

The geochemistry of oil in Cornish granites

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Abstract: Oil residues in Variscan granites in Cornwall, SW England, preserve biomarker data which indicate an origin from marine source rocks. The biomarkers also indicate a thermal maturity that excludes an origin from the Devonian-Carboniferous rocks intruded by the granites, but is similar to that of Jurassic-sourced oil to the east in the Wessex Basin. A suite of five different samples from the South Crofty tin mine are variably biodegraded, implying alteration after emplacement of oil in the granite. These characteristics are compatible with models for updip flow of fluids from offshore Mesozoic sediments into older granite topographical highs.

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There are many occurrences of hydrocarbons in granites and other basement rocks. Some are on a scale large enough to constitute commercial oil fields (e.g. [Petford & McCaffrey 2003](#)), so their origin is worthy of investigation. Possibly the earliest documentation of oil in granite is the occurrence of oil (including viscous/solid bitumen residues of oil) in the granites of Cornwall, where it was encountered during the underground mining of tin and other metals ([Klaproth 1787](#)), and even illustrated in the eighteenth century (plate 10 in [Rashleigh 1797](#)). Published observations, mostly from the nineteenth century, record oil at many mines (commonly described as mineral pitch; literature reviewed by [Parnell 1988](#)). Despite this heritage of observation, and much detailed study of the metalliferous mineralization (e.g. [Hawkes 1974](#); [Jackson *et al.* 1989](#); [Alderton 1993](#); [Gleeson *et al.* 2000](#)), the origin of the oil has remained enigmatic.

The mechanisms by which oil may enter granite can be divided into two broad categories: those in which the heat of granite intrusion has generated oil from the pre-existing country rocks; and those in which the granite forms a structural/topographical focus for the updip migration of hydrocarbons from source rocks that may post-date the granite intrusion ([Parnell 1988](#)). In Cornwall ([Fig. 1](#)), both possibilities have been inferred (see below), but a lack of published geochemical evidence has limited the matter to one of conjecture. This paper reports detailed organic biomarker data, to constrain the origin of oil in Cornish granites.

The granites of Cornwall were emplaced during the Hercynian/Variscan Orogeny, and are dated predominantly at about 295–290 Ma ([Chen *et al.* 1993](#)). They intruded sedimentary country rocks of Devonian-Carboniferous age, which in the mining district of SW Cornwall were metamorphosed to slates and traditionally termed ‘killas’. The granites were veined by tin and other metals, during multiple episodes of fracture-hosted mineralization. Early Sn–W–Cu mineralization was followed by Pb–Zn–Ag–Fe mineralization ([Jackson *et al.* 1989](#); [Alderton 1993](#)). Observations of mineral paragenesis place solid oil residues in the younger phase of mineralization along with quartz, haematite and kaolinite ([Dominy *et al.* 1994](#)). The younger veins show evidence of reactivation, including brecciation structures and the development of drusy cavities ([Dominy *et al.* 1994](#)). Oil residues occur as a late-stage filling of these veins. Historical records describe them filling vugs (e.g. ‘vugs often full of mineral pitch’ at South Wheal Towan: [Henwood 1843](#)), and in the modern era they exude from fractures

dilated by drilling ([Harrison & Beer 1977](#)). There is no evidence for post-oil mineralization.

The present study presents organic biomarker data from seven samples of viscous/solid oil residue from mines in Cornwall. The objectives for these data are to:

- measure thermal maturity;
- determine any constraints on the environment of deposition for the source rock;
- determine levels of biodegradation, and assess if this reflects modern and/or ancient alteration;
- compare with data from samples in other fractured basement.

Methods

Five of the seven samples are from South Crofty Mine in the Carnmenellis Granite ([Fig. 1](#); [Table 1](#)) but collected at different times, allowing the measurement of a set of samples with variable degrees of alteration. The samples, coded South Crofty A, B, Y, H and NHM, were provided by A. Bromley, A. Bath, B. Young, R. Harrison and the collections of the Natural History Museum (specimen 14433, recorded as Eastwell Crofty, assumed East Wheal Crofty which is now subsumed into South Crofty, archived in 1840–41), respectively. Samples were also measured from North Treskerby Mine, from the collection of the Royal Cornwall Museum, Truro, and from the Wheal Speed Mine, from the collection of the British Geological Survey. The occurrences of oil residues at South Crofty, North Treskerby and Wheal Speed were recorded by [Harrison & Beer \(1977\)](#) and [LeBoutillier \(1996\)](#), by [Tweedy \(1842\)](#), and by [Harrison & Taylor \(1966\)](#), respectively. The sample from North Treskerby is exceptional in containing crystals of sulphide minerals, and the Wheal Speed sample is intermixed with uranium minerals. Gas chromatography of Cornish samples had been attempted previously ([Harrison & Beer 1977](#); [Bath *et al.* 1984](#)) but no evidence of the results has been presented. Samples of ‘killas’ slate from Treskillard and Looe were extracted to assess if they could yield meaningful data. Data from the Cornish samples were compared with new analysis of a previously studied Jurassic-sourced oil seep at Mupe Bay, Dorset, 200 km to the east in the Wessex Basin ([Parfitt & Farrimond 1998](#)), and from organic-rich samples at several other stratigraphic levels. The samples were from black Devonian limestone in the Quantock Hills near Bridgwater,

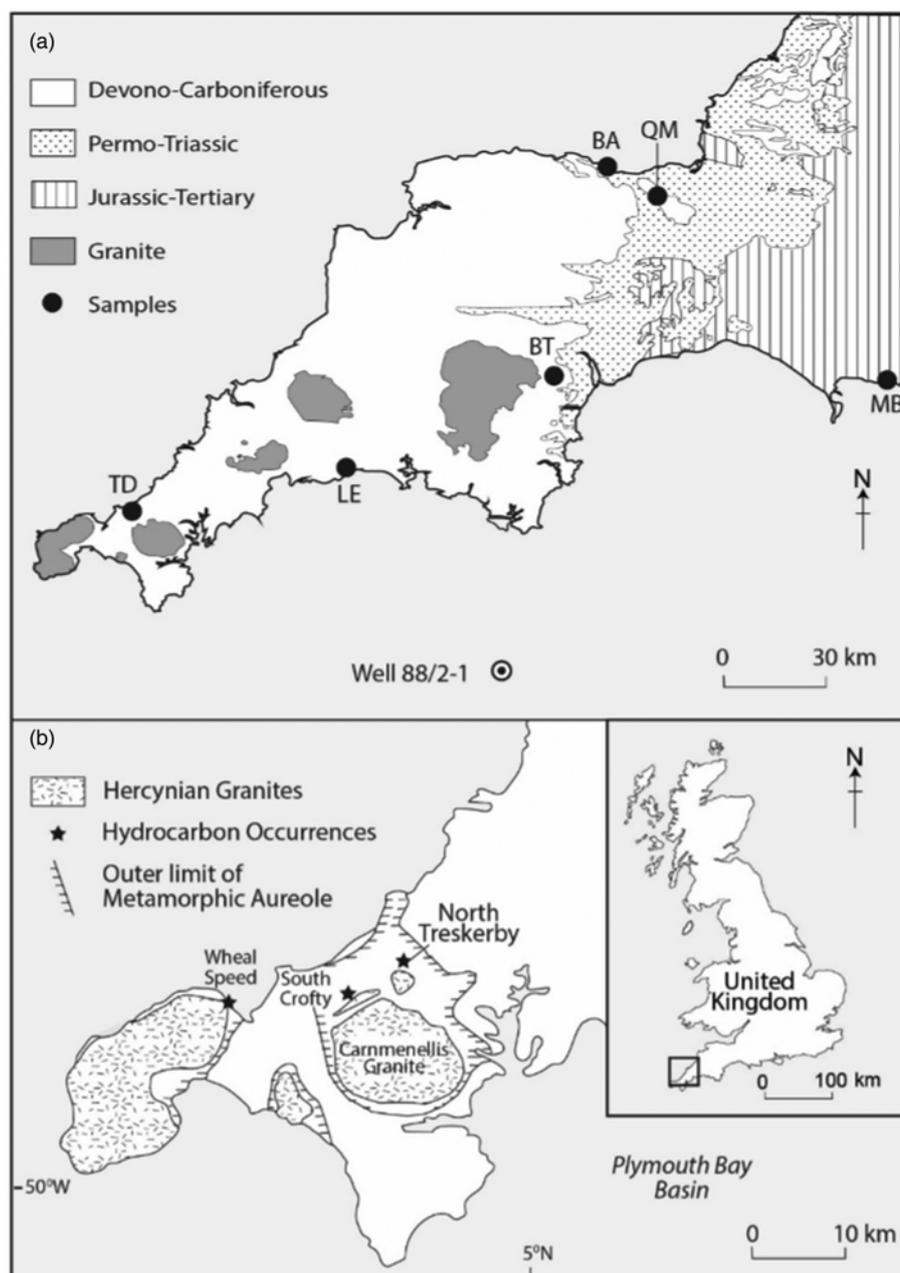


Fig. 1. Map of SW England (after Moon 2010), showing sample sites for oil residues at Wheal Speed, North Treskerby and South Crofty, and samples used for comparison. Oil residues occur close to the margin of granites with Devono-Carboniferous 'killas' country rock. BA, Triassic black shale, Blue Anchor; BT, Oligocene lignite, Bovey Tracey; LE, Looe; MP, Mupe Bay; QH, Devonian, Quantock Hills; TD, Treskillard.

Triassic black shale from Blue Anchor and Oligocene lignite at Bovey Tracey (Webby 1965; Edwards 1976; Warrington & Whittaker 1984) (Fig. 1).

Rock samples were prepared by rinsing with distilled water two times, and again with dichloromethane (DCM). The dry rocks were crushed and extracted using a Soxhlet apparatus for 48 h. Solid bitumen and tar samples were ultrasonicated with DCM and methanol (MeOH). All glassware was thoroughly cleaned with a 93:7 mixture of DCM–MeOH. Crushed samples were weighed, recorded and transferred into pre-extracted thimbles. The extracts were then dried down using a rotary evaporator, and separated into aliphatic, aromatic and polar fractions via a silica column chromatography using hexane, hexane–DCM in the ratio 3:1 and DCM–MeOH, respectively. Prior to gas chromatography mass spectrometry (GC–MS) analysis, an internal standard (5 β -Cholane, Agilent Technologies) was added to the saturate fraction before injection into the GC–MS machine and subsequent biomarker identification. This was done using an Agilent 6890N gas chromatograph fitted with a J&W DB-5 phase 50 m mass selective detector (MSD) and a quadruple mass spectrometer operating in

selected ion monitoring (SIM) mode (dwell time of 0.1 s per ion and ionization energy of 70 eV). Samples were injected manually using a split/splitless injector operating in splitless mode (purge 40 ml min⁻¹ for 2 min). The temperature programme for the GC oven was 80–295°C, holding at 80°C for 2 min, rising to 10°C min⁻¹ for 8 min and then 3°C min⁻¹, and finally holding the maximum temperature for 10 min. Quantitative biomarker data were obtained for isoprenoids, hopanes, steranes and diasteranes by measuring responses of these compounds on *m/z* 85, 125, 191, 217 and 218 mass chromatograms and comparing them to the response of the internal standard. Biodegradation was assessed using the ratio of phytane to the C₁₈ *n*-alkane (Ph/*n*C₁₈), which increases with degradation as *n*-alkanes are altered more rapidly (Peters & Moldowan 1993). Biodegradation also causes the breakdown of steranes at a faster rate than diasteranes, including in the shallow subsurface in aerobic conditions; thus, the diasterane/sterane ratio (D/S) can be elevated due to shallow biodegradation (Seifert & Moldowan 1979) but is also controlled by thermal maturity and source rock lithology (Burton *et al.* 2018). Thermal maturity was estimated from the 20S/(S + R) ratio for C₂₉ steranes, based on the

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Table 1. Quantitative biomarker data for granite-hosted bitumen and rocks sampled for comparison

Sample description	D/S	C ₂₉ 20S/(S+R)	C ₃₂ 22S/(S+R)	Ts/Tm	Pr/Ph	Pr/nC ₁₇	Ph/nC ₁₈	C ₂₇ (%)	C ₂₈ (%)	C ₂₉ (%)
South Crofty A	0.17	0.16	0.58	0.44	0.42	0.45	2.22	28	28	44
South Crofty B	0.21	0.38	0.48	0.34	0.54	1.19	1.15	32	28	40
South Crofty H	0.45	0.47	0.78	0.57	0.84	0.61	0.68	40	20	40
South Crofty NHM	0.25	0.52	0.37	0.51	0.25	0.92	1.25	47	28	25
South Crofty Y	0.35	0.37	0.65	0.62	0.95	1.93	0.99	30	30	40
North Treskerby	0.66	0.31	0.52	0.65	0.62	0.53	0.68	28	30	42
Wheal Speed	0.55	0.49	0.56	0.55	0.89	0.57	0.92	50	24	26
Mupe Bay Jurassic	0.74	0.38	0.68	0.63	ND	ND	ND	35	25	40
Quantocks Devonian	1.59	0.42	0.67	0.39	0.55	0.10	0.20	60	18	22
Blue Anchor Triassic	0.13	0.45	0.61	0.42	2.41	1.21	0.68	31	13	56
Bovey Tracey Oligocene	ND	0.15	ND	ND	ND	ND	ND	9	6	85

ND, no data; Pr/Ph, pristane/phytane; C₂₉ 20S, C₂₉ 20S/(20S + 20R); D/S, C₂₉ β₂₉ diasterane/αβ₂₉R sterane; C₃₂ 22S/(22S + 22R); Ts, C₂₇ 18α-22,29,30-trisnorhopane; Tm, C₂₇ 17α-22,29,30-trisnorhopane.

increasing proportion of the S isomer with maturation (Peters & Moldowan 1993), and was also determined from the relative proportions of hopane peaks Ts (C₂₇ 18α(H)-22, 30-trisnorhopane) and Tm (C₂₇ 17α(H)-22,30-trisnorhopane) peaks, and the C₃₂ 22S/(S + R) hopane ratio.

Results

The granite-hosted samples all yielded extracts adequate for GC-MS. Some chromatograms for the samples show prominent 'humps' (unresolved complex mixtures) that indicate strong alteration (Fig. 2) but, nonetheless, the data allow determination of quantitative parameters (Table 1). The proportion of diasteranes (Fig. 3), as indicated by the diasterane/sterane ratio, is relatively low for all five samples from South Crofty but higher for the samples from North Treskerby and Wheal Speed (Figs 4 and 5). The South Crofty samples have a wide range of Ph/nC₁₈ ratios (Fig. 5). The sterane thermal maturity parameter C₂₉ 20S/(S + R) ratios of 0.35–0.5 indicate onset of oil generation to early oil generation. The hopane thermal parameters of Ts/Tm 0.34–0.65 and C₃₂ 22S/(S + R) ratio 0.37–0.65 (excluding one aberrant value of 0.78) similarly indicate early oil generation.

The 'killas' slate samples yielded a very limited extract that was too degraded to allow meaningful interpretation. However, other organic-rich samples from further east in SW England yielded extracts from which environmental and thermal maturity data could be obtained.

The relative proportions of C₂₇, C₂₈ and C₂₉ steranes are clustered between C₂₇ and C₂₉ predominance (Fig. 6). The Jurassic-sourced oil sample from Mupe Bay plots in the middle of this array. The samples of Devonian, Triassic and Oligocene rocks plotted distinctly from the array.

Discussion

Oil composition

The chromatograms are typical of the residues of oils derived from marine source rocks. The consistently low content of C₂₈ steranes makes a non-marine source very unlikely. Some samples have unresolved complex mixtures indicative of alteration. The South Crofty samples exhibit variable degrees of biodegradation, as evidenced from the range of Ph/nC₁₈ values. This is to be expected where the samples were collected from different sites and fluid ingress has continued up to the present time (Edmunds *et al.* 1984). The least degraded sample is relatively fresh, and suggests that biodegradation occurred once the oil had entered the granite rather than prior to migration. If biodegradation had occurred in an intermediate reservoir, the Ph/nC₁₈ ratios should be less variable. The least degraded sample is oil that has exuded from fractures which dilated during mining activity (Harrison & Beer 1977), and so experienced negligible exposure to alteration. Some other samples may have been in vuggy cavities, where they had much greater exposure to alteration. The samples from the other two mines also have very low Ph/nC₁₈ ratios, but have a higher content of diasteranes. This distinction may be related to the evidence of metalliferous mineralization coeval with the oil emplacement, which suggests the possibility of hydrothermal alteration.

The spatial relationship with uranium mineralization at Wheal Speed could have caused the alteration of the organic matter by irradiation from the uranium (Landais *et al.* 1990; Court *et al.* 2006). Irradiation causes cross-linking of organic bonds, which results in greater molecular complexity and lower solubility, so that biomarker compositions can become altered. However, such alteration is not evident in the data from Wheal Speed.

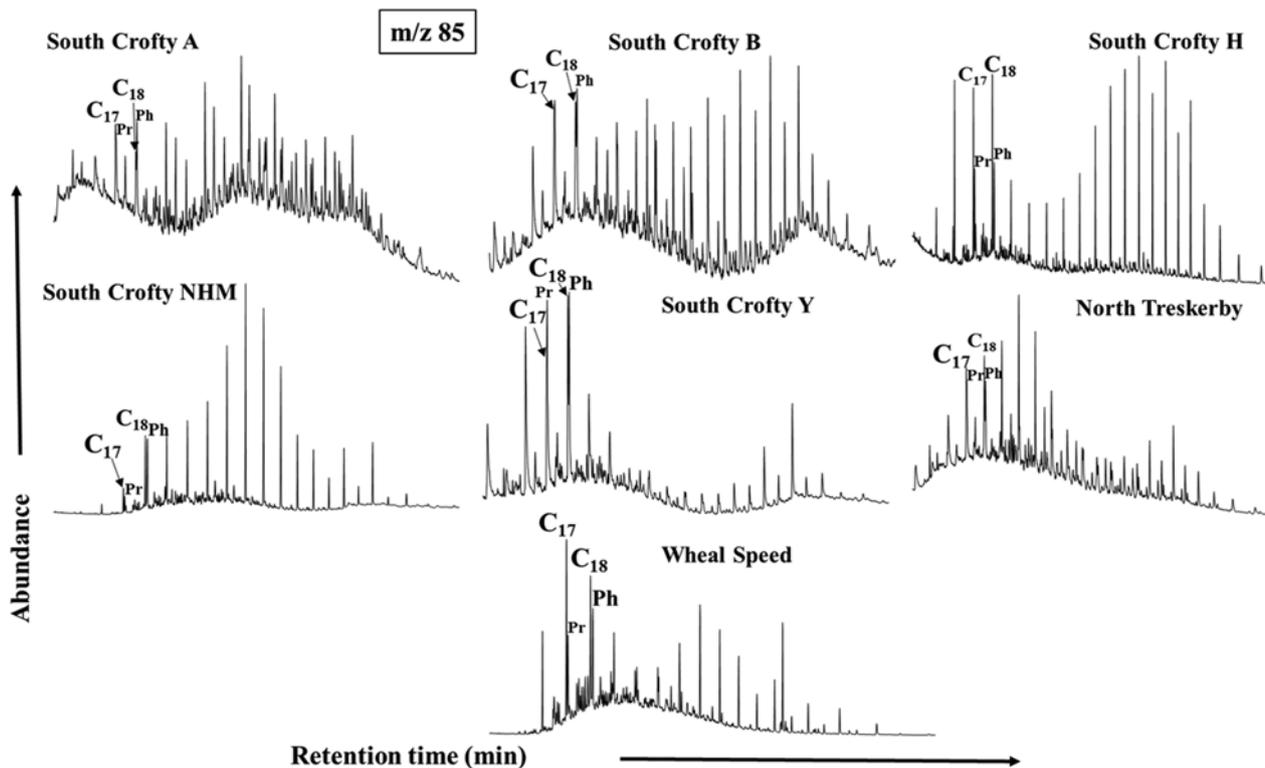


Fig. 2. Selected ion chromatograms for m/z 85 for oil residues, Cornwall, highlighting normal alkanes.

Where Mesozoic rocks are preserved further east in SW England, in the Wessex Basin, oils exposed at the current surface exhibit variable biodegradation, and thermal maturity C_{29} 20S/(S+R) ratios in the same range as the Cornish samples (Parfitt & Farrimond 1998). Their sterane composition is also comparable (Fig. 6) and it is possible that the Cornish oil residues are derived from a similar Jurassic source rock. Well 88/2-1 in the Plymouth Bay Basin (Fig. 1) contains organic-rich Jurassic shales which are oil-prone, and further indicates the possibility of a Jurassic source in the region (Evans *et al.* 1981; Evans 1990). The oil seep at Mupe Bay has an assumed Liassic source, and the rocks penetrated in the Plymouth Bay Basin are Liassic (Evans *et al.* 1981), but oil has also been generated at other levels within the Jurassic. The data reported here do not distinguish different levels of the Jurassic. Of the other samples from SW England, the two sample of Devonian-Carboniferous 'killas' slates yielded very limited extracts which were inadequate for any interpretation, while the Devonian sample remote from granitic metamorphism and the

Triassic and Oligocene samples gave measurable extracts. However, their sterane compositions, which are rich in C_{27} (Devonian) or C_{29} (Triassic, Oligocene), are distinct from those of the granite-hosted samples, and suggest they are not correlative.

Thermal history

The circumstantial evidence of oil occurrences in a region where the country rocks were metamorphosed to dark slates during the Variscan Orogeny led Harrison & Beer (1977) and Parnell (1988) to speculate that the shale precursors of the slates had yielded the oil during intrusion. The intruded Devonian-Carboniferous rocks of SW England have subsequently yielded vitrinite reflectance values mostly above 2% (equivalent to the dry gas zone) (Cornford *et al.* 1987, 2011), presenting conceptual difficulties that they could be a source of oil. Measurement of an offshore Devonian-Carboniferous well sample similarly gave a reflectance of 4.52% (Evans *et al.* 1981). Further, the country rocks had already been metamorphosed before granite intrusion (Chen *et al.* 1993), and intrusion occurred at a depth of 7–9 km (Charoy 1986), making oil generation during this event very unlikely. Selley (1992) suggested that rocks well above the level of granite intrusion might still be in the oil window and could yield oil into mineralizing convection cells but the reflectance data are equally inconsistent with that possibility. The thermal maturity data reported here indicate typical early oil window temperatures, and show no evidence of anomalous heating that would be expected if the organic matter had experienced mild metamorphism. The data from two samples (South Crofty NHM, Wheal Speed) indicate slightly higher maturities than the others, which could reflect some homogeneity in the oil. Higher maturity is also reflected in the slightly increased proportion of C_{27} steranes (Sajó 2000).

Oil generation from a source rock deposited after the intrusion of the granites and associated orogenic deformation is conceivable, given the much lower thermal maturities in the post-intrusion section for SW England (Macquaker *et al.* 1986; Suan *et al.* 2012). This alternative possibility was difficult to sustain

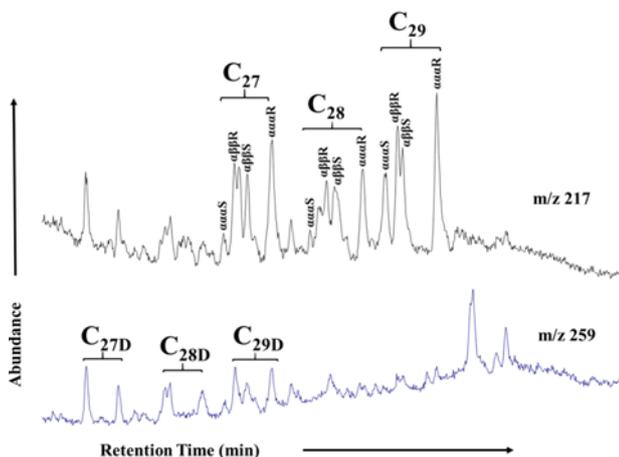


Fig. 3. Ion chromatogram for m/z 217 and 259 highlighting steranes and diasteranes for South Crofty B sample.

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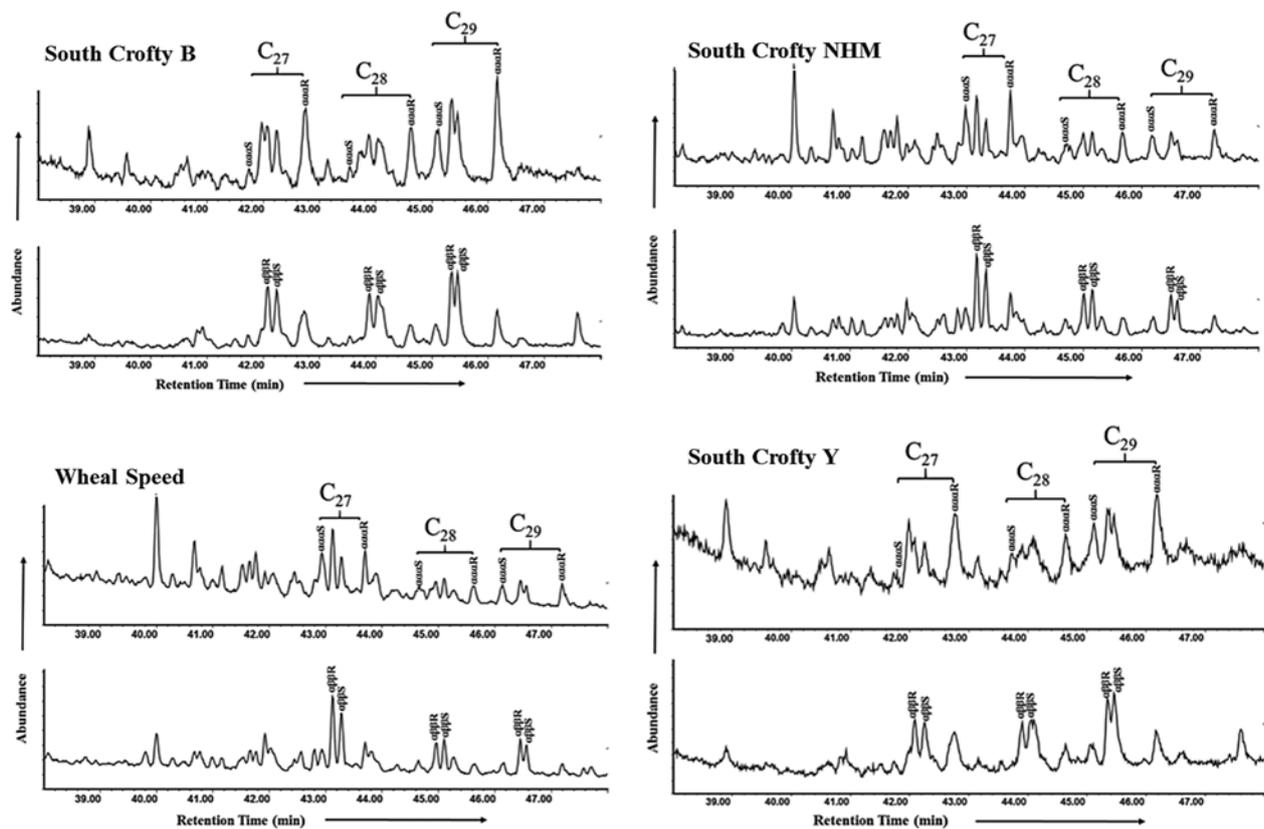


Fig. 4. Selected ion chromatograms for m/z 217 and 218 for oil residues, Cornwall, highlighting steranes.

when data from the offshore Plymouth Bay Basin indicated that in most wells the oil-prospective Jurassic section was missing (Ruffell *et al.* 1995). However, palaeogeographical and burial history reconstructions suggest that there had formerly been a thick cover of Jurassic sediments now largely removed by erosion (Cope 2004), and oil-prospective Jurassic sediments are preserved in well 88/2-1 in the Plymouth Bay Basin (Evans *et al.* 1981; Evans 1990). Importantly, there is strong evidence from isotopic and fluid-inclusion data that at least the younger stages of mineralization were derived from basinal brines, expelled from the offshore basins (Gleeson *et al.* 2000; Psyrillos *et al.* 2003).

The thermal history of the Carnmenellis Granite has been studied in some detail, and may be relevant to the origin/composition of the

oil. Apatite fission-track analysis for the surface of the pluton indicates cooling to below *c.* 125°C at 155–137 Ma (Chen *et al.* 1996). The composition of the oil suggests that it is unlikely to have experienced long-term heating at above 125°C, and thus post-dates this late Jurassic age. This is compatible with derivation of the oil from a Mesozoic source rock. The groundwaters currently penetrating the granite are meteoric and up to 50°C (Edmunds *et al.* 1984). These fluids could readily cause alteration, including biodegradation, up to the present day.

Biodegradation in basement rocks

Other studies of hydrocarbons in basement rocks have similarly shown that they underwent biodegradation within the basement (Parnell *et al.* 2017a, c). This would have been enhanced by the high susceptibility to fluid flow in such rocks. Basement rocks which contain hydrocarbons do so especially where the basement forms a topographical high updip from adjacent sedimentary basins, and/or the basement is separated from a basin by a basin-bounding fault; both of which can allow fluid ingress from basin to basement. The fluid flow is not limited to hydrocarbons, and hydrocarbon emplacement could be accompanied or followed by aqueous fluids that might alter the hydrocarbons. Where basement rocks form a topographical high, this also makes them more likely to be penetrated by meteoric water. The enhanced susceptibility to updip and meteoric fluid is evident in some granites of SW England where they have been extensively altered to kaolinite (Bristow 1993; Psyrillos *et al.* 2003). Meteoric water, in particular, has the potential to introduce microbial communities from the surface that could cause the biodegradation of hydrocarbons.

Comparison of oil residues in UK basement

There are several other examples of oil residues within basement rocks within the UK, including Longmyndian, Moinian and

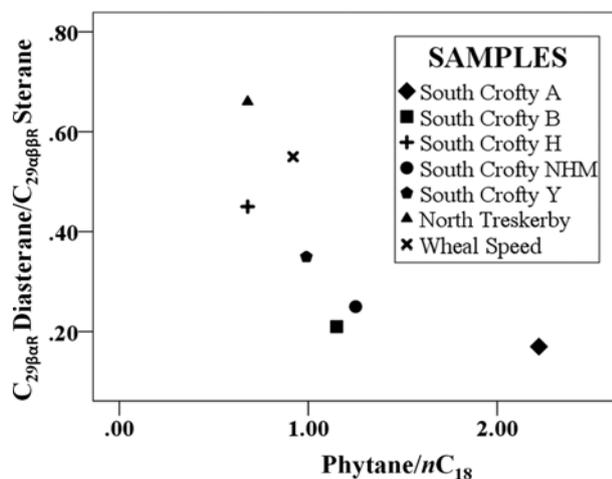


Fig. 5. Cross-plot of diasterane/sterane ratios and Ph/nC_{18} ratios for oil residues, Cornwall. South Crofty samples show a wide range of Ph/nC_{18} ratios, suggesting variable biodegradation after emplacement in granite.

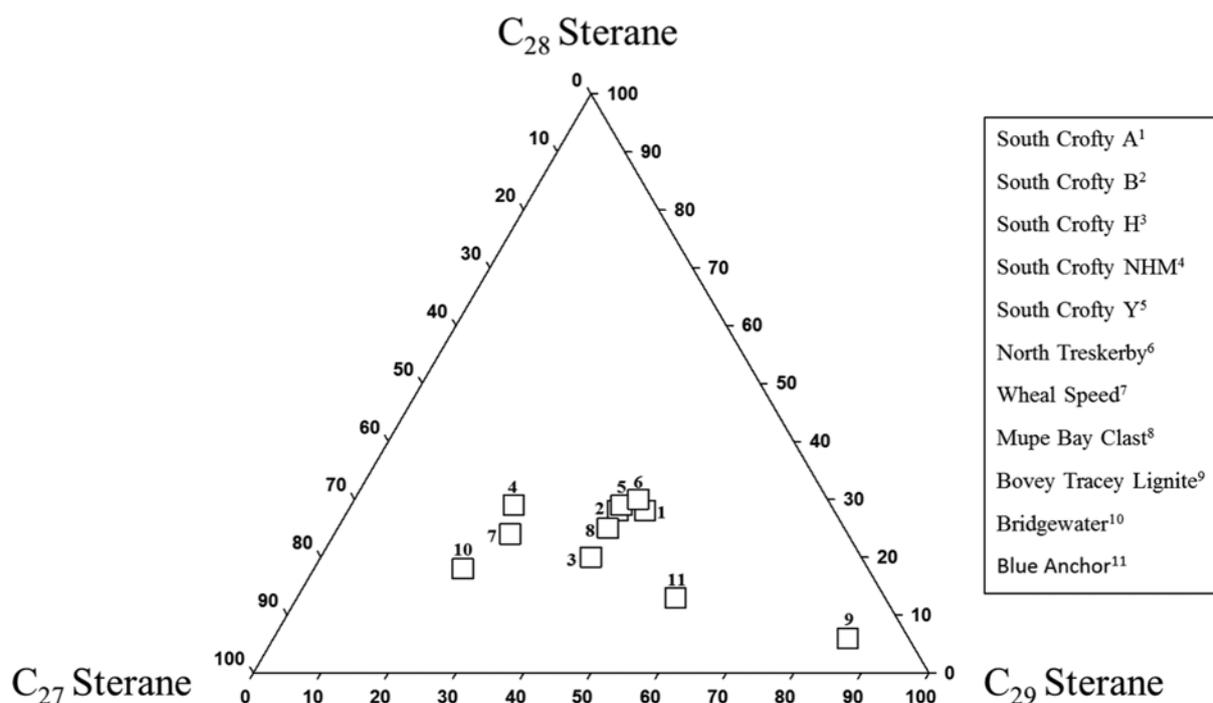


Fig. 6. Composition of C_{27} , C_{28} and C_{29} steranes ($\alpha\beta$ S + R) in samples from Cornwall, determined from m/z 218 chromatograms. Compositions cluster between C_{27} and C_{29} predominance. Jurassic-sourced oil from Mupe Bay, Dorset, plots within the cluster. However, the sterane compositions of the Devonian, Triassic and Oligocene samples are distinct from those of the granite-hosted samples, and suggest that they are not correlative.

Lewisian metasediments, and the Weardale and Helmsdale granites (Parnell 1988; Trice 2014; Parnell *et al.* 2017*a, b, c*). However many factors control the fate of such residues, including the time gap between basement and oil, temperature, origin of porosity and proximity to the surface, so the residues are diverse.

The basement rocks are all topographical highs, which is why they have been amenable to sampling. This has allowed oils to enter them, updip or laterally, from adjacent sedimentary basins. Fracturing associated with basin development facilitated oil ingress into the Helmsdale Granite from the adjacent Moray Firth Basin, into Longmyndian metasediments from the adjacent Carboniferous and into Moinian metasediments from the adjacent Devonian. In the Helmsdale and Moinian cases, the sedimentary rocks were juxtaposed against basement by basin-bounding faults, while the Longmyndian was penetrated partly beneath the sub-Carboniferous unconformity. The Cornish granite was similarly penetrated below an unconformity surface. The other pluton, the Weardale Granite, was distinct in incorporating oil into an active hydrothermal convection system. Only some of the residues exhibit strong biodegradation, found in Moinian and Longmyndian

metasediments. In both of these cases the basement had been uplifted so that oil at a shallow level (<2 km depth, at temperatures allowing microbial life) could enter the basement surface. Recent biodegradation of oil in the Cornish granite was similarly at a shallow level. By contrast, oil entered the Helmsdale Granite and Weardale Granite at deeper levels, and so was not susceptible to biodegradation.

Fluid source

Notably, despite a wealth of fluid-inclusion data for mineralization in the Carnmenellis Granite and other plutons in Cornwall (e.g. Dominy *et al.* 1994; Gleeson *et al.* 2000; Psyrrillos *et al.* 2003), there are no published records of oil fluid inclusions. This is in contrast to some other occurrences of oil in fractured basement, where oil inclusions were entrapped in vein minerals (e.g. Feely *et al.* 2017; Parnell *et al.* 2017*c*). The absence of oil inclusions in Cornwall implies that the ingress of oil occurred later than the youngest measured vein minerals (generally quartz in north-south cross-courses), although there is evidence of syn-oil mineralization at

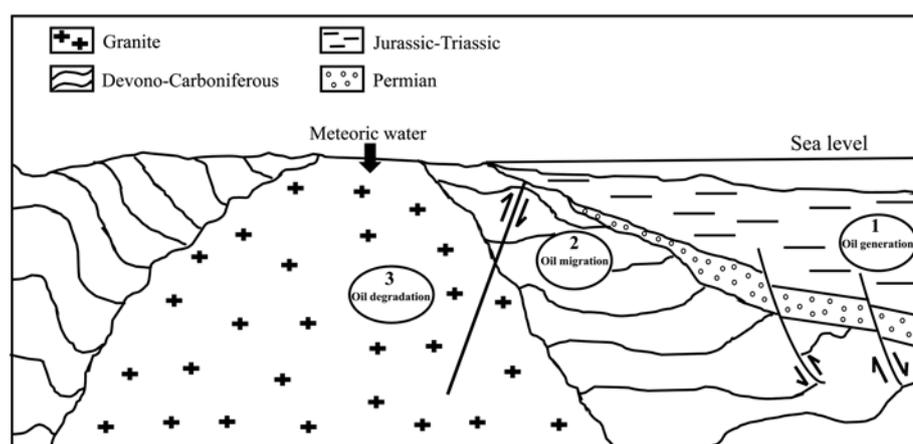


Fig. 7. Schematic model of hydrocarbon generation, migration and degradation in SW England (context adapted from Psyrrillos *et al.* 2003).

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North Treskerby and Wheal Speed in intermixtures with ore minerals, and the oil represents a relatively late reactivation of fluid flow through the mineralized structures.

Models for the migration of mineralizing brines from offshore basins in the region emphasize derivation from the Permo-Triassic offshore section, based on geochemical modelling and the age of late vein mineralization (Scrivener *et al.* 1994; Gleeson *et al.* 2000; Psyrrillos *et al.* 2003). However, fluid migration probably continued through the Cretaceous (Psyrrillos *et al.* 2003), when any Jurassic section that survived erosion could have contributed oil, and there is evidence of post-Jurassic expulsion of basin fluids elsewhere in SW England (Haggerty *et al.* 1996). This is consistent with the late context of the oil in the paragenesis. The model of Psyrrillos *et al.* (2003) can be adapted to the story of hydrocarbon generation, migration and degradation deduced in this study (Fig. 7).

Much of the mineralization in the granites occurs close to their upper margins; hence, most of the observations of mineral species, and oil residues, are in this setting. This may reflect the focusing of fluids updip from offshore basins, along the sub-Mesozoic unconformity, which was probably not far above the present erosion surface (Cope 2004). Notably, in a counterpart on the south side of the English Channel, mineralization in the Hercynian granites of the French Massif Central similarly is attributed to updip migration of fluids from the Aquitaine Basin along the Mesozoic granite unconformity (Boiron *et al.* 2002). The granite in the Massif Central likewise contains oil residues (Powers 1932).

Conclusions

The organic biomarker data for oil samples from Cornish granites can be interpreted as follows:

- Thermal maturity data indicate early oil window temperatures but not anomalous heating, so the oil has not experienced Variscan metamorphism.
- The samples exhibit variable levels of biodegradation, ranging from low to high. The large range suggests that degradation was relatively recent, reflecting emplacement of oil in different sites in the granite.
- The oil composition is typical of a marine source rock, and comparable with data from Jurassic oil in the Wessex Basin, but does not match Devonian, Triassic and Oligocene samples so well.
- The implication of a post-granite, possibly Jurassic, source makes it likely that the oil migrated updip into the granites from offshore sedimentary basins, which were the depocentres of post-granite sedimentation.

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