

HIGH RESOLUTION TRANSMISSION ELECTRON MICROSCOPY (TEM)  
IN THE STUDY OF OIL SHALES

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Abstract

In the broadest terms, the TEM work reported here has greatly extended knowledge and understanding of the nature and origin of the organic matter in oil shales. The study has shown the limitations which exist when light microscopy alone is used to assess the nature and properties of organic matter. Much important information is available only at the resolutions possible with transmission electron microscopy.

The nature and, in many cases, the source of the vitrinite-like (bituminite) organic matter have been established through TEM and carbon-isotope analysis, and it is shown to consist of bacteria and their degradation products. The microbial remains may occasionally be recognised in TEM observations, which also allows them to be clearly distinguished from algal remains. The lack of fluorescing properties of the vitrinite-like organic matter can be understood, since the alteration of lipids due to biological decomposition is very extensive. Vitrinite-like organic matter of oil shales, although generally of lower reflectance than vitrinite, displays a range of reflectances depending on sources and diagenetic history.

The source of some trace elements present in high concentrations in the Rundle-Condor and other oil shales have been established by TEM/microprobe and carbon-isotope analysis, and it is shown that these have been leached and mobilised from the hinterland by humic acids, and transported into the depositional basin. Humic acids are clearly distinguishable from other organic components in TEM.

## Methods of Study:

Light microscopy has been carried out on polished rock surfaces with the aim of observing relationships between the organic matter and the mineral matrix. Ultraviolet (UV) mode with blue filter excitation was also applied. Whole rock fragments were examined by scanning electron microscopy (SEM). Transmission electron microscopy (TEM) observations were made on ultra-thin sections of organic matter concentrates. After demineralisation of the samples by HCl and HF, the organic matter concentrates were embedded in polyester resin and sectioned on an ultramicrotome to a thickness of 0.03 to 0.05  $\mu\text{m}$ . Sections were then lifted on to formvar-coated copper grids for observation in a JEOL 100 C, H500 and Zeiss 109 electron microscopes. Humic acids were extracted by sodium hydroxide treatment and acid precipitation. The dry humic acids were then embedded in polyester resin, ultra-thin sections prepared and observed in TEM. Lead citrate and colloidal iron stains were used on duplicate sections for comparative observations.

The carbon isotopic composition of the organic matter was determined by the method of Kaplan et al., (1970).  $\text{CO}_2$  from calcium carbonate samples was collected following phosphoric acid treatment. Isotope ratios were determined on a Micromass 602D mass spectrometer. In selected samples, humic acids were analysed separately.

Major elements analysis of C,H,O,N and S was carried out on organic matter concentrates. Yeh's (1963) method was used for C and H determinations, while O,N and S were analysed on a Carlo Erba model 1106 elemental analyser.

## Results and Discussion

### 1. Toolebuc oil shales

Oil shales of the Early Cretaceous Toolebuc Formation in the Eromanga Basin, Queensland, consist of irregularly spaced calcareous and organic-rich laminae suggestive of cyanobacterial mats. Observations of the predominant organic matter in reflected light microscopy reveal it to be

of low reflectance ( $R_0 = 0.1-0.3\%$ ) with a vitrinite-like nature. Vitrinite reflectance is about 0.5%. The low maturity of the Toolebuc Formation is also confirmed by the relatively high H/C vs O/C atomic ratios.

TEM observations of ultra-thin sections of organic matter concentrates revealed, for the most part, organic matter of low electron density (i.e. light grey appearance), where occasionally filamentous structure could be distinguished particularly when enhanced by metal staining. Light microscopy combined with TEM have shown that unaltered algae (chlorophytes), chrysophytes) in sediments are represented by highly fluorescing organic matter in UV light (blue filter excitation), i.e. Botryococcus, Pediastrum and dinoflagellates. On the other hand, bacterial remains (including cyanobacteria), their degradation products and metabolites do not exhibit fluorescing properties. The vitrinite-like organic matter predominant in Toolebuc Formation oil shales does not fluoresce. When viewed as dispersed matter in transmitted light it appears amorphous, which is characteristic of degraded organic matter. Framboids of pyrite within the organic matter are common. Pyrite also appears as specks disseminated throughout the organic matter in association with humic acids. The humic acid content is small and usually less than 1%. Following alkali separation from remaining organic matter, embedding, ultra-thin sectioning and observing in TEM, the humates display the form of very small spheres or globules, usually in aggregates. These structures are seen to be irregularly dispersed in small concentrations throughout the rest of the organic matter. Most Toolebuc Formation samples studied in TEM, with one exception, have revealed an irregular mode of humic acid distribution, in small clusters throughout the rest of the vitrinite-like organic matter. However one sample showed a higher concentration of humic matter and filling of vacant spaces within the remaining organic matrix, rather than irregular distribution. The irregularly dispersed humic acids throughout the remaining organic matter in Toolebuc Formation oil shales, suggest a local source for their formation. The in situ formation of the humic acid/alkali-soluble fraction in these samples is supported by C-isotope studies. Electron

dense particles were occasionally associated with the humic fraction. These, when analysed by electron probe proved to contain pyrite. Another metal detected was copper in electron dense coccoid bacterial forms. The predominant light grey (low electron density) organic matter displayed a loosely packed, almost sponge-like appearance. Filamentous organisms were recognised in several instances. Single filaments are rarely distinguishable, since the organisms mostly merge into a mass of loosely compacted matter. Most filaments do not exhibit any internal structure, although occasionally cross walls can be recognised. The filaments are non-branching and show a straight or curved character. Individual filaments are about  $0.25\ \mu\text{m}$  wide and  $1-2\ \mu\text{m}$  long. On one occasion a bundle of smaller filaments was observed possibly belonging to another type of organism, the disintegration of which is clearly visible. Filamentous structure may be enhanced by metal staining. Lead citrate stain used in the present study is responsible for the coarse granular precipitate. Glycogen granules, which are found in cyanobacteria as well as in other microbial organisms, have a special affinity for lead.

Among the filamentous structures, two main types can be recognised, namely individual relatively large and thick filaments ( $0.5\ \mu\text{m}$  wide, up to  $5\ \mu\text{m}$  long) and smaller filaments (less than  $0.2\ \mu\text{m}$  wide, less than  $2\ \mu\text{m}$  long) usually appearing in bundles. The former type are compressed into a more or less homogeneous substance where borderlines of filaments are no longer discernible without staining. It is therefore likely that a significant part of the vitrinite-like organic matter, where no structure is visible in TEM, has been derived from compressed cyanobacteria and possibly sulphate-reducing bacteria. Compression or homogenisation of individual filaments may occur due to both dewatering and probably also the breakdown of a major part of cell walls.

On occasions calcareous outlines or replicas of micro organisms closely resembling cyanobacteria of Oscillatoria type were also observed in SEM examination of whole rock samples.

Other microbial remains are rare. However, occasionally clumps of a stalked organism resembling Caulobacter were encountered. This organism forms rosettes which in turn aggregate into clumps of up to 2 $\mu$ m across. The stalked organism appears in association with a highly electron dense coccoid form. An organism resembling the living form Flectobacillus marinus was observed occasionally. The micro organism appears in chains or clusters, individual forms being of a doughnut shape with one convex side, as is characteristic of the living form. The Flectobacillus-like organism and the electron dense coccoid forms may have been part of the aerobic microbial assemblage responsible for degradation of primary organic matter while in the oxygenated water column. It is noteworthy that the above mentioned microbial remains were only observed in isolated cases, and do not compose a significant portion of the organic matter. The latter is dominated by filamentous or loosely compacted cryptogranular organic matter of low electron density.

## 2. Cambrian Camooweal oil shales

TEM observations of the Camooweal oil shales have led to an understanding of the origin of the main types of organic contributors to the deposit. Vitrinite-like organic matter displaying varied reflectances (0.3-0.6Rm) could be recognised from polished rock surfaces of this Cambrian oil shale. However, only TEM is capable of indicating that the component of higher reflectance consists of humic acids. The other predominant organic component of an extremely low reflectance (0.09-0.1%Rm) displayed filamentous structure, possibly of cyanobacterial origin. Carbon-isotope compositions supported two sources for the organic matter in the Cambrian oil shales and also for some other Lower Palaeozoic black shales.

## 3. Oil shales of the Rundle complex

The Tertiary fresh water deposits of the Rundle complex in Queensland, appear to be those most likely to be worked commercially in Australia. These deposits extend over an area of about 1600x200 km in sub-surface basins along the central coast of Queensland. They include

the Rundle, Stuart, Condor, Nagoorin, Lowmead and Yaamba deposits. The oil shale sequence has been deposited in a number of grabens east of the Great Dividing Range, in what may have resembled the present day Great Lakes system in the East African Rift Valley. As these Tertiary deposits are all part of the same geologic event and depositional environment they will be referred to in the present study as the Rundle Complex regardless of local variations within each sub-deposit.

The organic matter of the Condor and Rundle oil shales, is of a predominantly algal nature unlike the microbial remains and degradation products in the Toolebuc shales and is therefore high in aliphatic compounds with H/C = 1.7. In TEM observations of ultra-thin sections of the organic matter concentrate, two categories of organic matter can be distinguished: (1) the predominant algal lipidic matter; and (2) humic acids filling in spaces between algal accumulations.

Humic acids may constitute up to 30% of the total organic matter in these oil shales and are characterised by a large number of electron dense particles. Electron probe analysis of these particles showed Ti as the metal responsible for the electron density. Concentrations of up to 0.6% Ti have been found in trace-element analysis of the Rundle oil shales. TEM observations indicate that most of the Ti is concentrated and contained within the humic acid fraction. The volcanics associated with the Rundle-Condor oil shale deposits must have acted as source for the large quantities of Ti. It is evident from studies conducted on the interaction of humates with phytoplankton and humates with metals, that the latter are mobilised and carried by humic acids. When the amount of metal exceeds the carrying capacity of the humic acids it is precipitated together with the carrier humic acids. C-isotope compositions of the phytoplankton remains show typical values of  $\delta^{13}\text{C} = 21.2$  and  $-22.2\text{ppt}$  in Rundle and Condor, respectively. The humic acid fraction separated and analysed isotopically yielded values of  $-26.7\text{ppt}$ , which is typical for soil humates. Therefore it is reasonable to assume a terrigenous source for the high humic acid content of these deposits. The allochthonous origin of the Rundle-Condor humates may also be deduced from TEM observations, whereby the humic acids can be seen as filling in spaces

between algal matter and never being part of the predominant algal lipidic matter. This phenomenon is in contrast to observations in oil shales of the Toolebuc Formation. In the latter, the minute humic acid fraction is irregularly dispersed throughout the rest of the organic matter. These TEM observations are supported by C-isotope compositions of same or very close values obtained for the humic and non-humic acid fractions. The humic acids in the Toolebuc Formation are therefore considered to be in-situ formed marine humates.

#### 4. Green River oil shale

In light microscopy, using UV light/blue filter excitation, the predominant organic matter in the Green River samples exhibits bright yellow fluorescence, while some organic matter displays orange-brown fluorescence. Both types display amorphous nature in transmitted light. TEM observations have shown the organic matter to have the characteristics of algal components, probably Botryococcus. Humic acids associated with electron dense particles were seen to fill-in cavities within the predominant organic matter. The mode of appearance of this organic matter, however, is unusual in being interconnected, as though part of one continuous mass. Flow lines are obvious where electron dense particles have been carried through the organic matrix. Brines percolating through these deposits may have brought about certain chemical alterations which obliterated any structures of the precursor organisms through a homogenisation process such as severe alkaline hydrolysis. Carbon-isotope compositions support an allochthonous source for some of the humic acids. The electron dense particles associated with this fraction as well as those dotted throughout the lipidic matter proved to be an association of Cr-Ti-Fe, and may have been brought into the depositional basin with the humates. This is supported by trace element analysis of Green River oil shale which showed a very high Cr content.

Further indirect evidence for algae as precursors of the Green River oil shale are the very high H/C ratios which plot within the field of Type I kerogen, as do the torbanites and Rundle oil shales. It is clear from this study that biodegraded organic matter and cyanobacterial remains tend

to produce lower H/C ratios than non-degraded Botryococcus or Pediastrum accumulations.

### Summary and Conclusions

TEM studies of the different oil shales have shown that non-degraded, algal remains do not adsorb lead citrate metal stain as readily as degraded organic matter, namely bacterial metabolites and bacterial remains. Algal remains exhibit a homogeneous and more or less compact nature whereas the vitrinite-like matter is heterogeneous in TEM displaying an aggregate nature. Filaments of micro organisms attributable to bacteria are often discernible throughout this type of organic matter.

Humic acids in general cannot be recognised as a separate entity in light microscopy, but are clearly distinguishable from other organic components in TEM. Examination of the alkali-soluble fraction revealed an ultra structure consisting of minute globules which form aggregates. The allochthonous or autochthonous source of humic acids is consistent with their mode of distribution within the rest of the organic matrix. It was observed that when humates were irregularly distributed throughout the rest of the organic matter in isolated globules or small aggregates, their in situ origin is evident from carbon-isotope analysis. However, when humic acids were observed by TEM to form large accumulations within empty spaces in the organic matrix, or to be present in massive concentrations between algal remains, such as displayed in the Rundle-Condor oil shales, carbon-isotope compositions point to a terrigenous allochthonous source. In the Lower Palaeozoic Camooweal oil shales, the humic acids have also proved to be of a different source from the rest of the organic matter, possibly derived from another part of the water column. An external source for the Green River humates is also evident from TEM observations as well as carbon-isotope analysis.



Electron density is a function of the mass number and therefore the lipid-rich or lipid-poor nature of the organic matter will be reflected in TEM observations, and a direct correlation exists between electron transparent material and high H/C ratios and between electron dense material and low H/C. Very high electron dense particles are metal accumulations or concentrations.

TEM of spent shale has shown that most trace elements and pyrite are concentrated and adsorbed in the humic residue. Some lipidic material is seen to be adsorbed on to clay particles, thus explaining the loss of some heavy oil fraction from the retorted product.