Comment


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It is with some concern that we note in Boreham et al. (1998) detailed reference to our earlier work on the origin of coal bed methane (CH₄) in the Sydney and Bowen Basins of Australia (Smith and Pallasser, 1996), together with a totally erroneous description of the conclusions we drew from our data. Due to their error, the detailed discussion, Fig. 2 and Table 1 provided by Boreham et al. (1998) to illustrate shortcomings in our propositions are in themselves incorrect.

In the past we have paid particular interest to the origins and δ¹³C contents of coal-associated carbon dioxide (CO₂) as a guide to the environments and processes of methane generation. In essence it appears that the experience of Boreham and co-workers has been largely related to the gaseous products of laboratory carbonisation tests and with those resulting from direct coal/intrusive interaction in regions of thermal metamorphism. Other mechanisms responsible for much of the CO₂ generation (<500 m) in the Eastern Australian coalfields are not considered, although long since described (e.g. Gould et al., 1981). One of these sources is the coal itself which, via oxidation, decarboxylation, etc., at shallow levels of burial, generates CO₂ with a δ¹³C value similar to that of the coal (−23 ± 1‰ PDB). It is this coal-associated CO₂ that we believe undergoes kinetic reduction to the “light”, dry CH₄ and the resulting ¹³C enriched, isotopically related, residual CO₂. δ¹³C (CO₂–CH₄) values of 60±10‰ PDB are commonly measured in these product gases (Smith and Pallasser, 1996). Such a fractionation is in itself a feature strongly associated with biogenic rather than physical processes.

The second source of CO₂ is of external magmatic origin (−7±2‰ PDB) and may be present in proportions sufficient to completely displace methane from the coal seam. In our recent description of this magmatic CO₂ (Smith and Pallasser, 1996, p. 891), we report that where it occurs in seam gas in highly variable proportions, the relatively constant isotopic composition of the CH₄ shows that “neither reduction of CO₂ to CH₄, nor isotopic equilibration between CO₂ and CH₄ has occurred; that is, the introduced CO₂ behaves as an inert diluent”. Nevertheless, although this carbon dioxide is identified as having no active role in our model for seam gas generation, Boreham et al. (1998, p. 348) state that we have “argued for a predominantly microbiological origin for methane based on reduction of CO₂ (sourced from a magmatic origin) by methanogenic bacteria”.

In this regard, our much earlier data (Smith et al., 1984), quoted in Table 1 of Boreham et al. (1998), show the largely magmatic CO₂ component of a gas from Nattai to vary from 5 to 95% v/v and the CH₄ content to vary correspondingly from 95 to 5% v/v. In such circumstances, the absence of significant variation between the δ¹³C values of both components over this compositional range again clearly illustrates a complete lack of interaction between CO₂ and CH₄. Accordingly, it should not surprise Boreham and co-workers that isotopic differences between CO₂ and the CH₄ are commonly unrelated to equilibrium values and that correspondingly, under such non-equilibrium conditions, calculated values of ε (the isotopic enrichment) are meaningless.

In support of these findings, exhaustive laboratory studies of the interaction between CO₂ and CH₄ under a wide range of conditions at temperatures to 500°C provided no evidence of chemical or isotopic exchange between these gases (Sackett and Chung, 1979). Unfortunately, it seems that the conclusions of Boreham et al. (1998) were reached without reference to the bulk of this work (including Smith and Pallasser, 1996), in which the
supporting evidence of some 300 seam gas analyses is presented. These data show that during biogenic reduction the $^{13}\text{C} / ^{12}\text{C}$ isotopic fractionation between the residual CO$_2$ and the dry product CH$_4$ is $60 \pm 10\%$, whereas the relatively minor wet gases found in enclosing sandstones and those generated in our experimental pyrolyses have markedly lower $\Delta^{13}\text{C} [\text{CO}_2–\text{CH}_4]$ values. This progressive decrease in $\Delta^{13}\text{C} [\text{CO}_2–\text{CH}_4]$ values is illustrated in Fig. 1, showing the approximate isotopic boundaries of dry biogenic gas (Area A), minor wet thermogenic gas (Area B) and gases generated in our laboratory pyrolyses (Area C). These particular experimental pyrolyses, although few in number, are of considerable significance because the CO$_2$ and CH$_4$ generated have similar isotopic compositions to gases (Area D) recovered from open pyrolysis of Bowen Basin coals (Boreham et al., 1998). In our model, these isotopically distinct, wet thermogenic gases (Areas B and C Fig. 1) are considered to be genetically unrelated, and of little consequence in relation to the huge preponderance of dry biogenic CH$_4$. On the other hand, Boreham et al. (1998) accept the chemical and isotopic compositions of wet gases, derived from open laboratory pyrolysis (Area D), as being representative of naturally occurring Bowen Basin gases. Neither comparison with a published value for a directly recovered seam gas sample nor comment on carbon monoxide (CO) contents is made. Whilst it is true that gases recovered from a region of thermal metamorphism may indeed reflect the results of direct coal/intrusive interaction, the generation of gas of similar composition by the laboratory pyrolysis of coal is not in itself a guide to seam gas origin. Clearly as demonstrated here, other evidence is required to support the gas origins proposed by Boreham et al. (1998).

Data on the deuterium contents of the coals and CH$_4$ provide additional evidence in support of a CH$_4$ origin via the biogenic reduction of CO$_2$ (Smith and Pallasser, 1996). The average measured $\delta D$ value for coal-associated gas is $-217 \pm 17\%o$. This compares well with $-227\%o$ SMOW, the value for methane calculated using the measured $\delta D$ values of coal ($-132 \pm 14\%o$), the calculated palaeo-value for Permian water ($-47\%o$ SMOW) and a fractionation value for $\delta D$ of 180 $\%o$ SMOW when all the hydrogen atoms in the CH$_4$ are derived from the formation water.

We are grateful for this opportunity to describe, defend, and expand upon our model for gas generation at shallow levels of the Sydney and Bowen Basins. At the same time, we advance an explanation for the differing origins of gas components that give rise to the varying isotopic compositions reported.

References


