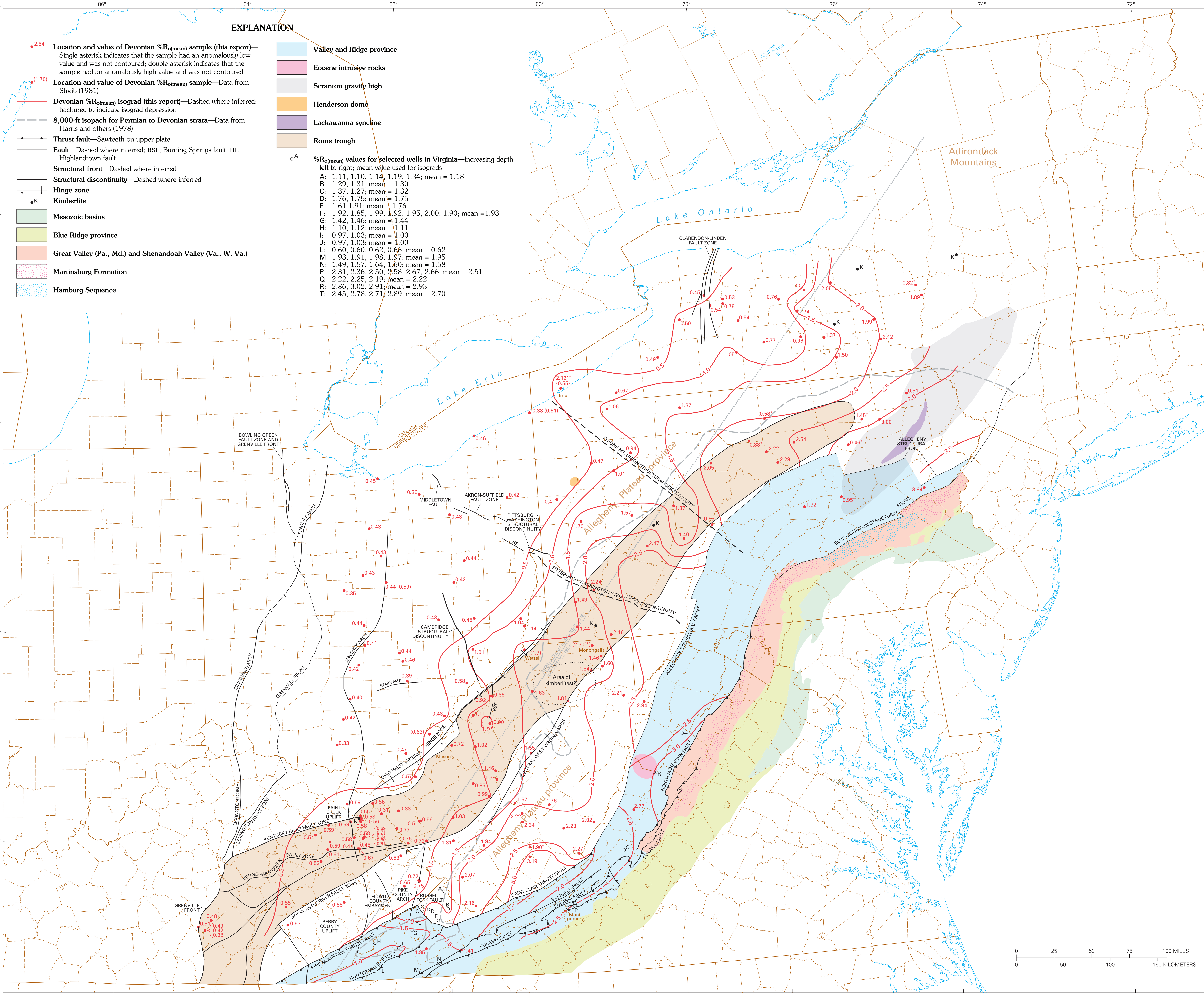

Figure 9.—Devonian vitrinite reflectance (%$R_{o(mean)}$) isograds superimposed on selected structural features and provinces.

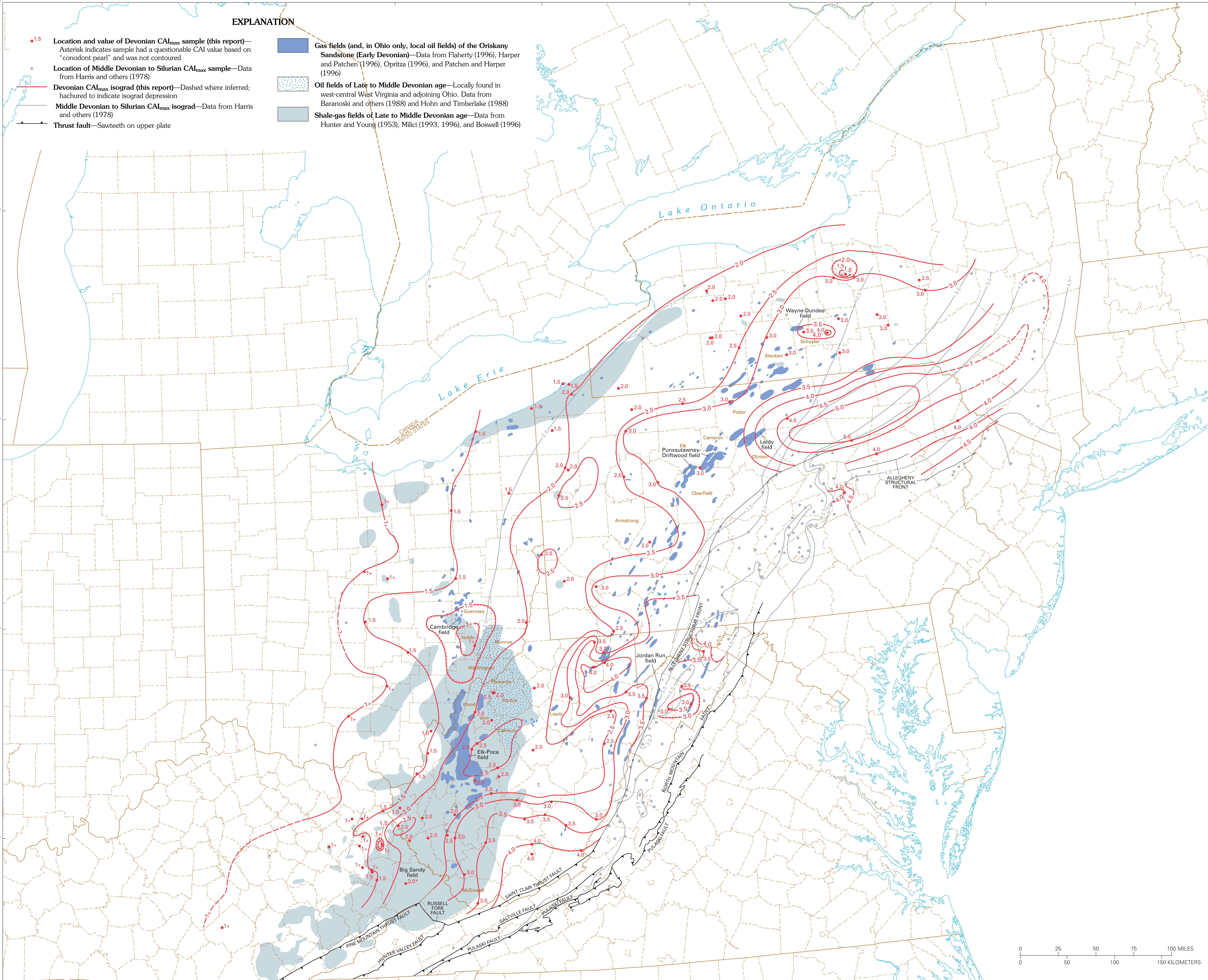

Figure 10.—Devonian conodont color alteration index (CAI_{max}) isograds superimposed on oil and gas fields in Lower Devonian Oriskany Sandstone and Devonian shale reservoirs.

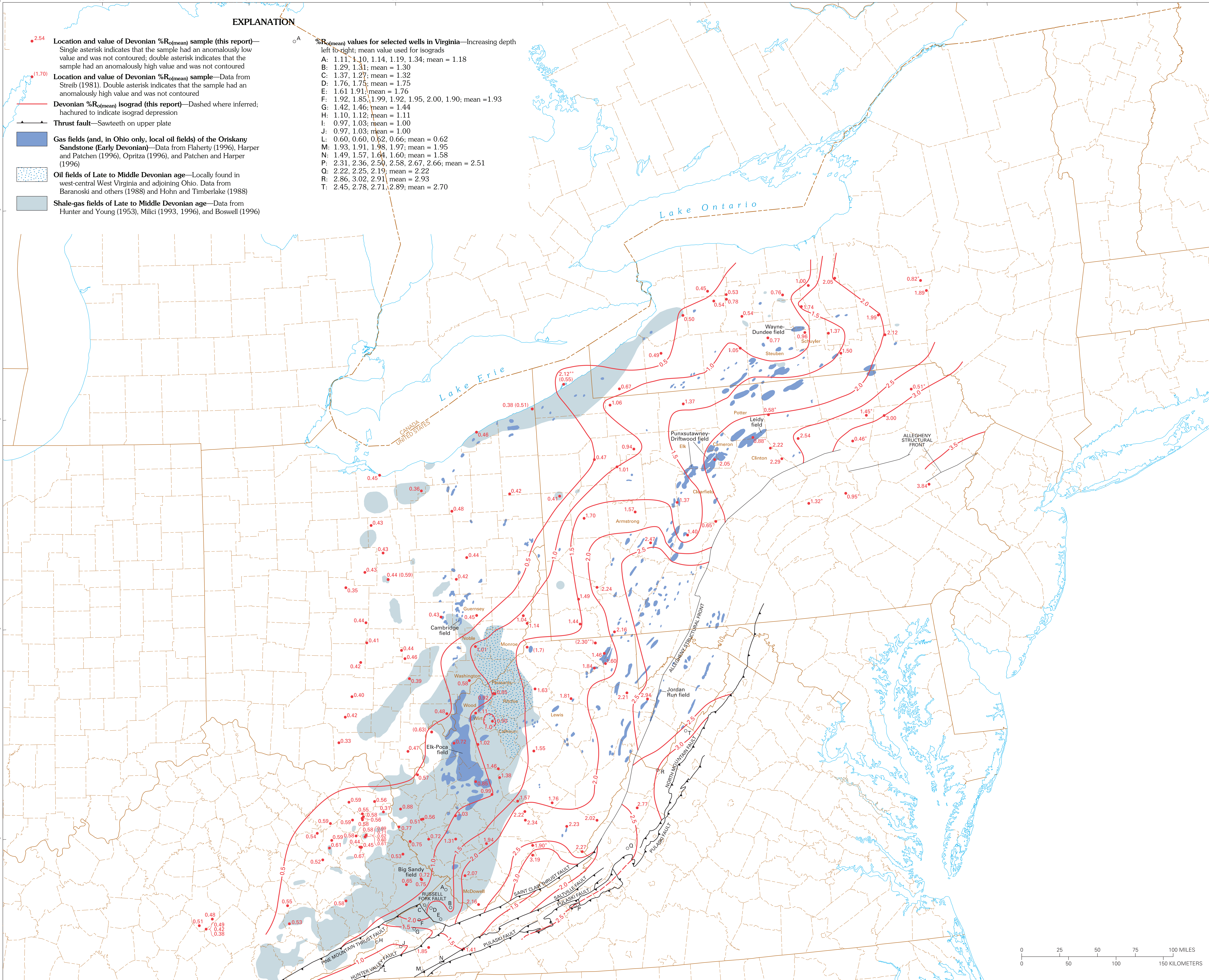

Figure 11.—Devonian vitrinite reflectance (%R$_{o(mean)}$) isograds superimposed on oil and gas fields in Lower Devonian Oriskany Sandstone and Devonian shale reservoirs.