

Session 35: Mineralogy of petroleum reservoirs

WH1: Improved Mineralogical and Petrographic Characterisation of Cuttings and Cores from Petroleum Reservoir Sequences Based on Established Automated SEM-based techniques

A.R. Butcher¹, D. Pirri², P. Gottlieb¹ and P. K. Hughes¹

¹CSIRO Minerals, PO Box 883, Kenmore, Queensland 4069, Australia

alan.butcher@csiro.au.

²Camborne School of Mines, University of Exeter, Redruth, Cornwall TR15 3SE, UK

The mineralogy of petroleum reservoirs in exploration and extraction has continued to play a key role in the fundamental understanding of stratigraphic sequences within hydrocarbon-containing sedimentary basins. Given that cores and cuttings are generally the only samples available to the geologist for direct examination of the sequence through which the drill bit has penetrated, great importance is often placed on documenting them as accurately as possible, both at the time of drilling and post-drilling.

Traditional optical, SEM, EPMA, and XRD mineralogical analysis methods are well established and used widely within the industry. In this study, we have used a proven technology, developed over 20 years for the mining industry, to measure cuttings and cores from reservoir sequences around the world. The technology, known as QemSCAN, utilises a fully-automated scanning electron microscope-based analysis system. It is able to rapidly scan cuttings and cores, and identify on-line, most rock-forming minerals. Mineral identification is based on compositional information gained from rapidly acquired EDS X-ray spectra. Mineralogical parameters that can be quantified automatically include: modal proportions, average grain size, chemical composition, and rock type.

Results will be presented in the form of a series of case studies carried out since 1999. Some of these studies were designed to demonstrate QemSCAN's ability to discriminate a high level of sedimentary textural complexity, such as resolving different clay cements in siliciclastic rocks, intricate bedding features in diamictite sequences, and replacement features in ironstone horizons. Other studies were aimed at solving specific problems, such as inter-well correlation based on layer-by-layer fingerprinting of detrital heavy mineral assemblages; or quantifying the nature and efficiency of seal rocks on a local and regional scale.

While QemSCAN will not replace real-time mud-logging methods, it has been shown to be a useful and valuable off-site mineralogical and petrographic tool that can provide the geologist with new eyes through which he or she can view key stratigraphic sequences within petroleum reservoirs.

WH2: Experimental calibration of reaction products among drilling fluids and rock cuttings as a function of drilling style

J.M. Evensen, G.A. Otten and M.E. Schaps

jmevens@upstream.xomcorp.com

ExxonMobil Upstream Research Company, PO Box 2189, Houston TX 77252, USA

An increasing amount of textural and chemical evidence suggests that melting or metamorphism likely occurs during the drilling process, where the thermal regime at the bit may exceed 600 °C. The degree of alteration experienced by oil-based (mostly diesel + barite) and water-based drilling fluids (mostly water + hydrocarbon liquids + barite) was evaluated experimentally over a range of drilling conditions. The results constrain scenarios for genesis of drill cuttings and their coexisting fluids, and the interpretation of such materials.

Fresh drilling muds were added to a matrix of coarse Boise Fm. sand (Qtz₈₁Or₉Ab₂Il₁Ch₁Hem₁), which was thermally pre-fractured to facilitate trapping of fluid inclusions in quartz at run conditions. Starting materials were evaluated at a constant pressure of 100 MPa (P_{Δ}) as a combined function of time and temperature (T): 14 days at 325, 7 days at 450, or 1 h at 600 °C. Run products were analysed by a combination of (A) direct plus extraction Gas Chromatography/Mass Spectrometry (GC/MS), (B) Magnetic Sector GC/MS, and (C) mass spectrometry of crushed fluid inclusions.

Going from 325° to 600°C, several parallel trends are observed among the water and oil-based series experiments. Contents of propane, butane and pentane rise then fall, whereas nitrogen plus some thermally stable aromatic hydrocarbons (e.g., methane, naphthalenes, phenanthrenes, diphenyl, dibenzothiophenes, pyrenes,

chrysenes) greatly increase. Over the same conditions, differences between water- and oil-based series are noted in contents and trends of ethane, benzene, toluene, carboxylic acids, CO₂, and helium.

While fluid compositions at the drill bit may clearly be affected by high- T interactions, the scale of potential melting/metamorphism remains an outstanding question. Compared to small cross-sectional areas of boreholes likely subjected to petrotexis, large volumes of circulating fluid probably facilitate loss of high- T fluid signatures via dilution. Rock cuttings, on the other hand, are more likely to retain evidence of high- T process. Tracking pre-drill vs. post-drill evolution of fluids is critical for differentiating drilling products from geologic hydrocarbons, and designating downhole intervals subject to alteration. Challenges include (1) the increasingly invisible signal present in water-based muds, which complicates the tracking of high- T events, and (2) that the extent of reaction is appreciably unknown in the high- T portion of the system quartz-feldspar-water-oil. The most common manifestations of petrotexis appear to be hydrocarbons bearing anomalous amounts of refractory aromatic compounds (cf. maturity indices) that likely correspond to downhole intervals where diamond or coring bits were used.

WH3: Metamorphic and thermal history of a marine volcanoclastic forearc basin: correlation of geothermometers

S. Miller¹ and D. I. M. Macdonald²

¹Department of Geology & Zoology, National Museums of Scotland, Chambers Street, Edinburgh, EH1 1JF

s.miller@nms.ac.uk

²Department of Geology & Petroleum Geology, University of Aberdeen, Aberdeen, AB24 3UE

We present a study of the low temperature metamorphism of a single sedimentary sequence from a little-deformed fore-arc basin of Mesozoic age in Antarctica. This basin has been inverted and its volcanoclastic fill is well exposed, allowing us to correlate various geothermometers to stratigraphic and structural height and hence to define constraints on models of basin burial history and geothermal gradients more clearly.

Samples were selected from the Late Jurassic Himalia Ridge Formation (HRF) to test the effects of grain size, depositional facies and stratigraphic height on the mineral paragenesis; the HRF is 2,200m thick at the study locality. The authigenic mineral assemblages were examined by light microscopy, SEM/EDAX and XRD techniques. In addition, oxygen isotopes, illite crystallinity and vitrinite reflectance were measured. Fission track methods were used to constrain depths of burial. The diagenetic effects include compaction, pore-space reduction and cementation by clay minerals, calcite, chlorite, laumontite, prehnite, quartz, haematite, pyrite and epidote. There is also dissolution and replacement of volcanic fragments by calcite, chlorite, laumontite, prehnite, pumpellyite, albite and mica. Chlorite "crystallinity" increases with increasing depth. Detrital organic matter has values ranging from $R_o = 2.3 - 3.7\%$, indicative of semi-anthracite to anthracite coal rank. The mineral assemblages presented here define two metamorphic grades; the uppermost 2000m belong to the zeolite facies, while the lowest 200m of the HRF are prehnite-pumpellyite grade. The results indicate a probable diagenetic/metamorphic temperature range of between 150°C and 250°C. The data and field observations imply maximum burial times of between 80 and 97 Ma for base and top of the HRF respectively. This suggests a geothermal gradient for the sequence of approximately 45°Ckm⁻¹. This is higher than the continental "average" palaeogeothermal gradient and implies that the HRF underwent significantly more heating than most forearc basins, which tend to be hypothermal (30-70% of global average heat flow values).

The high heat flow may be associated with recently documented volcanism due to active rifting. The higher metamorphic gradient may also be a result of increased heat flow in the basin due to arc relocation from the Peninsula area to western Alexander Island during early Tertiary times. The observations on the thermal history of the HRF would therefore indicate that the top of the section was buried by 3000-3500 m of younger sediment, rather less than the maximum possible overlying sediment thickness of close to 5000 m.

Session 35 Abstracts

WH4: Geochemical interactions between reservoir minerals and petroleum

Richard H Worden

Department of Earth Sciences, University of Liverpool, UK, L69 3GP

It is assumed typically that minerals do not affect the geochemistry of petroleum in subsurface accumulations: the organic and inorganic are thought to be entirely separate realms. Petroleum is stored naturally in the pores between mineral grains although some initial water remains following petroleum-filling. Residual water adheres to mineral surfaces if a specific mineral is water-wet although if a mineral is oil-wet, the surface will be coated with petroleum. Although minerals and petroleum do not easily interact, residual water provides a mechanism for geochemical interaction between the petroleum and minerals in the reservoir.

Petroleum contains reduced compounds. Oxidised minerals are unstable in the presence of petroleum and redox reactions are the likely consequence. Oxidised minerals found recurrently in reservoirs include sulphates and ferric-iron bearing minerals. Gypsum and anhydrite are common in sandstone and carbonate reservoirs and yet they are thermodynamically unstable in the presence of petroleum. At low temperature (<80°C), the process is mediated by bacteria; at higher temperature (>120°C) the kinetics of thermochemical reaction become favourable. The consequences of SR are replacement of sulphates by carbonates and loss of reactive hydrocarbon compounds from the petroleum. Ferric iron reduction also is common, the consequences being bleaching of rocks by petroleum and the increasing availability of ferrous iron for incorporation into carbonate and other late stage mineral cements.

Another result of SR is the conversion of sulphate into sulphide. In the presence of iron, the sulphide leads to late diagenetic pyrite, common in many reservoirs. In the absence of iron, the sulphide may accumulate as H₂S in petroleum fluids. H₂S can also back-react with remaining petroleum and lead to an increase in the petroleum-sulphur content with increasing amounts of thiol and thiophene compounds.

Non-hydrocarbon gases from petroleum source rocks, such as CO₂, can have significant effects on reservoir minerals. Increasing CO₂ fugacity leads to either carbonate mineral dissolution or precipitation depending on the strength of the pH buffer. Long-term, organically-derived CO₂ routinely gets incorporated into late stage mineral cements. Ammonia incorporated into diagenetic Krich minerals (feldspars and illite) has been assigned to petroleum source origins and, of course, organic H₂S from S-rich source rocks will react with iron-minerals in reservoirs to produce late diagenetic pyrite.

Controversially, it is being recognised that clay minerals catalyse reactions of organic compounds. Light hydrocarbon populations may be the direct result of catalysis by specific clay minerals in source rocks or reservoirs.

WH6: Relation between microstructure, mineralogy and permeability evolution during diagenesis: a study of Gulf of Mexico mudstones

D. Charpentier¹, R.H. Worden¹, Q.J. Fisher², A.C. Aplin³

¹University of Liverpool, 4 Brownlow Street, Liverpool, L69 3GP, United Kingdom.

dcharpen@liverpool.ac.uk

²University of Leeds, Leeds, LS2 9JT, United Kingdom.

³University of Newcastle, Newcastle upon Tyne, NE1 7RU, United Kingdom.

Mudstone microstructure is poorly understood even though it is an important characteristic of mudstone evolution and has a profound impact upon caprock sealing capacity. Microstructure, mineralogy and macrostructure are initially controlled by the depositional environment and then modified by diagenetic processes:

- mechanical compaction may lead to a reduction in volume due to reorientation and breakage of grains;
- chemical reactions require dissolution of material and precipitation of newly formed minerals.

The aim of this study was to determine the relation between mineralogy, microstructure and macroscopic characteristics. The study has been realised on a suite of samples of Gulf of Mexico mudstone, with samples from 19,000 to 25,000ft depth. Mineralogy was determined by electron microscopy and X-ray diffraction. Microstructure was studied by backscattered electron microscopy analysis and transmission electron microscopy on ion-beam thinned samples. Permeability, pore size distribution and porosity data have also been collected.

Mineralogy of the shallowest mudstone sample is dominated by quartz, K-feldspar, plagioclase, calcite (bioclastic and detrital grains), iron oxide and clay minerals. Halite was also detected in this sample. The <5µm clays minerals are micas and Fe,Mg-chlorite. Clay minerals >2µm are mainly K-smectite (80%). The particles are randomly organised. Permeability and porosity are respectively $1.2 \cdot 10^{-30} \text{ m}^2$ and 19%.

The mineralogy of the deepest samples consists of quartz, minor K-feldspar, plagioclase, siderite or ankerite, pyrite, chlorite, micas and kaolinite. Clay minerals >2µm are mainly illite. The grains in these samples are orientated approximately parallel to the bedding. Permeability and porosity are respectively $4.8 \cdot 10^{-21} \text{ m}^2$ and 12%.

The principal mineralogical reactions observed are thus: (1) transformation of smectite into illite and dissolution of K-feldspar. The proportion of smectite decreases from 80% to 20% with an important decrease at depth greater than 24400ft; (2) dissolution of calcite and precipitation of siderite or ankerite at depths greater than 20200ft; (3) formation of kaolinite and/or chlorite in primary pores in bioclasts; and (4) dissolution of iron oxide and the precipitation of pyrite at depths greater than 20,200 ft.

The transformation of smectite into illite is closely associated with the re-orientation of the clay particles. The decreases in both permeability and porosity also coincide with clay mineral transformation.

The results obtained on the mudstone from the Gulf of Mexico show that there is a good relationship between permeability, microstructure and diagenetic reactions. These results have allowed the generation of a model of the evolution of mudstone rock properties during burial diagenesis.

WH7: Fibrous illite records the onset of oil charge to the Penguin Field, Northern North Sea

Andrew J. Cavanagh¹, R. S. Haszeldine¹, and G. D. Couples²

¹Department of Geology and Geophysics, The University of Edinburgh, Edinburgh EH9 3JW, UK.

acavanagh@glg.ed.ac.uk

²Department of Petroleum Engineering, Heriot-Watt University, Edinburgh EH14 4AS, UK.

The Penguin Field of the Northern North Sea is a complex array of four distinct hydrocarbon traps spanning the Magnus and Brent Provinces of the East Shetland Basin. The field is also juxtaposed between the petroleum systems of the Viking Graben and the More Basin. The field has been diagenetically altered during the later stages of burial by fibrous illite. K-Ar ages for fine fractions of illite cement extracted from reservoir sandstones within the Penguin field display an unusual range of ages with respect to other studies for the East Shetland Basin and the Magnus oil field. Ages for the Penguin field appear to range from as much as 120 Ma to 30 Ma. Data sets similar to this exist for other fields in the vicinity, and have, without exception, been interpreted as artefacts of detrital contamination resulting from the separation method employed. However, the Penguin field separates appear to be of high quality after characterisation by XRD, and TEM analysis. An alternative geological model is proposed to explain these unusual ages. Namely, fibrous illite diagenesis in the Penguin Field is a response to the onset of oil migration in both local kitchen areas and deeper, more remote source areas associated with the Atlantic margin. This model is additionally supported by oxygen and deuterium stable isotope data. The general population of illite ages published for the East Shetland Basin is reinterpreted in light of these findings.

WH8: Oil charge preserves porosity in sandstones and limestones

R Stuart Haszeldine Department of Geology and Geophysics,

University of Edinburgh, EH9 3JW

s.haszeldine@glg.ed.ac.uk

The porosity and permeability of a sandstone is a function of its depositional grain size and sorting, followed by its diagenetic cementation. The dominant mineral to reduce porosity is quartz cement around detrital grains. Porosity reduction by this process is about 8% per km in the North Sea. Oil companies such as Exxon or Statoil do not appear to be convinced that porosity preservation can occur, whereas BP does. Porosity preservation could, theoretically, be achieved by halting quartz cementation by "waterproofing" sandstone pores with hydrocarbons.

Session 35 Abstracts

We have made a detailed study of the Brae, Miller and Kingfisher submarine fan sandstones of the Upper Jurassic Brae Formation in the North Sea (Marchand *et al.*, Geology 2001, AAPG 2002). Quartz cementation is systematically halted by progressive oil charge, lasting for 40 Ma duration. This forms 10-15% quartz cement in the aquifer at 4.0 km burial, which can successfully be predicted by EXEMPLAR modelling. However the oil zone has porosity typical of 2km burial. Extrapolating aquifer porosity and dynamic permeability during oil production from cores taken in the oil zone is incorrect.

Chalk in the UK and Danish North Sea decreases in porosity with increased burial, with locally derived calcite forming by a self-cementing process analogous to quartz in sandstones. The progress of cementation can be tracked by decreases of measured porosity, or by progressive reduction of the delta 18O of the whole rock. Data from several fields shows that the first 600 m of burial are characterized by compaction without significant cementation. Deeper than that, there is a progressive cementation, which completely eliminates porosity by 3.0 km. Chalk oilfields all have anomalously high porosity, sometimes 40% at 3.0 km, and rapid gradients of increased cementation with depth, corresponding to rapid porosity decline with depth. This is the same pattern as that seen in sandstones. Chalk cementation has been prevented by oil charge, sometimes from less than 1km burial; the porosity has been preserved through 2 km of burial.

The importance of this process is that gradients of porosity decline in gradually-charged sandstones and limestones are often 40% per km. These produce step changes of reservoir quality at the oil water contact, which are important for positioning development and production wells. A series of high porosity anomalies can be targets for satellite developments around existing fields, or targets for deep drilling in offshore deepwater exploration.

WH9: Evidence for multiple hydrocarbon charges from diagenetic evidence, UK North Sea sandstones: Brent Group and Fulmar Formation

M. Wilkinson¹, R.S. Haszeldine¹ and A. E. Fallick²

¹Department of Geology and Geophysics, Grant Institute, University of Edinburgh, Edinburgh, Scotland, UK, EH9 3JW

m.wilkinson@glg.ed.ac.uk

² Scottish Universities Environmental Research Centre, East Kilbride, G75 0QF, Scotland, UK.

Paragenetic sequences proposed for reservoir sandstones from the UK North Sea show only a single phase of hydrocarbon filling as the last diagenetic event. The paragenetic sequences show no interplay between the emplaced hydrocarbon and diagenetic reactions ongoing in the sandstone, except to stop (or dramatically slow) reactions within the oil-leg. However, there is sometimes evidence from the chemistry of reservoir petroleum that reservoirs fill in multiple stages, from multiple sources. Also, as some potential reservoirs lack a current hydrocarbon charge but have evidence of a previous charge, it is clear that reservoirs sometimes lose their petroleum charges into overlying formations, due to seal failure for example. Combining these observations, we conclude that some reservoirs may have had a complex history of filling and emptying, potentially with several 'cycles'. If this is the case, then this history should be recorded in the diagenetic minerals grown within the reservoir. Here we present diagenetic evidence for multiple episodes of reservoir filling and emptying from the Brent Group and the Fulmar Formation of the North Sea.

Authigenic kaolin from the Cormorant Field (Brent Group, UK North Sea) shows a strong correlation between oxygen isotopic composition and depth. This is interpreted as kaolin growth synchronous with hydrocarbon charging. The first filling event was a relatively early, slow, phase (45 - 70°C; 80 - 50 Ma) which filled the reservoir to substantially below the present day oil-water contact. The hydrocarbons subsequently leaked off, allowing diagenetic activity to recommence. The arrival of the present day hydrocarbon charge was a comparatively recent event.

In the dry well in the Fulmar Formation (UK well 29/10-2), K-Ar ages from illite show a younging-downwards trend interpreted as oil-filling from 64 to 84 Ma ago, when the reservoir was at only 50°C. The hydrocarbon was derived from an adjacent deep graben, and was probably subjected to biodegradation producing some of the ubiquitous bitumen. The hydrocarbon pre-dates most of the diagenesis, including dissolution of K-feldspar and formation of quartz overgrowths and ankerite. These authigenic reactions almost certainly occurred when the reservoir was largely empty of hydrocarbons, so that the early charge must have leaked off. However, the ankerite and authigenic quartz are overgrown by bitumen, implying a second phase of hydrocarbon filling. As the reservoir is dry at present day, this later hydrocarbon must also have leaked off, possibly coincident with an episode of grain fracturing which preserves fluid inclusions.

WH10: ⁴⁰Ar/³⁹Ar ultraviolet laser microprobe (UVLAMP) dating of complex K-feldspar overgrowths: from sandstone burial to lead-zinc deposition

S.C. Sherlock¹, T. Lucks² and S.P. Kelley¹

¹Dept Earth Sciences, The Open University, Milton Keynes, MK7 6AA, U.K.

s.sherlock@open.ac.uk

²School of Earth Sciences, University of Leeds, Leeds, LS2 9JT, U.K.

Dating diagenesis is riddled with problems, not least due to the low temperatures of mineral formation, which results in isotopic disequilibrium in most systems, but also the fine grain size of minerals. We present new ⁴⁰Ar/³⁹Ar data from complex authigenic K-feldspars obtained using the high spatial resolution UV laser microprobe (UVLAMP). Analysis is performed in situ, and at a resolution which enables a good distinction between both detrital, and two phases of authigenic K-feldspar growth. Samples from the Laisvall sandstone-hosted Mississippi Valley-type (MVT) lead-zinc deposit in the Swedish Caledonides have yielded three groups of ages. Detrital K-feldspars are Proterozoic, and range from 1600 to 600 Ma. There are two groups of authigenic K-feldspar ages - one mid Cambrian/early Silurian, with ages ranging from ca. 480 to 550 Ma, and a younger group of late Silurian, ca. 425 to 435 Ma. There is no spread of ages between these three distinct age groupings, arguing against there being significant mixing, either analytically or isotopically, between them. The deposition age of the sandstone is considered to be between 640 Ma and ca. 520 Ma, based on palaeontological evidence, and the oldest group of authigenic ages are interpreted as reflecting initial burial of the sandstone. The younger authigenic age group is considered to be genetically related to early phases of MVT deposition, and at ca. 435 to 425 Ma coincides with early compression within the Caledonides, which is thus considered a possible fluid-source for the MVT metallogenesis. The high spatial resolution ⁴⁰Ar/³⁹Ar UVLAMP technique is ideally suited to resolving age information in complex diagenetic K-feldspar overgrowths. K-feldspars are naturally highly potassic, and with a UV laser there is negligible heating of surrounding areas of ablation, preventing the problem of obtaining mixed detrital/authigenic ages from small areas of sample.

WH11: The influence of provenance on the diagenetic reactions of detrital feldspars

P. Thompson¹, M.R. Lee², I. Parsons¹

¹ Dept. of Geology and Geophysics, University of Edinburgh, Kings Buildings, West Mains Road, Edinburgh EH9 3JW

² Division of Earth Sciences, Lilybank Gardens, University of Glasgow, Glasgow, G12 8QQ

Pauline.Thompson@glg.ed.ac.uk

Detrital feldspars preserve intracrystal microtextures which reflect the igneous or metamorphic conditions under which they formed. These control their dissolution rate during diagenesis and susceptibility to replacement reactions. We have examined 35 samples from the Fulmar sands in four Central North Sea wells (30/16-7, 22/30b11, 22/23b6 and 22/30-8) by optical microscopy, SEM, TEM, CL, and EPMA. We have seen feldspars whose microtextures indicate at least 5 different ultimate provenances: 1. *Granulite facies metamorphic rocks*. Distinctive mesoperthitic granulite textures suggest a probable origin in the Norwegian Caledonides or possibly the Scottish Lewisian. These feldspars are pristine and devoid of microtextures aiding dissolution. 2. *Low-temperature metamorphic rocks*. Detrital plagioclases have compositions from Ab₀₀ to ~Ab₈₀An₂₀. TEM shows that many are rarely-reported sub-microscopic peristerite intergrowths. Their characteristic composition may indicate a specific source. They are usually partially replaced by albite. 3. *Acid or alkaline volcanics*. These optically featureless sanidines are abundant in the Fulmar. Their source is obscure as North Sea volcanicity is mainly basaltic or nephelinitic. Defect-free sanidines are resistant to dissolution and their abundance may be due to this characteristic. 4. *Granites/amphibolite facies gneisses*. These are fine lamellar perthites with bulk compositions characteristic of calc-alkaline granites. They are poor in defects that lead to rapid dissolution. 5. *Deuterically altered granites*. Most alkali feldspars from

Session 35 Abstracts

granitic source rocks are deuterically altered and are optically turbid. They are profoundly recrystallised and exceptionally reactive in low-*T* fluids. Intense dissolution of such grains is common. Much of the feldspar lost from the Fulmar during burial was probably of this type. Albitisation is common but it is not obvious whether this occurred in the parent rock or diagenetically. There are many potential sources for types (4) and (5) in the Scottish or Norwegian Caledonides.

Diagenetic changes are highly variable between neighbouring grains and hence the provenance of grains is the most important control in their authigenic histories. Albite and K-feldspar both occur in the same samples as overgrowth and replacive phases and partial dissolution of overgrowths is common. Authigenic textures record events involving changes in pore fluid chemistry in a framework of changing temperature. Thus clastic feldspars with their inventory of authigenic changes act as sensitive recording devices of diagenetic reactions. They provide a window onto these processes that is independent of changes in overall provenance, modal variation caused by local sedimentological factors, and large-scale export or import of components into the rock during diagenesis.

WH12: Scaling-up diagenesis for macro-scale modelling: an example from an Upper Jurassic sandstone reservoir of the Outer Moray Firth, North Sea, UK

G.L. England¹, S. Haszeldine¹, P.W.M. Corbett², D.K. Potter², S.A. Barclay^{1*}

¹Dept. Geology and Geophysics, Grant Institute, University of Edinburgh, Edinburgh, EH9 3JW, UK, Gavin.England@glg.ed.ac.uk

²Dept. Petroleum Engineering, Heriot-Watt University, Riccarton, Edinburgh, EH14 4AS, UK

* Present Address: CSIRO Petroleum, PO Box 136, North Ryde, NSW, 1670, Australia

It is well established that during the deep burial of sandstones, diagenetic processes can greatly reduce (or increase) porosity by 50-70% and permeability by a factor of 500-100,000. These diagenetic processes are usually identified at the micro-scale (thin-section/core), but modelling is often required at the macro-scale (e.g. engineering-scale fluid-flow in a reservoir or basin-scale computer modelling). Accurate extrapolation is required away from the points of measurements, but this depends on the validity of sampling to capture and represent the variation within the sandstone reservoir. To achieve this, the petrographer needs to consider: 1) how much of an effect the diagenetic variable has on reservoir quality; 2) what analytical technique best represents the diagenetic variable; and 3) how many analyses are required for each diagenetic variable and where they should be positioned to accurately characterise the reservoir.

This study examines a shoreface unit within an Upper Jurassic sandstone reservoir of the Outer Moray Firth, UK North Sea. The study applies a "genetic unit" approach and intensively samples the same sedimentary unit at different depths (12,000 and 14,000 ft) to compare the effects of diagenesis. Various analytical techniques were applied and compared, including thin section point counting, quantitative XRD, SEM/CL to quantify quartz cement, $\delta^{18}\text{O}$ of authigenic quartz and magnetic susceptibility measurements to quantify illite content. The study demonstrated that syntaxial quartz overgrowths and pore throat-inhibiting illitic clays were the major contributors to reduced porosity and permeability in the deeper well. In many cases, the diagenetic cementation matched sedimentation and permeability trends. It was also evident that some techniques that characterised various diagenetic components appeared more responsive to trends in permeability, such as magnetic susceptibility compared to quantitative XRD of illite.

Once the "genetic unit" was characterised, the diagenetic phases were then statistically validated and up-scaled (i.e. averaged) to be applied to well-, reservoir- or basin-scale computer models. This involved the application of statistical methods developed for reservoir description by petroleum engineers. One approach was testing the degree of heterogeneity (coefficient of variation) of a given diagenetic variable within the genetic unit, and then subsequently determining if the optimum sample density was acquired for that variable (i.e. "N₀ testing"), given a particular tolerance level (this depending on the purposes of the up-scaling). Initial results from the example demonstrated that while some variables were adequately characterised (e.g. illite%), others required more sampling due to higher degrees of heterogeneity (e.g. Kh).

WH13: Geochemical evaluation and computer simulation of diagenetic changes in the Ravenscar Group sandstones (middle Jurassic, Yorkshire, UK)

D. Garcia¹, B. Maréchal¹ and E. Brossé²

¹Ecole des Mines, 158 cours Fauriel, 42023 Saint-Etienne, France
garcia@emse.fr

²Institut Français du Pétrole, 1 avenue de Bois-Rueil Malmaison, France

Sandstone facies ranging from nearshore (shoreface) to continental (deltaic, estuarine) environments are subaerially exposed in the middle Jurassic Ravenscar Group (Yorkshire coast, UK), an analogue of the Brent Group (offshore North Sea). The Ravenscar Group reached maximum burial conditions (2500m, 90°C) less severe than many Brent sections, and the sands record a different diagenetic history, involving the development of early Fe carbonate, abundant kaolinite and quartz overgrowths, and the complete elimination of K-feldspar in the most permeable reservoirs; however, diagenetic illite was not observed.

An extensive whole-rock geochemical study was focused on six reservoir-bearing units in a km-scale drilled block. The most inert trace elements were used to establish robust stratigraphical correlations and to check for lateral connectivity of the reservoirs, while the major elements were used to assess how mineral contents vary laterally and vertically. Within a given reservoir, the distribution of diagenetic silicates remains rather homogeneous, and only smooth variations in mineral proportions are recorded. But different reservoirs, which have different geochemical signatures for the most inert elements, may bear either different silicate assemblages, or substantially different proportions of the same silicates. Subsequently, both initial variations in sand mineralogy as well as diagenetic modifications may have interfered to generate the present-day range of chemical compositions in these reservoirs.

The observed range of mineralogical/chemical variations was then compared with the results of numerical simulations of the diagenetic changes driven by various scenarios of fluid circulations, on a set of reservoir types representing the most likely initial mineralogies. Relevant diagenetic scenarios include the flushing of the reservoirs by meteoric waters during basin inversion, under isothermal conditions or along a temperature gradient due to block tilting, and the reaction with basinal brines acidified by the maturation of organic matter. The reaction-transport computer code DIAPHORE was used to perform these simulations and to explore the range of possible final reservoir compositions as a function of time and distance from the water inlet (1D). The influence of initial mineralogy, of fluid-rock exchange scenario and of other boundary conditions like temperature and fluid composition was examined.

WH14: Mineralogic signatures of diffusion controlled diagenesis in clastic systems

G. D. Thyne¹, A. J. Park² and P. Ortoleva²

¹Colorado School of Mines, 1500 Illinois Street, Golden, CO, 80401, USA

gthyne@mines.edu

²Lab for Computational Geodynamics, Indiana University, Bloomington, IN, 47405, USA

There are numerous reported occurrences of authigenic mineralization in sedimentary rocks whose spatial distribution is related to contacts between compositionally different units (i.e. sandstone-shale). Composition Driven Diagenesis (CDD) is a conceptual model that postulates many of these authigenic mineral features are controlled by the initial compositional variations that are themselves related to common stratigraphic and depositional processes. The models show that rapid aqueous diffusion through connecting pores is triggered by initial compositional disequilibrium as sediments are heated past a threshold temperature. Compositional disequilibrium is the normal condition for sediments that contain reactive detrital components such as organic matter, feldspars, volcanic glasses, smectitic clays, and biogenic silica and carbonate fragments. Diagenesis related to these local effects is intrinsic since only heating of compositionally unstable sedimentary systems is required to produce the redistribution of mass.

Past a threshold temperature, units with more reactive components produce higher solute concentration per unit time, resulting in the chemical gradients. Mass transfer continues until the reactants are depleted or the pore space becomes completely filled with the authigenic mineral. The reactions are modelled as, kinetic and temperature dependent. The reactions, coupled with solute-specific and porosity dependent diffusion rates, result in conditions where the local rate of surface reaction is greater than the local rate of transport. Thus, burial of units with multiple reactive components can produce sequential diffusion gradients throughout the burial history that produce multiple cementing episodes. Examples of contact-related patterns of

Session 35 Abstracts

diagenetic carbonate, quartz and clay cements, and secondary porosity are modelled and results compared to field data to demonstrate the utility of the CDD concept.

The coupling of the CDD conceptual model to the WRIS.TEQ software creates an effective tool for evaluating the process. WRIS.TEQ is a general multi-mineralic water-rock interaction simulator that implements advective and diffusive mass transfer, and kinetic and equilibrium reactions among minerals and water. The effects of compositional variations between units, grain size, chemical compaction, compactional flow and intra-unit variation can be assessed with this reaction – transport model. The CDD model can define the dimensions of an isochemical system where the intrinsic properties are responsible for patterns of authigenic mineralization. Furthermore, this assessment allows the modelling of diagenetic conditions where extrinsic factors, such as regional and significant flow, are important.

WH16: Significant overprint of the geochemical and magnetic properties of carbonates by a Fe-bearing fluid – a study from the La Vid Group, Cantabrian Mountains, NW-Spain

J. Schneider¹, T. Bechstäd¹, H.G. Machel²

¹Geologisch-Paläontologisches Institut, Universität Heidelberg, INF 234, 69120 Heidelberg, Germany

jo.schneider@uni-hd.de

²Department of Earth and Atmospheric Sciences, University of Alberta, Edmonton, Canada

The Lower Devonian La Vid Group in the Cantabrian Mountains (NW-Spain) is composed of marine sandstones, carbonates and shales, which were deposited during increased deepening of a carbonate ramp. Combination of petrography and geochemistry highlight a significant overprint of these sediments by a Fe-bearing fluid precipitating siderite, ferroan saddle dolomite and ankerite. These minerals show a characteristic distribution in the host rocks of the La Vid Group. At the transition from the underlying sandstones to the carbonates of the La Vid Group siderite crystallized among detrital quartz grains. Throughout the carbonates ferroan saddle dolomite occurs in veins, fossil moulds, and in recrystallized high-Mg shells. Ankerite precipitated in open pore spaces of the uppermost bed of crinoidal grainstones right below the overlying shales. Primary fluid inclusions are rare in these cements. Rare aqueous inclusions in ferroan saddle dolomite have homogenization temperatures between 114 to 119°C. Some samples contain fluorescing petroleum inclusions, which indicate highly mature hydrocarbons.

Trace element and stable isotope data of these cements reveal enrichments in Fe and Mn coinciding with depleted Sr values compared to brachiopods (Veizer *et al.*, 1999). Siderite has $\delta^{13}\text{C}$ values of -6.5‰ VPDB, in contrast to ferroan saddle dolomites that have $\delta^{13}\text{C}$ values of 1.9 to 3.3 ‰ VPDB similar to the hosting carbonates. Only the uppermost bed of the succession, cemented by ankerite, exhibits significant depletions with values of -2.5‰ VPDB compared to brachiopod values of -0.4‰ PDB (Veizer *et al.*, 1999). The $\delta^{18}\text{O}$ values of these cements (-8 to -11‰ V-PDB) are lower than those of presumed unaltered Devonian marine brachiopods (-4 to -6‰ V-PDB, Veizer *et al.*, 1999). Oxygen values of whole rock analyses show variations in the carbonates of the La Vid Group (-4 to -9‰ V-PDB). Coarse-grained layers reveal a shift to depleted values in comparison to fine-grained carbonates showing values similar to marine brachiopods (Veizer *et al.*, 1999).

Negative $\delta^{13}\text{C}$ values of the ferroan carbonate cements can be attributed to interaction of the Fe-bearing parent fluid with organic matter. Depleted oxygen isotope ratios indicate increased temperatures during cementation and reveal a significant overprint of the hosting carbonates. The homogenization temperatures of 114°C together with oxygen isotopes result in a fluid composition between 1 and 3‰ SMOW. This suggests sea water as a possible parent fluid.

Furthermore high magnetic susceptibilities of these carbonate cements coincide with elevated Fe and Mn contents and depletions in Sr and $\delta^{13}\text{C}$, whereas there is an inverse correlation between $\delta^{18}\text{O}$ values and magnetic susceptibilities. These variations occur at lithological boundaries especially between coarse-grained and fine-grained beds.

WH17: Diagenetic sealing of fault-controlled hydrocarbon migration pathways: The Moab fault, SE Utah, USA

P. Eichhubl¹, N. C. Davatzes¹ and A. Aydin¹

¹Rock Fracture Project, Stanford University, Stanford, CA 94305-2115, USA

eichhubl@pangea.stanford.edu

The Moab fault is a basin-scale normal fault with up to 1 km of stratigraphic offset across Pennsylvanian to Cretaceous units of the Paradox Basin, SE Utah. We mapped fault-related diagenetic alteration patterns relative to the fault structure in the northwestern extension of the fault where 200-300 m of normal slip juxtaposes upper Jurassic to Cretaceous mud- and sandstones against Lower to Middle Jurassic aeolian sandstone. The fault is segmented along strike, with segments separated by branch points and step-overs. Fault branch points are associated with extensive carbonate cementation of the adjacent sandstone whereas one step-over zone is associated with predominant silica cementation. Carbonate cementation is observed as veins and as concretions that are up to 5 cm in diameter and composed of poikilotopic calcite. Vein filling calcite extends as pore filling cement 1-2 cm into the adjacent host sandstone. Abundance of concretions and veins and the diameter of concretions decrease with distance from the fault. Carbonate is consistently associated with bleaching of the reddish hematite-cemented Jurassic sandstones. Stringers of bleached sandstone extend away from the fault for 20-50 m in the more cemented Slickrock member of the Entrada Formation and >100 m in more porous sandstone of the Navajo Formation and Moab Tongue member of the Entrada Formation. Pore and fracture-filling dead oil in bleached and carbonate cemented zones is indicative of bleaching due to reducing aqueous fluids in association with hydrocarbon migration along the fault. We envision that fault-related cementation is controlled by two processes: (1) rapid upward fluid flow along the fault and (2) degradation of hydrocarbons in contact with meteoric water. Evidence for rapid fluid flow is provided by clastic dykes associated with the fault. Cooling of rapidly upward flowing fluid would favor silica precipitation whereas a drop in CO₂ partial pressure and exsolution would favor carbonate precipitation. Evidence for carbonate precipitation due to hydrocarbon degradation is observed through malachite precipitated along margins of residual oil stains. Release of CO₂ by the microbial degradation of oil in the presence of organic acids may increase alkalinity resulting in carbonate precipitation. Both sealing processes may occur in repeated cycles, with extended episodes of slow flow and concurrent oil degradation alternating with short events of rapid flow. These processes of localized cementation may thus result in sealing of initially preferred fluid migration pathways along faults even in otherwise permeable sandstone units unless continued fault slip maintains fracture and fault permeability.

WH18: Geochemical signatures of carbonate vein and pore cements in Tertiary sediments of the Upper Rhine Graben

G. D. Lorenz¹ and S. Zeeh¹

¹Geologisch-Paläontologisches Institut Universität Heidelberg, Im Neuenheimer Feld 234, 69120 Heidelberg, Germany
Gesine.Lorenz@urz.uni-heidelberg.de

Vein and pore cements give information about fluid circulation in the Upper Rhine Graben during Cenozoic times. Samples of blocky calcites (phases A, B, C and E) and iron-rich dolomite (phase U) have been collected from drill cores of the basin and outcrops along the uplifted margins. Origin and genesis of precipitating fluids were interpreted from analytical data on trace elements and oxygen, carbon and strontium isotopes of the cements. Microthermometry of fluid inclusions gave salinity and ion content.

Three calcite phases (A, B and C) and dolomite U are related to late diagenesis indicated by depleted oxygen isotope values in comparison to host rock. Strontium isotopes of cement A show a meteoric signal similar to shallow groundwater and river water. The cements B, C and U have values as expected of deep ascending fluids circulating through granite and gneiss of the basement. Fluid inclusions of A and U have high, inclusions of B and C have reduced salinities. The precipitating fluids were probably mixtures of meteoric and formation waters of the graben. There may be admixture of basement brines to B, C and U. Carbonate veins are delivered from formation water (or the host rock). Basement brines serve as source for strontium. Low saline fluid inclusions of cement B and C indicate a high content of salt-poor meteoric water. Saline formation waters are responsible for high salinities of inclusions in A and U.

Calcite cements of phase E possess fluid inclusions of low salinity. The signal of strontium isotopes as well as the carbon isotopes depleted in comparison to host rock identify cement E as precipitate of meteoric water. The strontium ratio is enriched compared to host rock and marine water during Tertiary times.

Session 35 Abstracts

The cement generations took place between lower Miocene and lower Pliocene. Sinistral shear stress and uplift of graben and shoulders may have opened veins and the possibility for deep circulation of fluids in widespread areas.

There was no geochemical hint that the upper Miocene volcanism of the Kaiserstuhl with accompanying magmatic fluids influenced the fluid flow. Only volcanic rocks bear late volcanic hydrothermal minerals in addition to younger meteoric cements.

WH19: Calcite as an indicator of vertical fluid transport in hydrocarbon systems

J.R. Boles

University of California @ Santa Barbara. Santa Barbara, CA 93106
boles@magic.ucsb.edu

Calcite associated with faults in petroleum basins can provide evidence of the timing and magnitude of vertical fluid transport. A number of examples have been documented in the hydrocarbon basins of Southern California by our research at UCSB. The calcite is found within fault zones and the associated country rock. Field and petrographic evidence, including breccia and twinned crystals, suggests that calcite is formed at the time of deformation, rather than as a passive filling of void space long after fault movement. Uranium series dating of the calcite in some areas allows direct timing estimates of faulting and fluid movement. Some of these systems were active as recently as a few hundred thousands years ago.

The carbon and calcium components of calcite come from separate sources. The reaction of pore water with hydrocarbon releases dissolved carbon for calcite. In cases in which the calcite $\delta^{13}\text{C}$ is particularly light (35-45 per mil), the carbon is from oxidation of methane to carbon dioxide. The source of the calcium for the calcite varies depending on whether the system is rich in clastic or biogenic components. In general, the calcite is not simply a result of calcite dissolving deep in the basin and precipitating at shallow levels in fault zones.

Several techniques have been used to demonstrate the magnitude of vertical fluid transport. One is comparing crystallization temperatures of calcite within the fault to the maximum burial temperature for the wall rock. A second technique is the application of Sr isotope stratigraphy in marine rocks. Given the fact that there are predictable changes in Sr isotopic ratio of Tertiary marine biogenic carbonate, it is possible to infer the vertical component of transfer from the Sr isotopic ratio of the calcite vein-fill. This has been particularly successful in the biogenic-rich, clastic-poor Miocene Monterey and equivalent strata in the Southern California area, where interference from clastic components is minimal.

Several examples will be discussed from the Santa Barbara coastal area and the San Joaquin basin of California. Both areas have undergone transpression during the late Tertiary. These examples demonstrate that the vertical component of fluid transport associated with faulting is on the order of one to two kilometers. In some examples, the rupture of an over-pressured section is required to explain the magnitude of vertical transport and the crystallization temperatures.

WH20: The relationship between early authigenic dolomite and stable isotope data

Susanne Schmid¹, Richard H Worden¹, Quentin J. Fisher²

¹ Department of Earth Sciences, University of Liverpool, UK, L69 3GP

² Department of Earth Sciences, University of Leeds, UK, LS2 9JT

Early Triassic Sherwood Sandstone Group deposits in the Corrib gas field (offshore west of Ireland) show a development of dolocretes in the fluvial dominated facies. This non-ferroan dolomite occurs as microcrystalline rhombs and poikilotopic patches. It represents 2-24 volume percent with a mean of 9%. Very minor ferroan dolomite is also present as rims to the non-ferroan forms of dolomite. Evidence are provided by optical analysis from SEM, CL and thin section work that the non-ferroan dolomite precipitated very early in the paragenetic sequence.

The relationship between the microcrystalline and the non-ferroan poikilotopic dolomite is described by a dissolution and amalgamation of the primary microcrystalline dolomite and the subsequent precipitation of the poikilotopic dolomite on the rims of the amalgamated former dolomite. Ferroan dolomite formed later as discrete crystals and as rims on the non-ferroan dolomite. XRD/SEM data show a higher Ca content (Ca/Mg ratio) in the centre of these zoned microcrystalline dolomite.

Carbon isotope data have been collected from throughout six wells. These wells currently have up to 500 m depth variation to top Sherwood Sandstones. Graphs of $\delta^{13}\text{C}$ against stratigraphically normalised depth show identical carbon isotope trends within all of the six wells. The stable carbon isotope ratios from the authigenic

dolomite must not have been influenced by burial diagenesis for the stratigraphic patterns to have been preserved in wells with different burial histories. Unusually, the carbon isotope data have thus proved to be useful for stratigraphic correlation. In contrast, oxygen stable isotope data have been influenced by burial diagenesis and are different for the different types of dolomite.

POSTERS for Session 35

B35-1: The importance of phase composition in quantitative mineral inversion

P. K. Harvey and T. S. Brewer

Department of Geology, University Road, University of Leicester, Leicester, LE1 7RH, UK.
pkh@le.ac.uk

The derivation of quantitative mineral assemblages requires that the specific minerals required in a model be known, and also the composition of these minerals be known, or at least, known within reasonably tight limits. Using both theoretical and log examples this contribution shows that changes simply in the composition of the modelled phases (minerals and/or fluids) can cause significant differences in the final computed mineral percentages. The problem of mineral composition is particularly acute in shaly sediments where compositional colinearity is an additional, though related, problem. Unfortunately too few log curves are normally measured on a routine basis to enable these mineral inversion problems to be easily solved. This is a real and limiting problem if there is a need to have a reasonable estimation of the quantitative mineral proportions.

B35-2: Structural CO₂ in the apatite of the phosphorites in Egypt: its effect on the crystal parameters and isotopic composition

H. M. Baioumy

Central Metallurgical Research and Development Institute, 87 Helwan, Cairo, Egypt
hassanbaioumy@hotmail.com

Phosphorite deposits in Egypt, known as the Duwi Formation, are part of the Middle East to North Africa phosphogenic province of late Cretaceous to Paleogene age. Based on the petrographical observation, the phosphatic grains in the phosphorite grains are classified into phosphatic mudclast and phosphatic bioclast. Both of them are composed of carbonate fluorapatite, francolite.

The structural CO₂ contents in the francolite range from 3.32 to 7.21% with an average of 5.28%. Results indicated that the substitution of CO₃ for PO₄ in the carbonate fluorapatite decreases the unit cell volume and a-cell dimension and increases the c/a ratio. Effect is more obvious in the a-cell dimension; therefore, it is more significant in distinction between the different apatite species.

The $\delta^{13}\text{C}_{\text{PDB}}$ and $\delta^{18}\text{O}_{\text{PDB}}$ values of the samples studied are highly variable but are, nevertheless, all large negative numbers. The $\delta^{13}\text{C}_{\text{PDB}}$ values range from -4.04 to -8.7‰ while the $\delta^{18}\text{O}_{\text{PDB}}$ values range from -4.3 to -10.7‰.

Negative $\delta^{13}\text{C}$ values and low $\delta^{18}\text{O}$ values of structural CO₂ suggest that the CO₂ was derived from degradation of organic matter. The linear relationship between $\delta^{13}\text{C}$ and CO₂ that as the medium became more negative with shallow burial there was a progressive increase in the substitution of CO₃ for PO₄ in the carbonate fluorapatite. These data along with the higher CO₂ contents in the apatite from Duwi Formation in Egypt compared to the Recent authigenic phosphorites indicate that the chemical composition of apatite has been changed after the formation and during diagenesis by taking CO₂ into the structure from the surrounding medium and the studied apatite has been francolitized during diagenesis.

B35-3: Rotliegend aeolian sandstones of Western Poland in CL, SEM and EDS studies

A. Maliszewska, M. Sikorska, M. Kuberska, H. Kiersnowski

Session 35 Abstracts

Polish Geological Institute, 4 Rakowiecka Str., 00-975 Warszawa,
Poland
amal@pgi.waw.pl

Sandstones which form fossil dune fields in the Wielkopolska area (Western Poland), known as the Eastern Erg were petrologically analysed. Their thickness reaches 1000 m. These sandstones occur in the association with the playa lake and wadi deposits and have in places natural gas accumulations. The sandstones have been classified as fine and medium grained quartz and subarkose arenites, less frequently - as sublithic arenites or wackes. The cements of the sandstones were studied to establish of the history of the sandstone diagenesis and the evolution of the reservoir properties. Studies comprised also a grain framework in the aspect of the determination of the directions of the detrital material transport. The analyses were performed by means of the polarizing microscope and SEM/EDS.

The cathodoluminescence analysis has shown that calcite cements are varied. They do not luminesce at all or display either red or yellow-orange luminescence. The non-luminescent calcite (no Fe and Mn) crystallised as the earliest cement, being followed by later generations as Fe-calcite and Mn- or Mn/Fe-calcite. In some places, these cements are accompanied by the red-luminescent dolomite as well as sporadically - by non-luminescent ankerite. Calcites usually display subhedral forms, while dolomite and ankerite always occur as rhombohedrons, sometimes of zonal structure. Fine tables of anhydrite are often present in the sandstones.

In the quartz cements syntaxial overgrowths on the grains and fine prisms developed perpendicularly to the grain surface have been observed. The authigenic quartz and K-feldspar overgrowths either display luminescence in brown colours or are non-luminescent. All mentioned components of the cements observed in SEM have traces of dissolution. This points to a frequent chemical variation of the pore fluids during diagenesis. The feldspar grains have also been strongly dissolved.

SEM studies of the authigenic clay minerals show the presence of fibrous illite and Fe- or Fe/Mg-chlorites in form of flake aggregates of the honeycomb structure.

In the detrital material of the sandstones, quartz grains showing blue-violet luminescence are numerous. They may originate from the eroded Lower Rotliegend volcanic cover. Quartz grains with a brown luminescence and quartz-feldspar fragments may have been transported from the south from the complexes of metamorphic rocks of the Fore-Sudetic ridge.

(Grant of the Committee of Scientific Research No. 6PO4D 034 19)