Making Oil from Magma.

D. K. MUIRHEAD*[1], M. DUFFY[1], N. SCHOFIELD[1], N. MARK[1], & M. D. ROWE[2]

[1]*Department of Geology and Petroleum Geology, School of Geosciences, University of Aberdeen, Aberdeen AB24 3UE, UK*

[2]*Halliburton Energy Services, Lafayette, Louisiana, USA*

Corresponding author (e-mail: dmuirhead@abdn.ac.uk)

Abstract: Petroleum systems within rifted margin basins affected by volcanism continue to remain challenging for the exploration of hydrocarbons, most notably due to the volume of intrusions that pose imaging, drilling and exploration problems. Typically, intrusions possess small thermal aureoles, but despite this, there is evidence that intrusions could none the less be responsible for the generation of commercial volumes of hydrocarbons. Here we shed new light on this petroleum systems challenge by integrating organic geochemical and Raman spectroscopic techniques to produce potential volumetric data for hydrocarbons generated as a result of igneous intrusion. Results indicate that in areas with immature source rock intervals, it may be possible for intrusions to generate volumes of oil that would be capable of comfortably filling likely known oil reservoirs. This is a critical step forward in integrating several analytical techniques, indicating that under the right conditions there is the potential for hydrocarbon generation as a result of igneous intrusion.

The hydrocarbon prospectivity of sedimentary basins within rifted continental margins can be affected by the variable thermal alteration of sedimentary organic matter situated within the metamorphic aureoles of igneous intrusions (dykes and sills). Relative to mineralogical effects, the extent of thermal alteration of organic compounds can be noted at much greater distances from an intrusion (Calvin, 1969; Bostick, 1971), with a number of intrusive regimes having shown variations in the extent of alteration on

sedimentary organic matter, alongside the efficacy of specific biological markers (aromatic hydrocarbons, amino acids, alkylphenanthrenes, alkylnaphthalenes, tricyclic terpanes) to examine these effects, alongside the determination of the potential oil window locations (e.g. Perregaard & Schiener, 1979; Saxby & Stephenson, 1987; Raymond & Murchison, 1988, 1991, 1992; George, 1992; Bishop & Abbott, 1995; Muirhead *et al,* 2017). Thermal alteration of organic materials in proximity to intrusions is often expressed in terms of percentage intrusion thickness (e.g. a dimensionless number based on the thickness of the intrusion) for example, a 4m thick intrusion that was sampled at 50% *i.t.* (intrusion thickness) was sampled at exactly 2m from the intrusion contact, 100% *i.t.* would be 4m from the intrusion contact.

There are many known occurrences of intrusions interacting with petroleum systems worldwide (Fig. 1) and the tectonic histories of rifted margin basins, emplacement mechanics of intrusions, controls on aureole width, possible effects on hydrocarbon kinetics, migration and source rock quality have been closely scrutinized (Dalziel, 1991; Galushkin, 1997; Aarnes *et al,* 2010; Aarnes *et al,* 2011; Iyer *et al,* 2013; Muirhead *et al,* 2012; Rateau *et al,* 2013; Muirhead *et al,* 2017; Iyer *et al* 2017). However, there is currently very little comprehensive work on the impact (either beneficial or detrimental) of igneous intrusions on the potential volume of recoverable or migrated hydrocarbons from a commercial viewpoint. A significant factor on such understanding is the pre-intrusion maturity of the host rocks and the extent of organic matter alteration (a factor of the extent of the contact metamorphic aureole).

In this paper we present calculations of potential oil generation volumes within intrusive igneous systems in rifted margin basins as a factor of pre-intrusion maturity and aureole width, a unique example of employing many different forms of analytical methods to a petroleum systems problem. Findings from this project have important implications for our global understanding of the evolution of petroleum systems associated with rifted margins that have experienced considerable volcanism during their history (e.g. Brazil and Africa – Gladczenko et al., 1997; Australia – Holford et al., 2012, 2013; Greenland – Skogseid et al., 2000). For example, some of the largest intrusions in the NE Atlantic Margin are in excess of 20 x 10km in dimension (Schofield et al 2017) with metamorphic aureoles thus of considerable size,

allowing for potentially economic volumes of hydrocarbons to be produced if hosted in organic facies with appropriate source rock potential.

Geological context

Organic-rich sedimentary rocks adjacent to six intrusions were studied to calculate the volume of extractable organic matter (%EOM) within each system, alongside empirical organic geochemical measurements on *n*-alkanes, hopanes, methylphenanthrenes, alongside %TOC (See Muirhead *et al*, 2017 for further details) with further EOM data from published sources (Perregaard & Schiener 1979; Saxby & Stephenson 1987; Raymond & Murchison 1988, 1991, 1992; George 1992; Bishop & Abbott 1995). Samples were collected from: *1. North of Birsay Bay, Orkney*. Samples were adjacent to a 46cm wide camptonite dyke, which had been intruded into Orcadian laminite of the Old Red Sandstone; *2. Staffin Bay, Isle of Skye.* The intrusion is a 4m thick Palaeogene dolerite dyke intruded discordantly into Jurassic Oxford Clay shales; *3. Flodigarry, nr Staffin Bay, Isle of Skye.* The intrusion is 3.8m thick basic dyke emplaced into Jurassic shales. *4. Midland Valley, South Queensferry, near Edinburgh*. A 40cm thick Carboniferous basic sill intruded into mudstones of the Upper Oil-shale Group of the Dinantian Carboniferous Limestone Series; *5. Mingary Castle, Kilchoan, Ardnamurchan.* The intrusion was a 2.2m Dolerite sill within the Lower Jurassic Pabay shale; *6. Raton, New Mexico.* The intrusion was a 9m thick basaltic dyke intruded into the Cretaceous Pierre shale. (Table 1).

This study will focus solely on the potential for oil generation from immature sources as a result of intrusion-induced maturation.

Methodology

Sample Collection

The country rocks associated with five of the intrusions (those named above, except Raton) were exposed on shore-faces, and as such the top 5cm of each sample were discarded to minimise input from non-indigenous organic matter. A hammer and chisel was used to extract samples every 10% *i.t.* (intrusion thickness) from the intrusion contacts up to a distance of 150% *i.t.* Further samples were collected as extant from the intrusions as exposure would allow providing a control for the unaltered country rocks.

Extraction of Organic Matter

Gas chromatography–mass spectrometry (GC–MS) was used for extractable organic matter and identification of *n*-alkanes. Powdered samples were contained in sealed zip-lock plastic bags and kept cool and dry until soxhlet extraction. Approximately 40 g of each powdered sample was soxhlet extracted for 48 h using 250 ml of a solvent mixture of dichloromethane (DCM)/methanol (MeOH) (93:7 v/v). Procedural blanks were carried out by subjecting an empty soxhlet thimble to the same extraction procedure as the samples. The remaining extracts were dried and weighed before being separated into their relevant saturate, aromatic and polar fractions using silica gel column chromatography: hexane to elute saturate fraction; 3:1 v/v Hexane:DCM to elute aromatic fraction; 2:1 v/v DCM:MeOH to elute polar fraction. Gas chromatography-mass spectrometry (GC-MS) was performed on saturate and aromatic fractions using an Agilent Technologies 6890N Network GC System with a 5975 inert Mass Selective Detector, along with MSD Chemstation to analyse the data. Between one and three microlitres of sample were injected onto a fused silica capillary column (30m long and 0.32mm internal diameter with a film thickness of 5µm) and heated from 80 °C (which is held for an initial two minutes) with the temperature increasing by 4 °C/min up to a temperature of 290°C (which is held for 30 mins). The degree of order in the carbon was determined by Raman spectroscopy on kerogen isolates, using a Renishaw inVia Raman spectrometer–microscope and 514 nm laser, with Renishaw WIRE curve-fitting software (see Muirhead *et al* 2016, 2017 for procedure).

Extractable Organic Matter (EOM) data from this study and those previous (noted above) were incorporated to provide a broad range of cummulative percent extractable organic matter (%EOM) (Fig. 2, main) to demonstrate the extent of hydrocarbon generation (or exhaustion) from host rocks with either an initial high (greater than 0.5%R_o) or initial low (less than 0.5%R_o) vitrinite reflectance profile (Fig. 2, inset). These values represent pre-intrusion maturities of the host rocks studied. EOM data from six intrusions along with organic geochemical and Raman spectroscopic responses (Fig. 3) were used to produce a general trend for the effect of intrusion aureoles on immature sedimentary organic matter, with all techniques locating the onset of thermal alteration at approx. 100% *i.t.*. By utilising empirical data from several intrusion regimes, it is possible to provide potential typical maturation windows (Fig. 3) adjacent to intrusions based on the pre-intrusion maturity of the host rocks, in this case we are focusing on immature sources prior to intrusion. Hydrocarbon windows defined from these experiments and the data from other sources (Fig. 2) can then be used to quantify the possible volumetrics that may be associated with thermal heating of organic matter in the vicinity of intrusions. Typically, within immature source rocks, we see an oil window being developed between 40-100% *i.t.*.

Calculation of Oil Volume

To gauge potential oil volumes that may be generated via igneous intrusions we calculate maximum generative potential of the source rock within the thermal aureole. This assumes the duration of the intrusion was sufficient to transform the entirety of the source rock's potential and provides the maximum estimation for source rock maturation volumes for a given intrusion regime.

For volumetric calculations we use equations from Schmoker (1994) (Equations (1), (2) & (3)) in addition to gas to oil ratio for kerogens (Pepper & Corvi 1995) (Equation (3); Oil Gas Fraction) to calculate the oil generative portion of kerogen within the thermal aureole and then convert to barrels of oil equivalent (BOE). There are four primary stages to this method: 1. Calculate source rock volume defined by thermal aureole. 2. Calculate mass of organic carbon in source rock. 3. Determine the mass of

generated hydrocarbons calculated from HI (Hyrdrogen Index) and OGF (Oil Generative Fraction). 4. Conversion to barrels of oil equivalent (BOE). Stage one determines the volume of source rock within the thermal aureole. This is dependent on the size of intrusion and extent of thermal aureole as defined above with the likely response of the organic matter dependant on the pre-intrusion maturity of the host rocks. We take the average maximum extent of the thermal aureole to be 100% *i.t.* (intrusion thickness) based on our findings from intrusions into immature source rocks (Figs. 2 & 3). The extent of the aureole will of course differ in other systems. Within this volume we assume 60% of the affected source rock to be in the oil window (40-100% *i.t.,* Figs 2 & 3) based on EOM, Raman, Total Organic Carbon (TOC) and organic geochemical parameters including n-alkane envelopes and other biomarkers (homohopanes from Muirhead et al 2017 and this study; aromatic hydrocarbons, methylphenanthrenes from George, 1992; Bishop & Abbott, 1995; Muirhead et al 2017 and others noted above). Moving from the intrusion-county rock contact to the outside of the aureole, the first 0-20% of intrusion thickness is typically a hydrocarbon-loss zone due to proximity to the intrusion contact, at 20-40% intrusion thickness there is a gas zone and 40-100% *i.t* there is an effective oil window (see Muirhead *et al,* 2012 for indicative temperatures; Muirhead et al, 2017). Once these data are gathered the volumetric calculations can be performed. To perform calculations the following organic geochemical data is required; total organic carbon (TOC wt %), volume of source rock (cm^3), source rock density (g/cm^3), mass of convertible organic carbon (based on hydrogen Index) and the gas-oil ratio to account for the oil generative fraction (OGF) of the immature source rock. The final stage is to convert to barrels of oil equivalent (BOE) at standard temperature and pressure (surface).

Results

The volume of the intrusion is simplified to a cuboid and multiplied by two to account for volume of shale within the aureole above and below the intrusion. This provides the total volume of shale exposed to

thermal alteration by an intrusion. As discussed above only 60% of the shale volume is assumed to be within the oil window (1).

$$V \ (cm^3) = [V_{intrusion} \ (cm^3) \times 2] \ 0.6 \qquad\qquad (1)$$

To calculate the mass of organic carbon, (g TOC) available, the volume of the source, V (cm^3), is multiplied by average formation density, ρ (g/ cm^3) and TOC (wt. %). Multiplication of these parameters gives the mass of organic carbon within the source rock, equation (2).

$$M \ (g \ TOC) = [TOC \ (wt. \ \%) \ / \ 100] \times \rho \ (g/ \ cm^3) \times V \ (cm^3) \qquad\qquad (2)$$

For our calculations the average density used was 2.45 (g/cm³), a reasonable average for lithified and compacted mudrocks, not yet buried to depths likely to equate to the oil window in most sedimentary basins (Schmoker 1994). This permits a thermally immature source rock to be used as a base-case, and therefore reductions in TOC caused by prior periods of hydrocarbon-generation need not be considered. Equation (3) is for the mass of hydrocarbons generated by intrusive activity (kg HC), and is obtained by the multiplication of the HI (mg HC / g TOC) and OGF to calculate only the convertible portion of total organic carbon.

$$HCG \ (kg \ HC) = M \ (g \ TOC) \times HI \ (mg \ HC \ / \ g \ TOC) \times OGF \times 10^{-6} \ (kg/mg) \qquad\qquad (3)$$

Hydrogen index (HI = S2/TOC × 100) represents the convertible portion of kerogen. The remaining portions of kerogen are thus ignored in this equation, and the initial petroleum (S1) is assumed to be small for a thermally immature source rock. Average HI (mg HC / g TOC) typifies the kerogen type, based on approximate field data. For an immature source rock only the initial HI is used for the equation. However,

if prior periods of oil generation had occurred, a value of HI at the time of intrusion would be used. Convertible kerogen is split into oil and gas fractions. In the equation we use the oil generative fraction (OGF) determined from published source data (Pepper & Corvi, 1995).

The generated hydrocarbons, (kg HC) is then converted to barrels of oil equivalent HCC (BOE). The conversion divides 1 kilogram (Kg) by the weight of 1 barrel of oil (1 US barrel = 158.9L) which depends on specific gravity (SG). For most oils (10-45° API) SG ranges from 0.8-1. Equation (4).

HCC (BOE) = HCG (kg HC) x (1/(158.9 x SG))   (4)

For our calculations we assume the API of 37°, typical for oil discoveries on the NE Atlantic Margin which has a calculated SG of 0.83. One Kg of hydrocarbons equalling 0.00749 barrels which is the conversion factor used to convert barrels of oil equivalent (BOE).

Example calculation for oil only

Volume of source rock with thermal aureole:

1) V (cm³) = [$V_{intrusion}$ (cm³) x 2] 0.6

$V_{intrusion}$ = [(10000 cm³ x 2000000 cm³ x 1000000 cm³)x2] 0.6 = 24000000000000000 cm³

Mass of organic carbon with source rock:

2) M (g TOC) = [TOC (wt. %) / 100] x ρ (g/ cm³) x V (cm³)

M= (2/100) x 2.45 g/cm^3 x 24000000000000000 cm^3 = 1176000000000000 g TOC

Hydrocarbons generated:

   3) HGC (kg HC) = M (g TOC) x HI (mg HC / g TOC) x OGF x 10^{-6} (kg/mg)

HCG= 1176000000000000 g TOC x 600 mg HC/g TOC x 0.82 x 10^{-6} = 578592000000 kg HC

Hydrocarbons converted:

   4) HCC (BOE) = HCG (kg HC) x (1/(158.9 x SG)

HCC= 578592000000 kg HC x 1/(158.9 x 0.83976) = **4336,027,000 barrels.**

Discussion

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From our example we calculate a 100m thick intrusion covering an area of 200km^2 could potentially generate 4336 million barrels of oil equivalent provided the intrusion duration was sufficient to cook the entirety of the oil generative portion (Aarnes et al 2010, Muirhead et al 2012). Intrusions on such a scale and duration are not uncommon in rifted margin settings, for example West of Shetland, with some suggestion of intrusion-induced oil to gas cracking (Fig. 4) (Schofield *et* al 2017). Critically, although the volume of oil generated is very large, when charging and expulsion efficiencies are taken into consideration (McDowell, 1975), less petroleum is available to the system. Using system efficiencies of 2.8% for the North Sea (Evans, 2003) and 13% for the Greater Oseberg area, Norway (Dahl & Yukler 1991), a total of 20-560 MMBOE is potentially available to charge a reservoir. Efficiencies are likely to be on the lower end of these ranges due to the complex migration associated with intrusions (Schofield et. al, 2017). These

volumes would be comparable to the volumetric size of many of the fields located along the NE Atlantic Margin (Schofield et al, 2017, Mark et al, 2017).

Implications for hydrocarbon generation in volcanic affected basins

It is highly unlikely that an entire rifted margin petroleum system can be brought to the point of oil generation solely by heating within the thermal aureoles of igneous intrusions. However, clearly there is the potential for such a mechanism to contribute, however small, to the generative potential of these basins where source rocks are immature prior to intrusion. Already mature or over-mature source rocks have the potential for the generation of an extended gas phase (Muirhead et al 2017) with examples of such systems indicating gas reserves adjacent to intrusions (Schofield et al 2017 and Figure 4). However, these cases are not common, with intrusions likely to affect mature systems in a negative manner, due to complete over-maturation or graphitisation (Lindgren & Parnell, 2006). The majority of hydrocarbon accumulations associated with intrusions are not typically commercial, although there are occurrences of operating petroleum systems in close proximity to intrusion networks (Schofield et al, 2017). Understanding basin heat flow with respect to igneous intrusions, alongside the geochemical responses of potential source rocks may help to elucidate the mechanisms by which source rocks have been brought to maturation.

It is important to note here the need for careful appraisal of discrete basins in regions such as West of Shetland, where thermal and burial histories vary significantly over a small geographical area (Schofield *et* al 2017; Mark *et al* 2017). Spatially, there is evidence for discrete sub-basins only a few 10s of kilometres apart to display vastly different intrusion regimes and hydrocarbon potential; typical basin modelling that relies on large, often basin-wide (on the scale of the Faroe-Shetland Basin, for example) assumptions will miss some of the nuances noted above in the geochemical responses and thus not fully consider the implications for intrusion induced maturation.

A further area for consideration is the duration of maturation of the host rocks. Intrusions can generate hydrocarbons rather rapidly compared with burial maturation (Galushkin, 1997; Muirhead *et al*, 2012) and thus there is potential for any immature sources within sub-basins in regions such as the Faroe-Shetland Basin (FSB) (Mark *et al*, 2017) or indeed the Sea of Hebrides Basin to be brought to maturation potential (Muirhead *et al*, 2017). Over 70% of intrusions penetrated in the FSB are <15m thick (Schofield et al 2017) and the generation potential from such intrusions when compared to the 100m thick scenario above is minimal. However, recent modelling of multiple intrusions suggests that the compound heating could initiate large scale/basin wide thermal input beyond thermal aureoles (Aarnes 2011) with calculated responses well within typical commercial volumes (Aarnes 2015, Iyer, 2017).

Furthermore, the cases considered above display the need to carefully evaluate the organic geochemical responses of intrusions in rifted-margin basins, with several petroleum systems worldwide operating within intrusive regimes, it would be prudent to try to constrain the end-member mechanisms by which source rocks can be induced to generate petroleum. More detailed geochemical analyses have the potential to not only deepen our understanding of the maturation histories of the host rocks, but determine whether the organic matter was brought to maturation via typical burial routes or as a result of rapid thermal maturation induced by igneous intrusions. Most discoveries in rifted settings can of course be explained by thermal maturation due to burial, however all basin models have non-unique solutions.

The cases we present here are based on surface-data and show that even at first consideration large volumes of petroleum are generated in relatively small areas by igneous intrusions. Crucially, these large volumes of petroleum have been generated from source kitchens that could not be predicted by conventional burial models alone, and are potential source rocks that would otherwise have been predicted to be thermally immature yet have produced commercial volumes of oil.

Conclusion

This study adds some clarity to the potentially crucial impacts that intrusions may have on developing working petroleum systems. Critically, the basis for these estimates relies on the integration of several petroleum systems techniques to gauge the extent of thermal alteration surrounding intrusions. Without these empirical data it would not be possible to present the potential for intrusions to generate commercial volumes of oil. Of significant importance in such studies is the understanding of the host rock and intrusion interactions and the likely extent of the thermal aureoles. As discussed above, thermal aureoles can vary significantly and therefore one must approach maturation volume estimates with caution. When quantified, the potential volume of oil generated by thermal maturation within igneous intrusions can be shown to be commercially important. Despite the assumptions in these data, this report allows for a greater appreciation and appraisal of the potential extent of alteration and thus volume of hydrocarbons produced as a result of igneous intrusion.

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Fig. 1. Distribution of known intrusive regimes within petroleum systems or potential petroleum systems in sedimentary basins. Large Igneous Provinces highlighted in red, black arrows basins with associated igneous activity. (Adapted after Ganino *et* al (2008); Svensen & Jamtveit (2010); Uenzelmann-Neben (2013)).

Fig. 2. Cumulative percent Extractable Organic Matter (EOM) with respect to percent intrusion thickness, depending on pre-intrusion maturity (either <0.5 %R_o (dots) or >0.5 %R_o (crosses)) of the host rock. EOM *(inset)* showing averaged response from the six intrusions in this study alongside those from previous work (Raymond & Murchison 1988; Bishop & Abbott, 1995; Galushkin, 1997; Stewart *et al,* 2005). Greyed out area indicating location of oil window as a result of intrusion.

Fig. 3. Typical responses of immature source rocks in the metamorphic aureole of intrusions studied. **A:** *n*-Alkane envelope (modified after Muirhead *et al,* 2012; 2017) showing full range of response from immature background, through oil window and towards gas window; **B:** representative *n*-alkane envelopes from Raton and Flodigarry sample sites within the gas window, oil window and prior to heating; **C:** Raman spectroscopic response (modified after Muirhead *et al,* 2012; 2017 and data from this study); **D:** %TOC (averaged response from this study and others noted in text). Vertical dotted lines indicate the zone of petroleum generation as noted by both solid organic matter responses (Raman) and soluble organic matter (*n*-alkanes from this study, homohopanes after Muirhead *et al* 2017).

Fig. 4. – Geoseismic interpretation (modified after Schofield *et al.* 2017) though the Benbecula Gas discovery, NE Atlantic Margin. Isotopic analysis carried out on the gas, found that it possessed a 'very unusual isotopic signature' with the favoured explanation being that the gas is a mixture of a small amount of normally generated 'oil-associated' gas, plus a more extensive amount of dry methane caused by extensive 'oil to gas' cracking, potentially caused by cracking via igneous intrusions (highlighted in red).

Table 1. Location and summary or each intrusion from this study.