

ISOTOPIC STUDIES OF GEOCHEMICAL FACTORS IN OUTBURSTING

By

K.W. GOULD¹ and J.W. SMITH²

ABSTRACT

Studies of ¹³C/¹²C ratios of carbon dioxide in seam gases and in secondary calcites show that

1. In mines prone to carbon dioxide outbursting, the source of this gas is external to the coal.
2. Faults draining reservoirs of magmatic or primary carbon dioxide, rather than intrusives, are the most likely points of entry of carbon dioxide into mines.
3. The higher the concentration of carbon dioxide in seam gas and the wetter the mine, the lower the likelihood of secondary calcite occurring as a filling in cleats, fractures etc.
4. A role played by carbon dioxide in promoting outbursting may be the conversion of calcite to soluble bicarbonate, the removal of this in mine water and the subsequent weakening of the resistance of the bulk coal to stress.

INTRODUCTION

Variations in the natural ratio of the stable isotopes of carbon, ¹³C/¹²C, may result from chemical, physical, biological and geological processes. ¹³C/¹²C ratios are commonly and conveniently expressed relative to

the International Standard, Pee Dee Belemnite (PDB) in the following form

$$\delta^{13}\text{C} \text{ ‰ PDB} = \left(\frac{^{13}\text{C}/^{12}\text{C unknown}}{^{13}\text{C}/^{12}\text{C standard}} - 1 \right) \times 10^3$$

These changes in ratio may frequently be interpreted in terms of the histories and sources of geological materials and, in addition, are of particular value in providing otherwise unobtainable information in these respects. Since fossil fuels and their maturation products are largely comprised of carbon, the measurement of ¹³C/¹²C ratios has promise of wide application.

However, until recently, coal has remained a generally unfashionable rock, although it was included in the initial upsurge of fundamental interest in stable isotope ratios generated in the 1950's (Craig, 1953; Jeffery *et al.*, 1955). Notwithstanding this trend, stable isotope studies of Australian coals have been continuing at the CSIRO Fuel Geoscience Unit at North Ryde since 1971.

Although no isotopic measurements have previously been made on outbursting gases, some indirect information with regard to the ¹³C/¹²C ratio of carbon dioxide in mine gas was provided by earlier exploratory investigations of the isotopic composition of carbonates associated with liquid and solid fossil fuels (Gould and Smith, 1978; Smith, 1978; Gould and Smith, 1979). In the most recent study the distribution and isotopic composition of

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1. Experimental Officer, CSIRO Fuel Geoscience Unit, North Ryde, NSW.
 2. Principal Research Scientist, CSIRO Fuel Geoscience Unit, North Ryde, NSW.

carbonates in 124 coal samples from bores and mines in the Bowen, Galilee and Sydney Basins were determined. Calcite was recovered from 68 samples by handpicking the crushed coals. Isotopic analyses of these calcites showed that in normal, apparently unaltered Permian coals, when calcite occurred in higher concentrations, it was unexpectedly and remarkably enriched in the heavy carbon isotope, ^{13}C , whereas when in low concentration, the ^{13}C content was frequently relatively depleted. This relationship is shown in Fig. 1 together with average $\delta^{13}\text{C}$ values for marine carbonates and coals. In addition Gould and Smith (1979) noted that calcites from heat-altered coals from the Bowen Basin showed a definite trend towards depletion in ^{13}C .

The variability in the isotopic composition of carbonates, particularly in heat-altered zones, suggested that similar isotopic variations, dependent on source, might be found in the carbon dioxide in seam gas. Therefore this study was commenced in the expectation that outbursting seam gas might possess specific isotopic properties characteristic of its source and history that could be utilized in combating the outburst problem.

DEFINITION OF PROBLEM

Outbursting in coal mines could presumably be described simply as the violent ejection of coal and/or gas in widely varying proportions into underground openings. This definition would most probably not find universal acceptance and a host of amendments and modifications might be required to satisfy all requirements. In order to overcome this difficulty in definition we recognize outbursting as being a problem or hazard when, or wherever the management or staff of a mine report that such a situation exists or is believed to be pending. On this understanding and on the basis of data collected so far, it appears that a feature of Australian mines suffering from outbursting is a

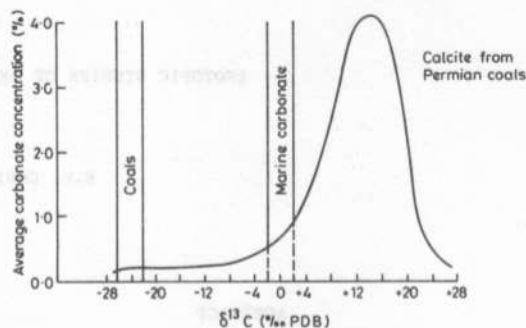


Fig. 1 - $\delta^{13}\text{C}$ values of carbonates associated with fossil fuels. Adapted from Smith (1978). Data presented by Gould and Smith (1979).

high concentration (i.e. >2% and often up to 70%) of carbon dioxide by volume in the seam gas on an air-free basis. This carbon dioxide is characterized by a $\delta^{13}\text{C}$ value of -7 ± 2 ‰ PDB.

It is not suggested that these are the only common factors, indeed associated igneous activity and faulting seem similarly related. It is not even known whether gas composition is a critical factor, but an association of outbursting with high concentrations of carbon dioxide of this isotopic composition does occur.

Does this carbon dioxide represent material released in the earliest stages of diagenesis and since retained within the coal structure, or is it a relatively recent maturation product? In which generation of carbon dioxide do carbonate minerals have their origins? In addition, if the coal is intruded, to what extent will coal/magma/water interactions alter the distribution and concentration of carbon dioxide and carbonates within the seam? What will be the effects of regional thermal metamorphism and are there possible external sources of the carbon dioxide?

Although Hargraves (1973) has invoked a pneumatolytic origin for high concentrations of

carbon dioxide in seam gas, unequivocal evidence regarding the source of the carbon dioxide is still required. Therefore attention has been focussed on

1. determining and distinguishing between the sources of carbon dioxide in coal seams, in particular that associated with outbursting, and
2. the possible role of carbon dioxide/carbonate interaction in promoting outbursting.

In addition, isotopic measurements have been made on gaseous hydrocarbons in seam gases, principally methane, in order that any other valuable relationships might be observed.

Because very little direct information exists on the sources and the isotopic composition of secondary carbonates in coal seams and none for carbon dioxide, a broad survey of the situation has been commenced. It is expected that this will allow meaningful comparisons to be drawn between gas and carbonate occurrences and isotopic ratios in stable mines and in those mines where outbursting is a recognised or possible hazard.

EXPERIMENTAL

In the course of this survey 14 mines have been visited and gas and carbonate samples taken from more than 80 locations covering 8 seams. Gases were collected whenever possible from holes freshly drilled to a depth of 3 m in virgin coal. Water occurring with the gas was collected, as were samples of coal and carbonate from the immediate vicinity of the holes. Details of the methods used in chemical and isotopic analyses of these products are described elsewhere (Smith and Gould, 1980). Collection sites, relevant analytical results and brief general descriptions of carbonate minerals are given in Table 1. More detailed analyses of the carbonates are contained in the Appendix.

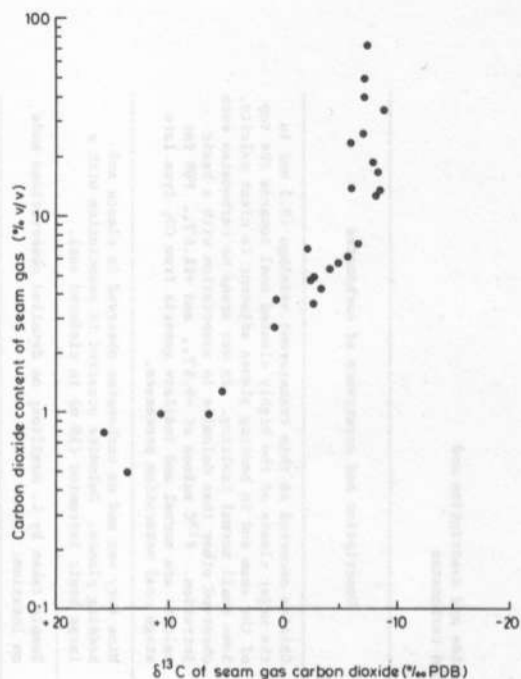


Fig. 2 - Isotopic changes accompanying the dilution of normal seam gas by externally derived magmatic carbon dioxide at West Cliff Colliery.

Major variations were observed in the chemical and isotopic composition of seam gases within individual mines. When this was so, gases were arbitrarily classified as (A) and (B) on the basis of their carbon dioxide analyses. The gases from West Cliff are classified in this way for the purposes of simple comparison and illustration. In fact, owing to the extreme variability of gas composition at West Cliff and a proneness to outbursting, this colliery was selected for a detailed study. This work has been described in detail elsewhere (Smith and Gould, 1980) and is presented here diagrammatically in Fig. 2.

Although included in the original survey, seam gas data from the Awaba State and Liddell

Table 1
 $\delta^{13}\text{C}$ values for coal and carbon dioxide and description and occurrence of associated carbonates

Mine	Seam	No. of locations	CO_2^* (% air free)	$\delta^{13}\text{C}$ CO_2^* (‰ PDB)	$\delta^{13}\text{C}$ Coal (‰ PDB)	Description and occurrence of carbonates
Munmorah State	Great Northern	3	0.8 [†]	n.d.	-23.9	Calcite occurred as thin transparent veinings (0.5 mm) in the major cleats of the highly cleated coal towards the top of the seam and in bedding planes adjacent to cleat calcite. Some small normal faulting. In wet areas no carbonates were observed other than dolomite in association with a basic intrusion. $\delta^{13}\text{C}$ values of +9.6‰ and +14.6‰ PDB for calcite are normal and indicate genesis from CO_2 from late stage coal maturation processes.
Newstan	Borehole	4	0.9 [†]	n.d.	-24.4	Mine very wet and no carbonates observed in cleats and bedding planes. Dolomite occurred in association with a large basic intrusion (10 m) in cindered coal.
Liddell	Liddell	1	0.4	-11.5	-23.7	Sample taken by L. Hamilton; no detailed observations made on location.
Appin	Bull1	1	0.8	+4.5 +5.0	-24.9	Dolomite abundant in cleats and roof to floor fractures in J. Panel. Siderite present in minor quantities as small rhombs. $\delta^{13}\text{C}$ values of CO_2 indicate product of late coal maturation. Dolomite with $\delta^{13}\text{C}$ value of +3.9‰, not directly related to current mine CO_2 . Water in boreholes.
Colliery 1	Bull1	2	77/83	-5.4	-24.0	Mine very wet; no carbonates observed.
Darke Forest	Bull1	2(A) 2(B)	11/17 55/63	-6.4 -7.8 -7.0	-23.3	Calcite seen in bedding planes near roof $\delta^{13}\text{C}$ values of calcite +4.9‰ to +5.6‰ PDB indicate this to be a late stage coal maturation product. Both dolomite and siderite occurred as vertical veinings adjacent to a basic intrusion. Dolomite predominated in more cindered coal, calcite in vugs. Dolomite occurred as traces in cleat fillings, otherwise carbonates entirely absent in wet regions.
Colliery 2	Bull1	1	96	-7.6	-25.0	Dry mine section; no significant carbonate at this location.
Coal Cliff	Bull1	1(A) 1(B)	76 31	-12.6 -10.0	-22.3 -25.0	Dry section with calcite in cleats and bedding planes towards roof. $\delta^{13}\text{C}$ values of calcite +9.0‰ to +16.8‰ indicate these to be late stage coal maturation products. These carbonates are not related to current CO_2 in seam gases. Dry section with dolomite in cleats and bedding planes. $\delta^{13}\text{C}$ values of dolomite +5.0‰ PDB indicate this to have different genesis from seam gas.

Table 1 continued

Mine	Seam	No. of locations	CO ₂ * (% air free)	δ ¹³ C CO ₂ * (‰ PDB)	δ ¹³ C Coal (‰ PDB)	Description and occurrence of carbonates
West Cliff	Bulll	6(A)	0.5	+5.4	-24.5	Generally dry section with minor calcite occurring in cleats and adjacent bedding plane towards the roof. δ ¹³ C values for calcite of +12.9‰ to +17.3‰. PDB indicate these to be late stage coal maturation products.
			1.3	+15.7		
		23(B)	2/75	+0.8 -8.7		Calcite rare and entirely absent in wetter sections.
Colliery 3	Bulll	4	82/93	-4.3	-24.4	Calcite lenses and veins occurred only in a persistent vitrinite band (2-3 cm) at roof. Mine generally wet and no other carbonates seen. δ ¹³ C values of carbonate +5.9‰ to +7.1‰ indicate these to be late coal maturation products.
				-5.3		
	Wongawilly	1	92	-7.7	-23.8	Calcite present in cleats in seam exposure. Location dry. δ ¹³ C value of +3.1‰ for calcite suggests this to be late stage coal maturation product.
Leichhardt	Gemini	3	0.9	+14.9	-24.8	Prominent calcite mineralization in cleats, joints and bedding planes (3 mm) near roof in both dry and moist sections. δ ¹³ C value for calcite from +4.8‰ to +29.8‰. PDB confirm these to be products of late coal maturation. Cross-cutting veins (3 cm) of sparry calcite at major faults appear to originate from fluids traversing these faults. δ ¹³ C value of these latter carbonates +0.8‰ to -9.1‰ further confirm that these are unrelated to the present CO ₂ in the mine
			4.4	+16.7		
Collinsville Bowen		4(A)	100 [†]	-8.8 -18.8	-21.2	Old oxidised mine section; some wet areas; no carbonates seen.
			6(B)	91/99	-6.0 -9.3	-22.5
Preston Extended	Hoskisson	1(A)	3.7 [†]	-21.6	-21.5	Carbonates only seen in immediate association with dykes. Dykes appear to be only source of all water and gas. Coal is tight and virtually cleat-free. Dykes calcitic and of variable δ ¹³ C values -0.6‰ to -16.0‰. PDB; possibly reflecting either some interaction of originally magmatic CO ₂ -bearing fluids with coal (or coal derived products) or isotopic fractionation accompanying a paragenetic precipitation of carbonates derived from an external CO ₂ source of δ ¹³ C value -7‰. PDB.

* Where two values are shown these represent the range of values determined

† Samples contained significant quantities of air

State mines are not reported here. The gases collected at these mines consisted mainly of air and otherwise contained only traces of carbon dioxide, presumably resulting from the oxidation of long exposed coal surfaces.

As shown in the footnote to Table 1, several of the other gas samples, or groups of samples, also contained significant quantities of air. Some caution in interpreting these data was required because it was not always possible to ascertain whether the air was entrained during the collection procedure, or whether it represented air that was permeating the coal and giving rise to oxidation products. When seam gases consisted largely of carbon dioxide in addition to air, and when the nitrogen/oxygen ratio approximated that in the atmosphere, as found for the Collinsville (A), Colliery 1 and Preston Extended (B) samples, it was assumed safe to accept that this carbon dioxide had not resulted from aerial oxidation of the coal. However, although the Munmorah, Newstan and Preston Extended (A) samples consisted largely of air, the remainder was almost entirely methane with only a trace of carbon dioxide. Consequently, in view of the difficulties normally encountered in separating and analysing such a small component and, in addition, the low level of confidence that might be attached to any result, no attempt was made to analyse the carbon dioxide in Munmorah and Newstan samples.

DISCUSSION

Sources of carbon dioxide

Carbon dioxide is released in rapidly diminishing quantities with increase in rank throughout the entire history of the maturation of preserved land plant residues to high grade bituminous coals. On this evidence alone some doubt must exist with regard to the precise origins and histories of outbursting concentrations of carbon dioxide and of carbonates in mature coals.

The isotopic data in Table 1 together with previously published information on carbonates in Australian coals (Smith, 1978; Gould and Smith, 1979) exclude many of the known possible sources of carbon dioxide and by so doing allow the most probable source of outbursting concentrations of carbon dioxide to be defined.

In discussion of the sources of carbon dioxide and carbonates in coal seams and of their possible roles in outbursting, it is perhaps timely to emphasize that the essential origin of all coal is atmospheric carbon dioxide. The global carbon cycle and the exchange of carbon dioxide between the atmosphere and the oceans has kept the isotopic composition of these reservoirs constant at $\delta^{13}\text{C} -7\text{‰ PDB}$ and $\delta^{13}\text{C}$ zero ‰ PDB respectively for possibly almost 2×10^9 years. Photosynthetic fixation of atmospheric carbon dioxide proceeds principally via the Calvin cycle and thus, as might be expected, whole land plants are generally of a uniform isotopic composition with a $\delta^{13}\text{C}$ value near -25‰ PDB . The decrease in the ^{13}C content of land plants relative to atmospheric carbon dioxide results from discrimination against $^{13}\text{CO}_2$ during photosynthesis.

On the death of a plant and its deposition in an early coal-forming swamp, two major reactions which chiefly affect the less-resistant plant components, e.g. cellulose and starch, may occur. If the water cover is shallow, acidic oxidising conditions prevail and these components are oxidised to products, including carbon dioxide of $\delta^{13}\text{C}$ value of -25‰ PDB that is lost from the sedimentary system. When the water cover is deeper, reducing conditions suitable for anaerobic fermentation may be established. In this situation methane and carbon dioxide are co-produced, probably via acetate, in a state approaching isotopic equilibrium (Rosenfeld and Silverman, 1959; Oana and Deevey, 1960). The methane ($\delta^{13}\text{C} -70\text{‰ PDB}$)

is lost from the system as marsh gas and the carbon dioxide may be deposited as early authigenic sideritic nodules ($\delta^{13}\text{C} +4 \pm 3 \text{‰}$ PDB) enclosed within the coal substance (Gould and Smith, 1979).

With deeper burial and increasing sediment temperatures the more-resistant, preserved plant residues progress through the peat stage to brown coal. No isotopic changes accompany the transformation of land plants to brown coal and the $\delta^{13}\text{C}$ values of total land plants and brown coal remain essentially indistinguishable near -25‰ PDB. Previous analyses of the functional group distribution in Australian brown coals (Brooks and Sternhell, 1957) have shown carboxyl groups to be much in evidence at this stage of diagenesis. These groups are readily decomposed, with the release of carbon dioxide, at relatively low temperatures and thus represent a positive source of carbon dioxide with increasing sediment temperatures and maturation. Laboratory experiments, in which the carbon dioxide liberated from Yallourn brown coals heated to 175°C was collected, show this carbon dioxide to differ little isotopically from the parent coal and to have a $\delta^{13}\text{C}$ value of -24‰ PDB (Smith, Gould and Rigby, unpublished data, 1980). Therefore, if this carbon dioxide is the source of carbonates appearing in coals of greater rank, these carbonates will be isotopically similar, or related by an established factor (Friedman and O'Neil, 1977), to this carbon dioxide. In fact, as mentioned previously, calcites with $\delta^{13}\text{C}$ values markedly less than zero ‰ PDB are rare in normal, apparently unaltered Australian coals (although they are common in locally heat-altered zones). Thus it appears that little, if any, of the ^{13}C -depleted carbon dioxide resulting from decarboxylation reactions is deposited as calcite and, on this evidence, it is assumed that retention of carbon dioxide gas as such in the seam is also minimal. In any event, the isotopic com-

position of this carbon dioxide ($\delta^{13}\text{C} -24 \text{‰}$ PDB), is so far removed from that of carbon dioxide associated with outbursting ($\delta^{13}\text{C} -7 \pm 2 \text{‰}$ PDB) that the contribution from this source cannot be large.

Other possible sources of carbon dioxide in bituminous coal seams, together with details of associated carbonates, are shown in Fig. 3. An evaluation of the role of carbon dioxide from these sources in promoting outbursting conditions follows.

1. In older mine workings, the coal is frequently permeated with air. Samples of gas drawn from fresh drill holes in these coals mainly reflect the high air content but are also likely to contain traces of carbon dioxide resulting from the oxidation of long-exposed coal faces. This carbon dioxide has a range of $\delta^{13}\text{C}$ values from -16‰ to -24‰ PDB and, in view of both its isotopic composition and small absolute volume, cannot be regarded as a serious contributor to the outbursting situation.
2. Gases from normal, apparently-unaltered, medium volatile, bituminous coal seams are comprised essentially of methane and traces of higher hydrocarbons together with 2% or less of carbon dioxide. This carbon dioxide is highly enriched in ^{13}C to $\delta^{13}\text{C}$ values of $+10 \pm 5 \text{‰}$ PDB, possibly as a result of isotopic exchange with methane during formation. Secondary calcites filling cleats and partings in such seams are commonly even more enriched in ^{13}C and appear to be genetically related to the seam carbon dioxide (Gould and Smith, 1979).

The disparity between the ^{13}C contents of the carbon dioxide in normal seam gases and that of the carbon dioxide-rich gases, associated here with outbursting, precludes a significant contribution of the former to the latter. In addition, since the former are comprised largely of methane, a substantial contribution of the former is also prohibited if the outbursting gases are to retain their abnormally high carbon

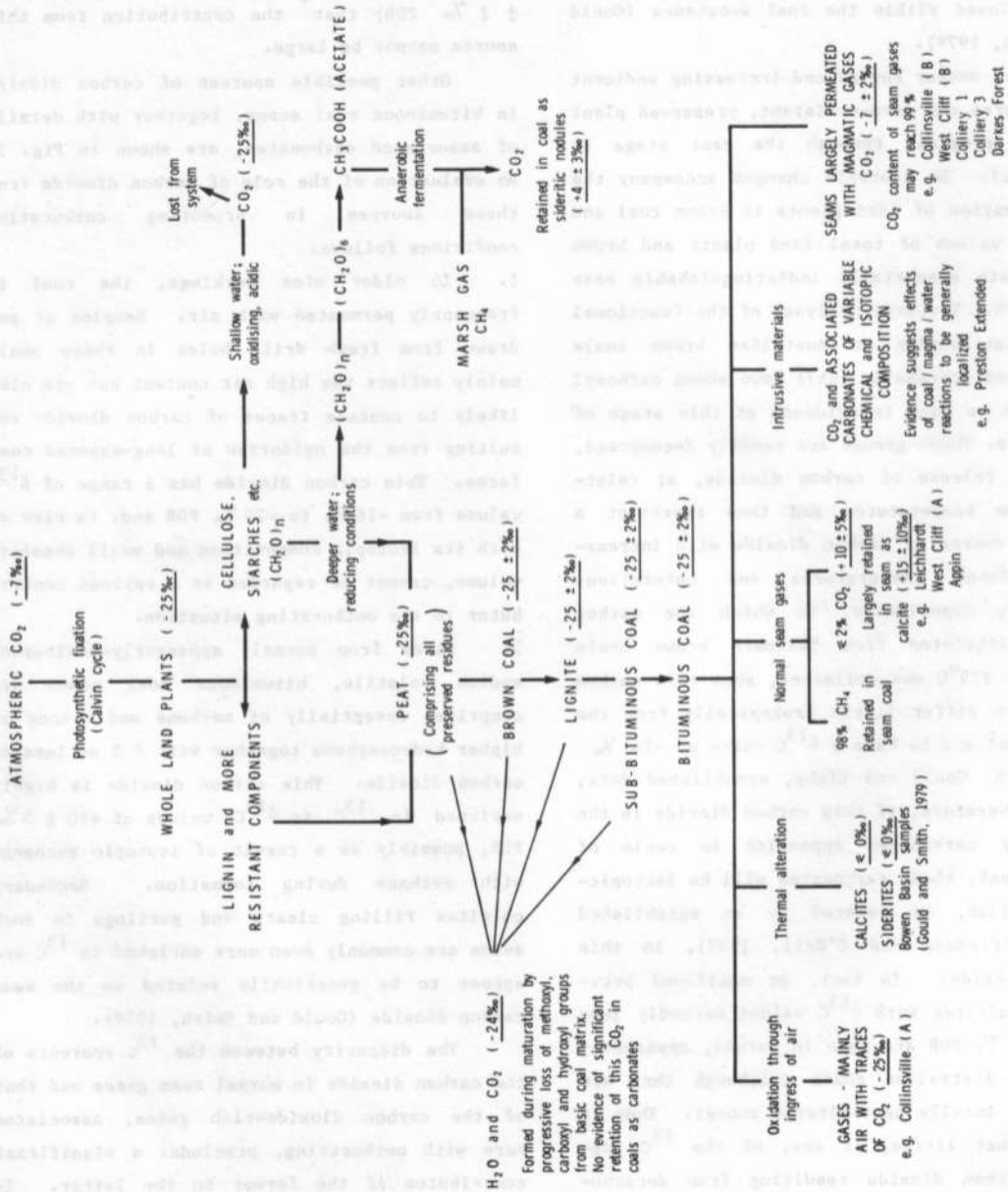


Fig. 3 - Distribution of ¹³C in carbonates and carbon dioxide generated during the formation and maturation of coals. Values in parentheses are δ¹³C in ‰ PDB

dioxide content.

Although the seam gases and the bulk of the calcites at Leichhardt have isotopic compositions to be expected in unaltered bituminous coals, calcites which occur as cross-cutting veins near faults are strongly depleted in ^{13}C to a $\delta^{13}\text{C}$ value of -9‰ PDB. Clearly these have different geneses from the bulk of the carbonates: they are not related to the seam gas carbon dioxide and a source, possibly igneous, but certainly external to the seam must be considered.

3. Intrusives represent another possible source of carbon dioxide, either as free gas accompanying the intruding magma, or as gas resulting from the interaction between magma, water and the coal. Dyke carbonates have been commonly encountered and consist either of calcite and/or siderite and/or dolomite. Isotopic analyses of these (Appendix) give a mean $\delta^{13}\text{C}$ value of $-4.9 \pm 6.3\text{‰}$ PDB for calcite. In fact, greater depletions in ^{13}C were expected owing to an envisaged major interaction and isotopic exchange between the magma and the coal ($\delta^{13}\text{C} -25 \pm 2\text{‰}$ PDB). This depletion was not generally observed and thus it appears that the degree of participation of coal in these reactions is generally limited. If a $\delta^{13}\text{C}$ value of $-7 \pm 2\text{‰}$ PDB and an external magmatic source are also accepted as characteristic of the carbon dioxide associated with intrusives, the variations of from -10‰ to $+4\text{‰}$ PDB seen in dyke calcite can be explained in terms of acceptable equilibration temperatures (Friedman and O'Neil, 1977). Only at Preston Extended were more substantially ^{13}C depleted dyke carbonates seen ($\delta^{13}\text{C} -16.0\text{‰}$ PDB).

Normally, major variations in gas composition and concentration were not observed in the vicinity of dykes. In this respect, Preston Extended again appears to be anomalous as it is reported that significant gas flows in

the mine occur only when dykes are breached during mining operations. Isotopic measurements on the most carbon dioxide-rich gas samples taken at Preston Extended showed these to be very strongly depleted in ^{13}C ($\delta^{13}\text{C}$ value -21.6 to -24.1‰ PDB), possibly in this case, as the result of extensive participation of coal in the reaction. Thus these gases appear to be genetically related to the dyke carbonates but not to be a source of the carbon dioxide regarded in this paper as promoting outbursting.

Other isotopically distinctive carbonates are the thermally altered calcites and siderites reported in bores from the Bowen Basin (Gould and Smith, 1979). Variable $\delta^{13}\text{C}$ values considerably more negative than zero ‰ PDB also generally characterize these carbonates, but whether they are in any way related to the isotopically similar vein carbonates at Leichhardt or to those carbonates normally associated with dykes remains unknown.

As stated previously high concentrations of carbon dioxide in seam gas, whether the seam be regarded as outbursting or not, are characterized by $\delta^{13}\text{C}$ values of $-7 \pm 2\text{‰}$ PDB, e.g. Colliery 1, Darkes Forest (A) and (B), Colliery 2, West Cliff (B), Colliery 3 (Bull and Wongawilly seams) and Collinsville (B). Only Coal Cliff where the carbon dioxide has a $\delta^{13}\text{C}$ value of -10.0‰ to -12.5‰ PDB shows any significant departure from this isotopic pattern. On the basis of this isotopic evidence and the immediately preceding discussions on the possible origins of carbon dioxide in coal mines, there can remain little doubt that the coal itself is not the source of these high concentrations of carbon dioxide but that they are produced externally to the seam.

In the Southern Coalfields of the Sydney Basin and in the northern extremities of the Bowen Basin, igneous activity and associated faulting are prominent geological features. Carbon dioxide associated with magma and

volcanism is generally credited with a $\delta^{13}\text{C}$ value approximating -7‰ PDB, although substantial variations have been reported (Hoefs, 1973). On this evidence, a magmatic source for the outbursting carbon dioxide appears to be most acceptable.

As discussed earlier, intrusions of magma into coal seams are not generally a major source of carbon dioxide but, if so, as at Preston Extended, the ^{13}C content of the carbon dioxide is very different from that expected for outbursting gas. When in high or hazardous concentrations, carbon dioxide tends to permeate the whole seam section rather than to be associated with specific intrusions. Entire mines may be so permeated and the conclusion gained from these early studies is that in these circumstances, vast reservoirs of magmatic carbon dioxide are being drained via fault systems. When this is so, replacement of methane by carbon dioxide and a gradual change in the chemical and isotopic composition of the seam gas occurs as the external source of the carbon dioxide is approached. Such a change is particularly evident at West Cliff where extensive sampling of the seam gases has permitted a detailed survey of the changing composition of the carbon dioxide to be made (Smith and Gould, 1980). Fig. 2 clearly demonstrates the effects of increasing flows of externally derived carbon dioxide on the general composition of the seam gas.

Carbon dioxide/carbonate interaction

Apart from the purely physical effects on coal seam stability of high volumes and pressures of carbon dioxide, early observations (Smith and Gould, 1980) suggested that chemical reactions might also be of significance. Although the number of mines visited so far is small and sampling within mines is generally inadequate, at times being restricted to a single location, some well-defined trends emerge.

Where high concentrations of carbon di-

oxide are found in seam gases and where the mine sections are described as wet, secondary calcites are generally absent, e.g. Colliery 1, Darkes Forest (B), West Cliff (B), Colliery 3 (Bulli Seam), Collinsville (B). The section sampled at Colliery 2 was dry and again no significant secondary carbonate mineralization was seen, however, in other dry sections as at Collinsville (B), Coal Cliff and Colliery 3 (Wongawilly Seam) calcite occurred. Isotopic comparisons between these carbonates and the seam gas carbon dioxide showed not only that they were not related but that the carbonates were typical maturation products of bituminous coal whilst the carbon dioxide had been introduced from an external source presumably at a later stage.

Secondary carbonate mineralization was also prominent in most of those sections sampled where the carbon dioxide content of the seam gas was low, e.g. Appin, Leichhardt and to a limited extent West Cliff (A). In these sections, carbonate and carbon dioxide were genetically related, both being enriched in ^{13}C and both representing normal coal maturation products.

Accordingly the emerging trend is that the higher the concentration of carbon dioxide in seam gas and the wetter the mine, the less the likelihood of the occurrence of secondary calcite. Although further analyses are required to confirm this relationship, a likely explanation of the present situation appears to be that the absence of calcite may commonly be ascribed to the action of carbon dioxide-rich water, i.e. carbonic acid. When this acid is present in significant concentration either conditions for calcite precipitation are not attained, or earlier deposited calcite is converted to the soluble bicarbonate and transported from the seam in mine waters.

In a single laboratory experiment the rapidity with which calcite, filling fractures in coal from the Young Borehole Seam, may be

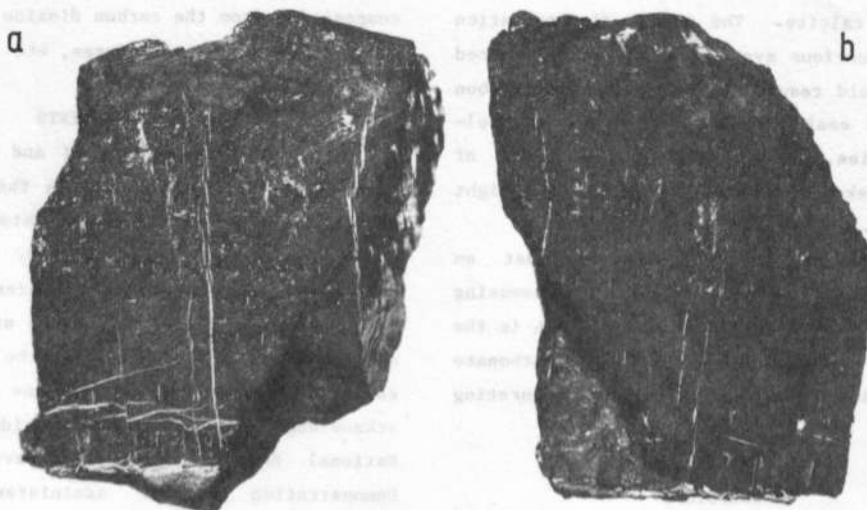


Fig. 4 - Illustration of removal of vein carbonate by the action of carbonic acid on coal from the Gemini Seam. a) Untreated coal b) Mirror image slice of the same coal treated with carbonic acid.

dissolved by carbonic acid has already been demonstrated (Smith and Gould, 1980).

In a similar experiment using coal from the Gemini Seam the rate of attack on carbonates was not only generally much slower but appeared to be highly selective. However the general effect was much the same, as shown in Fig. 4, and presumably reaction with carbonic acid should proceed underground, possibly even more rapidly.

If this is so, and calcite filling cleats, joints, fractures, etc. in the seam coal is removed by this reaction, some change in the physical properties of the coal may be expected. It could be argued that removal of carbonate will increase the permeability of the coal and decrease the outbursting hazard by allowing the faster drainage of otherwise potentially outbursting gases. In some circumstances this may be so. Conversely the action of carbonic acid may be seen as creating a more hazardous situation as follows.

Since the major sources of carbon dioxide are recognized as being external to the seam, the initial effects of interaction with carbonic acid are likely to be deep within the virgin coal in the vicinity of a fault. Fluid flows induced by mining will be towards the seam working faces. If mining is towards the fault, fluid flow towards the working face will be accelerated as the bulk of virgin coal between the fault and the face is decreased. The result of this increased flow will be the solution of mine calcite, particularly along the paths of least resistance to flow. No sign of these physical changes deep within the coal need be observable at the face other than perhaps an increase in the flow of water. Therefore, a critical situation may be visualized, particularly when the rate of coal cutting is fast, where huge volumes of carbon dioxide under high pressures are being constrained by inadequate thicknesses of coal, physically altered, if not demonstrably weakened, by the

removal of calcite. The sudden disintegration of this precarious system by natural or induced stresses would result in the ejection of carbon dioxide and coal into mine openings. Tunnel-like cavities, possibly following lines of physical weakness created by fluid flow, might be expected.

Accordingly it is suggested that an additional factor to be considered in assessing the outbursting character of a coal seam is the extent of interaction between carbonate mineralization and potentially outbursting fluids.

CONCLUSIONS

High concentrations of carbon dioxide in coal seam gases, whether the seam is outbursting or not, originate in sources external to the coal and are generally characterized by $\delta^{13}\text{C}$ values of $-7 \pm 2\%$ PDB. Faults draining reservoirs of magmatic or even primary carbon dioxide are postulated as the source of this gas.

Interactions between carbon dioxide, water and calcite filling fractures, joints, etc. in the coal result in the conversion of the calcite to soluble bicarbonate. In this form the mineral may be removed from the coal by water flow and, as a result, the coal may become weakened and made more prone to outbursting.

Working coal mines should therefore be regarded as dynamic systems. As well as the better documented, and often more easily observed, mechanical stresses and physical changes induced by mining, the less obvious interactions between water, carbon dioxide and minerals should also be monitored and their effects upon seam stability evaluated.

From the geochemical viewpoint, obviously unstable situations exist in wet mines where high concentrations of carbon dioxide occur in seam gases and where earlier deposited calcite, invariably differing markedly in isotopic

composition from the carbon dioxide, persists as fillings in cleats, fractures, etc.

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APPENDIX CARBON ISOTOPE DATA FOR CARBONATES IN APPARENTLY UNALTERED COAL SEAM SECTIONS

Colliery	Seam	Sample location	Mode of carbonate occurrence	Carbonate identity	Carbonate $\delta^{13}\text{C}(\text{‰PDB})$		
Munmorah State	Great Northern	3 North panel	Cleats	Calcite	+ 9.6		
		" "	Roof bed plane	Calcite	+14.6		
Newstan	Borehole		(Dyke carbonate)				
Liddell	Liddell	-	Thin veinings in vitrinite	Dolomite	- 4.3		
Appin	Bulli	J. panel	Cleats	Dolomite	+ 3.9		
Colliery 1	Bulli	406 panel	(Carbonates not observed)				
		400 panel	(Carbonates not observed)				
Darkes Forest	Bulli	422 panel	Roof bed plane	Calcite	+ 5.6		
		430 panel	Roof bed plane	Calcite	+ 4.9		
		314 panel	Cleats	Calcite	+ 2.7		
		395 panel	(Carbonates not observed)				
Coal Cliff	Bulli	227 panel	Cleats	Calcite	+ 9.0		
			Roof bed plane	Calcite	+16.8		
		291 panel	Cleats	Dolomite	+ 4.9		
West Cliff	Bulli		Roof bed plane	Dolomite	+ 5.0		
		211 panel	Cleats	Dolomite	+ 6.9		
		211 panel	Cleats	Calcite	+17.3		
		102 panel	Cleats	Calcite	+16.3		
		102 panel	Cleats	Calcite	+14.8		
		402 panel	Roof bed plane	Calcite	+12.9		
		Colliery 3	Bulli	Development 1	Lenses in)	Calcite	+ 7.1
				headings 3	persistent)	Calcite	+ 5.9
Bulli 4	vitrinite band)			Calcite	+ 5.7		
	Wongawilli	Drift end 5	Cleats	Calcite	+ 3.1		
Leichhardt	Gemini	SE.PNL.Dhdg	(Carbonates not observed)				
		SE.PNL.Bhdg6C/T	Cleats	Calcite	+28.4		
		SE.PNL.Ahdg7C/T	Roof bed plane	Calcite	+26.4		
		IE.PNL.Chdg3C/T	Vein at fault	Calcite	- 9.1		
		IE.PNL.Chdg3C/T	Roof bed plane	Calcite	+24.7		
		N.PNL.Bhdg4C/T	Cleats	Calcite	+29.8		
		N.PNL.C/Dhdg6C/T	Cleats	Calcite	+26.8		
		N.PNL.Ahdg	Vein at fault	Calcite	+ 0.8		
		W.PNL.Dhdg3C/T	Vein at fault	Calcite	- 6.8		
		W.PNL.Dhdg3C/T	Roof bed plane	Calcite	+ 4.8		
		W.PNL.Bhdg3C/T	Cleats (near fault)	Calcite	+11.7		
		S.PNL.Bhdg2C/T	Roof bed plane	Calcite	+27.7		
		S.PNL.Bhdg2C/T	Cleats	Calcite	+28.9		
Collinsville No.2	Bowen	65 level	Cleats	Calcite	+ 3.4		
		66-67 level	Cleats	Calcite	+ 5.5		
		66½ level	Cleats	Calcite	+ 8.4		
		67 level	Cleats	Calcite	+ 6.3		
		67-68 level	Roof bed plane	Calcite	+ 6.9		
		69 level	Cleat	Calcite	+ 7.4		
		68 level 7hdg	Vein	Aragonite	+ 4.4		
Colliery 2	Bulli		(Carbonates not observed)				

APPENDIX CARBON ISOTOPE DATA FOR CARBONATES COLLECTED FROM IGNEOUS INTRUSIONS IN COAL SEAMS

Colliery	Seam	Sample location	Mode of carbonate occurrence	Carbonate identity	Carbonate $\delta^{13}\text{C}$ (‰ PDB)	CO_2 $\delta^{13}\text{C}$ (‰ PDB)
Darkes Forest	Bullf	410 panel	Vertical vein in coal 3 m from dyke	Dolomite	- 0.2	- 7.8
		"	"	Siderite	- 0.3	- 7.8
		"	Vertical vein in coal at contact zone	Dolomite	- 3.0	- 7.8
		"	Dyke section close to above site. Sample containing dyke material and distinct carbonate zones	Calcite Siderite Calcite	+ 3.3 - 1.5 + 2.9	- 7.8 - 7.8 - 7.8
Liddell State	Liddell	West panel	Vein carbonate in dyke	Dolomite	- 0.3	-
		4hdg	Massive dyke carbonate	Calcite	+ 7.2	-
Munmorah State	Great Northern	48th panel	Vein carbonate in cindered coal	Dolomite	- 4.2	-
		18th panel	Vein carbonate in cindered coal	Dolomite	- 4.6	-
Preston Extended	Borehole	9-10C/T	Vein carbonate in cindered coal	Dolomite	- 0.3	-
		5W panel	Vein in coal away from dyke contact zone	Calcite	- 11.2	- 21.5
		"	Fibrous dyke carbonate	Calcite	- 16.0	- 21.5
		"	Crystalline dyke carbonate	Calcite	- 7.9	-
		1W panel	Large rhombs at dyke	Calcite	- 10.0	-
		"	Vein on dyke rock	Calcite	- 1.8	-
		"	Vein on dyke rock	Calcite	- 9.4	-
		"	6mm vein in dyke - fibrous carbonate	Calcite	- 1.4	-
		"	- crystalline carbonate	Calcite	- 0.6	-
		"	Carbonate rhombs	Calcite	+ 0.2	-
Wongawilli	Wongawilli	7W06	Carbonate rhombs	Dolomite	- 1.4	-
		7W06	With dyke mass	Siderite	- 4.4	-
		7W02	With dyke mass	Siderite	- 0.4	-
		7W03	With dyke mass	Siderite	- 3.6	-
		7W05	With dyke mass	Dolomite	+ 0.4	-
6W03	With dyke mass	Siderite	- 3.7	-		
					- 2.5	-