Metal enrichments in solid bitumens: A review

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Abstract. The association of oils and solid bitumens with ore deposits is widely recorded. The oils and bitumens may actually be enriched with metals. Unlike oils, metal enrichments within bitumens do not reflect the role of petroleum as a transporting agent for metals. By contrast, they may be a result of the reduction of metal ions on contact with bitumen, and may reach levels so high that ore mineral inclusions are precipitated. Metal determinations of British bitumens suggest that new metal anomalies can be detected by this approach, that some metal anomalies within bitumens may be related to ore mineralization, and that bitumens from different sources may be distinguished by their metal contents. The potential use of bitumen distribution and/or metal enrichment within bitumen for ore exploration is dependent on the metal concerned, and in particular whether the metal is *transported* by association with organic materials or *reduced* in the presence of organic materials.

It is well known that many occurrences of metalliferous minerals, including large ore deposits, are associated with oil or bitumens (*sensu lato;* discrete *solids* based upon hydrocarbons and organic NSO compounds). In the literature, attention has focused predominantly on the association of bitumens with Mississippi Valley-type lead-zinc deposits (e.g. Anderson and McQueen 1982) and uranium deposits (e.g. Breger and Deul 1959). However, several other metalliferous minerals also regularly occur in association with bitumens. This is not surprising as hydrocarbons and metals are both transported in aqueous media, particularly under hydrothermal conditions (Roberts 1980). In some cases the association may be casual, but in others the hydrocarbon-bearing fluids may have influenced ore deposition. Their role might simply be the deposition of metals and/or sulphides by reduction processes where metal-bearing and hydrocarbon-bearing fluids meet. Alternatively, hydrocarbons may play a role in the transport of metals through the formation of organometallic complexes. Both mechanisms have been proposed for Mississippi Valley-type ore genesis (see Giordano 1985 for a recent review). Dunsmore and Shearman (1977) have suggested a synthesis of both, in which an oil-brine emulsion might carry metals, hydrocarbons *and* sulphates, and then sulphate reduction is triggered at the site of ore deposition by some localised biochemical/geo-

chemical processes. The significant metal contents in many samples of oils and oilfield brines (Sverjensky 1984; Manning 1986) suggest that petroleum may play an important role in ore metal transport. This study assesses the occurrence of high metal contents in *solid* bitumens, many of which are oil residues, and reviews the range of ore deposits with which bitumens are associated.

Metal determination in bitumens

The determination of trace metal concentrations in petroleum has been greatly assisted by neutron activation analysis (Filby and Shah 1975; Bergerioux and Zikovsky 1978; Bannikova et al. 1984). This technique is particularly advantageous because it utilizes very small samples, sensitivity is high, interferences and matrix effects are minimal, the technique is non-destructive, and volatile elements are not lost because heating is not involved (Filby and Shah 1975). In this study metals in handpicked solid bitumen samples from Great Britain were determined using neutron activation analysis.

The samples were irradiated in the Imperial College reactor at Silwood Park, Ascot. Vanadium, copper and dysprosium were determined by irradiation for 5 minutes in a pneumatic irradiation system (cyclic activation system, see Burholt et al. 1982) in the reactor core (thermal neutron flux $10^{12} \text{n cm}^{-2}\text{s}^{-1}$) and counted for 5 minutes after 30 seconds decay. Cobalt, iron, uranium and molybdenum were determined by re-irradiation for an average of 22.5 hours and counted for 90–120 minutes after 4 days decay. A few very active samples were measured after irradiation for 10 seconds under a cadmium filter in the epithermal neutron irradiation tube (flux $4 \times 10^{10} \text{n cm}^{-2}$ s^{-1}) and counted for 60 seconds after a 1-second decay. Analyses were performed using a ND 6620 analyser system with software packages for peak search and evaluation. Hydrogen and carbon were determined using a Perkin-Elmer PE240 elemental analyser.

Data

The bitumen samples from Great Britain yielded a range of metal concentrations from negligible values up to the *per cent* level. Some of the data has been reported elsewhere in studies of individual regions (Parnell 1983a, 1984).[*] Points of interest from the data base include the

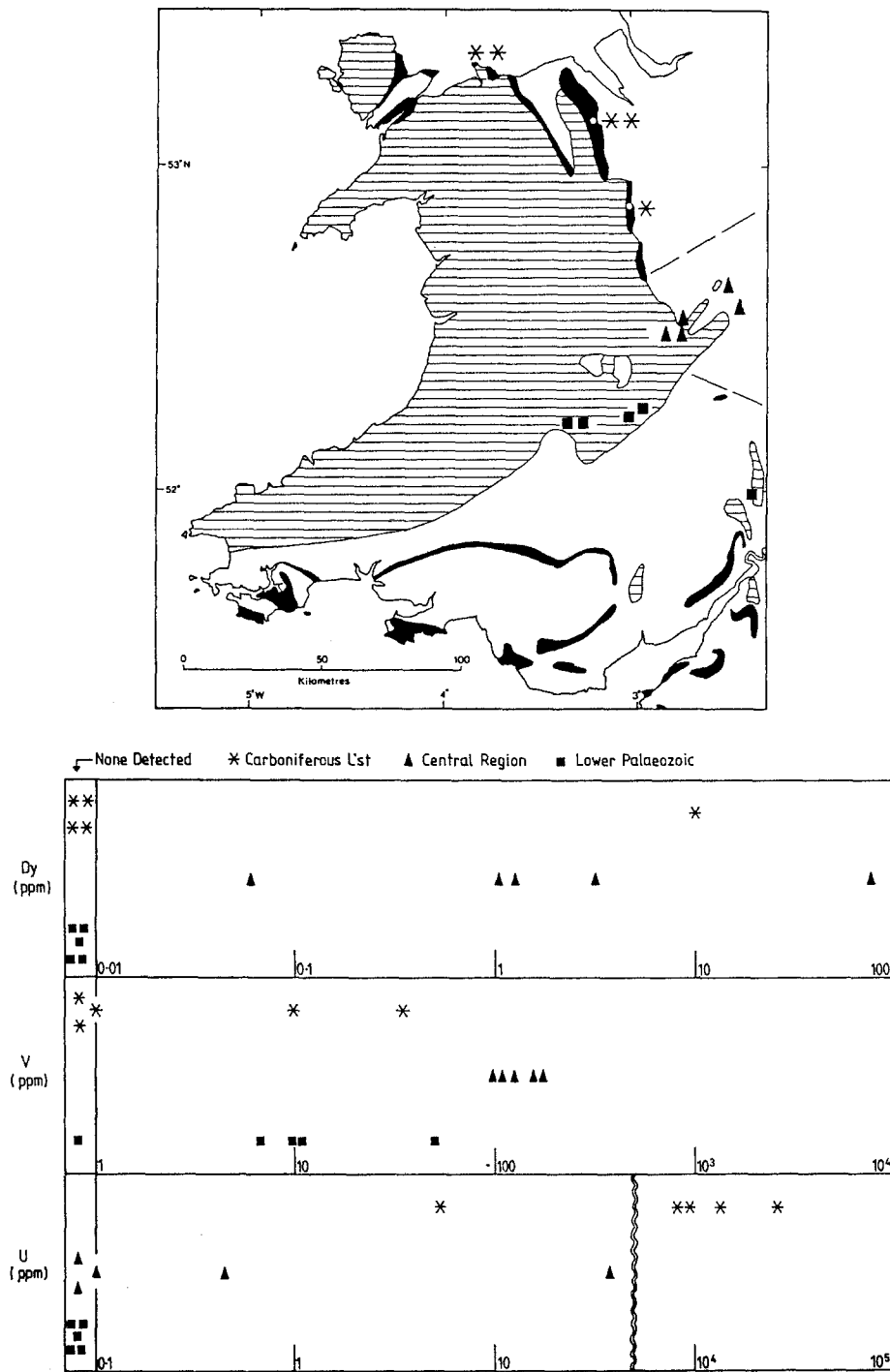*Note:* The complete data set is available from the author

Fig. 1. Bitumen sample localities in the Welsh Borderland for Dy/V/U determination by neutron activation analysis. Pre-Devonian outcrop is ruled, Carboniferous limestone outcrop is solid. Data plot shows different patterns from 3 regions (see Text). Scales are logarithmic; note break in uranium scale

following:

(1) Uranium is present in measurable quantities (up to 20%) in many samples associated with hydrothermal mineralization. In the richest samples, from Laxey, Halkyn, Great Ormes Head and Southwick (Fig. 4), discrete inclusions of uraninite can be identified using electron microscopy (Fig. 3). Some localities were already known to yield uranium-rich material. The occurrences of uranium mineralization at Halkyn and Craig Well (Parnell and Eakin 1987) were first established during this survey.

(2) Iron and cobalt are commonly present in the ranges 0.1%–1% and up to 10 ppm, respectively.

(3) Copper is present in concentrations of up to several thousand ppm in bitumens associated with copper ore mineralization in the Welsh Borderland and the Midland Valley of Scotland (details of the association with copper deposits are given in Parnell 1983 a, 1984).

(4) Vanadium was usually detected in the range 0–200 ppm as was expected because of the affinity of vanadium for organic matter (Lewan and Maynard 1982). Specimens of jet (i.e. fossil wood impregnated with bitumen) yield vanadium values higher than 200 ppm.

(5) The contents of dysprosium (and possibly other rare earth elements) may be of value in discriminating between bitumens from different sources. In the Welsh Borderland,

some bitumens are probably the residues of oil sourced from Carboniferous rocks, whilst other bitumens are derived from Lower Palaeozoic rocks (Parnell 1983a, 1987). Dysprosium, vanadium and uranium were determined in five samples from each of three areas; (1) a region of Carboniferous limestone in the north, (2) a central region adjacent to Upper Carboniferous Coal Measures and (3) a region of Lower Palaeozoic rocks in the south (Fig. 1). The data in Fig. 1 show different patterns for the three regions. Samples from the northern region generally contain high uranium, low vanadium and low dysprosium. Samples from the central region contain low uranium, significant vanadium and significant dysprosium. Samples from the southern region contain measurable vanadium, but no measurable uranium or dysprosium. These results suggest that metal determinations in bitumen deposits may have a value in delimiting samples from different sources. However, epigenetic enrichments of bitumens by metals (see below) negate a simple relationship between source and metal content. Whilst the difference between areas 2 and 3 in Fig. 1 may reflect a genuine difference in source, the high uranium values from area 1 strongly suggest epigenetic enrichment of the bitumens there so that areas 1 and 3 cannot be discriminated by source.

(6) Qualitative assessment of peak search data suggests that many samples also contain nickel and calcium, but very few contain detectable lead or zinc. Mercury was not recorded in any sample (see below).

It is plausible that the metal content of bitumens may be partly controlled by the mode of origin of the bitumen. A plot of atomic H/C ratio against vanadium concentration (Fig. 2) helps to assess this. The bitumens are distinguished according to whether they are formed by the alteration of reservoir hydrocarbons (reservoir bitumens of Rogers et al. 1974), by local mobilization from hydrocarbon source rocks during diagenesis/early catagenesis or by hydrothermal differentiation and hydrothermal-igneous contact metamorphism (see Mueller 1972 for detailed classification of mobilizates). The origins of most of the bitumens analysed in this study are discussed by Parnell (1983a, 1983b, 1984). The three types of bitumen plot in

distinct fields. The hydrothermal bitumens generally have lower H/C ratios (more thermally altered), and both types of local mobilizate contain relatively low vanadium contents compared with reservoir bitumens. The possibility that metal content might be related to thermal maturity (as expressed by the H/C ratio) is not supported by this data set. Rather, vanadium is concentrated in those samples which are residues of petroleum, and therefore probably migrated in the petroleum from the source rock. By contrast, vanadium does not appear to have been transported with the bitumens generated by rapid thermal processes or by localised diagenetic processes.

Interpretation is limited because the bitumens were collected from many regions and therefore represent many different source rocks, which are likely to have had different metal concentrations. Further investigations using a range of samples from a single basin are desirable.

Discussion

Metal-organic interactions

Metals which occur as an intrinsic component of bitumens could have been either (a) inherited from the hydrocarbon source rock as organometallic complexes (all living tissues contain organically bonded metals, and although much metal will be released after death, some will survive to form an enrichment within the enclosing sediment and in subsequently generated oils. Organophilic elements include vanadium, nickel, molybdenum, selenium and rhenium; Poplavko et al. (1978) (b) scavenged by migrating hydrocarbon-bearing fluids or (c) deposited in the bitumens at the site of mixing of metal-bearing and hydrocarbon-bearing fluids (e.g. Roberts 1980). Hydrogen sulphide for sulphide precipitation would be generated by redox reactions between petroleum and sulphates, or directly from sulphurous petroleum by thermal maturation or biodegradation. Saxby (1976) distinguished five modes of interaction between the dissolved metals and organic materials (bitumens and source rocks) which would result in mobilization or immobilization of the metals: (1)
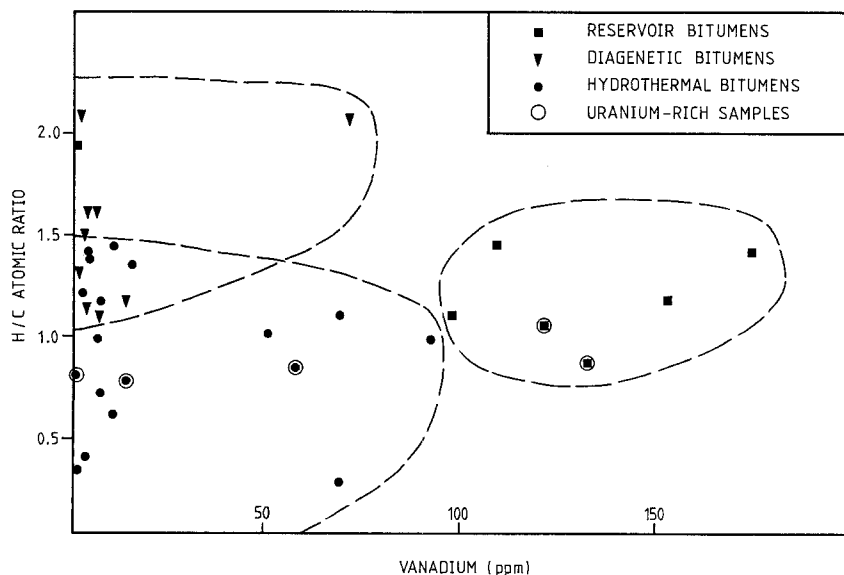

Fig. 2. Plot of atomic H/C ratios of British bitumens against vanadium concentration. Bitumens plot in different fields according to their origin. Uranium-rich samples are further distinguished, but do not correlate with vanadium enrichment
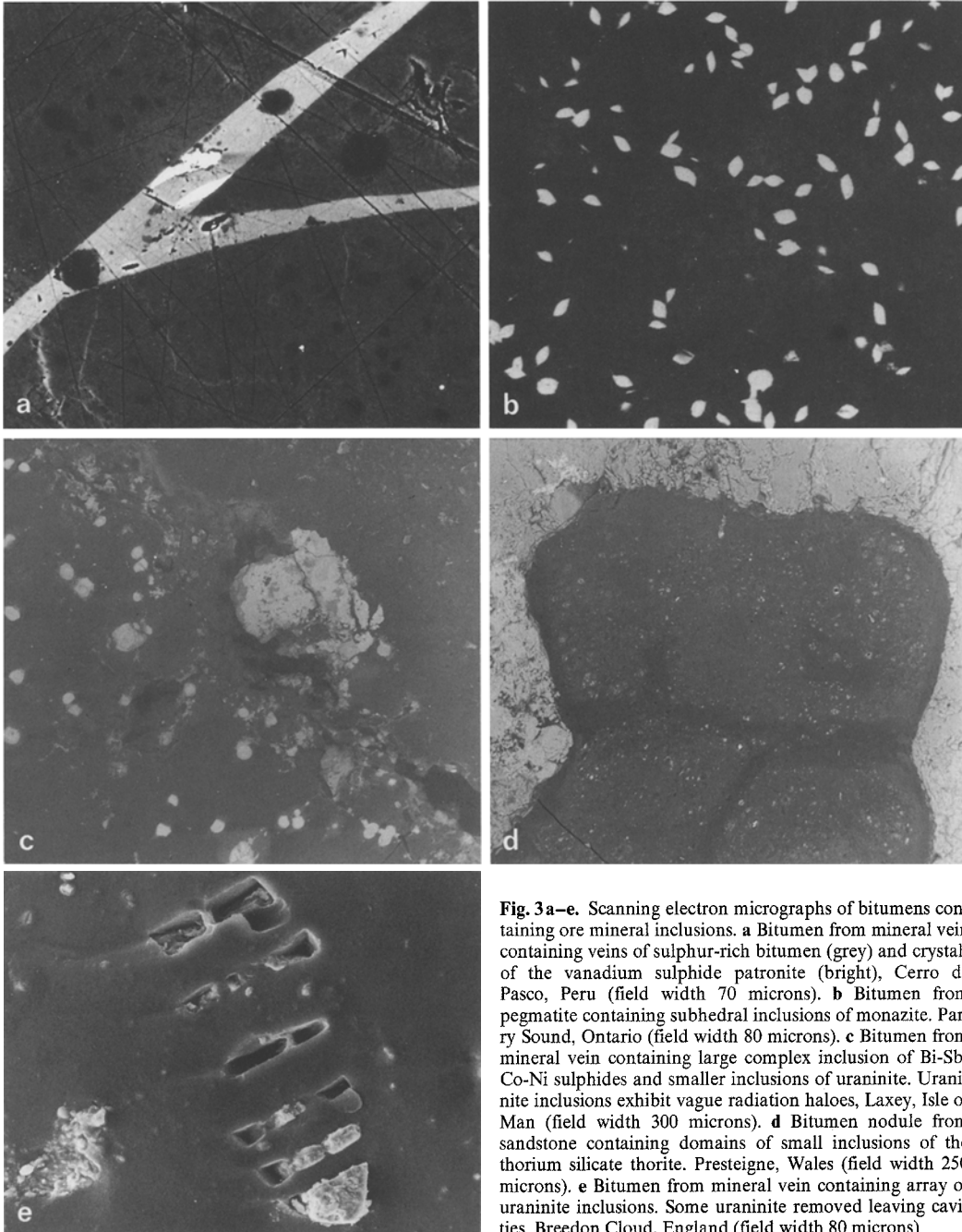
Fig. 3a–e. Scanning electron micrographs of bitumens containing ore mineral inclusions. **a** Bitumen from mineral vein containing veins of sulphur-rich bitumen (grey) and crystals of the vanadium sulphide patronite (bright), Cerro de Pasco, Peru (field width 70 microns). **b** Bitumen from pegmatite containing subhedral inclusions of monazite. Parry Sound, Ontario (field width 80 microns). **c** Bitumen from mineral vein containing large complex inclusion of Bi-Sb-Co-Ni sulphides and smaller inclusions of uraninite. Uraninite inclusions exhibit vague radiation haloes, Laxey, Isle of Man (field width 300 microns). **d** Bitumen nodule from sandstone containing domains of small inclusions of the thorium silicate thorite. Presteigne, Wales (field width 250 microns). **e** Bitumen from mineral vein containing array of uraninite inclusions. Some uraninite removed leaving cavities. Breedon Cloud, England (field width 80 microns)

chemisorption of metals into organic materials, (2) physical adsorption of metals onto organic materials, (3) precipitation of organometallic compounds by reaction of metals with organic ligands, (4) change in oxidation state, particularly reduction of metals by organic materials and consequent mineral precipitation and (5) mobilization of metals by the formation of organometallic complexes and subsequent deposition of ore minerals after destabilization of the complex.

Ore mineral inclusions. Very high metal enrichments necessitate the existence of microscopic inclusions of ore minerals within the bitumens. The mineralogy of the inclusions was investigated using backscattered electron imagery, in which the intensity of a mineral's image increases with the atomic number of the constituent elements and is therefore high for metallic ore minerals. A range of examples is illustrated in Fig. 3. Pyrite is particularly common as inclusions and is responsible for the very high iron contents recorded above.

The inclusions within bitumens could be formed in the following ways:

(1) The inclusions may represent remnants of a mineral which has been partially replaced by the bitumen. Many instances of uraninite inclusions have been interpreted as
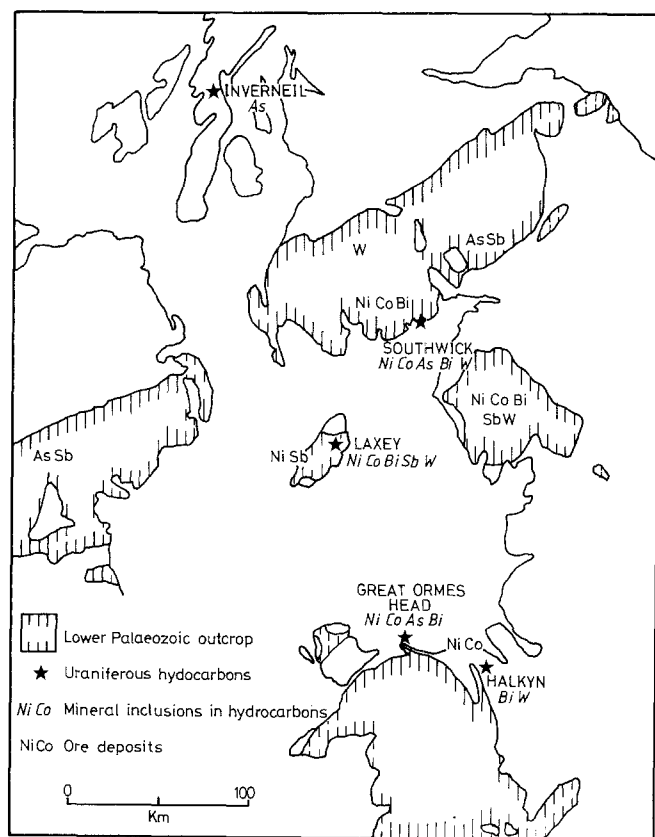
Fig. 4. Localities for uraniferous bitumens, indicating content of inclusions of the Co-Ni-Bi-W-Sb-As assemblages, and proximity of ore deposits of the same assemblage in the central British Isles

residual after replacement by bitumen which nucleated about the uraninite (e.g. Davidson and Bowie 1951).

(2) The inclusions may be ore minerals physically transported within the once fluid hydrocarbon; Mueller (1951) and Leventhal et al. (1987), for example, interpreted the irregular sulphide fragments within bitumens from England and Canada, respectively, to represent fragments abraded from a mineralized zone by migrating hydrocarbons.

(3) The bitumen and ore mineral inclusions may be coeval, precipitated from a common fluid. Spherular interfaces between inclusions and the host bitumen and inclusions of bitumen within the ore mineral suggest synchronous precipitation.

(4) When a metal is concentrated within a bitumen by continuous absorption of metal or loss of hydrocarbons, at some stage the metal can no longer be accommodated as an organometallic complex and will have to precipitate as an inorganic mineral. Thus, bitumens with exceptionally high vanadium contents contain the vanadium sulphide patronite (Fig. 3a) and uraniferous bitumens contain uraninite (Fig. 4e). Sulphide and oxide anions can be derived from sulphur and oxygen involved within the organometallic complexes (see Yen 1975 and Rouzaud et al. 1980 for the role of sulphur and oxygen in complexing vanadium and uranium, respectively). With increasing time and/or temperature and consequent decreasing H/C ratio of the bitumen, metals originally bound in organic form may precipitate out. This process has been demonstrated experimentally using uranium-organic complexes by Rouzaud et al. (1980).

(5) During the maturation of bitumens, loss of the more volatile fractions results in the development of contraction fractures. Bitumens formed by gas deasphalting may contain gas bubbles (Rogers et al. 1974). Such fractures and cavities may be filled by ore minerals precipitated by reduction from metalliferous fluids. Bitumens deposited in pegmatite veins (see below) often contain exotic fracture-fills (Fig. 3b).

(6) Uraniferous bitumens often contain very small inclusions of galena even where no other lead mineralization is present in the deposit. The galena can occur within the bitumen matrix, but particularly occurs within the uraninite inclusions. The lead in the galena is a daughter product of the radioactive decay of uranium (e.g. Borshchevskii 1959).

The metal enrichments in solid bitumen can clearly be much higher than in petroleum or oilfield brines, especially if the bitumens contain metal inclusions (see Manning 1986 for summary of metal contents in petroleum). In addition, metals which are normally transported in oxidizing conditions and do not reach high levels in petroleum, including copper and uranium, may be highly enriched within bitumens. Some elements, such as lead and antimony, may be almost entirely restricted to mineral inclusions as opposed to organometallic complexes. The metal contents of bitumens are therefore not a guide to the role of petroleum as a transporting agent for metals. On the contrary, the metal enrichments are in some cases due to the reductive properties of organic materials which would make transport in petroleum improbable.

Organometallic complexes include compounds in which metallic cations are bonded to heteroatoms (including N, S, O) in a variety of structures and polar complexes in which cations are bonded electrostatically to polar functional groups such as carboxyl radicals (Yen 1975). Tetrapyrrole groups are an important type of complex in which cations are bonded to four nitrogen atoms. The role of these complexes in metal transport and deposition remains to be fully assessed, but it is clear that some compounds such as humic acids are particularly effective in the transport of metals, including copper, lead and zinc (Ong et al. 1970). Metals transported in this way could ultimately be enriched within solid organic materials. On the other hand, the interception of migrating hydrocarbons by metal-rich groundwaters, rather than hydrocarbon/metal cotransport, is probably responsible for a substantial number of metalliferous hydrocarbon occurrences. The nature of the bitumen-ore association and its consequence for ore exploration varies according to the relative importance of transport as organometallic complexes and fluid mixing.

Metal-bitumen associations and their significance for exploration

Vanadium, nickel. Vanadium and nickel have a marked facility for forming organic complexes, including tetrapyrroles which are found in living organisms, organic sediments and oil (Lewan and Maynard 1982). Tetrapyrroles are still preserved in some bitumens (e.g. Sugihara and McGee 1957). During diagenesis in source rocks, the metals in most organometallic complexes will be substituted by vanadium and nickel (Saxby 1976). Vanadium and nickel tetrapyrroles, including porphyrins, have a high

thermal stability compared to other organometallic complexes (Lewan and Maynard 1982). Hence, enrichments of these metals in the organic matter of source rocks are reflected as enrichments within petroleum. The metals are progressively concentrated in bitumens over their petroleum precursors (Curiale and Harrison 1981). Metals, sulphur and asphaltene contents show good correlations. Metals are particularly concentrated in the asphaltene fraction of oils and bitumens (Reynolds et al. 1984); hence degraded oils and bitumens, which are enriched in asphaltenes, contain more vanadium and nickel than their non-degraded equivalents. The proportion of asphaltenes increases with sulphur content (Huc et al. 1984), and non-porphyrin-bound vanadium is probably in coordination with sulphur (Yen 1975; Reynolds et al. 1984).

The role of bitumens in exploration for vanadium is straightforward. Bitumens may contain concentrations of vanadium so great that they themselves constitute vanadium ores. Bitumen veins in Cretaceous limestones in Peru and Argentina were once mined as a source of vanadium (Abraham 1945). The vanadium-rich bitumens contain inclusions of the vanadium sulphide patronite (Fig. 3a). The organic-rich shales which are the probable source rocks for the bitumens also contain high vanadium contents (Baragwanath 1921), which supports the hypothesis that the vanadium is organically bound and migrates within petroleum (see Manning 1986 for discussion of vanadium and nickel transport with petroleum). The bitumen veins in Peru, Argentina and Venezuela are also enriched in nickel. High levels of vanadium and nickel in Venezuelan oils and coals have been related to vanadium and nickel ore deposits which are likely to have been in the watershed during coal and oil source rock deposition (Kapo 1978). Venezuelan and Colombian oils and bitumens also contain high molybdenum levels (1000 ppm in a Colombian bitumen), and by analogy Kapo (1978) suggests that this may reflect a molybdenum ore deposit in a palaeowatershed which remains to be discovered.

Lead, zinc, Lead-zinc ores are associated with bitumens in two particular settings, i.e. limestone and black shale sequences. Bitumens are very commonly observed in Mississippi Valley-type (MVT) lead-zinc deposits, where they occur in mineral veins and fillings of vuggy porosity. Well-known examples of bitumen-bearing MVT deposits are in the type area in the Mississippi Valley (Marikos et al. 1986), the Pine Point orefield in Canada (MacQueen and Powell 1983) and the Cambro-Ordovician limestones of the United States and Canadian Appalachians (e.g. Sangster 1980). A much-studied locality at Windy Knoll in England exposes bitumen containing crystals of sulphides and gangue minerals at an unconformable contact between Carboniferous limestone and overlying Carboniferous shales (Pering 1973). Hydrothermal fluids were channelled along the unconformity, where oil had accumulated in a topographic trap (Pering 1973). Bitumen also occurs in lead-zinc deposits in the Carboniferous limestone of Wales (Parnell 1983a), Eire and Scotland (Parnell 1984). In none of these deposits have the bitumens been found to be enriched in lead or zinc.

The widespread presence of hydrocarbons in MVT deposits is interpreted as evidence for their role as a sulphate reductant in limestone-hosted deposits (Anderson and MacQueen 1982; and see MacQueen and Powell 1983

for organic geochemical evidence) or for organometallic complexing as a means of lead/zinc transport (Giordano 1985). In a sandstone-hosted MVT deposit at Laisvall, Sweden, sulphate-rich brines are similarly considered to have precipitated sulphides after encountering an oil reservoir (Rickard et al. 1981). Many bitumens in ore deposits have suffered *recent* bacterial degradation (e.g. Curiale and Harrison 1981). Biodegradation of bitumens by sulphate-reducing bacteria may also have been involved in the sulphide mineralization process. (Connan 1979).

The temperature ranges for petroleum maturation/expulsion and MVT ore deposition show considerable overlap in the 100°–150°C region (Anderson and MacQueen 1982), and fluid inclusion analyses and theoretical considerations show that MVT ore solutions are similar to oil and gas field brines (Sverjensky 1984). Petroleum generation and MVT ore deposition are both normal aspects of the evolution of a sedimentary basin, and it would be remarkable if the two products were not frequently associated.

Black shale sequences commonly include bitumens filling bedding plane and cross-cutting fractures. Localised maturation of organic matter adjacent to igneous intrusions and hydrothermal mineral deposits often results in shows of oil or bitumen. Several examples are known from mineral deposits in lacustrine-epicontinental black shale sequences in extensional settings, including the Lower Palaeozoic of the Oslo Graben, the Proterozoic Nonesuch Shale in the Keweenawan Rift and Triassic-Jurassic rift basins of the eastern United States (Parnell 1986).

Since they are often associated, the distribution of hydrocarbons has value as a pointer towards the distribution of lead-zinc ore deposits. Studies of MVT deposits in western Canada in particular emphasize the importance of organic matter as a favorable indication in ore exploration (Anderson and MacQueen 1982). Anomalous concentrations of hydrocarbon gases have been detected around carbonate-hosted lead-zinc deposits in Ireland, and this phenomenon also has a possible potential for the exploration for new orebodies (Carter and Cazalet 1984).

Copper, Copper mineralization in limestones is often associated with bitumens, e.g. in the Lower Palaeozoic of Quebec (Sangster 1980). Black shale sequences containing copper-bitumen associations include the Oslo Graben (Dons 1956) and the Proterozoic Nonesuch Shale in Michigan. The Nonesuch Shale was the source of bitumen which is mixed with native copper and chalcocite and locally replaced by copper (Barghoorn et al. 1965; Kelly and Nishioka 1985). Igneous rocks intruded into Triassic-Jurassic sequences in New Jersey and Connecticut and generated bitumens which are associated with copper mineralization within the intrusions. Mixed copper-bitumen deposits are also recorded from extrusive igneous rocks, such as in the Carboniferous of Alaska (Knopf 1910).

Bitumens are intimately related with chalcopyrite in the Carboniferous limestone of Great Britain at Laxey, Isle of Man (Davidson and Bowie 1951), Great Ormes Head (Bath et al. 1986) and Hilderstone, West Lothian (Parnell 1984). Studies in the Welsh Borderland and Scotland show that in regions of copper ore mineralization, copper may be enriched within bitumen in concen-

trations of over 1000 ppm, even where no copper mineral inclusions are visible (see above). Possibly in regions where traces of bitumen are more widely distributed than traces of copper mineralization, copper enrichments in bitumen could help to locate copper ore mineralization.

Uranium, thorium, gold. The enrichment of uranium within organic materials is commonplace in both organic-rich sediments and bitumens (e.g. Breger and Deul 1959). Bitumens from vein and sandstone-hosted deposits contain uranium concentrations of up to several *per cent,* at which level the uranium occurs predominantly as mineral inclusions. Uraninite inclusions occur in bitumens from British ore deposits in the Isle of Man, Kirkcudbrightshire, Caithness, Cornwall, North Wales and the East Midlands (Bath et al. 1986). Sandstone-hosted bitumen-uranium deposits are particularly abundant in Utah and Colorado and exhibit partial replacement of the sandstone by the bitumen (Parnell and Eakin 1987).

Thucholites (bitumens containing Th, U, C, H, O) occur locally within many orefields, particularly in Precambrian terranes. Thucholite in the Witwatersrand deposits contains particles of gold, galena, sphalerite, chalcopyrite and irregularly shaped uraninite. Although some workers have interpreted the irregular uraninite to be partially replaced by bitumen (e.g. Davidson and Bowie 1951), Boyle and Steacy (1973) have interpreted similarly shaped uranium minerals in thucholite from Ontario to represent an exsolution phenomenon. Boyle (1979) also believes that the exsolution of uraninite and gold from a hydrocarbon-gold-uranium compound best explains the Witwatersrand occurrences, and Kucha (1983) suggests a similar origin for palladium arsenides and gold in thucholite from the Zechstein copper deposits of Poland. Gold does also occur in association with non-radioactive bitumens (Boyle 1979).

Many thucholites are additionally rich in lead: Plumbiferous thucholites are known from pegmatite deposits in Ontario, Quebec, Sweden and the Karelian SSR (Hoekstra and Fuchs 1960), and uraniferous bitumens occur in pegmatites in southern Norway (Dons 1956) and Japan (Davidson and Bowie 1951).

The association of uranium with organic matter offers potential exploration for both uranium and petroleum. The association takes the form of organic complexing of uranium with organic ligands, physical adsorption of uranium onto the surface of large organic molecules, reduction of UO_2^{2+} ions by organic matter to precipitate UO_2 and also radiation-induced condensation-polymerization of fluid hydrocarbons to precipitate solid bitumens (see Curiale et al. 1983). Clear evidence for this latter process is found in petroleum source rocks where thin coatings of bitumen are precipitated around uraninite and zircon grains (e.g. McKirdy and Kantsler 1980). Bitumen occurrences in pegmatites are similarly formed by a reaction between uraninite and migrating hydrocarbons.

Because uranium commonly occurs associated with organic materials, bitumens are a good sampling media during uranium exploration (Boyle 1982). As noted above, some uranium-mineralized localities in Great Britain were discovered in this survey through metal determination of bitumens. The property of uranium-bearing minerals to nucleate the deposition of solid hydrocarbons has important consequences for petroleum exploration. A weak flow of gaseous or dissolved hydrocarbons leaking from a reservoir could be recorded by radiation-induced precipitation, but might otherwise go undetected. The process is particularly likely where hydrocarbons pass through red-bed sediments containing uranium-rich groundwaters. Several examples are documented in the literature. In Kazakhstan, hydrocarbons leaking from an anticlinal trap merged with uraniferous groundwaters in a sandstone aquifer and precipitated uranium-rich bitumens (Roberts 1980). In Oklahoma, petroleum leaking along deep faults suffered degradation and then mixed with groundwaters flowing off uranium-rich granitic basement to form uraniferous, bituminous nodules in Permian red beds (Curiale et al. 1983). In Scotland, petroleum migrating along faults through a Devonian conglomerate precipitated uraniferous bitumen nodules in an overlying sandstone bed, which led to the discovery of bituminous reservoir sandstones below the conglomerate (Parnell and Eakin 1987).

Silver, cobalt, nickel, arsenic. An ore assemblage of silver-cobalt-nickel arsenides is typically associated with felsic and basic igneous rocks, but there are some exceptions which appear to be the product of remobilization of preexisting deposits, including deposits in the organic-rich Kupferschiefer and vein mineralization at Kongsberg, Norway (Badham 1976). Bitumen is abundant at Kongsberg, and its presence is significant to the distribution of silver ore. Dons (1956) reported that the bitumen can be found coating silver minerals and that "workers there had a rule saying that where there is no coal blend (i.e. *bitumen*) or bituminous calcite, there will be no native silver". Another example of hydrocarbon minerals directly linked with native silver is reported from mineral veins in Colorado by Koenig and Stockder (1881).

Silver-cobalt-nickel-arsenide vein mineralization in the Thunder Bay district of Ontario includes veins of bitumen (Ellsworth 1934). In central Scotland, silver-cobalt-nickel-arsenide ores occur with bitumens at Hilderston and Alva (Parnell 1984). Bitumens have been noted in other "red-bed"-type silver deposits and have yielded inclusions of silver and nickel-cobalt arsenides in the Witwatersrand gold deposits (Boyle 1979).

The contents of the metals within bitumens may reflect the nature of the ore mineralization. The Ontario bitumens from arsenide veins contain substantial nickel and traces of cobalt (Ellsworth 1934). Bitumens from the Alva silver deposit in Scotland contain silver selenide minerals (author's unpublished observations). Some other British bitumens have been found to contain inclusions of cobalt-nickel-arsenic-antimony-bismuth minerals and traces of bismuth and tungsten within uraninite inclusions. These occurrences are restricted to regions where these metals also occur as ore deposits (Fig. 4), although at individual localities the *only* occurrence of a metal may be within bitumen. Therefore, the mineralogy within the bitumens expresses to a certain degree the nature of the ore mineralization in the same region.

Mercury. Oil or bitumen occur in mercury ore deposits in California, Texas, Peru, Germany, Austria, Czechoslovakia, Italy and Spain (e.g. Abraham 1945; Geissman et al. 1967; Mueller 1972). Petrographic studies of Californian material by Bailey (1959) and of Russian material by

Shabo et al. (1983) suggest that cinnabar and bitumen were in each case deposited from a common fluid. The association of bitumens with mercury ores led to an assumption that organic matter caused the precipitation of the mercury. It may be significant however that in many cases the mercury occurs with oil rather than solid bitumens. Recent data for trace element concentrations in petroleum fractions (Chakhmakchev et al. 1981) shows that mercury is enriched within lighter oils, whilst many other metals are enriched within heavier oils. Mueller (1972) has suggested that the near-surface, low-pressure conditions prevailing during mercury mineralization are conducive to the deposition of a number of organic sublimates which are peculiar to this type of deposit. They include curtisite, idrialite and pendletonite, i.e. a series of polycyclic, aromatic, crystalline organic minerals (Wise et al. 1986).

Russian workers have suggested the use of hydrocarbon analyses in prospecting for mercury. In a study of the Plamennoye mercury-antimony deposit Vershkovskaya et al. (1972) found that the maximum bitumen (sensu stricto) concentrations in organic matter were associated with ores containing the highest mercury contents. Mercury is so abundant in some oil and gas fields that mercury anomalies are also used in prospecting for hydrocarbons (Rudakhov 1973).

Conclusion

The roles of organic materials in the transport and deposition of metals, and the physicochemical nature of metal-organic interactions are both variable. In general, organometallic complexing enhances the transport of metals in hydrocarbon-bearing fluids, and reduction by organic matter enhances ore deposition. The relative importance of these processes determines the significance of metal-bitumen associations in ore exploration as follows:

a) Organophilic elements, including vanadium and nickel, may be initially concentrated within the petroleum source rock and further concentrated within bitumen following hydrocarbon generation, migration and degradation.
b) Low-temperature ore deposits may be associated with bitumen because both are generated and deposited over the same (low) temperature range during normal basin evolution. In particular, MVT ore solutions show similarities with oilfield brines. Mercury-bitumen ores are another low-temperature association.
c) Metals transported in oxidizing environments, particularly copper and uranium, are deposited through reduction by organic materials and may be incorporated within those materials.
d) In some instances the role of organic materials is not clear but the metals concentrated within bitumens are also the metals which may form ore deposits in the same region.

With the exception of category (b), in each case solid bitumens may become enriched with metals, even where not associated with separate ore mineralization. Determinations undertaken in this study suggest that (1) metal anomalies can be detected by bitumen analysis, (2) metal anomalies can be related to the distribution of ore mineralization, (3) bitumens from different sources may be distinguished by metal content, although the relationships

could easily be obscured by epigenetic metal enrichments, and (4) metal concentrations in bitumens may be strongly dependent upon the mode of genesis of the bitumen. The last factor is one which has not been considered in the limited literature on this subject, and which should be the object of further research.

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