The replacement of sandstones by uraniferous hydrocarbons: significance for petroleum migration

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Abstract

Hydrocarbons (bitumens *sensu lato*) in sandstones have been recorded in several instances to have partially replaced their host rock, including quartz grains. Many replacive hydrocarbons are uranium-rich: associated non-uraniferous hydrocarbons are not replacive. Uranium is transported as carbonate complexes, which may be decomposed by organic acids to yield UO_2^{2+} ions and CO_2. The UO_2^{2+} will be absorbed onto hydrocarbons before reduction to a mineral phase, generally uraninite; and the CO_2 may be aggressive towards the silicate grains of the host sandstone. Accretionary nodules of replacive uraniferous hydrocarbon in red beds (e.g. at the cores of reduction spots) can provide valuable information about petroleum migration. They occur particularly in the vicinity of faults, and may record the interactions between metal-rich groundwaters and hydrocarbons leaking along a fault from an underlying reservoir. A trial study in Devonian sandstones of Easter Ross successfully traced a hydrocarbon-bearing sandstone reservoir from an occurrence of uraniferous hydrocarbon nodules.

KEYWORDS: hydrocarbons, sandstones, uranium, uraninite, petroleum migration.

Introduction

IT is widely recognised that the porosity in many hydrocarbon-bearing sandstones is secondary (see Schmidt and McDonald, 1979, for Mesozoic and Cenozoic examples where substantial hydrocarbon accumulations occur in secondary sandstone porosity). Observations in Carboniferous sandstones of the USSR (Chepikov *et al.*, 1961) first led to the concept that the dissolution of cement and concomitant increase in porosity might be related to the migration of hydrocarbons into/through a sandstone reservoir. Cements and detrital grains are leached by dissolved CO_2, which may be derived from organic matter by the biogenic generation of gas and oil, the thermal generation of gas, and the biodegradation of oil (Al-Shaieb and Shelton, 1981). Sakhibgareyev (1978) suggests that at stable oil–water contacts the products of bacterial oxidation of oil cause the dissolution of minerals (including quartz), an accumulation of biodegraded oil residues and often extensive pyritization. A possible example of this process in the U.K. is in the Row Brook district of Shropshire, where at the surface of an oil-impregnated Carboniferous sandstone (Parnell, 1983*a*) the sandstone is massively replaced by solid hydrocarbon and pyrite (Fig. 1A). Reaction between petroleum and sulphate ions may yield CO_2 or bicarbonate ions. Dunsmore and Shearman (1977) suggest that the reaction of an idealized hydrocarbon C_7H_{12} might be:

$$C_7H_{12} + 4H_2O + 2SO_4^{2-} \rightarrow 4HCO_3^- + 2HS^- + 2H^+ + 3CH_4.$$

CO_2 is also produced by inorganic diagenetic reactions (Shanmugam, 1985).

Where minerals which have partially replaced silicate grains (principally carbonates) are themselves leached by CO_2-rich fluids, the secondary porosity so produced may appear to indicate the direct leaching of silicates. Sandstones showing corrosion of quartz and other silicate minerals should therefore be interpreted with caution. However, in hydrocarbon-bearing sandstones in which the hydrocarbon is uranium-rich, quartz replacement may have occurred without an intermediate sequence of cementation–replacement–cement dissolution.

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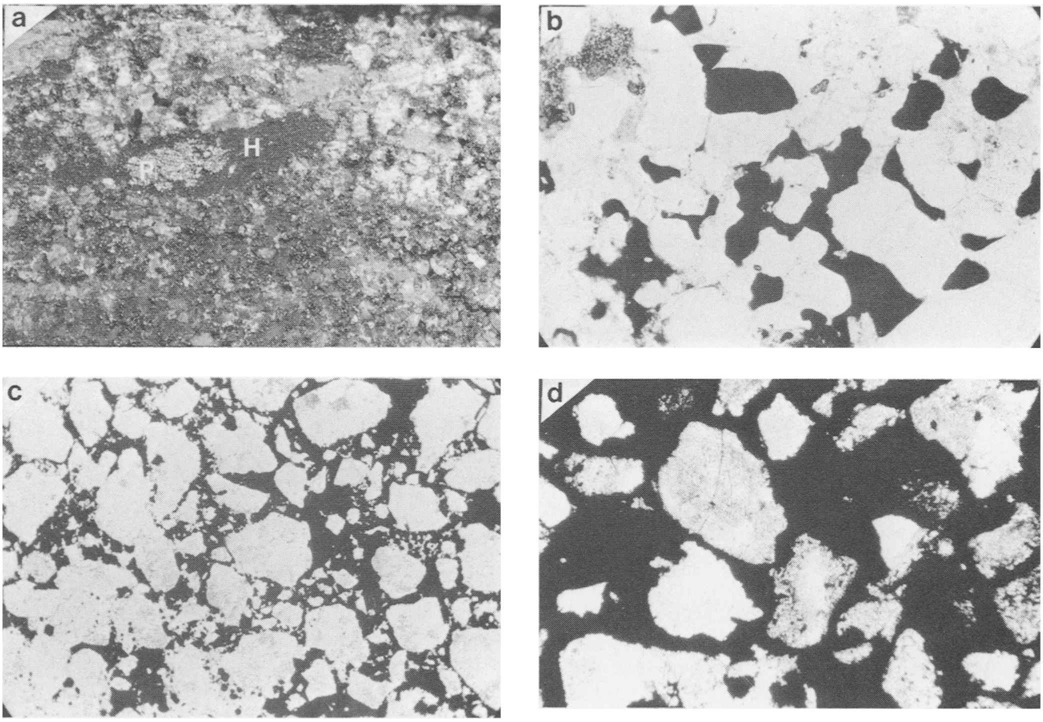

FIG. 1. Photomicrographs of sandstone exhibiting replacement by hydrocarbons (*a*) hydrocarbon H (non-uraniferous) and pyrite P replacing Carboniferous sandstone, Shropshire, possibly representing an oil-water contact, ×7. (*b*) to (*d*) show progressive degrees of replacement by uraniferous hydrocarbon, in thin sections. (*b*) Triassic, North Mesa Mine, Temple Mountain, Utah; hydrocarbon botryoids concentrated at grain boundaries, ×50. (*c*) Devonian, Allt Briste, Sutherlandshire, hydrocarbons show intricate replacement of grains, ×50. (*d*) Cretaceous, Cerro Heumul (Eva Peron deposit), Malargue, Argentina; highly corroded grains floating in hydrocarbons, ×45.

Replacive uraniferous hydrocarbons. There is a widespread and well-documented association of uranium with carbonaceous materials. A diverse range of organic materials, including plant remains, accretionary nodules and oil residues are found to be greatly enriched in uranium (e.g. Breger and Deul, 1959; Bell, 1960; Vassiliou, 1980; Rouzaud *et al.*, 1980). The most commonly offered explanations for these associations are based on the radioactive property of the uranium, and the presence of oxygen-bearing ligands in the organic material. Radiation from the uranium causes polymerization and condensation reactions in hydrocarbons and so solidifies and precipitates them (Colombo *et al.*, 1964). Uranium, or uranium (VI) ions, can be easily bonded to the oxygen atoms in various functional groups (Nash *et al.*, 1981).

Uraniferous hydrocarbons (we shall use this term *sensu lato* to include all oils and petroleum derivatives which are enriched in uranium) exhibit several properties which distinguish them from their non-uraniferous equivalents. For example they are notably insoluble in organic solvents (Haji-Vassiliou and Kerr, 1972), they are harder (Moench and Schlee, 1967), they have abnormally low atomic H/C ratios and high O/C ratios (Curiale *et al.*, 1983; Leventhal *et al.*, 1986) and heavy carbon isotope ratios (Leventhal and Threlkeld, 1978). An unusual property exhibited by uraniferous hydrocarbons within siltstones and sandstones is their apparent ability to replace the silicate grains (including quartz grains) of the host rock. This phenomenon allows their occurrence within some siltstones and fine sandstones in which the porosity would be otherwise inadequate for the accumulation of hydrocarbons between the grains. Accretionary nodules of uraniferous hydrocarbon within red bed sequences, often forming the cores of reduction spots (e.g. Parnell, 1985*a*), are an example of this mode of occurrence. In other instances uraniferous hydrocarbons exhibit

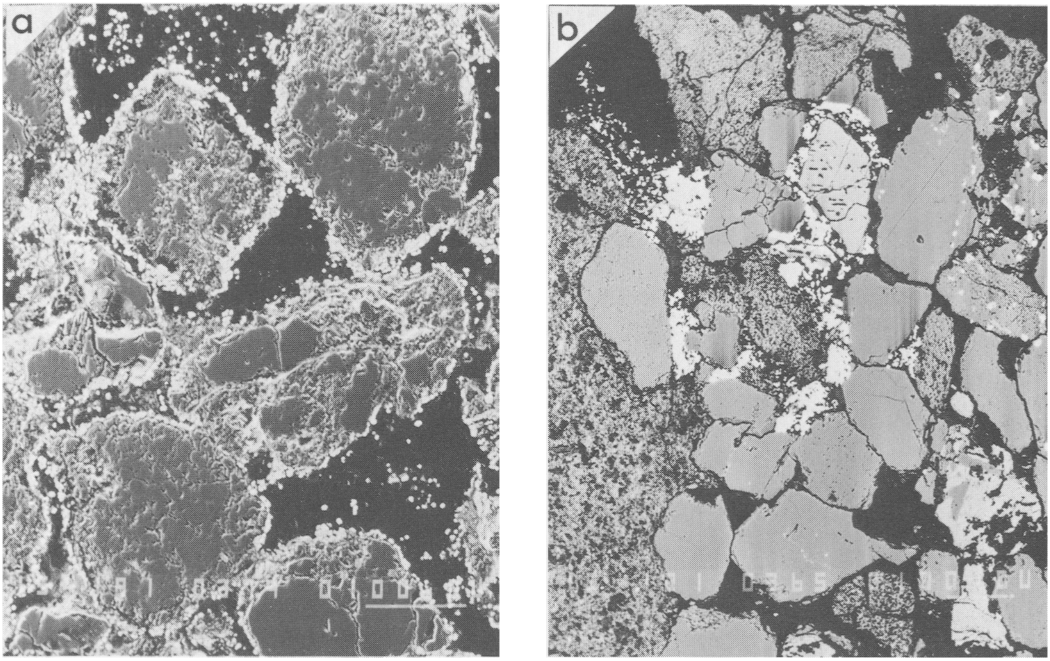

FIG. 2. Scanning electron micrographs of uraniferous hydrocarbons in sandstones. (*a*) Malargue, Argentina. Uraninite botryoids (bright) in hydrocarbon (black), concentrated near boundaries with corroded detrital grains, ×130. (*b*) Temple Mountain Utah. Grains show marginal replacement. Note irregular distribution of uraninite (v. bright) in hydrocarbon (black), ×90.

replacement on a massive scale. The replacive property of uraniferous hydrocarbons in siliciclastic rocks has in the past been a matter for incidental comment in studies of uranium mineralization. We describe several examples together here, and suggest that in some cases the occurrence of accretionary nodules can provide valuable information about petroleum migration.

Replacive hydrocarbons in sandstones: examples

Mendoza Province, Argentina. Sandstone-hosted uranium ore from the Malargue district, Mendoza Province, Argentina, contains replacive uraniferous hydrocarbons (Darnley, 1958). The ore deposits are described by Angelilli (1956) and Linares (1956). Petroleum shows are widespread in the vicinity (Lahee, 1932), and petroleum is concluded to be the precursor of the uraniferous hydrocarbons. The hydrocarbon contains uraninite and rare chalcopyrite inclusions. The sandstone is extensively replaced such that highly corroded detrital grains are left floating in a hydrocarbon 'cement' (Fig. 1D). Quartz, feldspar and lithic fragments are corroded to an equal degree. Internal grain boundaries within lithic fragments were also a focus for replacement. Examination of the ore using electron imagery shows botryoidal uraninite inclusions concentrated particularly near the boundaries of the hydrocarbon with remnant detrital grains (Fig. 2A).

Temple Mountain, Utah. Uranium ores in the Triassic sandstones of the Colorado Plateau include replacive uraniferous/vanadiferous hydrocarbons. The hydrocarbons are particularly prevalent at Temple Mountain, Utah (Hess, 1922; Isachsen, 1956; Breger and Deul, 1959). The hydrocarbons are probably petroleum derivatives, as there are rapid lateral transitions between uraniferous hydrocarbons, solid non-uraniferous hydrocarbons and petroleum (Hausen, 1956; Kelley and Kerr, 1958; Hawley *et al.*, 1968). The uraniferous hydrocarbons contain uraninite inclusions (Hawley *et al.* 1965), and we have additionally recorded a calcium uranium phosphate mineral, probably ningyoite $CaU(PO_4)_2$, at the margins of hydrocarbon masses. Petroleum samples have yielded up to 440 ppm uranium (Hawley *et al.*, 1965), an extremely high value for fluid hydrocarbons.

The host rock is grain-supported, medium quartzose sandstone with minor highly altered feldspar. Hydrocarbons occur (i) in clay-lined voids, representing an infill of secondary porosity after feldspar dissolution, and (ii) as replacive masses. Various degrees of replacement are observed, from replacement of interstitial clay minerals, progressively extending to detrital grains until the grains consist of 'a few scattered corroded remnants' in 'a massive body of urano-organic material' (Kelley and Kerr, 1958). A sample of sandstone showing a moderate degree of replacement (Figs. 1B, 2B) exhibits replacement of quartz grains along grain boundaries. The replacive masses occur up to 1m+ width (Keys, 1956). Kelley and Kerr (1958) noted that sandstone cemented by pyrite or carbonate had suffered less replacement. This observation confirms that the hydrocarbons are not simply infilling secondary porosity after leaching of a cement. No corrosion of quartz occurs in samples impregnated by *non*-uraniferous hydrocarbons.

Grants, New Mexico. Ores in the Grants uranium region, New Mexico, include replacive hydrocarbons in sandstones of the Upper Jurassic Morrison Formation. The uraniferous hydrocarbons have been interpreted as derivatives of humic acids rather than of petroleum (Moench and Schlee, 1967; Turner-Peterson, 1985). Humic substances can fix large quantities of uranium because they have a high content of oxygen-bearing functional groups (see above). In the New Mexico instance, the humic substances are thought to be derived from lacustrine mudrocks released at surface/near-surface temperatures (Turner-Peterson, 1985). The hydrocarbons contain coffinite and/or uraninite inclusions. Like most uraniferous hydrocarbons they are insoluble in organic solvents (Adams *et al.*, 1974). The hydrocarbons coat sand grains, and where abundant, partially replace them (Granger *et al.*, 1961; Moench and Schlee, 1967).

United Kingdom. Replacive uraniferous hydrocarbons have been recorded in several sandstones in the U.K. Nodules of replacive hydrocarbon in Upper Carboniferous arkosic sandstones of Heysham, Lancashire, have been well described by Harrison (1970). The hydrocarbons contain inclusions of chalcopyrite and pyrite. Uranium and vanadium were determined chemically by Harrison (1970), and although no uranium mineral inclusions were noted, a radiographic examination indicated point sources of radiation rather than a homogenous distribution. The hydrocarbon extensively replaces both matrix (clay minerals, feldspar) and detrital grains (quartz, feldspar).

Uraniferous hydrocarbons in Lower Devonian sandstones from western Orkney (Michie and Cooper, 1979) show marginal alteration of quartz and feldspar grains and lithic fragments. Numerous shows of non-uraniferous hydrocarbon occur nearby (Parnell, 1983*b*). Small masses (up to 3 cm) of uraniferous hydrocarbon in Middle Devonian sandstones in east Sutherlandshire are similarly replacive (Fig. 1C and see Parnell, 1985*a*). At Dingwall, Easter Ross, replacive uraniferous hydrocarbon nodules, up to 2 mm diameter, form the cores of reduction spots in Middle Devonian sandstones. The nodules were reported from a single locality by Parnell (1985*a*) but are now recorded throughout a 600 m+ section of sandstone and siltstone. The uranium is concentrated in uraninite and as traces in xenotime and (?) brannerite inclusions. The inclusions are restricted to the hydrocarbon nodules. Their replacive character and spherical morphology (Fig. 3) shows that the hydrocarbons do not represent detrital organic matter, which is found at the core of many reduction spots. The nodules in Easter Ross and at Heysham represent a distinctive type of replacive hydrocarbon, accretionary nodules, which have a particular significance to studies of petroleum migration (see below).

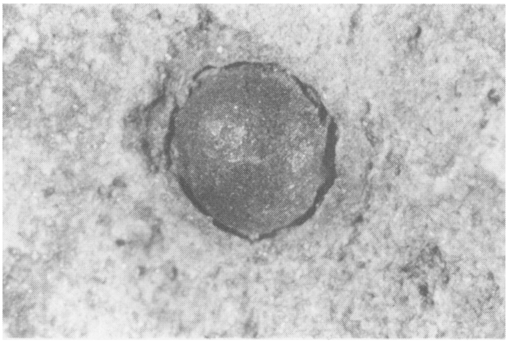

FIG. 3. Uraniferous hydrocarbon core of reduction spot, Devonian sandstone, Easter Ross, ×11. Note spherical morphology.

Paragenesis of uranium and hydrocarbons

In accounting for uraniferous hydrocarbons, we might envisage that either (i) migrating uranium, complexed in solution, is reduced upon contact with reservoired/migrating hydrocarbons, (ii) migrating hydrocarbons are nucleated (solidified) about uranium mineral grains due to the effects of radiation, or (iii) uranium and hydrocarbons migrate together and are co-precipitated by a change in the physico–chemical environment. Given that uranium concentrations in solid hydrocarbons often greatly exceed the highest concentrations found in oil (e.g. Hawley *et al.*, 1965), the last possibility cannot be the general explanation. Isachsen (1956) and Hausen (1956) believed that in the case of Temple Mountain, uranium mineralization preceded the introduction of hydrocarbons because they could envisage the replacement of quartz grains by uraninite more readily than by hydrocarbons. We do not believe that this is likely because:

(i) all uraniferous hydrocarbons in sandstones appear to be replacive. If uraninite was responsible for replacement of the sandstone, that would imply that hydrocarbons only interact with uraninite that is replacive.

(ii) it necessitates that in each instance the original uranium mineral was replaced by hydrocarbons, which upon introduction would have been non-uraniferous and exhibiting 'normal' properties. The morphology of the uraninite inclusions (Fig. 2A and see Hawley *et al.*, 1965) does not suggest that they have been replaced.

In the case of the accretionary nodules, uranium mineral grains are much more abundant within the nodules, than without, suggesting that they were localized by a local organic concentration rather than *vice versa*.

If we accept that uraniferous hydrocarbons are formed where uranium-bearing fluids encounter static/migrating hydrocarbons, this does not imply the immediate precipitation of uranium minerals. Experimental work by Rouzaud *et al.* (1980) suggests that the process of uranium absorption by organic materials occurs progressively. Initially, the uranium is probably absorbed onto or complexed with the organic material before being reduced to a mineral phase. Several workers (e.g. Calvo, 1974; Corniciuc, 1974) suggest that during the carbonization (lowering of H/C ratio) of organic material, uranium originally present in an organic form precipitates out as inorganic minerals. Heat treatment experiments (Rouzaud *et al.*, 1980) show that precipitation progresses with increasing temperature and time. The uraninite inclusions in many uraniferous hydrocarbons (e.g. Davidson and Bowie, 1951; Pierce *et al.*, 1964), including sandstone-hosted deposits (e.g. at Temple Mountain; Hawley *et al.*, 1965) form annular arrays. Orderly arrays of inclusions are more suggestive of exsolution from an organo–uranium complex than of a replacement of uraninite by hydrocarbons. The process of uraninite precipitation by the interaction of uranium-bearing fluid with organic materials has also been demonstrated by experiments using wood and coal (Breger and Deul, 1959).

Role of carbonate. A regular aspect of sandstone-hosted uraniferous hydrocarbon deposits is the occurrence of calcite cement. In the sandstones from northern Scotland, portions of sandstone not replaced by hydrocarbon are cemented/replaced by calcite (Parnell, 1983*b*, 1985*a*). The Carboniferous hydrocarbon-bearing sandstones described by Harrison (1970) are similarly cemented and replaced by calcite. Where Triassic sandstones of the Colorado Plateau are not impregnated/replaced by hydrocarbon they are cemented by calcite (Isachsen, 1956). Harshman (1970, Fig. 4) illustrates a close relationship between calcite cement and uranium ore at a roll front between grey sandstone and sandstone leached of organic carbon, in Eocene sandstone from Wyoming. Calcite is not present in the sandstone from Mendoza. However, the impregnation and replacement of the sandstone by hydrocarbon is so thorough that if calcite had formerly been present it would probably have been entirely replaced. Adjacent unimpregnated sandstones *are* calcite-cemented (Linares, 1956).

A simple explanation for sandstones in which hydrocarbon locally appears to adopt the cementing/replacive role of calcite would be that the calcite had been leached to yield secondary porosity which was subsequently occupied by hydrocarbon. There is no doubt that hydrocarbon infilling of secondary porosity is of widespread occurrence, but we do not believe that it explains the replacive nature of uraniferous hydrocarbons. In the more extreme examples, hydrocarbon occupies over 50% of the rock by volume and the relic grains are hydrocarbon-supported. If the hydrocarbon were removed, the grains would collapse. Furthermore, the ubiquitously replacive nature of sandstone-hosted uraniferous hydrocarbons suggests that the replacement is due to some special feature of uraniferous hydrocarbon deposits. The hydrocarbon in uraniferous hydrocarbons presumably has the same source as the associated non-uraniferous hydrocarbons, which do not exhibit replacement (see examples above). Therefore the hydrocarbons alone are not responsible for the replacement. We must seek an answer to the problem in the chemistry of the uranium-bearing fluid which interacts with the hydrocarbon to produce uraniferous hydrocarbons.

Uranium is thought to be readily transported as uranium (VI) carbonate complexes, such as the $\{UO_2(CO_3)_2\}^{2-}$ and $\{UO_2(CO_3)_3\}^{4-}$ anions (e.g. Nash *et al.*, 1981). Thermodynamic calculations suggest that the dicarbonate complex is prevalent in neutral solutions and the tricarbonate complex in alkaline solutions (Hostetler and Garrels, 1962). High concentrations of CO_2 in fluid inclusions in some hydrothermal uranium deposits (e.g. Poty *et al.*, 1974) suggests that carbonate complexes are likely to be an important means of uranium transport to those and other uranium deposits. Leroy (1978) argues that two separate reactions are necessary for the precipitation of UO_2 from a uranium carbonate complex. Firstly the complex must be broken down;

$$\{UO_2(CO_3)_2\}^{2-} + 2H^+ \rightleftharpoons 2HCO_3^- + UO_2^{2+}$$

followed by the reduction of UO_2^{2+} and precipitation of UO_2. Rich *et al.* (1977) view these stages as a single reaction:

$$\{UO_2(CO_3)_2\}^{2-} + H_2O \rightleftharpoons UO_2 + \tfrac{1}{2}O_2 + 2HCO_3^-$$

which shows that $a_{\{UO_2(CO_3)_2\}^{2-}}$ is proportional to $a_{\{HCO_3\}^-}$. Where calcium ions are available, the reaction

$$Ca^{2+} + 2HCO_3^- \rightarrow CaCO_3 + CO_2 + H_2O$$

may result in $CaCO_3$ precipitation and a decrease in HCO_3^- concentration upon CO_2 loss. Observations by Leroy (1978) suggest that CO_2 loss by boiling in a hydrothermal environment drives the reactions to the right, releasing UO_2^{2+} which could be reduced by hydrocarbons or another reductant.

Although uranium mineralization *is* associated with carbonate in several sandstone-hosted deposits, CO_2 loss by boiling is not plausible. An alternative mechanism for the breakdown of uranium (VI) carbonate complexes in sandstones especially where hydrocarbons are present, is their decomposition by organic acids. Koglin *et al.* (1978) have demonstrated that humic acids in a coaly sediment cause the decomposition of the relatively very stable $\{UO_2(CO_3)_3\}^{4-}$ anion, with consequent uptake of the uranium by the carbonaceous material. They summarised the reaction with humic acid (HA) as

$$6HA + \{UO_2(CO_3)_3\}^{4-} \rightarrow 6A^- + 3H_2O + 3CO_2 + UO_2^{2+}$$

The UO_2^{2+} cation may then be complexed with carboxylate groups of the humic acids (the importance of oxygen-bearing ligands in the retention of uranium was noted above; Nash *et al.*, 1981). Alternatively UO_2^{2+} ions may combine with electron donor free radicals within organic material (see Rouzaud *et al.*, 1980). Thus, adsorption and reduction to precipitate uraninite could occur in a single stage. CO_2 becomes available as a source of carbonate, which could be locally precipitated as a calcite cement. The CO_2 could also be aggressive towards the silicate grains of the sandstone, giving rise to their dissolution and a secondary porosity of which the hydrocarbons would take advantage.

Accretionary nodules: significance for petroleum migration

There are many cases of mineralization in red beds which are concentrated in and around accretionary (i.e. non-detrital) nodules of replacive organic matter. In particular, some reduction spots are nucleated around spheroidal carbonaceous cores (Fig. 3) rather than detrital organic particles. Many such nodules are enriched in U, Cu, V and other metals (e.g. Harrison, 1970; 1975; Curiale *et al.* 1983). The non-detrital organic matter which constitutes these nodules is bitumen (*sensu lato*) and is related to petroleum. In an example from Permian red beds in Oklahoma, Curiale *et al.* (1983) have used carbon isotope measurements to show that the organic matter in replacive uraniferous nodules is derived from petroleum. They assumed that the petroleum was leaking from deep reservoirs, although the hydrocarbon source-rock could not be identified. Evidence from other sequences suggests that interactions between metals in red bed sediments and hydrocarbons may be commonplace. For example Germanov (1963, and summarised by Roberts, 1980) has described the interaction of uraniferous and cupriferous groundwaters in a sandstone aquifer with hydrocarbons leaking from a buried petroleum reservoir to yield uraniferous hydrocarbons. Leakage of other reductant species (e.g. H_2S gas or aqueous sulphide species) from buried hydrocarbons may also lead to red bed mineralization (e.g. uranium ores in the Tertiary of South Texas; Reynolds *et al.*, 1982).

All petroleum reservoirs leak to some extent (Roberts, 1980). The interaction between escaping hydrocarbons and metals in red bed sediments to form metalliferous, carbonaceous nodules (Fig. 4) may be of value in the exploration for petroleum, in addition to metalliferous mineralization. The very low quantities of leaking hydrocarbons involved might otherwise go undetected.

We have investigated several instances of metalliferous, carbonaceous nodules in the U.K. Details of three are presented here (Figs. 5, 6, 7); two have been mentioned above. They have in common that they are adjacent to faults, which

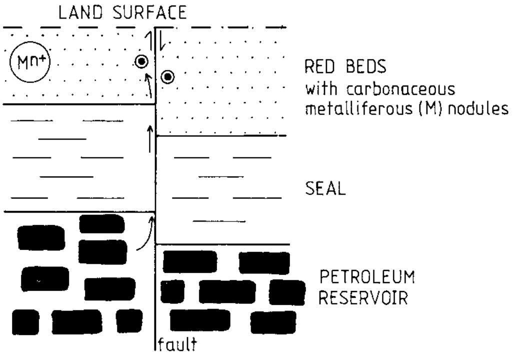

FIG. 4. Schematic interaction of hydrocarbons, leaking along a fault plane, with metalliferous groundwaters in red beds. Red beds may have sufficiently low vertical permeability to act as the seal, whilst allowing lateral flow of groundwaters.

would have acted as conduits for migrating hydrocarbons:

(i) uraniferous/cupriferous nodules in Upper Carboniferous sandstones (Harrison, 1970), immediately adjacent to the faulted eastern margin of a Permo-Triassic basin at Heysham. The basin includes the Morecambe Bay Gas Field, in which gas is being produced from the Triassic (Ebbern, 1981). Oil seeps in the Permo–Triassic rocks are also related to faulting (Cope, 1951).
(ii) vanadiferous nodules in Triassic (Keuper) siltstones near the Larne Lough Fault. Petroleum exploration has been instigated in the close vicinity of Larne, where a methane show has been detected (Griffith, 1983).
(iii) uraniferous nodules in Middle Devonian siltstones/fine sandstones in an Easter Ross section showing numerous faults of small throw (Parnell, 1985*a*). Nodules also occur in sandstone interbeds in an underlying conglomerate.

Occurrences (i) and (ii) are summarized in Fig. 6. In these cases, there was already evidence, or reason to suspect, that buried hydrocarbon deposits occur at depth beneath the nodule localities. This was not the case with occurrence (iii). Occurrence (iii) was chosen for detailed study to test the viability of using carbonaceous nodules in red beds as a guide to buried hydrocarbons. It is suitable because the nodule-bearing beds are separated from a Precambrian gneissose basement (which cannot be a source of oil) by only 700–800 m of sedimentary rocks. If the nodules reflect the presence of buried hydrocarbons then the hydrocarbon reservoir must occur in these underlying rocks, although there is no previous record of such a reservoir. The outcrop to the north and west of the nodule-bearing exposures provides a cross-section through the underlying sequence.

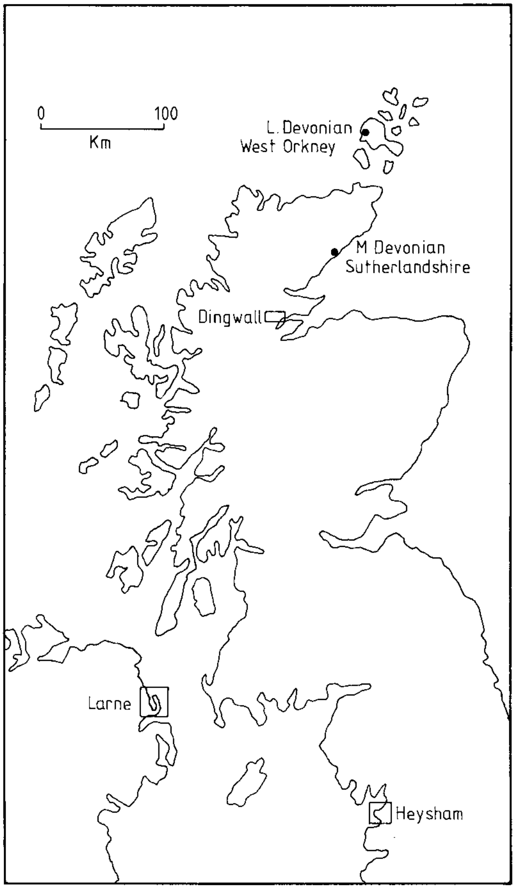

FIG. 5. Location of U.K. replacive hydrocarbons discussed in text, and of accretionary nodule occurrences in Figs. 6 and 7.

Mapping of the region (Fig. 7) showed that the nodule-bearing red beds are underlain by a conglomerate with no primary porosity. Underneath the conglomerate are sandstones, dolomitic siltstones and a lower conglomerate in descending order, resting on basement (Horne and Hinxman, 1914). The siltstones are kerogenous and plausible source rocks for petroleum (Parnell, 1985*b*). The sandstones immediately underlying the upper conglomerate were found to be locally black, in which cases they contained pore-filling hydrocarbon. Sandstone interlenses within the conglomerate were also found to be hydrocarbon-bearing. The conglomerate is fractured; some fractures are normal faults of small throw. Several fault planes

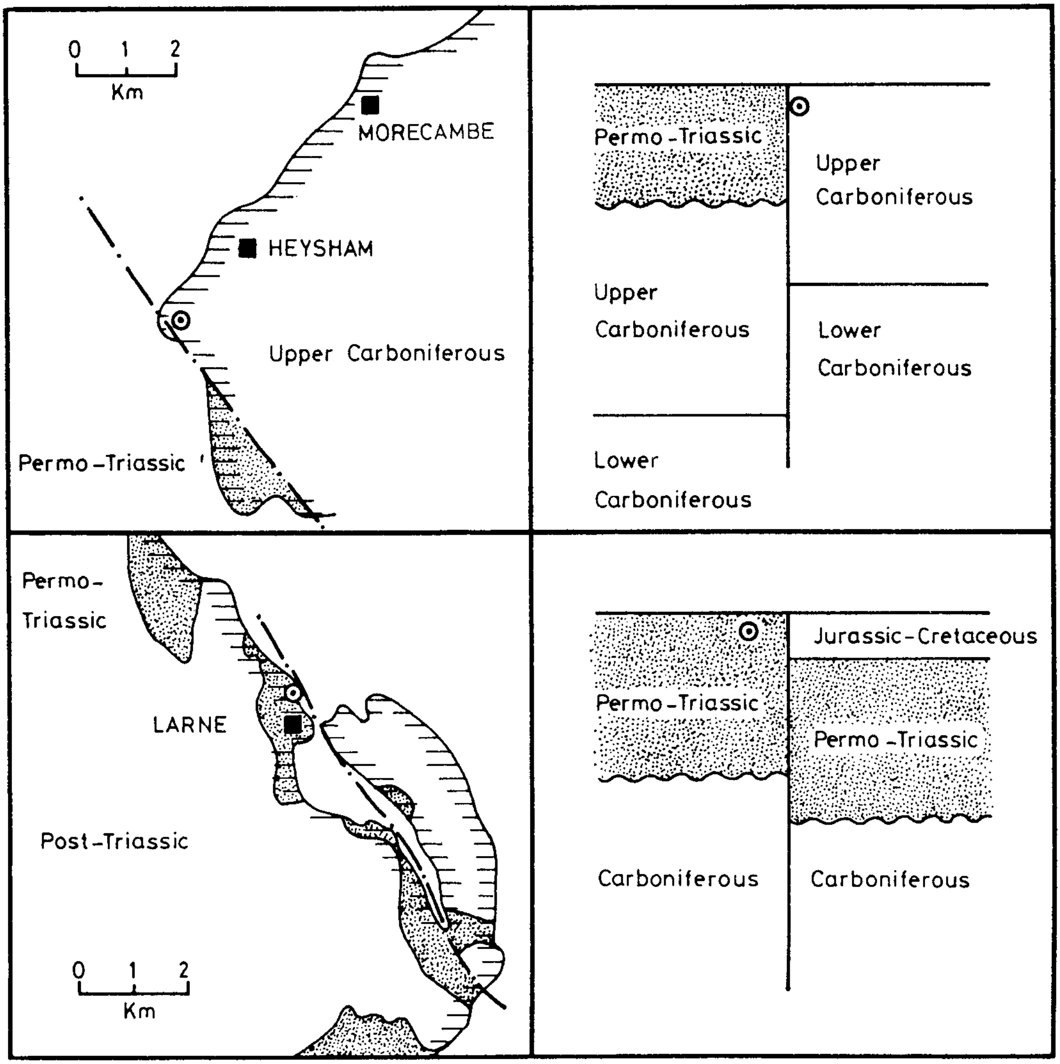

FIG. 6. Locations and schematic cross-sections of accretionary nodule occurrences at Larne and Heysham.

are now occupied by a solid brittle hydrocarbon. Detached fragments of wallrock occur in the hydrocarbon. Cobbles of Precambrian gneiss and quartzite in the conglomerate were fractured and the fractures were then coated with hydrocarbon and recemented by quartz.

These observations suggest that hydrocarbons accumulated in the sandstones underlying the impermeable conglomerate. Fracturing and faulting of the conglomerate then allowed the injection of hydrocarbons upwards through the conglomerate and into the overlying sandstone. There they were available for interaction with uraniferous groundwaters to form uraniferous, carbonaceous nodules. The uranium in Devonian red bed sediments in northern Scotland is believed to be derived from granitic basement (see Watson and Plant, 1979, for details).

In this study of an occurrence of replacive hydrocarbon nodules, hydrocarbons have been proven in an underlying sandstone reservoir which had not been previously recorded. There are however numerous instances of metalliferous carbonaceous nodules which are not spatially related to faults and/or hydrocarbon reservoirs. Similarly, we know of many examples of uraniferous

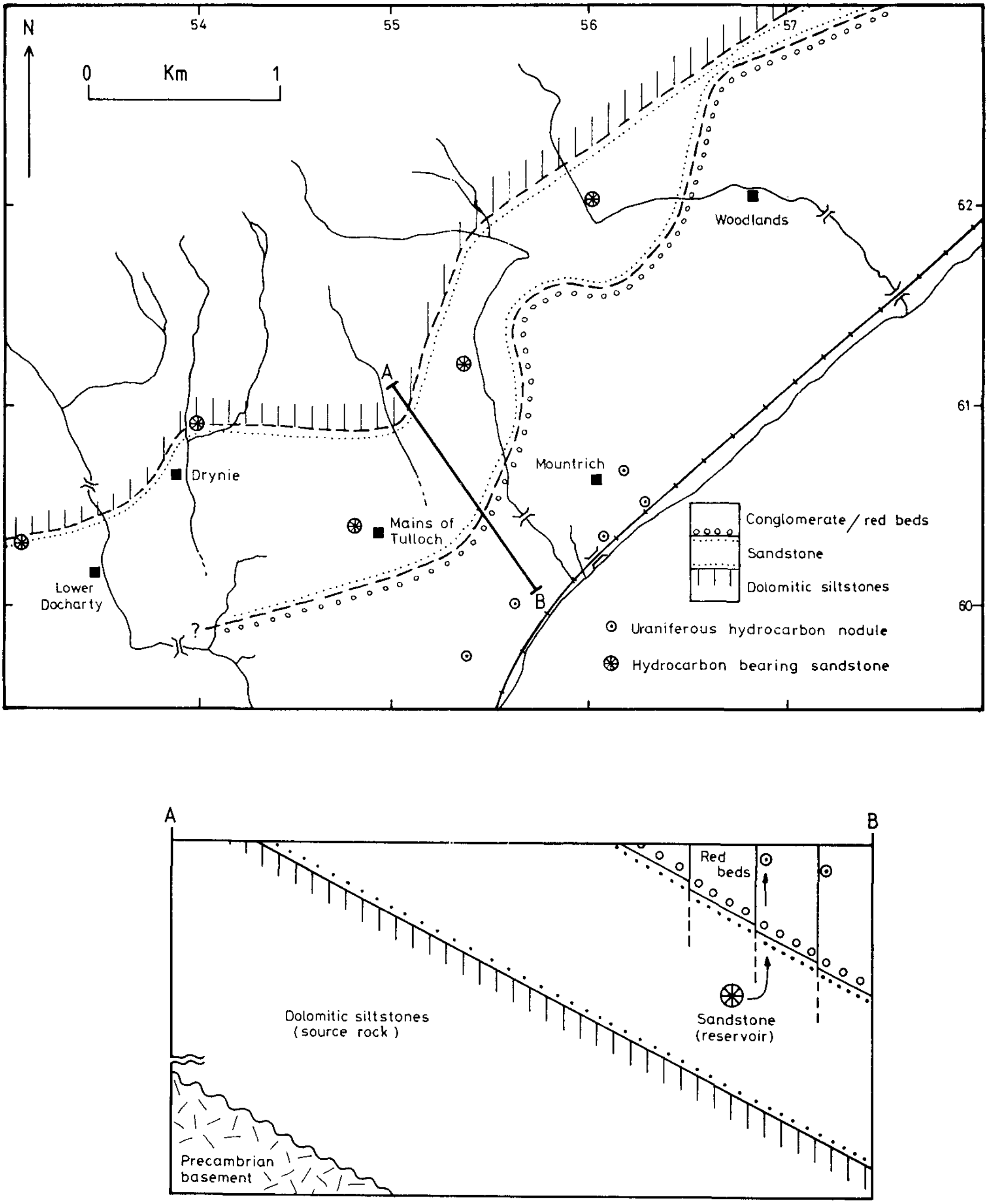

FIG. 7. Location and schematic cross-section of uraniferous hydrocarbon nodule occurrences and hydrocarbon-bearing sandstones in Devonian near Dingwall, Easter Ross. Occurrences of nodules led to mapping of underlying rocks and discovery of hydrocarbon-bearing sandstones.

hydrocarbons which are unlikely to indicate hydrocarbon reservoirs, particularly those in hydrothermal mineral deposits (e.g. Davidson and Bowie, 1951). Nevertheless metalliferous, carbonaceous nodules occur in the UK in several red bed sequences of Devonian to Triassic age and some are in basins where there is active prospecting for hydrocarbons. Normally when nodules are discovered they are studied for the concentration and distribution of metals within them, and the possible implication of more extensive mineralization. The successful exploration for hydrocarbons in this small-scale test case shows that it may be equally valuable to investigate the source of the carbon in these nodules.

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