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Original research paper

Secondary origin of negative carbon isotopic series in natural gas[☆]

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Abstract

The carbon isotopic series of alkane gases were divided into three types: (1) positive carbon isotopic series: $\delta^{13}C$ values increased with increasing carbon numbers among the C_1−C_4 alkanes, which is a typical characteristic for primary alkane gases; (2) negative carbon isotopic series: $\delta^{13}C$ values decreased with increasing carbon numbers among the C_1−C_4 alkanes; and (3) partial carbon isotopic reversal, which had no increasing or decreasing relationship between the $\delta^{13}C$ values and carbon numbers. Negative carbon isotopic series were further divided into primary and secondary origins. The primary is a typical characteristic of abiogenic gases, while the secondary is a result of the secondary alteration imposed on biogenic gases usually observed in over-mature shale gas and coal-derived gas. Previous research has proposed several possible explanations for negative carbon isotopic series of secondary origin, such as secondary cracking, diffusion, and the Rayleigh fractionation of ethane and propane through redox reaction with the participation of transition metal and water at 250−300 °C. After a comparative study, the authors found that the negative carbon isotopic series of secondary origin for both shale gas and coal-derived gas appeared in areas where source rocks (shales) were at an over-mature stage, but not in areas where source rocks (shales) were only at a high-maturity stage. As a result, high maturity (>200 °C) was the main controlling factor for the occurrence of negative carbon isotopic series of secondary origin in thermogenic gases. Within this maturity interval, secondary cracking, diffusion, and Rayleigh fractionation of ethane and propane could happen separately or together.

Keywords: Carbon isotopic series; Negative carbon isotopic series of secondary origin; Shale gas; Coal-derived gas

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1. Introduction

Some distribution regularities are observed in carbon isotopic series of alkane gases: (1) positive carbon isotopic series: $\delta^{13}C$ values increased with increasing carbon numbers among the C_1−C_4 alkanes ($\delta^{13}C_1 < \delta^{13}C_2 < \delta^{13}C_3 < \delta^{13}C_4$), which is a typical character for biogenic alkane gases; (2) negative carbon isotopic series: $\delta^{13}C$ values decreased with increasing carbon numbers among the C_1−C_4 alkanes ($\delta^{13}C_1 > \delta^{13}C_2 > \delta^{13}C_3 > \delta^{13}C_4$); and (3) when the $\delta^{13}C$ values did not increase/decrease with increasing carbon number, this is called a carbon isotopic reversal [1,2].

2. Negative carbon isotopic series

2.1. Negative carbon isotopic series of primary origin

Negative carbon isotopic series of primary origin were observed in abiogenic gases from inclusions in magnetite, found in the volcanically active area of Yellowstone Park in the U.S., the Mid-Ocean Ridge of the North Atlantic, and meteorolite of Australia (Table 1) [3−7].

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2.2. Negative carbon isotopic series of secondary origin

In recent years, large-scale distributed alkane gases (especially shale gas) with negative carbon isotopic series were observed in some over-mature sedimentary basins; i.e., shale gas from the Wufeng–Longmaxi Formation in the southern Sichuan Basin, China (Table 2) [8,9], Fayetteville shale gas from the Arkoma gas field in the U.S. [10], and shale gas from the Horn River gas field in the Western Canadian Sedimentary Basin (Table 3) [11]. These shale gases have high wetness values and are derived from source rocks with high TOC values and maturities (over-mature). As shown in Table 2, the Wufeng–Longmaxi shale gas had wetness and *R*o values of 0.34%–0.77% and >2.2% [12] (or of 2.2%–3.13% [13]), respectively. As shown in Table 3, the Fayetteville shale gas had wetness and *R*o values of 0.86%–1.60% and 2%–3%, respectively. The Horn River shale gas had a wetness value of 0.2% (Table 3). The helium associated with the Wufeng–Longmaxi shale gas had a R/Ra ratio of 0.01–0.04, indicating a crustal origin (Table 2). Thus, the negative carbon isotopic series in these alkane gases were the result of secondary alteration that is different from that of the negative carbon isotopic series of primary origin in abiogenic gases. In this study, it is defined as "negative carbon isotopic series of secondary origin".

Large-scale distributed alkane gases with negative carbon isotopic series were not only observed in over-mature shale gas, but also in over-mature coal-derived gas from the southern Ordos Basin in China (Table 4, Fig. 1). Gas source-rocks in this area are coals and dark mudstones in the Carboniferous Benxi (C_2b), the Permian Taiyuan (P_1t), and the Shanxi (P_1s) formations. Coal seams mainly occur in the Taiyuan and Shanxi formations with the thickness of 2–20 m. The coal measures belong to humic coals with average TOC values and chloroform bitumen "A" of 70.8%–74.7% and 0.61%–0.80%, respectively. Dark mudstones have average TOC

Table 1
Geochemical parameters of abiogenic natural gas with negative carbon isotopic series of primary origin.

Sample location	$\delta^{13}C$/‰, VPDB				References
	CH_4	C_2H_6	C_3H_8	C_4H_{10}	
Magma rock in Khibiny massif Russia	−3.2	−9.1	−16.2		[3]
Mud volcano, Yellowstone Park USA	−21.5	−26.5			[4]
Chimera, Turkey	−11.9	−22.9	−23.7		[5]
Lost City in the North Atlantic Mid-Ocean Ridge	−9.9	−13.3	−14.2	−14.3	[6]
Australian Murchison meteorite	9.2	3.7	1.2		[7]

Table 2
Geochemical parameters of Wufeng–Longmaxi shale gas from the Jiaoshiba and Changning-Weiyuan gas fields in the Sichuan Basin.

Well	Formation	Molecular composition/%					Wetness/%	$\delta^{13}C$‰, VPDB			$^3He/^4He$ (10^{-8})	R/Ra	References
		CH_4	C_2H_6	C_3H_8	CO_2	N_2		CH_4	C_2H_6	C_3H_8			
JY1	O_3w,S_1l	98.52	0.67	0.05	0.32	0.43	0.72	−30.1	−35.5		4.851 ± 0.944	0.03	This study
JY1-2	O_3w,S_1l	98.80	0.70	0.02	0.13	0.34	0.73	−29.9	−35.9		6.012 ± 0.992	0.04	
JY1-3	O_3w,S_1l	98.67	0.72	0.03	0.17	0.41	0.75	−31.8	−35.3				
JY4-1	O_3w,S_1l	97.89	0.62	0.02		1.07	0.65	−31.6	−36.2				
JY4-2	O_3w,S_1l	98.06	0.57	0.01		1.36	0.59	−32.2	−36.3				
JY-2	O_3w,S_1l	98.95	0.63	0.02	0.02	0.39	0.65	−31.1	−35.8		2.870 ± 1.109	0.02	
JY7-2	O_3w,S_1l	98.84	0.67	0.03	0.14	0.32	0.70	−30.3	−35.6		5.544 ± 1.035	0.04	
JY12-3	O_3w,S_1l	98.87	0.67	0.02	0.00	0.44	0.69	−30.5	−35.1	−38.4			
JY12-4	O_3w,S_1l	98.76	0.66	0.02	0.00	0.57	0.68	−30.7	−35.1	−38.7			
JY13-1	O_3w,S_1l	98.35	0.60	0.02	0.39	0.64	0.62	−30.2	−35.9	−39.3			
JY13-3	O_3w,S_1l	98.57	0.66	0.02	0.25	0.51	0.68	−29.5	−34.7	−37.9			
JY20-2	O_3w,S_1l	98.38	0.71	0.02	0.00	0.89	0.74	−29.7	−35.9	−39.1			
JY42-1	O_3w,S_1l	98.54	0.68	0.02	0.38	0.38	0.71	−31.0	−36.1				
JY42-2	O_3w,S_1l	98.89	0.69	0.02	0.00	0.39	0.71	−31.4	−35.8	−39.1			
JY1HF	S_1l	97.22	0.55	0.01		2.19	0.56	−30.3	−34.3	−36.4			[8]
	S_1l	98.34	0.68	0.02	0.10	0.84	0.70	−29.6	−34.6	−36.1			
	S_1l	98.34	0.66	0.02	0.12	0.81	0.69	−29.4	−34.4	−36.1			
	S_1l	98.41	0.68	0.02	0.05	0.80	0.71	−30.1	−35.5				
	S_1l	98.34	0.68	0.02	0.10	0.84	0.70	−30.6	−34.1	−36.3			
JY1-3HF	S_1l	98.26	0.73	0.02	0.13	0.81	0.77	−29.4	−34.5	−36.3			
	S_1l	98.23	0.71	0.03	0.12	0.86	0.74	−29.6	−34.7	−35.0			
Wei201	S_1l	98.32	0.46	0.01	0.36	0.81	0.48	−36.9	−37.9		3.594 ± 0.653	0.03	[8]
Wei201-H1	S_1l	95.52	0.32	0.01	1.07	2.95	0.34	−35.1	−38.7		3.684 ± 0.697	0.03	[9]
Wei202	S_1l	99.27	0.68	0.02	0.02	0.01	0.70	−36.9	−42.8	−43.5	2.726 ± 0.564	0.02	
Ning201-HI	S_1l	99.12	0.5	0.01	0.04	0.30	0.51	−27.0	−34.3		2.307 ± 0.402	0.02	
Ning211	S_1l	98.53	0.32	0.03	0.91	0.17	0.35	−28.4	−33.8	−36.2	1.867 ± 0.453	0.03	
Zhao104	S_1l	99.25	0.52	0.01	0.07	0.15	0.53	−26.7	−31.7	−33.1	1.958 ± 0.445	0.01	
YSL1-H1	S_1l	99.45	0.47	0.01	0.01	0.03	0.48	−27.4	−31.6	−33.2	1.556 ± 0.427	0.01	

Note: Wetness = $\sum(C_2\text{-}C_5)/\sum(C_1\text{-}C_5)$, %.