Reflected-light microscopy of uraniferous bitumens

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Abstract

Uraniferous bitumens from Great Britain, Scandinavia and South Africa have been studied by oil-immersion reflected-light microscopy and categorised into those formed either by replacement of pre-existing uraninite and pitchblende or by complexation/reduction mechanisms in pre-existing hydrocarbons. The former are characterised by displaying normal replacive textures, and containing high concentrations of non-mineral-bound uranium, or later, occasionally exotic, uraniferous fracture-filling phases. Uraniferous bitumens formed during complexation/reduction reactions display monotonous mineralogies and ordered mineral-inclusion distributions.

Radiolytic alteration of uraniferous bitumens induces both chemical and mechanical alteration. Early alteration is marked by the generation of mobile hydrocarbons during 'cracking reactions' with subsequent within-sample migration to form globular bitumens and dendritic interspersions of mineral-rich and -poor uraniferous bitumen. Mobile hydrocarbons may act as lubricants during mechanical deformation. Advanced organic alteration is characterised by well-documented increased reflectance around uraniferous grains, and by fracturing of the bitumens.

KEYWORDS: bitumens, uranium, reflected-light microscopy, hydrocarbons.

Introduction

THE intimate association of uranium with organic matter has been known since the last century (see Dons, 1956, and Welin, 1966, for reviews). The close association arises both from the ability of mobile hydrocarbons to replace pre-existing uranium minerals (Dubinchuk et al., 1977) and the oxygen-bearing ligands in organic matter to form soluble U^{6+} complexes (Nash et al., 1981). The latter process may account for occurrences of uranium-enriched peat, lignite, coal, humate, bitumen, coalified wood and kerogen, and can participate in the genesis of economically viable uranium deposits (e.g. the Lodève deposit in France and sandstone–hosted tabular uranium deposits of the U.S.A.).

One problem encountered in studying uraniferous bitumens is their reduced solubility in common organic solvents, and hence inaccessibility to gas chromatographic–mass spectrometric studies. Prolonged irradiation of bitumens tends to result in dehydrogenation and aromatisation, with loss of more informative 'biomarkers' (Zumberge et al., 1978; Landais et al., 1987; Eakin, 1989c) coupled with poorly understood shifts in carbon isotopic ratios (Leventhal and Threlkeld, 1978; Eakin, 1989a). Reflected-light microscopy is a standard organic petrographic technique (Stach et al., 1982), and can yield information on sources of geological organic matter, thermal maturity, and the influences of processes such as stress, oxidation and radiation.

Despite their widespread geological occurrence and importance in a large number of economic uranium deposits, little effort has been made to relate the fabrics observed in uraniferous bitumens to a common mode of genesis or pathway of post-formational alteration. We report here on several features common to many of our own samples and those documented by other authors.

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The samples studied are associated with (i) lead–zinc–copper sulphide mineralisation in northeast Wales, the Isle of Man, and southern Scotland, U.K., (ii) base metal (especially iron) mineralisation and granitoid pegmatites in the Scandinavian Precambrian basement, and (iii) Precambrian quartz pebble conglomerates, forming the 'Carbon Leader' seams of the Witwatersrand region, South Africa. The geological occurrences of the samples are summarised in Table 1, and detailed descriptions of each of these occurrences are available elsewhere (Eakin, 1989a).

The results are interpreted as representing textures developed at two stages. The first is developed during the formation of the uraniferous bitumens, and the second results from post formational radiation-induced alteration.

Previous work

Several petrographic features of uraniferous organic matter have been previously documented. For example, radiation is known to induce increased organic reflectance around radioactive minerals (e.g. Breger, 1974; Schidlowski, 1981; Leventhal et al., 1987), the increased reflectance being related to the size of the radioactive mineral grain (Jedwab, 1966; Eakin, 1989b). Radiation-induced ordering of organic matter has been demonstrated (Penkov, 1980; Eakin, 1989a). The presence of globular structures in uraniferous bitumens has been documented (Grip and Odman, 1944; Cortial et al., 1990), and in the latter case, interpreted as resulting from precipitation of uranium minerals around pre-existing hydrocarbon masses.

The mineralogy of several uraniferous hydrocarbon occurrences has been published (e.g. Brodin and Dymkov, 1964; Miller and Taylor, 1966; Dubinchuk et al., 1977). Few, however, have attempted detailed investigation of the paragenesis of the samples. One notable exception is the early work of Davidson and Bowie (1951) who described in detail the uraniferous bitumens from Laxey, Isle of Man, and suggested that two stages of uraninite development were

Table 1. Summary of geological occurrences of uraniferous bitumen samples

Sample locality	Occurrence	References
Great Britain		
Laxey, Isle of Man; Northeast Wales orefield (Ty Gwyn and Llandulas)	Botryoidal masses or veins in Carboniferous limestones or sub - Carboniferous basement; associated with Pb/Zn/Cu sulphide mineralisation	Davidson and Bowie, (1951); Parnell, (1988a); Eakin, (1989a).
Dalbeattie, Scotland.	Pitchblende mineralisation in sub - Carboniferous basement. Associated with minor sulphide mineralisation	Miller and Taylor, (1966).
Scandinavia		
Boliden, northern Sweden.	"Titano - thucholite" in botryoidal masses and veins in Precambrian basement - hosted sulphide deposit.	Grip and Odman, (1944)
Hiddingsta and Samsala, Orebro County, Sweden.	Basement - hosted Fe / U skarn mineralisation.	Welin, (1966) and references therein.
Naresto, southern Norway.	Hydrocarbon masses in Precambrian pegmatite	Dons, (1956); Eakin, (1989b).
South Africa		
Witwatersrand "Carbon Leader"	Seams and "fly specks" in uraniferous and auriferous Precambrian quartz - pebble conglomerates	Leibenburg, (1955); Schidlowski, (1981) and references therein.

responsible for the mineral morphologies observed. Uraninite precipitated during the main phase of base-metal mineralisation was subsequently corroded by fluid hydrocarbons. Uranium thus released to the hydrocarbons later reprecipitated as pitchblende inclusions.

Parnell (1988a) considered organised mineral fabrics in uraniferous bitumens from the northeast Wales orefield deposit to be the product of an 'exsolution' process, forming uraninite from a uranium-saturated hydrocarbon precursor. It was also suggested that spherical inclusions of minerals in hydrocarbons may result from the coprecipitation of hydrocarbons and minerals at a common site of deposition (Parnell, 1988b). Several peculiar mineral fabrics have been observed in uraniferous bitumens. For example Pierce et al. (1964) described 'capillary structures' in uraniferous hydrocarbon nodules from the Panhandle gas field, U.S.A., although no explanation of the features was attempted.

Methods

Reflected-light petrography was performed on a Zeiss UMSP 50 microscope controlled through a IBM Personal Computer, using ×40 and ×100 oil immersion lenses (R.I. of the oil = 1.5150). Precision and accuracy were better than 0.04%, based on repeated determinations of internal standards. Microprobe analyses were performed on a Jeol 733 Superprobe, utilising energy dispersive X-ray analysis. Quantitative analyses were obtained at 15 keV accelerating voltage, and the raw data processed through computer software provided by the manufacturer. A 5 μm beam diameter was used throughout. Occasionally qualitative analyses were performed at 25 keV accelerating voltage. The analytical system yielded precision and accuracy both better than 2% based on the repeated determination of commercial native U and Th standards. The standards were cleaned at regular intervals to remove oxide layers etc. For the elements analysed in this study, the detection limit was taken as 0.5%. The system was calibrated against an internal iron reference every 30 minutes. Where applicable to the analysis of mineral phases, oxygen abundance was calculated by stoichiometry.

Results: uranium mineralogy

British uraniferous bitumens. Reflected-light microscopy confirms the presence of pitchblende in the bitumens from the northeast Wales orefield (Parnell, 1988a), Laxey in the Isle of Man

(Davidson and Bowie, 1951) and Dalbeattie, southern Scotland (Miller and Taylor, 1966). The shapes of the mineral grains are variable. The sample from Laxey, exhibits grains (5–19 μm in diameter) with smooth boundaries, some forming perfectly spherical crystals (Fig. 1.1) or more commonly fragments of spheres which appear to have separated within the bitumen mass (Fig. 1.2). Some grains appear to be exploded, resulting in inclusion trails between larger mineral fragments (Fig. 1.3), or whole grains transformed to a mass of small mineral inclusions (Fig. 1.4).

In the northeast Wales orefield, for example the Ty Gwyn deposit, mineral inclusions are arranged in clusters of submicroscopic grains each cluster being surrounded by larger pitchblende inclusions up to 3 μm in diameter (Fig. 1.5). The latter have spherical outer edges. Alternatively wedge-shaped inclusions are arranged in an annulus (Parnell, 1988a), forming structures 5–20 μm in diameter (Fig. 1.6).

A second Welsh sample, from Llandulas, contains highly altered, wedge-shaped mineral inclusions, cored by uraninite(?) (Fig. 1.7). Similar 'capillary structures' have been described elsewhere (Pierce et al., 1964). Microprobe analyses indicate that the alteration rim may be brannerite $\{(U,Ca,Ce)(Ti,Fe)_2O_6\}$. Areas of dispersed, sub-microscopic mineral (Fig. 1.8) were tentatively identified, using microprobe evidence, as highly altered pitchblende.

A sample from Dalbeattie, Scotland, contains abundant irregularly shaped inclusions of pitchblende up to 50 μm in diameter, often substantially altered at the edges (Fig. 2.1). Trogerite, $(UO_2)_3(AsO_4).12H_2O$, occasionally coats the inclusions and fills fractures through the hydrocarbon.

Scandinavian uraniferous bitumens. The petrography of the 'titano–thucholite' from Boliden has been described by Grip and Odman (1944). The fine-grained (<1 μm) uranium minerals, identified as brannerite by microprobe analysis, are restricted to positions between bitumen masses (Figs. 2.2 and 2.3) or are aligned in a common orientation (Fig. 2.4), the aligned zones being commonly cross-cut by the elongated mineral-free zones (Figs. 2.3 and 2.5). Inclusions are also arranged to form 'fingerprint structures' (Grip and Odman, 1944).

Bitumens from Hiddingsta and Samsala, Orebro, Sweden, contained dispersed fine-grained pitchblende, most grains being irresolvable by microscopy (Fig. 2.6), although some single grains are distinguishable in the slightly coarser Samsala sample. The mineral distributions are not even, nor are they related to a
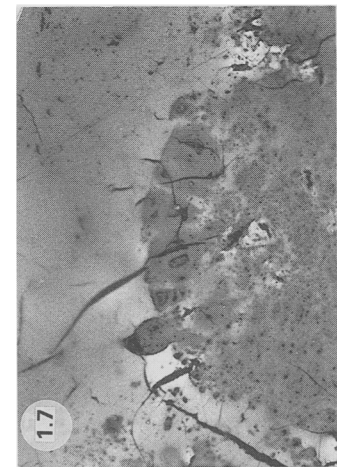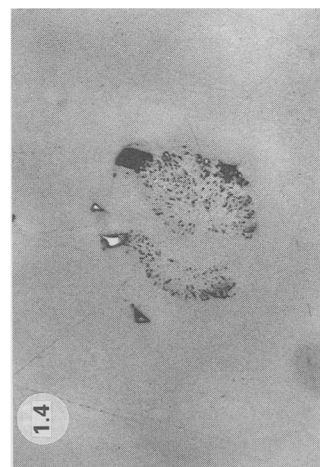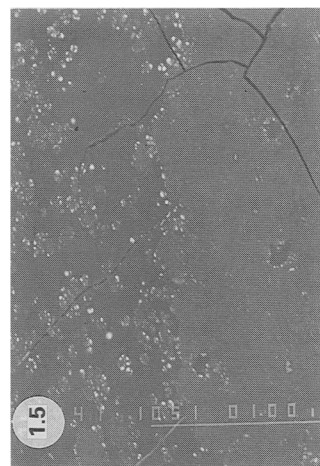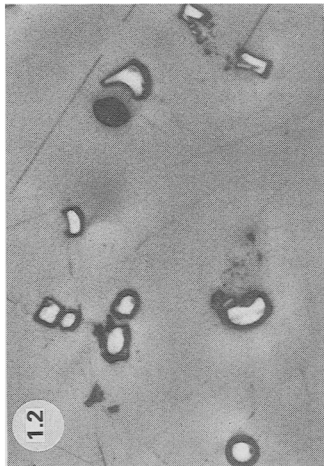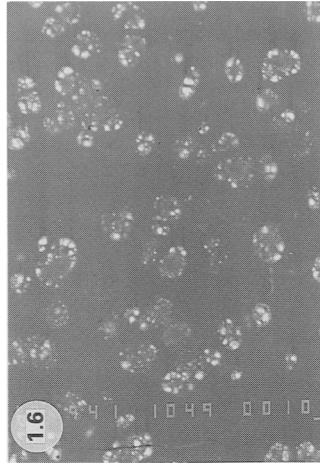
mineral fabric, but are controlled by the presence of bodies of mineral-free bitumens within the sample.

Uraniferous and thoriferous bitumens from Narestø, Norway, contain evenly distributed, irregular grains of thorium-rich uraninite, reaching 20 μm in diameter, often altered at the edges (Figs. 2.7 and 2.8). Veins of uraniferous aeschynite, $(Ce,Ca,Fe,U,Th)(Ti,Nb)_2(O,OH)_6$, crosscut the hydrocarbon (Eakin 1989b).

South African uraniferous bitumens. The reflected-light petrography of the Witwatersrand uraniferous bitumens has been extensively described elsewhere (e.g. Davidson and Bowie, 1951; Leibenberg, 1955; Schidlowski, 1981). The organic matter consists of bitumen granules, nodules and seams bearing inclusions of thorium-rich uraninite (Grandstaff, 1981), gold and sulphides. Uraninite inclusions are of two types (Davidson and Bowie, 1951). The first consists of grains up to 50 μm in diameter forming aggregates in which the shape of an orginally larger grain can be distinguished, but the constituent fragments of which have parted (Fig. 3.1). The second form of uraninite (and brannerite) forms granules and fills minor fractures in the bitumens and has an average grain size of less than 1 μm (Fig. 3.2).

Organic petrography

There is a marked similarity in the textures exhibited by uraniferous bitumens despite differences in the host geological environment.

Globular bitumens. Two types of globular structure occur in uraniferous bitumens. The first has been observed in the samples from the northeast Wales orefield. Small globules occur towards the outer edge of the massive bitumen and coalesce to form botryoidal masses (Fig. 3.3). The second type of globular texture is best observed in those samples containing mineral matter distributed evenly through the bitumens. The structures occasionally consist of coalescing rounded masses of mineral-free bitumens (Fig. 3.4). The textures in Fig. 3.5 suggests that the globules form by displacement of sub-microscopic uraninite grains along a 'front' at the outer edge of the bitumen globule, forming a concentration of uraninite. In the Boliden sample, the globules reach 100 μm in diameter and are rimmed by brannerite (Fig. 2.2). In some samples a marked reflectance variation within the bitumen is observed (Fig. 3.5).

A variety of other textures based on irregularly shaped areas of minerals-free bitumen forming elongate structures up to 30 μm in length, or dendritic arrangements dispersed through pitchblende concentrations have also been observed (Fig. 3.6), and are assumed to be genetically related to the mineral-free globular structures described above.

Fracturing. Fractures are common in uraniferous bitumens, their form being controlled by the presence and nature of the uraniferous grains, and the internal structure of the bitumens.

The simplest form of fracture consists of cracks of varied length radiating from radioactive grains in the bitumens. In the Narestø sample they occur around the larger, more altered grains and are restricted to a zone of increased bitumen reflectance surrounding the uraninite grains (Fig. 2.8).

In those bitumens bearing a large amount of very fine grained uraniferous mineral matter (e.g. Llandulas, Hiddingsta, and Samsala), fissures are found in concentrations of sub-microscopic pitchblende and have a randomly oriented, branching form (Fig. 3.7). These fissures are largely absent from the mineral-free areas of the bitumens.

Other fractures (Fig. 2.3) have been previously described as 'gash veins' (refer to Fig. 5, Grip and Odman, 1944) and form in the centre of, and perpendicular to, elongated areas of mineral-free bitumen. The structures are dilated towards their centre, forming openings up to 1 μm wide.

Bitumen mobility. Many uraniferous bitumens display evidence of post-formational movement. This may result in the separation of mineral grains (for example, along cleavage planes etc), or the development of irregular fabrics in the hydrocarbon which are best highlighted under crossed polars (Fig. 3.8).

FIG. 1 (oil immersion, reflected, plane-polarised light, field width 27 μm unless otherwise stated). Figs. 1.1 to 1.4 progressive uraninite alteration and fragmentation in the Laxey uraniferous bitumen (1.1) unaltered spherical uraninite (field width 12 μm), (1.2) 'drifted' fragments of uraninite spheres, (1.3) drifted fragments of uraninite with inclusion trails between the larger fragments, (1.4) an 'exploded' uraninite grain. Figs. 1.5 and 1.6: uraninite distribution in the Ty Gwyn uraniferous bitumen (backscaterred-electron images), (1.5) bodies of sub-microscopic inclusions bordered by larger uraninite grains (Field width 234 μm), (1.6) annular arrays of wedge shaped inclusions (field width = 117 μm). Figs. 1.7 and 1.8 mineral fabrics in Llandulas uraniferous bitumen: (1.7) large wedge-shaped inclusions with uraninite cores and brannerite (?) outer, (1.8) small-scale radial structures resembling the 'capillary structures' of Pierce et al. (1964).
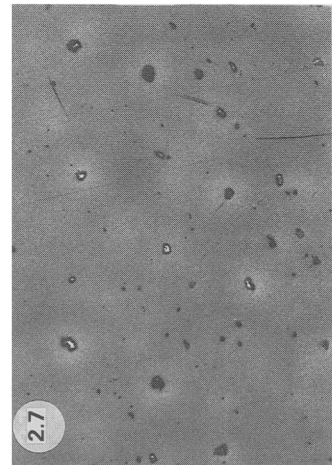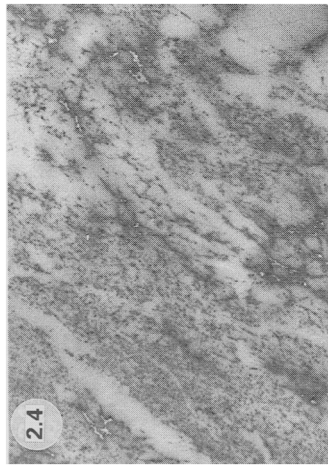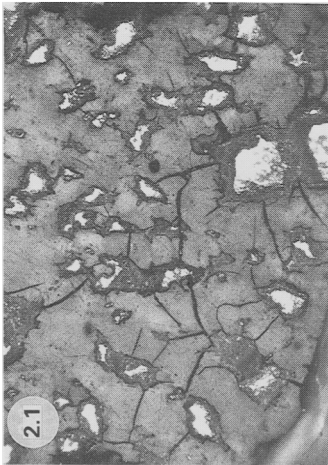
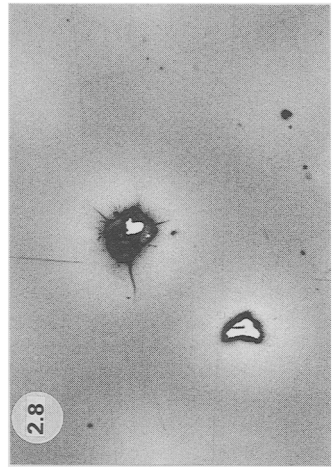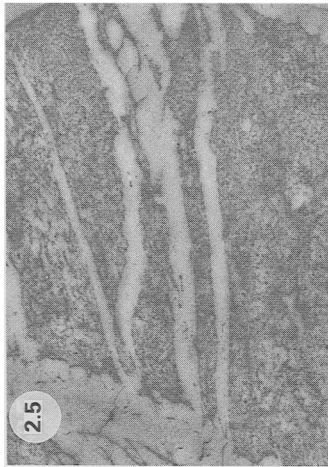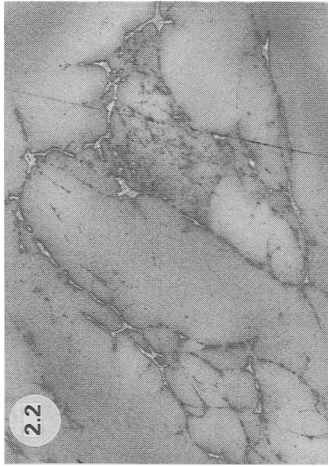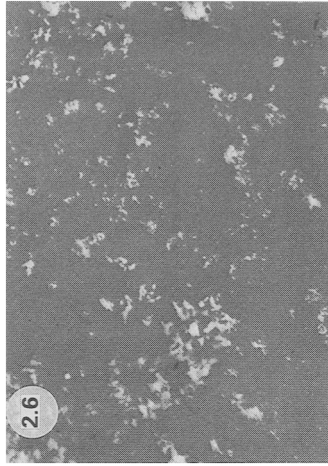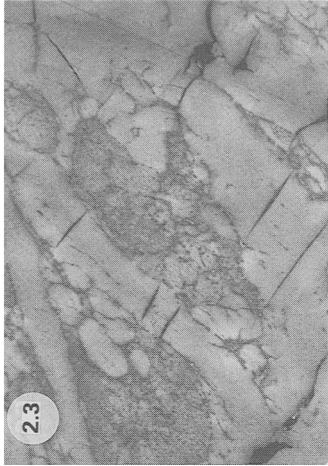Fig. 1.1 to 1.4 reflects progressive fragmentation of spherical uraninite crystals as a result of secondary bitumen movements. Mineral inclusions have split into angular fragments (Fig. 1.2), occasionally with inclusion trails between them (e.g. Fig. 1.3). Advanced fragmentation is exhibited in Fig. 1.4. In the Ty Gwyn sample, the annular arrangements of inclusions may have formed by the separation of originally spherical grains into segments (Fig. 1.6). Additionally, some of the groups of inclusions show a marked elongation as further indication of post-formational movement. The areas of aligned inclusions (Fig. 2.4) and 'veins' (Fig. 2.3 and 2.5) in the Boliden sample, and the pronounced bireflectance in the Witwatersrand sample (Fig. 3.8), further indicate post-formational movement. Similar structures have been observed and described from other occurrences of uraniferous bitumens (e.g. Penkov, 1980; Leventhal et al., 1987).

Microprobe analysis

Uraninite composition. Representative microprobe analyses of uraninite samples from Great Britain and Scandinavia are shown in Table 2. The results indicate that most of the uraninite and pitchblende compositions have thorium concentrations lower than the accurate detection limit of the analyser (approximately 0.5%), suggestive of formation under low-temperature conditions (Durrance, 1986). In contrast, in the Narestø sample thorium levels in the uraninite reach 7.9%, indicative of high-temperature formation (Eakin, 1989b). No zoning was evident in any sample.

It is notable that the most visibly altered minerals (e.g. Samsala, Hiddingsta, and Dalbeattie) yield the lowest analytical totals. In contrast the comparatively 'fresh' Laxey and Narestø samples yields total close to 100%. This presumably reflects the presence of H_2O or small quantities of U^{6+} mineral in the alteration products.

Discussion

The remarkable similarity in the textures observed in samples from a variety of geological settings implies a common petrogenesis for these features. We have attempted to interpret the fabrics described above within the framework outlined in Table 3. The petrographic features observed have been categorised temporally in to those arising from (1) formation of the uraniferous bitumens, (2) alteration of uranium minerals in uraniferous bitumens and (3) post-formational radiolysis of the organic matter.

In addition to the temporal (or paragenetic) sequence of events, we have attempted to differentiate textures on a mechanistic basis. In a previous study of non-uraniferous bitumens which had been coked, Gize (1985) was able to attribute bitumen textures on the basis of physical or chemical mechanisms. Included in physical processes were textures resulting from aqueous insolubility, the effects of multiple pulses of hydrocarbons or bitumens, and a change from ductile to brittle response to stress. In this earlier study, the bitumens have been coked by a variety of thermal processes. A predominant chemical mechanism would have been 'cracking' at relatively high temperatures (250 °C+), probably involving free-radical mechanisms. In the present study, the uranium radiation will also promote free-radical mechanisms, but contrasts with the textures produced in natural cokes by being a relatively low temperature process.

Genesis of uraniferous bitumens. The association of uranium with organic matter has historically been attributed to two processes. These are either a syn- or epigenetic enrichment of organic matter by complexing and reduction of hexavalent uranium from solution with O-bearing organic functional groups (Nash et al., 1981), or precipitation of mobile hydrocarbons around pre-existing uranium minerals as a result of radiation-induced polymerisation processes (Hoekstra and Fuchs, 1960). The latter process is often accompanied by simultaneous dissolution of the uranium mineral (e.g. Miller and Taylor, 1966).

FIG. 2 (oil immersion, reflected plane-polarised light, field width 27 μm unless otherwise stated): (2.1) uraninite grains with fresh cores and altered rims in the Dalbeattie uraniferous bitumen. Figs 2.2 to 2.5: petrographic features of the Boliden uraniferous bitumen, (2.2) titaniferous uranium minerals restricted to the edges of large, mineral-free globules, (2.3) elongated mineral free zones with 'gash-vein' fracturing, (2.4) commonly orientated mineral inclusions, (2.5) bitumen 'veins'. (2.6) Ultra-fine grained uraninite evenly dispersed through the Hiddingsta sample. Note the small dendritic segregations of mineral-free bitumen. (2.7) Narestø uraniferous bitumen displaying increased bitumen reflectance around uraninite grains. (2.8) Radial cracks emanating from altered uraninite grains in the Narestø bitumen.
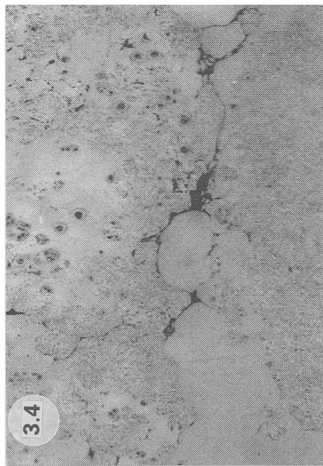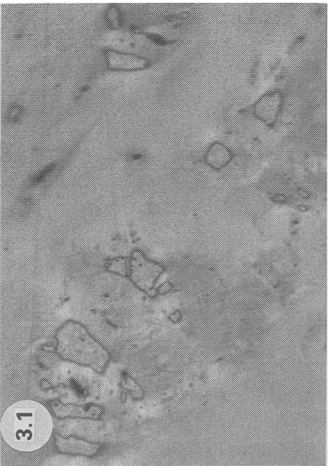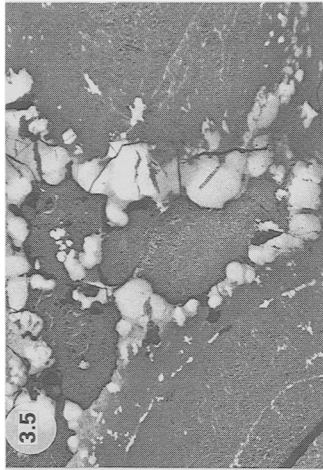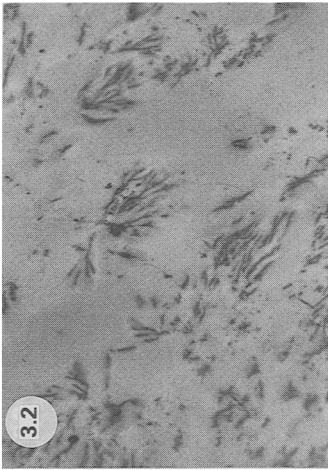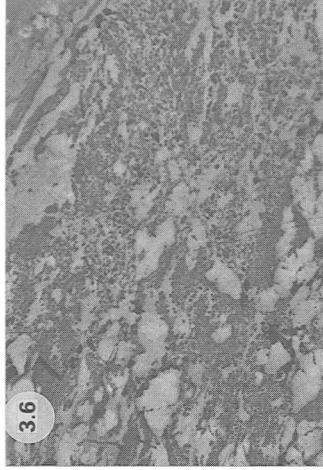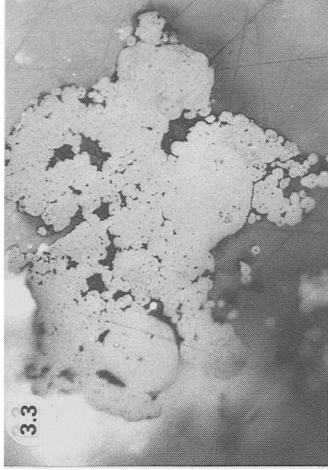
Therefore textual information on uranium minerals within the hydrocarbon may indicate which of these processes was responsible for the formation of the sample under investigation. However, one of the potential problems in determining the genetic history of uraniferous bitumens is that if dissolution of uranium minerals can be an integral part of their formation, there is no obvious reason why it should not also occur as a later alteration phenomenon in uraniferous phases formed within the bitumen by the complexation/reduction process. Therefore, primary diagnostic features of uraniferous organic matter may be lost as a result of later alteration reactions.

Uranium mineralisation of bitumens. Chemically, it is difficult to envisage how organised mineral morphologies and distributions, e.g. in the Laxey (Fig. 1.1 to 1.4) and northeast Wales orefield samples (Fig. 1.5 to 1.8), could have formed by replacement of pre-existing minerals. Therefore they probably reflect formation by the complexation/reduction process. The ubiquitous association of the two phases in the Laxey and northeast Wales orefield deposits implies a common genesis. Similarly, the absence of uraninite not associated with bitumen does not support the suggestion that pre-existing uraninite was the source of the uranium. Where uraniferous bitumens have formed by the dissolution/precipitation mechanism, free uraninite or pitchblende

are found elsewhere in the deposits (Miller and Taylor, 1966; Welin, 1966).

Mineralisation of the British uraniferous bitumens may be related to an increased capability for uranium fixation by oxidised petroleum (Lisitsin, 1960). Fig. 3.3 is interpreted as reflecting primary coagulation of oil globules. Liquid hydrocarbons could develop oxygenated functional groups by development and regeneration of oxygenated functional groups during contact with oxidising U-mineralising fluids (Landais *et al.*, 1987), thus enabling urano-organic complexes to form. This 'preconcentration' stage has been argued to be essential for the precipitation of uranium from weak mineralising solutions (Kochenov *et al.*, 1977). It is postulated that this mechanism accounts for the absence of uranium mineralisation without the involvement of organic matter in the Laxey and northeast Wales orefield deposits.

After enrichment, a second stage of uranium precipitation must occur to form the regular arrays of uranium minerals. A process of 'exsolution' (Parnell, 1988b) does not seem viable as it does not take into account a compulsory stage of chemical reduction which takes place during the precipitation of U^{4+} minerals from U^{6+}/organic matter complexes. The reduction of U^{6+} complexed to mineral-bound U^{4+} ions can be achieved by several processes: oxidation of alcohol groups in the organic matter to generate

Table 2. Representative electron - microprobe analyses of uraninite in uraniferous bitumens from Great Britain and Scandinavia.

SAMPLE	UO$_3$	ThO$_2$	PbO	SIO$_2$	TOTAL[1]
HIDDINGSTA	91.02	bdl[2]	bdl	7.18	96.33
SAMSALA	87.54	bdl	4.16	3.63	95.33
NARESTØ	79.94	7.45	10.41	1.69	99.49
DALBEATTIE	91.43	0.6	bdl	0.52	94.95[3]
LAXEY	94.27	bdl	2.55	1.00	98.23

[1]Low totals probably due to alteration to hydrated alteration assemblages. [2]bdl = below detection limits (see methods section for details). [3]Sample contains 2.3% Bi.

FIG. 3 (all oil immersion, reflected plane-polarised light, field width 27 μm), uraninite/pitchblende morphologies in the Witwatersrand organic matter: (3.1) primary uraninite inclusions formed by fragmentation of parent grains, (3.2) secondary pitchblende filling fractures and forming veins through the bitumen. Figs. 3.3 to 3.6, globular and dendritic structures in uraniferous bitumens: (3.3) bitumen globules from the Ty Gwyn locality possibly preserving orginal immiscibility textures. Figs 3.4 to 3.6, globular structures formed during radiation-induced alteration by gathering of low-molecular weight products of irradiation: (3.4) Ty Gwyn (3.5) Hiddingsta (note the concentration of mineral matter around the globules and the reflectance variation within them) (3.6) dendritic segregations of mineral-rich and poor bitumen in the Hiddingsta bitumen formed as precursors to globule formation. (3.7) randomly orientated fissures within mineral-rich areas of the Llandulas samples. (3.8) marked bitumen anisotropy in the Witwatersrand bitumen generated by shear-type movement. Note the augen-type textures around the mineral grains.

aldehydes, acids, and ultimately CO_2 and H_2O (Andreyev and Chumenenko, 1964; Nakashima *et al.*, 1984), direct reduction by organic matter at temperatures in excess of 500 °C (Rouzaud *et al.*, 1980), reduction by hydrogen from the organic matter (Nakashima *et al.*, 1984), and by reduced sulphur species (Breger, 1974). Given the abundance of sulphide minerals intimately associated with the bitumens, and their close proximity to sulphide ore bodies (Davidson and Bowie, 1951; Eakin, 1989*a*), sulphide species are the likely reductants active in the precipitation of uranium minerals in the Manx and Welsh bitumens.

Our results indicate that the range of minerals present in uraniferous bitumens is markedly restricted, relative to the large number of minerals which have been reported in the literature. This is consistent with the conclusions of Kochenov *et al.* (1977) that the enrichment process outlined above should result only in the formation of uranium minerals such as uranitite and coffinite. One reason for this restriction is presumably that the organic matter acts as a redox (Eh) buffer. Uraninite has been synthesised during experimental studies of uranium/organic-matter complexes under hydrothermal conditions (Nakashima *et al.*, 1984).

The precipitation of minerals involves nucleation and growth. The northeast Wales orefield samples are characterised by containing large

Table 3. Petrographic features associated with genesis and alteration of uraniferous bitumens.

TEXTURE	GENESIS	EXAMPLE
	uraniferous bitumen formation	
Spherical mineral inclusions; inclusion clusters; monotonous mineralogy and inclusion size; "capillary structures"	precipitation of $^{4+}$U minerals within hydrocarbon masses	Figs.1.1, 1.5, 1.6, 1.7 and 1.8
Irregularly sized and shaped mineral inclusions often with alteration rims	replacement of primary uranium mineralisation by mobile hydrocarbons	Figs.2.1,2.7,2.8 and 3.1
	uranium - mineral alteration	
Alteration of grain rims; dispersion of uranium in hydrocarbons; precipitation of fracture - filling and grain - coating uraniferous phases.	Replacement of uraninite and pitchblende by hydrocarbons coupled with reprecipitation of free uranium in veins and mineral overgrowths.	Figs.2.1, 2.7, 2.8 and 3.1 Figs.1.7 and 3.2
	hydrocarbon alteration	
Early alteration: Globular bitumen, dendritic structures, mineral - free hydrocarbon "veins".	Formation of mobile hydrocarbons during radiolytic cracking reactions; within hydrocarbon migration.	Figs. 2.2 to 2.5, 2.6,3.4 to 3.7
plasticity and deformation of hydrocarbons	Mobile hydrocarbons as "lubricants" under stress.	Fig. 3.8
drifting of mineral fragments; "exploded" mineral inclusions; alteration of minerals to sub - microscopic grains; "capillary structures".	Mobilisation of hydrocarbons and reprecipitation at mineral - hydrocarbon interface in fractures and cleavage planes.	Figs. 1.2 to 1.4, 1.6 to 1.8 and 3.1
Advanced alteration: Increased reflectance and bireflectance.	Continuous polymerisation and structural ordering of bitumens.	Figs. 2.7, 2.8 and 3.8: see more complete work in Jedwab, (1966); Leventhal *et al.*,(1987); Eakin, (1989a).
Bitumen fracturing.	Embrittlement of bitumens during devolatisation; volume changes associated with mineral alteration.	Figs. 2.1, 2.3, 2.8 and 3.7.

numbers of small inclusions. In contrast, the Laxey sample has a much higher uranium content (Eakin, 1989a) but contains a relatively small number of large inclusions. Since the number of crystals formed is proportional to the number of nuclei available, the Laxey sample must have contained relatively few uraninite nuclei and the northeast Wales orefield samples a large number. The nuclei could form on impurities in the hydrocarbon, and the availability of uranium should then determine the ultimate size of the crystals formed. The structures exhibited in Fig. 1.5 may result from the existence of concentrations of impurities which, after mineral nucleation and growth, formed large numbers of small inclusions. Bordering the areas of high inclusion density, larger inclusions will form in response to greater availability of uranium. The spherical morphology of the pitchblende inclusions (Fig. 1.1) is commonly adopted by uraninite and pitchblende (Heinrich, 1958).

Replacement of uranium minerals by hydrocarbons. The reaction of mobile hydrocarbons with uraninite involves two steps which may proceed independently but which combine to form features characteristic of uraniferous bitumens formed by corrosion of pre-existing uraninite. Firstly, radiation-induced polymerisation reactions precipitate solid bitumens from mobile precursors. Secondly, reaction of the organic material corrodes the uraniferous phase. The latter process is held reponsible for the massive dissolution of the uranium mineral (uraninite or pitchblende). Formation of uraniferous bitumens by these processes result in fabrics exhibited by the Dalbeattie (Fig. 2.1), Narestø (Figs. 2.7 and 2.8), and Witwatersrand (Fig. 3.1) samples. Common features include the presence of irregularly shaped uraninite fragments, often with fresh core and highly altered rim, 'floating' in the bitumen (Figs. 2.1, 2.7, and 3.1). In the cases of very advanced alteration, sub-microscopic mineral inclusions may result (Figs. 2.4, 2.6, 3.5, 3.6 and 3.7). Genesis of uraniferous bitumen by this mechanism can usually be easily identified by the occurrence of uraniferous minerals not associated with bitumen elsewhere in the deposit.

There have been few attempts to construct a detailed mechanisms for the replacement of uraninite by hydrocarbons. Indeed, Hoekstra and Fuchs (1960) have questioned the viability of such a process since '(1) uranium could only be separated from the uraninite by oxidation to the hexavalent state, and. . . (2) the presence of oil indicates reducing conditions'. However, Dubinchuk et al.(1977) have suggested a role for free radicals in the replacement of uraninite. High

concentrations of free radicals have been noted in uraniferous organic matter (Zumberge et al., 1978).

Silica mobilisation. A side issue stemming from this study is the behaviour of silica in uraniferous bitumen deposits. The presence of coffinite, $U(SiO_4)_{1-x}(OH)_{4x}$, in some uraniferous bitumens (Dubinchuk et al., 1977) indicates co-precipitation of U and Si. The migration and deposition of silica related to ore precipitation is also suggested by quartz overgrowths in sandstone-hosted tabular uranium deposits (e.g. Fishman et al., 1985), and quartz veins and overgrowths through the Narestø uraniferous bitumen (Eakin, 1989b).

The ubiquitous corrosion of uraniferous hydrocarbon host rocks (including substantial dissolution of quartz grains) has been reported (Parnell and Eakin, 1987). The action of carbonic acid, released on dissociation of U^{6+} ion-carbonate complexes in the mineralising fluids, was considered responsible. However, this mechanism does not account for the alteration of host rocks associated with uraniferous bitumens formed by the dissolution/precipitation process, which does not involve the dissociation of metal–carbonate complexes in solution. We propose that a free radical-based reaction could be responsible for dissolution of minerals both in uraniferous bitumens and in the surrounding host rock.

The high concentrations of free radicals and hydrogen formed during irradiation of the organic matter would result in the development of an extremely reducing micro-environment within and immediately surrounding the bitumen. This micro-environment is evidenced by the previously noted restricted uranium mineralogy in bitumens, together with stability of sulphide minerals. It has been suggested that under such conditions uranium and silicon oxides can be reduced to alkoxy compounds (J. Rooney, pers. comm., 1988), formed with aliphatic and aryl organic compounds. In uraniferous bitumens, such organo–silicon and uranium compounds may form through intimate association of free radicals and oxygen present in mineral lattices. The result would be corrosion of uraninite and silica, and release of these elements into the bitumen. Inferred support for such a process has been provided by several authors (Brodin and Dymkov, 1964; Dubinchuk et al., 1977; Penkov, 1980) who have reported the distribution of non-crystalline uranium throughout bitumens replacing uraninite veins. An alternative mechanism for uranium and silicon mobility would be increased solubility resulting from radiation damage of mineral surfaces. Such anomalously enhanced

solubilities have been described from experimental studies and attributed to surface-limited mechanical damage (Beckwith and Reeve, 1969; Rimstidt and Barnes, 1980). It is not possible to verify either mechanism in this study.

Schidlowski (1981), in supporting a replacement mechanism for the genesis of the Witwatersrand bitumen, has noted the absence of uranium in the bitumen surrounding the uraninite. This situation may be explained by the reprecipitation of the dispersed uranium as later fissure-fills within the bitumen (Fig. 3.2). Similarly, uranium-enriched minerals such as trogerite at Dalbeattie, aeschynite at Narestø (Eakin, 1989b) and brannerite in the Llandulas sample suggest that later mineralising processes may scavenge uranium dispersed through the bitumen and incorporate it into later fracture-filling minerals.

One limiting factor which will impede and may eventually stop dissolution of the minerals may be the restriction in movement imposed on the free radicals as the hydrocarbons progressively solidify (the so-called 'cage effect'; Charlesby, 1960). Solid uraniferous bitumens still contain large numbers of free radicals but which are immobile. Therefore, normal radical-termination reactions (reactions which destroy free radicals and prevent their propagation) are not responsible for the cessation of corrosion (Zumberge et al., 1978).

Precipitation of bitumen around the uraniferous grain progresses concurrently with the corrosion process described above. Radiation-induced solidification, by free-radical polymerisation processes, has been demonstrated experimentally (e.g. Charlesby 1954, 1960; Swallow, 1960; Bolt and Carrol, 1963). Further, descriptions of bitumens precipitated around uraniferous zircon and monazite grains (McKirdy and Kantsler, 1980; Rasmussen et al., 1989) provide evidence that the solidication process is truly radiation-induced, and is not an artifact of the chemical reaction between UO_2 and the bitumens.

Organic petrography. The variety of textures exhibited by uraniferous bitumens can be related to irradiation of the organic matter. Our interpretation has been aided by the wealth of experimental data from laboratory irradiation of organic materials (Charlesby, 1954, 1960; Swallow, 1960; Bolt and Carrol, 1963: Colombo et al., 1964). Charlesby (1954) concluded that on irradiation of paraffinic hydrocarbons, polymerisation processes were accompanied by cracking of chain structures, resulting in the formation of lower molecular weight products. The globular textures observed in several samples (Figs. 2.2, 3.4 and

3.5), and the separation of the samples into mineral concentrations and mineral-free bitumens (Fig. 3.6 and 3.7), including the formation of dendritic structures (Figs. 2.6 and 3.6), may represent accumulation of mobile hydrocarbons generated by hydrocarbon irradiation.

Condensation and polymerisation of such mobile bitumens at the mineral/organic interface may be responsible for the precipitation of hydrocarbon in the cracks and the gradual drifting apart of the constituent grains observed by Schidlowski (1981). This process could also account for the formation of annular arrays of inclusions (Fig. 1.6), and in advanced stages the impression of grain explosion (and severe alteration) may be gained (Fig. 1.4).

In the light of these suggestions, we conclude that only one phase of uraninite growth is necessary in many uraniferous bitumens, for example in the Laxey deposit. This involved growth of spherical uraninite inclusions in pre-existing bitumens, which were disrupted by later bitumen movement to give the impression of uraninite replacement (Fig. 1.2 to 1.4). Some inclusions were unaffected by the bitumen movements and maintained their original spherical form (Fig. 1.1).

The presence of mobile hydrocarbons may also influence other characteristics of uraniferous bitumens noted above. For example elongated structures and fabrics have been interpreted as evidence of 'marked plasticity' of the bitumens from the Witwatersrand region (Schidlowski, 1981) evidenced by the distinct bireflectance of the materials, and the formation of augen-type structures surrounding uraninite grains (Fig. 3.8). Such fabrics may result from deformation during early irradiation, the mobile hydrocarbons possibly providing 'lubrication' to facilitate such deformation.

The presence of mineral-free bitumen 'veins' (Grip and Odman, 1944), provides further indication of movement within the uraniferous bitumens (e.g. Fig. 2.3 and 2.5) although the exact origin of these structures is unclear. The linear, mineral-free nature of these structures may arise from lines of shear movement in the bitumen mass.

Structures produced as a result of plastic deformation and hydrocarbon movement within uraniferous hydrocarbons need not, therefore, result unequivocally from liquid hydrocarbon precursors (e.g. Leventhal et al., 1987). For example, uraniferous bitumens formed as a result of polymerisation of gaseous hydrocarbons (as has been suggested for the Witwatersrand hydrocarbons) may, as a result of radiolysis and tectonic

stress, develop fabrics indicating fluid movement of the hydrocarbon mass.

With continued irradiation other facets of alteration may become evident in the bitumens. Such features include well documented increased reflectance (Jedwab, 1966; Breger, 1974; Schidlowski, 1981; Leventhal *et al.*, 1987), for example in Fig. 2.8, and ordering of the organic matter (Eakin, 1989*a*).

The fissuring of uraniferous bitumens reflects advanced radiation-induced alteration. Crosslinking and polymerisation promote solidification of the bitumen (Charlesby, 1954), leading ultimately to the embrittlement of the solid (Bolt and Carrol, 1963) which becomes prone to brittle failure. Therefore, it is not surprising that in uraniferous bitumens fracturing is most pronounced in the vicinity of the greatest uraninite concentrations (e.g. Fig. 3.7). Textures such as those shown in Fig. 2.3 also suggest that the development of 'gash veins' can be controlled by the internal structure of the organic matter. Teichmuller and Teichmuller (1966) produced similar structures experimentally by degassing of coal macerals. Their results are of interest since they simulate the volatile loss which accompanies irradiation of organic matter (Colombo *et al.*, 1964). Gize (1985) attributed the formation of the similar fissures in naturally coked bitumens to a final devolatisation of the organic matter. The 'gash veins' are, therefore, interpreted as forming during the final stages of severe radiation-induced alteration of the organic matter.

The radial cracks surrounding the uraninite grains in the Narestø sample (Fig. 2.8) are restricted to areas of high bitumen reflectance Eakin, 1989*a*). However, it is unlikely that radiation damage alone is responsible for the fracturing development. High reflectance halos in the Witwatersrand bitumen, which display even more pronounced reflectance around the uraninite grains do not show radial fracturing (Fig. 3.1). It is suggested that the volume increase which accompanies alteration of uraninite to hydrous secondary minerals, is responsible for forming the radial fissures. In this case therefore, the radial cracks are not a direct result of radiation-induced alteration.

The underlying chemical mechanism leading to some of the textures reported here is a free radical process at relatively low temperatures. The other geological situation under which free-radical mechanisms occur is during coking (Gize, 1985). In spite of similar organic mechanisms, the textures observed in uraniferous bitumens reported in this study are markedly different to those reported previously for natural cokes. In natural cokes, marked optical anisotropy as sharp optical domains, is superimposed on textures resulting from physical processes such as aqueous immiscibility. Although uraniferous bitumens are also anisotropic, no development of clear optical domains has been observed: variations in anistropy are diffuse and may indicate crude ordering under stress (Fig. 3.8). The anisotropy in cokes has been ascribed to the ordering of planar aromatics produced by 'cracking' to form liquid crystals. The formation of a liquid crystalline phase is temperature dependent (experimentally above 300 °C, and geologically at 250 °C+), and can be considered as an intermediate phase between a true solid and a true liquid. No such transition has been observed in the uraniferous bitumens studied to date. This may simply be a reflection of sampling bias: uraniferous bitumens from high-temperature environments have not been examined.

Summary

The uranium mineralogy of uraniferous bitumens is simple, consisting primarily of uraninite, coffinite and pitchblende. This restricted mineralogy is interpreted as resulting from the reducing micro-environment imposed by the organic matter.

Microscopic investigation of uraniferous hydrocarbons indicates that two processes are responsible for the genesis. These are (1) corrosion of uraninite and pitchblende combined with radiation-induced precipitation of hydrocarbons around the mineral relics and (2) mineralisation of bitumens by uranium from mineralising solutions. The former process may also affect minerals formed by the enrichment process, and the host rock surrounding the uraniferous organic matter. Uranium released to the bitumens during the corrosion process may form exotic uraniferous phases during later mineralisation events, or may form fine uranium-rich disseminations through the bitumen.

Radiolysis promotes mobility of the hydrocarbons by cracking of large molecules to yield mobile low-molecular-weight products. Where the hydrocarbons are not exposed to external stress these mobile hydrocarbons may accumulate, displacing mineral grains, to form globular accumulations of mineral-free hydrocarbons. Where the organic matter has been exposed to thermal or tectonic stress, the products of radiolysis may act as a lubricant, promoting movement and deformation of the hydrocarbons. Such movements can alter the arrangement and morphology of the included mineral grains. Severe

radiolytic alteration may ultimately promote fracturing of the hydrocarbons, the fracturing being controlled firstly by the concentration of radioactive mineral grains, secondly by the internal structure of the organic matter and thirdly by alteration of the radioactive minerals.

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