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Hydrochemical characteristics of the hot spring waters in the Kangding district related to the Lushan M_S 7.0 earthquake in Sichuan, China

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Abstract

Hydrogeochemistry of 10 hot springs in the Kangding district was investigated by analyzing cation and anion concentrations of the spring waters. The water samples were collected within 5 days after the Lushan earthquake. The spring waters are classified into 7 chemical types based on the hydrochemical compositions. Comparison with the hydrochemical data before the Lushan earthquake, concentrations of Ca^{2+}, HCO_3^- and TDS of the waters from the Guanding, Erdaoqiao, Gonghe, Erhaoying, Tianwanhe and Caoke springs evidently increased, which resulted from enhancing interaction between deep-earth fluids and carbonate rocks by the increment of dissolved CO_2 in the groundwater. Concentrations of Na^+, Cl^- and SO_4^{2-} of the waters from the Guanding, zheduotang, Xinxing and Gonghe springs were decreased, indicating dilution of precipitation water. Concentrations of Na^+ and SO_4^{2-} of the Erhaoying spring water increased, which may be attributed to the more supplement of fluids enriched in sulfur. The results indicate that hydrochemical components of spring water can be used as an effective indicator for earthquakes.

1 Introduction

The great earthquakes usually associate with the physical-chemical variations of groundwater. The short-term hydrogeochemical precursors for the earthquakes (King et al., 1995; Favara et al., 2001; Quattrocchi et al., 2003; Du et al., 2008; Dadomo et al., 2009), co-seismic response of hydrochemistry (Song et al., 2006; Yang et al., 2006; Reddy et al., 2011) and post-seismic geochemical changes of the hot springs have been observed throughout the world (Thomas, 1988; Woith et al., 1988; Italiano et al., 2010; Zhou et al., 2010; Malakootian and Nouri, 2010; İnan et al., 2012). Claesson et al. (2004) observed changes in multicomponent constituents and $\delta^{18}O$ of groundwater due to the seismic event (M 5.1) in northern Iceland. Isaksen et al. (1997) observed increased Cl^- concentration in the spring water 5 days prior to the M_L 5.2 earthquake.

NHESSD
2, 7293–7308, 2014

The geochemical anomalies may be mainly caused by the alteration of groundwater in the specific circulating system under the action of increasing crustal stress before and after the earthquakes (Song et al., 2006; Italiano et al., 2010; Wang et al., 2012; Miller et al., 2013).

The origins, contaminations, chemical classifications and heat reservoirs of the hot spring waters in the Kangding district in western Sichuan have been investigated widely (Luo, 1994; Jia et al., 1997; Zhang and Hu, 2000; Li et al., 2005; Cao et al., 2006; Du et al., 2006; Shen, 2007; Liu, 2008; Lu et al., 2008). Chen et al. (2014) observed the geochemical variations of the waters sampled from the hot springs in the Kangding district before the Wenchuan M_S 8.0 earthquake in Sichuan Province, Southwest China on 12 May 2008.

This paper aims at investigating hydrochemical characteristics of the spring waters in the Kangding district before and after the Lushan M_S 7.0 earthquake in Sichuan Province, southwestern China and the relationship between the geochemical variations and seismic activity.

2 Geological setting

The studied area is located in a "Y" shape intersection of the Longmenshan fault (LMSF), Xianshuihe fault (XSHF) and Anninghe fault (ANHF) (Fig. 1). Those faults incise each other and deeply cut the lithosphere, and act as an important passage for upward migration of thermal fluids from the deep earth, which is indicated by distribution of many hot springs with high temperature and Yanshanian granite widely exposed around the "Y" intersection area (Fig. 1) (Luo, 1994).

Historically, a number of great earthquakes ($M_S > 7.0$) have occurred surround the Kangding district since 1800. The most hazardous earthquakes are the 1850 Xichang M_S 7.5 earthquake occurred in the ANHF zone, the M_S 7.5 one of 25 August 1933 in the LMSF zone, and the M_S 7.5 one of 1955 and the M_S 7.9 one of 1973 in the XSHF zone (Zhou et al., 2010), the 2008 M_S 8.0 Wenchuan earthquake in the LMSF zone

NHESSD
2, 7293–7308, 2014

(Chen et al., 2014) and the Lushan M_S 7.0 earthquake on 20 April 2013 in Lushan district, Sichuan Province, Southwest China, which is 95 km from the Kangding district (Fig. 1).

3 Methods

The spring waters were collected at 10 sites of wells and springs in the southeast segment of XSHF zone (Fig. 1) on 23–25 April 2013. The water samples were sealed quickly after the sampling and stored in 25 mL plastic bottles. The water temperatures were measured in the field with a digital thermometer with an error of ±1 %. The concentrations of cations (K^+, Na^+, Mg^{2+} and Ca^{2+}) and anions (F^-, Cl^-, Br^-, NO_3^- and SO_4^{2-}) of the water samples were measured with the Dionex ICS-900 ion chromatography in the Seismic Fluid Laboratory of Institute of Earthquake Science, China Earthquake Administration, with the reproducibility within ±2 %. The CO_3^{2-} and HCO_3^- concentrations were measured by the standard titration procedures with a ZDJ-100 potentiometric titrator (reproducibility within ±2 %). For calibrating the chromatography, the standard samples were measured before and after measuring each batch of the water samples. Deviation of the measurements is within ±2 %. The data were evaluated by the ion balance (ib) calculated according to the Eq. (1) (Woith et al., 2013),

$$\mathrm{ib}[\%] = \frac{\sum \mathrm{cations} - \sum \mathrm{anions}}{0.5(\sum \mathrm{cations} + \sum \mathrm{anions})} 100. \quad (1)$$

4 Results

The physico-chemical parameters of the water samples are showed in Table 1. The ib values of measured chemical data are less than 5 %.

The temperatures of the spring waters were in the range from 30.4 to 83.0 °C. The TDS values ranged from 132.1 to 2130.5 mg L^{-1}. Concentrations of K^+, Na^+, Ca^{2+}

NHESSD
2, 7293–7308, 2014

and Mg^{2+} ranged from 0.0 to 53.3, 35.0 to 518.4, 3.7 to 80.5 and 0.0 to 48.1 $mg L^{-1}$, respectively. Concentrations of F^-, Cl^-, Br^-, SO_4^{2-} and HCO_3^- ranged from 0.0 to 27.1, 2.4 to 336.2, 0.0 to 1.3, 6.7 to 161.9 and 60.0 to 1270.9 $mg L^{-1}$, respectively (Table 1).

5 Discussion

5.1 Chemical types of the spring waters

The triangular diagrams illustrate the proportions of the milli-equivalent of the anions (Cl^-, SO_4^{2-} and HCO_3^-) and cations (K^+, Na^+, Mg^{2+} and Ca^{2+}) for the spring waters (Fig. 2). Each of the triangular diagrams were divided into 7 blocks. The water samples were mainly plotted in the blocks i, ii, vi and II, III and IV respectively, which indicated that Na^+ and HCO_3^- were the main chemical components for most of the spring waters. Using the Shoka Lev's classification method, the spring waters were classified into 7 types: Na-HCO_3, NaMg-HCO_3, NaMg-HCO_3SO_4, CaNa-SO_4HCO_3, CaNa-HCO_3SO_4, Na-$ClHCO_3$ and Na-HCO_3Cl (Fig. 2, Table 1). The differential chemical types of the spring waters indicated the variation of water-rock interactions in the hydrological system in the study area (Fig. 1).

5.2 Chemical variations of the spring waters

The hydrochemical parameters of the spring waters before and after the Lushan M_S 7.0 earthquake evidently varied with the amplitudes ranging from −73.3 to 231.9 $mg L^{-1}$.

After the Lushan earthquake, the concentrations of Ca^{2+}, HCO_3^- and TDS of the waters from the Guanding, Erdaoqiao, Gonghe, Erhaoying, Tianwanhe and Caoke springs showed obviously increase, with the amplitudes ranging from 9.9 to 43.1 $mg L^{-1}$, 59.1 to 172.3 $mg L^{-1}$ and 56.7 to 231.9 $mg L^{-1}$ respectively, but the TDS of the Guanding spring water decreased by 20.0 $mg L^{-1}$ (Fig. 3a–c). Furthermore, the concentrations of Ca^{2+} and HCO_3^- of the waters from the Guanding, Erdaoqiao, Gonghe, Erhaoying, Tianwanhe and Caoke springs moved toward the Ca^{2+} and HCO_3^- corners in the triangular diagrams (Fig. 2), and the chemical types of the waters from the Guanding and Caoke springs changed from Na-$ClHCO_3$ to Na-HCO_3Cl and CaNa-SO_4HCO_3 to CaNa-HCO_3SO_4, respectively (Table 1).

The water-rock interaction has been proposed as a possible mechanism for the geochemical parameters variations before and after earthquake (Du et al., 2010; Reddy et al., 2011). Experiments on CO_2-water-rock interaction indicated that injection of CO_2 into geothermal waters would promote the release of Ca^{2+} from the surrounding carbonate rock as the Eq. (2) (Ueda et al., 2005; Liu et al., 2012). The dissolution rate of carbonate rocks can be enhanced by increasing the dissolved CO_2 into geothermal waters in response to the elevated partial pressure of CO_2 (Robert et al., 2005).

$$CaCO_3 + H_2O + CO_2 \rightarrow Ca^{2+} + 2HCO_3^- \qquad (2)$$

CO_2 is the main gas phase of the waters from the Guanding, Erdaoqiao, Gonghe, Erhaoying, Tianwanhe and Caoke springs, with the concentrations ranging from 4.2 to 90.0 vol. % (Zhou, 2011). Before the Lushan earthquake, the regional stress field surround the Kangding district had been building up (Wu et al., 2013; Wang et al., 2014), which might strengthen the partial pressure of the CO_2 in the spring waters and accelerated its dissolution rate. Consequently, the increment of dissolved CO_2 in the spring waters would accelerate the interaction between water and carbonate rocks which widely exist in the strata, resulting in the increase of TDS and concentrations of Ca^{2+} and HCO_3^- of the waters from the springs during the earthquake generation. Furthermore, the chemical types of the Guanding and Caoke spring waters changed from Na-$ClHCO_3$ to Na-HCO_3Cl and from CaNa-SO_4HCO_3 to CaNa-HCO_3SO_4, respectively. The milli-equivalent values of Ca^{2+} and HCO_3^- of the waters from the Guanding, Erdaoqiao, Gonghe, Erhaoying, Tianwanhe and Caoke springs increased lineally ($R^2 = 0.93$, Fig. 4), which indicated the enhanced dissolution of carbonate rocks. Whereas, the TDS of the Guanding spring water decreased, which may be the result of the dilution of precipitation water.

NHESSD
2, 7293–7308, 2014

Hydrochemical characteristics of the hot spring waters in the Kangding district

Z. Chen et al.

The concentrations of Na^+, Cl^- and SO_4^{2-} of the waters from the Guanding, Zheduotang, Xinxing, Erhaoying and Gonghe springs varied complexly. After the Lushan earthquake, Na^+ concentration of the waters from the Xinxing and Gonghe springs decreased by 21.9 and 19.1 $mg\,L^{-1}$ respectively, but that of the water from the Erhaoying spring increased by 36.5 $mg\,L^{-1}$. Cl^- concentrations of the waters from the Guanding and Xinxing springs decreased by 39.1 and 73.3 $mg\,L^{-1}$, respectively (Fig. 3d). SO_4^{2-} concentrations of the waters from the Zheduotang and Gonghe springs decreased by 9.7 and 9.2 $mg\,L^{-1}$ respectively, while that of the Erhaoying spring water increased by 10.6 $mg\,L^{-1}$ (Fig. 3a).

The high $^3He/^4He$ ratios for the gas from the Guanding, Zheduotang, Xinxing, Erhaoying and Gonghe spring waters (between 1.43 and 3.73 Ra, $Ra = 1.39 \times 10^{-6}$) suggested the contribution of mantle fluids to the springs (Zhou et al., 2010), which resulted in the high temperatures (between 42.8 and 83.0 °C, Table 1) and high concentrations of Cl^- and SO_4^{2-} of the spring waters (Chen et al., 2014). Therefore, the decrease of the concentrations of Na^+, Cl^- and SO_4^{2-} of the waters from the Guanding, zheduotang, Xinxing and Gonghe springs may be the result of dilution of precipitation water. Otherwise, the increase of the concentrations of Na^+ and SO_4^{2-} in the Erhaoying spring water may be attributed to the more supplement of fluids enriched in SO_4^{2-} resulted from the oxidation of H_2S.

6 Conclusions

The following conclusions can be drawn from our study:

1. Based on the Shoka Lev's classification method, the waters from the hot springs in the Kangding district can be classified into 7 chemical types: Na-HCO_3, NaMg-HCO_3, NaMg-HCO_3SO_4, CaNa-SO_4HCO_3, CaNa-HCO_3SO_4, Na-ClHCO_3 and Na-HCO_3Cl.

NHESSD
2, 7293–7308, 2014

2. The concentrations of Ca^{2+}, HCO_3^- and TDS of the waters from the Guanding, Erdaoqiao, Gonghe, Erhaoying, Tianwanhe and Caoke springs increased evidently after the Lushan earthquake, with the amplitudes ranging from 9.9 to 43.1 $mg\,L^{-1}$, 59.1 to 172.3 $mg\,L^{-1}$ and 56.7 to 231.9 $mg\,L^{-1}$, respectively, which resulted from the enhanced interaction between carbonate rocks and water enriched in CO_2.

3. The concentrations of Na^+, Cl^- and SO_4^{2-} of the waters from the Guanding, Zheduotang, Xinxing and Gonghe springs decreased after the Lushan earthquake, which may be related to the dilution of precipitation water. However, the increase of the concentrations of Na^+ and SO_4^{2-} of the waters from the Erhaoying spring after the Lushan earthquake may be the result of the more supplement of fluids enriched in SO_4^{2-} resulted from the oxidation of H_2S.

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NHESSD

2, 7293–7308, 2014

Hydrochemical characteristics of the hot spring waters in the Kangding district

Z. Chen et al.

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Table 1. Physico-chemical parameters of the spring waters.

No.	Site	Date	Longitude (E)	Latitude (N)	T °C	TDS mg L^{-1}	K^+ mg L^{-1}	Na^+ mg L^{-1}	Ca^{2+} mg L^{-1}	Mg^{2+} mg L^{-1}	F^- mg L^{-1}	Cl^- mg L^{-1}	Br^- mg L^{-1}	SO_4^{2-} mg L^{-1}	HCO_3^- mg L^{-1}	Chemical type
16	Guanding	15 Jun 2008*	101.96	29.98	80.5	1306.1	41.2	396.8	13.2	13.2	1.5	336.2	0.5	52.0	440.3	Na-ClHCO$_3$
	Spring	26 Oct 2008*			80.0	1395.4	40.6	367.2	13.4	13.6	2.6	328.5	1.1	50.0	485.5	Na-ClHCO$_3$
		25 Jun 2009*			83.0	1353.8	42.7	367.4	13.7	13.5	2.4	320.9	0.5	49.7	443.1	Na-ClHCO$_3$
		17 Apr 2010*			83.0	1273.6	41.5	349.7	13.8	13.8	0.1	300.8	0.0	50.6	447.2	Na-ClHCO$_3$
		25 Apr 2013			n.d.	1453.6	44.3	346.2	23.7	16.2	2.2	261.8	0.0	52.8	506.4	Na-HCO$_3$Cl
17	Longtougou	15 Jun 2008*	101.96	29.98	70.8	2044.9	53.2	510.8	16.0	31.4	3.1	220.7	1.0	8.3	1200.4	Na-HCO$_3$
	Spring	26 Oct 2008*			70.2	2130.5	52.7	518.4	17.4	31.0	3.2	227.4	1.0	8.6	1270.9	Na-HCO$_3$
		25 Jun 2009*			73.1	2025.9	52.3	516.7	16.7	30.8	3.0	226.2	0.7	8.3	1171.3	Na-HCO$_3$
		17 Apr 2010*			70.2	2096.9	51.6	507.9	16.3	31.1	3.2	207.6	0.0	8.3	1270.9	Na-HCO$_3$
		25 Apr 2013			n.d.	2086.8	53.3	506.6	13.9	32.1	2.8	220.2	0.0	8.0	1250.0	Na-HCO$_3$
18	Zheduotang	15 Jun 2008*	101.86	30.01	54.5	681.6	3.1	208.8	4.9	0.1	26.7	10.6	0.0	17.6	342.1	Na-HCO$_3$
	Spring	26 Oct 2008*			53.8	705.5	3.1	219.8	4.4	0.1	26.4	10.6	0.0	17.3	338.1	Na-HCO$_3$
		25 Jun 2009*			53.4	650.3	3.0	207.1	4.4	0.1	27.0	9.6	0.0	16.6	346.6	Na-HCO$_3$
		17 Apr 2010*			53.8	663.2	2.9	208.8	4.7	0.1	27.1	9.8	0.0	16.4	305.1	Na-HCO$_3$
		25 Apr 2013			n.d.	683.4	2.0	207.4	3.7	0.0	26.8	8.9	0.0	6.8	340.0	Na-HCO$_3$
19	Erdaoqiao	15 Jun 2008*	101.95	30.09	39.1	843.4	23.5	150.5	22.1	44.1	1.2	43.9	0.0	114.6	443.5	NaMg-HCO$_3$
	Spring	26 Oct 2008*			39.4	919.7	22.5	150.7	22.1	44.7	1.4	40.4	0.0	107.1	530.9	NaMg-HCO$_3$
		26 Jun 2009*			40.6	926.4	22.4	146.3	20.2	44.5	1.2	43.9	0.0	109.5	538.4	NaMg-HCO$_3$
		16 Apr 2010*			40.6	935.5	23.7	157.1	20.9	43.8	1.1	41.0	0.9	111.6	535.4	NaMg-HCO$_3$
		25 Apr 2013			n.d.	1094.1	26.2	156.1	57.1	47.8	3.6	43.6	0.0	104.6	655.0	NaMg-HCO$_3$
20	Xinxing	16 Jun 2008*	102.06	29.75	45.6	1287.5	9.4	422.7	12.5	9.7	3.8	148.0	1.0	28.9	545.2	Na-HCO$_3$
	Spring	27 Oct 2008*			44.1	1167.8	9.7	365.0	12.8	9.4	3.8	144.0	1.3	24.7	597.2	Na-HCO$_3$
		24 Jun 2009*			42.8	1289.9	9.2	360.6	12.0	9.4	3.4	148.4	1.0	24.1	597.2	Na-HCO$_3$
		23 Apr 2010*			48.2	1038.5	9.2	303.1	12.0	9.0	3.9	156.2	0.3	21.3	523.4	Na-HCO$_3$
		24 Apr 2013			n.d.	1028.5	9.1	281.2	13.3	12.9	3.4	82.9	0.0	20.6	545.0	Na-HCO$_3$
21	Gonghe	16 Jun 2008*	102.11	30.62	48.8	577.9	9.9	108.4	19.3	22.1	1.9	18.4	0.0	60.3	337.5	Na-HCO$_3$
	Spring	27 Oct 2008*			47.6	598.2	10.0	106.5	20.1	22.1	2.0	17.8	0.0	60.1	359.5	Na-HCO$_3$
		24 Jun 2009*			50.0	610.2	9.6	107.6	18.5	21.3	1.9	17.4	0.0	65.1	369.0	Na-HCO$_3$
		23 Apr 2010*			44.8	585.9	9.4	111.8	19.3	21.5	2.6	17.9	0.0	64.1	339.3	Na-HCO$_3$
		24 Apr 2013			n.d.	642.7	9.8	92.7	35.9	28.5	2.2	13.7	0.0	54.9	405.0	Na-HCO$_3$
22	Erhaoying	17 Jun 2008*	102.03	29.59	65.5	597.3	18.3	154.1	13.5	4.6	2.7	37.1	0.0	59.3	307.6	Na-HCO$_3$
	Spring	27 Oct 2008*			67.4	645.1	18.3	156.5	13.5	4.6	2.9	36.8	0.5	62.2	349.9	Na-HCO$_3$
		25 Jun 2009*			63.0	585.6	18.5	153.0	13.2	4.7	3.0	35.3	0.2	62.4	295.1	Na-HCO$_3$
		24 Apr 2010*			67.4	631.7	18.3	150.4	13.0	4.8	0.4	36.0	0.0	59.9	349.0	Na-HCO$_3$
		24 Apr 2013			n.d.	863.6	24.1	186.9	48.6	5.8	3.0	44.4	0.0	70.4	480.4	Na-HCO$_3$
23	Tianwanhe	17 Jun 2008*	102.14	29.49	53.0	613.9	17.6	76.9	13.1	45.3	2.4	24.6	0.2	152.3	281.5	NaMg-HCO$_3$SO$_4$
	Spring	25 Jun 2009*			n.d.	632.2	16.9	73.4	12.7	45.7	2.2	23.4	0.6	139.6	317.7	NaMg-HCO$_3$SO$_4$
		24 Jun 2009*			54.0	611.7	17.6	79.1	12.8	43.6	1.7	24.9	0.3	145.2	286.5	NaMg-HCO$_3$SO$_4$
		24 Apr 2010*			53.2	644.8	17.4	79.1	12.7	44.4	2.3	25.7	0.0	145.4	317.7	NaMg-HCO$_3$SO$_4$
		23 Apr 2013			n.d.	867.9	21.4	79.9	55.8	48.1	4.5	28.9	0.0	139.4	490.0	NaMg-HCO$_3$SO$_4$
24	Caoke		102.10	29.39	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	
	Spring	28 Oct 2008*			41.4	407.8	3.0	48.7	50.1	6.2	1.0	4.0	0.0	155.6	139.2	CaNa-SO$_4$HCO$_3$
		24 Jun 2009*			42.9	363.1	3.0	46.2	44.4	6.1	0.9	3.9	0.0	160.5	98.1	CaNa-SO$_4$HCO$_3$
		24 Apr 2010*			41.4	369.4	3.0	46.3	45.6	6.2	0.9	3.6	0.0	161.9	101.9	CaNa-SO$_4$HCO$_3$
		23 Apr 2013			n.d.	527.1	5.9	47.8	80.5	6.2	0.0	3.9	0.0	157.8	225.0	CaNa-HCO$_3$SO$_4$
25	Shimian		102.22	29.44	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	
	Well	28 Oct 2008*			30.4	150.3	2.4	38.6	7.0	1.2	11.1	2.6	0.0	17.8	69.6	Na-HCO$_3$
		23 Jun 2009*			31.3	149.1	2.4	37.6	6.5	1.2	10.9	2.4	0.0	17.3	70.8	Na-HCO$_3$
		24 Apr 2010*			31.2	137.8	2.3	35.1	6.9	1.2	10.2	2.4	0.0	17.2	62.5	Na-HCO$_3$
		23 Apr 2013			n.d.	132.1	0.0	35.0	7.0	0.0	12.3	2.4	0.0	15.4	60.0	Na-HCO$_3$

The * data were from Chen et al. (2014), the "n.d." represents no samples were colleted.

NHESSD
2, 7293–7308, 2014

Hydrochemical characteristics of the hot spring waters in the Kangding district

Z. Chen et al.

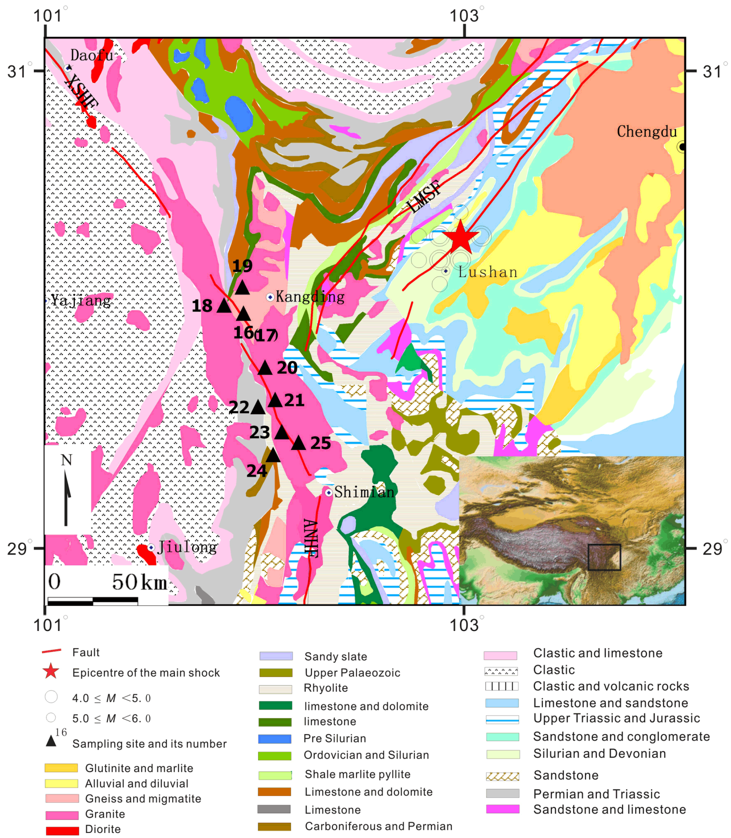

Figure 1. Geological map of the studied region, the insert showing Asia map in which the square shows the location of studied region, the sampling sites distribute in the southeast segment of XSHF zone.

NHESSD
2, 7293–7308, 2014

Hydrochemical characteristics of the hot spring waters in the Kangding district

Z. Chen et al.

Title Page
Abstract Introduction
Conclusions References
Tables Figures
◀| |▶
◀ ▶
Back Close
Full Screen / Esc
Printer-friendly Version
Interactive Discussion

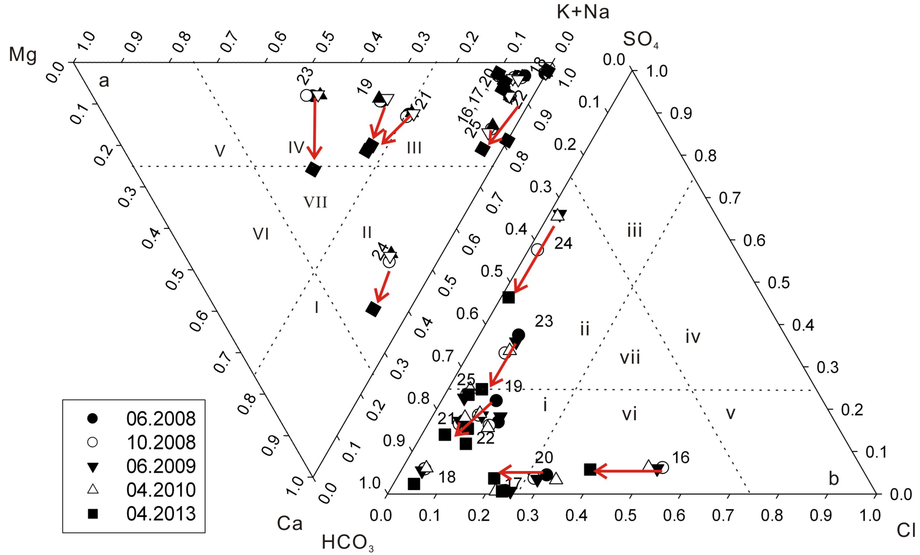

Figure 2. Ternary plots of the cation and anion for the hot spring waters, **(a)** is the plot of cation and **(b)** is the plot of anion.

NHESSD
2, 7293–7308, 2014

Hydrochemical characteristics of the hot spring waters in the Kangding district

Z. Chen et al.

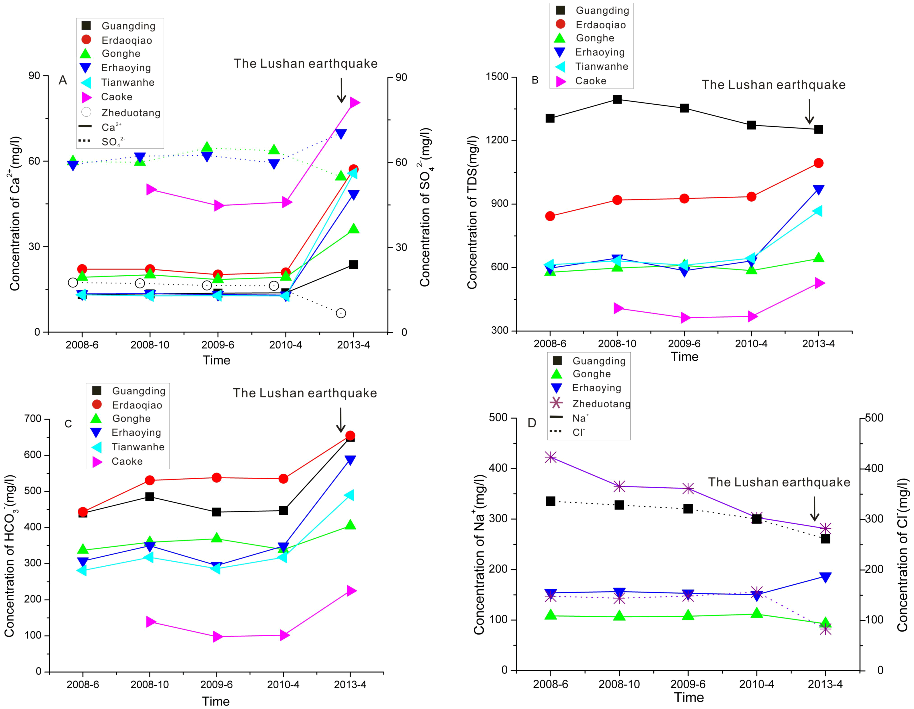

Figure 3. Temporal ion variations of the spring waters before and after the Lushan earthquake.

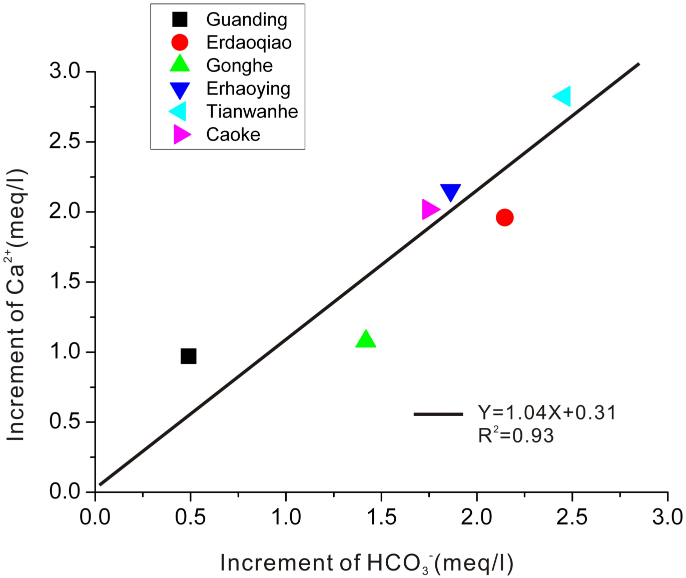

Figure 4. The plot of Ca^{2+} vs. HCO_3^- milli-equivalent, showing Ca^{2+} and HCO_3^- were most possibaly derived from dicomposition of carbnates. The abscissa indicates the Ca^{2+} increment of the water samples being relative to Ca^{2+} concentration in 2010 and the ordinate indicates the HCO_3^- increment of the water samples compared to that collected in 2010.

NHESSD
2, 7293–7308, 2014

Hydrochemical characteristics of the hot spring waters in the Kangding district

Z. Chen et al.