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Gas emission from the Qingzhu River after the 2008 Wenchuan Earthquake, Southwest China

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ABSTRACT

Four gas and six water samples were collected from the Qingzhu River in Qingchuan County, one of the regions affected by the 2008 *Ms*8.0 giant Wenchuan Earthquake. Gases were discharged soon after the earthquake, but such emissions ceased in October 2008. The predominant gases are CH_4, CO_2, N_2 and O_2. The N_2, O_2 and noble gases are of atmospheric origin. In contrast, the CH_4 and CO_2 have typical biogenic signatures, with high $C_1/(C_2+C_3)$, $\delta^{13}C_{CH4}$ (−56.1 to −56.6‰); δD_{CH4} (−328 to −345‰); and $\delta^{13}C_{CO2}$ (−6.7 to −4.9‰). These measurements indicate that the gases are discharged from a shallow reservoir through faults or fractures caused by the earthquake. The discharging gases are significantly distinct from the natural gas fields nearby, suggesting that there are no direct pathways, such as faults or fractures, between the surface and the natural gas reservoir.

1. Introduction

On May 12, 2008 a giant earthquake occurred near Wenchuan in Sichuan Province, southwestern China. This *Ms*8.0 event induced numerous secondary effects, including rock falls, surface ruptures, landslides, soil and debris flows, and the dammed lakes (Fu et al., 2008; Li et al., 2008; Parsons et al., 2008; Fu et al., 2009; Dai et al., 2011; Fu et al., 2011). In common with many great earthquakes elsewhere, the Wenchuan earthquake was followed by unusual geological phenomena with flammable gas bubbling in the Qingzhu River, moist fogs in some valleys, and hot spring activity (Zhou et al., 2010). The emission of flammable gas was of great concern as the gas release was considered to announce further shocks. In consequence, urgent questions arose concerning: (i) the composition and the origin of the gases; (ii) their release mechanism; (iii) indications of correlation between the gas release and shocks; and (iv) local significance of gas release. In order to clarify these questions, field investigations were carried out in February 2009 soon after completion of emergency work on the dammed lake. The chemical characteristics of the emitted gases are reported in this paper and some related questions are also discussed.

2. Local geological settings

The destructive Wenchuan earthquake occurred along the NE–SW trending Longmenshan fault zone (Fig. 1), which provides the tectonic boundary between the Tibetan Plateau to the west and the Sichuan Basin in the southeast. Regional tectonic activities along this boundary have been frequent and commonly very strong since the Late Cenozoic (Wang and Meng, 2008), resulting in the formation of the extraordinary topography with closely spaced high mountains and deep valleys. Difference in elevation of 4000 m exists within less than 50 km across the Longmenshan (Royden et al., 1997; Clark and Royden, 2000; Fu et al., 2011). The Wenchuan earthquake (*Ms*8.0) of May 12, 2008 signaled the continuation of tectonic activity along the Longmenshan faults.

The Qingzhu River is located at the northern end of the Longmenshan fault zone which it crosses at about 90°. The river rises from the south slope of the Motianling Mountains at Qingxi Town (Clean Stream Town) and the Dacaoping (giant grass plateau) at the northern end of the Longmenshan Mountains. Flowing through Qingchuan County, the Qingzhu River first joins the Bailongjiang and then the Jialingjiang, one of the largest rivers in the region (Fig. 1). The source of the Qingzhu River lies 3837 m above sea level (asl) and the river is about 204 km long with a catchment area of 2873 km^2. Flood disasters occur frequently along the river during the summer season, a consequence of the high annual precipitation and the deep slope of the river valley. Debris generated by the Wenchuan earthquake produced a dammed lake in the river valley near Donghekou town, behind which a lake rapidly formed within

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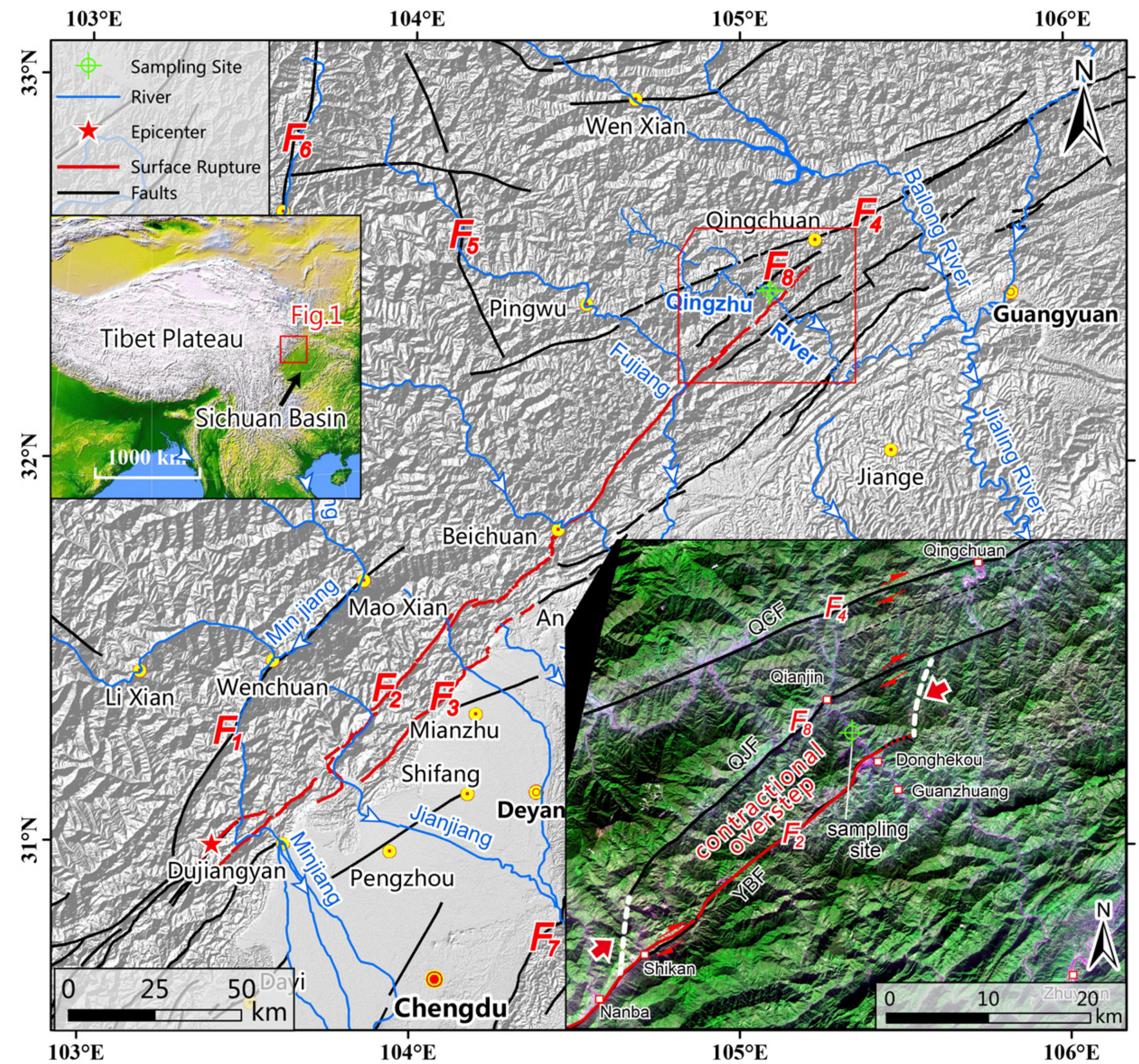

Fig. 1. Location map showing the Qingzhu River and areas effected by 2008 *Ms8.0* Wenchuan earthquake. Located on the northeast part of the map, the Qingzhu River is flowing southeast and crossing the Qingchuan fault where the Donghekou quake dam formed along with the main shock of the *Ms*8.0 Wenchuan Earthquake. The epicenter of the main shock is located at southwest corner on the map. The major faults on the map include *F1*—Maoxian fault; *F2*—Yingxiu-Beichuan fault; *F3*—Guanxian-Anxian fault; *F4*—Qingchuan fault; *F5*—Huya fault; *F6*—Minjiang fault; *F7*—Longquanshan fault; *F8*—Qianjin fault. The sampling site is just located in the overstep region between F2 and F8.

several days. In January 2009, after the water had subsided and rescue work had been completed, much bubbling of gas was observed in the river. Although it is not known when the bubbling began, there is no doubt that its occurrence is directly linked to the earthquake.

Tectonically, the Qingzhu River region is located on an overstep bounded by two parallel right-lateral strike-slip faults, the Yingxiu-Beichuan fault (YBF as F2 in Fig. 1) and Qianjin fault (QJF as F8 in Fig. 1). A contractional overstep in tectonic geology normally indicates a discontinuous interval between two sub-parallel faults (strictly speaking between similar structures). If the normal to the tip of one overstepping fault intersects the other faults, there is overlap. During the 2008 Wenchuan earthquake, the YBF was ruptured by both the mainshock and the large aftershocks. However, the vertical and dextral coseismic displacements of the YBF around the study area are just about 30–50 cm, much less than at the southern and central parts (Fu et al., 2011). Our study area is located at the northeasternmost termination of the surface rupture zone. The QJF was not involved in the 5.12 Wenchuan earthquake, but its correlated location with the YBF induced the overstep with lots of fractures on the surface and in the shallow layer which lies in close proximity to the Qingzhu River. The flammable gas emission just occurred within the overstep (Fig. 1).

The study area includes Cambrian to Silurian sequences (Fig. 2), which mainly consist of marine carbonate rocks, carbonaceous sandstone, siltstone and argillites. Phyllites and low-degree metamorphic rocks occur locally. Quaternary deposits in the valleys are mainly composed of gravels and sands. Very thick sandy sediments were newly deposited in the dam lake as direct or indirect consequences of the earthquake.

3. Samples and experiments

Field investigations and sampling were carried out in February 2009 shortly after completion of rescue work at the dammed lake. Thick river-bed sedimentary deposits had emerged along the Qingzhu River as the waters of the newly-formed lake subsided. Many gas emission pits (Fig. 3) were observed, and the gas was noted to be flammable (Fig. 3D).

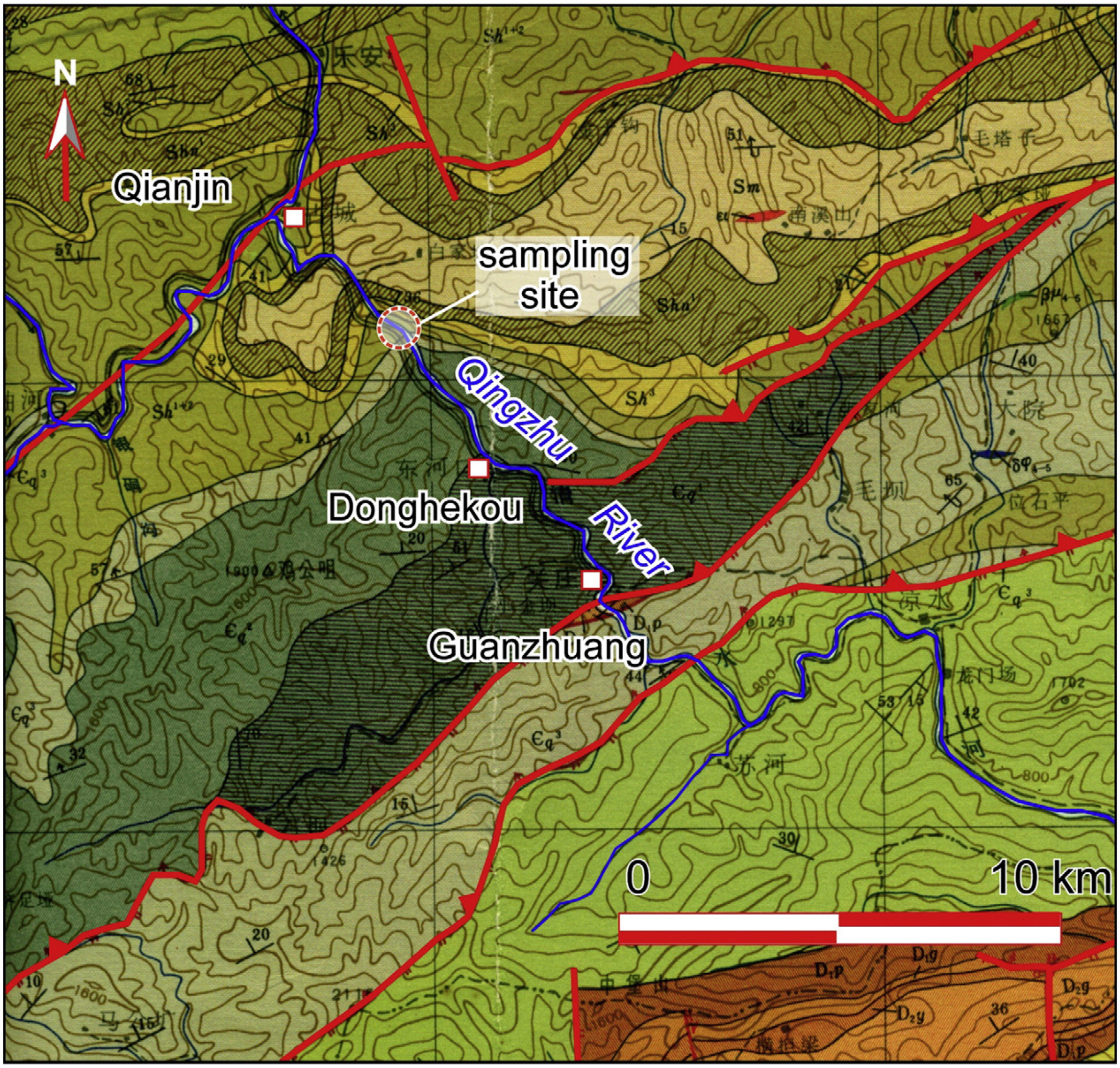

Fig. 2. A geological map showing the local sequences and major faults. The Qingzhu River flows from west to east. In the figure, ∈—Cambrian; S—Silurian; D—Devonian.

During the field investigation, four gas samples were collected using conventional water displacement methods. Four water samples were also collected from the same locations as the gas samples. For comparison, an additional water sample was collected 500 m upstream of the gas sites, and another from approximately 2 km downstream of the lake.

Hydro-geochemical parameters, including pH, Eh, salinity, conductivity and dissolved oxygen content, were measured on site using a handy lab pH/LF12-Set of portable multi-parameters. All gas samples were analyzed in the Key Laboratory of Petroleum Resources Research, Chinese Academy of Sciences at Lanzhou. Major gas compositions were determined by gas chromatography (model GC5890A) with errors <10% given by repeat measurements of in-house standards and limits for main gas as 1 ppm. Carbon and hydrogen isotopic compositions were determined by a gas chromatograph–pyrolysis–isotope ratio mass spectrometer (model HP6890-DeltaPlusXP) with uncertainties of $\pm 0.3‰$ for $\delta^{13}C$ and $\pm 3‰$ for δD. Noble gas compositions were analyzed by a static mass spectrometer (model MAT271) with an uncertainty of 10%. $^{3}He/^{4}He$ and $^{40}Ar/^{36}Ar$ ratios were determined by a static mass spectrometer (model VG 5400).

4. Results and discussion

4.1. In-situ characteristics of water

The pH, Eh, salinity, conductivity and dissolved oxygen of the water samples are given in Table 1. There is a distinct difference between water samples from the dammed lake and the river, and samples HST-02W and HST-03W taken near the small pits emitting the gases. Consistent pH values (7.85–8.42) of water from the dammed lake and from the river indicate a slightly alkaline aquatic system due to the carbonates in the river catchments presumably derived from the limestones, muddy limestones, and metamorphic marbles that dominate sequences in the study area (Fig. 2). However, pH values of 6.78 and 6.91 of water samples from the gas emitting pits indicate relatively weak acidic condition. There are abundant reddish precipitates in the gas pits (Fig. 3C) as well as film floating on the water (Fig. 3D), and iron hydroxide on the bottom of gas pits, typically indicating iron bacteria (Fortin and Langley, 2005; Zheng et al., 2007). The bacteria are presumed to use methane as their source of energy. Such bacteria activity, involving methane and iron oxidation,

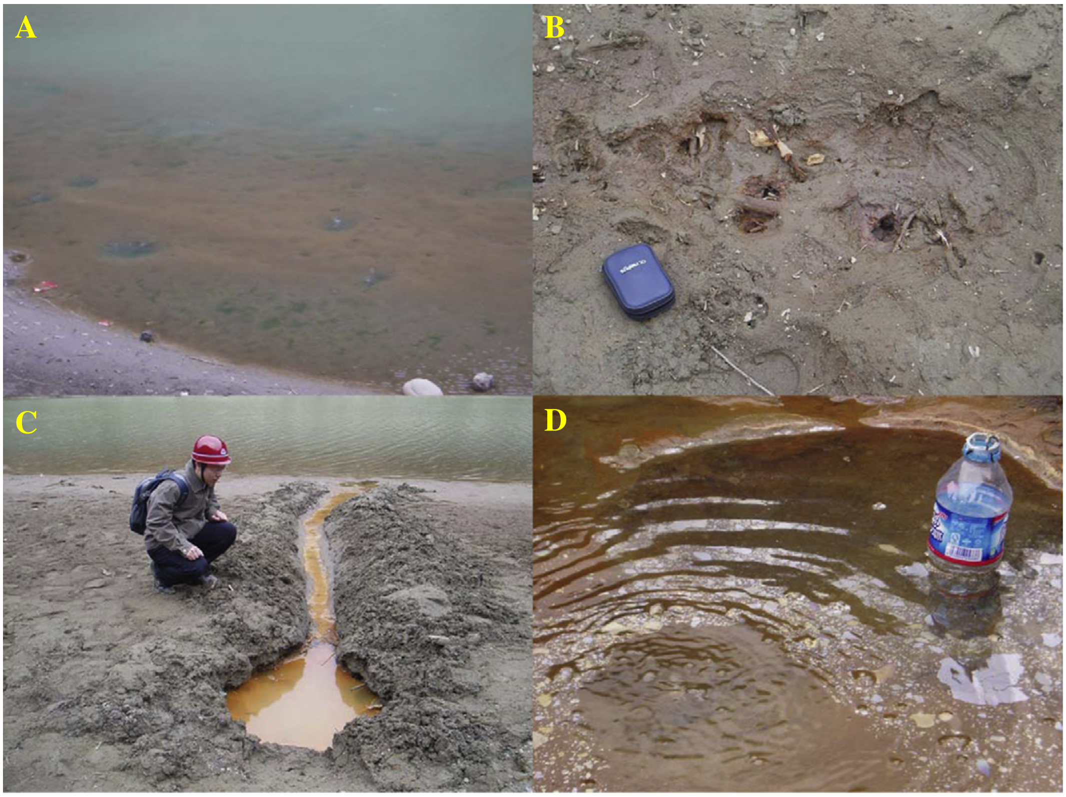

Fig. 3. Photographs of the gas release pits along the Qingzhu River. (A) Underwater gas releasing pits on the river bed; (B) gas pits on the river bed without surface water cover; (C) artificial pit at a gas releasing point with water flow and reddish precipitate; (D) flammable gas babuls and iron bacteria film floating on the water surface.

is considered to have introduced organic acids into the environment and to have then induced the acidic conditions in waters at the gas emitting pits. The weak acidic environment in the vicinity of the gas releasing pits also increases the conductivity of the water to 1210~1265 μS cm^{-1}, far higher than in the other river water samples of 316~342 μS cm^{-1}. This is presumably due to the increase of ionic activity under acidic conditions. Similar changes also occurred in redox potential, salinity and dissolved oxygen content (Table 1).

4.2. Composition and origin of discharging gases

The chemical and isotopic compositions of the Qingzhu gas samples are listed in Table 2. Qingzhu gases are relatively simple in chemical composition, mainly consisting of N_2, O_2, CH_4 and CO_2. H_2, H_2S, SO_2 and heavy hydrocarbons (C_2, C_3, …) are below the detection limits.

The concentration of N_2 is in the range of 6.96%~44.67%, and O_2 concentration varies in the range of 1.91%~12.02%. The average N_2/O_2 ratio (3.74 ± 0.11) is identical to the atmospheric value of 3.71, indicative of an atmospheric origin, as is commonly observed elsewhere in the world. The low concentration of dissolved oxygen also suggests strong anaerobic conditions, with the small quantities of oxygen most probably introduced during the sampling process.

Concentrations of the noble gases ^4He, ^{20}Ne and ^{40}Ar vary from 0.86 ppm to 3.4 ppm, 1.75 ppm to 19.1 ppm and 816 ppm to 7440 ppm respectively. The average $^4He/^{20}Ne$, $^4He/^{40}Ar$ and $^{20}Ne/^{40}Ar$ ratios are almost consistent with the atmospheric values within the margin of analytical errors.

Atmospheric origin is further confirmed by the isotopic compositions of helium and argon, with $^3He/^4He$ and $^{40}Ar/^{36}Ar$ ratios range of 1.02~1.08 Ra and 296.2~297.5 respectively, in good agreement with the atmospheric values of 1 Ra and 295.5 within the margin of analytical error, By contrast, the weighted average $^3He/^4He$ ratio (1.05 ± 0.03 Ra) is significantly distinct from 8 ± 0.5 Ra for typical mantle-derived helium, or values <0.1 Ra which characterize the average radiogenic helium component in the crust. The weighted average $^{40}Ar/^{36}Ar$ ratio (296.9 ± 2.9) in Qingzhu samples is similarly much lower than the values observed in mantle-derived and crustal components.

In contrast to atmospheric origin for N_2, O_2 and the noble gases, the origins of the CH_4 and the CO_2 are clearly different. CH_4, the only hydrocarbon compound detected, had concentrations ranging from 29.44% to 60.33%. CO_2 concentration varies from 13.3% to 30.7%. There

Table 1
In-situ characteristics of surface waters along the Qingzhu River and the quake lake.

Sample No.	Locations	Latitude	Longitude	pH	Eh (mv)	Temperature (°C)	Salinity (%)	Conductivity (μS cm^{-1})	Dissolved oxygen (mg L^{-1})
HST-07W	River water upstream	N32°27′36.7″	E105°04′30.8″	8.42	−92	25	0.01	328	0.34
HST-01W	Lake water	N32°27′32.3″	E105°04′58.2″	7.85	−59	25	0.00	342	0.07
HST-02W	Pit water with gas emission	N32°27′31.8″	E105°04′58.3″	6.91	−2	25	0.40	1210	0.05
HST-03W	Red pit water with gas emission	N32°27′32.2″	E105°04′58.7″	6.78	6	25	0.40	1265	0.03
HST-04W	Lake water	N32°27′31.9″	E105°04′56.8″	8.05	−70	25	0.00	353	0.08
HST-06W	River water downstream	N32°26′48.2″	E105°05′42.0″	8.28	−84	25	0.00	316	0.05

Table 2
Chemical and isotopic composition of gas samples from the Qingzhu River.

Sample no.	Latitude	Longitude	CH_4 (%)	CO_2 (%)	N_2 (%)	O_2 (%)	He (ppm)	Ne (ppm)	Ar (ppm)	$d^{13}C_{CH4}$ (‰)	dD_{CH4} (‰)	$d^{13}C_{CO2}$ (‰)	$^3He/^4He$ (Ra)	$^{40}Ar/^{36}Ar$
HST-02G	N32°27′32.3″	E105°04′58.2″	29.44	13.33	44.67	12.02	3.4	10.67	4470	−56.1	−345	−4.9	1.08 ± 0.05	297.4 ± 6.7
HST-03G	N32°27′31.8″	E105°04′58.3″	46.91	18.2	27.43	7.12	2.64	6.96	2930	−56.5	−328	−5.5	1.05 ± 0.08	296.2 ± 5.6
HST-04G	N32°27′32.2″	E105°04′56.8″	–	–	–	–	6.66	19.1	7440	–	–	–	1.02 ± 0.03	296.7 ± 5.9
HST-05G	N32°27′31.9″	E105°04′58.8″	60.33	30.7	6.96	1.91	0.86	1.75	816	−56.6	−339	−6.7	1.05 ± 0.04	297.5 ± 5.3
Air			0.001	0.032	78	21	5.4	18	9340			−7	1	295.5

is a positive correlation between CH_4 and CO_2 with r = 0.95 (not shown), suggesting a common origin of the two components. The CH_4 and CO_2 vary simultaneously with $CH_4/CO_2 = 2.2 \pm 0.3$ during biogenic gas formation process. The main reason for variations in the CH_4 and CO_2 contents is attributed to dilution by atmospheric gases. For example, CH_4 and CO_2 have clear negative correlations with N_2 (r > 0.98) and O_2 (r > 0.97).

The high CH_4-content of the released gases is responsible for their flammability. The proportion of CH_4 in a hydrocarbon gas mixture can be expressed on a volume percentage basis by the "Bernard parameter", $C_1/(C_2 + C_3)$ (Bernard et al., 1978). In CH_4 formation zones from which thermogenic hydrocarbons are absent, $C_1/(C_2 + C_3)$ values are typically 10^3 to 10^5. Such high values are also typical for thermogenic gases with high maturity. In CH_4 consumption zones the $C_1/(C_2 + C_3)$ ratio can decrease to values of less than 10. But $C_1/(C_2 + C_3)$ ratios less than 50 are also typical for thermogenic hydrocarbon gases. In consequence, difficulties in the interpretation of natural gas sources may arise in the presence of CH_4 oxidation.

In the absence of detectable heavy hydrocarbons in Qingzhu gas samples, the high $C_1/(C_2 + C_3)$ ratios can be qualitatively considered and interpreted as indicating a biogenic source or a highly matured thermogenic gas. The choice between these possibilities can then be made on the basis of carbon isotopic compositions, biogenic gases being richer in ^{12}C (i.e. more negative $\delta^{13}C_{CH4}$) whereas thermogenic gases are enriched in ^{13}C (less negative $\delta^{13}C_{CH4}$).

The $\delta^{13}C_{CH4}$ and δD values of Qingzhu gases range from −56.6‰ to −56.1‰ and from −345‰ to −328‰ respectively, and the $\delta^{13}C_{CO2}$ values vary from −6.7‰ to −4.9‰. These values are comparable with those for typical biogenic gases in China. Zhang et al. (2009) compiled a dataset of typical isotopic compositions of biogenic gases in China with $\delta^{13}C_{CH4}$ from −89.1‰ to −55.1‰; $\delta^{13}C_{CO2}$ from −39.1‰ to +0.95‰; and δD from −277‰ to −108.5‰. Although the $\delta^{13}C_{CH4}$ and $\delta^{13}C_{CO2}$ values for Qingzhu gas lie within the range reported by Zhang et al. (2009), the δD values are more negative.

Bacterial production of methane is a widespread phenomenon in nature occurring in marine sediments, lake sediments, salt marshes, and glacial till deposits and other environments. Methane in shallow dry gas deposits has also been described as being of biogenic origin (e.g. Schoell, 1980). Wolin (1976) and Cappenberg (1976) have summarized various types of enzymatic reactions in methane-producing bacterial food chains. These can be divided into two groups:

(i) Reduction of CO_2: these reactions comprise two steps, i.e. production of CO_2 and H_2 by non-methanogens, followed by reduction of CO_2 with H_2 by methanogens.
(ii) Hydrogenation of CH_3 radicals, i.e. complete transformation of the CH_3 radical to CH_4.

In either of these reactions, the hydrogen in the CH_4 molecule is mainly derived from two sources: organic matter and water hydrogen. The isotopic composition of organic material in natural sedimentary environments does not vary systematically. However, the deuterium concentrations in natural waters do vary considerably. Precipitation in continental environments is depleted in deuterium (δD is from −20‰ to −90‰), whereas marine waters and interstitial waters are comparatively enriched with δD from about 0‰ to −20‰). Collection of data from worldwide occurrences generated a characteristic relationship between δD_{CH4} and δD_{H2O} for all natural biogenic gases (Schoell, 1980).

$$\delta D_{CH4} = \delta D_{H2O} - (160 \pm 10)$$

A slope of 1 in this relationship suggests that 100% of the hydrogen in these methanes is derived from their associated waters. By contrast, CH_3 hydrogenation by methanogens (important in Lake Vechten sediments in the Netherlands; Cappenberg, 1976) is clearly of minor importance for the formation of natural biogenic gases. Woltemate et al. (1984) reported δD values of −291‰ to −338‰ for gases from the shallow freshwater lake of Würmsee in Germany. The δD values of the Qingzhu gases are similar to those of Würmsee's, neither of which fit the above δD_{CH4} and δD_{H2O} relationship for natural methanes. A very unlikely δD_{H2O} of −150‰ would be necessary to fit this relationship. A fermentation process similar to that investigated in sewage sludge (rather than CO_2 reduction) would have to be invoked in order to explain this particular isotopic composition from freshwater environments.

Fig. 4 shows the relationship between the hydrogen and the carbon isotopic composition of methanes from different types of natural gas. The $\delta^{13}C/\delta D$ boundaries given in this figure are referred from Whiticar (1999). It is clear that the Qingzhu and Würmsee gases both plot within the range typical for methyl-type bacterial fermentation. Fig. 5 shows a

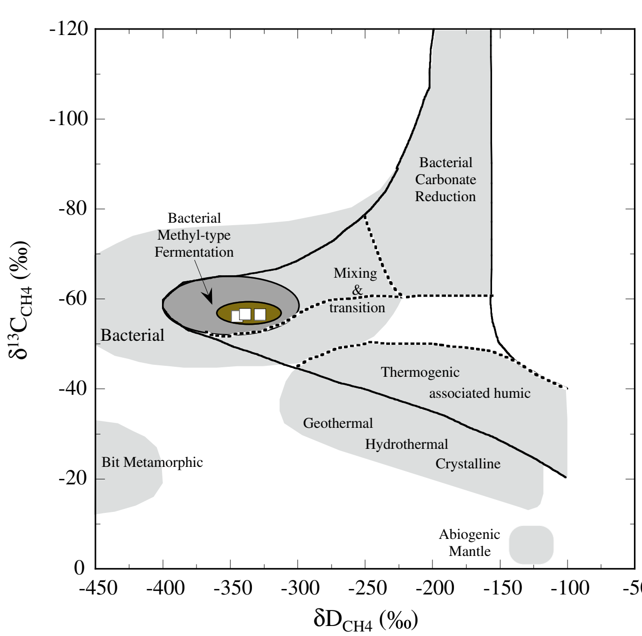

Fig. 4. CD-diagram for classification of bacterial and thermogenic natural gas by the combination of $\delta^{13}C_{CH4}$ and δD_{CH4} information (Whiticar, 1999). The Würmsee gas samples are also plotted as brown for comparison (Woltemate et al., 1984). The thermogenic gases in SW Sichuan natural gas fields are in the range of thermogenic origin.

cross plot of $\delta^{13}C_{CO2}$ vs $\delta^{13}C_{CH4}$ in gas samples. The lines depict varying values of fractionation factor α_C [$\alpha_C = (\delta^{13}C_{CO2} + 1000) / (\delta^{13}C_{CH4} + 1000)$]. Whiticar (1999) concluded that values of α_C that would be characteristic of acetate fermentation would range from α_C ~1.040 to 1.055. Values characteristic of CO_2 reduction would range from α_C ~1.055 to 1.090. It is clear that the Qingzhu and Würmsee gas samples, ranging from α_C ~1.053 to 1.054, plot within the range of methyl fermentation.

In summary, the chemical and isotopic compositions of the Qingzhu gas samples are typical of gases of biogenic origin associated with methyl-type bacterial fermentation in a freshwater environment. Such gases are usually produced and trapped in shallow sediments. Biogenic gases generated in such circumstances can be directly released to the atmosphere if the cap rocks are fractured.

4.3. Implication of further earthquake activity

Many giant earthquakes are characterized by deep seismic waves with accompanying violent shaking of the ground, soil liquefaction, tsunamis, and other hazardous phenomena. The Wenchuan Earthquake induced a 285 km long surface rupture zone within the Longmenshan fault zone along the pre-existing Yingxiu-Beichuan, Guanxian-Anxian, and Qingchuan faults (Fig. 1). Maximum thrust slip distance was estimated to be about 10 m, accompanied by 9 m of shortening across the rupture zone (Li et al., 2008). Slip distance and shorting along the YBF decreased to the northeast.

Zhou et al. (2010), who measured soil gases at numerous sites along the YBF following the May 12 Wenchuan earthquake, failed to find methane in the soil gases. The sites they investigated were mainly located along the south and central parts of the YBF. Their results may indicate that the flammable gases at Qingzhu were due to extremely local circumstances, with no direct relationship to the Yingxiu-Beichuan fault. Yet the emission site of the flammable gas is located in the overstep area right between the YBF and QJF (Fig. 1). The YBF was the main causative fault of the Wenchuan Earthquake with displacements during the main shock and aftershocks. Quake activity along the YBF may have induced or activated shallow and surface fractures, producing pathways for gas emission after the Wenchuan earthquake. The QJF did not rupture during the Wenchuan earthquake,

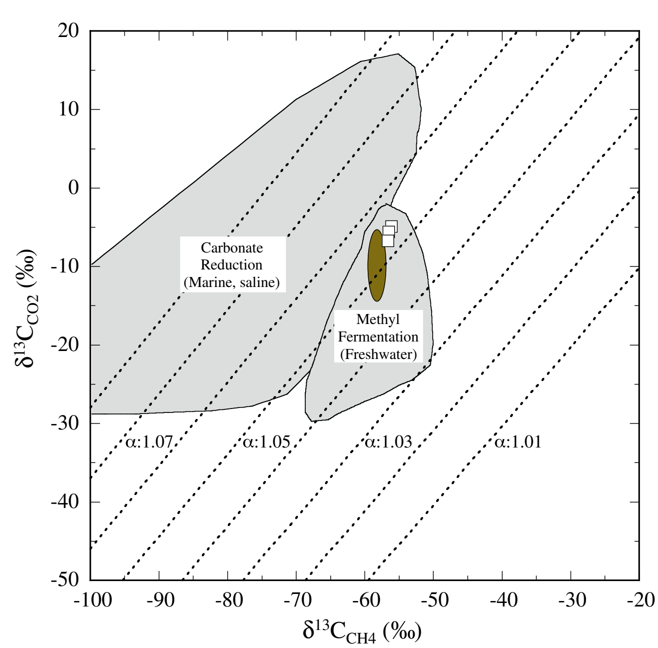

Fig. 5. Cross plot of $\delta^{13}C_{CO2}$ vs $\delta^{13}C_{CH4}$ in gas samples. The Würmsee gas samples are also plotted as brown for comparison (Woltemate et al., 1984).

The Sichuan Basin, where oil and gas explorations commenced during the 1950s, is one of the largest sedimentary oil- and gas-bearing basins in China. It is bounded to the northwest by the Longmenshan fault zone, a major tectonic control (Zhu et al., 2006). Several natural gas fields have been discovered and developed in front of the Longmenshan fault zone. Accordingly, there were discussions whether the gases discharged following the quake were derived from natural gas reservoirs beneath the Longmenshan thrust.

Shen et al. (2010) compiled geochemical data for natural gases in the western Sichuan gas fields, obtaining a $C_1/(C_2+C_3)$ range of 10 to 175; $\delta^{13}C_{CH4}$ from −39‰ to −24‰; and δD_{CH4} from −200‰ to −140‰. This falls within the field of gases of thermogenic origin (Fig. 4), indicating that natural gases of the western Sichuan gas fields, for the most part are associated with sediments of Jurassic, Triassic and Permian age, are of predominantly thermogenic origin. Yet most natural gases in the western Sichuan gas fields have high contents of H_2S (Shen et al., 2010). This means that the gases discharged from the bed of the Qingzhu River differ from those observed in the nearby natural gas fields, strongly suggesting that there is no direct conduit between the surface and the natural gas reservoirs. In the western Sichuan, natural gas reservoirs are usually distributed below 2000 m (Zhu et al., 2006), and the results of the present study show no evidence that the gases of the western Sichuan Basin had migrated towards the surface during the principal quake or its aftershocks.

The Wenchuan earthquake broke through to the surface and provided upward fracture pathways for biogenic gases. But the faults or fractures that were activated during the earthquake and its aftershocks did not provide direct pathways to the surface for natural gas from deep reservoirs beneath the Longmenshan thrust. In other words, there might be less evidence to suggest further earthquake activity, which is supported by recent cessation of gas emission in the Qingzhu River.

5. Conclusions

This study reported analytical results for gas and surface water samples from the Qingzhu River in Qingchuan County, a region affected by the 2008 *Ms*8.0 Wenchuan Earthquake. Gases present in the Qingzhu River soon after the earthquake are chemically and isotopically dominated by CH_4 and CO_2 of typical bacterial origin, plus N_2, O_2 and noble gases of atmospheric origin. They differ significantly from the thermogenic gases in deep natural gas reservoirs nearby. Our samples were of shallow biogenic origin and were composed of gases that had migrated upwards through faults or fractures produced by the earthquake. In contrast, direct pathways from the underlying natural gas reservoirs to the surface do not appear to exist.

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