Thorium–bitumen mineralization in Silurian sandstones, Welsh Borderland

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Abstract

The Llandovery Folly Sandstone near Presteigne, Powys, contains disseminated thorium mineralization. The thorium occurs as inclusions of thorite and thorianite within sub-millimetre-scale bitumen nodules throughout the sandstone. The nodules grew replacively *in situ*. The two square kilometres outcrop/subcrop of the sandstone may contain over 500 tonnes thorium.

KEYWORDS: thorium, thorite, thorianite, bitumen, Silurian, Wales.

Introduction

THORIUM mineralization is reported from Llandovery sandstones near Presteigne, Powys, in the Welsh Basin. The mineralization occurs throughout a 2 km long outcrop which spans the Wales–England border. The thorium occurs as thorite and thorianite inclusions within spherical bitumen nodules in the sandstone.

The host rock is the Folly Sandstone, a 30 m+ thick marine shelf sandstone of Llandovery C1 to C2 age (Ziegler *et al.*, 1968). The Folly Sandstone is overlain by the Wenlockian Nash Scar Limestone, but the base of the sandstone is not exposed. The Llandovery and Wenlock rocks form an inlier, amongst younger Silurian rocks, along the line of the Church Stretton Fault. Another inlier of early Silurian rocks along the fault at Old Radnor, 5 km to the south west, exposes underlying Longmyndian (Precambrian) basement of sandstones and shales (Kirk, 1951). This basement probably also occurs below the Folly Sandstone.

Samples were collected along the length of the sandstone outcrop at Corton House Quarry, Folly Road, several localities along the B4362 in Nash Wood, and above Nash Scar Limestone Quarry (Fig. 1). Details of localities are given by Ziegler (1966). Samples from all localities contain bitumen nodules with thorium mineralization.

Occurrence

The host sandstones are fossiliferous, subarkosic, fine to medium grained, with lensoid pebble bands. The sandstone matrix consists of chloritic clays and iron oxides, and fresh samples contain traces of calcite cement. The bitumen occurs as nodules up to 1 mm diameter and average 0.3 mm diameter (Fig. 2). A cubic centimetre of sandstone contains up to 200 nodules (0.3% of volume) and an average of 30 to 50 nodules. Excepting in pebble bands, the bitumen nodules are significantly larger than the grains in the sandstone. Rare examples of coalesced nodules have been observed, which suggest growth *in situ* rather than a detrital origin. The nodules are of a replacive nature. The margins of round quartz grains are replacively disrupted by the nodules and, remarkably, nodules even occur within the outer parts of quartz pebbles (Fig. 3). Replacement is a characteristic property of uraniferous bitumens in sandstones (Parnell and Eakin, 1987) and replacive spherical bitumen nodules rich in uranium are described by several workers (e.g. Harrison, 1970; Curiale *et al.*, 1983; Parnell, 1985). However, thorium-rich bitumen nodules are not documented elsewhere.

Composition

The bitumen nodules in the sandstone have been studied by electron microprobe analysis/electron microscopy. Each nodule contains several domains of thorium mineral inclusions (Fig. 4) separated by zones of thorium-free bitumen. The largest inclusions (2–5 μm across) are the oxide thorianite. Most inclusions of less than 2 μm are the silicate thorite. (N.B. probe analyses have not excluded the hydrated silicate thorogummite). The thorite

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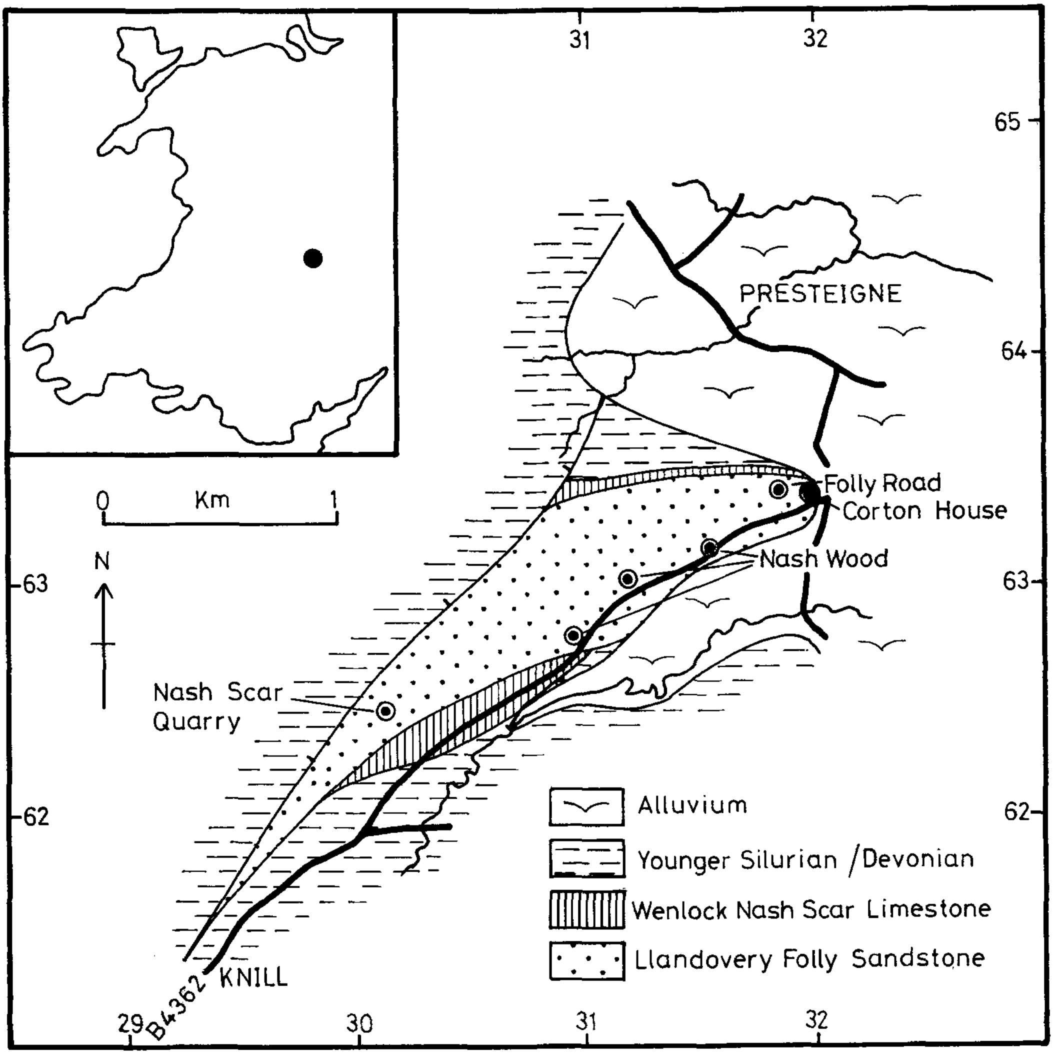


FIG. 1. Location of Folly Sandstone, and of particular localities where thorium-bearing nodules were collected (see text).

characteristically contains variable traces of calcium and phosphorus. Uranium has not been detected. In addition to thorium minerals, micron-scale inclusions of quartz and baryte are sparsely scattered within the nodules. The bitumen is rich in sulphur (up to 3%) which does not appear to be related to metals and is therefore probably organically bound.

Analyses of whole nodules show that the bitumen has an average thorium content of about 0.75%. Assuming a minimum thickness of 30 m sandstone over an area of 2 km^2, a density of 40 nodules per cm^3, and a measured rock density of 2710 kgm^{-3}, we calculate that the outcrop holds in excess of 500 tonnes thorium.

Discussion

Thorium mineralization normally occurs in pegmatites, metasomatized limestones and hydrothermal veins; and economic deposits take the form of thorite, thorianite or thorium-rich monazite placers. Thorium enrichments are reported from solid bitumens elsewhere, in which the thorium may be evenly distributed as metallo-organic complexes, or as discrete inclusions of thorite or

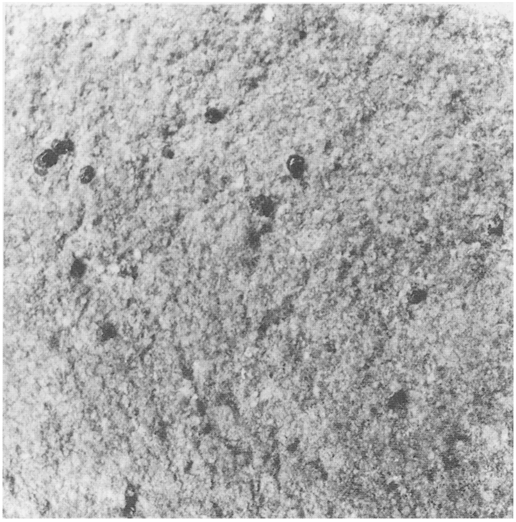
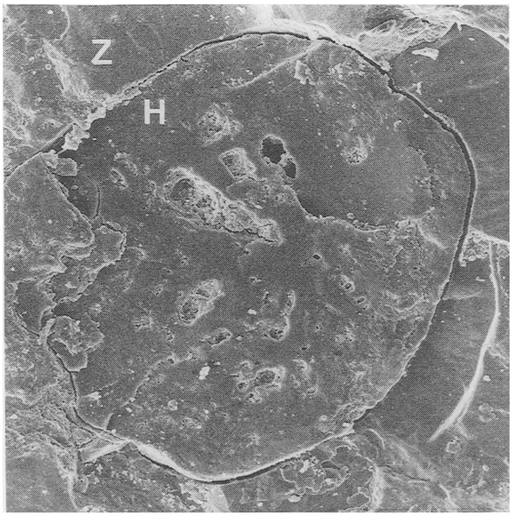


FIG. 2. Bitumen nodules on bedding surface of Folly Sandstone, Nash Wood (field width 15 mm).

thorianite (Boyle, 1982). However these occurrences are generally vein-hosted or occur within pegmatites (e.g. Davidson and Bowie, 1951). Sandstone-hosted thorium–bitumen mineralization is exceptional.

Genesis. Vein-hosted bitumens in the Nash Scar Limestone do not contain thorium minerals; nor do other bitumens analysed from Powys. This suggests that the thorium-rich nodules in the Folly Sandstone were formed by an interaction of migrating bitumen with thorium in the sandstone. Uranium-rich bitumen nodules in red beds elsewhere have similarly been interpreted as the result of merging petroleum fluids with uraniferous groundwater (Roberts, 1980; Curiale *et al.*, 1983; Parnell and Eakin, 1987). The thorium could be concentrated by bitumens due to absorption or by fixation as thorium–organic complexes. Subsequently, radiation from the decay of thorium would cause polymerization of the organic molecules and the precipitation of thorium minerals from the carbonized bitumen (Boyle, 1982). The occurrence of replacive nodules in quartz pebbles is typical of sandstone-hosted uranium and thorium mineralization with or without bitumen, and the replacement process is therefore probably due to a property of the thorium-bearing groundwaters.

Alternatively, the thorium may have been in mineral form when the interaction took place. The formation of thucholites (bitumens rich in thorium, uranium, and rare earth elements) is often initiated by the precipitation of bitumen around a pre-existing grain of a thorium/uranium mineral. The precipitation process would be caused



FIGS. 3 and 4. FIG. 3 (*left*). Bitumen nodule (H) within quartz pebble (Z) in Folly Sandstone, Nash Wood. Bitumen must have replacive origin. Cavities in nodule represent sites of large inclusions, weathered out (field width 250 μm). FIG. 4 (*right*). Bitumen nodule in sandstone. Nodule consists of domains of thorite inclusions (dark grey) cross-cut by thorium-free veins (black). Largest inclusions (as arrowed) are thorianite. Host sandstone consists of quartz (light grey) in matrix of chloritic clays and iron oxides (white) (backscattered image of polished surface, field width 500 μm).

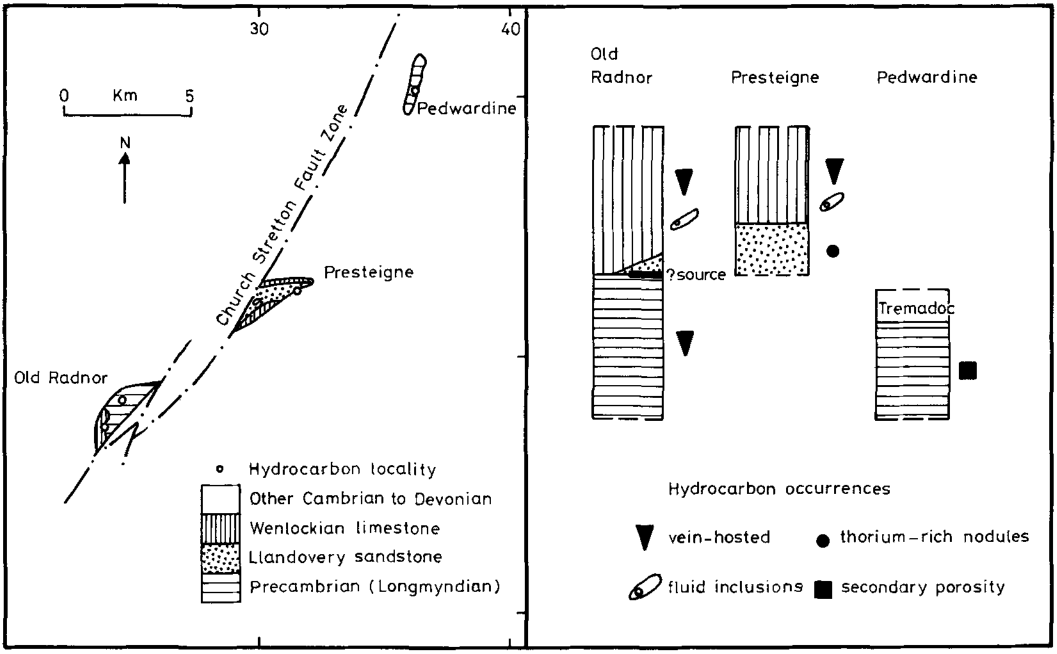


FIG. 5. Presteigne and other inliers along Church Stretton Fault Zone, with schematic successions and distribution of hydrocarbon types. The source rock exposed at Old Radnor is black shale which may be of Longmyndian or Llandovery age (see text).

by the polymerization of fluid hydrocarbons due to radiation from the radioactive element(s) (see Schidlowski, 1975, and Curiale *et al.*, 1983, for discussion of this mechanism). In many instances thucholites exhibit subsequent replacement of a uraninite nucleus by the bitumen (e.g. Welin, 1964; Schidlowski, 1975). One explanation for the nodules in the Folly Sandstone is that detrital grains of a thorium mineral nucleated the precipitation of bitumens, and the thorium mineral was partially replaced by the bitumen with some redistribution of the thorium. The size of the nodules necessitates expansion from the original grain size. Expansion could be due to (*a*) mineralogical changes and/or (*b*) thermal expansion of the thorium mineral due to the heat of radioactivity. Uraninite replaced by bitumen often exhibits a volume increase (e.g. Welin, 1966*a*, *b*) and the affect of radioactive heating is recorded even in minerals with a relatively low thorium content such as allanite (Heinrich, 1958). The cross-cutting zones of thorium-free bitumen could be formed during the expansion process. Welin (1964) similarly records uranium-rich bitumens cut by a network of non-radioactive bitumen veinlets. If the replacement theory is correct, the primary mineral was probably thorite or thorianite, as there are no traces of cerium or lanthanum which would have been expected from replaced monazite. A source rich in thorite or thorianite but without monazite is difficult to envisage, and an authigenic origin for the thorium minerals seems more likely.

Provenance. The likely source of the bitumens can be assessed from the distribution of bitumens in other rocks in the region (Fig. 5). The Nash Scar Limestone which overlies the Folly Sandstone is cross-cut by calcite veinlets which contain brittle solid bitumens and quartz crystals with hydrocarbon fluid inclusions. Heating of the inclusions caused the irreversible precipitation of solid bitumen within them. The nearby Old Radnor inlier similarly contains bitumens within Wenlockian limestones and the Longmyndian basement. There, the bitumens are similarly vein-hosted and occur as brittle solids, waxy solids and fluid inclusions. Bitumens in the Pedwardine inlier occur in secondary porosity after the dissolution of feldspar grains. A thick sequence of deformed black shales outcrops in the Old Radnor inlier, possibly of Longmyndian or Llandovery age (see Davies *et al.*, 1983). Organic geochemical studies of limited extracts from the shales and solid bitumens suggest that they can be correlated (Bath *et al.*, 1986). Other bitumen shows in Powys are also of Lower Palaeozoic origin (Parnell, 1983), and it seems likely that the bitumens in the Folly Sandstone have a similar source. The nearest Carboniferous rocks containing hydrocarbons are Dinantian limestones at Merthyr Tydfil, 50 km distant, and Westphalian sandstones at Row Brook, Shropshire, 45 km distant. Carboniferous rocks do not seem to be a plausible source, although the Merthyr rocks do contain quartz crystals with hydrocarbon fluid inclusions very similar to those at Nash Scar and Old Radnor. Inclusions from all three localities yield uncorrected homogenization temperatures in the range of 90 to 140 °C.

The source of the thorium is unknown. Lower Palaeozoic rocks in the main part of the Welsh Basin to the west are widely mineralized by lead, zinc and copper (Ball and Nutt, 1975). Minor baryte-chalcopyrite-tennantite mineralization was recorded during this study in the Old Radnor inler. However, there are no records of thorium minerals in these deposits. The nearest bitumens which are significantly uraniferous are in Triassic rocks at Knowle, 85 km to the east (Harrison *et al.*, 1983) and in Carboniferous Limestone at Halkyn, 110 km to the north (Bath *et al.*, 1986). They do not contain thorium. If the thorium was originally present as detrital grains, a possible source would be Malvernian (Precambrian) rocks which were exposed 45 km to the east during Llandovery times (Parnell, 1987). The Malvernian basement is locally rich in pegmatite veins, although petrographic studies have not revealed thorium-bearing minerals (Lambert and Holland, 1971). Petrographic studies of the Longmyndian sandstones similarly do not show anomalous concentrations of monazite.

Read *et al.* (1987) have recently reported the occurrence of abundant monazite nodules in sedimentary rocks of Ordovician and Llandovery age, to the west in central Wales. The monazites are recrystallized and/or overgrown on detrital monazites from a granite/pegmatite source. However, the thorium contents are low for granitic monazites, and Read *et al.* (1987) suggest that thorium has been selectively lost from the monazite during weathering, sedimentation and recrystallization. The thorium lost from these monazites elsewhere in the Lower Palaeozoic of the Welsh Basin may be responsible for the nodular concentrations of thorium in the Folly Sandstone.

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