## Diagenesis and Fluid Flow History in Sandstones of the Upper Permian Black Jack Formation, Gunnedah Basin, Eastern Australia

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Abstract: The fluid flow history during diagenesis of sandstones in the Upper Permian Black Jack Formation of the Gunnedah Basin has been investigated through integrated petrographic observations, fluid inclusion investigations and stable isotope analyses. The early precipitation of mixed-layer illite/smectite, siderite, calcite, ankerite and kaolin proceeded at the presence of Late Permian connate meteoric waters at temperatures of up to 60°C. These evolved connate pore waters were also parental to quartz, which formed at temperatures of up to 87°C. The phase of maximum burial was characterized by development of filamentous illite and late calcite at temperatures of up to ~90°C. Subsequent uplifting and cooling led to deep meteoric influx from surface, which in turn resulted in dissolution of labile grains and carbonate cements, and formation of second generation of kaolin. Dawsonite was the last diagenetic mineral precipitated and its formation is genetically related to deep-seated mamagtic sourced  $CO_2$ .

Key words: diagenesis, fluid flow history, Gunnedah Basin, fluid inclusion, stable isotope

## **1** Introduction

The Gunnedah Basin (Fig. 1) forms the central part of the Sydney-Gunnedah-Bowen Basin system in eastern Australia from the southern New South Wales to central Queensland. It is a foreland basin with sediments lapping unconformably onto the deformed and metamorphosed rocks of the Lachlan Fold Belt in the west and abutting the New England Fold Belt in the east along the east-dipping Hunter-Mooki Thrust System. It is separated from the Sydney Basin by the Mount Coricudgy Anticline and from the Bowen Basin by Narrabri High (Tadros, 1993). The configuration of the Gunnedah Basin forms a N-S trending elongated structural trough up to 200 km long and ~120 km across at its widest point. The Gunnedah Basin took its final structural form after the mid-Permian onset of the orogeny in the New England Fold Belt and persisted as a structural entity until the end of Middle Triassic time (Korsch, 2004).

The stratigraphy of the Gunnedah Basin was reviewed in Tadros (1993). It is characterized by two coal-bearing sequences: the Lower Permian Maules Creek and Upper Permian Black Jack Formations, which are separated by largely marine Porcupine and Watermark Formations (Fig. 2). The Maules Creek Formation is underlain by the Lower Permian alluvial and lacustrine Goonbri and Leard Formations and the Black Jack Formation is overlain unconformably by Triassic alluvial and lacustrine sediments of the Digby and overlying Napperby Formations. The Black Jack Formation consists of sandstone, siltstone, conglomerate, tuff and coal seam. It has a viable thickness from less than 40 m in the west to more than 400 m in the southeast. It is divided by the Hoskissons Coal Member into two parts (Fig. 2). The lower part of the formation was deposited in shallow marine and deltaic environments (Hamilton, 1991) and the upper part in interfingered fluvial and lacustrine environments (Tadros, 1993).

In contrast to the extensive study of stratigraphy and sedimentology of the Black Jack Formation (e.g. Hamilton, 1991; Tadros, 1993), no comprehensive investigation of the diagensis and fluid flow history of sediments in the formation has ever been attempted. In this study, the main aims are twofold. One is to document the diagenetic features of sandstones in the formation. The other is to attempt to constrain the temperature, timing, chemistry

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Fig. 1. Location map of the Gunnedah Basin and wells used in this study. Wells are represented by the designated letter. Well name abbreviation is given in brackets. a = DM Morven 1 (MOR), b = DM Cookabingie 1 (COE), c = DM Wilson 1 (WIL), d = DM Purlawaugh 1 (PUR), e = DM Bando 1 (BAN), f = DM Brigalow 2 (BRW), g = DM Brigalow 1 (BRI), h = DM Coogal 1 (COL), i = DM Benelabri 1 (BEN), j = DM Benelabri 2 (BEE), k = DM Denison 1 (DEN), 1 = DM Dewhurst 1 (DEW), m = DM Parkes 2 (PAR), n = DM Tullamullen 1 (TUL), o = DM Dampier 1 (DAM), p = DM Gorman 1 (GOR), q = DM Blake 1 (BLA), r = DM Turrawan 2A (TUR), s = DM Narrabri 1 (NAR).

and source of pore fluids during the diagenetic history of the sandstones through combined applications of petrographic observations, fluid inclusion investigations and stable isotope analyses.

## 2 Methods

A total of 66 sandstone samples were taken from 19 wells (Fig. 1) in the northern part of the basin (no core data available in the southern part) with most being selected from the western bed-load quartz-rich unit defined by Hamilton (1991). Thin sections cut for all the samples were examined under a standard petrological microscope to observe grain size, framework mineralogy, texture, porosity, dissolution features and cementation history. Modal analyses were carried out on 40 of the samples. Of these samples, the majority were subjected to scanning electron microscope (SEM)/energy dispersive X-ray (EDX) analyses to identify carbonates and clay minerals. Seven sandstones with well developed quartz

overgrowths were selected for fluid inclusion investigations. Isotopic studies were carried out for authigenic minerals (quartz, clay, and carbonate) in 27 samples.

Fluid inclusions were investigated by petrological examinations of wafers about 50 µm thick and polished on both sides. fluid inclusions Hydrocarbon were identified by fluorescence using ultra violet and violet illumination and short wavelength barrier. Homogenization temperatures (bubble disappearance temperatures) and ice melting point temperatures of aqueous fluid inclusions were measured on pieces cut from the wafer using a Chaix Mecca heatingfreezing chamber mounted on a standard petrological microscope.

For isotopic studies, the sandstone samples were initially cleaned on exterior surfaces and then grounded to a specified size, depending upon the grain size of the monocrystalline quartz in the sandstone, by disc milling. An aliquot of 200 g sample was used to yield a <10  $\mu$ m clay fraction for 14 of the samples and a pure quartz (>180  $\mu$ m) separate for 5 samples following the techniques outlined by Jackson (1979). Pure carbonates (ankerite, calcite, dawsonite, and siderite) were obtained by repeated magnetic and heavy liquid treatments. Finer size clay fractions

were prepared by gravitational and centrifuge settling and analyzed by X-ray diffractions. Only pure (>90%) clay separates were used for isotopic analyses. The >180 mm pure quartz separates were used to derive the values of overgrowth oxygen isotope composition following the method of Lee and Savin (1985). The quartz separate was etched in H<sub>2</sub>SiF<sub>6</sub> (50%) for 10 hours. After neutralizing the acid by repeated distilled water washing, they were treated with ultra-high frequency sonic vibration in distilled water and then sieved into six size fractions: >180, 180–125, 125–75. 75–53, 53–20, and < 20  $\mu$ m, which were used for oxygen isotope analyses.

For isotopic analyses of carbonates,  $CO_2$  was released from calcite and dawsonite by reaction overnight with 100% phosphoric acid at 25°C and from siderite and ankerite by reacting with phosphoric acid for 3 hours at 100°C. The produced  $CO_2$  was cleaned through a cold trap (~80°C). Oxygen was released from clay, which was preheated in a 200°C oven for at least four hours to remove absorption water, and quartz by reaction overnight



Fig. 2. Generalized stratigraphic column of the Gunnedah Basin (modified from Hamilton, 1991; Tadros, 1993).



Fig. 3. Schematic illustrations of the order of precipitation of diagenetic minerals in sandstones of the Black Jack Formation, the Gunnedah Basin.

with bromine pentafluoride at 550°C and then converted to CO<sub>2</sub> by reacting with a hot graphite rod using a platinum catalyst (Clayton and Mayeda, 1963). Oxygen and carbon isotope ratios were measured in a Finnigan Mat 252 mass spectrometer. The isotope data are presented in per mil ( $\delta$ ‰) with respect to Standard Mean Ocean Water (SMOW) for oxygen and Belemnitella americana from the Peedee Formation (PDB) for carbon. Analytical precision is ±0.1‰ for  $\delta$ <sup>18</sup>O and  $\delta$ <sup>13</sup>C of the carbonates and ± 0.25‰ for  $\delta$ <sup>18</sup>O of the silicates.

## **3 Petrography**

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Sampled sandstones are fine to coarse grained sandstones with an average grain size of 0.21 to 0.91 mm, but the majority of them are medium to coarse grained sandstones. They are very poorly to well sorted with the coarser sandstones tending to be very poorly and poorly sorted and the finer sandstones moderately to well sorted. Clay (including both detrital and authigenic) matrix constitutes 0.2 to 27.2% of the total rock volume with an average content of 10.4%. Its abundance is reversely related to that of carbonate cements in the sandstones.

The 40 sandstone samples, on which modal analyses were carried out, are divided into two groups in terms of composition: quartz-rich and lithic-rich. Thirty of them, which are from the lower quartz sandstone unit and Clare Sandstone Member (Fig. 2), are quartz-rich and classified as quartzarenites, sublitharenites, subarkoses and quartzrich litharenites (Folk et al., 1970). The average composition of these sandstones

is  $Q_{81.3}F_{2.7}R_{16}$ . The other ten samples, three of which are from the basal lithic unit of lower delta plain facies and the rest from the lithic conglomeratic unit of fluvial facies (Fig. 2), are quartz-poor and classified as lithic-rich litharenites with an average composition of  $Q_{39.0}F_{1.5}R_{59.5}$ .

Cements and replacive minerals include carbonates (ankerite, calcite, dawsonite, and siderite), clay minerals (kaolin, mixed-layer illite/smectite and illite), and quartz (overgrowths and outgrowths). They (excluding diagenetic clays) together constitute 1.6% to 41.8% of the total rock volume with an average content of 7.4%.

## **4** Paragenetic Sequence

On the basis of the textural relationships observed under the petrological microscope and the SEM, the relative timing of the major diagenetic mineral was deduced and shown in Fig. 3. Grain coating illite/smectite is enclosed by carbonates and quartz overgrowths so that it is considered to be the earliest product of diagenesis. Siderite occurs within pore-filling ankerite cement, suggesting that siderite pre-dated ankerite. Our observation that ankerite is enclosed by quartz overgrowths suggests that quartz overgrowths formed later. The enclosing of kaolins by quartz overgrowths, intergrowth of kaolins and quartz



Fig. 4. Histogram of homogenization temperatures for aqueous fluid inclusions in quartz overgrowths in six samples of the Black Jack Formation.

overgrowths, and the presence of kaolins on quartz overgrowths imply that quartz crystallization was partly coeval with precipitation of kaolins. The presence of calcite cement on euhedral quartz overgrowths indicates that calcite was precipitated after quartz. Growing of illite on quartz overgrowths and calcite is interpreted as such that illite post-dated quartz and calcite. Dawsonite abuts ankerite, quartz overgrowths and illite. The textural relationships suggest that it post-dated all these diagenetic minerals. The presence of dissolved ankerite and calcite and the partial filling of secondary pore spaces by dawsonite indicate that dissolutions process happened after precipitation of calcite but before crystallization of dawsonite.

## **5 Fluid Inclusions Investigations**

Aqueous fluid inclusions give information on the palaeotemperature and composition, in particular the salinity, of pore water at the time of crystallization of host minerals. They provide temperature inputs for interpreting the isotope compositions of diagenetic cements. Observation of hydrocarbon fluid inclusions in diagenetic minerals gives the timing of oil migration relative to diagenesis.

#### 5.1 Petrography of fluid inclusions

In all the seven samples subjected to the investigation, aqueous fluid inclusions are recognized to occur at the boundary between detrital quartz grains and overgrowths and within overgrowths. They are normally  $4-20 \mu m$  in diameter and have rounded, elongated or irregular shapes. At room temperature, they consist of a colorless liquid and a variable (2 to 20% by volume) vapor bubble. Hydrocarbon fluid inclusions were found in four of the samples where they occur in healed fractures cutting detrital grains. They have an orange-yellow and a light blue to white fluorescence colors. Their size and shape are similar to those of aqueous fluid inclusions. At room temperature, they consist of a colorless liquid and a variable (2 to 80% by volume) vapor bubble.

#### 5.2 Fluid inclusion thermometric results

Homogenization temperatures were measured for 44 different aqueous fluid inclusions at the boundary between detrital quartz and overgrowths and within overgrowths in the seven samples. The results are summarized in Fig. 4. The aqueous fluid inclusions have a large range of homogenization temperatures from  $72^{\circ}$ C to >  $140^{\circ}$ C. For the same samples, the homogenization temperature also varies greatly as shown in Fig. 4.

An ice melting point temperature was measured for only one aqueous fluid inclusion at the boundary between detrital quartz grain and overgrowths in one sample from Wilson 1 (WIL587.2). It is  $-1.5^{\circ}$ C, which corresponds to a salinity of about 2.56% (wt) NaCl equivalent. This low salinity suggests that aqueous fluid inclusions are of meteoric origin, which is supported by the calculated negative  $\delta^{18}$ O composition of pore waters (see later section).

# **5.3** Geological temperatures from fluid inclusion temperatures

The variable (2 to 20% by volume) vapor in aqueous fluid inclusions at room temperature and the wide range of homogenization temperatures of the inclusions suggest that the fluid inclusions trapped mixtures of water and gas. Trapping of a second phase increases the recorded homogenization temperature so that the minimum homogenization temperatures are the best estimate of the geological temperatures (Roedder, 1981; Burruss, 1992).

The seven samples for fluid inclusion investigations are from six wells with two from Wilson 1. The two samples from this well give different minimum homogenization temperatures. In this case, the minimum homogenization temperature from the same well is used as the best estimate of the true geologic trapping temperature for

| Table 1 Stable isotope data for authiger | iic carbonates |
|--|----------------|
|--|----------------|

| Sample No. | Mineral     | $\delta^{18}$ O (‰ <sub>SMOW</sub> ) | $\delta^{13}$ C (‰ <sub>PDB</sub> ) |  |
|------------|-------------|--------------------------------------|-------------------------------------|--|
| BAN575.2   | ankerite    | 10.2                                 | -3.2                                |  |
|            | duplicate   | 10.0                                 | -3.2                                |  |
|            | calcite     | 10.1                                 | -3.5                                |  |
| BEE217.9   | dawsonite   | 16.1                                 | 0.6                                 |  |
| BEE223.1   | dawsonite   | 16.4                                 | 0.6                                 |  |
| BLA432.5   | ankerite    | 11.6                                 | -11.7                               |  |
| BLA460.0   | ankerite    | 10.4                                 | -10.8                               |  |
| BLA476.1   | dawsonite   | 14.1                                 | -1.4                                |  |
| BRW510.1   | calcitecite | 5.1                                  | -5                                  |  |
| COL390.8   | dawsonite   | 17.7                                 | 0.8                                 |  |
| COL400.7   | dawsonite   | 16.6                                 | -0.1                                |  |
|            | duplicate   | 16.7                                 | 0.11                                |  |
| DEN160.0   | dawsonite   | 15.2                                 | -0.2                                |  |
|            | duplicate   | 14.8                                 | -0.3                                |  |
| GOR539.3   | siderite    | 16.1                                 | -3.3                                |  |
| MOR330.1   | siderite    | 8.1                                  | -1.9                                |  |
|            | duplicate   | 8.3                                  | -1.9                                |  |
| MOR332.1   | siderite    | 12.7                                 | -1.5                                |  |
| NAR557.4   | dawsonite   | 18.6                                 | 0.2                                 |  |
| PAR442.6   | dawsonite   | 15.4                                 | 2.5                                 |  |
|            | duplicate   | 15.3                                 | 2.5                                 |  |
| PAR445.2   | dawsonite   | 15.4                                 | 2.2                                 |  |
| PUR314.5   | siderite    | 14.8                                 | -0.6                                |  |
| TUR318.1   | ankerite    | 15.8                                 | -2.6                                |  |
|            | dawsonite   | 14.4                                 | 2.4                                 |  |
| TUR322.3   | ankerite    | 14.2                                 | -2.9                                |  |
|            | dawsonite   | 14.1                                 | 2.3                                 |  |
|            | duplicate   | 14.3                                 | 2.3                                 |  |
| WIL587.2   | ankerite    | 9.8                                  | -1.9                                |  |
|            | calcite     | 6.5                                  | -8.7                                |  |
|            | duplicate   | 6.5                                  | -8.7                                |  |
|            | siderite    | 9.4                                  | -8.5                                |  |
|            | duplicate   | 9.2                                  | -8.5                                |  |
| WIL590.9   | ankerite    | 9.7                                  | -3.3                                |  |
|            | calcite     | 10.4                                 | 0.0                                 |  |
|            | siderite    | 9.5                                  | -7.4                                |  |

Note: Sample No. is named with the well name abbreviation and the drilling depth (in meters) from which the sample was collected. Sample BAN575.2 means that it was collected from the drilling depth of 575.2 m in Bando 1 well.

inclusions at the particular well location. In the sample from Brigalow 1 (BRI379.6), only one homogenization temperature was obtained and higher than 130°C, which is assumed not to be the minimum temperature. Samples from these wells (except Brigalow 1) have minimum homogenization temperatures ranging from 72°C to 86.5 °C. Thus, the trapping temperatures of fluid inclusions in quartz overgrowths lie between 72°C to 86.5°C, which are taken as the estimated crystallization temperatures of quartz overgrowths in these sandstones.

### **6** Stable Isotope Investigations

The diagenetic cements subjected to isotope determinations include carbonates, clay minerals and quartz overgrowths. Carbonates from 21 samples, clays from 14 samples and pure quartz separates from 5 samples were isotopically analyzed.

#### **6.1 Carbonates**

A total of 29 carbonates, which consist of 7 ankerites, 5 calcites, 11 dawsonites, and 6 siderites, were subjected to isotopic measurements. Duplicate analyses produced very good repeats. The results are presented in Table 1.

Ankerite: Seven pore filling ankerite samples yielded a wide range of  $\delta^{18}$ O values of 9.7% to 15.8% and an even wider range of  $\delta^{13}$ C values of -11.7% to -1.9% with samples from the same well having similar  $\delta^{18}$ O and  $\delta^{13}$ C values (Table 1). The  $\delta^{18}$ O values cluster into two distinct groups: 9.7% to 11.6% (five samples) and 14.2% to 15.8% (two samples).

Calcite: Five pore filling calcite samples (two early calcites and three late calcites) recorded  $\delta^{18}$ O values of 5.1‰ to 10.4‰ and  $\delta^{13}$ C values of -8.7‰ to 0‰. The  $\delta^{18}$ O values cluster into two groups: 5.1‰ to 6.9‰ (two early calcites and one late calcite) and 10.1‰ to 10.4‰ (two late calcites). In contrast to ankerites, calcites from the same well have quite different  $\delta^{18}$ O and  $\delta^{13}$ C values. The two samples from Wilton 1 well yielded  $\delta^{18}$ O values of 6.5‰ and 10.4‰ and  $\delta^{13}$ C values of -8.7‰ and 0‰ respectively (Table 1).

Dawsonite: Eleven dawsonite samples yielded quite similar  $\delta^{13}$ C values ranging from -0.3% to 2.5‰. Their  $\delta^{18}$ O values fall in the range of 14.2‰ to 18.6‰. Dawsonites from the same well except those from Coogal 1 have very similar  $\delta^{18}$ O values (within 0.5‰).

Siderite: Six siderite samples recorded a wide range of  $\delta^{18}$ O values of 8.2‰ to 16.1‰ which cluster into two distinct groups: 8.2‰ to 9.5‰ (three samples) and 12.7‰ to 16.1‰ (three samples). Their  $\delta^{13}$ C values vary from -8.5‰ to -0.6‰.

#### 6.2 Clays

A total of 33 clay samples (12 kaolins and 21 illites) were subjected to oxygen isotope analyses. The analytical results are presented in Table 2. Twelve pure kaolin samples yielded  $\delta^{18}$ O values of 8.1% to 11.7% with different size fractions from the same sample having similar  $\delta^{18}$ O values. Twenty one pure illite samples were analyzed for oxygen isotope. The  $\delta^{18}$ O values fall in a very narrow range from 5.6% to 8.7%. Different size fractions from the same sandstone generally have quite similar  $\delta^{18}$ O values.

#### 6.3 Quartz

The  $\delta^{18}$ O values of the various size fractions are presented in Table 3. Reproducibility is generally good, particularly for finer size fractions. For three of the five samples (BRW379.6, PAR442.6 and WIL587.2), a significant difference (> 1‰) exists between coarse and fine fractions. For these samples, it can be assumed that

| Sample No. | Size fraction | Mineral | <sup>18</sup> O‰* |  |
|------------|---------------|---------|-------------------|--|
| -          | (µm)          |         | (SMOW)            |  |
| BAN575.2   | <0.5          | illite  | 8.5, 8.5          |  |
| BEE216.7   | <0.5          | illite  | 6.6, 6.6          |  |
|            | 0.5-1         | illite  | 6.4               |  |
|            | 1–2           | illite  | 6.7               |  |
| BEN206.5   | <0.5          | illite  | 7.0               |  |
|            | 0.5-1         | illite  | 7.5, 7.2          |  |
| BLA432.5   | <2            | kaolin  | 11.7              |  |
|            | 5-10          | kaolin  | 11.5, 11.1        |  |
| BLA460.0   | <0.5          | kaolin  | 10.4              |  |
|            | 0.5-1         | kaolin  | 9.9               |  |
|            | 1–2           | kaolin  | 10.3              |  |
| BRI379.6   | <0.5          | illite  | 5.7, 5.6          |  |
|            | 0.5-1         | illite  | 5.7, 5.5          |  |
|            | 1–2           | illite  | 5.9, 5.7          |  |
| BRW514.7   | <0.5          | illite  | 5.8               |  |
|            | 0.5-1         | illite  | 6.2               |  |
| DEW565.7   | <0.5          | illite  | 6.1               |  |
|            | 0.5-1         | illite  | 6.1               |  |
| GOR539.3   | 0.5-1         | kaolin  | 8.1               |  |
|            | 1–2           | kaolin  | 8.5               |  |
|            | 2-5           | kaolin  | 9.1, 9.5          |  |
| MOR330.1   | <0.5          | illite  | 6.3               |  |
|            | 2-5           | kaolin  | 8.2, 7.9          |  |
| PUR314.5   | <0.5          | illite  | 7.9, 7.6          |  |
|            | 0.5-1         | illite  | 6.8, 7.1          |  |
| TUL140.7   | <0.5          | kaolin  | 9.1, 9.6          |  |
|            | 0.5-1         | kaolin  | 9.6, 9.2          |  |
|            | 1–2           | kaolin  | 10.4              |  |
| WIL547.7   | <0.5          | illite  | 8.1               |  |
|            | 0.5-1         | illite  | 8.0, 7.7          |  |
| WIL587.2   | <0.5          | illite  | 8.2               |  |
|            | 0.5-1         | illite  | 8.7               |  |
|            | 1–2           | illite  | 8.3, 7.9          |  |

Table 2 Stable isotope data for clay minerals

Table 3 Oxygen isotope data for different size quartz separates

| Sample No. | <sup>18</sup> O‰ (SMOW) for different size fractions ( $\mu$ m) |         |        |       |       |      |
|------------|---|---------|--------|-------|-------|------|
|            | >180  | 180-125 | 125-75 | 75-53 | 53-20 | <20  |
| BRI379.6   | 11.7  | 11.6    | 12.3   | 12.1  | 12.1  | 11.6 |
|            | 12.2  |         |        |       | 11.2  | 11.6 |
| BRW514.7   | 11  | 9.8     | 10.1   | 10.3  | 11.2  | 13.6 |
|            |   | 10.1    | 9.7    | 9.8   | 11.1  |      |
| PAR2.6     | 12.4  | 12.5    | 12.1   | 11.7  | 13.5  | 14.0 |
|            | 12.4  |         |        |       | 13.7  |      |
| TUL140.7   | 12.5  | 12.8    | 12.8   |       | 11.7  | 11.9 |
|            | 12.7  |         |        |       |       |      |
| WIL587.2   | 11.7  | 12.1    | 12.2   | 12.8  | 13.1  | 13.3 |
|            | 11.3  |         |        |       |       |      |
|            |   |         |        |       |       |      |



\* Note: Some samples have a second duplicate for measurement so that two values are obtained.

quartz overgrowths increase with the decrease in fraction size (cf. Lee and Savin, 1985). The  $\delta^{18}$ O values of quartz overgrowths are estimated to be between 13‰ and 15‰. For the other two samples, there is no difference in  $\delta^{18}$ O values between coarse and fine size fractions. Thus, it is assumed that the H<sub>2</sub>SiF<sub>6</sub>-sonic treatment has not worked for efficient separation of overgrowths from detrital quartz because detrital core material has also contributed to finer size fractions (cf. Brint et al., 1990).

#### **7** Pore Water Evolutions

Petrographic, fluid inclusion and stable isotope data can be combined to deduce changes in the oxygen isotope composition of formations waters, as demonstrated by Ferket et al. (2003). A similar approach is used here to investigate the isotopic changes during the diagenesis of sediments of the Black Jack Formation. These changes can be related to the burial history of the basin.

As emphasized by Longstaffe (1986), it is essential to evaluate the possibility of recrystallization of the minerals in the evolving pore waters before attempting to deduce Fig. 5. Evolution of pore water  $\delta^{18}$ O composition with temperature for Black Jack Formation samples.

Temperature estimates are derived from the fractionation of oxygen isotope between pore water and a precipitating oxygen-bearing mineral according to equations given in Friedman and O'Neil (1977) for calcite and quartz, Dutton and Land (1985) for ankerite, Carathers et al. (1988) for siderite, and Savin and Lee (1988) for illite. The fractionation of oxygen isotope for calcite is used for dawsonite. The curved lines are fractionation curves that describe the relationship between temperature and parental pore water  $\delta^{18}$ O for specific mineral  $\delta^{18}$ O compositions.

the oxygen isotope composition of pore waters. If recrystallization occurred after the mineral precipitation from pore waters, the measured isotope signature would be indicative of late waters involved in the recrystallization rather than the early waters involved originally in forming the mineral.

Siderite and ankerite are relatively early diagenetic minerals present in the Black Jack Formation. Dissolution of them has created secondary porosity. No evidence was found to indicate simple dissolution and reprecipitation of siderite and ankerite. Thus, siderite and ankerite preserved probably have not undergone any recrystallization. Their measured  $\delta^{18}$ O values can be used to indicate isotopic compositions of pore waters originally involved in their precipitation.

Pore water compositions of early diagenesis can be approximated by the isotopic signature of early diagenetic Vol. 81 No. 3

siderite. Siderite commonly forms in the methanic zone during early diagenesis. If it formed at temperatures of 20-40°C, the  $\delta^{18}$ O values of pore waters in equilibrium with siderites of  $\delta^{18}$ O values of 14.8‰–16.1‰ (samples PUR314.5 and GOR539.3) and  $\delta^{18}$ O values of 8.2% – 9.5‰ (Samples MOR330.1 and WIL590.9) would have been -18‰ to -12.5‰ (Fig. 5) and -24.5‰ to -19‰ respectively. Given that Early Permian meteoric waters in the area had  $\delta^{18}$ O value of -17% (Bird and Chivas, 1988) and Early Triassic meteoric waters in the adjacent Sydney Basin area had  $\delta^{18}$ O value of about -15% (Bai et al., 2001), the pore water  $\delta^{18}$ O values of -18% to -12.5%imply that early diagenetic pore waters are largely of Late Permian meteoric waters with some contribution of Permian marine waters, which had  $\delta^{18}$ O value of -2% to 0‰ (Bird and Chivas, 1988). Considering that the two samples with measured siderite  $\delta^{18}$ O values of 14.6% to 16.1‰ were selected from the lower quartz rich sandstone unit which overlies and interfingers with the marine Arkarula Sandstone Member, it is not unexpected that early pore waters in the unit had some contribution of Late Permian marine water.

The  $\delta^{18}$ O values of -24.5‰ to -19‰ of pore waters involved in precipitation of siderites with  $\delta^{18}$ O values of 8.2‰–9.5‰ are much lower than the calculated  $\delta^{18}$ O value of -17‰ for Early Permian meteoric water and thus untenable. One alternative explanation is that these siderites formed in higher temperature but should not be higher than the precipitation temperatures of quartz overgrowths (72-86.5° C) as they predated quartz overgrowths. If it is assumed that they were precipitated in temperatures of 50°C to 60°C, the pore waters involved would have  $\delta^{18}$ O values of -18% to -15%. Such low  $\delta^{18}$ O values indicate pore waters are probably representative of meteoric waters at the time of the deposition of the Late Permian Black Jack Formation, which is consistent with the depositional environment of the formation.

Like siderite, ankerite also has a wide range of  $\delta^{18}$ O values of 9.7‰–15.8‰. A similar approach as used in discussing siderite is applied here. If they formed at temperatures of 30°C to 50°C, pore waters in equilibrium with ankerites with  $\delta^{18}$ O values of 14.2‰ to 15.8‰ would have  $\delta^{18}$ O values of -16.5% to -11% (Fig. 5), indicating that pore waters were mixed waters and very similar to those involved in forming earlier siderites. At the same temperature range, the  $\delta^{18}$ O values of 9.7‰–11.6‰ were -21% to -15.5%. Given that Early Permian meteoric waters had  $\delta^{18}$ O value of -17% (Bird and Chivas, 1988) and earlier siderites crystallized in pore waters are same temperature to -12.5%, the calculated  $\delta^{18}$ O values are

probably too low. Thus, the ankerites with lower  $\delta^{18}$ O values are very likely to have formed at higher temperatures. If they formed at temperatures of 50°C to 60°C, the involved pore waters would have  $\delta^{18}$ O values of -17% to -14%, which are slightly higher than the  $\delta^{18}$ O values of -18% to -15% for pore waters involved in precipitation of siderites with lower  $\delta^{18}$ O values (Fig. 5).

Very early calcite in sample BRW510.1 has a  $\delta^{18}$ O value of 5.1‰. There are two explanations for the measured low  $\delta^{18}$ O value of the early calcite: 1) calcite formed very early at temperatures of 20°C to 40°C from pore waters with  $\delta^{18}$ O values of -20% to -24% and retained its original isotopic signature; or 2) the present calcite is the product of recrystallization and reflects isotopic composition of pore waters at the time of recrystallization. Given that the pore waters had  $\delta^{18}$ O values of -18‰ to -12.5‰ during the precipitation of early siderite (Fig. 5), the pore water isotopic composition indicated by first explanation is considered to be unlikely. The second exploration is preferred. Although it is of early diagenetic origin, therefore, the calcite probably precipitated from late diagenetic pore waters at higher temperatures and cannot be used to infer the isotopic compositions of early pore waters.

During the precipitation of siderite and ankerite, the fluid flow regime is a very much open system (Fig. 5). Pore waters were replenished frequently by Late Permian meteoric waters with  $\delta^{18}$ O values of -17% to -15%. The  $\delta^{18}$ O value of pore waters did not change much with the temperature increase from 20°C to ~60°C. The overall similarity of  $\delta^{13}$ C values for carbonate precipitation is compatible with carbon sourcing from atmospheric CO<sub>2</sub> dissolved in the flowing meteoric water system.

Using the same approach, pore water composition during later diagenesis was inferred from measured isotope signatures of late diagenetic minerals and an idealized pore water evolution path is shown in Fig. 5. With the precipitation temperature of 72°C to 86.5°C and the measured  $\delta^{18}$ O values of 13‰–15‰, the  $\delta^{18}$ O values of the pore waters from which quartz overgrowths crystallized are calculated to be -12.5% to -8.5% (Fig. 5). Considering that the maximum burial temperature was ~ 80°C to 90°C for the Black Jack Formation, the precipitation temperature for the post-quartz overgrowth calcite should not be higher than 90°C. At temperatures of 80°C to 90°C, the pore waters in equilibrium with the late calcites with  $\delta^{18}$ O values of 6.5% to 10.4% would have  $\delta^{18}$ O values of -13% to -8%. If it is assumed that illite formed at a similar temperature range of calcite, the pore waters involved in precipitating illite with  $\delta^{18}$ O values of 5.6‰–8.7‰ would have  $\delta^{18}$ O values of -9.5‰ to -5.5‰ (Fig. 5).

During the precipitation of quartz overgrowths to postquartz overgrowth calcites, the  $\delta^{18}$ O value of pore waters increased to -12.5% with the temperature increasing from 50–60°C to 80–90°C (Fig. 5). The enrichment of <sup>18</sup>O of oxygen isotopes for the pore waters is considered to have resulted from water-rock interactions during progressive burial. Dissolution of <sup>18</sup>O enriched detrital minerals such as feldspar and mica can lead to the increase of the pore water  $\delta^{18}$ O value.

From quartz overgrowth to illite, the  $\delta^{18}$ O value of pore waters had a significant jump (~4‰) without temperature increase (Fig. 5). In addition to the water-rock reactions, this jump is probably largely due to invasion of <sup>18</sup>O enriched pore waters from the underlying marine sequence of the Watermark Formation into the Black Jack Formation during the formation of illite. Thus, these diagenetic minerals are considered to have precipitated in a semi-closed to closed fluid flow system.

The loci of kaolin curves do not overlap with those of quartz curves (Fig. 5), indicating that kaolins with  $\delta^{18}$ O values of 8.1‰-11.7‰ were not co-precipitated with quartz as indicated by the intergrowths of kaolins and quartz overgrowths. Thus, these kaolins are considered to be of generation II. Depending upon the precipitation temperature, the involved pore waters have variable  $\delta^{18}$ O values. If kaolin formed at the maximum burial at the temperatures of 80°C to 90°C, the  $\delta^{18}$ O of pore waters would be -9% to -4.5% and the loci of kaolin curves overlap with those of illite curves, which implies that they crystallized simultaneously from pore waters. Considering that kaolin and illite form under different conditions (Garrel and Christ, 1965), it is unlikely that kaolin and illite could co-precipitate from pore waters. Thus, kaolin formed at either a lower or higher temperature than illite. Given that the maximum burial temperature of the Black Jack Formation is not higher than 90°C, kaolin is very likely to have formed at a lower temperature, indicating that the basin was uplifted after illite precipitation. In the Denison Trough of the adjacent Bowen Basin, a late kaolin was reported to have formed at temperatures of the order of 40°C to 70°C. If this temperature range is assigned for the precipitation temperature, the  $\delta^{18}$ O of pore waters must have been in the range of -14.5% to -6.5%. From illite to kaolin, the  $\delta^{18}$ O value of pore waters decreased (Fig. 5), suggesting that the basin uplifting exposed the Black Jack Formation and led to infiltration of <sup>18</sup>O depleted meteoric water from the surface. Kaolin formed as a result of meteoric water infiltration is widely reported in the literatures.

The precipitation of the last diagenetic mineral dawsonite is of Tertiary event. In a review of dawsonite occurrences worldwide and with particular emphasis on the frequent occurrence in the Sydney-Gunnedah-Bowan Basin system of eastern Australia, Baker et al. (1995) suggested that its formation is genetically linked with hydrothermal/igneous activities, which provided the excessive CO<sub>2</sub> required for its formation. It seems that magma-derived CO<sub>2</sub> occurs widely in the world. More recently, magma-originated CO<sub>2</sub> is reported to be present and has contributed to the formation of gas accumulations in the Songliao Basin (Wang et al., 2007). Thus, we propose that the formation of dawsonite is closely associated with deep-seated magmatic sourced CO<sub>2</sub>. Its formation temperatures were similar to present day formation temperatures of ~30°C to 40°C. At these temperatures, the  $\delta^{18}$ O value of pore waters precipitating dawsonite with  $\delta^{18}$ O values of 14.2‰–18.6‰ must have been in the range of -13% to -7% (Fig. 5), which is largely consistent with the reported  $\delta^{18}$ O value of presentday mine waters of -7‰ for the Sydney Basin and around -10‰ for the Bowen Basin.

During the precipitation of generation II kaolin and dawsonite, the pore water evolution path was reversed to lower temperatures and lower  $\delta^{18}$ O compositions, which is the effects of meteoric water invasion subsequent to the 100 Ma uplifting event. This is consistent with the existence of current freshwater aquifers in parts of the Gunnedah Basin.

### **8** Conclusions

(1) Diagenesis of sandstones in the Upper Permian Black Jack Formation began with the precipitation of mixed-layer illite/smectite, siderite, calcite, ankerite and kaolin. The following diagenetic events include the cementation by quartz overgrowths, late calcite, illite and late kaolinite (generation II). Dawsonite is the last diagenetic mineral.

(2) The early precipitation of mixed-layer illite/ smectite, siderite, calcite, ankerite and kaolin took place at the presence of Late Permian connate meteoric waters at temperatures of up to 60°C in an open flow regime where meteoric waters were periodically replenished.

(3) Quartz overgrowths were formed at temperatures of 72°C to 86.5°C. They, together with the following illite and late calcite, proceeded at temperatures of 72°C to 90° C in a semi-closed to closed fluid flow system where the interaction between the <sup>18</sup>O rich detrital minerals and pore waters led to a significant increase (~4‰) of the  $\delta^{18}$ O value for the pore waters.

(4) The basin uplifting at 100 Ma exposed the Black Jack Formation and led to infiltration of <sup>18</sup>O depleted meteoric water from the surface. Late kaolin (generation II) and the last diagenetic mineral of dawsonite formed at

temperatures of  $\sim 30^{\circ}$ C to  $70^{\circ}$ C in an open fluid flow system. The formation of dawsonite is genetically related to deep-seated magmatic sourced CO<sub>2</sub>.

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