Asian Journal of Chemistry; Vol. 25, No. 3 (2013), 1541-1546

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2013.13132

Chemical Characteristics and Formation of Karst Water in Guilin Area, China

HUI QIAN[1,2,*], JIANHUA WU[1,2] and PEIYUE LI[1,2]

[1]School of Environmental Science and Engineering, Chang'an University, No. 126 Yanta Road, Xi'an 710054, Shaanxi, P.R. China
[2]Key Laboratory of Subsurface Hydrology and Ecology in Arid Areas, Ministry of Education, No. 126 Yanta Road, Xi'an 710054, Shaanxi, P.R. China

*Corresponding author: Fax: +86 29 82339952; Tel: +86 29 82339327; E-mail: qianhui@chd.edu.cn

(*Received*: 28 November 2011; *Accepted*: 19 September 2012) AJC-12156

In present study, the chemical characteristics and evolution law of the Guilin karst water are reported. The chemical compositions of 74 karst water samples and one local rain water sample were compared and analyzed. The dissolved amounts of minerals and gas in the 74 karst water samples were calculated using mass balance approach. The forming environments of the karst water were analyzed and discussed. The results show that the karst water in this region is formed by the dissolutions of gypsum, calcite, dolomite and atmospheric CO_2 on the basis of the chemical compositions of the local rain water and the Guilin karst water is formed in a relatively open environment.

Key Words: Karst water, Dissolution of mineral and gas, Mass balance calculation, Forming environment, Water chemistry.

INTRODUCTION

Karst regions are characterized by limestones and other soluble rocks at or near land surface that have been modified by solution erosion[1]. Interest in karst hydrology has increased greatly in the past decades, which has resulted in international exchange of many topical karst problems. The history of the research on karst water in China can be traced back to the 1960s, when a national karst conference was held by the Geological Society of China in Guilin[2]. Since then a number of scholars have focused on karst water research at different levels in China. Gu[3] put forward several experiments about shallow karst water service to agricultural production. At this time, some international scholars have also noticed the interesting research. Pitty[4] proposed an approach of correlating both solute fluctuations and flow rate of karst water with climatic data to study karst water. In their work, nearly 100 karst water samples were collected and analyzed for determining the quantity of dissolved calcium carbonate in the limestone areas of the southern and central Pennines. In the 1970s, some specific investigations and calculations on karst water were carried out in some river basins[5-7] and the runoff features of karst water and the effects of karst features on water circulation were studied[8,9]. Entering into the 1980s, more studies on karst problems were conducted. These studies nearly covered every aspect of karst study such as chemical characteristics of karst water[10-12], chemical classification of karst water[13], karst water pollution[14], movement and dynamics of karst water[15], karst landscape[16,17], the formation of karst water[18-20] and karst water resource evaluation and management[21-24]. Since the 1990s, the studies on various aspects of karst related issues have become more complex and with the popularity of computers, numerical modeling on kasrt water movement has become more and more common[25-28].

At present, there are typically two ways for karst phenomenon research: one is the direct way which studies directly the changing characteristics of dissolvable minerals when water flows through them and the other is the indirect way which discusses the changing characteristics of dissolvable minerals indirectly by studying the physicochemical property changes of water which flows through these minerals. Actually, the latter way is to calculate the dissolution and precipitation of minerals by discussing the physicochemical property changes of the water flowing through the dissolvable rocks. This paper attempts to discuss the dissolution and precipitation of minerals in Guilin karstic region by the latter way.

EXPERIMENTAL

Study area: Guilin area, one of the most popular areas for karst research in China and the world, is situated between longitude 110º09' -110º42'E and latitude 24º40' -24º40' N, and covers an area of 7420 km^2. It is covered by limestone all over the area and is the most typical and developed area for karst landforms and karst groundwater in China. The first international karst research institute is located in the area. The area is dominated by subtropical monsoon climate and is characterized

TABLE-1
CHEMICAL ANALYSIS RESULTS AND STATISTICAL ANALYSIS OF KARST WATER (UNIT: mg/L EXCEPT pH AND TEMPERATURE)

Sample No.	pH	T (ºC)	Cl^-	SO_4^{2-}	HCO_3^-	Na^+	K^+	Ca^{2+}	Mg^{2+}	CO_3^{2-}
Rain water	6.40	18.50	3.50	0.00	6.00	0.20	0.00	1.60	0.04	0.00
1	8.23	19.00	4.25	15.37	214.79	0.50	0.00	79.76	0.91	7.20
2	8.60	18.00	2.84	14.41	112.88	0.30	0.00	44.09	1.00	4.80
3	8.48	18.50	2.84	18.25	61.02	0.30	0.00	32.06	0.96	4.80
4	8.18	18.50	4.25	14.41	222.11	0.30	0.00	82.16	1.16	2.40
5	8.62	12.00	2.84	18.25	165.97	0.30	0.00	64.13	1.05	9.60
6	8.12	17.30	3.55	20.17	170.86	0.75	0.00	70.94	0.54	9.60
7	8.26	20.00	4.96	12.49	234.23	1.00	0.00	85.37	0.44	4.80
8	7.49	18.00	6.38	17.29	273.37	0.90	0.00	98.20	0.91	0.00
9	7.82	17.00	4.96	15.37	297.87	0.55	0.00	107.40	1.24	0.00
10	7.80	10.20	4.96	16.33	256.28	0.50	0.00	92.18	1.16	0.00
11	8.34	18.00	4.25	13.45	122.04	0.30	0.00	56.91	0.96	9.60
12	8.36	16.80	2.84	15.37	126.92	0.00	0.00	53.71	1.16	2.40
13	8.26	19.80	3.55	14.41	124.48	0.35	0.30	48.90	0.50	7.20
14	7.98	16.00	2.13	18.25	124.48	0.30	0.00	18.50	1.06	0.00
15	8.76	13.00	2.55	18.25	146.54	0.30	0.00	64.93	0.74	14.40
16	7.38	17.00	2.13	4.80	241.63	0.30	0.00	78.16	1.46	0.00
17	7.49	15.50	2.13	1.92	129.36	0.50	0.50	38.88	2.19	0.00
18	7.67	17.50	3.55	3.84	151.33	0.40	0.00	52.10	0.97	0.00
19	7.40	17.00	3.55	2.88	288.01	0.20	0.00	92.99	1.46	0.00
20	7.38	16.20	8.51	5.76	234.32	2.25	0.50	76.95	1.22	0.00
21	7.96	17.00	3.55	5.76	131.80	0.25	0.00	48.50	0.73	0.00
22	7.48	17.80	21.98	14.41	205.03	6.10	2.55	78.16	4.86	0.00
23	7.50	16.00	5.76	11.53	222.11	1.50	0.60	75.75	1.22	0.00
24	7.47	16.00	3.55	15.37	224.55	0.37	0.00	77.76	1.22	0.00
25	7.60	15.50	3.55	17.29	234.32	0.37	0.00	83.37	0.24	0.00
26	7.36	16.00	4.25	5.76	53.70	1.05	0.86	18.04	0.97	0.00
27	7.94	20.00	2.13	2.88	178.21	0.40	0.30	55.31	3.89	0.00
28	7.87	20.00	2.84	4.80	180.65	0.40	0.30	58.11	1.22	0.00
29	7.56	20.00	0.00	0.96	151.33	0.46	0.00	51.30	0.97	0.00
30	7.86	20.00	0.00	0.00	207.47	0.00	0.00	62.52	4.37	0.00
31	7.96	19.20	2.84	0.96	170.86	0.40	0.50	44.09	6.81	0.00
32	7.50	25.30	3.55	0.96	214.79	0.55	0.30	57.72	8.03	0.00
33	7.52	19.20	3.55	0.96	288.01	0.20	0.00	91.38	2.19	0.00
34	7.24	18.50	2.13	0.96	258.72	0.20	0.00	80.56	2.68	0.00
35	7.31	18.00	2.84	4.80	263.61	0.30	0.50	87.37	0.97	0.00
36	7.61	18.20	2.13	3.84	212.35	0.40	0.50	63.33	3.89	0.00
37	7.61	18.60	3.55	4.80	205.03	0.40	0.30	64.53	1.70	0.00
38	7.50	19.10	4.25	3.84	209.91	0.40	0.30	64.53	3.16	0.00
39	7.50	22.70	2.84	2.88	200.15	0.85	0.65	63.33	2.68	0.00
40	7.31	19.60	2.84	0.00	229.44	0.20	0.00	72.54	2.43	0.00
41	7.68	23.50	2.84	2.88	195.26	0.75	0.50	58.52	3.89	0.00
42	7.42	21.00	2.84	0.00	226.99	0.65	0.50	70.14	2.19	0.00
43	7.45	18.50	2.84	1.92	231.86	0.50	0.33	75.35	2.67	0.00
44	7.61	19.50	2.13	1.92	241.63	0.40	0.33	68.94	6.56	0.00
45	7.44	21.30	3.55	5.76	205.03	0.50	0.29	60.12	5.59	0.00
46	7.37	19.00	4.25	6.72	205.03	0.60	0.83	58.52	6.56	0.00
47	7.30	20.00	19.85	43.23	212.35	10.83	0.29	86.57	2.19	0.00
48	7.57	18.50	3.55	2.88	263.61	0.37	0.00	85.77	1.94	0.00
49	7.31	19.00	2.13	3.84	263.59	0.30	0.17	82.16	3.40	0.00
50	7.30	13.00	4.25	12.49	214.79	0.40	0.80	75.35	1.70	0.00
51	7.46	7.30	3.55	3.84	117.16	0.25	0.45	33.27	5.10	0.00
52	7.42	19.50	2.13	10.57	207.47	0.00	0.00	69.73	0.49	0.00
53	7.36	19.00	4.25	9.61	139.13	0.00	0.00	49.70	0.73	0.00
54	7.62	10.50	2.84	6.72	146.45	0.00	0.00	51.70	1.46	0.00
55	7.24	16.50	4.25	15.37	229.44	0.25	0.30	79.76	0.24	0.00
56	7.16	13.00	2.84	6.72	73.24	0.60	0.30	23.25	2.92	0.00
57	8.24	31.00	2.84	0.00	61.02	0.60	0.30	20.04	2.92	4.80
58	7.60	14.50	2.84	7.68	109.85	0.60	0.30	32.06	1.22	0.00
59	7.63	25.20	2.13	3.84	119.60	0.45	0.30	36.07	0.97	0.00
60	7.70	14.50	2.84	5.76	107.41	0.60	0.30	33.27	1.46	0.00
61	7.27	21.00	3.55	24.02	100.07	0.70	0.55	48.90	0.73	0.00
62	7.70	16.50	3.55	13.45	336.89	0.80	0.30	109.02	2.92	0.00

63	7.90	17.00	2.84	9.61	205.06	0.40	0.30	68.54	0.73	0.00
64	8.44	12.50	2.13	11.53	180.65	0.40	0.00	67.74	0.00	7.20
65	8.37	13.00	3.55	12.49	124.53	0.30	0.00	45.69	0.49	2.40
66	7.41	18.00	2.13	7.68	12.42	0.20	0.00	103.81	3.19	0.00
67	7.40	18.00	2.13	7.68	280.68	0.20	0.00	91.78	1.94	0.00
68	7.48	18.20	2.13	7.68	207.46	0.20	0.00	70.94	0.97	0.00
69	7.72	16.50	2.84	6.72	170.86	0.62	0.29	53.71	2.19	0.00
70	7.74	19.50	2.84	9.61	163.53	50.50	0.00	55.31	1.22	0.00
71	7.66	18.20	2.13	24.02	180.62	0.40	0.00	67.33	0.49	0.00
72	7.46	19.20	3.55	23.06	263.61	0.65	0.00	92.99	2.92	0.00
73	7.62	15.50	1.42	62.44	153.76	0.40	0.00	73.75	1.70	0.00
74	7.50	17.50	1.42	24.98	180.61	0.30	0.00	63.33	2.67	0.00
Mean	7.71	17.89	3.66	10.28	191.51	0.67	0.23	65.27	2.05	1.23
Min	7.16	7.3	0.00	0.00	12.42	0.00	0.00	18.04	0.00	0.00
Max	8.76	31	21.98	62.44	336.89	10.83	2.55	109.02	8.03	14.4
SD	0.38	3.46	3.16	9.12	64.18	5.96	0.36	20.98	1.70	2.95

Mean, Min, Max, and SD are mean, minimum, maximum and standard deviation of indices of karst water, respectively.

by hot and rainy summer, cold and dry winter. The average annual temperature is 18-19 ºC and increases from north to south. The average annual precipitation in the area is 1897.3 mm with over 60 % concentrated during April to July[29]. The main minerals forming the rocks are dolomite, calcite and gypsum which can easily dissolve under specific conditions. The world famous scenery in the area is formed by the dissolution of these minerals. Rain water, the most important source for karst water, is essential for the forming of karst landforms. All the karst water bodies including karst surface water and karst groundwater are formed on the basis of rain water through the water-rock interaction.

RESULTS AND DISCUSSION

Chemical characteristics of Guilin karst water: To carry out the study, a total of 74 karst water samples and a rain water sample were used. Because of the inadequate of available data, all these data used in the paper were abstracted from the monograph[30]. The chemical analysis results and the statistical analyses of karst water samples were included in the Table-1 in which the rain water chemical analysis results were also listed. The temperature of rain water is the local average air temperature. Compared the chemical compositions of local rain water with those of karst water, it can be found that the karst water possesses the following characteristics:

(i) Compared with the rain water, the concentrations of Cl^-, Na^+ and K^+ in karst water do not change significantly. The concentrations of Cl^-, Na^+ and K^+ in rain water are 3.50, 0.20 and 0.00 mg/L and the mean values of the three chemical parameters in karst water are 3.65, 1.35 and 0.23 mg/L. The highest concentration of Na^+ is 10.83 mg/L observed in sample 47 and the lowest is 0. The concentrations of K^+ are lower than 1.0 mg/L in all karst water samples except in sample 22 which possesses the highest K^+ concentration of 2.55 mg/L.

(ii) The increases of the concentrations of SO_4^{2-}, HCO_3^- in karst water samples are significant compared with those in the rain water sample. In the rain water, no SO_4^{2-} was detected, but in karst water samples the mean concentration of SO_4^{2-} reaches to 10.28 mg/L and its biggest concentration is 62.44 mg/L. The maximum concentration of HCO_3^- in karst water samples is 336.89 mg/L and the mean concentration is 187.46 mg/L which is over 31 times higher than that in the rain water. A significant increase of Ca^{2+} content in karst water was also observed. The mean Ca^{2+} content in karst water is 40.79 times of that in rain water.

(iii) A slight increase of Mg^{2+} concentration in karst water was observed. The mean Mg^{2+} concentration in karst water is 2.05 mg/L which is 51.26 times of that in the rain water. The concentration of CO_3^{2-} in karst water is mainly controlled by pH. Generally speaking, only when pH value is higher than 8.0 can the CO_3^{2-} exist and be detected in water.

Based on the geology, hydrogeology of the study area and the above comparison, it can be concluded that the changes of the chemical compositions in karst water relative to those in rain water are resulted from the dissolution of calcite, dolomite, gypsum and carbon dioxide (CO_2).

Dissolution calculation of the minerals and gases in karst water: Since the chemical changes of the karst water relative to the local rain water are resulted from the disolution of calcite, dolomite, gypsum and CO_2, it is of great concern to determine how much dissolution of these minerals is needed to form current chemical constituents of karst water on the basis of the rain water chemistry. According to the elements mass balance among minerals, gases and water, the amounts of minerals and gases dissolved in karst water can be calculated.

There are four main elements in gypsum, calcite, dolomite and CO_2 that are our most concern, namely, S, C, Ca and Mg. Assume that X_1 mmol/L gypsum, X_2 mmol/L CO_2, X_3 mmol/L calcite and X_4 mmol/L dolomite are dissolved to form the existing chemical compositions of the karst water, then the dissolved amounts for element S, C, Ca and Mg are X_1, $(X_2 + X_3 + 2X_4)$, $(X_1 + X_3 + X_4)$ and X_4, respectively. At the same time, the above dissolution makes the element S, C, Ca and Mg contents in water solution also increase. If dS, dC, dCa and dMg are used to denote the increase of element S, C, Ca and Mg per liter water, respectively, the following relationships according to the principle of mass balance should be met:

$$X_1 = dS \quad (1)$$

$$X_2 + X_3 + 2X_4 = dC \quad (2)$$

$$X_1 + X_3 + X_4 = dCa \quad (3)$$

$$X_4 = dMg \quad (4)$$

TABLE-2
RESULTS OF MASS BALANCE CALCULATION FOR GUILIN KARST WATER

Sample No.	Gypsum		CO_2		Calcite		Dolomite		Ratio
	mmol/L	mg/L	mmol/L	mg/L	mmol/L	mg/L	mmol/L	mg/L	
1	0.160	21.77	1.713	75.35	1.758	175.76	0.036	6.66	1.9358
2	0.150	20.14	0.870	38.28	0.872	87.21	0.040	7.36	1.9139
3	0.190	25.85	0.372	16.38	0.533	53.31	0.038	7.05	1.6105
4	0.150	20.41	1.672	73.58	1.817	181.72	0.047	8.59	1.8753
5	0.190	25.85	1.367	60.14	1.331	133.06	0.430	7.82	1.9655
6	0.210	28.57	1.318	58.01	1.503	150.26	0.021	3.83	1.8538
7	0.130	17.69	1.841	80.99	1.947	194.75	0.017	3.07	1.9292
8	0.180	24.99	2.112	92.93	2.199	219.66	0.036	6.68	1.9299
9	0.160	21.77	2.248	98.93	2.435	243.49	0.050	9.20	1.8870
10	0.170	23.13	1.962	86.32	2.048	204.77	0.047	8.59	1.9163
11	0.140	19.05	0.781	34.38	1.204	120.43	0.038	7.05	1.6099
12	0.160	21.77	0.833	36.65	1.096	109.60	0.047	8.59	1.7004
13	0.150	20.41	1.011	44.47	1.013	101.32	0.019	3.53	1.9612
14	0.190	25.85	0.917	40.37	0.940	93.99	0.043	7.82	1.8951
15	0.190	25.85	1.120	49.28	1.364	136.40	0.029	5.37	1.7876
16	0.050	6.80	1.940	85.34	1.805	180.48	0.059	10.89	2.0086
17	0.020	2.72	1.021	44.91	0.822	82.24	0.090	16.49	2.0191
18	0.040	5.44	1.121	49.33	1.184	118.38	0.039	7.14	1.8890
19	0.030	4.08	2.309	101.60	2.196	219.56	0.059	10.89	1.9980
20	0.060	8.16	1.870	82.28	1.775	177.46	0.049	9.05	1.9985
21	0.060	8.16	0.921	40.52	1.084	108.38	0.029	5.28	1.8070
22	0.150	20.41	1.298	57.12	1.563	156.31	0.201	36.95	1.6607
23	0.120	16.33	1.760	77.44	1.684	168.45	0.049	9.05	1.9872
24	0.160	21.77	1.790	78.75	1.695	169.47	0.049	9.05	1.9981
25	0.180	24.49	1.870	82.30	1.856	185.58	0.008	1.53	1.9989
26	0.060	8.16	0.392	17.26	0.312	31.23	0.039	7.12	2.0063
27	0.030	4.08	1.350	59.40	1.152	115.23	0.160	29.51	1.9164
28	0.050	6.80	1.451	63.85	1.314	131.36	0.049	9.05	2.0278
29	0.010	1.36	1.111	48.89	1.194	119.38	0.039	7.14	1.8741
30	0.000	0.00	1.599	70.37	1.343	134.26	0.180	33.19	1.9389
31	0.010	1.36	1.368	60.21	0.770	77.02	0.282	51.91	2.0254
32	0.010	1.36	1.697	74.66	1.060	106.01	0.333	61.25	1.9832
33	0.010	1.36	2.299	101.16	2.145	214.49	0.090	16.49	1.9892
34	0.010	1.36	2.069	91.04	1.854	185.40	0.110	20.24	1.9976
35	0.050	6.80	2.009	91.96	2.056	205.55	0.039	7.12	1.9799
36	0.040	5.44	1.719	75.64	1.343	134.28	0.160	29.51	2.0333
37	0.050	6.80	1.670	73.50	1.454	145.41	0.069	12.73	2.0490
38	0.040	5.44	1.679	73.90	1.403	140.33	0.120	23.92	2.0098
39	0.030	4.08	1.559	68.62	1.403	140.33	0.110	20.24	1.9607
40	0.000	0.00	1.790	78.76	1.674	167.39	0.100	18.33	1.9556
41	0.030	4.08	1.549	68.16	1.233	123.26	0.160	29.51	1.9973
42	0.000	0.00	1.820	80.07	1.624	162.39	0.090	16.49	2.0092
43	0.020	2.72	1.769	77.85	1.714	171.42	0.110	20.17	1.9151
44	0.020	2.72	1.928	84.81	1.392	139.18	0.272	49.99	1.9961
45	0.060	8.16	1.628	71.65	1.172	117.18	0.231	42.56	1.9965
46	0.070	9.52	1.638	72.08	1.081	108.13	0.272	49.99	2.0083
47	0.450	61.24	1.619	71.25	1.584	158.44	0.090	16.49	1.9182
48	0.030	4.08	2.070	91.07	1.995	199.51	0.079	14.57	1.9611
49	0.040	5.44	2.109	92.79	1.834	183.40	0.140	25.76	1.9975
50	0.130	17.69	1.640	72.16	1.645	164.45	0.069	12.73	1.9199
51	0.400	5.44	0.860	37.83	0.541	54.09	0.211	38.79	1.8931
52	0.110	14.97	1.691	74.40	1.574	157.44	0.019	3.44	2.0490
53	0.100	13.61	1.051	46.26	1.074	107.36	0.029	5.28	1.9294
54	0.070	9.52	1.061	46.68	1.123	112.33	0.059	10.89	1.8543
55	0.160	21.77	1.861	81.87	1.786	178.56	0.008	1.53	2.0325
56	0.070	9.52	0.511	22.48	0.351	35.12	0.120	22.08	1.8643
57	0.000	0.00	0.401	17.64	0.341	34.10	0.120	22.08	1.6901
58	0.080	10.88	0.972	42.76	0.632	63.23	0.049	9.05	2.3300
59	0.040	5.44	1.002	44.08	0.783	78.30	0.039	7.14	2.1642
60	0.060	8.16	0.872	38.35	0.673	67.26	0.059	10.89	2.1019
61	0.250	34.03	0.581	25.57	0.904	90.35	0.029	5.30	1.6046
62	0.140	19.05	2.759	121.40	2.425	242.54	0.120	22.08	2.0351
63	0.100	13.61	1.661	73.09	1.545	154.46	0.029	5.28	2.0368

64	0.120	16.33	1.451	63.86	1.535	153.51	-0.002	-0.31	1.9475
65	0.130	17.69	0.992	43.63	0.953	95.34	0.019	3.46	2.0008
66	0.080	10.88	2.417	106.34	2.344	234.40	0.131	12.14	1.9272
67	0.080	10.88	2.249	98.97	2.095	209.53	0.079	14.57	1.9981
68	0.080	10.88	1.610	70.86	1.615	161.48	0.039	7.14	1.9516
69	0.070	9.52	1.380	60.73	1.143	114.32	0.090	16.49	2.0438
70	0.100	13.61	1.291	56.79	1.194	119.35	0.049	9.05	1.9991
71	0.250	34.03	1.451	63.84	1.374	137.43	0.019	3.44	2.0277
72	0.240	32.67	2.059	90.58	1.924	192.45	0.120	22.08	1.9510
73	0.650	88.45	1.200	52.79	1.084	108.42	0.069	12.73	1.9814
74	0.260	35.39	1.470	64.67	1.173	117.35	0.110	20.17	2.0554

In the above equations, dS, dC, dCa and dMg can be obtained according to water chemistry analysis results. Solving the equations of l, 2, 3 and 4, the amounts of dissolved gypsum, calcite, dolomite and CO_2 can be obtained. This method is called mass balance calculation (MBC). The calculated results of MBC for the 74 karst water samples are shown in Table-2. Ratio in Table-2 denotes the ratio of the dissolved element C to the sum of dissolved Ca and Mg by calcite and dolomite which in value equals to $(X_2 + X_3 + 2X_4)/(X_3 + 2X_4)$.

Table-2 reveals that all the samples are formed by gypsum, calcite, dolomite and CO_2 on the basis of rain water except sample 64 which is formed by the dissolution of gypsum, calcite and CO_2, and the precipitation of dolomite (denoted by minus number for dolomite, -0.31 mg/L). The average amounts of dissolved gypsum, calcite, dolomite and CO_2 are 14.56, 140.08, 15.41 and 65.71 mg/L. The largest amount for dissolved gypsum is 88.45 mg/L observed in sample 73. The largest amount for dissolved CO_2 is observed in sample 62, being 121.40 mg/L. The biggest amounts for dissolved calcite and dolomite are, respectively observed in samples 9 and 32 and they are 243.49 and 61.25 mg/L, respectively.

If the amounts of dissolved CO_2 in the processes of forming the chemical compositions of the local surface water and groundwater in Guilin area are estimated, some very meaningful results can be obtained. The Guilin area covers an area of 7420 km^2 and the annual average rainfall in the area is 1897.3 mm. Seventy percent of the rainfall forms surface water and groundwater, and the total surface water and groundwater formed by the precipitation is 9.8546×10^9 m^3 per year. If the mean amount of dissolved CO_2 is taken into account, then 6.475×10^5 t CO_2 will dissolve into the rain water to form the local surface water and groundwater each year. Even if the minimum amount of dissolved CO_2 of the 74 karst water samples is used to calculate the annual dissolved CO_2 amount, the result is 1.614×10^5 t per year. This result is of particular importance for protecting earth's environment, especially in these years when the emission of CO_2 is increasing.

The dolomite precipitation occurred in the sample 64, seems impossible according to its chemical compositions. It may because that there is no Mg^{2+} in sample 64 and when the average Mg^{2+} concentration of rain water which is higher than that in sample 64 is used for calculation, incorrect result may arise.

Forming environment of karst water in Guilin: There are two typical environments where dolomite and calcite dissolve into the rain water, namely, closed environment (closed system) and open environment (open system). In a closed system, calcite and dolomite usually dissolve into water by the following formulas:

$$CaCO_3 \rightleftharpoons Ca^{2+} + CO_3^{2-}$$

$$CaMg(CO_3)_2 \rightleftharpoons Ca^{2+} + Mg^{2+} + 2CO_3^{2-}$$

In closed systems, there is no CO_2 recharge during the reactions and the ratio of the dissolved element amount of C to the sum of Ca and Mg calculated by calcite and dolomite dissolution (ratio in Table-2) should be 1. Whereas, in an open system there is continuous CO_2 recharge during the reactions and the reactions are expressed as follows:

$$CaCO_3 + CO_2 + H_2O \rightleftharpoons Ca^{2+} + 2HCO_3^-$$

$$CaMg(CO_3)_2 + 2CO_2 + 2H_2O \rightleftharpoons Ca^{2+} + Mg^{2+} + 4CO_3^-$$

The ratio in the open system should be equal to 2 according to the above reaction formulas.

The last column of Table-2 indicates that the mean value of ratio for the 74 karst water samples in Guilin is 1.9469 and the minimum value is 1.6046. So it can be conclude that the karst water in Guilin is formed in an open environment.

Conclusion

The chemical compositions of the karst water in Guilin are formed by dissolution of calcite, dolomite, gypsum and CO_2 on the basis of the chemical compositions of the local rain water. Mass balance calculation can be used to calculate the dissolved amounts of the minerals and gases of the karst water relative to the local rain water in Guilin. The least amount of dissolved CO_2 estimated is 1.614×10^5 t per year and average is 6.475×10^5 t per year, which is particularly important and useful for CO_2 storage and improving and protecting the earth's environment, and is also of significance in controlling CO_2 emission and global climate warming. Overall, the karst water in Guilin is formed in an open environment.

ACKNOWLEDGEMENTS

The research was supported by Special Fund for Basic Scientific Research of Central Colleges, Chang'an University (CHD2011TD003), the Doctor Postgraduate Technical Project of Chang'an University (CHD2011ZY025 and CHD2011ZY022) and the National Natural Science Foundation of China (41172212).

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