Hydrocarbons and Mississippi Valley-type Sulfides in the Devonian Reef Complexes of the eastern Lennard Shelf, Canning Basin, Western Australia

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Abstract

A wide range of maturation parameters indicates that near-surface Devonian sequences of the eastern Lennard Shelf are immature (peak temperatures of 70–90°C). Fluid inclusion microthermometry indicates that peak temperatures in the Palaeozoic were probably around 60 to 70°C for presently exposed or near-surface rocks.

Mississippi Valley-type (MVT) deposits on the eastern Lennard Shelf appear not to have thermal anomalies around them. Negative anomalies in vitrinite reflectance and Tmax associated with mineralisation appear to be caused by chemical, rather than thermal processes. This suggests that mineralisation occurred under conditions of regional burial, with uniformly elevated temperatures. Petrologic evidence indicates that hydrocarbons entered the carbonates contemporaneously with MVT mineralisation on the Lennard Shelf at about 350 Ma.

The reservoir-shaped geometry of the Cadjebut Zn-Pb deposit, together with the presence of stalactitic sulfide textures from a number of deposits suggest that buoyant phases like gaseous hydrocarbons have played a role in sulfide precipitation. We suggest that at around 350 Ma, in-situ, low temperature (<90°C) bacterial sulfate reduction occurred in association with migrated hydrocarbons to produce H2S-rich reservoirs in the reef complexes. The sulfate was probably derived from local Givetian evaporites and other sources. These sour gas accumulations then reacted with metalliferous brines from the Fitzroy Trough to produce the economic base-metal sulfide deposits of the Lennard Shelf.

Introduction

Many researchers have suggested a genetic relationship between organic maturation and Mississippi Valley-type (MVT) Pb-Zn mineralisation. In their landmark paper, Jackson & Beales (1967) suggested that Mississippi Valley-type (MVT) sulfide precipitation was a normal consequence of basinal brine evolution and organic maturation. More recently, Anderson (1991) has championed the idea of a link between organic maturation and mineralisation.

One problem in this general field of study is that organic maturation studies of mineralised sequences are often considered quite separately from the mineralisation itself. In this paper, we attempt to integrate data on organic maturation and thermal history analysis with results from MVT deposit research with the aim of better understanding both processes.

The Canning Basin, and particularly the Lennard Shelf with the outcropping Devonian reef complexes (Fig. 1), has a stratigraphy which resembles that of the Western Canada Sedimentary Basin and this has spurred much petroleum exploration in the region. To date however, there has only been limited success, with oil having been produced from five small fields: Blina, Sundown, West Terrace, Lloyd and Boundary (Jackson et al., 1992). Only Blina’s production is from the Devonian–Carboniferous carbonates.

Mineral exploration has enjoyed greater success, with many MVT lead-zinc deposits having been discovered in the outcropping Devonian reef complexes over the last thirty years. Four Zn-Pb deposits have proved to be economic on the eastern Lennard Shelf: Cadjebut, Goongewa (formerly Twelve Mile Bore), Pillara (formerly Blendevale) and Kapok (Fig. 2). Further south in the basin, the giant Admiral Bay Pb-Zn deposit was discovered as part of an oil exploration program (McCracken et al., 1996) (Fig. 1). This is a subsurface deposit, and at this stage, appears to be uneconomic because of its depth.
Hydrocarbons and sulfides, Lennard Shelf

Geological Setting

The structure of the northern Canning Basin is dominated by the NW–SE trending Fitzroy Trough which contains up to 15 km of sediments. Bordering the Fitzroy Trough are relatively thin successions that are a few kilometres thick: the Jurgurra Terrace–Barbwire Terrace system to the south and the Lennard Shelf to the north (Fig. 1). This structural geometry was principally developed during mid Devonian–Early Carboniferous extension (Shaw et al., 1994). Maximum subsidence and sedimentation in this structural system also occurred during this period of rifting. This major period of extension has been called the Pillara Extension by Shaw et al. (1994) who have subdivided it into three separate pulses of movement: the Gogo Extension (~375–370 Ma), the Van Emmerick Extension (~363–366 Ma), and the Red Bluffs Extension (~340–354 Ma).

The Lennard Shelf is separated from the Fitzroy Trough by a series of predominantly south-dipping NW–SE trending listric normal faults and these are well illustrated on the deep seismic line BMR88–03 (Shaw et al., 1994). Accommodation zones along the Lennard Shelf have produced regions that are dominated by NE–SW fault systems (e.g. NW Pillara Range, Fig. 2).

During the mid to Late Carboniferous, a major period of uplift and erosion took place across the basin and this appears to coincide with what Shaw et al. (1994) called the Meda Transpressional Movement. This erosional episode also coincides with the Gondwanan glaciation. Sediments immediately overlying the unconformity produced by this erosion are of fluvial or marine origin with common glacial deposits (Upper Carboniferous Reeves Formation and Permian Grant Group, Apak and Backhouse, 1998) (Fig. 3).

In the Permian and Mesozoic, a period of subsidence occurred across the basin and this corresponds with extension offshore. The Fitzroy Transpressional Movement in the Late Triassic–Early Jurassic initiated a major period of uplift and erosion (Forman & Wales, 1981; Shaw et al., 1994). The structural history has therefore produced two major subsidence-burial events (Late Devonian–Early Carboniferous and Permian Mesozoic) and two uplift-erosion events (mid–Late Carboniferous and late Mesozoic to Tertiary) on the Lennard Shelf.

The stratigraphy of the Lennard Shelf is dominated by the spectacularly preserved Devonian reef complexes which have been well documented by Playford and others (Playford & Lowry, 1966; Playford, 1980, 1984; Playford et al., 1989).

Figure 1: Map showing location of Canning Basin, with simplified structural elements and location of study area (modified from Playford, 1980).
The Lennard Shelf carbonates range in age from Givetian through to Famennian, but barrier reef systems are best developed in Frasnian–Famennian age sequences (Fig. 4). Givetian and Early Frasnian carbonates are characterised by ramp and low-relief bank systems (Playford, 1984). The oldest Devonian carbonate sequence is the Cadjebut Formation (Hocking et al., 1996) and this is evaporitic in nature. In most areas of the Lennard Shelf, Precambrian metamorphic basement rocks directly underlie the Devonian sequence. However, on the eastern Lennard Shelf, Ordovician sequences (Emanuel Formation and Gap Creek Dolomite) can underlie the Devonian sequence.

Potential carbonate reservoir rocks on the Lennard Shelf include coarsely crystalline regional dolomites which constitute about 10% of the volume of the Devonian carbonates and are more common towards the basement (Kerans, 1985; Wallace et al., 1991). These dolomites are the most porous carbonates present in the Devonian reefs, the limestones typically having a very low porosity, with virtually all primary porosity having been destroyed by burial calcite cementation (Wallace et al., 1991). The regional dolomite is of early burial diagenetic origin and the porosity is of secondary origin (Kerans, 1985; Wallace et al., 1991).

Other potentially important reservoir lithologies on the Lennard Shelf are siliciclastic sediments interspersed with the Devonian carbonates (Fig. 2). Large masses of sandstone and conglomerate interfinger with the outcropping Devonian reefs at many localities on the Lennard Shelf (Playford, 1980). Mineral and petroleum exploration drilling indicates that sandstones become volumetrically more important in the...
sulfides on the Lennard Shelf (e.g., the Pillara, Fossil Downs and Kapok deposit). In contrast, the Cadgebaut mineralisation is markedly stratabound, with an obvious stratigraphic and evaporitic control on sulfide distribution. The stratabound ore at Cadgebaut has a banded fabric (Tompkins et al., 1994b; Wallace et al., 1994), whereas the less significant ore type at Cadgebaut is a breccia (Figs. 5a, g).

The Goongewa deposit is situated in the hanging wall of a normal fault (Cadgebaut Fault). Stratigraphically, the mineralisation occurs around a Givetian platform margin and also occurs at the boundary between dolomitised and undolomitised carbonates. MVT sulfides are largely present as cavity-filling cements within large hydrothermal karst caverns (Figs. 5c, d). The nearby Kutarta mineralisation (close to the old Price’s Creek prospect, Fig. 2) has a quite different style again, with much of the base-metal sulfide mineralisation being a replacement of dolomitised and brecciated back-reef carbonates (Pittari, 1999).

Stromatolite-barite-sulfide mounds (Fig. 5f) are present at a number of localities on the eastern Lennard Shelf (notably Lake Bore and Longs Well areas, Fig. 2) and are interpreted as synsedimentary exhalative deposits (Playford & Wallace, 2001). The stromatolite mounds occur near the top Gogo Formation–base Virgin Hills Formation contact and are associated with extensive gossans in outcrop. In drill core, iron sulfides (marcasite and pyrite) are dominant, with base-metal sulfides only occurring as later stage cross-cutting veins.

The timing of MVT sulfide precipitation is well constrained by a number of techniques. Using carbonate cement stratigraphic relationships in host rock primary porosity, McManus & Wallace (1992) suggested that a single, widespread sulfide precipitation event (pyrite, sphalerite, galena, marcasite) occurred during early burial diagenesis during latest Devonian–earliest Carboniferous time (350 ± 15 Ma) within the reef complexes of the Lennard Shelf. This mineralisation age has since been confirmed by both Rb-Sr dating of sphalerite at the reef complexes of the Lennard Shelf. This mineralisation age has since been confirmed by both Rb-Sr dating of sphalerite at Blendevale and U-Pb dating of ore-stage calcites from Goongewa (Christensen et al., 1995; Brannon et al., 1996).

The stromatolite barite-sulfide mounds are of late Frasnian age and are interpreted to have been produced by cool fluids exhalting onto the sea floor, driven by dewatering of the Gogo Formation shales. Carbonate, barite and sulfide precipitation is believed to have been driven by early diagenetic bacterial reactions like sulfate reduction occurring within the Gogo Formation shales. The exhalative mineralisation is therefore not directly linked with MVT sulfides, which were precipitated some 15 million years later.

Methods

Samples for vitrinite reflectance analysis and Rock-Eval pyrolysis are from either core, cuttings, or mine samples (Ellyard, 1984a,b; Diekman, 1990; Kufpec, 1988, and results from this study). Outcrop samples were not included. Keiraville Konsultants, Australia, carried out all vitrinite

Sulfide mineralisation

MVT sulfides occur at many localities within the Devonian reefs and are hosted by carbonates ranging from Givetian evaporitic dolomites, through to Famennian fore-reef carbonates (Fig. 4). The eastern Lennard Shelf has been the most prolific region for Zn-Pb mineralisation, hosting most of the economic deposits to date. Lead-zinc sulfides were also mined from the Narlarla deposit, which was located on the western Lennard Shelf, about 150 km east of Derby (Ringrose, 1989). Faults and fractures (Fig. 5e) host the majority of MVT substrate portions of the shelf to the south of the outcropping reef complexes. These subsurface sandstones occur predominantly within the slope facies of the reef complexes and have been interpreted by Southgate et al. (1993) as being of lowstand origin.

Figure 3: Generalised stratigraphy of the Northern Canning Basin. The coloured intervals occur on the Lennard Shelf (modified from Wallace et al., 1991) and distinguish major rock units; red lines represent periods of non-deposition and/or erosion. The Late Carboniferous to Permian stratigraphy is modified from Apak and Backhouse (1998).
reflectance determinations. Samples were mounted in cold-setting polyester and polished. A Leitz MPV1.1 photometer with separate fluorescence illuminator was used for reflectance determinations. Reflectance standards were: spinel 0.42%, YAG 0.91%, GGG 1.72%. The procedure for measurement follows the Australian Standard (AS) 2486, with slight modification for dispersed organic matter. Where possible, at least 25 fields were measured. The mean maximum reflectance is reported.

Rock-Eval Pyrolysis data on unmineralised samples was obtained from open-file reports (Ellyard, 1984a,b; Diekman, 1990; Kufpec, 1988). Rock-Eval Pyrolysis data on mineralised samples was carried out by Geotechnical Services Pty Ltd using the standard method and interpreted according to Espitalié et al. (1977) and Peters (1986).

Conodont Colour Alteration (CAI) studies were carried out on both outcrop and field samples. CAI was determined by comparison with the published data of Epstein et al. (1977). Fluid inclusion microthermometry was conducted on a Fluid Inc adapted U.S.G.S. gasflow heating/freezing stage, calibrated with Fluid Inc standard inclusion mounts (mounted on a Zeiss Universal microscope with a Nikon long working distance 40 X objective) using the techniques of Goldstein & Reynolds (1994).

Source Rock Analysis

Many of the upper Devonian carbonates of the Lennard Shelf have very low organic carbon contents, being dominated by high-energy platform and marginal slope facies. This is particularly so for the late Frasnian and Famennian reef complexes, which are characterised by strongly prograding platforms (Playford, 1984, Playford et al., 1989) with high energy, coarse-grained platform lithologies (Nullara Limestone) and relatively oxidised slope and basinal facies (Virgin Hills Formation, Piker Hills Formation, Napier Formation).

In contrast, the Givetian and most Frasnian (excluding lastest Frasnian) carbonates are characterised by vertically aggrading or back-stepping platforms margins (Playford, 1984), with lagoonal facies commonly developed. The Givetian–Frasnian Pillara Limestone (platform facies) is commonly slightly more organic-rich. The inter-reef Gogo Formation is also commonly organic-rich. The oldest carbonate sequence exposed on the Lennard Shelf is a Givetian age evaporitic unit that is now known as the Cadjebut Formation (Hocking et al., 1996). The Cadjebut Formation also has a relatively high organic content (Fig. 6).

Thick sections of Givetian to Famennian sandstones occur in outcrop (e.g. Sparke Range conglomerates) and have been
Figure 5: Mineralisation styles from the eastern Lennard Shelf.

A. Banded sphalerite. Cadjebut, lens 1.

B. Breccia ore of probable hydrothermal karst origin from the southern side of Cadjebut. Cadjebut, lens 1, 45–3S.

C. Hydrothermal karst cavern lined with sulfides and ore-stage calcite. Goongewa 1065 level.

D. Hydrothermal karst cavern filled by internal sediments, breccias and sphalerite cements. The cavern emanates from a stratigraphic contact at lower right of photo. Goongewa 1020 level.

E. Mineralised fault breccia cemented by ore-stage calcite and sulfides. Kapok, 735 level, west face.

F. Exhalative stromatolite mound, Lake Bore, East Pilbara Range.
intersected in the subsurface (e.g. Grevillea 1). However, these sandstones generally have low organic contents and have not been considered further as source rocks.

**Rock-Eval Pyrolysis**

A total of 63 samples with Rock-Eval data were available from a large number of localities across the study area (Fig. 2). Most samples were taken from near-surface cores (0–800 m), with deeper samples being available from the well Needle Eye Rocks 1 (Fig. 2).

Total organic carbon content (TOC) for the Gogo Formation ranges from 0–2 wt % (average 0.92%), while the Pillara Limestone and Cadjeput Formation have TOC values in the range 0–4.5 wt% (averaging 1.35% and 1.53% respectively) (Fig. 6). The Gogo Formation, Pillara Limestone and Cadjeput Formation appear to have similar organic compositions, with the majority of samples having organic matter with the chemical characteristics of type III organic matter (Hydrogen Index values ranging from 50 to 400, Fig. 7). Some samples have a minor type II chemical component. One sample of Ordovician Emanuel Formation has a higher Hydrogen Index (HI) value, more typical of Type II organic matter. Available data from the Early Permian Grant Group indicates that it is a poor source rock.

The best source rocks analysed in the region are therefore the Pillara Limestone and Cadjeput Formation, with TOC and HI values indicating they are potentially fair to good source rocks (Peters, 1986). By the same criteria, the Gogo Formation has a poor to fair source rock potential (Figs 6, 7). Alexander et al. (1985) found that some Gogo Formation samples gave slightly higher TOC and HI values and therefore suggested that it was a fair to good source rock.

**Regional Thermal and Burial History**

**Conodont Colour Alteration (CAI)**

Three near-surface (<200 m depth) samples of Givetian to Frasnian age from the Emanuel Range (Fig. 2) all yielded conodonts with CAI = 1. One of these samples was taken in close proximity to the base-metal mineralisation at Goongewa, while the other two were taken from unmineralised outcrop samples. Previous CAI data from the well Grevillea 1 (Fig. 2) ranged from CAI 1–1.5 at 800 m to CAI 2–3 at 2425 m. This is consistent with a surface CAI of 1 (Nicoll & Gorter, 1984a,b). Wells from other areas on the Lennard Shelf similarly show CAIs of 1 at the surface, with depths to the base of CAI 1 interval ranging from

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**Figure 6:** TOC values for major source rock units of the eastern Lennard Shelf.
400 m (Hawkstone Peak) to 2300 m (Blackstone 1). All available conodont data indicate a CAI of 1 for outcropping Devonian carbonates on the Lennard Shelf (Nicoll & Gorter, 1984a). Nicoll & Gorter (1984a) noted that some wells from the Lennard Shelf (including Grevillea 1) had the highest CAI gradients in the Canning Basin and suggested that this was due to the intrusion of Tertiary lamproites.

Rock-Eval Pyrolysis

On the HI vs Tmax diagram (Fig. 7), most near-surface samples from the Gogo Formation, Pillara Limestone and Cadjeput Formation fall in the sub-mature zone (vitrinite reflectance equivalent less than 0.5, Espitalié et al., 1977). Values for the Production Index (PI) are typically less than 0.1 for all units (except if they are mineralised, Fig. 8), indicating that the near-surface carbonates are immature. Samples from the Permian Grant Group and the Emanuel Formation display a similar level of low maturity.

There is little or no regional variation in any of the Rock-Eval parameters from near-surface samples. However, mineralised samples typically have lower Tmax and higher PI values (Fig. 8). Both Tmax and PI show a trend towards increasing with depth. At depths below 600 m, Tmax values are typically greater than 425°C and PI values generally range between 0.1 and 0.15.

Vitrinite Reflectance

A total of 127 samples with vitrinite reflectance (Ro) data were available from the eastern Lennard Shelf. There is very little regional variation in near-surface vitrinite reflectance data across the study area, with most samples falling in the range 0.35 to 0.55 % (Fig. 8). Samples from the southern Emanuel Range have slightly higher average Ro values than those from the Pillara Range, perhaps indicating slightly higher levels of maturation. Overall, the Ro data are consistent with other maturity data indicating that the near-surface Upper Devonian carbonates are immature. Using the Burnham & Sweeney (1989) kinetic model for vitrinite reflectance maturation, with a heating rate of 15 million years, indicates maximum palaeotemperatures in the range of 60 to 80°C for near-surface carbonates on the eastern Lennard Shelf.

Figure 9 shows a combined plot of vitrinite reflectance vs depth for the well Needle Eye Rocks 1 and near-surface samples from the Pillara Range (close by). A good correlation exists between vitrinite reflectance and depth, from which a palaeogeothermal gradient can be calculated. Using the methods of Bray et al. (1992) indicates a palaeogeothermal gradient of 44 ± 10°C/km (at 95% confidence limits).

The Ro vs depth plot indicates that near-surface carbonates in the Pillara Range – Needle Eye Rocks region are immature and that the top of the oil window (Ro ~ 0.6) lies at a depth of approximately 1000 m. Most of the Upper Devonian carbonate section in the Pillara Range region is therefore either...
immature or early mature (up to 0.7 Ro). This situation is probably valid for Upper Devonian carbonates across the whole of the eastern Lennard Shelf.

Three near-surface samples of the Grant Group give an average Ro of 0.52%, indicating that the Permian Grant Group has a similar level of maturity to the Upper Devonian carbonates. This suggests that the maximum heating event that produced the palaeogeothermal gradient in the Pillara Range–Needle Eye Rocks data was of post-Permian origin.

**Apatite Fission Track Analysis**

Detailed studies of the thermal history of the Lennard Shelf have been carried out (Arne, 1996; Arne et al., 1989) using apatite fission track analysis (AFTA). Arne (1996) concluded that Late Devonian–Early Carboniferous palaeotemperatures on the eastern Lennard Shelf probably did not exceed 90°C. Arne (1996) also found that the Devonian carbonates in this region had been heated to palaeotemperatures in the range of 70 to 90°C, prior to cooling at around 200 Ma during the Fitzroy Movement. These estimates are within the range indicated by Ro and Rock-Eval data from the same region and are consistent with CAI data.

**Fluid Inclusion Microthermometry**

Analysis of fluid inclusion homogenisation temperatures (ore-stage calcite) was carried on the Goongewa Pb-Zn deposit in order to constrain palaeotemperatures during and after mineralisation. The Goongewa deposit (formerly known as Twelve Mile Bore) displays a deposit-wide paragenetic

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**Figure 9:** Vitrinite reflectance vs depth plot for the petroleum well Needle Eye Rocks 1. Vitrinite reflectance values from Devonian carbonates near the well (Northern Pillara Range) have also been plotted. The modern geothermal gradient in the region is also shown.

**Figure 10:** A. Homogenisation temperatures for ore-stage calcite cements from the Goongewa Zn-Pb deposit. B. Same data with homogenisation temperature plotted against inclusion diameter. The slight correlation between homogenisation temperature and inclusion diameter indicates some degree of inclusion stretching to peak temperatures.
sequence of sulfides and carbonates, first described by Bradley (1994). At least three separate generations of coarse euhedral calcite cements are present within the sulfide precipitation sequence, indicating calcite precipitation during mineralisation. These ore-stage calcites have an abundance of large primary fluid inclusions (demonstrated by their occurrence in crystal growth zones, Goldstein & Reynolds, 1994), giving the calcite a milky appearance in hand-specimen. All samples analysed are from less than 400 metres depth.

The majority of inclusions within the ore state calcites are single-phase. Homogenisation temperatures from two-phase fluid inclusions within the ore-stage calcites fall predominantly in the range of 50 to 90°C, with a well-defined mode at 65°C (Fig. 10). There is no discernable difference in homogenisation temperature between the three ore-stage calcite generations analysed.

A plot of inclusion diameter (longest dimension) vs homogenisation temperature for ore-stage calcites (Fig. 10) indicates a slight positive covariance, with larger inclusions commonly having homogenisation temperatures greater than 70°C. This is consistent with mineralisation taking place prior to peak heating and the inclusions having been stretched during later heating (Goldstein, 1986; Barker & Goldstein, 1990). The general trend for larger inclusions is towards homogenisation temperatures of around 80°C, which may indicate a slight positive covariance, with larger inclusions typically having homogenisation temperatures greater than 80°C.

Figure 11: Burial-thermal history model for the well Needle Eye Rocks 1. Also shown is age of mineralisation determined for near-surface deposits.

Thermal and Burial History Modeling

A geohistory diagram constructed for the well Needle Eye Rocks1 is illustrated in Figure 11. Age and lithology data were taken from the Needle Eye Rocks well evaluation report (Kufpec, 1988). The present day geothermal gradient of 26°C/km (calculated by averaging corrected bottom hole temperatures from the wells Needle Eye Rocks1 and Grevillea1) was assumed to be constant over much of the burial history for the sequence. A period of elevated geothermal gradients (44°C/km) was assumed to occur during Mesozoic burial. This assumption is based on the palaeogeothermal gradient calculated from Ro data discussed above (Fig. 9). The timing for this heating event is based on AFTA data that indicates a heating event at around 200 Ma (Arne, 1996). This timing is also consistent with the observation of a post-Permian heating event implied from maturity levels in the Grant Group.

The depth of burial during the Palaeozoic is constrained by paragenetic and diagenetic considerations. Using carbonate cement stratigraphic relationships in host rock primary porosity, McManus & Wallace (1992) demonstrated that dolomitisation and lead-zinc mineralisation occurred during early burial diagenesis (probably during Latest Fammenian–Tournaïnian time) within the reef complexes of the Lennard Shelf. This mineralisation age was confirmed by radiogenic isotope techniques (Christensen et al., 1995; Brannon et al., 1996).

Significantly, both dolomitisation and mineralisation can be unequivocally shown to overprint well-developed high-amplitude (>1 mm) stylolites (Wallace et al., 1991; McManus & Wallace, 1992). Therefore, some high amplitude stylolites had formed prior to mineralisation during Palaeozoic burial. The depth of stylolite formation is a controversial issue, but two well-constrained studies indicate minimum depths of around 1 km are required for high amplitude stylolites to develop (Lind, 1993; Nicolaides & Wallace, 1997). Thus, a minimum depth of burial of 1 km for near-surface carbonates is geologically reasonable for Palaeozoic burial.

Maturity and Pb-Zn mineralisation

Mineralised samples (having visible base-metal sulfides) typically have slightly lower than average Ro values, ranging from 0.25 to 0.45 % (compared to values of 0.4 to 0.5 for near-surface unmineralised carbonates, Fig. 8). Similarly, Tmax values for mineralised samples are lower (400 to 420°C) than unmineralised near-surface samples (average Tmax around 420°C). Production Index values for mineralised samples are higher on average than unmineralised samples. However, only mineralised samples have anomalous maturation indices and no maturation haloes in unmineralised samples are distinguishable around the deposits (Figs 12, 13). Samples that are close to mineralisation (within a few hundred metres), but are unmineralised have maturation indices typical for the region.
From the lower than average Tmax and Ro values in mineralised samples, it could be argued that negative thermal anomalies exist around mineralisation. In contrast, the anomalous values for the Production Index could be interpreted as indicating higher levels of maturity for the mineralised samples, or that the mineralised samples contained excess quantities of hydrocarbons. However, many factors other than thermal maturation can affect both the Rock-Eval parameters and vitrinite reflectance.

The presence of elemental sulfur in samples is known to affect the Rock-Eval pyrolysis parameters (Sassen & Chinn, 1989). Heroux et al. (1989) have shown that the presence of sulfur in samples can dramatically lower the Tmax value. Similarly, the S1 peak becomes greatly enlarged as the sulfur content increases, thus increasing the value of the Production Index. Significantly, Page (1995) documented the presence of large amounts of elemental sulfur in mineralised samples from the Cadjebut deposit, and it appears likely that this is the situation for other deposits on the Lennard Shelf. Therefore, the presence of elemental sulfur almost certainly better explains the anomalous Rock-Eval parameters than any localised thermal effects.

Vitrinite reflectance values can also be altered by chemical, rather than thermal processes during mineralisation (Heroux & Tasse, 1990). Heroux & Tasse (1990) suggested that bacterial sulfate reduction can lead to a lowering of Ro values in associated organic matter, while thermochemical sulfate reduction can increase Ro values in organic matter. It therefore appears probable that the slightly lower vitrinite reflectance values in mineralised samples can also be explained by anomalous chemical, rather than thermal processes occurring around the mineralisation.

In summary, there is little evidence for the presence of thermal anomalies around the mineral deposits of the eastern Lennard Shelf. This could be explained by several scenarios; 1. No substantial thermal anomalies have ever existed in the Pb-Zn deposits and mineralizing fluids were emplaced at the regional palaeotemperatures; 2. Weak thermal anomalies were formed during mineralisation, but these were obliterated by subsequent heating during Mesozoic burial and/or the mineralisation process itself; 3. Heating during sulfide mineralisation was too short-lived to produce significant thermal haloes (Arne, 1996).

**Hydrocarbons and MVT Mineralisation**

**Organic Geochemistry of the Cadjebut Zn-Pb Deposit**

In order to investigate the relationship between MVT mineralisation and hydrocarbons, three mineralised and five unmineralised samples from within and around the Cadjebut Zn-Pb deposit were analysed by solvent extraction (Page, 1995). The three mineralised samples consisted of two samples of high-grade Pb-Zn ore (Cadjebut mine localities 120–1N, 60–1N) from Cadjebut lens 1 and one sample from the marcasite halo of Cadjebut lens 1 (locality 131–7N). In order to avoid contamination from organic materials within the host carbonate, only cavity-filling sulfides containing no carbonate were analysed from the mineralised samples. Unmineralised samples were analysed from the Lower Dolomite host around the Cadjebut deposit (ranging from 100 to 500 m distant from the ore lenses).

All samples were relatively lean, with the mineralised samples being particularly lean. Elemental sulfur was abundant in both mineralised and unmineralised sample extracts. Unmineralised Cadjebut Formation samples contained alkanes (excluding one sample) typically ranging from nC12 to nC38 (Fig. 14). However, the pattern > nC25 shows no signature that could be associated with higher plants. The lower mid-range (< nC25) is consistent with a microbial input (Tissot & Welte, 1984). In contrast to the unmineralised
samples, mineralised samples typically have a more limited carbon range, with the dominant alkanes in the range \( \text{nC}_{13} \) to \( \text{nC}_{19} \).

Changes in the hydrocarbon distribution of mineralised and unmineralised samples could be the result of variations in biological sources, thermal maturity, or hydrothermal alteration (Powell & McKirdy, 1973; Tissot & Welte, 1984; Gize, 1999). Large & Gize (1996) similarly found that mineralised samples from the Kupferschiefer deposit had generally lower molecular-weight n-alkane distributions than the host rocks underlying and overlying the deposit. They interpreted this as directly reflecting the host rock stratigraphy. This stratigraphic interpretation cannot be applied to the Cadjebut samples, as both mineralised and unmineralised samples are from the same stratigraphic unit (Cadjebut Formation). The lower n-alkane distribution of the mineralised Cadjebut samples may be due to locally higher maturation levels within the deposit. However, as discussed above, there is no evidence from any of the maturation parameters to indicate thermal anomalies around MVT mineralisation on the Lennard Shelf.

Another possibility is that the hydrocarbons in the mineralised samples are migrated oils, generated from a source different from the host Cadjebut Formation. Etminan & Hoffmann (1989) suggested this possibility in their study of hydrocarbons within the deposits of the Lennard Shelf. They documented significant quantities of hydrocarbons within inclusions from mineralised and unmineralised samples on the Lennard Shelf. They described purple sphalerite from Cadjebut that contained inclusions of aromatic and aliphatic hydrocarbons. In addition they documented the geochemistry of hydrocarbons from a Cadjebut dolomite sample. Using sterane maturity indicators, Etminan & Hoffmann (1989) suggested that the hydrocarbons in the Gogo Formation (a possible source rock on the Lennard Shelf discussed above) were much less mature than those found in the Lennard Shelf reservoirs and MVT deposits.

Etminan & Hoffmann’s (1989) conclusion that the MVT hydrocarbons (and reservoir hydrocarbons) were probably derived from a more mature, external source, is consistent with the maturity and organic geochemical data of this study. All maturity indicators suggest the near-surface source rocks of the eastern Lennard Shelf are immature or marginally mature for hydrocarbon generation, while sterane maturity data from mineralised samples indicate high levels of maturity.

Pristane/phytane (Pr/Ph) ratios of samples from the unmineralised Cadjebut Formation are low (1.0–1.7) and this is consistent with the hypersaline nature of the depositional environment (Ten Haven et al., 1987). The two mineralised samples for which Pr/Ph ratios could be measured have a bigger range (0.7–4.2) than the unmineralised host samples.

**Bitumen and hydrocarbon occurrences on the eastern Lennard Shelf**

Macroscopic bitumen occurrences are uncommon in the study area. The most prolific occurrences of bitumen visible in hand-specimen are from the Gap Creek region (Fig. 2). Here, bitumen has been found in the nodular calcareous shales of the Gogo Formation in at least nine BHP Minerals drill holes (GCD –11, –13, –14, –15, –16, –17, –19, –20, –23, –43, Diekman, 1990). In most cases, the bitumen occurs within fractures and along stylolites. In hole GCD–43, bitumen occurs in the Pillara Limestone in association with MVT sulfides. Similarly, in GCD–16, Diekman (1990) described bitumen in a vug filled by calcite, marcasite and sphalerite within the Gogo Formation.

Bitumen also occurs in the Brookong Gorge area of the SE Oscar Range (BHP Minerals hole BD–6–29 m). Here, bitumen occurs within primary porosity and is directly associated with iron sulfides and ore-stage calcite cements (Figs 15b–d). Furthermore, using cement stratigraphic relationships, the bitumen can be shown to have first entered the primary porosity contemporaneously with the sulfide and ore-stage calcite precipitation (Figs 15a–d). Bitumen from the Brookong Springs area (BD–6–17m and BD–3–13m) was analysed by Alexander et al. (1985) who suggested the samples were highly biodegraded.

Rayner (1991) also documented red-brown hydrocarbon material associated with marcasite-filled fractures near the Cadjebut Zn-Pb deposit. At the Goongewa Zn-Pb deposit, bitumen is relatively abundant. Orange-brown fluorescent
hydrocarbons were observed as primary fluid inclusions in ore-stage calcite, sphalerite and marcasite (Figs 16a, b, c). Blue-white fluorescent hydrocarbons were also observed as primary fluid inclusions from sphalerite (Fig. 16c).

Microscopic identification of bitumen and trace liquid hydrocarbons is common from lithologies on the Lennard Shelf. Organic petrologic descriptions (in Ellyard, 1984a,b; Diekman, 1990; Kufpec, 1988) commonly mention bitumen and droplets of liquid hydrocarbons. Similarly, Etminan & Hoffmann (1989) extracted hydrocarbons from Cadjebut and other deposits.

In only two occurrences can the timing of bitumen or hydrocarbon entry into the sequence be unequivocally determined (Goongewa & SE Oscar Range). The presence of primary hydrocarbons inclusions in various ore-stage phases (ore-stage calcite, sphalerite and marcasite) at Goongewa unequivocally indicates hydrocarbons were present during mineralisation (350 ± 15 Ma). Similarly, in the SE Oscar Range (drill hole BD–6), hydrocarbons entered the sequence contemporaneously with sulfides.

**Stalactitic textures in sulfides**

Well-formed stalactitic fabrics are present within sulfide cements at the Cadjebut and Goongewa Pb-Zn deposits (Fig. 17). At Cadjebut, small (generally < 1 cm long) well developed stalactites and stalagmites of colloform sphalerite occur sporadically in the banded ores (Fig. 17). At Goongewa, well-formed stalactites of marcasite were found in the uppermost mineralised cavities (Carney, 1997). Individual marcasite stalactites can be up to 10 cm long and range from 0.5 mm to 2 cm in diameter. Flowstone and “waterfall” textures have also been observed in marcasite at the Goongewa deposit.
Stalactitic and pendant textures are typically used as indicators of vadose diagenesis (James & Choquette, 1985). However, given that the sulfides were precipitated at elevated temperatures (70–90°C, discussed previously) during burial diagenesis (McManus and Wallace, 1992), it is extremely unlikely that vadose conditions can explain the stalactitic textures found in the sulfides. The presence of any gaseous phase (H₂S, CO₂ or CH₄ etc) or low-density water-immiscible liquid phase (e.g. hydrocarbons) during precipitation would produce stalactitic textures similar to those produced in a vadose environment. Therefore, the presence of stalactitic sulfide fabrics indicates that gaseous phases or liquid hydrocarbons were present during sulfide precipitation.

Reservoir Geometry of the Cadjebut Zn-Pb Deposit

The bulk of high-grade mineralisation at the Cadjebut deposit occurs in four stratabound lenses within the lower half of the Cadjebut Formation (Raetz & Bailey, 1990, Tompkins et al., 1994b). The ore lenses are mined at two levels, the upper and lower workings (each containing two lenses) that are termed lens 1 and lens 2 respectively (Fig. 18). The four ore lenses are all several tens of metres wide, less than a metre thick and around three kilometres long. Significant quantities of zinc and lead sulfides occur above, below and between the main lenses (e.g. Fig. 18). The ore lenses are all vertically aligned and form a linear to slightly meandering WNW–ESE-oriented ore zone (Fig. 18). Laterally equivalent marcasite or barite lenses flank the base-metal mineralisation. The barite lens is restricted to the northern side of the deposit. At least two of the ore lenses are stratigraphically equivalent to intraclastic breccias (of probable evaporite solution-collapse origin). Tompkins et al. (1994b) concluded that some of the ore lenses and flanking sulfide-sulfate lenses are stratigraphically equivalent to anhydrite units which occur to the north of the mine. The Cadjebut Fault system is present to the south of the ore body, but no major fault or system of faults is aligned with the ore deposit itself. The only minor fault cutting the deposit is a NNE–SSW trending normal fault with approximately twelve metres of total displacement (displacement and drag folding).

Bedding in the host carbonate dips ENE at approximately 6°. Significantly, the ore lenses are vertically
aligned within the hinge of a subtle anticlinal structure (Fig. 18), superimposed on the regional 6° dip. This anticlinal feature can be observed on north–south sections across the deposit, and can also be seen on structural contour maps for the base of the Cadjebut Formation (top of the Emanuel Formation) (Fig. 19). The anticline is a subtle feature and only has around ten metres of vertical relief over a distance of 1.5 kilometres.

The peculiar geometry of the Cadjebut deposit is highly suggestive of an anticlinal structure, which was host to a series of small reservoirs. The coincidence of a series of linear stratabound ore lenses, which are precisely stacked vertically over one another occurring within the hinge of a gentle anticlinal structure, is difficult to explain by other processes. This is particularly so in the absence of any faults which could act as feeders for the linear lenses.

**Discussion**

**Thermal History, Hydrocarbons and Fluid Flow**

A wide range of thermal maturity indicators consistently suggest that the outcropping and near-surface Devonian carbonates of the eastern Lennard Shelf are immature and have experienced maximum temperatures in the range of 70 to 90°C (Fig. 20). Of the maturity indicators used, apatite fission track analysis (Arne, 1996) gives the highest palaeotemperatures, while vitrinite reflectance values have a broader range and indicate somewhat lower palaeotemperatures. It is possible that the vitrinite reflectance values are slightly suppressed. However, given the ambiguities in correlation of the various maturity indicators, a remarkable degree of consistency is evident in the data.

The vitrinite reflectance profile for Needle Eye Rocks 1 (Fig. 9) suggests a relatively high maximum palaeogeothermal gradient (44 ± 10°C). Ro values reach the oil window at a depth of around 1 km in Needle Eye Rocks 1 and this can probably be extrapolated over most of the eastern Lennard Shelf. The fact that the Permian Grant Group has similar Ro values suggests that maximum heating may have occurred during the Mesozoic. This is supported by fluid inclusion data from Goongewa, suggesting some degree of stretching after their formation during Late Devonian–Early Carboniferous burial.

The low maturity values, combined with relatively lean source rocks on the eastern Lennard Shelf suggest that organic maturation has produced little or no petroleum in-situ. This is consistent with the relative scarcity of bitumens in the region. However, hydrocarbons are associated with MVT mineralisation at Cadjebut, Goongewa and in the SE Oscar Range (Etminan & Hoffmann, 1989; Carney, 1997) (Figs 15, 16). At Goongewa and in the SE Oscar Range, it is shown petrographically that hydrocarbons unequivocally entered the carbonates during the mineralisation episode. The chemistry of hydrocarbons from the Cadjebut deposit (Etminan & Hoffmann, 1989 and this study, Fig. 14) suggests that they have migrated from a more mature sequence. The most likely position of such a mature sequence is the Fitzroy Trough.

The age of mineralisation for the eastern Lennard Shelf, and hence associated hydrocarbons, is well established at 350 ± 15 Ma (McManus & Wallace, 1992; Christensen et al., 1995; Brannon et al., 1996). From stratigraphic reconstructions, seismic depth mapping (Dörling et al., 1996) and basin modeling, it is clear that large portions of the Ordovician to Devonian sequence in the Fitzroy Trough were within the oil window at 350 Ma. This is consistent with the hypothesis that MVT-associated hydrocarbons are derived.
from the Fitzroy Trough. The Fitzroy Trough also appears to be a likely source for metalliferous fluids.

The apparent lack of any thermal haloes around the sulfide deposits (Figs 12, 13) is significant and in accord with apatite fission track studies by Arne (1996). Sangster et al. (1994) similarly found that most MVT deposits do not have recognisable thermal haloes around them. The simplest explanation for this observation is that sulfides were precipitated during regional burial and heating. If this is so, it has important consequences for models of fluid flow during mineralisation. Since it is known that mineralisation occurred during active extension and subsidence in the region, the most appropriate fluid flow model for mineralisation on the Lennard Shelf is that of compaction-induced flow from the Fitzroy Trough (see also Dörling et al., 1996; Vearncombe et al., 1996). However, Cathles & Smith (1983) found that if significant thermal anomalies are required around the sulfide deposit, episodes of very intense dewatering are required, putting severe constraints on the compaction model. With no such thermal constraints required, the compaction model becomes a viable flow model. Compactional dewatering may also be responsible for carrying hydrocarbons that are associated with mineralisation from the Fitzroy Trough.

Eisenlohr et al. (1994) suggested that MVT mineralisation and associated hydrocarbons on the Lennard Shelf could have been emplaced by a eustatically induced hydrocarbon pulse from the Fitzroy Trough during the mid-Carboniferous (325 Ma). This model is untenable because it is based on an incorrect age for mineralisation (Tompkins et al., 1994a). It is also doubtful that the rise or fall of an oceanic thermocline as suggested by Eisenlohr et al. (1994) could produce a sudden pulse of heating at oil window depths (assuming that an oceanic thermocline existed at all in the Carboniferous Fitzroy Trough).

Lennard Shelf MVT Sulfide Deposits as Mineralised Sour Gas Accumulations

There is compelling evidence to suggest that buoyant and immiscible phases were present during sulfide precipitation on the Lennard Shelf. This evidence includes petrologic data for the paragenetic synchronicity of bitumens and sulfides, the
locally abundant and well-formed stalactitic fabrics in sulfides, and the peculiar anticlinal reservoir-like geometry of the Cadjebut deposit. Furthermore, the common concentration of mineralisation in pinnacle reefs across the shelf may also indicate buoyant phases associated with mineralisation being concentrated in stratigraphic traps.

These buoyant and immiscible phases may be gaseous or liquid hydrocarbons, or other non-hydrocarbon gaseous phases like CO₂, H₂S or N₂. Paragenetic data relating bitumens to sulfides provide direct and unequivocal evidence of hydrocarbons entering the sequence contemporaneously with sulfides. It is therefore possible that liquid or gaseous hydrocarbons have played a direct role in sulfide precipitation and localisation.

Jackson & Beales (1967) suggested that sour gas reservoirs played an important role in localising MVT sulfide precipitation. In their model, basinal brines carrying metals interact with H₂S-rich hydrocarbon reservoirs to produce MVT sulfide deposits. Anderson (1991) has similarly invoked gaseous hydrocarbon reservoirs as suitable environments for sulfate reduction and lead-zinc mineralisation to occur in.

The exact mechanism of sulfate reduction is problematic in these models. Most researchers agree that thermochemical sulfate reduction requires temperatures upwards of 140°C to occur at geologically reasonable rates (Worden et al., 1995; Worden & Smalley, 1996; Heydari, 1997). The Lennard Shelf has never experienced these temperatures and so thermochemical sulfate reduction is unlikely to have occurred in-situ. Evidence from the Cadjebut deposit however, suggests that sulfate reduction has occurred in or around the deposit at temperatures which never exceeded 90°C (maturity data from this study). The very similar sulfur isotopic composition of sulfides and associated evaporites, together with the gross replacement of stratiform evaporite units by stratabound sulfide lenses give virtually unequivocal evidence for in-situ sulfate reduction at Cadjebut.

Therefore, in the case of the Cadjebut deposit (and probably other MVT deposits on the Lennard Shelf), bacterial sulfate reduction is at present, the only viable mechanism for producing reduced sulfur. The discovery of thermophilic sulfate-reducing bacteria living at 65–70°C in petroleum reservoirs is pertinent to this issue (e.g. L’Haridon et al., 1995). L’Haridon and others were able to cultivate sulfate-reducing bacteria from petroleum reservoirs up to temperatures of 90°C. However, the sulfate-reducing bacteria studied can only tolerate salinities of up to 3–4 wt % NaCl, suggesting that they cannot exist in deep basinal brines.

Bacterial sulfate reduction could occur where hydrocarbons have migrated up dip into the shallow burial regime, in the presence of relatively low salinity brines. This is very likely the situation on the Lennard Shelf. It does appear that mature hydrocarbons have migrated from the Fitzroy
Trough into the Devonian carbonates of Lennard Shelf prior to significant burial of the carbonates (Etminan & Hoffmann, 1989, and this study). Being subject to low salinity fluids and relatively low temperatures (perhaps 60–70°C) within a sulfate-rich environment, the reservoir would very likely be subject to bacterial sulfate reduction and H2S accumulation. During continued burial, the biogenic H2S will eventually come into contact with metalliferous basinal brines, leading to metal sulfide precipitation. It is possible that the fluid chemistry of the mineralizing system fluctuated between high and low salinity, particularly during the initial stages of basinal brine influx. In this environment, bacterial sulfate reduction and H2S accumulation could occur when the fluids had a relatively low salinity (and low metal content), and metal sulfide precipitation could occur during times when basinal brines dominated the system. This fluid fluctuation would lead to alternate periods of H2S accumulation and metal sulfide precipitation and this might explain the paragenetic cycles of sulfides observed within many of the deposits.

In this scenario, the various ore deposit types (stratabound, fracture and fault-hosted and stratigraphically/diagenetic-controlled deposits) can be viewed as reflecting different trap types for sour gas. This scenario for MVT formation on the Lennard Shelf is illustrated diagrammatically in Figure 21.

**Conclusions**

1. A wide range of maturation parameters indicates that the near-surface Devonian carbonates of the eastern Lennard Shelf are immature. The oil window is present at a depth of approximately 1 km. A palaeogeothermal gradient of 44 ± 10°C per km is indicated from vitrinite reflectance data.
2. Peak temperatures of 70–90°C for near-surface carbonates are indicated and these were probably reached during Mesozoic burial. During Palaeozoic burial, temperatures of around 70°C are indicated from fluid inclusion data. Depths of burial for near-surface carbonates of around 1 km or more are indicated (by stylolite development) for Palaeozoic burial.
3. Evidence for the presence of liquid hydrocarbons is relatively scarce on the eastern Lennard Shelf. This is probably due to a combination of lean source rocks and low levels of maturity. Some hydrocarbons entered the carbonates contemporaneously with MVT mineralisation on the Lennard Shelf at around 350 Ma. These mineralisation-related hydrocarbons appear to be more mature than the carbonate host rocks and have most likely migrated from the adjacent Fitzroy Trough.
4. There are no detectable thermal anomalies present around any of the MVT sulfide deposits investigated and the simplest explanation for this is that mineralisation occurred during regional heating and burial.

5. The geometry, stratigraphic position and stalactitic textures associated with MVT sulfides indicate that a gas or immiscible liquid phase was present locally during mineralisation.

6. In-situ sulfate reduction must have occurred at temperatures less than 90°C in the Cadjebut deposit (and probably other sulfide deposits on the Lennard Shelf). This suggests that bacterial sulfate reduction in association with migrated hydrocarbons is the most likely scenario for in-situ sulfate reduction on the Lennard Shelf. These microbial processes may have occurred in a shallow (perhaps 1 km depth) burial setting.

7. Compartmental flow from the Fitzroy Trough appears to be the most likely mechanism for the delivery of metalliferous brines and mature hydrocarbons to the Lennard Shelf.

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