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## Characterisation of carbon components and their isotopic composition in gas shales

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### Abstract

Shales are an important reservoir of both organic and inorganic carbon that can be decoupled by incremental stepwise combustion without acid treatment. The study of shales from various depths of three cores of Haynesville-Bossier formation of Jurassic period indicates the presence of organic and inorganic carbon with comparable  $\delta^{13}\text{C}$  and nitrogen/carbon (N/C) ratios in all three. Both the isotopic and elemental ratios predominantly indicate a continental source but a minor N/C fraction corresponding to a marine/lacustrine source is also seen. This indicates either mixing from different sources and/or fractionation, perhaps due to preferential loss of nitrogen during organic matter degradation. Because some of the organic component is released at a high temperature of 1000–1200 °C although ungraphitised, it may be locked up in minerals like sulphides and K-feldspars, incorporated during diagenesis and hydrothermal alteration. Carbon locked in these minerals can be isolated from the carbon cycle for a longer period of time.

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### 1. Introduction

The ‘deep’ carbon cycle comprises the movement of carbon between rocks, soil, ocean and atmosphere taking millions of years, through chemical reactions and tectonic activity. The dominant carbon containing rock is limestone, where carbon occurs as carbonate minerals precipitated in oceans and sea or, derived from shells of organisms that sink to the sea floor after these organisms die. Subsequently, limestones can be weathered or subducted, contributing

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to the balance of the Earth's carbon budget [1]. A fraction of the carbon is also present as organic carbon locked up in shales, some of which can be converted to hydrocarbons under favourable conditions, making itself available to the carbon cycle.

Shales are common fine-grained sedimentary rocks composed mainly of mud that is a mixture of clay minerals and silt-sized particles of other minerals like quartz and calcite. They have formed on the Earth since Precambrian times and, in the Phanerozoic the content of their organic matter can be variable to significant and economic. In this context, the unconventional hydrocarbon reservoirs of gas shales, which are shales with entrapped natural gas can be particularly informative. Effectively, the carbon in gas shales consists of organic carbon, inorganic carbon mainly in the form of calcite and dolomite formed by cementation and recrystallization as well as the shale gas in the form of hydrocarbons (mainly methane CH<sub>4</sub>), trapped within the pore spaces and microfractures. The carbon isotopic compositions of the different carbon phases can sometimes be distinctive, and can be used to trace the chemical evolution during the transformation of organic matter to hydrocarbons, as well as the physical migration pathways of the hydrocarbons that are strongly influenced by the cementing carbonate minerals.

In this study, we analysed gas shales from different depths of three drill cores of the Bossier-Haynesville formation corresponding to an age of 156-145.5 Ma during the Jurassic. This is an organic, silty calcareous rich mudstone deposited in the tectonically formed East Texas Basin associated with a divergent tectonic plate margin development during the opening of the Gulf of Mexico province [2]. Compositionally, the Kimmeridgian-age Haynesville is significantly more calcareous than the overlying Tithonian-age Bossier shales.

Shales are highly friable and fissile. It is therefore very difficult to get undamaged samples for study. Here, we had access to relatively intact drill core samples of American shales from varying depths. The method of step-wise combustion used in this study enables different components to be released at different temperature steps depending on their host sites in the rocks and their occurrence in the samples (e.g. bound vs. fixed). Consequently, the different components and their isotopic and elemental signatures can be identified.

The main objective of the study was to investigate the carbon isotopic signatures of both the organic and inorganic fractions in shales by combustion without resorting to conventional acid treatment of the samples. Determining the carbon signatures of the organic and inorganic fractions, along with their elemental N/C ratios in these gas shales help in identification of their source(s) that have important implications for their hydrocarbon bearing potential, as well as identify any diagenetic effect in them. The later affects how the carbon is locked in the shales or may have been lost from them. For example, presence or absence of carbonate minerals can affect the porosity and permeability of the shales with implications for the physical entrapment or loss of fluids or volatiles, including hydrocarbons.

#### Abbreviations and symbols

C	Carbon
N	Nitrogen
(T)OM	(Total) organic matter
(T)OC	(Total) organic carbon
(T)IC	(Total) Inorganic carbon
C(1,2,3)	Core (1/2/3)
S-(1,2,...n)(1,2,3)	Sample-(1/2/.....n)Core(1/2/3)
$\delta^{13}\text{C}$	$[\{^{13}\text{C}/^{12}\text{C}_{\text{sample}}/^{13}\text{C}/^{12}\text{C}_{\text{standard}}\} - 1] \times 1000$ where PeeDee Belemnite/PDB is the standard used.
CIA	Chemical index of alteration
CIW	Chemical index of weathering

#### 1.1. Samples and experimental procedures

First the rock samples were extracted from the central portions of the three drill cores to minimise superficial effects of core retrieval and contamination from handling. Five samples from C-1 between depth of 3590 to 3652 m, 7 samples from C-2 between depth of 3540 to 3730 m and 7 samples from C-3 between depth of 3490 to 3520 m were analysed

for C simultaneously with N and nobles gases (to be reported elsewhere). Instrumental blank corrections for both C and N were below significance. Between 5 to 10 mg of samples were combusted from 200 to 1400 °C in incremental steps of 100-200 °C each, using 2 torr of O<sub>2</sub>, introduced in the system under ultra-high vacuum conditions.

C-1 and C-3 are in close proximity with a distance of ~ 8 km separating them while their distance from C-2 is ~220 km. Average mineralogical compositions based on X-ray diffraction analyses shows 34% clay, 32% carbonates and 34% others in C-1, 12% clay, 65% carbonates and 23% others in C-2 and, 46% clay, 14% carbonates and 40% others in C-3. The others include quartz, pyrite, K-feldspar, plagioclase and apatite. While the average content of pyrite (3-4%) and K-feldspar (~ 8%) are comparable between the cores, the quartz (13-25%), plagioclase (1-8%), and apatite (0-2%) are more variable. Alteration due to weathering was assessed based on Hannigan and Brookfield [3]. The CIA and CIW are comparable for C-1 and C-3 with average values of 80 and 69 respectively. C-2 is comparatively less weathered with lower CIA and CIW with averages of 67 and 58 respectively. TOC measured by LECO is 0.3-2.7 wt. % for C-2 with an average of 1.3 wt. % and, 0.7-2.7 wt. % for C-3 with an average of 1.7 wt. %.

Table 1:  $\delta^{13}\text{C}$  and C content ( $\pm 5\%$ ) of bulk samples with their corresponding depth in the cores.  $\text{TOC}_{\text{calc}}$  and  $\text{TIC}_{\text{calc}}$  are calculated TOC and TIC respectively based on bulk values (Appendix A). Elemental analyser (EA) measurement of TOC and TIC are provided where available, for comparison. N.D. not determined; N.A not analysed.

Sample	Depth (m)	C (wt %)	$\delta^{13}\text{C}$ (‰)	N/C (10 <sup>-3</sup> )	$\text{TOC}_{\text{calc}}$ (wt %)	$\text{TIC}_{\text{calc}}$ (wt %)	$\text{TOC}_{\text{EA}}$ (wt %)	$\text{TIC}_{\text{EA}}$ (wt %)
S-1(1)	3629.9	3.9	-18.7±1.1	26±2	2.9	1.0	3.4	1.6
S-2 (1)	3592.2	3.0	-19.7±0.4	34±1	2.3	0.7	1.5	1.1
S-3 (1)	3651	6.0	-14.1±2.9	19±1	3.4	2.6	3.4	1.6
S-4 (1)	3650.8	2.1	-31.8±2.0	28±2	1.5	0.7	N.A	N.A
S-5 (1)	3650.7	1.9	-15.8±2.0	49±3	1.2	0.7	N.A	N.A
S-1(2)	3616	3.6	-15.0±0.7	21±1	1.7	1.9	1.5	1.5
S-2(2)	3664	2.0	-4.5±0.4	29±1	0.2	1.8	N.A	N.A
S-3(2)	3542	0.9	-17.5±7.2	41±2	N.D.	N.D.	N.A	N.A
S-4(2)	3542.2	0.8	-16.3±3.0	36±2	N.D.	N.D.	N.A	N.A
S-5(2)	3726	0.7	-21.2±8.5	53±3	N.D.	N.D.	0.8	0.5
S-6(2)	3615	3.3	-18.2±10.1	21±1	N.D.	N.D.	N.A	N.A
S-7(2)	3646	3.3	-22.1±7.9	20±1	N.D.	N.D.	N.A	N.A
S-1(3)	3491	2.2	-16.3±0.1	42±2	1.2	1.0	N.A	N.A
S-2(3)	3495	2.1	-18.7±0.1	65±3	1.3	0.8	N.A	N.A
S-3(3)	3495.3	2.2	-16.6±1.2	41±2	1.2	1.0	1.1	1.2
S-4(3)	3518	3.5	-18.1±6.1	36±2	2.2	1.5	N.A	N.A
S-5(3)	3540	3.2	-9.5±1.8	53±3	1.0	2.2	N.A	N.A
S-6(3)	3491.4	2.7	-20.9±1.0	21±1	1.9	0.8	N.A	N.A
S-7(3)	3491.5	3.3	-12.9±2.7	20±1	1.4	1.9	1.1	1.0

## 2. Results

The bulk N/C and  $\delta^{13}\text{C}$  of the samples are listed in Table 1. The N/C and  $\delta^{13}\text{C}$  vary extensively between different temperature steps of each sample, from ~ 3 to 300 and ~ -37 to 0 ‰ respectively. Isotopic analyses of C, N and noble gases were conducted simultaneously and the variations are correlated to a first order with microscopic shale component mineral phases. For example, the peak nitrogen release at 400-500 °C (Figs. 1, 2, 3) and corresponding high <sup>40</sup>Ar/<sup>36</sup>Ar ratios, can be related to the decomposition of clay minerals and associated OM as potassium (<sup>40</sup>K<sup>+</sup>) decays to <sup>40</sup>Ar and, being equal in charge and radius can be readily substituted by ammonium (NH<sub>4</sub><sup>+</sup>) ions in clay [4]. The highest  $\delta^{13}\text{C}$  values ~ 600-800 °C with low N/C ratios correspond to the decarbonation breakdown of carbonate

(mostly calcite) and the release of IC as CO<sub>2</sub>. The gas release patterns are in agreement to those observed for standard rock eval pyrolysis experiments, corresponding to S3 (400 °C) and S5 (800 °C) peaks, related to the breakdown of kerogen and carbonate minerals respectively [5].

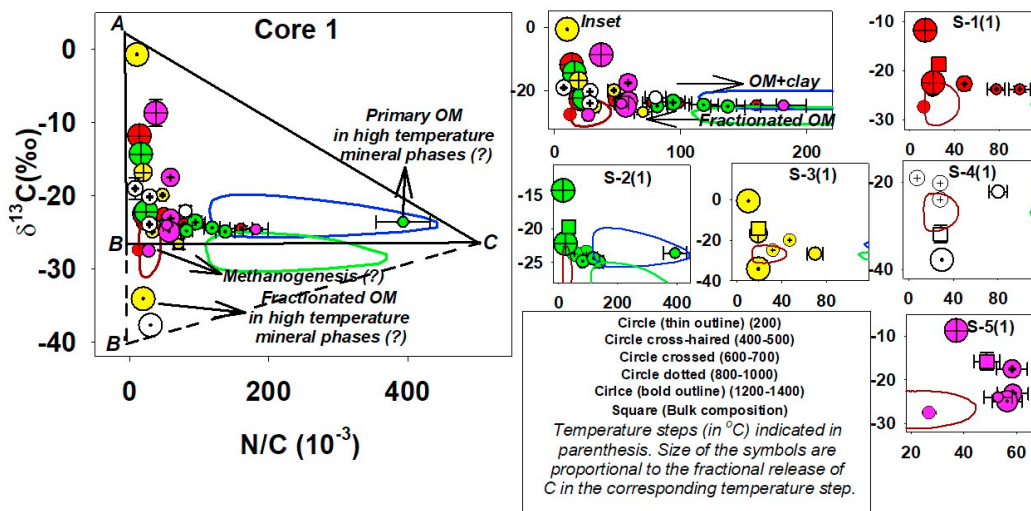


Fig. 1.  $\delta^{13}\text{C}$  vs. N/C for core 1. Symbols as described in legend. Compositional fields for marine, lacustrine and continental OM compositions are marked by blue, green and red solid lines respectively based on [6]. Inset and individual samples in side panels.

### 3. Discussion

#### 3.1. Core comparison

All data can be explained by the mixing between the three components A (inorganic carbon: carbonate), B/B' (OM) and C (clay minerals) (Figs. 1, 2, 3). The OM is predominantly of continental origin, based on measured N/C and  $\delta^{13}\text{C}$  of the samples at the low temperature steps of  $\leq 400$  °C and 400-500 °C, corresponding to discrete OM and OM associated with clay minerals respectively (Figs 1-3). Except for C-2, very few data points plot along the A-C trend reflecting a lack of well-mixed clay + carbonate matrix in C-1 and C-3. The well-cemented matrix of C-2 accounts for its lower porosity as compared to C-3, observed by standard porosity measurements. Also, the higher clay content in both C-1 and C-3 can account for the mixing trends observed between OM and clay /clay+carbonate matrix. Lack of such a trend for C-2 indicates that the OM may not be bound to the clay minerals. This also accounts for its lower TOC. In C-1, the B-C trend line shows the association of OM with the clay minerals, particularly for the samples S-1(1) and S-2(2).

#### 3.2. Primary OM: Mixing and/or fractionation

The range in N/C and  $\delta^{13}\text{C}$  observed in this study, spanning over marine/lacustrine and continental OM composition (Figs. 1, 2, 3), suggests that source characterisation based on  $\delta^{13}\text{C}$  and N/C signatures of bulk shales should be used with caution. The variation in composition can be related to fractionation during processes such as OM degradation or, selective weathering of the labile marine/lacustrine OM leading to preferential preservation of the more resistant continental OM component with depleted  $\delta^{13}\text{C}$  and N/C ratios [7]. Since they are liberated at temperature significantly higher than the breakdown of the clay or carbonate minerals, OC can be locked in minerals such as pyrite and K-feldspars formed during diagenesis and hydrothermal alteration [8]. It is possible that these phases store the unfractionated  $\delta^{13}\text{C}$  and N/C signatures. Alternatively, isolation of the organic molecules in them might have played a role in the fractionation process. Once OC is locked in these relatively resistant minerals they can be isolated from the carbon cycle for a longer period of time as compared to the rest of the OM fraction.

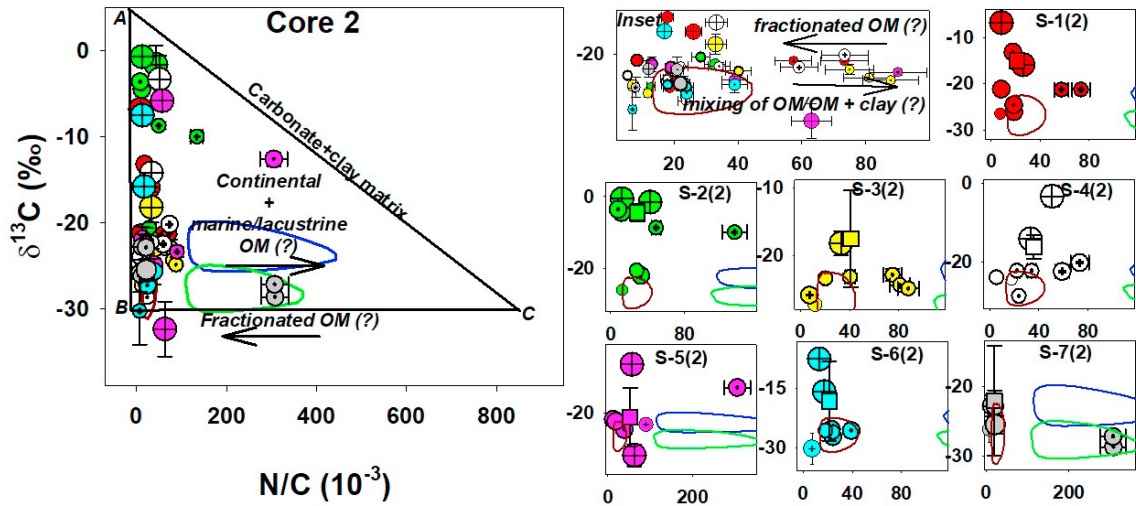


Fig. 2.  $\delta^{13}\text{C}$  vs. N/C for core 2. For details, see Fig. 1.

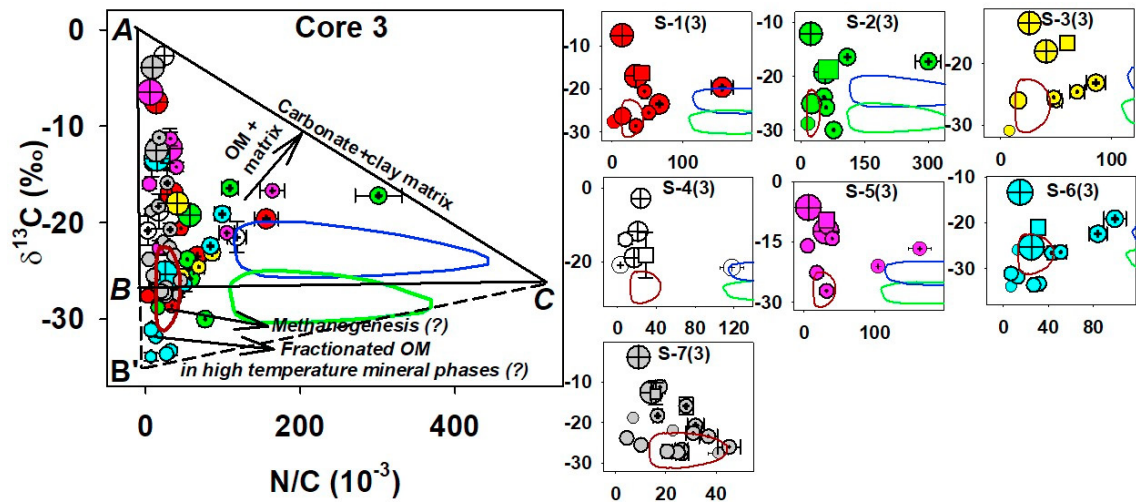


Fig. 3.  $\delta^{13}\text{C}$  vs. N/C for core 3. For details, see Fig. 1.

### 3.3. Assessment of TOC & TIC

Step combustion can also be used for assessing the TOC and TIC in shales without acid treatment (Appendix A). For example, The TOC for C-3 varies from 1.0 to 1.9 wt. % with an average of 1.5 wt. in agreement with observations from LECO measurements. The range of values for TOC in all the three cores lie between 0.2 to 3.4 wt. %, comparable to previous studies from Haynesville and Bossier cores [2]. TOC and TIC are comparable with elemental analyser measurements ( $\pm 15\%$ ) (Table 1), and the differences can be due to heterogeneity related to the variation in the amount of samples used by two methods.

### 4. Conclusions

The conventional  $\delta^{13}\text{C}$  and N/C of shales is not always the best provenance indicator as fractionation can lead to depletion of both  $\delta^{13}\text{C}$  and N/C ratios. Consequently, marine/lacustrine signatures of OM can be altered to that of

continental sources accounting for the range in composition observed during the step-combustion of Haynesville-Bossier gas shales. But, a fraction of the organic molecules (ungraphitised) can be locked up in sulphides and K-feldspars, released at high temperature of 1000-1200 °C post breakdown of clay minerals at 400-500 °C. This locked carbon in the OM trapped by these minerals will be isolated longer from the C cycle. Also, these minerals may be the point to look for primary, unfractionated OM signatures. Step combustion of shales can be used for assessing TOC and TIC without acid treatment.

### Appendix A. Methodology for assessing TOC and TIC

For each sample,  $\delta^{13}\text{C}_{\text{carbonate}}$  and  $\delta^{13}\text{C}_{\text{OC}}$  corresponds to components A and B/B' for its core (Figs. 1, 2, 3). The fraction of IC ( $F_{\text{carbonate}}$ ) and OC ( $F_{\text{OC}}$ ) can be calculated using equation (1), assuming all IC to be in carbonate minerals.  $\delta^{13}\text{C}_{\text{sample}}$  represents the total  $\delta^{13}\text{C}$  (inclusive of measurement from all temperature steps).

$$\delta^{13}\text{C}_{\text{sample}} = \delta^{13}\text{C}_{\text{carbonate}} \times F_{\text{carbonate}} + \delta^{13}\text{C}_{\text{OC}} \times F_{\text{OC}} \quad (1)$$

Since

$$F_{\text{OC}} + F_{\text{IC}} = 1, \quad (2)$$

the TOC and TIC can be calculated from the measured C content in the sample.

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