

Mississippi Valley–type deposits: Products of brine expulsion by eustatically induced hydrocarbon generation? An example from northwestern Australia

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ABSTRACT

Mechanisms for fluid flow such as compactive dewatering, gravity-driven hydrologic flow, and seismic pumping are not geologically plausible for Mississippi Valley–type (MVT) mineralization in the Lennard Shelf, Canning Basin, northwestern Australia. Sulfides at Cadjebut and the other Lennard Shelf MVT deposits precipitated from overpressured, hydrocarbon-rich brines. The deposits lie below a major mid-Carboniferous unconformity that is linked to a global sea-level fall. Independent evidence at Cadjebut also constrains the time of mineralization to the mid-Carboniferous. A sea-level fall at this time could have raised the sediment-water interface above the thermocline, thereby increasing the temperature of the basin by ~16 °C. Model calculations show that a rise in basin temperature would induce sufficient hydrocarbon gas maturation to expel 1005 km³ of brine. This brine volume would be more than sufficient to transport and deposit the metal budget of the known MVT deposits on the Lennard Shelf. The existence worldwide of MVT deposits below unconformities suggests that sea-level–induced hydrocarbon generation could have assisted MVT mineralization in other provinces.

INTRODUCTION

Mississippi Valley–type (MVT) Zn–Pb deposits are typically located within stable cratonic basins on or near basement highs. They are considered to have formed at 80 to 200 °C from brines that originated deep within basins and migrated toward basin margins. MVT deposits are commonly located below unconformities of regional extent (Callahan, 1967; Stanton, 1972; Sangster, 1988).

Fluid flow mechanisms commonly proposed to explain MVT mineralization include basin compaction, tectonic loading and compression, seismic pumping, and gravity flow from uplifted areas. None of these flow mechanisms are appropriate to explain formation of the Cadjebut Zn–Pb and other MVT deposits of northwestern Australia (Fig. 1). The Cadjebut deposit is hosted in Devonian carbonate rocks, and it formed after dolomitization and diagenesis during the mid-Carboniferous (Tompkins et al., 1994a). Episodic fluid expulsion associated with compaction of basin sediment (e.g., Cathles and Smith, 1983) is unlikely to have caused mineralization, because sedimentation rates were low after the Devonian (Fig. 2A). Tectonically induced fluid expulsion (e.g., Oliver, 1986) could have occurred during the Triassic when the basin was in a transpressional tectonic regime, but this event postdates the age of mineralization. The nearest uplifting terrain at the time of mineralization, the Alice Springs orogeny (Forman and Wales, 1981), lies 700 km southeast of the deposit, and intervening basement highs would have prevented fluids from reaching the deposit. Thus, topographic flow models (e.g., Sverjensky and Garven, 1992) are not applicable. Because the major extensional structures were inactive at the time of mineralization, seismic-pumping models (e.g., Clendenin and Duane, 1990) also do not apply. Four geologic facts stand out at Cadjebut: (1) metal deposition and hydrocarbon migration occurred simulta-

neously; (2) the deposit lies below a regional unconformity; (3) the deposit shows clear evidence of fluid overpressing; and (4) meteoric fluids mixed with the late ore fluids.

No explanation has been advanced previously for the association of MVT deposits, at Cadjebut and elsewhere, with unconformities. We show that surface temperature changes during sea-level regression could cause a pulse of hydrocarbon maturation, fluid overpressing, and brine expulsion of sufficient magnitude to produce the northwestern Australia MVT deposits. Hydrocarbons, especially hydrocarbon gases, could be produced in sufficient volume to rapidly expel the brine volume required to produce all the MVT deposits on the Lennard Shelf. Gas-driven expulsion has been sug-

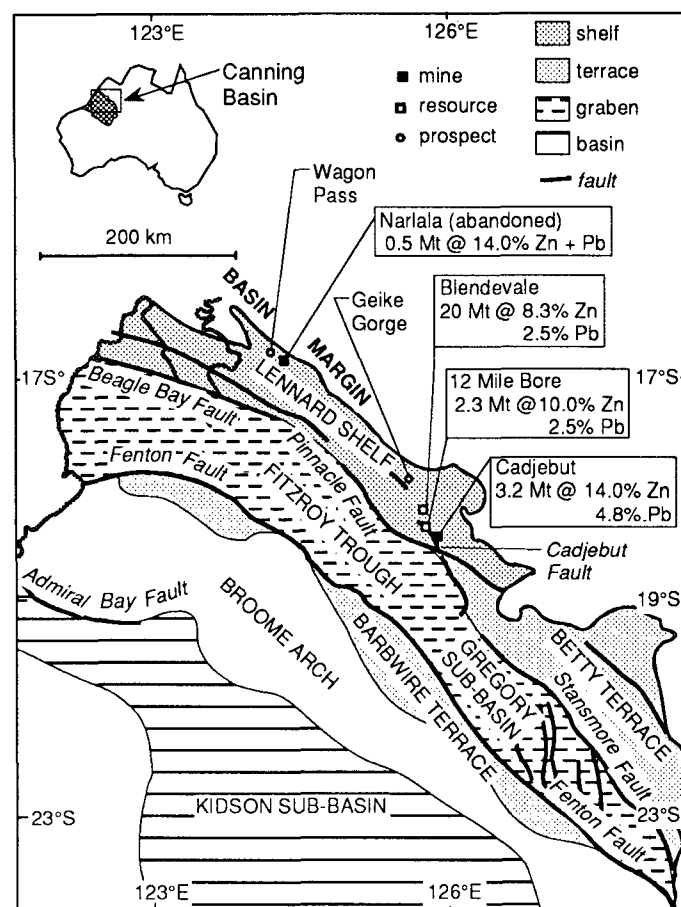
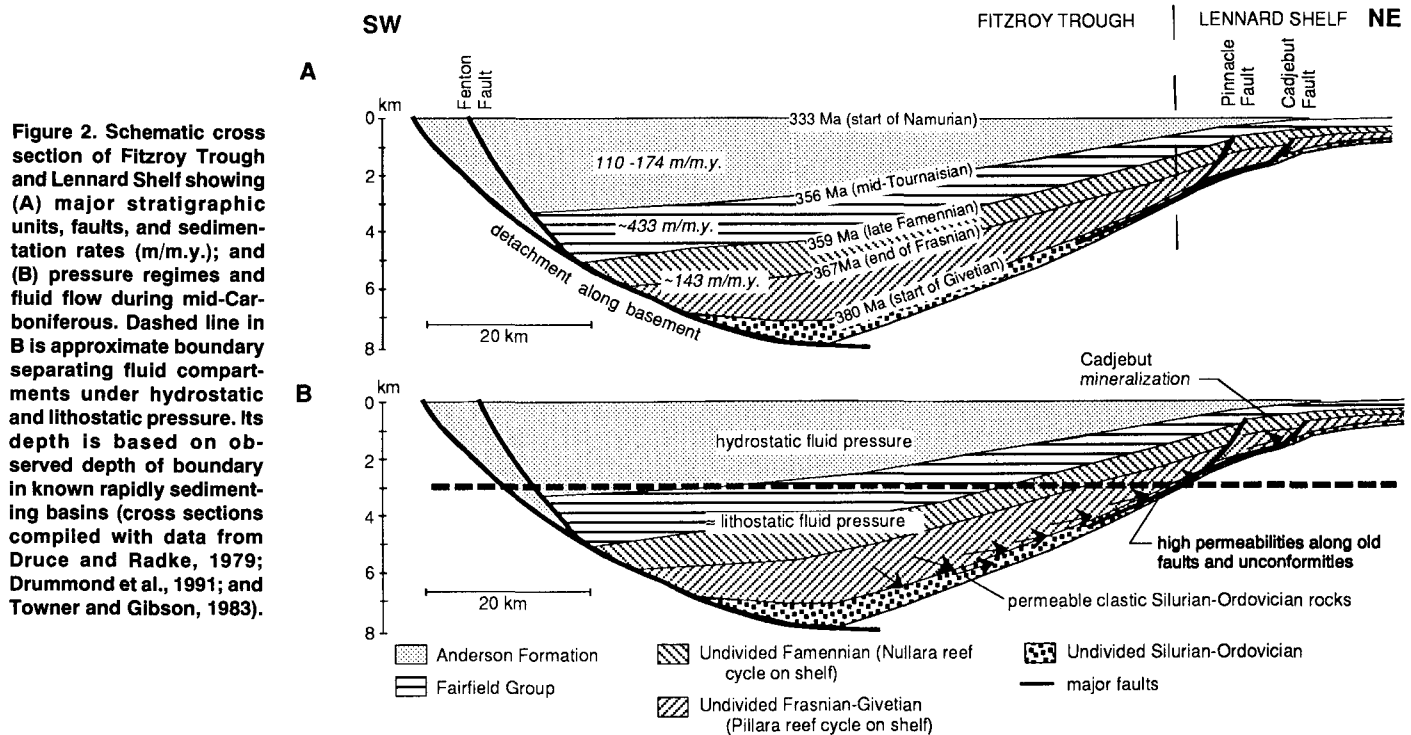


Figure 1. Simplified geology of Canning Basin showing Fitzroy Trough, Lennard Shelf, and other major tectonic units. Locations, ore reserves, and grades of known Mississippi Valley–type deposits and prospects are also shown. Total base metal content of these deposits is ~3.1 Mt (calculated from Murphy, 1990).



gested as a fluid drive for oil migration (Rich, 1927), but it has never been specifically tied to a sea-level fall or MVT mineralization.

FITZROY TROUGH AND LENNARD SHELF

The Lennard Shelf forms the northeastern margin of the Fitzroy Trough, within the Canning Basin (Fig. 1). The oldest sedimentary rocks are Ordovician and were deposited on Precambrian basement, followed by deposition of sand and silt during the Early Devonian. The Fitzroy Trough, which started to form during the Middle Devonian (Towner and Gibson, 1983), is a half graben bounded on the southwest side by a series of listric normal faults (Fenton fault system). The northeast margin of the trough is defined by the listric Pinnacle fault, which soles out along the top of the Ordovician succession and is interpreted as antithetic to the faults on the southwest side of the trough (Drummond et al., 1991). In total, about 8000 m of sediments were deposited in the Fitzroy Trough.

Depositional environments on the Lennard Shelf were shallow marine to supratidal through the Devonian to mid-Carboniferous. Maximum sediment accumulation on the shelf is about 3000 m; reef-fringed carbonate platforms developed in the Frasnian and Famennian (Towner and Gibson, 1983). Depositional facies in the Fitzroy Trough remained marine, and subsidence was concentrated along the southern margin of the trough between late Famennian time and the end of the Viséan, resulting in the deposition of the 2500 to 4000 m of sediment of the Fairfield Formation and Anderson Group (cf. Druce and Radke, 1979). The Anderson Group is restricted to the trough and was deposited in continental and marine environments, although little is known of the facies distribution (Fig. 2A). The mid-Carboniferous (Namurian) is marked by a lacuna on a subaerially eroded unconformity throughout the basin, including the Fitzroy Trough. Renewed sedimentation in the Fitzroy Trough began in the late Carboniferous (Stephanian), and glacially influenced sediment was deposited until the Triassic. The area was faulted, folded, and uplifted during the Late Triassic and Early Jurassic (Brown et al., 1984).

The mid-Carboniferous unconformity coincides with a second-

order eustatic event that began with a major regression and is recorded in basins all over the world (cf. Saunders and Ramsbottom, 1986). The unconformity also coincides with the transition from the Devonian-Viséan rift phase to the Namurian-Triassic sag phase of the basin (Brown et al., 1984; cf. Watts, 1982). The burial depths of Devonian and lower Carboniferous units in the Fitzroy Trough, and the calculated geothermal gradients for the Carboniferous, indicate that these units were within oil and/or gas generation windows during the Carboniferous, which is also interpreted as the time of primary hydrocarbon migration from the axis of the basin to its margins (Ellyard, 1984). On the basis of conodont color alteration, a Late Devonian-Carboniferous thermal event, with a probable peak during the Tournasian, has also been noted in the Fitzroy Trough (Nicoll and Gorter, 1984). Fission-track studies suggest that this event extended to the Lennard Shelf (Arne et al., 1989).

CADJEBUT MVT DEPOSIT

The Cadjebut orebody is located to the north of the Cadjebut fault, a growth fault that splays off the Pinnacle fault (Fig. 1). There are two texturally distinct types of zinc-lead mineralization at Cadjebut: (1) early rhythmically banded, bedding-parallel, Zn-rich ore considered to be an evaporite replacement (Tompkins et al., 1994b), and (2) a later, Pb-rich, crosscutting breccia ore. The breccia ore is associated with a set of 15° to 40° north-dipping reverse faults. These faults show displacements of 10 to 40 cm, tend to terminate upward in breccia zones, and delaminate along the base of the banded ore. A set of subhorizontal veins filled with ore identical to that in the reverse faults is associated with these faults and is also present throughout the mine. The veins crosscut the banded ore and are dilational, as shown by their matching opposite margins. In more fractured areas, breccia fragments can be restored to their original position if the vein fill is removed. This evidence suggests that high fluid pressures were involved in the formation of the faults and breccia ore. Veins of clear calcite and vein-associated hydraulic breccias, locally mineralized, crosscut breccias and clastic-filled fissures (neptunian dikes) relating to normal movement along the Cadjebut

fault, indicating that mineralization-associated veining and brecciation postdates normal fault movement.

Fluid inclusions in sphalerite and dolomite from Pb-Zn MVT deposits on the Lennard Shelf, including Cadjebut, contain aqueous fluid and an immiscible hydrocarbon (Etminan and Hoffman, 1989). Sphalerite at Cadjebut and Blendevalle also contains purple zones, constituting up to 30% volume, that consist of innumerable hydrocarbon-rich inclusions. The hydrocarbons originated from deep within the basin and were emplaced epigenetically into the host rock (Etminan and Hoffman, 1989).

The presence of abundant hydrocarbons in sphalerite, the mid-Carboniferous peak in hydrocarbon generation in the Fitzroy Trough, and the evidence for fluid overpressuring during mineralization all suggest a mid-Carboniferous (~325 Ma) age for ore deposition. Detailed regional (Pedone, 1990) and local (Tompkins et al., 1994a) diagenetic studies of the host-rock carbonates using cement stratigraphic, isotopic, and geochemical data at Cadjebut also indicate that mineralization occurred during the mid-Carboniferous. Oxygen isotope ratios of carbonates indicate that meteoric water mixed with the deep basinal ore fluids during the last stages of mineralization (L. Tompkins, unpublished); this suggests that the rocks were close to subaerial exposures (i.e., outcrops of the Namurian) and thus also supports a mid-Carboniferous age for mineralization.

GAS-EXPULSION MODEL

Temperatures in a basin depend on depth, the geothermal gradient, and the temperature on the surface of the basin. Temperatures change strongly across the ocean thermocline, which generally lies at a depth of 100 to 200 m. Temperatures below the thermocline are about 4 °C, assuming that ocean temperature profiles during the Carboniferous were similar to those currently observed (cf. Crowley, 1993), whereas above the thermocline temperatures are near ambient. Ambient temperatures would have been ~20 °C at the ~25°S position of the Fitzroy Trough in the mid-Carboniferous (cf. Forman and Wales, 1981). A change in sea level of several hundred metres, whether due to tectonic uplift or eustatic fall, could, therefore, have moved the sediment-water interface from below to above the thermocline and could have increased the temperature of the sediment-water interface over the entire Fitzroy Trough by ~16 °C. Such an increase in basin surface temperature will rapidly diffuse downward, resulting in the warming of sediments at all depths by 16 °C.

Relative sea-level changes of several hundred metres in magnitude during Earth's history have been documented (cf. Vail et al., 1977). The Namurian sea-level changes, of specific interest here, occurred rapidly, although the rate of change is unknown. The periodicity of the minor and major eustatic cycles in the mid-Carboniferous is estimated at 40 to 120 ka and 235 to 400 ka, respectively (Heckel, 1986). However, the mid-Carboniferous is poorly dated, and cycle periods of approximately half the above period are thought to be more likely (Klein, 1990). The duration of the Namurian sea-level fall was thus likely <100 ka. Namurian low sea levels are thought to have persisted for 1.9 to 4.5 m.y. (Saunders and Ramsbottom, 1986).

If sea level fell in less than 100 ka, then the rate of temperature change at ≥3 km depth would have been controlled by time required for heat to diffuse into the basin. Carslaw and Jaeger (1959, p. 60, equation 5) derived an expression for the rate of heating in a semi-infinite solid whose surface temperature is suddenly changed by T . The rate of change is maximum at the temperature front. The depth, z , of the front increases with time, t , such that $z = 2(Kt)^{1/2}$. Substituting the above expression for z in Carslaw and Jaeger's equation gives:

$$(dT/dt)_{\max} = (4TK)/(z^2\pi^{1/2}e)$$

for the maximum rate of temperature change as a function of depth. K is the thermal diffusivity of the sediments (in cm^2/s) and is typically ~0.01 cm^2/s ; T , the change in temperature of the top surface of the basin, is taken to be 16 °C at $t = 0$; z is depth (in cm); and e is the base of the natural logarithm. For $z = 3$ km, $(dT/dt)_{\max} = 46$ °C/m.y., and for $z = 6$ km, $(dT/dt)_{\max} = 12$ °C/m.y.

The "normal" rate of heating due to sedimentation and burial is the product of the burial rate and the geothermal gradient. Paleotemperature models for the Fitzroy Trough based on maturity measurements (vitrinite reflectance, thermal alteration index, and conodont alteration index) suggest geothermal gradients from 13 to 18 °C/km during the Paleozoic (Ellyard, 1984). Using 18 °C/km and a burial rate of <0.2 km/m.y. (Fig. 2A), the heating rate was <4 °C/m.y. Heating rates at 3 and 6 km depths in the Carboniferous Fitzroy Trough, due to a rapid sea-level-induced change in surface temperature, are thus four to 11 times greater than the rates due to sedimentation, and equal those observed in basins with rapid sedimentation (0.8 to 2.2 km/m.y.), where overpressures are almost always encountered.

On the basis of total organic carbon (TOC) contents measured in wells, Devonian siliciclastic and marine facies of the Carboniferous Fairfield Group within the Fitzroy Trough are considered the best hydrocarbon source. TOC contents are consistently >1% or 2%; there are a few highs of up to 8% for parts of the Fairfield Group and some of the Devonian basinal facies shales (cf. Ellyard, 1984; Horstman, 1984). Burial depths for these rocks during the Namurian were 2000 to 4000 m for the Fairfield Group and 2000 to 7000 m for the Devonian siliciclastic rocks; these depths place parts of these groups in the peak hydrocarbon generation window (cf. Ellyard 1984). If we assume an 18 °C/km gradient during the Carboniferous, a 16 °C temperature change caused by a fall in relative sea level would be equivalent to the deposition of 890 m of sediment, and would move 890 m of sediment through the oil and gas windows. Hydrocarbon production, especially gas, would lead to a significant volume change. For example, Ungerer et al. (1983) estimated a 6% overall increase in volume of type II (marine) organic matter if maturation has proceeded through oil generation (vitrinite reflectance $R_o = 1.3\%$), and a 77% increase if the organic material has fully matured to methane ($R_o = 2\%$).

The significance of these volume expansions if applied over the Fitzroy Trough is shown by simple calculations. (1) A column of sediment 890 m long and 1 cm^2 in cross section (the column that will be matured by sea-level change) contains 3916 g of kerogen, if we assume a sediment density of 2.2 g/cm^3 and a 2 wt% organic carbon (kerogen) content. If the kerogen density is 1.5 g/cm^3 it occupies 2611 cm^3 . (2) If there is a 77% volume increase when this kerogen matures to gas, 2010 cm^3 of basin pore fluids (mostly basin brines) will be expelled per square centimetre of surface area of the basin. (3) A 100 km by 500 km part of the Fitzroy Trough will thus expel 1005 km^3 of basin brine. (4) If that brine precipitates just 10 ppm Zn + Pb, 10 Mt of metal will be deposited, an amount that exceeds the <5 Mt metal resource estimated for the Lennard Shelf (Murphy, 1990). Because basinal brines can contain hundreds of parts per million base metals and can precipitate a large percentage of their metal content upon venting, the above estimate is considered to be conservative.

The 77% volume expansion used above is a low estimate; twice as much CH_4 could be formed during kerogen maturation (John Hunt, 1990, personal commun.). However, dissolution of CH_4 in the pore waters will reduce the volume expansion. At most, about 20 000 ppm CH_4 can be dissolved in pore waters at lithostatic pressures and reasonable basin temperatures (Bonham, 1978). A sediment with 10% porosity can thus dissolve 0.002 g CH_4/cm^3 . At 2 wt% organic matter content and a conversion efficiency of 0.15 g CH_4/g kerogen

(Ungerer et al., 1983), the sediment will produce $0.007 \text{ g CH}_4/\text{cm}^3$. Thus, pore water can dissolve about one-third of the CH_4 produced. If the basin matured only to the oil stage, smaller but still substantial volumes of brine would be expelled. Using Behar et al.'s (1985) estimate of 6% for organic matter volume expansion at the oil stage, 78 km^3 of basin brine would be expelled from the Fitzroy Trough. However, precipitation of $\sim 100 \text{ ppm Zn} + \text{Pb}$ from solution would be required to produce 7.8 Mt of metal. Although this amount would be sufficient to account for the metal budget of the Lennard Shelf, it would require high precipitation efficiency at the depositional sites. Therefore, only basins producing gas in addition to oil are likely to produce MVT deposits by the mechanism proposed in this paper, if the Lennard Shelf deposits and the Fitzroy Trough are typical.

CONCLUSIONS

We have shown that a significant pulse of hydrocarbon generation could have been produced by a several hundred metre sea-level drop in the mid-Carboniferous, and that this pulse of hydrocarbon generation could have rapidly expelled a large volume of basin brines and hydrocarbons from the Fitzroy Trough. The outflow is expected to have been focused in the permeable units, such as the Silurian and Ordovician clastic sediments at the bottom of the basin, and to have exited through the major listric normal faults near basin-basement contacts at the basin margins, where Zn-Pb sulfide ores were precipitated (Fig. 2B). Given the rapidity (a few hundred thousand years) of the maturation pulse, fluid pressures approaching, and locally exceeding, lithostatic at the shallow depths of ore deposition are expected. The mechanism is the only one proposed so far that can account for all the principal geologic features observed at Cadjebut.

High hydrocarbon contents in fluid inclusions in MVT mineralization and associated gangue minerals have been documented many times (e.g., Spirakis and Heyl, 1993), but the role of hydrocarbons has been largely considered from a chemical point of view only. It is suggested here that the relation can also be physical. Given that MVT deposits worldwide commonly occur below major unconformities (cf. Sangster, 1988), sea-level change and gas generation could have more generally assisted in the formation of MVT deposits.

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