A Possible Source for Hydrocarbons Observed in the Waddell-Duncan No. 1 Murrey Well, Cochise County, Arizona*

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Abstract

The Waddell-Duncan No. 1 Murrey well, drilled in 1950 in the southeastern corner of Cochise County Arizona, was reported to have oil shows in well cutting samples at approximately 1950 to 1960 feet, 2980 to 2990 feet, and 3345 to 3360 feet. There was also a gas show recorded between 2250 and 2260 feet. Whether these oil or gas shows were the result of hydrocarbons generated in situ, or the result of hydrocarbon contaminants in the drilling mud system, has remained a question for the past 35 years. Organic-matter slides, originally prepared in 1978-1979 from well-cutting samples from the above intervals, were re-examined to determine the source of the hydrocarbons.

All the hydrocarbon-containing zones (listed above) were found to be dominantly composed of lipid-rich algae. Plant-tissue fragments, with minor occurrences of trilete spores and pollen, were also observed. Nothing unusual was noted in the well samples from the stratigraphic sections 1950 to 1960 feet, 2250 to 2260 feet and 2980 to 2990 feet. Cuttings, from the stratigraphic interval 3350 to 3440 feet, contained minor accumulations of hydrogen-rich, oil-like globules, bubbles and scum-like stains. Some components exhibit a dull, yellow-gold to yellowish-brown fluorescence in ultraviolet radiation while others were a bright yellow to yellow-orange. Some had no fluorescence at all. These hydrogen-rich constituents are interpreted to be a product of the algae which makes up the bulk of the organic matter within this portion of the stratigraphic section.

Introduction

In the late 1970's the senior author asked Dr. H. Wesley Pierce, formerly with the Arizona Bureau of Mines (now the Geological Survey of Arizona), permission to examine a small quantity of well cutting samples from the Waddell-Duncan No. 1 Murrey well. The agreement between Dr. Pierce and Mr. Schwab was that a copy of his findings would be provided to the Arizona Bureau of Mines (Geological Survey of Arizona). Mr. Schwab, President and former Owner of Geo-Strat, Inc., provided that report in 1980. (See report entitled: Geochemical

Evaluation of the Waddell-Duncan No. 1 Murrey Well, Sec. 5, T22S, R27E, Cochise County, Arizona currently on file with the Arizona Geological Survey).

According to Thompson, et al. (1978), the Waddell-Duncan No. 1 Murrey well, drilled in 1950 in the southeastern corner of Cochise County, Arizona, was reported to have oil shows in the well-cutting samples taken at approximately 1950 to 1960, 2980 to 2990., and 3345 to 3350 feet (Figures 1 and 2). Mazzullo (2014) reported that there was also a gas show recorded in the section between 2250 and 2260 feet. As far as the writers are aware, no commercial quantities of oil or gas were found in the Waddell-Duncan No. 1 Murrey well.

Because the well cutting samples from the Waddell-Duncan No. 1 Murrey well were mud-pit samples, we wondered if the oil and gas shows were associated with in situ hydrocarbons or if they were the result of contaminants from some other source. This prompted the writers to re-examine the original visual kerogen slides prepared by Schwab. The primary objective was to see what evidence could be found in the organic matter suite that might substantiate the mud-loggers observations of oil and or gas shows in the well. That question forms the basis for this investigation and is the primary objective for the preparation of this manuscript.

Discussion

In an attempt to better understand the geochemistry of the sediments recovered from the Waddell-Duncan No. 1 Murrey well, the authors re-examined the original set of slides prepared by Schwab in his 1980 geochemical study. Our goal was is to try to determine what part of the stratigraphic section had the greatest likelihood for the generation of liquid and/or gaseous hydrocarbons. Of equal importance is our attempt to determine if the oil and gas shows that were reported in the well were a result of in situ hydrocarbon generation or a result of contaminates that were introduced into the mud-system during the drilling of the well.

During the re-examination of the visual kerogen slides the writers observed a number of things that were not recorded in Schwab’s original report. Observations included the recognition of a variety of new stalked alga as well as the presence of a couple of poorly preserved palynomorphs having morphology similar to the pollen genus *Aquilapollintes* sp. The latter, observed in samples taken at 2250 to 2340 and 2450 to 2540 feet, is often associated with Upper Cretaceous sediments and may be an indication of the age of the sediments in that portion of the stratigraphic column.

Of greater significance, was the observation of oil-like globular, bubble-shaped, and scum-like films (hydrocarbons), present in some of the visual kerogen slides. These oil-like constituents are the main focus of this report.

The writers believe that the presence of these oil-like constituents, especially those observed in the visual kerogen slides of the Waddell-Duncan No. 1 Murrey well, may be of primary importance in recognizing which stratigraphic zones offer the best chances for finding in situ liquid and gaseous hydrocarbons. Furthermore, the authors are of the opinion that the presence of these oil-like constituents may actually be related to, and contributed to, the “oil and gas” shows recorded by the well-site geologist.

Well-cutting samples, representative of the stratigraphic section from 1950 to about 2140 feet were observed to contain minor amounts of these oil-like constituents. The greatest concentrations of these components were found in the well cuttings that are representative of the stratigraphic section between 3350 and 3440 feet.

Results

Palynologists occasionally find hydrocarbons in palynological and organic-matter slides. The presence of this material in palynological and visual kerogen preparations has been commonly referred to as "bitumen" or "petro-fibrils". They have been interpreted by some palynologists and organic-matter analysts as an indication that hydrocarbons were generated within the stratigraphic unit, or as a tell-tale sign that liquid hydrocarbons have migrated through that particular part of the stratigraphic section. Groth (1980, 1981), Thompson-Rizer (1987), Graham, et al. (2000) and Wood et al. (2002) discuss this topic in more detail.

According to Graham, et al. (2000), "The angular or sub-rounded bodies (from which the fibrils emendate), are actually a form of organically sourced hydrocarbon classified as asphaltenes." These authors go on to say that these components may originate as amorphous kerogen and form as secondary pore fillings.

To the writer's knowledge, nothing as of this date has been mentioned of their direct association with, or relationship to, algae. In our study, most of the hydrocarbon (oil-like) constituents in the Waddell-Duncan well are totally unlike anything described by Graham et al., Wood et al., or Groth. Only one petro-fibril filament type was observed in the sample material at 3350 to 3440 feet in the Waddell-Duncan No. 1 Murrey well. Contrary to what Graham et al. (2000) state in their paper regarding the origin of the petro-fibrils, we believe the filaments, based on our observations, are more likely associated with algal constituents (Figure 3). Although the organic particle from which a petro-fibril has developed appears to be black in color, resembling solid bitumen, the opaque material does have structure. This can be seen in the photographs taken under high magnification using a variety of different lighting conditions. Even some of the petrol-fibril filaments described and illustrated by Wood et al. (2002, Plate 1, figures 5-8) appear to be of algal origin. Our examination of Wood et al.'s published photographs, which were enhanced using various lighting techniques available in our Adobe Photoshop Elements software program, shows that the material has internal structure. It is, in our opinion, not solid bitumen as the authors believe it to be. The amorphous debris associated with the petro-filaments, illustrated by Wood et al. (2002), is also interpreted to be algal in origin. When figures 1-5 in his Plate 1 were enlarged and carefully analyzed, algal cells could be clearly seen within the amorphous-like matrix.

The oil-like (lipid-rich) constituents in the well-cutting samples from the Waddell-Duncan No. 1 Murrey well have a morphology that is distinctly different than the petro-fibrils described by Groth (1980), Graham et al. (2000), and Wood et al. (2002). We have not seen any photomicrographs of various types of bitumen described by Thompson-Rizer (1987) and therefore cannot make any comments about them.

Most of the oil-like (lipid-rich) constituents occur as entrapped "bubbles," some having other globular-looking masses within them (Figures 4C-D, 5, 6, 7 and 8). Others occur as a transparent liquid-appearing "film" or "scum" within the organic matter assemblage. Many of the "bubble-like" forms have pale yellow to yellow-orange scaly fragments, possibly shards of oil-like detritus, adhering to what we interpret to have been the exterior surface of the bubbles (which since have ruptured leaving remnants of the organic matter behind). See Figures 5C-D and 7.

The majority of the oil-like (lipid-rich) constituents in the Waddell-Duncan No. 1 Murrey samples are considered to have been generated since the initial organic-matter slides were prepared in 1979. There is no conceivable way that these oil-like (lipid-rich) stains would have survived intact, and in the manner that we observed them, during the preparation of the visual kerogen sample. What is this oil-like (lipid-rich) material, where did it come from, and why did the senior author not observe its presence when the slides were first examined?

Because the majority of the oil-like (lipid-rich) material is found in association with a predominantly algal-rich organic-matter suite, the authors believe it was derived from the algal material itself. We do not believe it to be a product of contamination due to the migration of oil-like (lipid-rich) liquids within the rocks. Some oil-like (lipid-rich) residue can be seen within the "head" or "fan" of one of the algal components in the cutting samples from 3350 to 3440 feet (Figure 4A-B). When examined under high magnification, the oil-like or lipid-rich material appears to have flowed from the head portion of the algal constituent into the surrounding cell tissue. The staining pattern of the oil-like (lipid-rich) material suggests that it may have been liquid at some point in its geological past. Whether this oil-like (lipid-rich) substance was generated from high concentrations of lipids that occurred within the individual algal cells, as they do in the fresh to brackish water alga *Botryococcus braunii*, illustrated in the photomicrograph published by Kinross (2015) and by Canter-Lund and Lund (1998, p. 37) and shown in Figures 9 and 10, and then expelled through the cell membrane or along the margins of the cell walls that make-up the colony, we do not know. It is reasonable to assume, however, that this oil-producing process, or one similar to it, has continued in a similar fashion since the algae first appeared in the geologic record.

Why were these oil-like, lipid-rich, constituents not readily observed when the visual kerogen slides were first prepared and examined? The answers could be: 1) Schwab overlooked the presence of the oil-like constituents in the sample during his initial examination, or 2) The oil-like constituents had not formed to the extent they now appear. The writers suspect that the visual kerogen slides were stored away after the initial examination and during the 36 years since their initial preparation, the effect of the mounting media, a product called Elvacite, reacted with the organic matter in such a way as to cause the expulsion and release of the oil-like constituents from the organic matter or algal debris.

Another question pertains to the oil-like (lipid-rich) constituents themselves. How do we know they are an oil-like residue? We can never be totally sure based solely on visual observations. It would be necessary to do some geochemical work on the well-cutting samples to make this determination. Since the only sample material the writers have are the prepared visual kerogen slides, we cannot do a geochemical (extraction and/or gas generation) study. We can use another technique, however, fluorescence microscopy, to see if the oil-like material is really that, and not some stain on our Visual Kerogen slide. This technique will also help to determine if the chemical composition of the organic material is hydrogen-rich, an important factor in the generation of hydrocarbons.

Oil-Like Constituents in UV-Fluorescence

Fluorescence microscopy is commonly used by researchers to determine whether a particular sedimentary unit has source-rock qualities. In their book, entitled Petroleum Formation and Occurrence: A New Approach to Oil and Gas Exploration, Tissot and Welte (1978, p. 437) state that fluorescence microscopy can be used in several ways in the study of source rocks.

According to Tissot and Welte, geochemists considered fluorescence microscopy to be an excellent diagnostic tool for identifying the liptinite group (i.e., lipid-rich relics of plants) of macerals when analyzing coal samples during vitrinite-reflectance analyses. It has also been stated, based on scientific observations, that the oil-like components, termed exsudatinite, can readily be seen by using fluorescence microscopy (Teichmuller, 1974). Also, fluorescence microscopy is often used in helping palynologists to identify and quantify the various types of finely disseminated amorphous liptinitic particles observed in their organic-matter residue studies. Palynologists often have no other good method of visually identifying the finely dispersed particulate debris of algal or microbial origin commonly observed in their visual kerogen preparations.

In addition, fluorescence microscopy is a method that can be used to determine the level of thermal maturity of dispersed organic matter by estimating the intensity and color of the fluorescence. Lipid-rich organic matter having a low level of thermal maturity fluoresces more brightly than organic particles having higher levels of thermal maturity. It has been documented that there is a distinct color difference in the fluorescence when determining which constituents are at an immature stage of thermal maturity and those that are mature. Organics that are at an immature stage of thermal maturity generally fluoresce a bright yellow while organics that are at a more mature stage of thermal alteration tend to exhibit a dull orange to dull orange-brown fluorescence.

The importance of fluorescence microscopy was evident when the senior author examined Staplin's (1969) original set of Thermal Alteration Standards (TAI) for Exxon Production Research Company in the mid-1980's. It was observed that there was a notable change in the overall percentage and color of fluorescence between Staplin's TAI (Thermal Alteration Index) of 1.2 and 2.6 (Staplin samples 30-370, 30-363, 30-364, 30-362, 30-426, 30-365 and 30-606). Below Staplin's TAI Standard of 2.6 (sample 30-606), little to no visible fluorescence was observed (Figure 11).

Fluorescence is often used to determine if lipid-rich organic debris in a rock sample is in situ or the result of contamination. Contamination is a common problem associated with well-cutting samples and occurs primarily from the caving of rock fragments derived from sediments higher in the well bore. This is especially a problem in uncased well bores. Contamination can also occur in cored material although it is generally not a problem unless the rocks have a high level of fracturing, porosity and/or permeability. The recycling of liquids (including finite particulate organic matter) from older and perhaps more mature, rock units can migrate into a stratigraphic section due to the capillary movement of fluids in the sediments. Geologists, geochemists, and petrologists always have to be mindful of the drilling mud system used in the well. The type of drilling fluid being used, the casing points and the number of bit trips all should be recorded. Many of the mud additives being used in drilling are from sediments (bentonite, lignite, etc.) far removed (location and age-wise) from where a well may actually be drilled. Drilling mud can often contain organic matter not indigenous to the geographical area. This is precisely why organic-matter analysts should have a good background in palynology, so that they can easily recognize problems, should they occur.

In discussions that Schwab and Smith had with their colleague, the late Dr. Pieter van Gijzel, a pioneer in fluorescence microscopy and its application to petroleum exploration, he made mention of the fact that almost all crude oil fluoresces, to some degree, under ultraviolet radiation. He also mentioned that this was generally a good method whereby one could determine if the organic debris was hydrogen-rich or hydrogen-poor. Hydrogen-rich organics are generally rich in lipids (i.e., fats, oils, waxes, and most of the non-protein membrane of cells) the precursors of petroleum products. Therefore, it serves as a good indicator that the oil-like substances these writers observed in the cutting samples from the Waddell-Duncan No. 1 Murrey well are most likely composed of polyaromatic and heterocyclic hydrocarbons (oil). See Riecker (1962).

In our examination of organic matter, using reflected fluorescence microscopy (ultraviolet radiation), we observed that many of these oil-like constituents, including some of the lipid-rich material itself, exhibited good fluorescence qualities. Figures 12 and 13 illustrate the same stalked benthonic algae shown on Figure 4A-B in brightfield transmitted and reflected UV radiation. As can be seen in the photomicrographs, the oil-like substance is fluorescing brightly in UV radiation. It not only appears to be bleeding in an outward direction from the central portion of the algal colony but has completely saturated the surrounding cells. There is little doubt that the oil-like stains observed on the visual kerogen slides were once liquid and generated in situ from within the organic matter and portions of the algae itself. If the oil-like substance had migrated into the rock matrix after the organic debris had been fossilized, we would expect the entire algal specimen to have been covered by the substance, and the entire algal specimen would have fluoresced intently. We did not observe that.

Figure 14A-B illustrates the same oil-like residue presented on Figure 6A-B in brightfield transmitted and reflected UV fluorescence radiation. Note the dull dark orange color of the fluorescence compared to that which was observed in Figure 13A-B. This may indicate that the oil-like constituents are composed of two different chemical compositions, represent two different levels of thermal maturity or organic material representative of two different geological ages. The writers do not know which.

Figure 15A-B is a photomicrograph showing the same material in Figure 3A-D. Illustrated here is a bitumen-like petro-filament or algal residue, shown in brightfield transmitted illumination and in UV reflected fluorescence. A portion of the main body of the algal debris fluoresces while the hair-like filament extruding from it shows no color in UV radiation. It does not appear on the photomicrograph of the specimen observed in UV radiation. It is as if the fields of view shown in Figure 15A-B are totally different. If the fibril does not fluoresce, is it composed of a hydrocarbon substance? We do not know the answer to this question. Also, we are not aware of any studies published on the fluorescence capabilities of these petro-filaments

While recycled organic matter is a common contaminate found throughout the entire well, the writers believe that the fluorescence of the oil-like constituents in the well-cutting sample from 3350 to 3440 feet is in situ. If this were not true, we should have seen this contamination in all the other cutting samples, not just those from the stratigraphic interval between 3350 and 3440 feet.

In most samples, the oil-like substance showed various degrees in the intensity and color of the fluorescence as did the algal debris. In places, the oil-like scum or stain fluoresces while the surrounding material does not. If the oil-like (lipid-rich) material fluoresces, why does not the entire specimen fluoresce? We assume it is a matter of changes in the chemical composition of the organics.

Conclusions

From our re-assessment of 41 visual kerogen slides from the Waddell-Duncan No. 1 Murrey well, the writers have concluded:

1). The algal material in the samples of the Waddell-Duncan No. 1 Murrey well is most likely the source for much of the oil-like (lipid-rich) constituents found in the stratigraphic section where the well-logger initially noted the presence of oil or gas shows. This is especially true for the sample representing the stratigraphic interval between 3350 and 4,440 feet.
2). Because the oil-like (lipid-rich) constituents are most often found associated with large concentrations of algal debris, the writers postulate that the algal material acted as both the source and the trapping mechanism for the liquid and gaseous hydrocarbons that were generated during geothermal diagenesis.
3). Based on their fluorescence capabilities, the oil-like constituents encountered in the stratigraphic section between 3350 and 3440 feet in the Waddell-Duncan No. 1 Murrey well are interpreted to be at a mature stage of thermal maturity (i.e., within the oil generating stage for liquid and gaseous hydrocarbons) .
4). Although commercial quantities of hydrocarbons were apparently never found in the Waddell-Duncan No. 1 Murrey well, it is feasible that southeastern Arizona , including parts of northern Mexico, could contain significant amounts of liquid and gaseous hydrocarbons if the right geochemical and geological conditions are present. The question is not **"if"** oil and gaseous hydrocarbons are present in the sediments from this part of Arizona but rather, how much oil and gas has already been generated and where does one have to drill in order to find commercial accumulations of the product.

Acknowledgements

This paper is dedicated to the memory of Mr. Alan H. Miller, an extraordinary geologist, classmate and life-long friend.

The writers are indebted to the late Dr. H. Wesley Pierce for providing the samples used in this study. Dr. Pierce was an outstanding geologist, a good friend and an exceptional individual. We also remember and give thanks to our dear friends and colleagues, the late Dr. Pieter van Gijzel for his extraordinary work in fluorescence microscopy, the late Dr. Frank L. Staplin for his outstanding contributions in the field of visual kerogen assessment and the late Dr. Gordon D. Wood, an outstanding and world respected Palynologist. To all these gentlemen, as well as the countless others whom we worked with during our careers, thank you for the many contributions that you made to the study of Earth Sciences. Your pioneering spirit will live forever.

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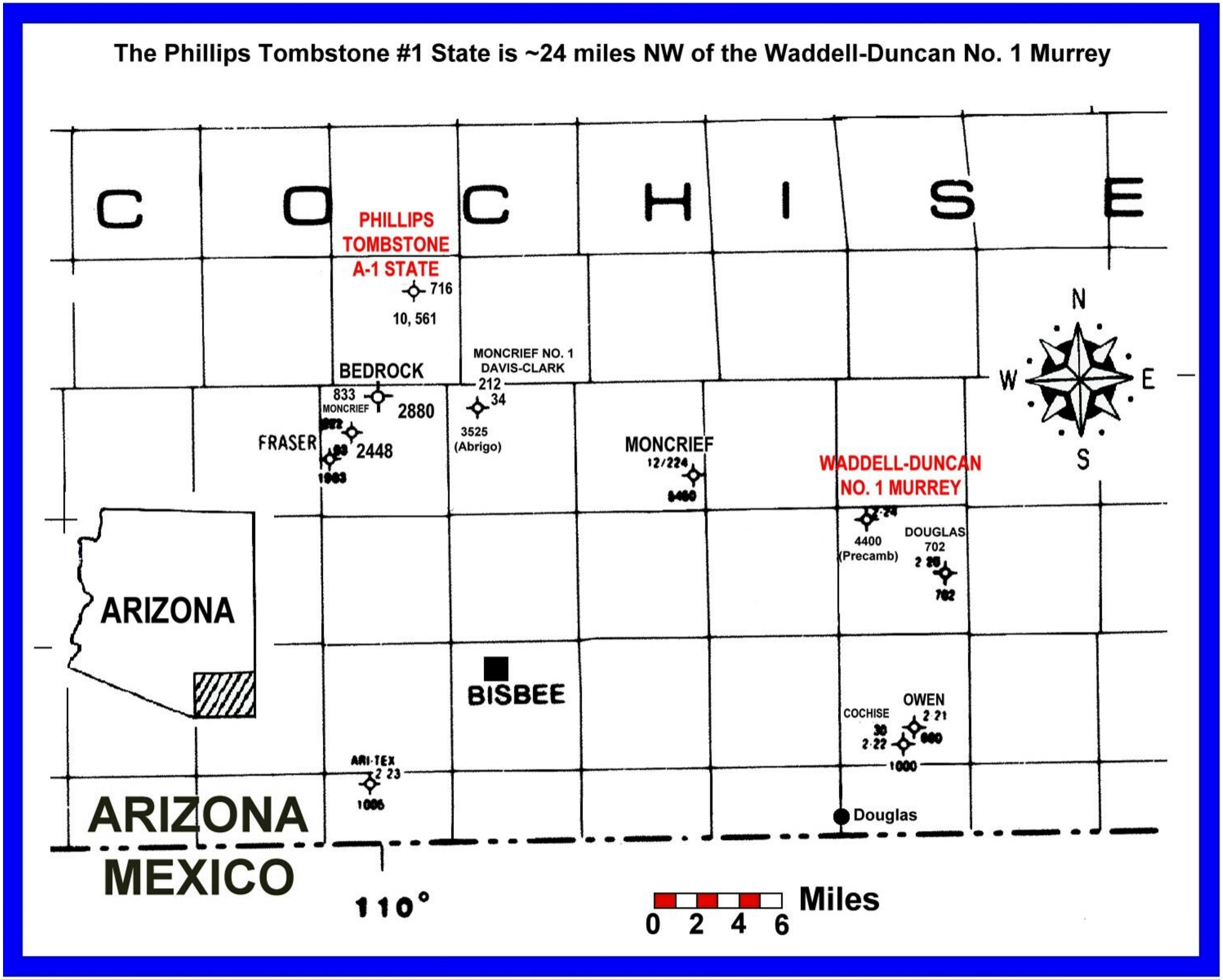

Figure 1. Location map of the Waddell-Duncan No. 1 Murrey and Phillips Tombstone No. 1 State wells, Cochise County, Arizona.

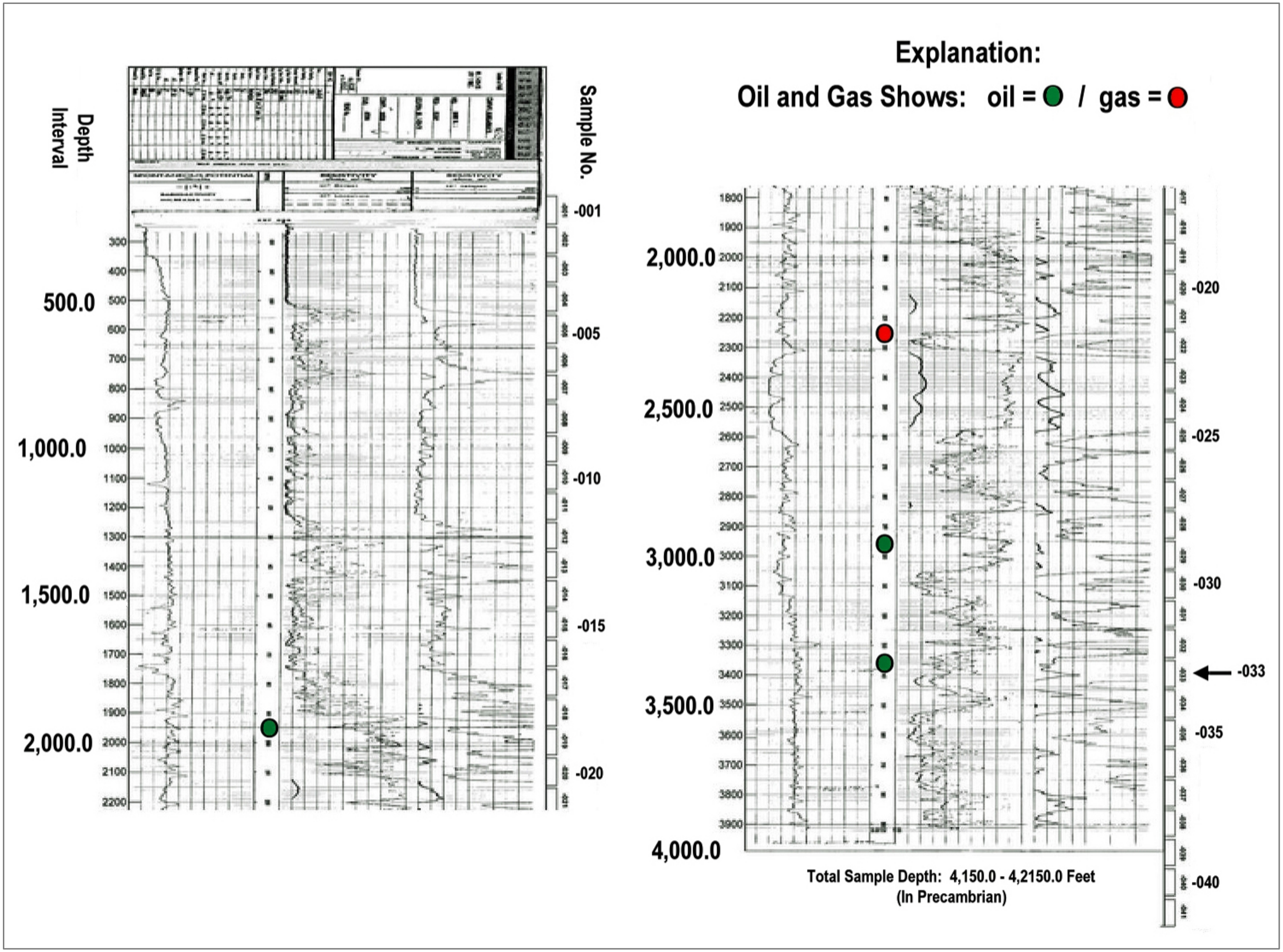

Figure 2. Electric log of the Waddell-Duncan No. 1 Murrey, Cochise County, Arizona, Section 5, T22S, R27E (courtesy of the Oil and Gas Conservation Commission of Arizona).

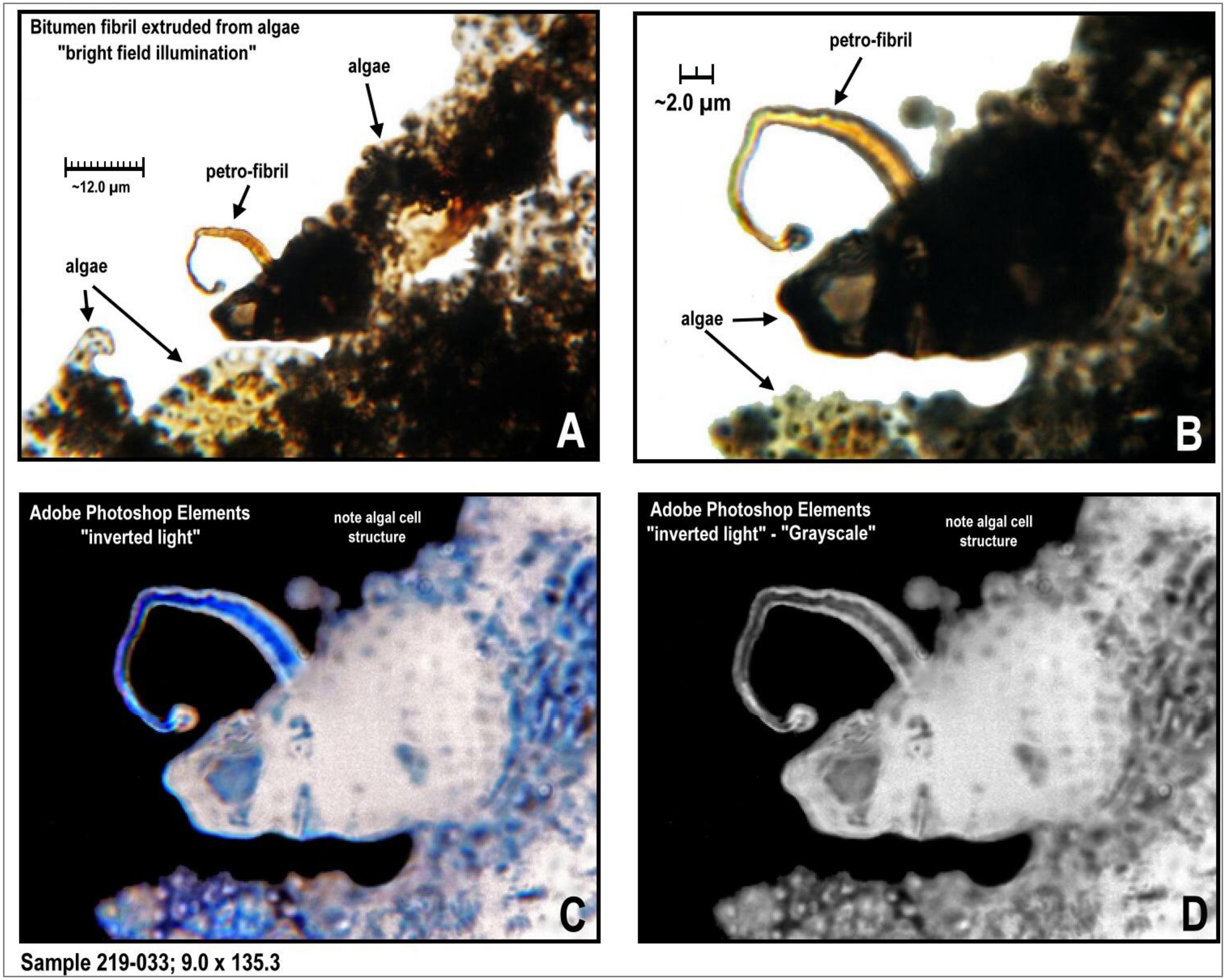

Figure 3. Waddell-Duncan No. 1 Murrey, Cochise County, Arizona, 3350-3440 feet. Photomicrographs illustrate a petro-fibril that has developed from the surface of algal debris.

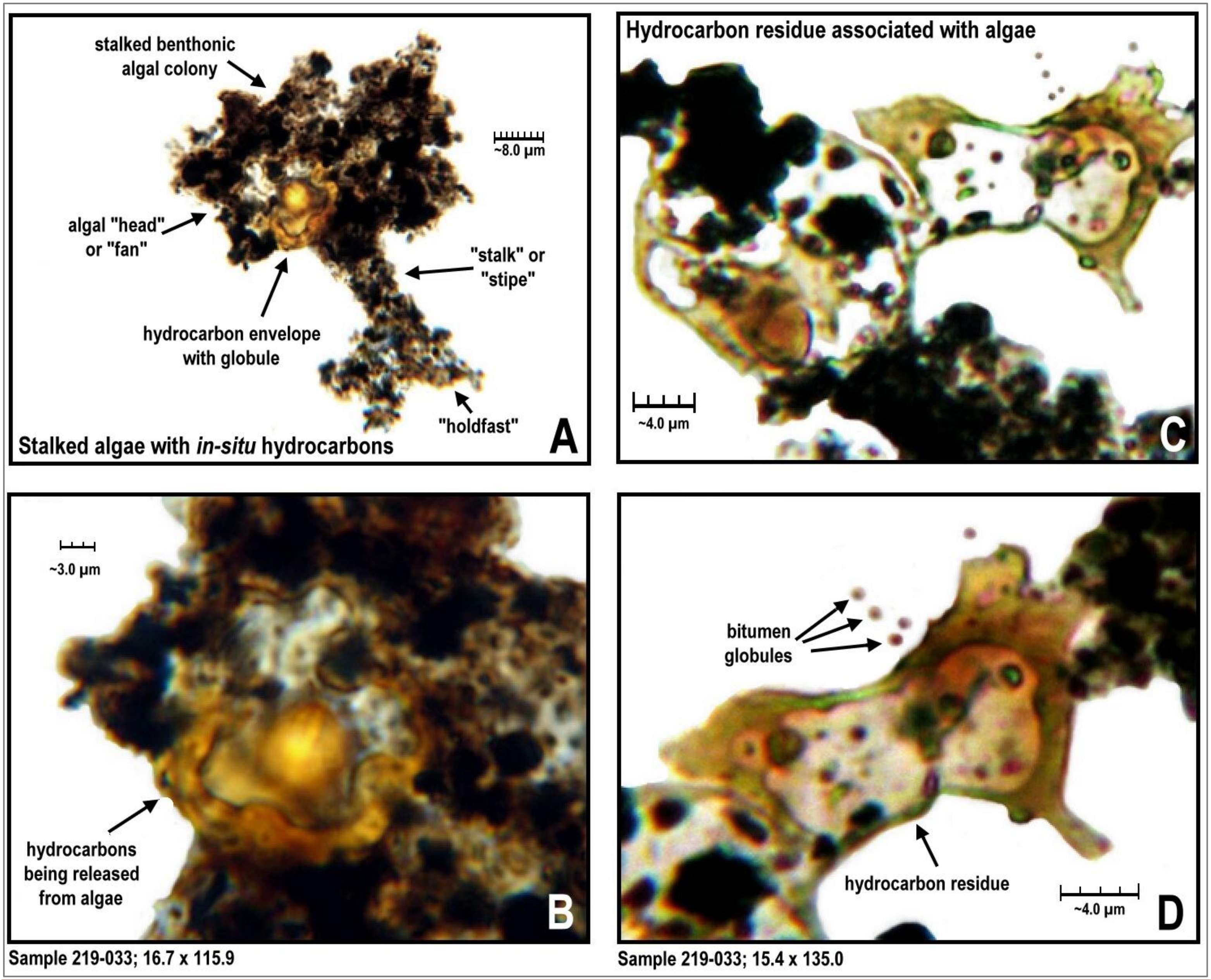

Figure 4. Waddell-Duncan No. 1 Murrey, Cochise County, Arizona, 3350-3440 feet. Photomicrographs A-B illustrate a stalked algal colony with hydrocarbons being released from lipid-rich cellular material. Photomicrographs C-D illustrate liquid-like globular hydrocarbon residue that is common on the organic-matter slide.

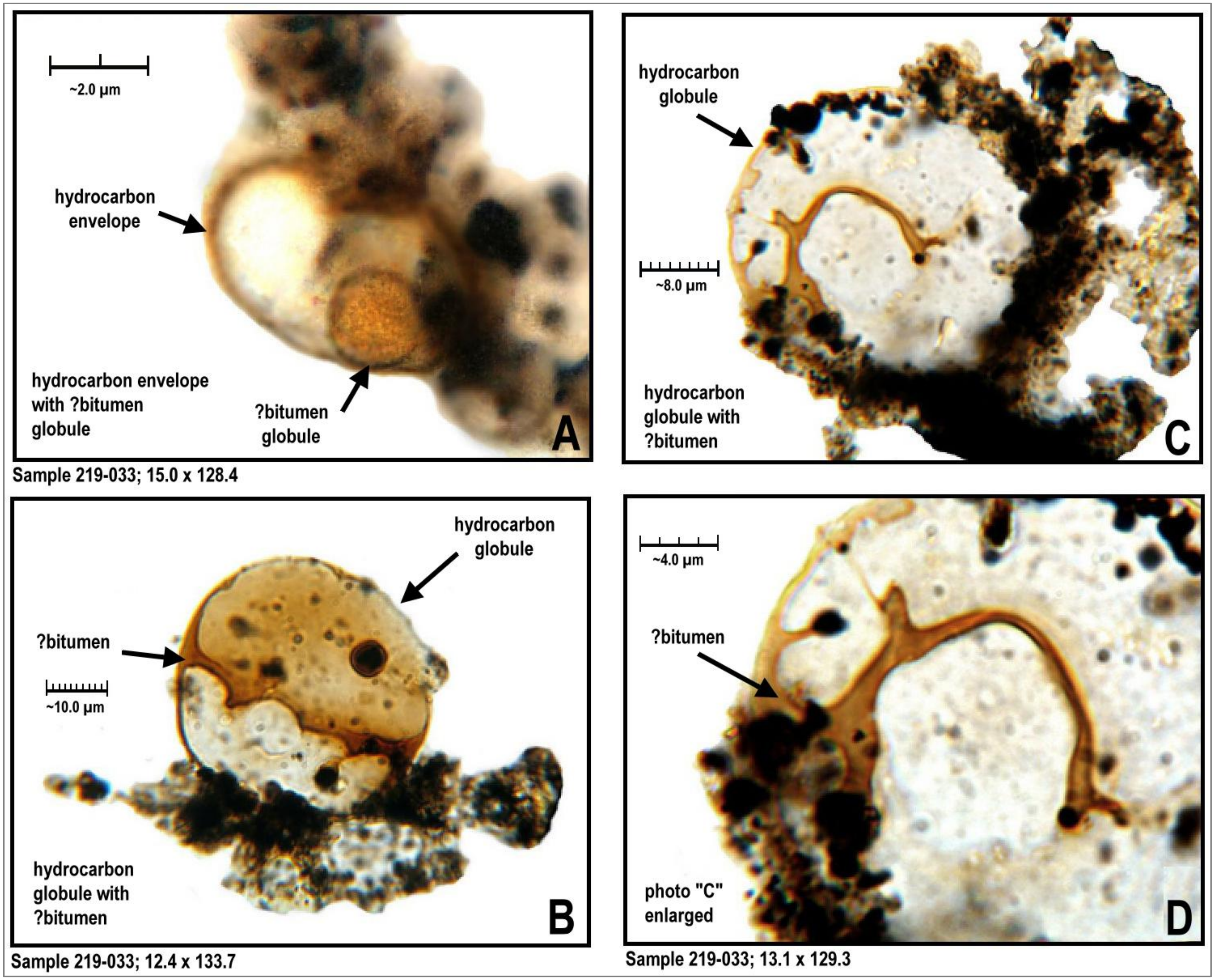

Figure 5. Waddell-Duncan No. 1 Murrey, Cochise County, Arizona, 3350- 3440 feet. Photomicrographs A-B illustrate various types of globular hydrocarbon residue. Photomicrographs C-D show a hydrocarbon bubble with hydrocarbon residue coating the surface of the bubble.

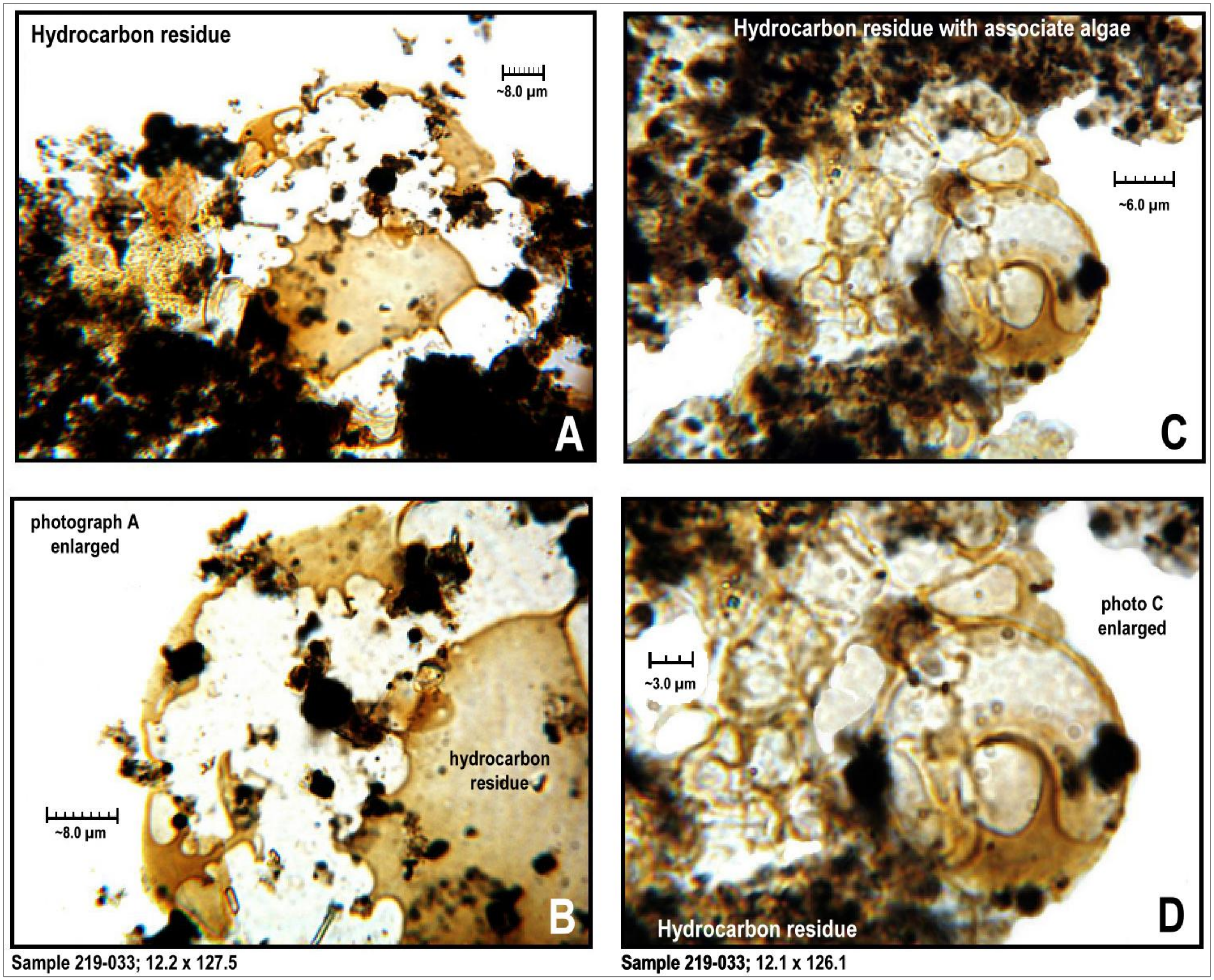

Figure 6. Waddell-Duncan No. 1 Murrey, Cochise County, Arizona, 3350-3440 feet. Photomicrographs A-B illustrate fragmented pieces of hydrocarbon residue, whereas photomicrographs C-D are examples of a bubble of liquid-like hydrocarbon residue.

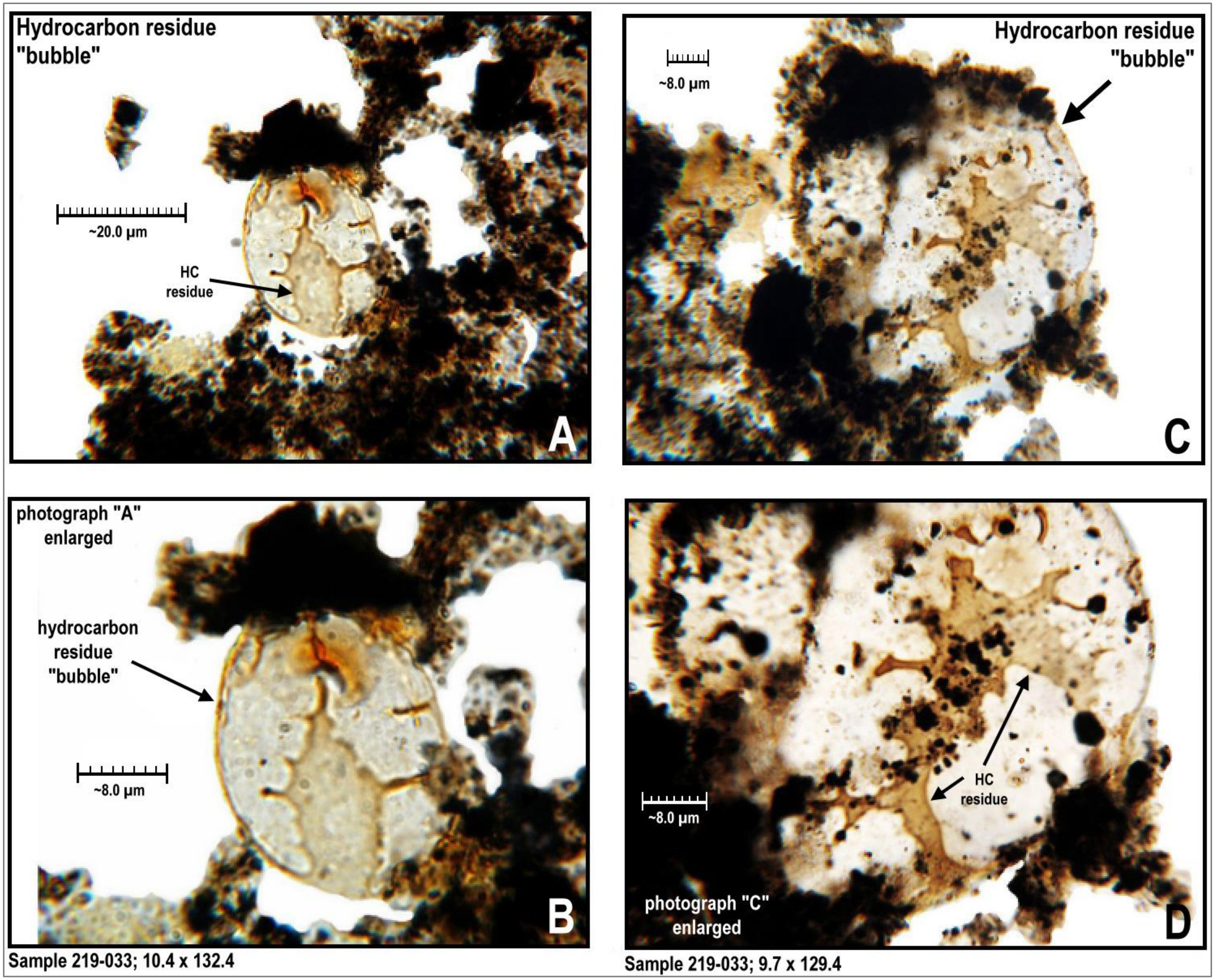

Figure 7. Waddell-Duncan No. 1 Murrey, Cochise County, Arizona, 3350-3440 feet. Photomicrographs A-D illustrate bubble-like forms of hydrocarbon residue covered with scaly, shard-like pieces of dark-colored hydrocarbon residue.

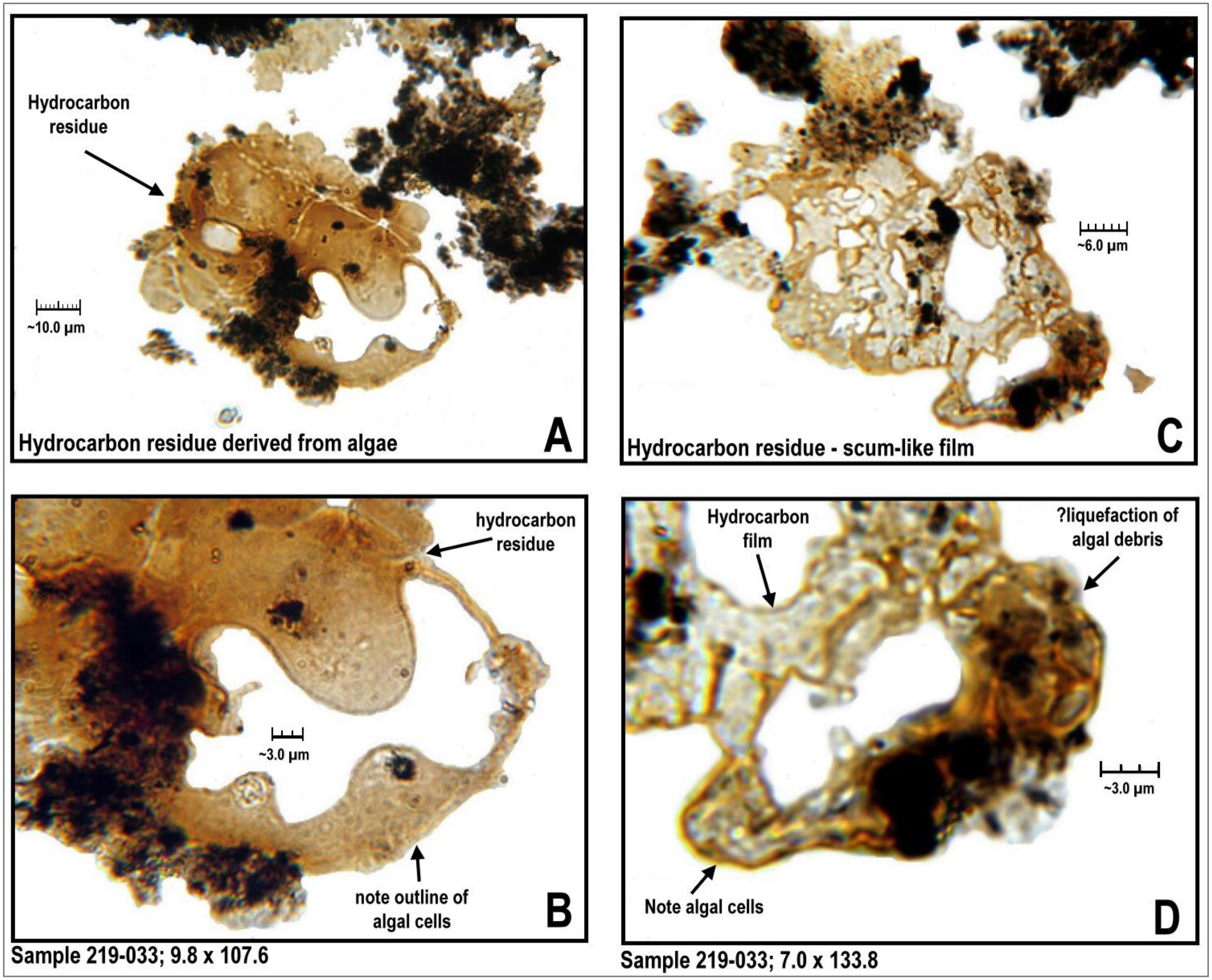

Figure 8. Waddell-Duncan No. 1 Murrey, Cochise County, Arizona, 3350-3440 feet. Photomicrographs A-D illustrate liquid-like accumulations of hydrocarbon residue having been generated from algal debris. Remnants of algal cells are clearly visible within the scum.

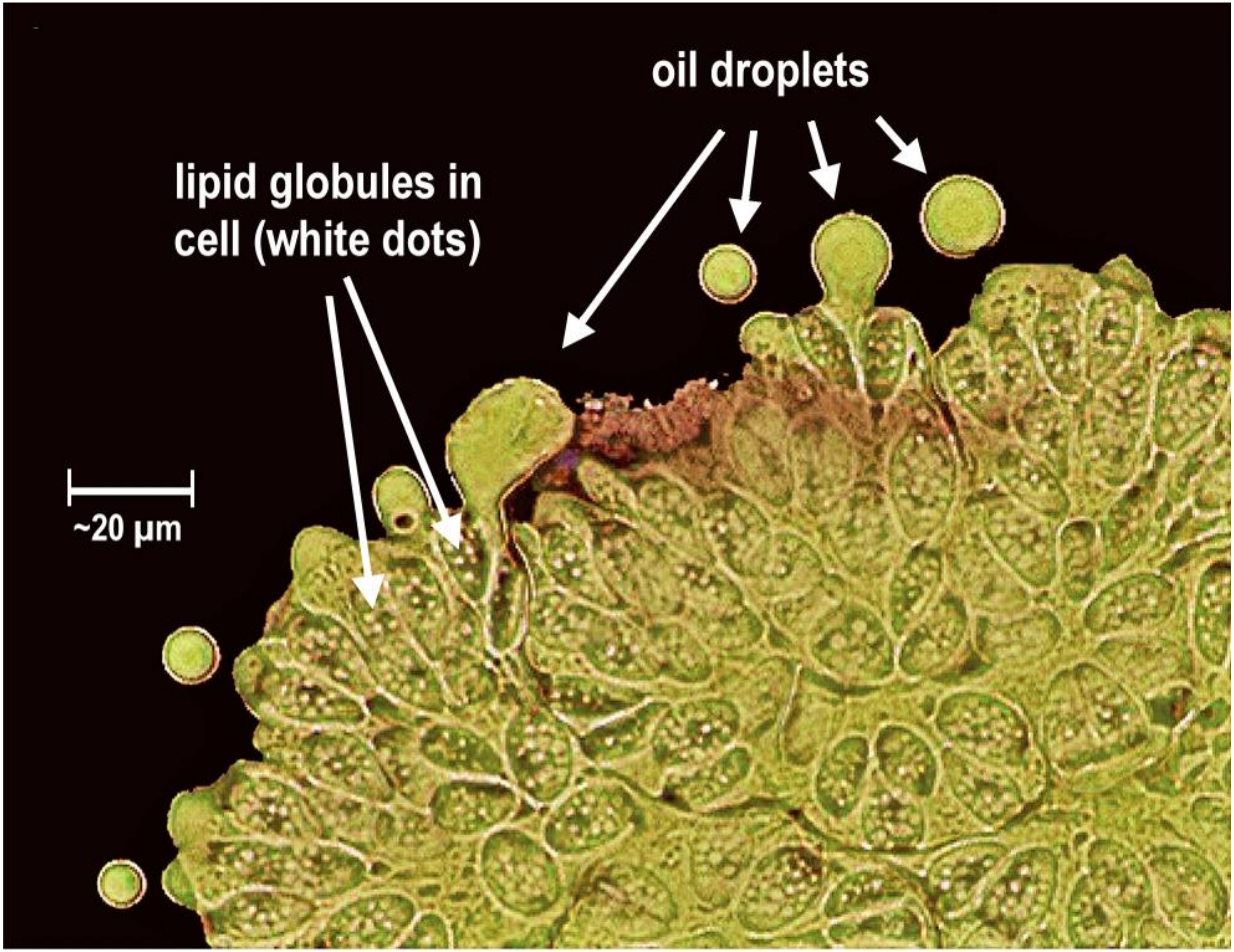

Figure 9. Photomicrograph of *Botryococcus braunii* by Dr. John Kinross, The Algan Web (http://www.algalweb.net) and used with his permission.

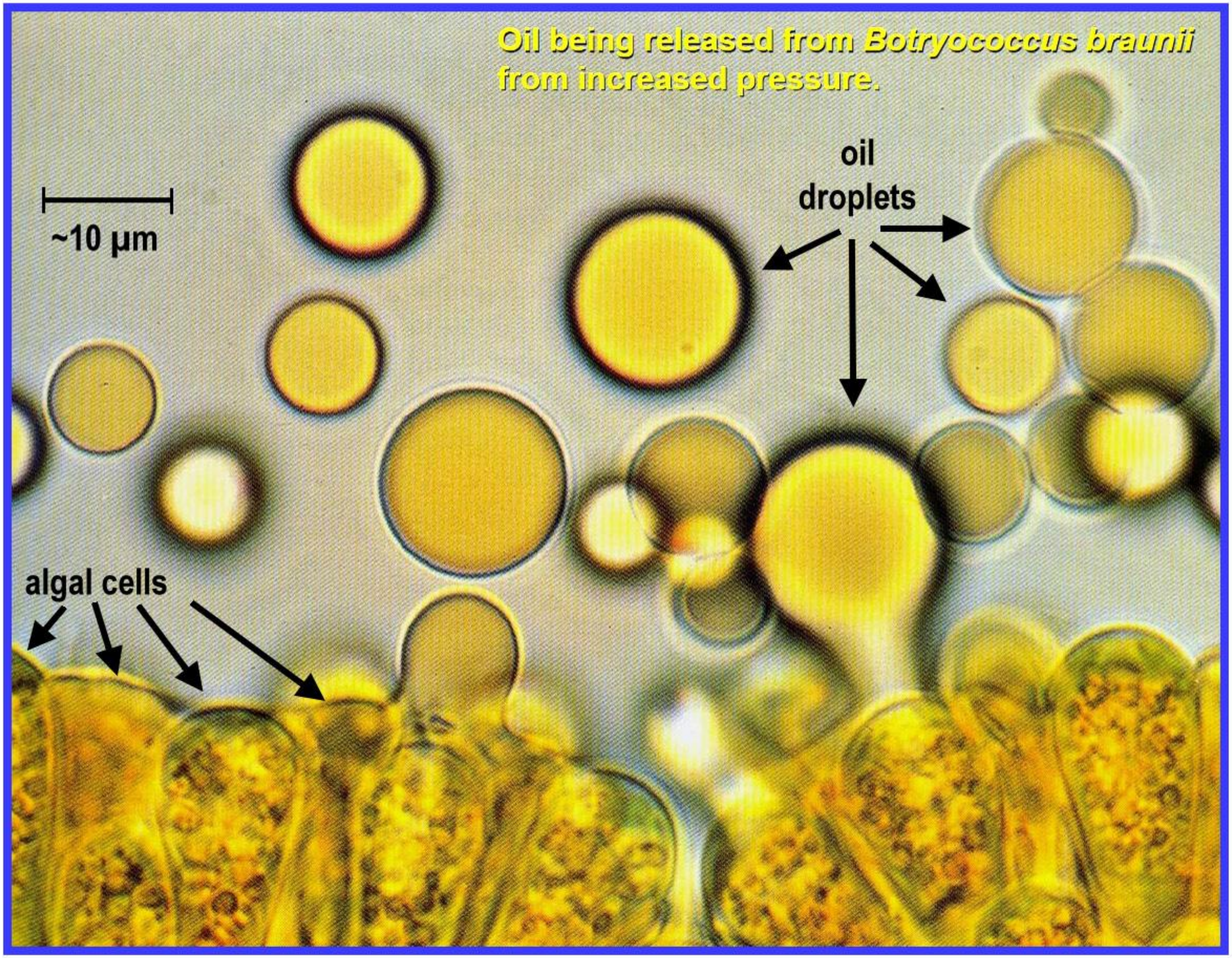

Figure 10. Enlarged view of the cells of *Botryococcus braunii*. Note the droplets of oil being generated from within the cells and along the cell walls. "H.M. Canter-Lund, photograph reproduced by permission of the Freshwater Biological Association," Cumbria, U.K.

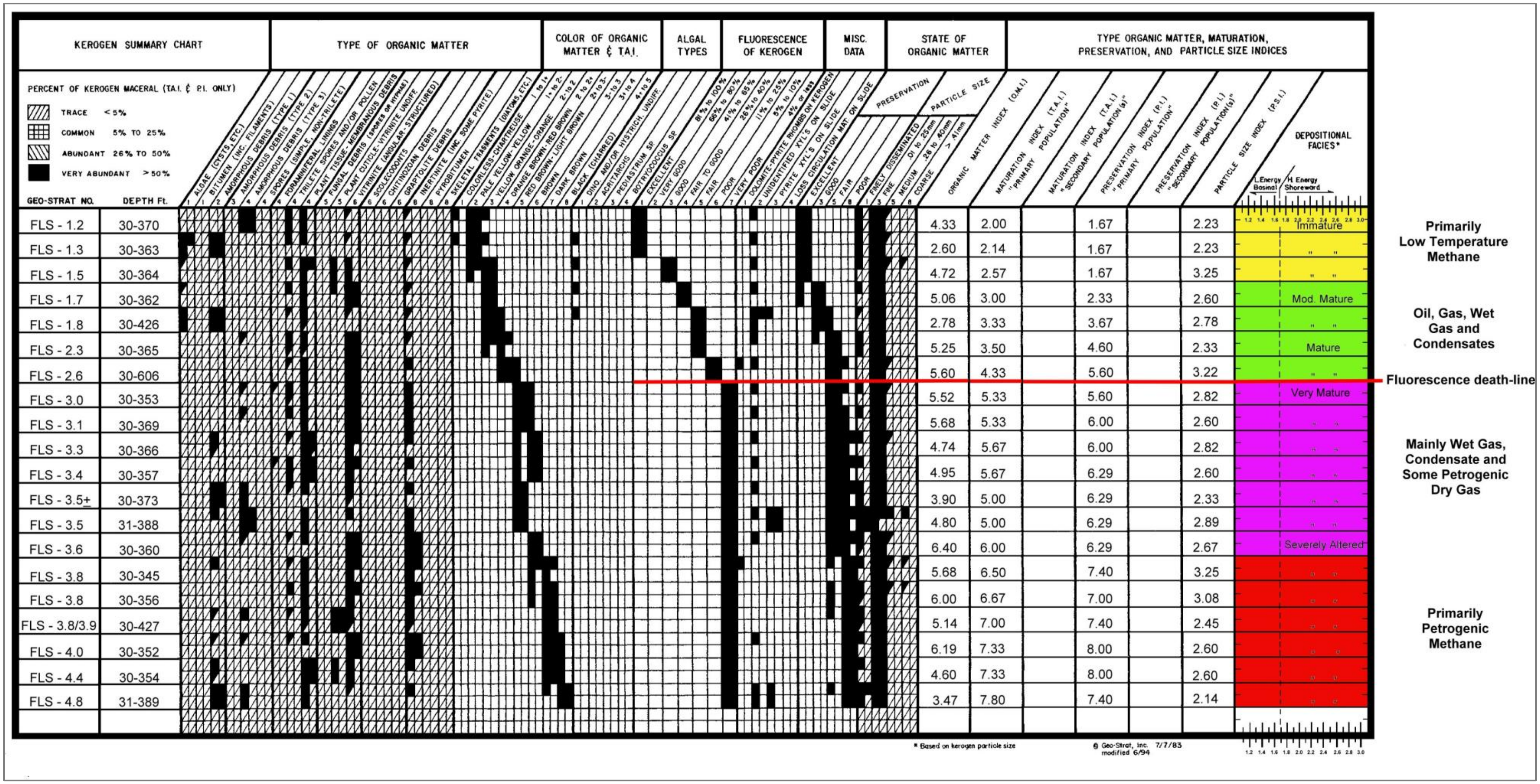

Figure 11. Interpretation of Staplin's original Thermal Alteration (TAI) standards (1969) by K.W. Schwab, Geo-Strat, Inc., July, 1983.

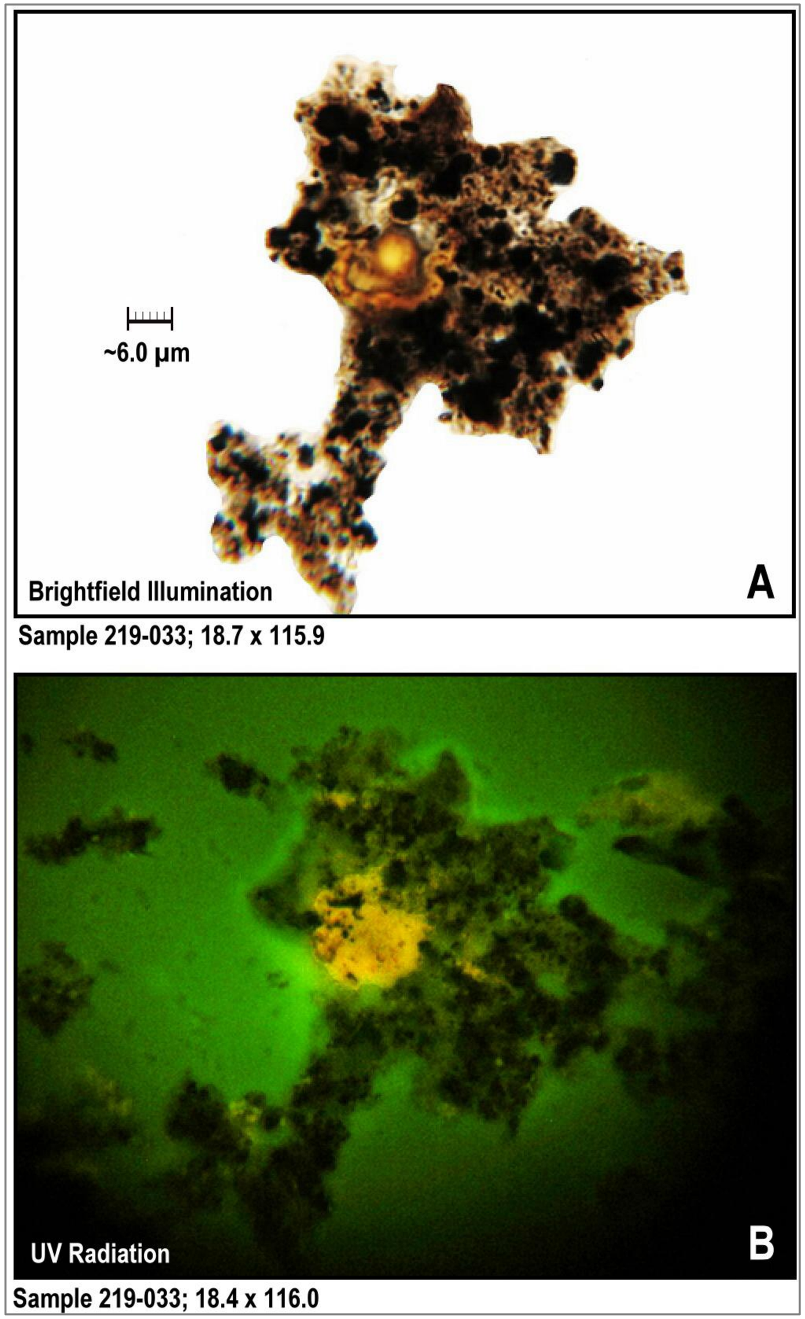

Figure 12. Waddell-Duncan No. 1 Murrey, Cochise County, Arizona, 3350-3440 feet. Same photomicrograph as shown in Figure 4A, but here illustrated in brightfield illumination and fluorescence (Blue-Light Irradiation). Note the fluorescence of the lipid-rich hydrocarbon residue that has been generated within the central portion of the algal colony.

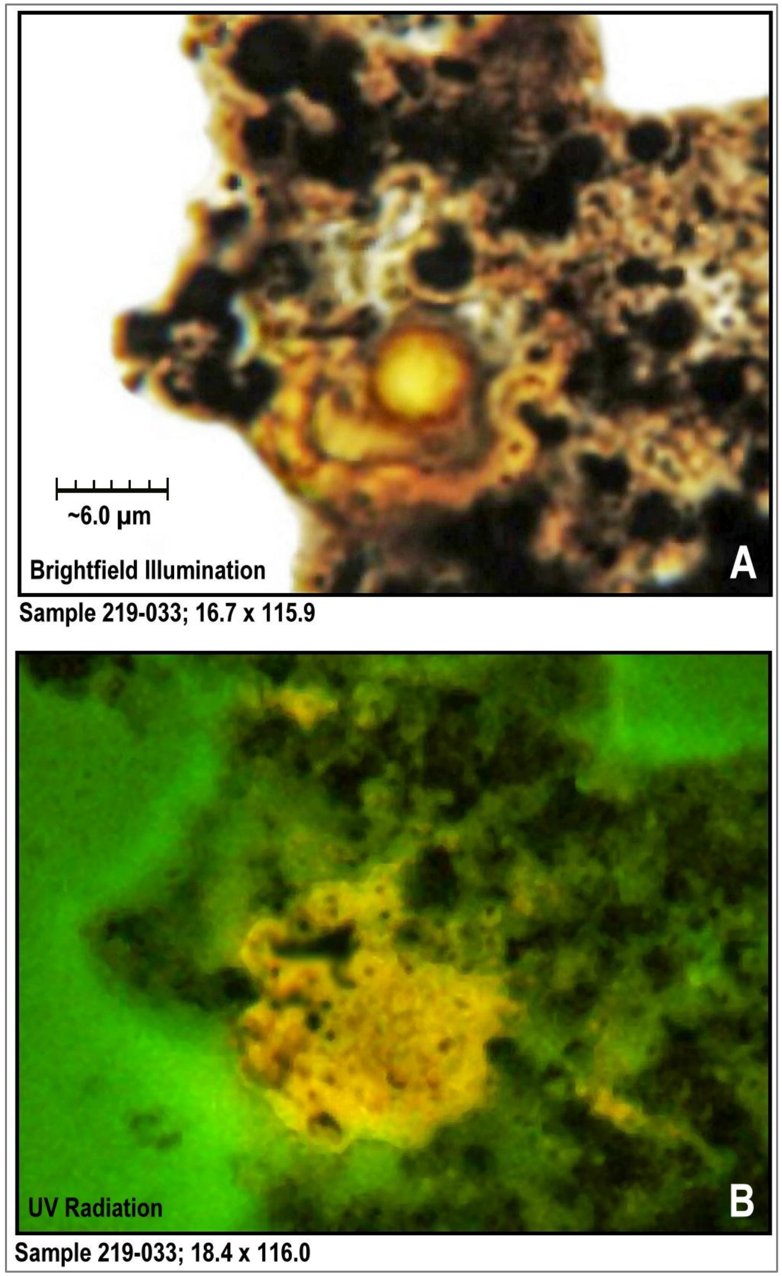

Figure 13. Waddell-Duncan No. 1 Murrey, Cochise County, Arizona, 3350-3440 feet. Photomicrographs of the algal colony shown in Figure 4B, enlarged to show the cellular detail. Note the bright, yellow-orange fluorescence of the lipid-rich material. We interpret this to be the source of the liquid hydrocarbons that are being squeezed-out of the cells.

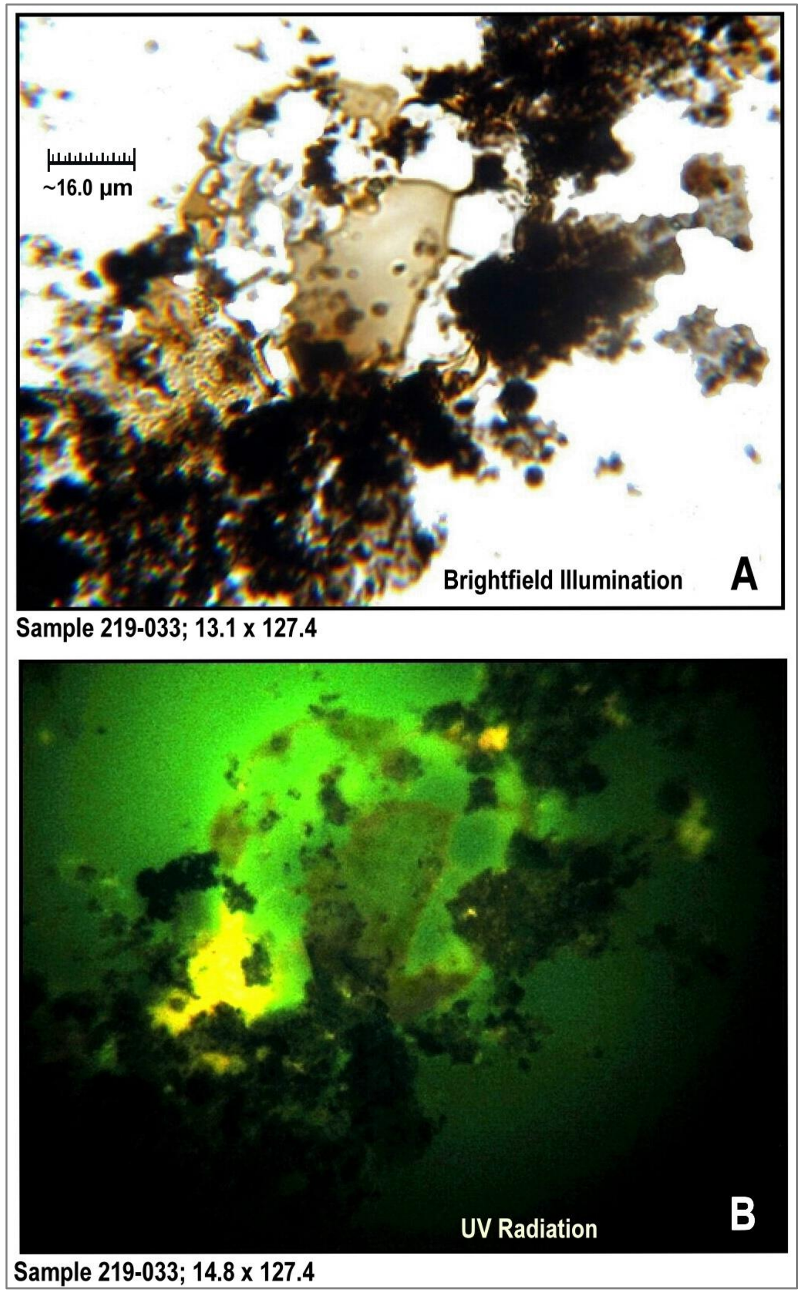

Figure 14. Waddell-Duncan No. 1 Murrey, Cochise County, Arizona, 3350-3440 feet. Same photomicrograph shown in Figure 6A-B but here in brightfield illumination and fluorescence (blue-light irradiation). Note the orange-brown color of the hydrocarbon residue in Photomicrograph B.

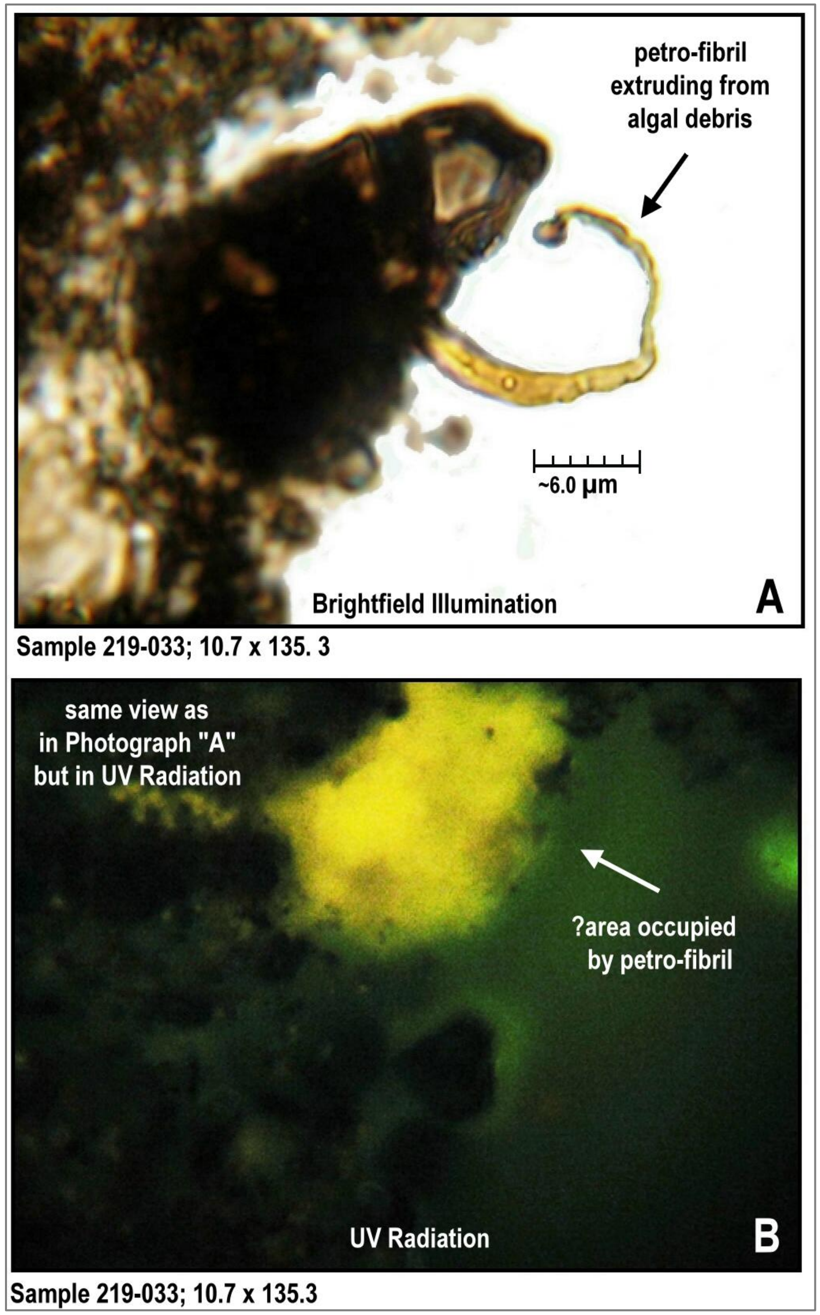

Figure 15. Waddell-Duncan No. 1 Murrey, Cochise County, Arizona, 3350-3440 feet. Same photomicrograph of the petro-fibril shown in Figure 3A-D but here illustrated in brightfield illumination and fluorescence (blue-light irradiation).