# Reports

## Hydrocarbon Resources of the Eastern Overthrust Belt: A Realistic Evaluation

Abstract. *By considering the present occurrence of hydrocarbons, past geologic conditions, and timing of deposition, deformation, and metamorphism, realistic limits to hydrocarbon occurrences in the Appalachians may be defined. Additional consideration of thermal gradients and present depths to possible sedimentary rocks in the footwall beneath the Blue Ridge–Piedmont overthrust indicates that hydrocarbon stability is unlikely beneath much of it today.*

Interest in potential hydrocarbon occurrences in the Appalachians beneath the Blue Ridge thrust sheet and the eastern Valley and Ridge has been spurred by the interpretation of newly acquired seismic reflection data from the external and internal parts of the Appalachian orogen (*1, 2*) (Fig. 1). Results of these studies confirm the earlier hypothesis (*3–5*), based on the interpretation of surface geologic data, that the Blue Ridge of Tennessee, North Carolina, and Georgia is allochthonous. A more recent idea, based on regional aeromagnetic and gravity data as well as surface geology, is that the Inner Piedmont is also allochthonous (*6*). In light of recent speculations that there may be hydrocarbons (particularly natural gas) beneath large portions of the Blue Ridge and Piedmont (*7*), an additional assessment should be made.

It is more difficult to evaluate the hydrocarbon resources of the Appalachian orogen than those of a Mesozoic-Cenozoic to Recent passive margin because of the complexity of the Appalachians. However, similar factors in the depositional environment influence the generation and initial containment of hydrocarbons in simple or complex reservoirs. But in a deforming orogen, where hydrocarbons may be forced to migrate several times and are subjected to steeper thermal gradients, the hydrocarbons have a greater probability of being destroyed. Perhaps the most crucial question is that of the timing of metamorphic-thermal events relative to the formation and emplacement of the major structures that are most likely to trap and contain hydrocarbons. Maturation is strongly influenced by the duration of burial of a mass and whether it has been heated. In the Appalachians, the timing of metamorphism in the Blue Ridge and parts of the Valley and Ridge relative to emplacement of the large thrust sheets is most important. Also important are the ambient temperatures of the thrust sheets at the time of emplacement. Emplacement of thrust sheets has the effect of emplacing a thermal blanket. Even if the thrust sheets were cool at time of emplacement, the additional crustal thickness at a particular point requires thermal reequilibration according to existing heat flow characteristics at that point.

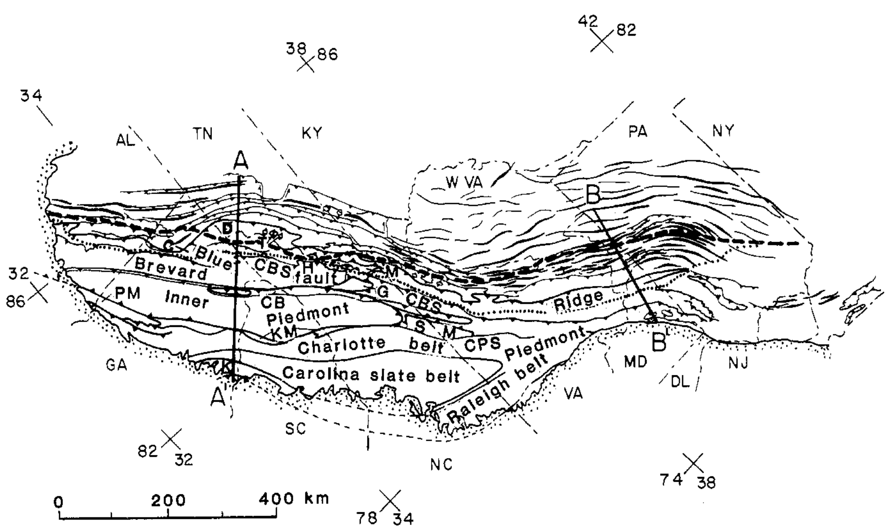


Fig. 1. Map showing the subdivisions of the southern Appalachians. The heavy dashed line in the eastern Valley and Ridge and western Blue Ridge represents the eastern limit for probable hydrocarbon occurrences in Ordovician and older rocks. The dotted line is a less well defined limit for exploration in post-Ordovician rocks, if they occur beneath the Blue Ridge–Inner Piedmont thrust sheet. Abbreviations: *A–A'* and *B–B'*, locations of cross sections shown in Fig. 3; *C* (Cartersville), *D* (Ducktown), and *H* (Hot Springs), locations of reported hydrocarbon occurrences in the crystalline Blue Ridge referred to in the text; *T*, Tuckaleechee Cove, Wear Cove, Cades Cove, and Calderwood windows; *M*, Mountain City window; *G*, Grandfather Mountain window; *CBS*, Central Blue Ridge suture; *CB*, Chauga belt; *PM*, Pine Mountain belt; *KM*, Kings Mountain belt; *SM*, Sauratown Mountains; *CPS*, Central Piedmont suture; and *K*, Kiokee belt.

Metamorphism in the Blue Ridge of the Carolinas, northeast Georgia, and Tennessee probably occurred during the Ordovician, 450 to 480 million years ago (*8*). Last movement on the Blue Ridge (Great Smoky–Cartersville) thrust occurred during the late Paleozoic (~ 290 million years ago), since Mississippian rocks occur in the footwall of the Great Smoky thrust in Tennessee (*9*). The coeval relationship of deformation and metamorphism, particularly the correlation between known movement histories of large faults and metamorphism in the Appalachians, has been discussed (*10*).

Rocks of the Valley and Ridge of Virginia and northeast Georgia are metamorphosed to the chlorite zone in Barrow's zones of progressive regional metamorphism and contain a strong slaty cleavage. Rocks of the central and southern Valley and Ridge and westernmost Blue Ridge of Tennessee are unmetamorphosed or only slightly metamorphosed. They contain a spaced cleavage or locally a weak slaty cleavage. Timing of metamorphism is uncertain in the Valley and Ridge. There is probably a component of Taconic metamorphism (~ 450 to 480 million years ago), but some of the younger rocks in Georgia, Alabama, and Virginia also possess a cleavage, probably superimposed in Pennsylvanian or Permian time.

Studies of illite crystallinity in the Cambrian shales of the Valley and Ridge of northwest Georgia and eastern Tennessee (*11*) indicate that the greatest degree of recrystallization is near Cartersville, Georgia, in a region where the trace of the Blue Ridge thrust is concave toward the Valley and Ridge. This also corresponds to the zone of greatest deformation and appearance of chlorite in the rocks of the Georgia and Tennessee Valley and Ridge, indicating that the pressure and temperature conditions of the lower portions of the greenschist facies of regional metamorphism were reached.

Studies of increasing conodont alteration with increased temperature by Epstein *et al.* (*12*) bring out the same relationships as the illite crystallinity studies. Values of conodont alteration index (CAI) above 4 correspond to lower greenschist facies temperatures. The CAI values in the Cartersville recess and those in northeasternmost Tennessee and the eastern part of the southwest Virginia Valley and Ridge in the Kingsport-Bristol-Roanoke recess are above 4. Limits of petroleum stability are probably reached well below a CAI value of 4. There appears to be a strong correlation between the westwardly convex parts of a large thrust sheet and the metamorphic grade of rocks in the footwall. The footwall rocks immediately northwest of the outermost part of the westwardly convex portion of the Blue Ridge thrust sheet in Tennessee are least metamorphosed. The same relationship holds within the convex parts of the Blue Ridge thrust sheet. The Ocoee and Chilhowee sequences in the outermost thrust block within the Great Smoky thrust sheet are less deformed and metamorphosed than the sequences immediately above the thrust sheet farther to the northeast and southwest, where the outcrop trace of the thrust becomes westwardly concave and extends farther southeast into the orogen.

Examination of mineral assemblages of rocks within windows or suspected windows brings out additional interesting relationships (Table 1). All rocks southeast of the Brevard zone exposed in windows have been metamorphosed to amphibolite facies assemblages. Those in the Grandfather Mountain window are in the upper greenschist facies (*3*), as are carbonate slices in the Brevard zone (Fig. 2) (*4, 13*), and are well above the limits of hydrocarbon stability. The only really low grade rocks in windows or slices are in the simple windows of the Great Smoky Mountains in Tennessee (*14*).

Additional evidence includes reports of methane in one or more of the mines at Ducktown, Tennessee, in staurolite-kyanite grade rocks, and asphaltic residues from the Great Smoky fault zone in the Hot Springs window, North Carolina

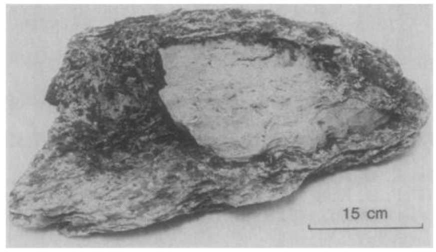


Fig. 2. Specimen of carbonate slice from the Brevard zone in South Carolina showing dark phyllitic interlayers and low-porosity dolomite, which are the products of greenschist facies metamorphism and strong deformation.

(*15*), indicate that hydrocarbons may still occur beneath the western part of the Blue Ridge thrust sheet. Another unsubstantiated hydrocarbon locality exists in the Blue Ridge east of Cartersville, Georgia (Fig. 1).

Thus any assessment of the hydrocarbon potential of the southern and central Appalachian overthrust belt should take into account factors such as the timing of deformational and thermal events, distribution of zones of low or higher metamorphic grade ascertained from mineral assemblages, illite crystallinity, CAI, and known occurrences of hydrocarbons. The part of the Blue Ridge where hydrocarbons may occur today is therefore restricted to a very narrow zone in the western Blue Ridge of the southern half of Tennessee, a slight portion in western North Carolina, and a small portion in north Georgia. It is also possible to use these data to restrict the likelihood of hydrocarbon occurrences to small segments of the eastern Valley and Ridge of Tennessee and most of the western Valley and Ridge and Plateau (Fig. 1).

Younger post-Ordovician rocks, if present beneath the Blue Ridge thrust sheet, may not be metamorphosed in the frontal zone, provided all metamorphism was Taconic (which it may not have been). This allows for the possibility of source rocks that were not affected by a thermal event prior to final emplacement of the thrust sheet. However, the area of greatest likelihood of occurrence of thermally unaffected rocks is again beneath the western edge of the Blue Ridge thrust sheet (Fig. 1). In this case the promising area is larger, particularly in Georgia, where Mississippian rocks are common along the leading edge of the thrust sheet.

It has been pointed out (*16*) that the overburden thickness covering footwall rocks in the Inner Piedmont would have been sufficient to produce geothermal equilibration temperatures in excess of the stability limits of hydrocarbons, making the probability of their occurrence here very low. The westward limit of this zone of geothermally reequilibrated high temperatures would depend on

Table 1. Metamorphic grades of rocks from beneath the Blue Ridge–Inner Piedmont thrust sheet.

| Locality | Grade |
|---|---|
| Tuckaleechee Cove, Wear Cove, Cades Cove, Calderwood windows | Unmetamorphosed |
| Mountain City window | Lower greenschist |
| Grandfather Mountain window | Upper greenschist |
| Brevard Zone slices | Upper greenschist |
| Sauratown Mountains | Upper greenschist to amphibolite (garnet-kyanite) |
| Pine Mountain belt | Upper amphibolite (kyanite-sillimanite) |

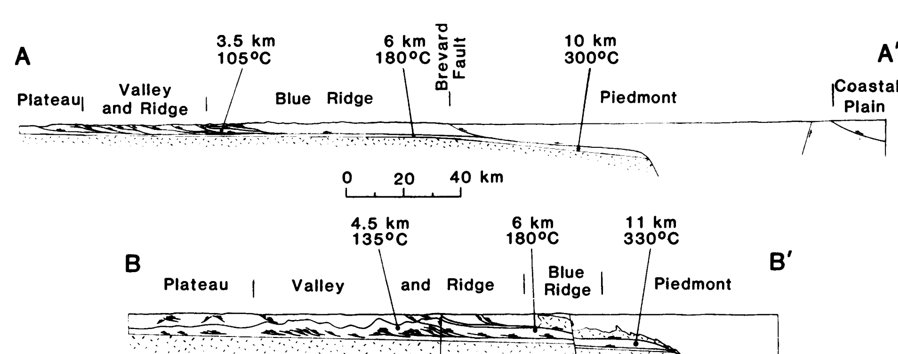


Fig. 3. Cross section through southern and central Appalachians (*17*) showing temperatures that would exist beneath the thrust sheet today, assuming a geothermal gradient of 3°C per 100 m. Cross-hatch pattern represents Precambrian basement rocks (not shown in the Blue Ridge thrust sheet in *A–A'*). Pre-Alleghenian faults are also not shown. Locations of sections are shown in Fig. 1.

the thickness and ambient temperature of the thrust sheet in the western part of the Blue Ridge at the time it was emplaced. This factor would affect any rocks beneath the thrust sheet regardless of their age. Assuming present thicknesses and a reasonable interpretation of southern and central Appalachian structure (*17*), temperatures would be too high today beneath most of the sheet for hydrocarbons to survive (Fig. 3), unless there is some process capable of creating and maintaining abnormally low temperature and pressure conditions over hundreds of millions of years. This is unlikely in light of observations in areas where deeply eroded crystalline thrust sheets occur, such as in the Scandinavian Caledonides. One of the best examples is near Åre in Sweden, where granulite facies (Caledonian metamorphism) rocks occur in the highest thrust sheet at the top of the mountain Åreskutan. However, some 1700 m lower, near the base of the mountain, Lower Silurian limestones contain identifiable crinoid fragments (*18*). It is obvious that metamorphism occurred before emplacement of the thrust sheets. However, despite the fact that fossils occur in the limestone near the base of the mountain, this limestone is penetratively deformed and metamorphosed at least to the greenschist facies. Minimal restored burial depth of the fossiliferous rocks to the elevation of the present topography is less than 1 km. The thickness of the thrust pile must have been several times this at the time of emplacement. The important conclusion both there and in the Appalachians is that the higher the metamorphic grade of the highest grade rocks in a pile of thrust sheets, the higher the metamorphic grade of the lowest grade rocks beneath the sheets, provided emplacement of the thrust sheets is related to one or more of the metamorphic and thermal events producing the high grade rocks.

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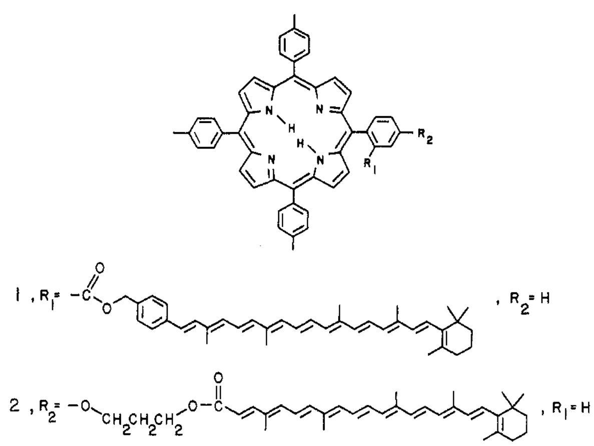
## Photoprotection by Carotenoids During Photosynthesis: Motional Dependence of Intramolecular Energy Transfer

Abstract. *A new carotenoporphyrin has been prepared in which a synthetic carotenoid is joined to a tetraarylporphyrin through a flexible trimethylene linkage. This molecule exists primarily in an extended conformation with the carotenoid chromophore far from the porphyrin π-electron system. In benzene solution, where large-amplitude molecular motions are rapid, the molecule can momentarily assume less stable conformations which favor triplet energy transfer, and quenching of the porphyrin triplet by the carotenoid is fast. In a polystyrene matrix or frozen glass such motions are slow, and energy transfer cannot compete with other pathways for depopulating the triplet state. These observations help establish the requirements for biological photoprotection.*

Carotenoid polyenes serve at least two functions in the photosynthetic apparatus of green plants. They are useful as antenna pigments which absorb light in regions of the spectrum where chlorophylls are not efficient and transfer excitation energy to the chlorophyll singlet manifold. They are vital as photoprotective agents which mitigate the harmful effects of singlet oxygen. Synthetic carotenoporphyrins such as **1** can serve as model systems which define the structural requisites for both photoprotection and antenna function (*1–3*). We now report studies of a new carotenoporphyrin showing that the dynamics of the molecule, as well as the static structure, play a crucial role in the photophysical events basic to the biological functions of these pigments.



In green plants the major potential source of singlet oxygen is sensitization by chlorophyll triplet states. Thus carotenoid polyenes can provide photoprotection by quenching the chlorophyll triplets before they can react with oxygen. In benzene solution at ambient temperatures, triplet energy transfer from the porphyrin chromophore of **1** to the carotenoid occurs with 100 percent efficiency and the porphyrin triplet state is completely quenched within ~ 25 nsec (*3*). Thus the porphyrin triplet lifetime is too short to allow singlet oxygen production under atmospheric conditions, and photoprotection in **1** is completely effective (*3*). Using similar techniques, we have determined that triplet-triplet energy transfer also occurs on the nanosecond time scale when **1** is irradiated in a deoxygenated polystyrene or cellulose triacetate matrix.