# Mechanisms for Coalbed Methane Formation

by

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## ABSTRACT

Isotopic measurements ($^{13}C/^{12}C$ and D/H ratios) on coal seam gases from the Sydney and Bowen Basins indicate the microbial reduction of carbon dioxide, rather than direct thermogenic reactions, to be mainly responsible for seam gas composition.

## INTRODUCTION

Methane and carbon dioxide are the principle gases observed to be generated in the thermal transformation of plant residues to bituminous coal. Changes in the elemental composition (C, H & O) of coaly organic material with increasing thermal maturation can be readily described in terms of the loss of $CO_2$ and/or $CH_4$ from the parent material. This has resulted in proposals for relatively, simple thermogenic models for the gas generating characteristics of coals (Mott, 1943; Hargraves, 1963).

In general all such models e.g. Figure 1, show remarkable similarity with carbon dioxide, the major product of the maturation of brown coals, being relegated to a minor component by the increased generation of methane at the bituminous stage of coal maturation.

However, such simple thermogenic mechanisms for gas generation from Australian coals have become increasingly untenable with the increasing availability of isotopic data on the composition of coals and seam gases. (Smith and Gould, 1980; Smith et al., 1982, 1985). In addition more recent evidence of other alternative microbial pathways for gas generation, and of isotopic fractionations accompanying these, (Claypool and Kaplan, 1974; Schoell, 1980,;Whiticar et al., 1986; Jenden and Kaplan, 1986) have promoted interest in the possibility of a microbial input in seam gas generation (Smith, 1992).

## PREVIOUS OBSERVATIONS

The Australian gases previously studied were largely collected directly at the coal face and thus no doubt with regard to origin exists. However, difficulty was experienced in reconciling the $^{13}C$ contents of these gases with those of coal seam gases described elsewhere (Stahl, 1976). Furthermore, in schemes for the classification of natural and coal seam gases on the basis of their D and $^{13}C$ contents (Schoell, 1980) Australian coal seam gases did not fall within the delineated zone.

Although often a prominent diagnostic feature of Australian coal seam gases no mention had been made elsewhere of the concentration and often excessively high $^{13}C$ content carbon dioxide in similarly derived gases. On this evidence it was suggested that the unexpected relative depletion of *13*C in Australian coal seam methanes and the co-occurrence of $^{13}C$- enriched carbon dioxide might provide a clue not only to the origins of these gases but also to their divergence in isotopic composition from coal seam gases from elsewhere. Accordingly the co-generation of carbon dioxide and methane in isotopic equilibrium was proposed as the mechanism of gas formation (Smith et al., 1982) although no pathway for equilibration of these gases at moderate temperatures is known.

## EXPERIMENTAL

### Sample Collection

Gas and coal samples were either collected underground by CSIRO personnel or were largely supplied by coal mining companies often as part of a survey of seam gas composition in relation to outbursting behaviour (Smith et al., 1984). 307 samples of gas, and in many cases of coal, were collected from 13 collieries and 17 exploratory bore holes into Permian coal seams in the Sydney and Bowen Basins.

### Chemical and Isotopic Analyses

The chemical composition of all gases was determined on a Hewlett Packard 5830A gas chromotograph, or, more recently on a SRI 8610 natural gas analyser.

In isotopic studies, methane, ethane and carbon dioxide were originally separated by cryogenic distillation at -196°C (Sakai et al., 1976) and preparative chromatography on Porapak 1 columns prior to combustion on copper oxide at 850°C. Product carbon dioxide and water from the combustion of each component were collected. This method has been updated to that of Jenden and Kaplan (1989). Gases generated in laboratory pyrolysis experiments were analysed by the later methods.

After acid-washing to remove carbonate, coals were combusted in oxygen at 1000°C (Kaplan et al., 1970). Product carbon dioxide and water were collected.

All collected water samples were reduced to hydrogen over depleted uranium ($^{238}$U) metal at 800°C for subsequent D/H ratio analysis.

The results of chemical and isotopic analyses are shown in Table 1.

### Mass Spectrometry

The prepared samples were analysed on a Vacuum Generator 602D isotopic ratio mass spectrometer. The data is reported in the usual delta per mille notation ($\delta^o/oo$) as the difference in parts per thousand between the isotope ratio, R, of the sample and that of a standard (Peedee Belemnite, PBD, for carbon and standard mean ocean water, SMOW for hydrogen).

$$\delta^o/oo(\frac{R_{sample}}{R_{standard}} - 1) \times 1000$$

where R = $^{13}C/^{12}C$ for carbon

where R = D/H for hydrogen

The precision for these measurements is < 0.2°/oo This value includes the error contributions from sample preparation and mass spectrometric analysis.

### Pyrolysis Experiments

Reactors (10ml) were filled with acid-washed Blair Athol coal -1mm (6g) and, after closing, heated at 250, 350 and 400°C for 3 days. After cooling, gas pressures were measured and the gas volumes calculated. These volumes are shown in Table 2 together with the chemical and isotopic analyses of the gases.

### RESULTS

The number of samples analysed, the ranges of values recorded and, where appropriate average values are listed in Table 1. In most of the 307 gases analysed higher n-alkane contents were negligible. However in 35 of the samples this content equalled or exceeded 0.1% by volume and in 21 of these, higher alkane contents exceeded 0.3% and maximised at 10.1%. Intersection by bores of prospective pockets in the Bulgo sandstone above the Bulli seams is held to be largely a source of these gases with the high ethane contents (Hargraves. Pers. Comm.). Otherwise the Blake Seam, Collinsville, is the main source of such gases.

$\delta^{13}C_{CO2}$ and $\delta^{13}C_{CH4}$ values for all gases are shown in Figure 2. Where measured, $\delta^{13}C$ and $\delta D$ values for both gases and coals are shown in Figure 3. Variations of isotopic composition with the concentration of carbon dioxide are illustrated in Figure 4.

### DISCUSSION

The large isotopic fractionation between $CO_2$ and $CH_4$, $\Delta^{13}C(CO_2-CH_4)$, commonly a feature of coal seam gases is clearly illustrated in Figure 2. Included in this Figure are lines representing calculated isotopic fractionations of 1.080, 1.060 and 1.040 corresponding to $\Delta^{13}C (CO_2-CH_4)$ values of 80, 60 and 40 °/oo PDB respectively. Another feature of this Figure is the clustering of the "wetter" gases in the region of lower isotopic fractionation.

The coals collected and analysed in this work have, as shown in Table 1 and Figure 3, a d13C value of -22.9± 1.0°/oo PDB which is in good general agreement with the published data on Australian coals -24.4± 1.4°/oo PDB Smith et al. 1982). There is no evidence of major carbon isotopic variability within or

between coals and thus the large isotopic fractionations between gaseous products, $\Delta^{13}C(CO_2\text{-}CH_4)$, and between these components and the parent coal are remarkable. This remarkability is further demonstrated by the isotopic analyses of the products from the pyrolysis of the Blair Athol coal (Table 2). From this Table it is evident that the $\delta^{13}CCO_2$ value approximates that of bituminous coals. In addition, the depletion of some -15°/oo PDB in $\delta^{13}C$ $CH_4$ values, relative to the coal, is commensurate with the greater ease of breakage of $^{12}C\text{-}^{12}C$ bonds, relative to $^{13}C\text{-}^{12}C$ bonds, and the generation of product methane depleted in $^{13}C$ relative to accompanying higher n-alkanes (Silverman, 1967; James, 1983) and the parent coal. Therefore, $\Delta^{13}C$ $(CO_2\text{-}CH_4)$ values are likely to be minimised in pyrolysis products as confirmed by the $\Delta^{13}C$ values of $16\pm 1$°/oo shown in Table 2. Another feature of theses pyroysis products are the high concentrations of gaseous higher n-alkanes associated with the methane. As hown in Figure 2, coal seam gases having lower $\Delta^1 3C$ $(CO_2- CH_4)$ values (Fractionatin factor < 1.040) also tend to be 'wet'. Thus, by analogy with the gases resulting from laboratory pyrolysis experiements, which exhibit these same properties, the assumption is made that such seam gases result from thermal processes.

Also shown in Figure 2 are data for gases derived by the microbial reduction of carbon dioxide or by acetate fermentation according to equation 1 and 2 respectively.

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$$

$$CH_3COOH \rightarrow CH_4 + CO_2$$
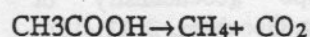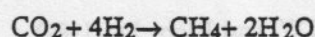
From the analysis of gases from marine sediments Jenden and Kaplan (1986), as shown in Figure 2 ascribe $\Delta 1^3C$ $(CO_2\text{-}Ch_4)$ values of 70 $\pm$ 10°\oo and of 50 $\pm$ 10°\oo to gases generated by carbone dioxide reduction and acetate fermentation respectively. Other areas outlined define the composition of gases investigated by Whiticar *et al.*, (1986) from both marine and frehwater sediments and the microbial pathways ytilised in their generation. The similarity in carbon isotope composition of the dry "dry" seam gases and

these microbially derived products iws well established by this comparison.

Other samples with carbon isotopic fractionations of less than 1.040 are largely from Wedderburn boreholes or the Collinsville region (Smith et al. 1984). Invasions of these areas by carbon dioxide of presumed deep-seated origin with a $\delta^{13}C$ value of -10± 5°/oo PDB is largely responsible for reducing fractionations below 1.040. Carbon dioxide concentrations in such gases commonly exceed 90% (Fig. 4) and thus residual coal-sourced gas has a greatly diminished diagnostic value.

The total data on the D contents of the coals and methane samples are given in Table 2 and Fig. 3. Calculated average $\delta^D$coal and $\delta^D CH_4$ values are -132±14°/oo and SMOW -217±17°/ooSMOW respectively.

When gases are microbially derived, as is suggested by the carbon isotopic composition of the dry coal seam gases, the product $\delta^D CH_4$ value reflects that of the formation water (Schoell 1980, Whiticar et al. 1986, Woltemate et al. 1986). In carbon dioxide reduction, as in equation (1), all the hydrogen in the methane is derived from the formation water and

$$\delta^D CH_4 = \delta^D water - 180°/ooSMOW \qquad 3$$

However, where methane is a product of acetate fermentation, as in equation (2), only one hydrogen in the methane is obtained from the formation water and

$$\delta^D CH_4 = 0.25\delta^D water - 321°/ooSMOW \qquad 4$$

Palaeolatitude studies of the environments of coal deposition (Smith etal. 1983, 1985) indicate

$$\delta^D coal = \delta^D water - 85°/ooSMOW \qquad 5$$

Then by substituting -132°/oo SMOW for $\delta$D coal in equation 5 the $\delta$D of the formation water is seen to be - 47°/oo SMOW. The substitution of this value in equations 3 and 4 gives $\delta^D CH_4$ values of -227°/oo and - 333°/oo respectively. A comparison of these calculated values with the measured value of $\delta^D CH4$ from Table 2 and Fig. 5 is -

217±17°/oo strongly indicates carbon dioxide reduction to be a major factor in the generation of coal seam methane.

A mixed origin for some Australian coal seam methane has previously been suggested on the basis of an over-large difference recorded in $\Delta^{13}C$ ($C_2H_6$-$CH_4$) °/oo values (Smith et al. 1985). The evidence presented here for an alternative microbial pathway for the generation of methane provides an excellent explanation for these earlier findings.

Although microbial activity at temperatures approaching 100°C now enjoys wide acceptance, the precise stage of coal maturity at which microbial reduction of carbon dioxide might occur has to be determined. Furthermore, if and when the reaction occurs what is its chemical role in the coal maturation process? More importantly does the method of methane generation affect its modes of emplacement, retention and release?

## CONCLUSIONS

Isotopic evidence suggests that in the Sydney and Bowen Basins microbial processes play a major role in determining coal seam gas composition.

Primary products from the thermal decomposition of coal are probably present as a minor component in all seam gases sampled. When dominant these thermogenic gases are readily distinguished by their chemical and isotopic compositions.

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| | Air-free basis % | $\delta^{13}C°/°°$ PDB | $\delta D°/°°$ SMOW |
|---|---|---|---|
| $CO_2$ Range | 0.0 to 99.7 | -15.5 to +16.7 | - |
| No. of samples | 307 | 305 | - |
| | | | |
| $CH_4$ Range | 0.3 to 100.0 | -18.0 to -78.9 | -152 to -255 |
| No. of samples | 307 | 307 | 88 |
| Mean | - | - | -217 ± 17 |
| | | | |
| Coal Range | | -21.6 to -26.6 | -93 to -162 |
| No. of samples | - | 45 | 44 |
| Mean | | -22.9 ± 1.0 | -132 ± 14 |

*Table 1.* Chemical and Isotopic Compsotion of Coals and Coal Seam Gases.

| Reaction Temp °C/3 days | 250 | 350 | 400 |
|---|---|---|---|
| Gas generated ml/grm | 5 | 12 | 30 |
| Air + $N_2$ content % | 10.5 | 5.8 | 1.6 |
| $CH_4$ % Air free | 1.7 | 19.5 | 45.6 |
| $C_2H_6$ % " " | 0.7 | 5.5 | 5.1 |
| $C_3H_8$ % " " | 0.3 | 1.0 | 1.3 |
| $iC_4H_{10}$ % " " | - | 0.1 | 0.3 |
| $C_4H_{10}$ % " " | - | 0.1 | 0.6 |
| $C_5H_{12}$ % " " | - | - | 0.3 |
| $CO_2$ % " " | 97.3 | 73.8 | 45.5 |
| | | | |
| $\delta^{13}C_{CH4}$ °/°° PDB | -34.4 | -38.8 | -37.0 |
| $\delta^{13}C_{CO2}$ °/°° PDB | -19.3 | -21.9 | -21.6 |
| $\Delta^{13}C(CO_2-CH_4)$ °/°° PDB | +15.1 | +16.9 | +15.4 |

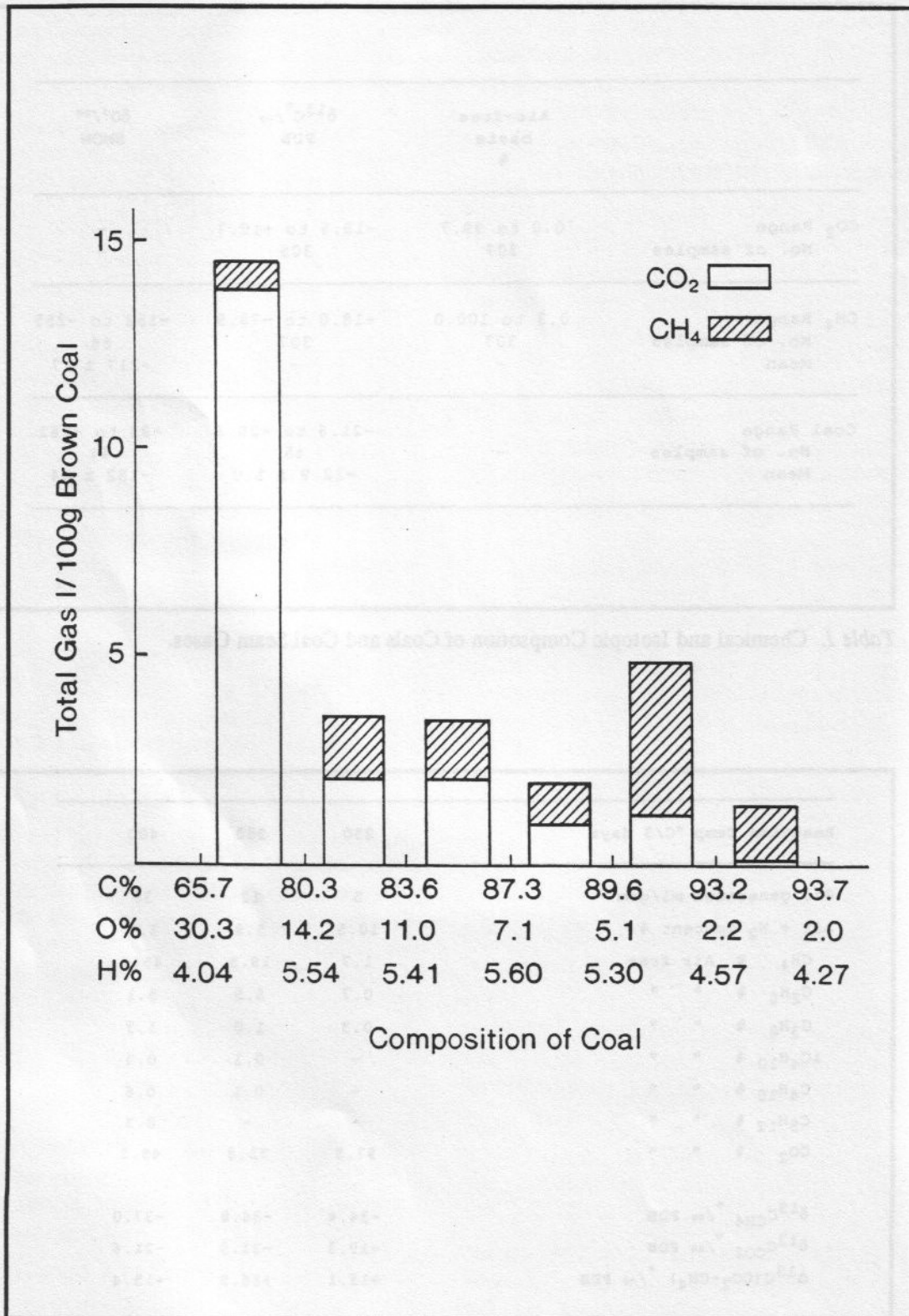*Table 2.* Yield and Composition of Coal Pyrolysis Products

*Figure 1* Calculated maximum volumes of gas generated during progressive maturation of brown coal.
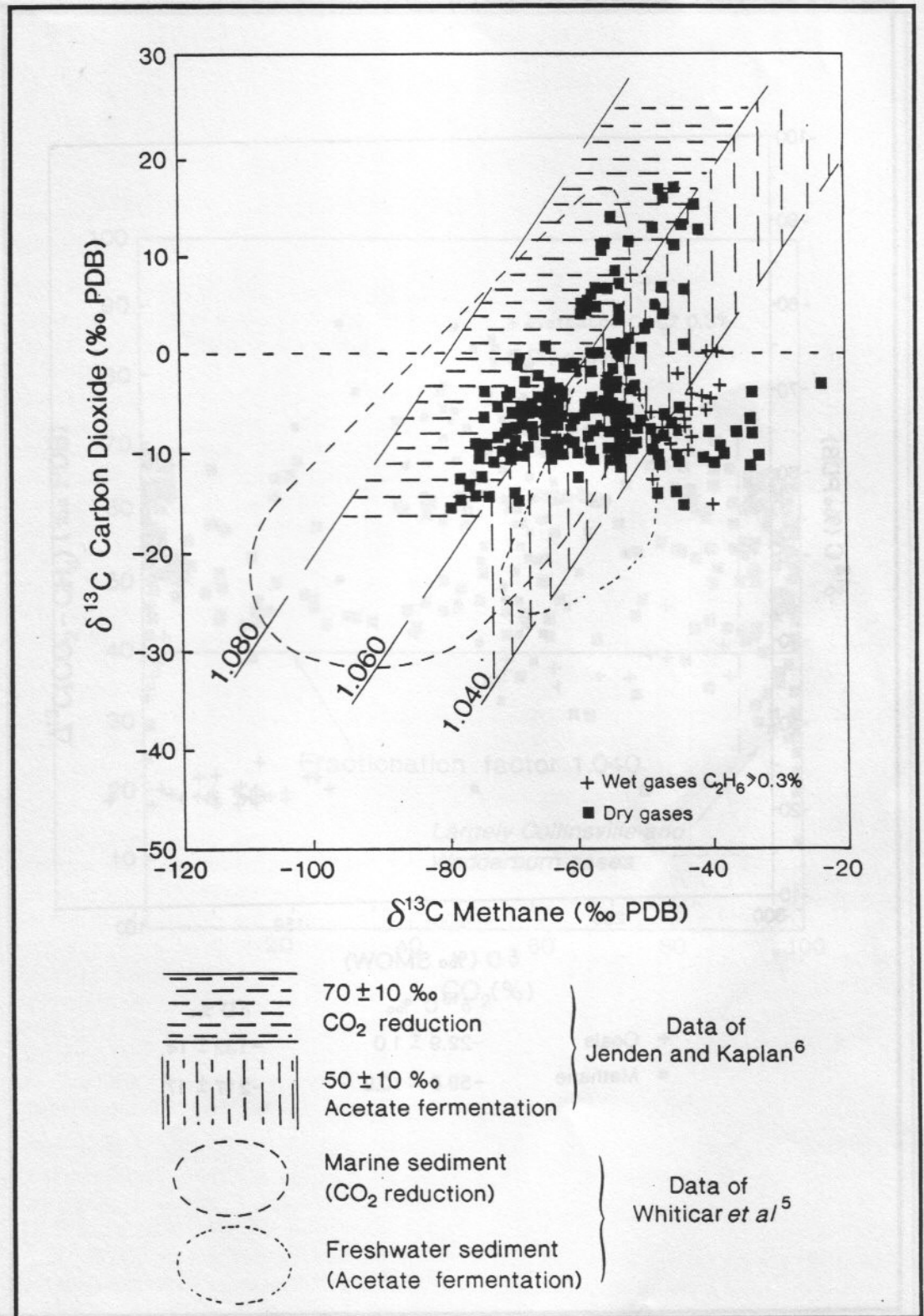
**Figure 2.** Carbon isotope composition of $CO_2$ and $Ch_4$ in coal seam and microbial gases.
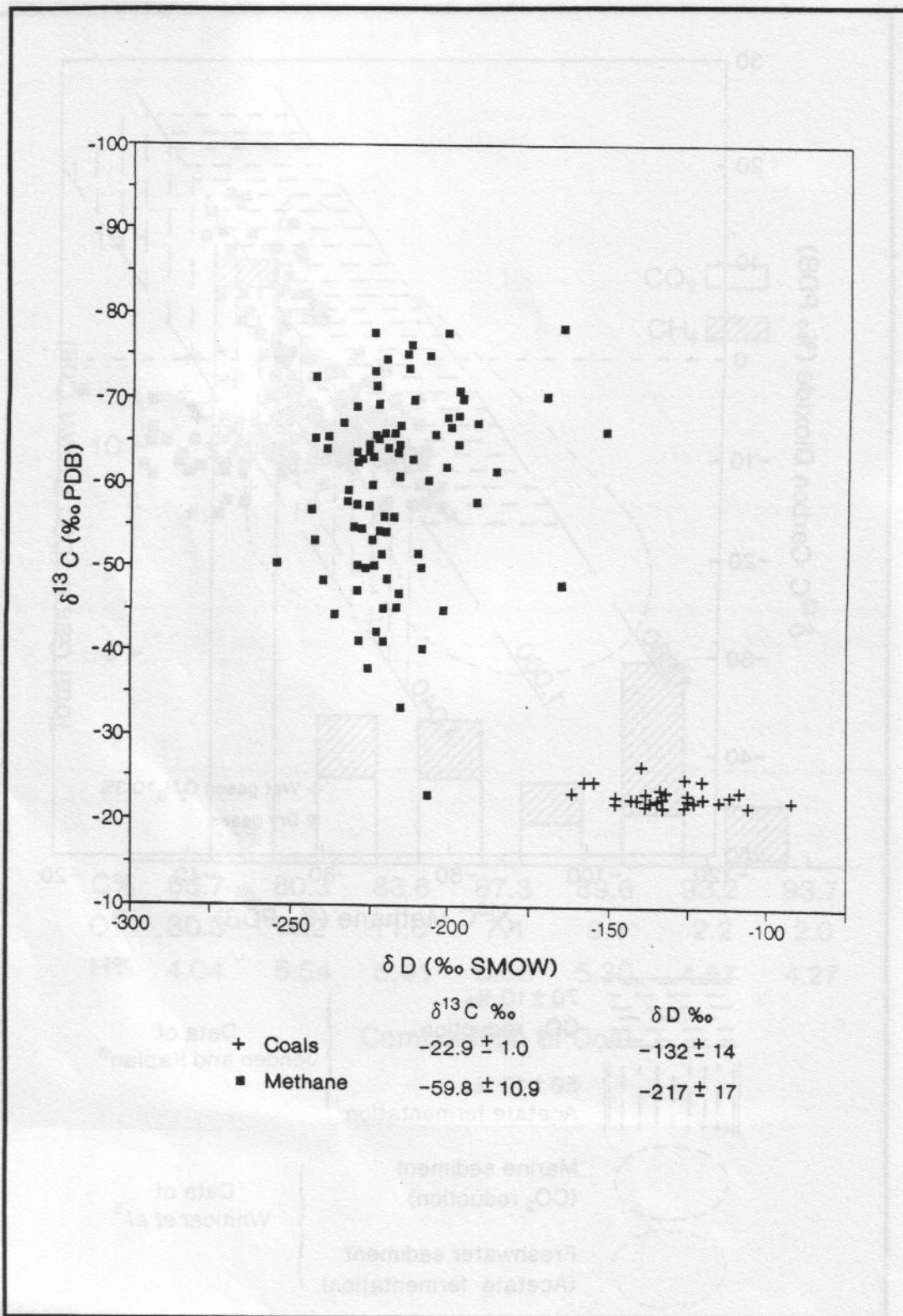
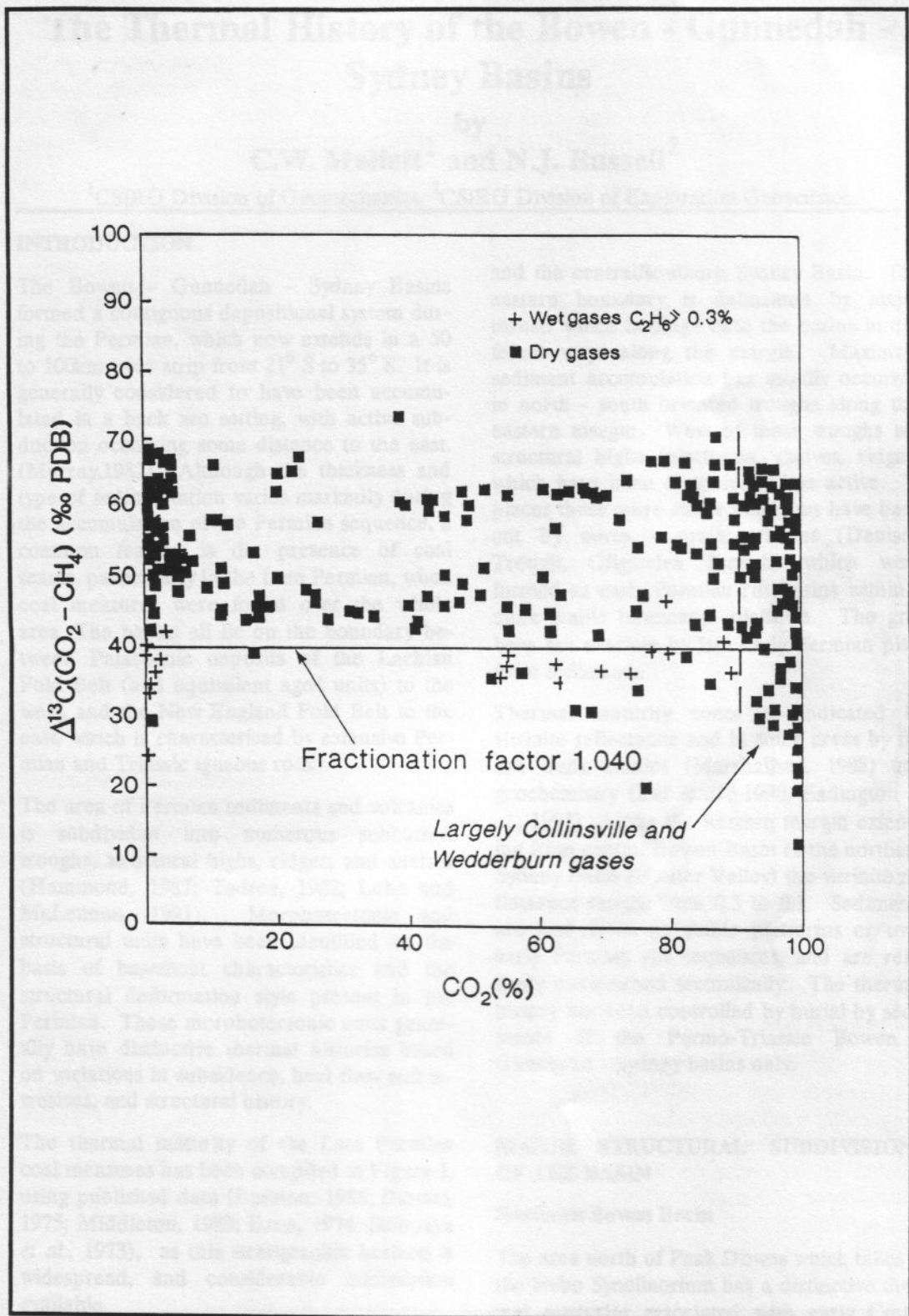*Figure 3.* Carbon and hydrogen isotope composition of coals and methane.

*Figure 4.* Variation of $\Delta\ ^{13}C$ ($CO_2$-$CH_4$) $^o$/oo with carbon dioxide concentration.