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# Carbon isotope variations in inorganic carbon materials: Implications for mud volcanic carbon cycling in the northern Tianshan fold zone, Xinjiang, China

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## ABSTRACT

Carbon isotopes of inorganic carbon-bearing materials (gaseous CO<sub>2</sub>, dissolved inorganic carbon (DIC) and solid carbonates) sampled from four mud volcanoes in the northern Tianshan fold zone were investigated to study the mud volcanic carbon cycling process. The analysed carbon isotopes showed <sup>13</sup>C enriched characteristics, the δ<sup>13</sup>C values of CO<sub>2</sub>, DIC and solid carbonates were in the range of 10.99–32.11‰, 17.02–36.22‰, and –7.28–12.40‰, respectively. The <sup>13</sup>C enrichment of CO<sub>2</sub> could be attributed to carbon isotope fractionation during the partial reduction of CO<sub>2</sub> by methanogenic bacteria. The positive δ<sup>13</sup>C values in DIC may be caused by the carbon isotope fractionation during CO<sub>2</sub>-water-rock interactions. The mixture of carbonate precipitates from DIC in the water and carbonate minerals from the host rock resulted in a relatively less positive δ<sup>13</sup>C value in carbonates of the mud samples. The reduction of CO<sub>2</sub> by methanogenic bacteria could be the primary mechanism for the <sup>13</sup>C enrichment of inorganic carbon during the carbon cycling process in the mud volcanic systems in the northern Tianshan fold zone.

## 1. Introduction

Extremely positive isotopic values of carbon in CO<sub>2</sub> (δ<sup>13</sup>C<sub>CO2</sub>), DIC (δ<sup>13</sup>C<sub>DIC</sub>) and carbonates (δ<sup>13</sup>C<sub>carb</sub>) have been widely reported in concentrated evaporated brines and anoxic sediments (Turner and Fritz, 1983; Stiller et al., 1985; Talbot, 1990; Valero-Garcés, 1999; Nakada et al., 2011). For examples, the extremely high δ<sup>13</sup>C value up to +13.4‰ has been observed in carbonates from Lake Kivu in Africa (Hassan, 2014). In Lake Apopka, Florida, the δ<sup>13</sup>C values in the pore water are +26.4‰ (Gu et al., 2004) and positive δ<sup>13</sup>C values as high as +23.6‰ are reported in soil-emitted CO<sub>2</sub> from biogas residues (Chen et al., 2011a,b). To explain the high <sup>13</sup>C content in CO<sub>2</sub>, DIC and carbonates, models proposed in the literature include the reduction of CO<sub>2</sub> by methanogenic bacteria (Jin et al., 2008), the reduction of organic matter by methanogenic bacteria (Zyakun, 1996), CO<sub>2</sub> outgassing from the liquid phase (Chen et al., 2011a,b), CO<sub>2</sub> dissolution and carbonate precipitation (Rovira et al., 2008), phytoplankton photosynthesis (Zhu

et al., 2013) and evaporation (Hassan, 2014). However, these models require specific geological settings or environments.

The carbon isotope composition of CO<sub>2</sub> from mud volcanoes in Azerbaijan (Bonini et al., 2013), Indonesia (Mazzini et al., 2007), Italy (Tassi et al., 2012), India (Chaudhuri et al., 2012), Japan (Etiope et al., 2011) and China (Chao et al., 2010; Nakada et al., 2011; Wan et al., 2013) also have extremely positive δ<sup>13</sup>C<sub>CO2</sub> values > +30.0‰ (Etiope et al., 2011; Bonini et al., 2013; Ray et al., 2013), as a result of the oxidative and fermentative destruction of saturated hydrocarbons (Zartman et al., 1961; Wilhelmset al., 2001; Feyzullayev and Movsumova, 2010). Extremely positive δ<sup>13</sup>C (up to +33.3‰) of CO<sub>2</sub> from the Dushanzi (DSMV) and Aiqigou (AQMV) mud volcanoes in the northern Tianshan fold belt are reported, and the mechanism has been briefly described (Nakada et al., 2011; Wan et al., 2013). Enriched <sup>13</sup>C has been reported widely in mud volcanoes worldwide, however there are few detailed reports which describe the origins of the <sup>13</sup>C enrichment. A thorough investigation of the origin of <sup>13</sup>C enrichment in

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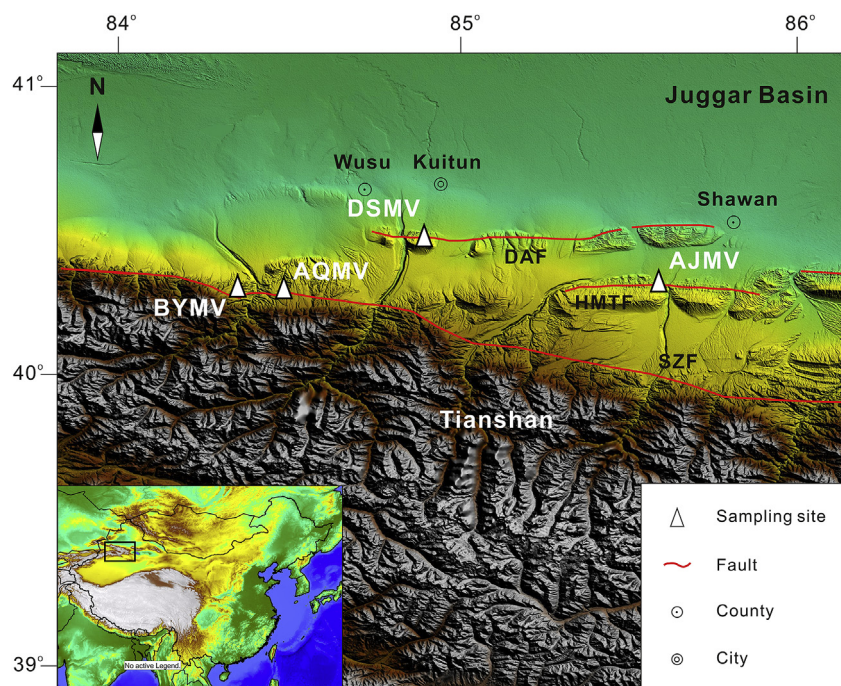


Fig. 1. Regional map of the studied area. Inset map shows the location of the studied region in NW China. (DAF: Dushanzi-Anjihai fault, HMTF: Huoerguosi-Manasi-Tugulu fault, SZF: southern margin of the Junggar Basin fault).

carbon materials from mud volcanoes is crucial in understanding the carbon cycling processes in mud volcanic systems.

The aim of this study is to determine the  $^{13}\text{C}$  enrichment in inorganic carbon materials ( $\text{CO}_2$ , DIC and carbonates) sampled from four mud volcanoes and to determine the geochemical source, thus providing insight into the carbon cycling process in the northern Tianshan fold belt, NW China.

## 2. Geological setting

The northern Tianshan fold zone, tectonically located at the transitional region between the northern Tianshan Mountains and the Junggar Basin, consists of three NWW-SEE fold belts distributed along the southern margin of the Junggar Basin, fold belts, from south to north. These fold zones are intersected by several parallel thrust faults (Zheng et al., 2010a, 2010b; Dai et al., 2012). There are four mud volcanic groups which occur on the northern Tianshan fold zone, named Anjihai (AJMV), Dushanzi (DSMV), Aiqigou (AQMV) and Baiyanggou (BYMV) from east to west (Yang et al., 2014) (Fig. 1).

The AJMV, located 40 km south of the Shawan County (Fig. 1), has one active crater with a diameter of  $\sim 1$  m containing muddy water with a slightly oily appearance (Fig. 2a). The frequency of gas bubbles release is approximately 60 times per minute, with a maximum bubble diameter of  $\sim 5$  cm. The DSMV, located 1 km southwest of the Dushanzi District (Fig. 1), has two active craters on the Dushanzi hill. Viscous muddy water flows out of the northern crater and forms a mud cone with a diameter of  $\sim 8$  m at the bottom and height of  $\sim 2$  m (Fig. 2b). Gas bubbles are released at a frequency of  $\sim 90$  times per minute with a maximum bubble diameter of  $\sim 5$  cm. The BYMV is located 43 km south of Wusu City (Fig. 1) with dozens of craters ( $> 20$  over  $1 \text{ km}^2$ ) which produce muddy water and gas. The smallest crater is characterized by a diameter of  $\sim 3$  cm and the largest crater has a diameter of  $\sim 5$  m. Due to the small amount of erupted muddy water, only a few spray-mud-cones craters have been formed and oil seepages have been observed in these craters (Fig. 2c). The most active mud crater has a bubbling frequency of  $> 120$  times per minute with a maximum bubble diameter of  $\sim 10$  cm. Twin volcanic spray-mud-cone craters occur in the AQMV

area, approximately 80 km south of Wusu City, which are  $\sim 15$  m in height. The crater in the southwest is extinct, but the northeast crater is active has a diameter of approximately 5 m. Muddy water discharged from the crater is cold and the surface is a silver and grey colour (Fig. 2d). It has a bubbling frequency of  $> 150$  times per minute with a maximum bubble diameter of  $\sim 25$  cm (Du et al., 2013; Chen et al., 2014).

The sedimentary sequences in the northern Tianshan fold belt from the Permian to Recent age are up to 16 km in thickness (Deng, 2000). The Permian, Triassic, Jurassic and Cretaceous strata consist primarily of sandstone and mudstone. The Tertiary formations consist primarily of mudstone, limestone, sandstone and conglomerate. The Quaternary formations consist of sandy loess and gravel deposits (Bai, 2008). Red Tertiary sandstone and conglomerate in the core part of the Dushanzi anticline have been bleached by oil and gas from the mud volcanic craters and their original colour of red have changed to yellow, green, grey and black. This phenomenon could be explained as a typical bleaching effect of hydrocarbons on the host rocks in a mud volcanic area (Zheng et al., 2010a, 2010b).

## 3. Methods

Gas, water and mud samples were collected from the craters of AJMV, DSMV, BYMV and AQMV. Gas samples were collected by placing a cylindroid glass bottle (500 mL in volume, 0.5 cm thickness, made of soda-lime glass) upside down, which was pre-filled with water from each sampling site and connected with a rubber tube to an inverted funnel fully sunk into the mud at the crater site (Wang, 1989). Gas released from the mud volcanoes passed through a tube and filled the soda-lime bottles, replacing the water inside the bottle, which was then sealed onsite using solid trapezoidal rubber plugs and adhesive plaster (Du et al., 2006; Dai et al., 2012). Three bottles of gas were collected for the analysis of gas composition, isotope ratios (He and Ne) and carbon isotopes. Water samples collected from the mud volcanoes were filtered using a membrane (hydrophilic PTFE) of  $0.45 \mu\text{m}$  pore size to remove the suspended solids, and then placed in 250 mL plastic bottles, sealed with corks and adhesive plastic. The gas in the bottles

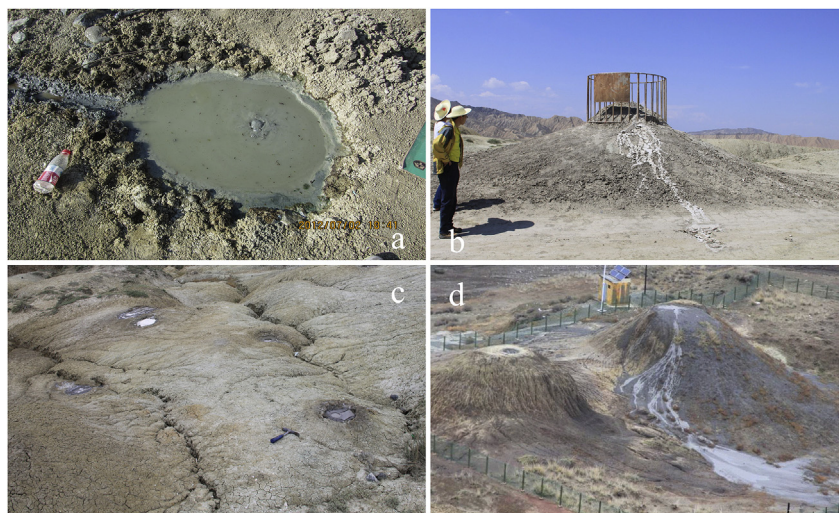


Fig. 2. Photos of the mud volcanoes in this study. a) AJMV; b) DSMV; c) BYMV; d) AQMV.

had been exhausted completely onsite. DIC in the water samples was precipitated out on site, carbonates in the water were precipitated out using barium hydroxide added to the sample bottle. The carbonate precipitant was collected and dried in an oven at 45 °C for 48 h, and then placed into 10 mL tubes. Mud samples were collected and fully sealed in 15-mL plastic bottles on site. Mud samples were also dried in an oven at 45 °C for 48 h before analysing.

The water temperature (T) and  $\text{HCO}_3^-$  concentrations were measured on site. The temperature was measured using a digital thermometer with an error of  $\pm 1\%$ , the  $\text{HCO}_3^-$  concentrations were determined using standard titration procedures with a ZDJ-100 potentiometric titrator (reproducibility within  $\pm 2\%$ ). The concentrations of cations ( $\text{Na}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$ ) and anions ( $\text{Cl}^-$  and  $\text{SO}_4^{2-}$ ) in the water samples were determined using Dionex ICS-900 ion chromatography in the Seismic Fluid Laboratory of Institute of Earthquake Science, China Earthquake Administration, with a reproducibility within  $\pm 2\%$ . Gas compositions and isotopic ratios were measured in the Laboratory of Gas Geochemistry (Lanzhou, China), Institute of Geology and Geophysics, Chinese Academy of Sciences. Gas compositions were determined using mass spectrometer MAT 271 characterized by relative standard deviations of  $< 5\%$ ,  $\delta\text{D}$  and  $\delta^{18}\text{O}$  in the water was measured using a Picarro L1102 mass spectrometer. The errors were 0.5‰ for  $\delta\text{D}$  and 0.1‰ for  $\delta^{18}\text{O}$ ,  $^3\text{He}/^4\text{He}$  (reported as R/Ra,  $\text{Ra} = 1.4 \times 10^{-6}$ ) and  $^4\text{He}/^{20}\text{Ne}$  were determined using mass spectrometry (VG 5400),  $\delta^{13}\text{C}$  values were analysed using a gas chromatography-pyrolysis isotope ratio mass spectrometer (HP6890-Delta Plus XL) with errors of  $\pm 0.3\%$ . Analysis of all samples were completed within 30 days from sampling.

#### 4. Results

The geochemical parameters of inorganic carbon from the mud volcanoes in this study are listed in Table 1. The concentrations of  $\text{CO}_2$ ,  $\text{CH}_4$  and  $\text{C}_2\text{H}_6$  in gas samples from the mud volcanoes were in the range of 1.1–18.0%, 59.1–94.7% and 2.8–10.1%, respectively.

The concentration of  $\text{HCO}_3^-$  in water samples was 800.5–5838.6  $\text{mg L}^{-1}$ , much higher than that reported for the hot springs in northern Tianshan fold belt ( $< 20 \text{ mg L}^{-1}$ ) (Chen et al., 2014). The concentrations of  $\text{Cl}^-$  were 1131.1–11022.8  $\text{mg L}^{-1}$ , and  $\text{Na}^+$  2085.8–8630.2  $\text{mg L}^{-1}$ . The temperature of the water emitted from the four mud volcanoes was 7.4–30.8 °C.

The  $^3\text{He}/^4\text{He}$  and  $^4\text{He}/^{20}\text{Ne}$  ratios of the gas samples varied from 0.0200 to 0.7780 and 4.0 to 2362.7, respectively. The  $\delta\text{D}$  values of water samples from the mud volcanoes were  $-97.56$  to  $-52.78\%$ . The

$\delta^{18}\text{O}$  values of water samples were  $-8.16$ – $-4.38\%$ .

All inorganic carbon (gas  $\text{CO}_2$ , DIC and carbonates) sampled from the four mud volcanoes showed  $^{13}\text{C}$  enriched characteristics. The  $\delta^{13}\text{C}$  values of  $\text{CO}_2$  for the gas samples from the mud volcanoes were 10.99–32.11‰, being comparable with that of DIC in water samples (17.02–36.22). DIC in water samples from the AQMV\* had the most positive  $\delta^{13}\text{C}$  of 32.11‰, and  $\delta^{13}\text{C}$  values of the carbonates in the mud samples were less positive ( $-7.28$ – $12.40\%$ ). The  $\delta^{13}\text{C}$  values of  $\text{CH}_4$  for the gas samples varied from  $-46.29$  to  $-35.12\%$ .

#### 5. Discussion

Enrichment in  $^{13}\text{C}$  from  $\text{CO}_{2(\text{g})}$ , DIC and carbonates from the four mud volcanoes was found (Table 1). Possible origins for the  $^{13}\text{C}$  enrichment are proposed below, with a discussion on the carbon cycling process in the mud volcanic systems.

##### 5.1. Origin of enriched $^{13}\text{C}$ in the $\text{CO}_2$ gas

The  $\text{CO}_2$  gas from the four mud volcanoes had  $\delta^{13}\text{C}$  values in the range of 10.99–32.11‰ (Table 1), which were more positive compared to reported  $\delta^{13}\text{C}$  values of  $\text{CO}_2$  gas in natural environments ( $< +0.2\%$ ) (Chen and Wang, 2004). The input of mantle-derived  $\text{CO}_2$  and the fractionation of carbon isotopes during the reduction of  $\text{CO}_2$  by methanogenic bacteria which can exist at depths  $> 2$  km have been proposed to cause enrichment of  $\delta^{13}\text{C}$  in  $\text{CO}_2$  gas in some natural environments (Blundy et al., 1991; Zyakun, 1996; Zhang and Duan, 2009; Nakada et al., 2011; Etiopie et al., 2011).

The reported  $\delta^{13}\text{C}$  of mantle-derived  $\text{CO}_2$  sampled from hydrocarbon drillings is  $\leq +28\%$  (Du, 1991). The  $^3\text{He}/^4\text{He}$  and  $^4\text{He}/^{20}\text{Ne}$  of gas from the mud volcanoes were 0.0200–0.7780 (R/Ra) and 4.0–2362.7, respectively. These values are clustered in the “crust” values on the cross plot of  $^3\text{He}/^4\text{He}$  and  $^4\text{He}/^{20}\text{Ne}$  (Fig. 3), with the exception of gas from the AJMV and DSMV sampled on June 26, 2012 which was located between “crust” and “air”. These were considered to be precursors for the Xinyuan-Hejing  $M_{\text{S}}6.6$  earthquake on 30 June 2012 due to the interfusion of gas from a shallower reservoir (Dai et al., 2012). This data suggests that  $\text{CO}_2$  gases from the four mud volcanoes could be primarily crust-derived, with small amounts of gas from the mantle (Du et al., 2013; Zhang et al., 2016).

The cross-plot of  $\text{C}_1/(\text{C}_2 + \text{C}_3)$  versus  $\delta^{13}\text{C}_{\text{CH}_4}$  suggests that gases from the mud volcanoes fall into the thermogenic zone (Fig. 4). The high  $\text{CH}_4$  content (59.1–94.7%) and values of  $\delta^{13}\text{C}_1$  ( $-46.29$  to  $-35.12\%$ ) and  $\delta^{13}\text{C}_2$  ( $-23.0$  to  $-20.5\%$ ) (Table 1) indicate a

**Table 1**  
Geochemical parameters of the ejecta from the mud volcanoes in the Northern Tianshan Fold zone.

Site	Date	T (°C)	Gas composition (vol.%)				C <sub>1</sub> /(C <sub>2</sub> +C <sub>3</sub> )	δ <sup>13</sup> C (‰)	Ion composition (mg L <sup>-1</sup> )							<sup>4</sup> He/ <sup>20</sup> Ne	<sup>3</sup> He/ <sup>4</sup> He (R/Ra)	δD (‰)	δ <sup>18</sup> O (‰)		
			CO <sub>2</sub>	CH <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	C <sub>3</sub> H <sub>8</sub>			Na <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Cl <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	HCO <sub>3</sub> <sup>-</sup>							
AJH-1	6.2012	22.4	2.5	59.1	2.8	0.0	21.1	-36.77	31.64	-	-	4595.5	13.9	108.9	6974.3	3.4	2075.2	7.8	0.4518	-73.27	-5.13
AJH-2	7.2012	30.8	6.1	87.6	4.1	0.0	21.4	-37.95	32.11	-	-	5654.8	25.1	106.7	7199.1	3.6	5838.6	277.1	0.0392	-69.41	-5.17
AJH-3	10.2012	11.1	11.8	74.4	3.1	0.0	24.3	-35.12	32.00	36.22	11.45	5881.3	25.3	119.4	6899.2	0.7	5821.3	121.8	0.0570	-74.34	-5.34
AJH-4	5.2013	22.1	3.6	77.7	3.8	0.0	20.3	-36.00	30.29	32.24	6.06	8630.2	29.8	166.1	11022.8	0.0	1670.4	124.6	0.0430	-72.75	-5.18
AJH-5	9.2013	22.0	3.1	79.5	4.4	0.0	18.1	-36.85	32.09	32.61	5.30	5832.6	26.8	115.8	7211.2	0.0	1885.6	148.8	0.0550	-73.08	-5.67
AJH-6	6.2014	24.3	3.8	78.6	3.9	0.0	20.2	-36.91	30.22	34.25	10.95	6958.5	27.9	123.3	9649.4	4.3	902.1	153.9	0.0420	-74.32	-5.54
DSZ-1	6.2012	24.9	3.9	88.1	4.4	0.0	19.9	-42.58	21.75	-	-	5460.0	66.7	142.4	8405.9	0.0	2781.4	4.0	0.7780	-52.78	-4.91
DSZ-2	7.2012	22.2	4.2	88.8	4.4	0.0	20.1	-42.57	19.89	-	-	5594.9	65.5	155.9	9059.7	0.0	2871.4	465.2	0.0442	-58.68	-4.78
DSZ-3	10.2012	7.4	7.6	88.0	4.4	0.0	19.7	-42.94	14.87	21.08	-4.77	5623.8	40.0	144.7	8621.1	0.0	1607.7	134.2	0.0460	-65.38	-5.07
DSZ-4	5.2013	14.9	3.4	87.6	4.6	0.0	19.0	-41.90	15.20	25.89	-2.03	5363.4	89.1	142.3	9930.7	0.0	1878.8	134.0	0.0370	-67.47	-5.02
DSZ-5	9.2013	16.0	1.7	87.5	5.0	0.0	17.5	-41.36	26.24	26.75	-1.64	5186.9	68.9	96.6	10239.9	13.3	1000.4	156.0	0.0460	-60.88	-5.13
DSZ-6	6.2014	20.1	4.5	85.4	4.0	0.0	21.4	-42.67	24.78	25.63	-3.44	4828.9	81.5	133.4	8861.3	0.5	800.5	230.0	0.0440	-65.12	-4.99
BYG-1	6.2012	25.0	1.6	85.2	9.9	0.0	8.6	-45.65	15.78	-	-	4161.1	7.5	49.4	4725.9	122.3	4564.0	1345.0	0.0195	-71.64	-5.09
BYG-2	7.2012	23.9	2.3	94.7	9.0	0.0	10.5	-46.03	15.20	-	-	4347.3	7.3	55.6	4881.9	121.1	4784.1	297.9	0.0268	-66.53	-4.38
BYG-3	10.2012	13.2	8.0	85.2	10.0	0.0	8.5	-46.29	10.99	17.74	-6.42	4181.3	14.0	50.9	3865.1	81.4	4465.0	160.2	0.0240	-72.51	-5.13
BYG-4	5.2013	20.2	2.3	85.3	9.8	0.0	8.7	-45.80	14.70	18.35	-3.59	4114.8	10.5	49.3	4222.6	90.3	4343.2	182.0	0.0220	-69.89	-4.53
BYG-5	9.2013	17.8	1.1	85.3	10.0	0.0	8.5	-45.84	13.93	17.02	-5.01	4866.0	12.0	60.6	5628.0	78.8	4806.4	190.4	0.0260	-71.01	-4.87
BYG-6	6.2014	24.9	2.4	80.1	10.1	0.0	7.9	-45.62	14.63	17.43	-7.28	4660.6	14.0	56.2	5663.7	18.7	4268.3	170.5	0.0230	-70.97	-5.06
AQG-1	6.2012	16.5	15.5	78.2	4.8	0.0	16.3	-41.12	29.20	-	-	2085.8	41.1	69.0	1397.9	109.4	3462.0	2362.7	0.0170	-85.39	-7.26
AQG-2	7.2012	20.5	15.1	76.6	5.1	0.0	15.0	-41.24	29.00	-	-	2085.9	41.4	69.2	1407.9	111.2	4098.1	131.9	0.0787	-90.03	-7.40
AQG-3	10.2012	10.4	16.7	76.6	5.1	0.0	15.0	-42.12	28.83	30.94	8.12	2493.2	24.6	82.2	1463.8	112.9	4114.4	209.2	0.0210	-89.18	-7.42
AQG-4	5.2013	18.0	17.9	75.3	5.1	0.0	14.7	-40.03	28.40	33.26	12.4	2110.8	27.5	54.0	1131.1	100.0	3611.2	503.0	0.0220	-97.56	-8.16
AQG-5	9.2013	16.0	14.0	77.5	5.3	0.0	14.6	-37.95	26.93	30.12	10.65	2344.6	23.0	82.2	1207.8	100.0	4733.6	430.8	0.0290	-82.55	-7.67
AQG-6	6.2014	21.8	18.0	77.4	5.4	0.1	14.1	-41.02	27.62	31.11	9.36	2128.1	41.4	65.5	1159.0	101.8	5032.2	279.9	0.0200	-80.76	-7.43

The “-”: not detected. <sup>3</sup>He/<sup>4</sup>He (R/Ra) was the measured <sup>3</sup>He/<sup>4</sup>He ratio divided by that of air (Ra = 1.4 × 10<sup>-6</sup>).

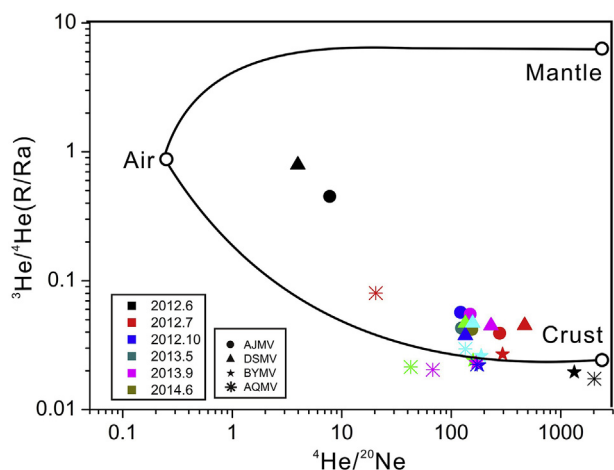


Fig. 3. Plots of  $^3\text{He}/^4\text{He}$  (R/Ra)- $^4\text{He}/^{20}\text{Ne}$ . End members in the plots are: R/Ra<sub>air</sub> = 1,  $^4\text{He}/^{20}\text{Ne}_{\text{air}}$  = 0.254, R/Ra<sub>mantle</sub> = 8,  $^4\text{He}/^{20}\text{Ne}_{\text{mantle}}$  = 1000, R/Ra<sub>crust</sub> = 0.02,  $^4\text{He}/^{20}\text{Ne}_{\text{crust}}$  = 1000 (Sano and Wakita, 1985).

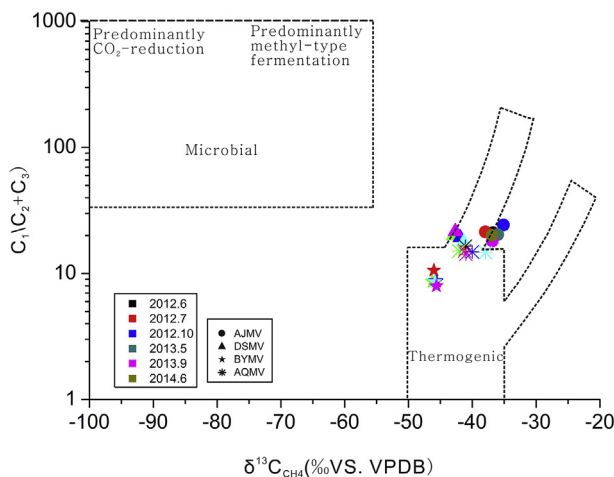


Fig. 4. Relationship between  $C_1/(C_2 + C_3)$  and  $\delta^{13}\text{C}_{\text{CH}_4}$  values of the gas samples.

thermogenic gas derived from the hydrocarbon reservoir approximately 3600 m beneath the surface (Nakada et al., 2011). Therefore,  $\text{CO}_2$  from the mud volcanoes could be the result of hydrocarbon degradation (Dai et al., 2012; Wan et al., 2013).  $\delta^{13}\text{C}$  of organic-derived  $\text{CO}_2$  from hydrocarbon degradation is usually  $< -10\text{‰}$  (Dai et al., 2012). Therefore, large isotope fractionations may have occurred during the upwelling of  $\text{CO}_2$  through mud volcanic vents and responsible for the  $^{13}\text{C}$  enrichment in  $\text{CO}_2$  found in this study.

Carbon isotope fractionation in the process of the reduction of  $\text{CO}_2$  by methanogenic bacteria is one of the possible genesis for  $^{13}\text{C}$  enrichment of  $\text{CO}_2$  in natural environments (Zyakun, 1996; Nakada et al., 2011). Methanogenic bacteria living in a  $\text{CO}_2$  and  $\text{H}_2$  environment can produce  $\text{CH}_4$  under anaerobic conditions. This process, equations (1) and (2), could induce carbon isotopic fractionation which leads to a continuous  $\delta^{13}\text{C}$  enrichment in the residual  $\text{CO}_2$  and reduction of  $^{13}\text{C}$  in produced  $\text{CH}_4$  (Zyakun, 1996; Nakada et al., 2011; Etiopie et al., 2011; Bonini et al., 2013; Ray et al., 2013; Hassan, 2014).



$$\delta^{13}\text{C}_{(\text{CO}_2)_f} = \delta^{13}\text{C}_{(\text{CO}_2)_0} + 1000f^{(1-\alpha)} - 1000 \quad (2)$$

Where:  $\alpha = 1.051$  for  $\text{CO}_2 \rightarrow \text{CH}_4$ ,  $\delta^{13}\text{C}_{(\text{CO}_2)_0}$  is the  $\delta^{13}\text{C}$  of  $\text{CO}_2$  substrate,  $\delta^{13}\text{C}_{(\text{CO}_2)_f}$  is the  $\delta^{13}\text{C}$  of residual  $\text{CO}_2$ , and  $f$  is the composition (%) of residual  $\text{CO}_2$ .

The  $\delta^{13}\text{C}$  values of residual  $\text{CO}_2$  from this reduction process can reach 32.7‰ (Chen et al., 2011a,b), which is slightly higher than that of  $\text{CO}_2$  discharged from the sampled four mud volcanoes (10.99–32.11‰) (Table 1). The concentration of  $\text{CO}_2$  gas between 1.1 and 18.0% (Table 1) and several species of methanogenic bacteria have been observed in these mud volcanoes, which are characterized by a methanosarcinales content to up to 86% (Yang et al., 2012), and  $\text{H}_2$  could be continuously produced as a result of hydrocarbon degradation and biochemical reactions under anaerobic conditions (Liu et al., 2014). Consequently, the kinetic isotope fractionation during the reduction of  $\text{CO}_2$  by methanogenic bacteria could be the primary origin for the  $^{13}\text{C}$  enrichment in the  $\text{CO}_2$  from the mud volcanoes. The same process could have lowered  $\text{CO}_2$  concentrations and produced  $\text{CH}_4$  depleted in  $^{13}\text{C}$ , leaving residual  $\text{CO}_2$  enriched with  $^{13}\text{C}$ . The  $\text{CO}_2$  content in the gas samples from the four mud volcanoes were relatively low, ranging 1.1–18.0%, indicating no correlation with  $\delta^{13}\text{C}$  of the  $\text{CO}_2$  gases (Table 1). This may indicate different  $\delta^{13}\text{C}$  of  $\text{CO}_2$  at the beginning of  $\text{CO}_2$  reduction or different reduction rates of  $\text{CO}_2$  reduction between different mud volcanoes.

$\text{CH}_4$  is the primary component of gas sampled from the four mud volcanoes (with concentration ranging 59.1–94.7%), with  $\delta^{13}\text{C} - 46.29 - 35.12\text{‰}$  comparable to those of  $\text{CH}_4$  from oil wells ( $-41.1 - 25.6\text{‰}$ ) in the study area (Du et al., 2013; Song et al., 2014) (Table 1), and which is a thermogenic gas (Dai et al., 2012; Wan et al., 2013), suggesting that the  $\text{CH}_4$  deriving from the reduction of  $\text{CO}_2$  by methanogenic bacteria should have made a subordinate contribution to the composition of  $\text{CH}_4$  from the mud volcanoes.

### 5.2. Mechanism of enriched $^{13}\text{C}$ in the DIC in water

Enriched  $^{13}\text{C}$  in DIC of the water samples was determined to be 17.02–36.22‰ (Table 1) and had a strong positive correlation with those in  $\text{CO}_2$  gas from the mud volcanoes ( $Y = 0.81X + 7.95$ ,  $R^2 = 0.88$ ) (Fig. 5). This could indicate that the DIC could have primarily transformed from  $\text{CO}_2$  in the mud volcanoes.

All water samples from the mud volcanoes were enriched with  $\text{HCO}_3^-$ ,  $\text{Cl}^-$  and  $\text{Na}^+$ , at concentrations of 800.5–5838.6  $\text{mg L}^{-1}$ , 1131.1–11022.8 and 2085.8–8630.2  $\text{mg L}^{-1}$ , respectively (Table 1). The chemical types of these water samples were  $\text{Na-ClHCO}_3$  and  $\text{Na-HCO}_3\text{Cl}$  (Fig. 6). The concentration of  $\text{Na}^+$  correlates strongly and positively with those of  $(\text{HCO}_3^- + \text{Cl}^-)$  ( $Y = 1.37X + 3019.70$ ,  $R^2 = 0.80$ ) (Fig. 7). The host rock in which the four mud volcanoes occur was red Tertiary sandstone, which had been deposited in a semiarid climate and contained halite ( $\text{NaCl}$ ). Extensive water-rock interaction between the groundwater and sandstone may have occurred

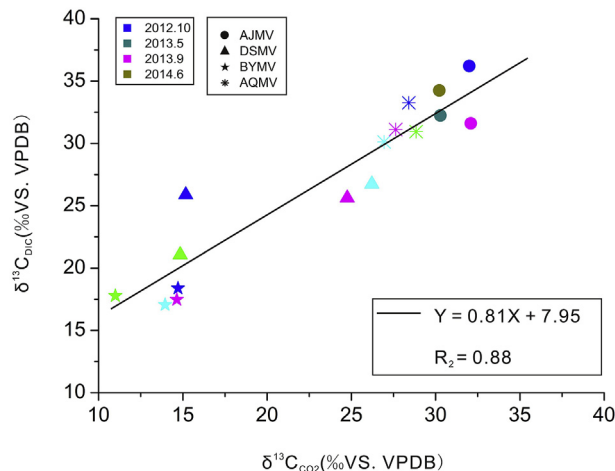


Fig. 5. Plot of  $\delta^{13}\text{C}$  values of DIC in the water samples versus  $\delta^{13}\text{C}$  values of  $\text{CO}_2$  in the gas samples.

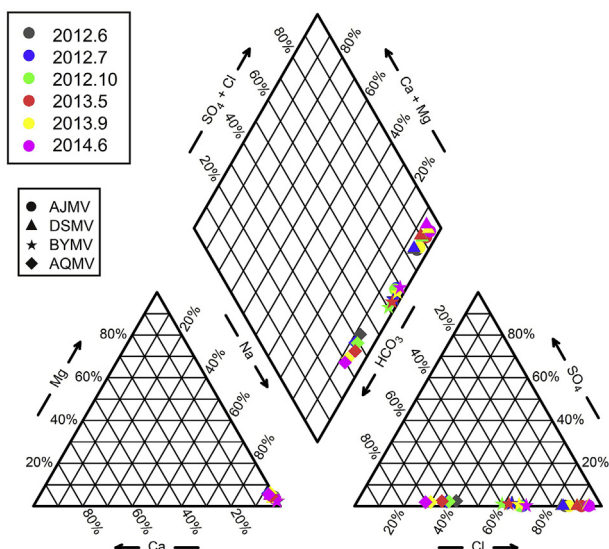


Fig. 6. Piper diagram of the water samples from the AJMV, DSMV, BYMV and AQMV.

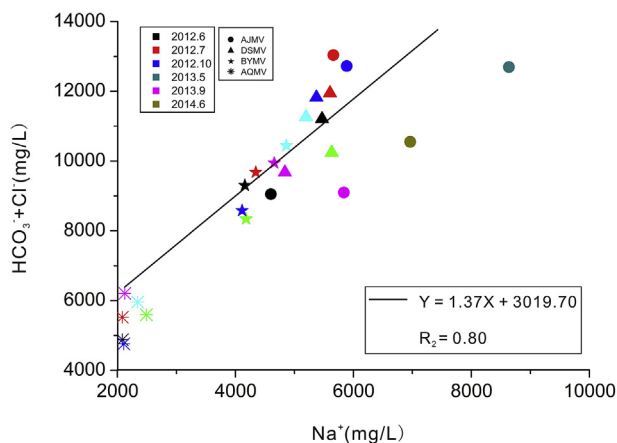


Fig. 7. The plot of  $\text{Na}^+$  vs  $\text{HCO}_3^- + \text{Cl}^-$ . Dashed line: water samples from the AJMV, DSMV, BYMV and AQMV.

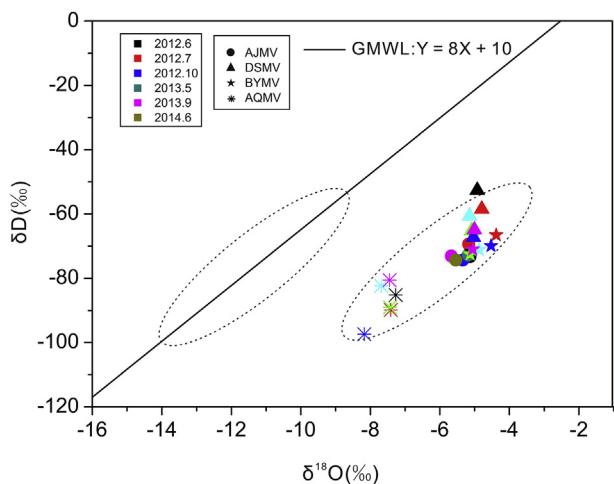
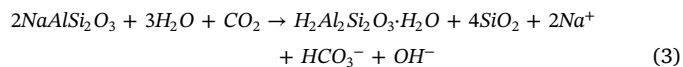


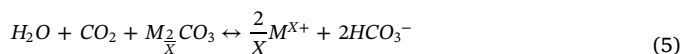
Fig. 8. Plots of  $\delta\text{D}$  and  $\delta^{18}\text{O}$  values of the water samples. Dashed line: the global meteoric water line (GMWL); solid ellipse: field of meteoric water in northern Xinjiang (Wei and Gasse, 1999); dashed ellipse: field including water samples from the AJMV, DSMV, BYMV and AQMV parallel to the field of meteoric water in northern Xinjiang.

in the mud volcanic systems, resulting in horizontal movement of  $\delta^{18}\text{O}$  values from the GMWL on the  $\delta^{18}\text{O}$ - $\delta\text{D}$  plot (Fig. 8) (Chen et al., 2014). Water samples from the AJMV, DSMV, BYMV and AQMV fall into an elliptical zone parallel to the zone of meteoric water in northern Xinjiang, on the  $\delta^{18}\text{O}$ -D plot (Fig. 8).

Laboratory experiments indicated that an injection of  $\text{CO}_2$  into groundwater can accelerate the water-rock interaction (Ueda et al., 2005; Liu et al., 2012). Therefore, the water-rock interactions which occurred in the mud volcanic systems could have been accelerated by  $\text{CO}_2$  gas upwelling from the mud volcanoes, which can be expressed by equations (3) and (4) (Chen et al., 2015).



Previous studies demonstrate that carbon isotope fractionation in the process of  $\text{CO}_2$ -water-sandstone interaction (i.e. equation (3)) can result in an increase of  $\delta^{13}\text{C}$  by +9.0‰ for DIC at 15 °C (Rovira and Vallejo, 2008), and 0.1–16.3‰ at 25 °C (Rustad et al., 2008). The temperature of the water from the four mud volcanoes ranged from 7.4 °C to 30.8 °C. Therefore,  $\text{CO}_2$ -water-sandstone interactions in the mud volcanic system



could result in 0.1–16.3‰ higher  $\delta^{13}\text{C}$  values in DIC, compared to those in  $\text{CO}_2$  gas.  $\delta^{13}\text{C}$  values of  $\delta^{13}\text{C}$  0.51–10.69‰ higher were observed in this study (Table 1) suggesting a strong  $\text{CO}_2$ -water-sandstone interaction could have occurred in the four mud volcanoes, which may be responsible for the positive  $\delta^{13}\text{C}$  values in DIC from the mud volcanic system.

### 5.3. Mechanism of enriched $^{13}\text{C}$ in carbonates in the mud

$\delta^{13}\text{C}$  values of precipitated carbonates extracted from the mud samples were -7.28 - 12.40‰ and had a strong positive correlation with  $\delta^{13}\text{C}$  values of the DIC ( $Y = 1.03X + 25.04$ ,  $R^2 = 0.85$ ) (Fig. 9). This could indicate that carbonate precipitation of DIC in water could be an important origin for carbonates in the mud samples from the mud volcanoes.

Previous studies report that the chemical reaction  $\text{HCO}_3^- \rightarrow \text{CaCO}_3$  during carbonate precipitation of DIC could result in an increase of  $\delta^{13}\text{C}$  in carbonates, up to 1.85‰ at 20 °C (Emrich et al., 1970). Carbonates ( $\text{CaCO}_3$ ,  $\text{MgCO}_3$ ,  $\text{NaHCO}_3$  and  $\text{Na}_2\text{CO}_3$ ) precipitation from DIC could

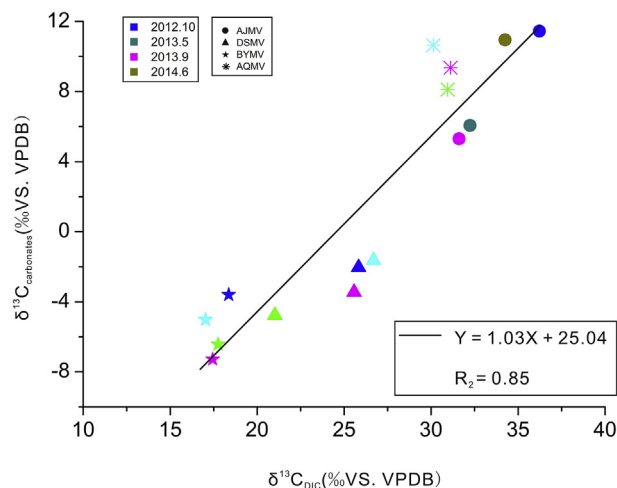


Fig. 9. Plot of  $\delta^{13}\text{C}$  values of DIC in the water samples versus  $\delta^{13}\text{C}$  values of carbonates in the mud samples.

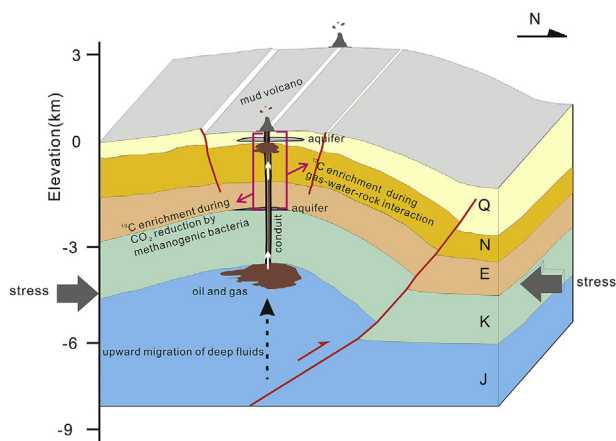


Fig. 10. Conceptual model of origin of  $^{13}\text{C}$  enrichment and the carbon cycling process in the mud volcanic systems.

have occurred in the shallower stratum due to the decreasing  $\text{CO}_2$  partial pressure during the upwelling of  $\text{CO}_2$  through the mud volcano system and resulted in enrichment of  $^{13}\text{C}$  in the carbonate precipitates. However,  $\delta^{13}\text{C}$  values of carbonate precipitant in the mud samples were at a much lower range ( $-7.28$ – $12.40\%$ ) than those of DIC from the mud volcano system (Table 1). In addition, carbonate minerals (such as calcite and dolomite) were found in the mud samples. The contents (%) of calcite in the mud samples from the AJMV, DSMV, BYMV and AQMV are 15%, 10%, 5% and 3%, respectively, and those of dolomite are 10%, 2%, 5% and 2%, respectively (Yang et al., 2014). The calcite and dolomite may have originated from carbonate minerals in the host rocks, with  $\delta^{13}\text{C}$  ranging from  $-10.0$  to  $+2.0\%$  (Deng et al., 2008). Therefore,  $\delta^{13}\text{C}$  values of carbonates in mud samples from the four mud volcanoes could be a result of mixing carbonate precipitates from DIC in the water and carbonate minerals from the host rock.

#### 5.4. The carbon cycling process in the mud volcanic systems

A conceptual model of the origin of  $^{13}\text{C}$  enrichment and the carbon cycling process in the mud volcanic system is summarized in Fig. 10. The  $\text{CO}_2$  gas from the mud volcanoes are likely to have resulted from hydrocarbon degradation, while the  $^{13}\text{C}$  enrichment of  $\text{CO}_2$  may have resulted from carbon isotope fractionation during the reduction of  $\text{CO}_2$  by methanogenic bacteria surviving up to 2000 m underground when  $\text{CO}_2$  gases upwelled through volcanic vents (Fu and Xin, 2009). The  $^{13}\text{C}$  enrichment in  $\text{CO}_2$  gas could be the original end-member responsible for the unusual positive  $\delta^{13}\text{C}$  values in the inorganic carbon during the carbon cycling process in the mud volcanic systems. During upward migration of fluid through the host rock,  $\text{CO}_2$ -water-sandstone interactions could have occurred, and the enriched  $^{13}\text{C}$  in  $\text{CO}_2$  transformed into the DIC in the water, resulting in DIC with more positive  $\delta^{13}\text{C}$  values. This can be attributed to carbon isotope fractionation in the procedure of  $\text{CO}_2$ -water-sandstone interactions. However, carbon isotope fractionation during the precipitation of DIC should have result in more enriched  $^{13}\text{C}$  in carbonates in mud compared to DIC in water, but the  $\delta^{13}\text{C}$  values in carbonates from the mud ( $-7.28$ – $12.40\%$ ) were much more lower than those in the DIC, which could be a result of mixing of carbonate minerals from the host rock and precipitation of DIC in the water.

## 6. Conclusions

The study describes the  $^{13}\text{C}$  enrichment in inorganic carbon ( $\text{CO}_2$ , DIC and carbonates) from four mud volcanoes in the northern Tianshan fold belt, NW China. The  $\delta^{13}\text{C}$  values of  $\text{CO}_2$  gas from the four mud volcanoes ranged from 10.99 to 32.11‰, those in DIC from the water

samples were more positive, 17.02–36.22‰. However, those in carbonates extracted from the mud samples were less positive, ranging from  $-7.28$ – $12.40\%$ .

$\text{CO}_2$  from the mud volcanoes is likely to have been a result of hydrocarbon degradation, and subsequent reduction by methanogenic bacteria. This is proposed as the primary factor in producing  $^{13}\text{C}$  enriched inorganic carbon during the carbon cycling process in mud volcanic systems.  $\text{CO}_2$  may have dissolved in water during  $\text{CO}_2$ -water-sandstone interactions during the upward movement of fluid through the conduit. This resulted in DIC with more positive  $\delta^{13}\text{C}$  values. The mixing of carbonate precipitates from DIC in the water and carbonate minerals from the host rock should have produced a relatively less positive  $\delta^{13}\text{C}$  value in carbonates from the mud samples.

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## References

- Blundy, J., Brodholt, J., Wood, B., 1991. Carbon-fluid equilibria and the oxidation state of the upper mantle. *Nature* 349 (6307), 321–324.
- Bai, B., 2008. Tectono-sedimentary Evolution and its Controls on Basic Petroleum Geological Condition of South Margin of Junggar. Doctoral thesis. Northwestern University, China (in Chinese with English abstract).
- Bonini, M., Tassi, F., Feyzullayev, A., Aliyev, C., Capecciacci, F., Minissale, A., 2013. Deep gases discharge from mud volcanoes of Azerbaijan: new geochemical evidence. *Mar. Petrol. Geol.* 43, 450–463.
- Chen, J., Wang, H., 2004. *Geochemistry*, vol. 418. Science Press, Beijing, pp. 124–129.
- Chao, H., You, C., Sun, C., 2010. Gases in Taiwan mud volcanoes: chemical composition, methane carbon isotopes, and gas fluxes. *Appl. Geochem.* 25, 428–436.
- Chen, R., Lin, X., Wang, Y., Hu, J., 2011a. Mitigating methane emissions from irrigated paddy fields by application of aerobically composted livestock manures in eastern China. *Soil. Use and Manag.* 27, 103–109.
- Chen, R., Senbayram, M., Lin, X., Dittert, K., 2011b. Origin of positive  $\delta^{13}\text{C}$  of emitted  $\text{CO}_2$  from soils after application of biogas residues. *Soil Biol. Biochem.* 43, 2194–2199.
- Chaudhuri, H., Ghose, D., Bhandari, R.K., Sen, P., Sinha, B., 2012. A geochemical approach to earthquake reconnaissance at the Baratang mud volcano, Andaman and Nicobar Islands. *J. Asian Earth Sci.* 46, 52–60.
- Chen, Z., Du, J., Zhou, X., Cui, Y., Liu, L., Li, Y., 2014. Hydrogeochemical changes of mud volcanoes and springs in North Tianshan related to the 30 June 2012 Xinyuan MS 6.6 earthquake. *Earthquake* 3, 97–107 (in Chinese with English abstract).
- Chen, Z., Zhou, X., Du, J., Xie, C., Liu, L., Li, Y., Yi, L., Liu, H., 2015. Hydrochemical characteristics of hot spring waters in the Kangding district related to the Lushan  $M_s=7.0$  earthquake in Sichuan, China. *Nat. Hazards Earth Syst. Sci.* 15, 1149–1156.
- Du, J., 1991. Origin of high content  $\text{CO}_2$  reservoir in China natural gas. *Nat. Gas. Geosci.* 2 (5), 203–208.
- Deng, Q., Feng, X., Zhang, P., Xu, X., Yang, X., Peng, S., Li, J., 2000. Active Tectonics of the Tianshan Mountains. Seismological Press, Beijing (in Chinese with English abstract).
- Du, J., Cheng, W., Zhang, Y., Jie, C., Guan, Z., Liu, W., Bai, L., 2006. Helium and carbon isotopic compositions of thermal springs in earthquake zone of Sichuan, Southwestern China. *J. Asian Earth Sci.* 26 (5), 533–539.
- Deng, S., Wu, C., Gu, X., Guo, Z., 2008. Sedimentary records and paleoenvironmental significance of stable isotopic evidences from the late Cenozoic, northern Tianshan. *Acta Petrol. Sin.* 24 (4), 689–698.
- Dai, J., Wu, X., Ni, Y., Wang, Z., Zhao, C., Wang, Z., Liu, G., 2012. Geochemical characteristics of natural gas from mud volcanoes in the southern Junggar Basin. *Sci. China Earth Sci.* 55, 355–367.
- Du, J., Zhou, X., Chen, Z., Cui, Y., Liu, L., Li, Y., Zhang, W., Gao, X., Xu, Q., Wang, H., 2013. Responses of mud volcanoes in the north Tianshan to the 30 June 2012 Xinyuan-Hejing MS 6.6 earthquake. *Acta Seismol. Sin.* 35 (6), 876–887 (in Chinese with English abstract).
- Emrich, K., Ehhalt, D., Vogel, J., 1970. Carbon isotopic fractionation during the precipitation of calcium carbonates. *Earth Planet Sci. Lett.* 8, 363–371.
- Etiotie, G., Nakada, R., Tanaka, K., Yoshida, N., 2011. Gas seepage from Tokamachi mud volcanoes, onshore Niigata Basin (Japan): origin, post-genetic alterations and  $\text{CH}_4$ -

- CO<sub>2</sub> fluxes. *Appl. Geochem.* 26, 348–359.
- Fu, L., Xin, M., 2009. Ecological diversity and industrial application of methanogens. *Chin. J. Appl. Environ. Biol.* 4, 574–578.
- Feyzullayev, A.A., Movsumova, U.A., 2010. The nature of the isotopically heavy carbon composition of carbon dioxide and bicarbonates in the waters of mud volcanoes in Azerbaijan. *Geochem. Int.* 48, 517–522.
- Gu, B., Schelske, C., Hodell, D., 2004. Extreme <sup>13</sup>C enrichments in a shallow hypereutrophic lake: implications for carbon cycling. *Limnol. Oceanogr. Meth.* 49, 1152–1159.
- Hassan, K., 2014. Isotope geochemistry of swan lake basin in the Nebraska sandhills, USA: large <sup>13</sup>C enrichment in sediment-calcite records. *Ch. Erde. Geochem.* <https://doi.org/10.1016/j.chemer.2014.03.004>.
- Jin, L., Guoyi, H., Zhang, Y., Yang, G., Cui, H., Cao, H., Hu, X., 2008. Application of carbon isotope fractionation during the reduction process from CO<sub>2</sub> to CH<sub>4</sub>. *Earth Sci. Fron.* 15 (5), 357–363.
- Liu, C., Ma, J., Yu, J., Jiang, X., 2014. The origin of hydrogen in the bio-methane production. *J. Chengde petrol. coll.* 4, 1–8.
- Liu, F., Lu, P., Griffith, C., Hedges, S.W., Soong, Y., Hellevang, H., Zhu, C., 2012. CO<sub>2</sub>-brine-caprock interaction: reactivity experiments on Eau Claire shale and a review of relevant literature. *Int. J. Greenh. Gas. Con. I* (7), 153–167.
- Mazzini, A., Svensen, H., Akhmanov, G., Aloisi, G., Planke, S., Malthe-Sørensen, A., Istadi, B., 2007. Triggering and dynamic evolution of the LUSI mud volcano, Indonesia. *Earth Planet Sci. Lett.* 261, 375–388.
- Nakada, R., Takahashi, Y., Tsunogai, U., Zheng, G.D., Shimizu, H., Hattori, K.H., 2011. A geochemical study on mud volcanoes along the southern margin of the Junggar Basin. *Appl. Geochem.* 26 (7), 1065–1076.
- Rovira, P., Vallejo, V., 2008. Changes in δ<sup>13</sup>C composition of soil carbonates driven by organic matter decomposition in a Mediterranean climate: a field incubation experiment. *Geoderma* 144, 517–534.
- Rustad, J., Nelmes, S., Jackson, Virgil, Dixon, David, 2008. Quantum-chemical calculations of carbon-isotope fractionation in CO<sub>2</sub>(g), aqueous carbonate species, and carbonate minerals. *J. Phy. Chem.* 112, 542–555.
- Ray, J., Kumar, A., Sudheer, A., Deshpande, R., Rao, D., Patil, D., Awasthi, N., 2013. Origin of gases and water in mud volcanoes of Andaman accretionary prism: implications for fluid migration in forearcs. *Chem. Geol.* 347, 102–113.
- Stiller, M., Rounick, J., Shasha, S., 1985. Extreme carbon-isotope enrichments in evaporite brines. *Nature* 316, 434–435.
- Sano, Y., Wakita, H., 1985. Geographical distribution of <sup>3</sup>He/<sup>4</sup>He ratios in Japan: implications for arc tectonics and incipient magmatism. *J. Geophys. Res.* 90 (B10), 8729–8741.
- Song, Z., Jiang, Z., Zhang, M., 2014. Origins and geochemical characteristics of unconventional natural gas in south margin of Junggar basin. *Petrol. Geo. Rec. Eff.* 21, 66–70.
- Turner, J., Fritz, P., 1983. Enriched <sup>13</sup>C composition of interstitial waters in sediments of a freshwater lake. *Can. J. Earth Sci.* 20, 616–621.
- Talbot, M.R., 1990. A review of the paleohydrological interpretation of carbon and oxygen isotopic ratios in primary lacustrine carbonates. *Chem. Geol.* 80, 261–279.
- Tassi, F., Bonini, M., Montegrossi, G., Capecciacci, F., Capaccioni, B., Vaselli, O., 2012. Origin of light hydrocarbons in gases from mud volcanoes and CH<sub>4</sub>-rich emissions. *Chem. Geol.* 294–295, 113–126.
- Ueda, A., Kato, K., Ohsumi, T., Yajima, T., Ito, H., Kaieda, H., Metcalfe, R., Takase, H., 2005. Experimental studies of CO<sub>2</sub>-rock interaction at elevated temperatures under hydrothermal conditions. *Geochem. J.* 39 (5), 417–425.
- Valero-Garcés, B.L., Delgado-Huertas, A., Ratto, N., Navas, A., 1999. Large <sup>13</sup>C enrichment in primary carbonates from Andean Altiplano lakes, northwest Argentina. *Earth Plan 171* (2), 253–266.
- Wang, X., 1989. *Isotope Geochemistry of Noble Gases and Cosmochemistry*. Science Press, Beijing, pp. 41.
- Wei, K., Gasse, F., 1999. Oxygen isotope in lacustrine carbonates of West China revisited: implications for post glacial changes in summer monsoon circulation. *Quat. Sci. Rev.* 18, 1315–1334.
- Wilhelms, A., Larter, S.R., Head, I., Farrimond, P., Di Primio, R., Zwach, C., 2001. Biodegradation of oil in uplifted basins prevented by deep-burial sterilization. *Nature* 411, 1034–1037.
- Wan, Z., Shi, Q., Guo, F., Zhong, Y., Xia, Bin, 2013. Gases in Southern Junggar Basin mud volcanoes: chemical composition, stable carbon isotopes, and gas origin. *J. Nat. Gas Sci. Eng.* 14, 108–115.
- Yang, H., Luo, K., Sun, J., Zhang, T., Ma, X., 2012. Prokaryotic diversity of an active mud volcano in the Usu City of Xinjiang, China. *J. Basic Microbiol.* 52, 79–85.
- Yang, X., Yu, H., Zhao, B., Xu, J., Gao, X., Zhang, T., 2014. Study on the solid products from mud volcano in north Tianshan Mountains, Xinjiang and discussion on its genetic mechanism. *Seismol. Geol.* 36 (1), 123–136 (in Chinese with English abstract).
- Zartman, R.E., Wasserburg, G.J., Reynolds, J.H., 1961. Helium, argon and carbon in some natural gases. *J. Geophys. Res.* 66, 277–286.
- Zyakun, A., 1996. Potential of <sup>13</sup>C/<sup>12</sup>C variations in bacterial methane in assessing origin of environmental methane. In: Schumacher, D., Abrams, M.A. (Eds.), *Hydrocarbon Migration and its Near-surface Expression*. AAPG Memoir 66. p. 341–352.
- Zhang, C., Duan, Z., 2009. A model for C-O-H fluid in the Earth's mantle. *Geochem. Cosmochim. Acta* 73 (7), 2089–2102.
- Zheng, G.D., Fu, B.H., Takahashi, Y., Kuno, A., Matsuo, M., Zhang, J.D., 2010a. Chemical speciation of redox sensitive elements during hydrocarbon leaching in the Junggar Basin, Northwest China. *J. Asian Earth Sci.* 39 (6), 713–723.
- Zheng, G.D., Fu, B.H., Kuno, A., Matsuo, M., 2010b. Iron speciation in bleached rocks by hydrocarbon leaching in Dushanzi Mud Volcano, NW China. *J. Phys.* <https://doi.org/10.1088/1742-6596/217/1/012048>. Conference Series 217 012048.
- Zhu, Z., Chen, J., Zeng, Y., 2013. Abnormally positive δ<sup>13</sup>C values of carbonates in Lake Caohai, southwest China, and their possible relation to lower temperature. *Quat. Int.* 286, 85–93.
- Zhang, W., Du, J., Zhou, X., Wang, F., 2016. Mantle volatiles in spring gases in the Basin and Range Province on the west of Beijing, China: constraints from helium and carbon isotopes. *J. Volcanol. Geoth. Res.* 309, 45–52.