1 **Application of hydrochemical and isotopic data to determine the origin and circulation**
2 **conditions of karst groundwater in an alpine and gorge region in the Qinghai–Xizang Plateau:**
3 **a case study of Genie Mountain**

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11 **Abstract**

12 Understanding of the recharge origin, runoff channels, and discharge characteristics of karst
13 groundwater is very important for construction of underground projects and identification of water
14 supply targets. Complex structural systems, lithological differences, and extreme heterogeneity of
15 aquifers combine to create a complex karst aquifer structure in alpine and gorge areas; however,
16 because of the topography, direct investigation of aquifer structure is difficult. In this study, field
17 survey, hydrochemical, and isotopic data are analyzed to reveal the development of karst
18 groundwater and to describe the karst water cycle in Genie Mountain, Qinghai–Xizang Plateau. The
19 results show that atmospheric precipitation and melting ice and snow are the groundwater recharge
20 sources, and groundwater circulation is shallow, with groundwater ages generally no more than 60
21 yr. The groundwater cycle can be divided into three levels: epikarst water circulation; mid to deep
22 karst water circulation; and deep geothermal water circulation. The karst springs located in the
23 outlet of the Huolong gully contain markedly higher levels of Na⁺ and SO₄²⁻ than other karst

24 springs because of the leaching effect of groundwater on mirabilite. The presence of evaporites also
25 indicates that the groundwater of Huolong gully is influenced by evaporation. The runoff of thermal
26 springs undergoes deep circulation and is controlled by faults. This water mainly dissolves
27 carbonate rock, with little influence of evaporation. This study shows that hydrochemical and
28 isotopic methods can be used to discriminate different water types, and can be applied to study the
29 characteristics of complex groundwater runoff in alpine and gorge areas.

30

31 **Key words**

32 karst groundwater circulation, hydrochemistry, isotopic analysis, alpine and gorge region, Qinghai–
33 Xizang Plateau

34

35 **1. Introduction**

36 Karst aquifers are an important threat to the safety of underground engineering. Globally, a
37 large number of underground projects have experienced water inrush from karst aquifers, resulting
38 in great casualties and property losses (Liu et al. 2019; Lin et al. 2020). There are many reasons for
39 water inrush in karst tunnels, but the most fundamental reason is that the structures of karst aquifers
40 and the process of groundwater circulation are not well understood (Zabidi and De Freitas 2013; Li
41 et al. 2015; Li et al. 2016; Fan et al. 2018).

42 A karst aquifer is the result of karstification, the phenomenon in which carbonate rock
43 dissolves under the action of water, which involves both physical and chemical processes. During
44 karstification, pre-existing discontinuities, fractures, joints, layers or macropores form a hydraulic
45 continuum from the surface to the spring water (Darnault, 2008). In general, karst systems exhibit

46 highly variable recharge processes (diffusion and concentration), storage areas (surface karst,
47 aeration zone, and phreatic zone), and flow types (by diffusion and along conduits) (White, 2002;
48 Perrin et al., 2003; Ford and Williams, 2007). The hydrological systems of karst catchments are
49 highly complex and karst aquifers exhibit strong heterogeneity. The roles of specific hydrological
50 processes and their effects in different hydrological conditions are often difficult to quantify. The
51 high heterogeneity of karst aquifers also causes challenges for research, because it is not possible to
52 extrapolate from small-scale processes to a larger-scale space such as a pore aquifer.

53 Owing to their unique hydrogeological characteristics, study of karst aquifers requires special
54 investigation methods (Goldscheider and Drew, 2007). Investigation of karst development, such as
55 studies of the characteristics of karst dissolution, measurement of the scale of karst development,
56 and tracer tests are useful; in addition, hydrochemical and isotopic methods can be applied to
57 accurately identify groundwater circulation. Directly describing the heterogeneity of karst aquifers
58 by means of hydrochemical data is difficult, but environmental isotopes (such as ^{18}O and ^2H) can
59 provide additional information about the specific groundwater flow path and water transport time of
60 a karst aquifer. This information is essential for describing the different components of an aquifer.
61 Environmental isotopes in water have been studied to provide some insights into the recharge
62 characteristics of karst aquifers under different flow conditions (Aldalla 2009; Yao et al. 2009;
63 Zhang et al. 2015; Bicalho et al. 2019; Rusjan et al. 2019; Tomasz et al. 2019). The mean migration
64 time of karst catchments has also been estimated by isotopic means (Maloszewski et al., 2002;
65 Perrin et al., 2003). Environmental isotopes in water are excellent conservative tracers because they
66 are naturally "injected" throughout the basin by diffusion during rainfall (McGuire and McDonnell,
67 2008; Yin et al. 2011) and do not react chemically in the environment at ambient temperature (Gat,
68 1996). Although there are many uncertainties in isotope geochemistry, these substances are still an

69 important means of improving understanding of karst aquifers.

70 The study area is Genie Mountain (highest peak 6204 m), which is located in the Hengduan
71 Mountains in the eastern Qinghai–Xizang Plateau. The plateau is the most tectonically active area
72 worldwide. The Jinshajiang Fault Zone and Batang Fault are still active and induce earthquakes
73 (Wu and Cai, 1992). Strong tectonic uplift and incision of river valleys have greatly changed the
74 hydrogeological structure, especially of karst aquifers. The karst aquifers developed in the plateau
75 area may be important in the development of high-altitude karst, which is affected by the high
76 altitude above sea level, cold climate, extremely complex geological structure, and the series of
77 changes caused by valley incision. The circulation of karst groundwater in the plateau is also
78 affected by the development of karst in the plateau, which intensifies the spatial and temporal
79 heterogeneity of the karst aquifer. Furthermore, the harsh natural environment and geomorphic
80 conditions cause great difficulties for research work. All of these factors are challenges for accurate
81 characterization of aquifer structure.

82 In this study, field survey, hydrochemical, and isotopic data are analyzed to reveal the
83 development of karst groundwater in Genie Mountain, to describe the karst water cycle process, and
84 to provide reference data for research on karst aquifers in similar conditions in other regions.

85 **2. Study area**

86 **2.1 Geographic setting and climate setting**

87 Genie Mountain is located in the west of Sichuan Province, China, and on the east bank of the
88 Jinshajiang River (30°10′–30°50′N, 98°30′–99°25′E) (Fig. 1). The highest peak is Mount
89 Dangjiezhenla, at an altitude above sea level of 6204 m. The lowest point is the Jinshajiang River, at
90 an altitude above sea level of 2240 m. The height difference between the highest and lowest points
91 is 3820 m. The gradient is generally ~45°, and up to 60° in some areas. The valley, which is a

92 typical V-shaped mountain canyon landform, generally does not exceed 1000 m in width.

93 The study area is influenced by the altitude, the presence of mountains, and atmospheric
94 circulation, and experiences an alpine plateau climate with an annual mean temperature of 8.0–
95 12.3 °C. The mean temperature in January is −1.6 °C. The temperature rises rapidly in spring, and
96 sunshine is abundant in summer, with a maximum temperature of >35 °C. In winter, the lowest air
97 temperature is below −10 °C. The annual maximum rainfall is 828.8 mm (1998), the minimum
98 rainfall is 291.5 mm (1994), and the mean rainfall is 503.69 mm. The rainy season is May to
99 September; approximately 90% of total rainfall occurs during that interval. Average annual
100 evaporation is 1711.4 mm. According to the karst classification of the Chinese Academy of
101 Sciences, the karst in Genie Mountain is temperate arid climate-type denudation karst of the
102 Qinghai–Xizang Plateau (Li et al. 2020).

103 The main river in the study area is the north- to south-flowing Jinshajiang River, which is the
104 terminal discharge point of groundwater from Genie Mountain. The annual total runoff is 29.719
105 billion m³. There are many major tributaries of the Jinshajiang River on the western side of Genie
106 Mountain, and the main tributaries in the east are the Jiangqu River, the Xiqu River (along the
107 Jinshajiang East Boundary Fault), the Huolong gully, and the Gangtonglong gully (along the
108 Gangtonglong Fault).

Fig. 1. Hydrogeological map of Genie Mountain indicating sampled springs

2.2 Geology

The study area is part of the Songpan–Ganzi block, and is located at the turning point of the structural belt on the eastern edge of the Qinghai–Xizang Plateau, to the west of the Ganzi–Litang deep fault. The main fault structure in the area is the Jinshajiang Fault Zone.

The Jinshajiang Fault Zone is approximately 700 km long and approximately 80 km wide. The structure of the zone is complex: it is composed of six to seven main faults, including the Jinshajiang East Boundary Fault, the Gangtonglong Fault, and the Edexi–Hongjunshan Fault. The maximum fault displacement is 25 km. The fault zone generally trends north–south and dips at a high angle. The zone contains many branch faults and traction structures.

121 Cambrian to Quaternary sedimentary rocks occur in the study area, but Jurassic and Cretaceous
122 rocks are absent. The main karst strata are Devonian to lower Permian limestone, dolomite, and a
123 small amount of marble. The total thickness of the karst-bearing strata is more than 5000 m. The
124 strata mostly crop out in fault-controlled, north–south-trending blocks. The karst-bearing strata
125 mainly occur between the Edexi–Hongjunshan Fault and the Jinshajiang East Boundary Fault. West
126 of the Edexi–Hongjunshan Fault and east of the Jinshajiang East Boundary Fault, there are
127 Devonian and Carboniferous sandstone, schist, and phyllite. Pure carbonate rocks are rare and of
128 limited spatial extent.

129 The fracture system is the main control on karst water in the study area. The spatial
130 development of karst strata is controlled by the Jinshajiang Fault zone. Devonian, Carboniferous,
131 and Permian carbonate rocks crop out in nearly north–south-directed blocks. The fault is bounded
132 by Lower and Middle Triassic sandstone and slate to the east and lower and middle Cambrian
133 schist, phyllite, and volcanic rock to the west, forming a boundary for karst water. In addition, the
134 influence of the fault zone, especially the development of structural fissures within the zone,
135 provides space for groundwater. After a long period of water–rock interaction, dissolved gaps and
136 pores develop gradually in carbonate rock; these gaps constitute a good channel for groundwater
137 movement. Therefore, karst development in the fault-affected zone is much more rapid than that in
138 unaffected areas. From the regional geological data, nearly 70% of karst is developed in the zone of
139 structural influence. Furthermore, the distribution of karst water follows the Jinshajiang Fault.
140 Faults to the east of the surface watershed are very well developed, whereas faults are relatively
141 sparse to the west of the surface watershed. The main groundwater discharge area is also in the
142 eastern part of Genie Mountain; thus, karst water is abundant in the eastern part of Genie Mountain,
143 and less abundant in the western area.

Under the influence of glacier plucking, a planation surface has formed above 4600 m altitude. The surface extends NNW, with its northern end at the outlet of the Huolong gully and the southern end located near the east–west surface watershed. The total length of the planation surface is approximately 21 km. The surface is U-shaped overall, 200–400 m wide, and contains many glacial lakes in relatively flat terrain. The thickness of the moraine is ≥ 1.5 m.

2.3 Hydrogeology

Karst water in Genie Mountain is mainly supplied by atmospheric precipitation and melted ice and snow, and runs along the karst channels formed along the structures. The altitudes of the Jiangqu and Xiqu rivers control the discharge height level of karst water, and are also mainly recharged by groundwater. Karst water forms a concentrated drainage zone at the intersection of multiple faults. The main discharge points can be divided into the northern, Huolong, eastern, and Gangtonglong groups on the basis of their location. From flow measurements obtained during July and August 2019, some karst springs have relatively large flow rates: springs Q309 (627 L/s), G06 (640 L/s), and G11 (21.6 L/s). The flow rate of other springs is generally ≤ 1.5 L/s. In addition, thermal springs (water temperature 45–64 °C) are exposed on the east side of the Jiangqu River.

3. Methods

3.1 Sampling

A total of 42 groups of samples were collected: 16 from karst springs, 2 from thermal springs, 23 from river water, and 1 snow sample from the top of the mountain. The locations of the sampling points are marked in Fig. 1.

Sampling bottles were rinsed with sample water at least three times before collection. The samples were filtered through 0.45- μ m membrane filters and poured into 1.5-L and 250-mL high-density

polyethylene bottles for analyses of major and trace elements. The 250-mL samples were acidified by adding double-distilled nitric acid until the pH was below 2; the 1.5-L samples were untreated. Samples were stored at 4 °C until analysis. Samples for stable isotope analysis ($\delta^{18}\text{O}$ and δD) were collected in 50-mL glass bottles, which were sealed with airtight caps.

3.2 Analytical methods

At the time of sample collection, the water temperature, pH, and total dissolved solids (TDS) were measured using a HANNA HI 991301 pH/EC/Temperature multi-parameter instrument (Hanna Instruments®, Woonsocket, RI, USA). Major anions, except HCO_3^- , were analyzed with a Thermo Scientific Dionex ICS-4000 (precision $\pm 1\%$). HCO_3^- levels were determined by phenolphthalein titration, and major cations and minor elements were analyzed by a PerkinElmer Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) Model Optima 8300 (precision $\pm 1\%$) at the Groundwater Mineral Water and Environmental Monitoring Center of the Institute of Hydrogeology and Environmental Geology, Chinese Academy of Geological Sciences, Shijiazhuang, China. The reliability of the hydrochemical data was assessed by checking ion balances. Ion charge imbalances were within $\pm 5\%$.

Stable isotope ratios are reported in parts per thousand (‰) using the conventional δ notation: δ sample (‰) = $[(R_{\text{sample}} - R_{\text{standard}})/R_{\text{standard}}] \times 1000$, where R represents the $^2\text{H}/^1\text{H}$ or $^{18}\text{O}/^{16}\text{O}$ ratio of the sample and the standard. The $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ and δD values for water samples were measured using a Picarro L2130-i Analyzer at the Institute of Hydrogeology and Environmental Geology, Chinese Academy of Geological Sciences. The results are reported in ‰ relative to Standard Mean Ocean Water, with a precision of $\pm 0.1\text{‰}$ for $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ and $\pm 1\text{‰}$ for δD .

Tritium samples analyzed by an ultra-low background liquid scintillation spectrometer (1220 Quantulus) after low-temperature electrolysis enrichment. The detection limit and test precision are

189 1 TU and ± 0.5 TU, respectively.

190 4. Results

191 4.1 Water composition

192 The pH values of the analyzed samples were between 6.74 and 8.79, which is neutral or
193 weakly alkaline overall, and the range of TDS values was large, between 114.7 and 1331 mg/L
194 (Table 1). The mean TDS value of the Huolong group was 589.60 mg/L, higher than those of the
195 northern (236.38 mg/L), Gangtonglong (132.14 mg/L), and eastern groups (330.34 mg/L), but
196 markedly lower than that of thermal springs (1008.86 mg/L). The Na^+ (128.85 mg/L) and SO_4^{2-}
197 (300.29 mg/L) values of the Huolong group were higher than those of other groups, whereas the
198 Ca^{2+} , Mg^{2+} , and HCO_3^- levels of the Huolong group were similar to those of the other groups.
199 There are seven springs in the Huolong group, of which Q201, Q309, and Q312 are of the $\text{Na}\cdot\text{Ca}-$
200 SO_4 , $\text{Na}-\text{SO}_4$, and $\text{Na}-\text{SO}_4\cdot\text{HCO}_3$ hydrochemical types (Fig. 2), and the others are mainly $\text{Ca}\cdot\text{Mg}-$
201 HCO_3 type. The springs of the northern, eastern, and Gangtonglong groups are $\text{Ca}\cdot\text{Mg}-\text{HCO}_3$ type.
202 This difference may indicate greater water–rock reactions in the Huolong group.

203 The pH values of river water were between 7.01 and 8.33, and the TDS values ranged from
204 101.8 to 1234 mg/L, mean 336 mg/L, which is not different from the values of groundwater. The
205 river water of H202, H205, H206, and H207 near the karst springs in the Huolong group exhibited
206 $\text{Na}-\text{SO}_4$ or $\text{Na}-\text{SO}_4\cdot\text{HCO}_3$ water chemistry. The karst springs numbered Q201, Q309, and Q312
207 and the four surface-water points numbered H202, H205, H206, and H207 plot in the same area
208 (Fig. 2), showing that the river water and groundwater in the Huolong group are strongly correlated.
209 Other points plot relatively close together. The rest of the river-water samples were $\text{Ca}\cdot\text{Mg}-\text{HCO}_3$
210 type, with TDS values of 101.8–239.97 mg/L, which may indicate a circulation depth smaller than
211 that of the Huolong group.

212 The TDS values of thermal springs were more than 1000 mg/L; however, thermal springs Q75
213 and SM04 possessed $\text{Na}-\text{HCO}_3$ and $\text{Ca}-\text{Na}-\text{HCO}_3$ water chemistry, respectively. This difference in

214 water type indicates that, on the one hand, the circulation depth of thermal-spring water is large and,
215 on the other hand, the circulation processes of the two thermal springs are different.

216 **Table 1 Hydrochemical water type and concentrations of major ions in water samples from the study area**

Sample ID	sample type	pH	TDS	Na ⁺	K ⁺	Mg ²⁺	Ca ²⁺	Cl ⁻	SO ₄ ²⁻	HCO ₃ ⁻	Water type
G04	GW	7.78	153.3	1.58	0.61	8.34	41.8	0.12	13.48	147.8	Ca-Mg-HCO ₃
G11	GW	8.3	219.36	3.03	0.92	10.4	63.6	0.16	25.75	173.2	Ca-Mg-HCO ₃
Q203	GW	7.75	226.9	13.24	1.79	16.8	44.08	2.1	35.12	201.4	Ca-Mg-HCO ₃
Q205	GW	7.69	287.6	9.96	1.35	17.12	72.21	2.1	33.53	274.6	Ca-Mg-HCO ₃
A03	GW	8.05	294.75	4.49	0.87	28.4	59.5	0.33	73.98	228.8	Ca-Mg-HCO ₃ -SO ₄
A07	GW	7.98	121.46	4.48	0.59	6.66	33.3	0.09	7.64	126.8	Ca-Mg-HCO ₃
G09	GW	8.08	242.11	2.48	1.16	15.2	61.7	0.36	45.9	204.1	Ca-Mg-HCO ₃ -SO ₄
Q201	GW	7.69	1014	262.4	0.67	6.15	61.06	1.75	579.6	189.2	Na-Ca-SO ₄ -HCO ₃
Q309	GW	7.79	1150	320.2	0.52	5.97	42.7	1.75	695.9	157.4	Na-SO ₄
Q310	GW	7.66	153.9	1.75	0.69	9.52	41.42	1.4	11.14	153.2	Ca-Mg-HCO ₃
Q312	GW	7.92	1331	310.6	2.17	37.62	57.9	2.45	754.8	299	Na-SO ₄ -HCO ₃
SM02	GW	7.68	114.7	0.005	0.22	5.62	33.46	1.4	7.06	122.6	Ca-Mg-HCO ₃
A10	GW	8	330.34	2.39	2	17.9	85.4	1.53	103.12	207.2	Ca-Mg-HCO ₃ -SO ₄
G06	GW	8.3	132.79	4.29	0.31	10.4	32.9	0.12	7.08	142.9	Ca-Mg-HCO ₃
A30	GW	8.28	132.34	0.36	0.29	11.4	33.9	0.12	9.11	142.3	Ca-Mg-HCO ₃
YQ04	GW	7.98	131.3	0.06	0.33	12.56	30.39	1.75	5.21	0	Ca-Mg-HCO ₃
Q75	TS	8.79	1015.72	274	15.4	0.15	2.15	40.66	48.96	476.2	Na-HCO ₃
SM04	TS	6.74	1002	119.6	18.38	26.93	208.3	8.73	76.83	993.6	Ca-Na-HCO ₃
H211	RW	7.63	101.8	3.31	1.5	2.6	26.4	1.05	2.9	97.63	Ca-HCO ₃
H212	RW	7.82	201.9	3.12	3.19	8.24	54.4	0	42.44	152.5	Ca-HCO ₃ -SO ₄
SM01	RW	7.71	149.8	1.2	0.65	7.76	39.28	1.4	13.23	149.6	Ca-Mg-HCO ₃
A04	RW	8.25	216.06	2.77	0.73	13.1	53	0.29	44.27	170.1	Ca-Mg-HCO ₃ -SO ₄
A05	RW	8.21	158.25	1.55	0.56	8.84	43.7	0.16	17.08	151.5	Ca-Mg-HCO ₃
H202	RW	7.77	1234	320.6	0.55	6.17	63.56	2.1	735.9	198.3	Na-SO ₄
H205	RW	7.73	981.5	257.4	0.73	6.12	53.41	1.75	553.7	195.3	Na-SO ₄ -HCO ₃
H206	RW	7.88	977.8	252.2	1.42	18.46	43.09	1.75	536.8	231.9	Na-SO ₄ -HCO ₃
H207	RW	7.58	1197	315.8	1.04	12.56	54.8	2.1	679.1	244.1	Na-SO ₄ -HCO ₃
SM05	RW	7.55	122.2	0.36	0.25	2.75	39.22	1.75	8.88	126.2	Ca-HCO ₃
A08	RW	8.12	255	2.69	1.43	16.3	64	0.66	49.31	210.3	Ca-Mg-HCO ₃ -SO ₄
SM06	RW	7.01	140.2	4.61	0.83	6.96	29.59	1.75	43.4	84.95	Ca-Mg-HCO ₃ -SO ₄
SM07	RW	7.94	194.5	1.14	0.59	8.93	52.75	2.1	39.16	164.5	Ca-Mg-HCO ₃ -SO ₄
A09	RW	8.28	216.45	2.77	1.1	10.6	59.9	0.3	28.19	194.8	Ca-Mg-HCO ₃
A15	RW	8.21	139.86	0.78	0.76	2.73	47.5	0.26	7.52	139.2	Ca-HCO ₃
A17	RW	8.24	128.3	0.82	0.43	3.93	42.8	0.1	9.39	126.8	Ca-HCO ₃
A21	RW	8.28	206.91	2.06	0.71	9.8	58.5	0.22	38.53	151.5	Ca-Mg-HCO ₃ -SO ₄
A24	RW	8.27	180.75	2.11	0.45	7.33	54.3	0.19	24.87	160.8	Ca-HCO ₃
B08	RW	8.29	232.97	3.06	0.6	13.8	57.1	0.25	36.58	139.2	Ca-Mg-HCO ₃ -CO ₃
YQ03	RW	7.73	122.5	0.07	0.31	9.97	30.72	1.4	6.47	0	Ca-Mg-HCO ₃
B11	RW	8.33	155.42	0.5	0.4	16	34.1	0.12	12.74	148.4	Ca-Mg-HCO ₃

CL03	RW	8.22	175.12	1.8	0.46	6.59	53.6	0.1	21.81	162.4	Ca-HCO ₃
CL10	RW	8.29	239.45	2.13	0.42	12	65.2	0.11	65.9	145.3	Ca-Mg-HCO ₃ -SO ₄
SNOW	Snow	6.53	15.66	0.21	0.24	0.45	4.4	0.25	0.63	12.37	Ca-HCO ₃ -NO ₃

1) Concentrations are given in mg/L

2) Sample type, GW—groundwater, TS—thermal spring, RW—river water.

Fig. 2. Piper plot of water samples

4.2 Isotopic composition of waters

Table 2 Measurements of δD and $\delta^{18}O$ in samples from the study area

	$\delta D(\text{‰})$			$\delta^{18}O(\text{‰})$		
	max	min	average	max	min	average
Northern	-122.0	-131.0	-128.0	-15.8	-17.4	-17.0
Huolong	-123.0	-142.0	-129.5	-16.0	-18.5	-17.2
Eastern	-122.6	-122.6	-122.6	-16.4	-16.4	-16.4
Gangtonglong	-127.0	-130.0	-128.9	-16.9	-17.6	-17.2
thermal spring	-142.0	-154.3	-148.2	-18.5	-18.8	-18.6
river water	-118.9	-129.2	-126.1	-15.8	-17.5	-16.8

The stable isotope values of karst spring samples ranged from -17.75‰ to -15.8‰ for ^{18}O , with a mean value of -17.04‰ , and from -132‰ to -122‰ for δD , mean -127.81‰ (Table 2).

Using the least-square method, the relationship between δD and $\delta^{18}O$ can be calculated to be $\delta D =$

226 $4.3725 \times \delta^{18}\text{O} - 53.304$ ($r^2 = 0.6518$).

227 The isotopic values of the northern group varied between -17.42‰ and -15.80‰ (mean value
228 -17.03‰) for $\delta^{18}\text{O}$ and between -131‰ and -122‰ (mean value -128.02‰) for δD . The isotopic
229 values of the Huolong group were -18.5‰ to -16.8‰ (mean -17.39‰) for $\delta^{18}\text{O}$ and -125.8‰ to
230 -142‰ for δD (mean -130.29‰), isotopically more depleted than the northern group. The $\delta^{18}\text{O}$
231 values of the eastern group were -16.38‰ , δD was -122.6‰ . And the $\delta^{18}\text{O}$ values of
232 Gangtonglong group ranges from -17.6‰ to -16.9‰ , δD ranges from -127‰ to -130‰ , with the
233 mean values of $\delta^{18}\text{O}$ and δD were -17.17‰ and -128.9‰ , respectively.

234 The δD and $\delta^{18}\text{O}$ characteristics of water points in the study area were compared with those of
235 the global meteoric water line, the Mount Gongga (approximately 500 km east of the work area)
236 water line (GGMWL), and the eastern Qinghai–Xizang Plateau meteoric water line (EQXMWL)
237 (Fig. 3). First, Mount Gongga is part of the eastern Qinghai–Xizang Plateau, and there is a large
238 difference in the isotopic characteristics of precipitation between the two meteoric lines, which
239 arises from the different origins and proportions of water and the precipitation caused by the local
240 water cycle in high mountain and valley areas. Second, most of the samples fall between the
241 EQXMWL and the GGMWL, indicating that there is a close relationship between groundwater and
242 precipitation. Third, the slope of the linear relationship between δD and $\delta^{18}\text{O}$ of all karst springs is
243 4.37, lower than that of the GGMWL (9.40) and EQXMWL (6.79), which results from the relatively
244 arid climate and high evaporation in the study area. The annual rainfall of the eastern Qinghai–
245 Xizang Plateau is 892.24 mm (Li et al., 2018) and that of Gongga Mountain is 1938 mm (Song et
246 al., 2015), both larger than the value of 503.69 mm in the study area.

247 The water samples can be divided into three groups (Fig. 3; Table 2). Group A contains thermal
248 springs, and groups B and C include both karst springs and river water. Obviously, the circulation

249 depth of samples in group A was greater than that in groups B and C. Group B includes samples
 250 A07, Q309, A30, G11, SM02, Q203, Q205, and surface water CL10. These spots are concentrated
 251 in three areas: the mouth of the Huolong gully, the Gangtonglong gully, and downstream of Q75.
 252 Most river-water samples are in group C, and the isotope dilution level is low, indicating that the
 253 groundwater and surface water in group C are closely related, and the circulation is shallow.

254
 255 **Fig. 3. Plot of $\delta^{18}\text{O}$ versus δD . GMWL, global meteoric water line; EQZMWL, eastern Qinghai–Xizang**
 256 **Plateau meteoric water line; GGMWL, Mount Gongga water line. The blue line is the linear fitting curve of**
 257 **all the karst spring samples.**

258 The tritium values of the samples in the study area can be divided into three groups (Fig. 4).
 259 Most of the tritium values of surface water and groundwater were between 3 and 10 TU, indicating
 260 that the groundwater is mainly derived from mixing of ancient water and modern precipitation.
 261 River water is mainly supplied by groundwater. The tritium values of thermal springs were all
 262 approximately 1 TU, suggesting that the water supply is mainly older than 1954, and the water

263 experiences a deep cycle. The tritium values of samples Q310 in the Huolong group and A10 in the
 264 eastern Group were greater than 10 TU, indicating that the groundwater is mainly supplied by
 265 modern precipitation and the cycle process is short.

266
 267 **Fig. 4. Plot of $\delta^{18}\text{O}$ versus T values of water samples**

268 **5. Discussion**

269 **5.1 Water origin**

270 **Table 3 Comparison of deuterium excess among the study area and nearby regions**

Area	Maximum value	Minimum value	Average value
Northern	11.46	4.4	8.24
Huolong	13.5	3.2	9.24
Eastern	8.44	8.44	8.44
Gangtonglong	11.1	-4.14	8.43
thermal spring	6	-4.14	0.93
Mount Gongga	21.82	-0.82	11.21
Asia and the western Pacific			10.14
Asia and northern Indian Ocean			8.36
Middle East			11.71
Global			10

271 The precipitation in the study area comes from the Indian Ocean, Pacific Ocean, and Central Asia
 272 (Song et al., 2015). Excess deuterium in Genie Mountain spring water was basically consistent with
 273 global values (Table 3), but lower than the values in the Western Pacific, Central Asia, and Gongga

Mountain, and slightly higher than that in the Indian Ocean, indicating that the water vapor source of local internal circulation is important. The short cycle leads to relatively insignificant fractionation effects, and the D values are low. The deuterium surplus of the Huolong group is the largest, and there is little difference among the other groups, which indicates that the karst water of the Huolong group has experienced marked evaporation.

In the process of water vapor transport, isotope fractionation occurs, resulting in the depletion of δD and $\delta^{18}O$ in the study area. As a result of the high mountain and valley topography, the study area is mainly dominated by the local water cycle. All karst springs fall between the EQXMWL and the GGMWL (Fig. 3), evidence of a meteoric origin for these waters.

The isotopic composition of groundwater in mountainous areas is often affected by altitude effects, which depend on the altitude of the groundwater recharge area. According to Li et al. (2019), the isotopes of atmospheric precipitation in the eastern part of the Qinghai–Xizang Plateau exhibit the following relationship:

$$\delta^{18}O = -0.0028h - 3.93 \quad (1)$$

where h is the altitude (m). According to formula (1), the recharge area elevations of the northern, Huolong, and Gangtonglong groups are not much different (Fig. 5). The average values are 4679, 4751, and 4727 m, respectively, but the average difference in elevation between the recharge and discharge areas for the Gangtonglong group is 1924 m, more than for the Huolong group (1533 m) and the northern group (1568 m). The eastern group karst water has the shortest vertical circulation distance: the elevation of the recharge area is only 4446 m, and the vertical difference is 961 m. Hence, the replenishment elevation and vertical circulation distance of groundwater sample A10 are shorter than for other samples. The elevation of approximately 4446 m does not reach the planation surface or the watershed of Genie Mountain, so the recharge area can

only be located on the half slope of the mountain. A10 is supplied by modern water (Fig. 4). Thus, A10 is recharged from the half slope on the east side of Genie Mountain, from shallowly circulating groundwater that runs through the shallow karst system.

Fig. 5 Estimated altitudes above sea level of recharge areas and measured data of discharge areas for groundwater samples

5.2 Water–rock reactions

In karst areas, a series of water–rock reactions occur between groundwater and aquifers. The molar concentration relationship of $\text{Ca}^{2+}/\text{Na}^{+}-\text{HCO}_3^{-}/\text{Na}^{+}$ and $\text{Ca}^{2+}/\text{Na}^{+}-\text{Mg}^{2+}/\text{Na}^{+}$ can be applied to qualitatively distinguish the influence of rock weathering and dissolution on groundwater in the study area (Zheng et al., 2020). Most of the samples fall within the dissolution range of carbonate rocks, whereas samples Q201, Q309, and Q312 of the Huolong group fall between the salt rock evaporation zone and the silicate rock zone (Fig. 6). Thus, these three springs experience different water–rock interactions from other karst springs.

Fig. 6. Plots of the relationship of $\text{HCO}_3^-/\text{Na}^+$ versus $\text{Ca}^{2+}/\text{Na}^+$ and $\text{Mg}^{2+}/\text{Na}^+$ versus $\text{Ca}^{2+}/\text{Na}^+$ in groundwater

A Gibbs diagram and the quantitative relationships of index ions in water were applied to analyze the process of groundwater circulation. Most of the karst springs are dominated by rock weathering (Fig. 7[a] and [b]).

The milliequivalent concentration relationship between $(\text{Na}^+ - \text{Cl}^-)$ and $(\text{Ca}^{2+} + \text{Mg}^{2+}) - (\text{HCO}_3^- + \text{SO}_4^{2-})$ can indicate the occurrence of cation exchange between groundwater and carbonate rocks.

When the slope is near -1 , there is obvious cation exchange, and the degree of cation exchange can be determined from the absolute value of the difference between the slope of the fitting curve and -1 . From fitting the data with the least-square method, we conclude that obvious cation exchange takes place in karst springs, except for the eastern group. From the slope of the linear-fitting results, cation exchange is greatest in the Huolong group, lower in the northern group, still lower in the Gangtonglong group, and lowest in the eastern group (Fig. 7[c]).

325

326

Fig. 7 Gibbs diagram (a and b) and ionic relationships diagram (c and d)

The three karst springs Q201, Q312, and Q309, which are located at the outlet of the Huolong gully, exhibit different hydrochemical characteristics from other karst springs, indicating that they have experienced different cyclic processes and water–rock interactions. The three karst springs of the Huolong gully and their downstream surface water points fall in the area of evaporation–crystallization dominance. The springs at the outlet of the Huolong gully mainly experienced evaporation or evaporite dissolution (Fig. 7[d]). Springs Q201, Q309, and Q312 possess Na–Ca–

SO₄–HCO₃ water, Na–SO₄ water, and Na–SO₄–HCO₃ water, respectively (Table 1), and have markedly higher Na⁺ and SO₄²⁻ concentrations than other karst springs. In general, the source of SO₄²⁻ in the groundwater of carbonate rock areas is gypsum sulfate rock. However, the three springs at the outlet of the Huolong gully do not fall in the range of halite evaporation and dissolution (Fig. 6).

Fig. 8. Plots of $Ca^{2+} + Mg^{2+} - HCO_3^-$ versus $SO_4^{2-} - (Na^+ - Cl^-)$ in groundwater

The milliequivalent ratio of $(Ca^{2+} + Mg^{2+}) - (HCO_3^-)$ and $(SO_4^{2-}) - (Na^+ - Cl^-)$ can be used to determine whether the SO_4^{2-} ions come from gypsum dissolution. $(Ca^{2+} + Mg^{2+}) - (HCO_3^-)$ represents the concentration of Ca^{2+} derived from gypsum dissolution, and $(SO_4^{2-}) - (Na^+ - Cl^-)$ represents the concentration of SO_4^{2-} derived from gypsum dissolution (Fig. 8). The karst springs at the outlet of the Huolong gully plot far from the gypsum dissolution line (Fig. 8), indicating that the SO_4^{2-} in karst water is not mainly derived from gypsum dissolution.

349

350 **Fig. 9. Plot of the relationship of $(\text{Ca}^{2+} + \text{Mg}^{2+})/(\text{HCO}_3^-)$ versus $(\text{SO}_4^{2-})/(\text{HCO}_3^-)$ in karst springs**

351

352 **Fig. 10. Ratios of main anions to main cations in karst springs**

353 The ratio of $(\text{Ca}^{2+} + \text{Mg}^{2+})/(\text{HCO}_3^-)$ versus $(\text{SO}_4^{2-})/(\text{HCO}_3^-)$ can be used to determine the
 354 contribution of carbonate rock and gypsum dissolution to groundwater components. In this diagram,
 355 the Huolong group is different from other karst water groups (Fig. 9), which mainly reflects
 356 dissolution of carbonate rocks and dissolution of gypsum. The Huolong group is located in the area
 357 above the 1:1 line in Fig. 10(a), indicating that other cations are the main ions to balance the
 358 solution. After adding Na^+ , all the points fall near the 1:1 line (Fig. 10[b]), meaning that Ca^{2+} , Mg^{2+} ,

359 and Na^+ are the main cations. The source of SO_4^{2-} in groundwater is dissolution of sodium-
360 containing minerals.

361 The Na^+ in the Huolong group groundwater has several possible sources: atmospheric precipitation;
362 dissolution of silicate minerals; and dissolution of sodium minerals such as halite. First, the
363 concentration of Na^+ in the snow samples is only 0.21 mg/L, indicating that atmospheric
364 precipitation is not the main factor. Second, the dissolution of sodium silicate minerals follows the
365 following process (Zheng et al. 2020):

366
$$2\text{NaAlSi}_3\text{O}_8 + 2\text{CO}_2 + 11\text{H}_2\text{O} \rightarrow \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 + 2\text{Na} + 4\text{H}_4\text{SiO}_4 + 2\text{HCO}_3^-$$

367 However, in the diagram of the milligram equivalent concentration relationship of Na^+ and HCO_3^-
368 (Fig. 11), all points fall far from the dissolution line of albite, so the dissolution of albite contributes
369 little to Na^+ in groundwater. In the same way, halite dissolution is not the main source of Na^+ (Fig.
370 11(b)).

371 From the diagrams in Figs 10 and 11, the source of Na^+ in the karst springs at the outlet of the
372 Huolong gully is sodium sulfate minerals, which may be mirabilite ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$) or glauberite
373 ($\text{Na}_2\text{SO}_4 \cdot \text{CaSO}_4$). Ca^{2+} is derived from the dissolution of carbonate minerals (Fig. 10); therefore,
374 the source of Na^+ in karst water at the outlet of the Huolong gully is the dissolution of mirabilite.

375 **Fig. 11 Plot of the relationship of Na^+ versus Cl^- and HCO_3^- in the Huolong group and river water near the**
376 **Huolong group**

378 Overall, there are two main chemical sources of karst water in Genie Mountain. Most of the karst
379 water is derived from filtration through carbonate karst, but the Huolong gully karst springs are also
380 influenced by mirabilite dissolution.

381 The study area is in an alpine and gorge region. The height difference between the groundwater
382 recharge area and the discharge area is generally more than 1500 m, and it is not easy to generate a
383 slow-flow, stagnant-water environment. Formation of mirabilite requires an arid environment with
384 relatively stagnant water; therefore, the groundwater recharge area of the Huolong group is likely to
385 be located on the planation surface of Genie Mountain above 4600 m altitude. The surface extends
386 in a NNW direction, the terrain is relatively flat, there are some moderately thick moraines, and the
387 area includes some lakes. The lakes are mainly replenished by atmospheric precipitation and
388 seasonal melting of ice and snow. In the drought environment, the lake water and pore water in
389 moraines continuously undergoes evaporation and filtration, which increases the ion concentration
390 in groundwater. Lake water, pore water, and melt water from snow and ice continuously seep into
391 the karst groundwater circulation system.

392 **5.3 Thermal springs**

393 The study area is located at the western edge of the Litang–Batang geothermal zone in the eastern
394 part of the Qinghai–Xizang Plateau, and experiences relatively intense geothermal activity. Two
395 thermal spring samples were collected, in which the main types of groundwater are Na–HCO₃ and
396 Ca–Na–HCO₃ and the main source of water is atmospheric precipitation. These two thermal springs
397 have experienced a long thermal cycle at depth (3300–3700 m) (Zhao et al., 2019). Groundwater
398 flows through the deep runoff of karst or fissure channels controlled by the Chalo–Songduo Fault
399 (Cao, 2020), and is heated by deep magma heat sources (Li et al., 2019). Driven by deep thermal
400 power to circulate to the surface, more intense ion exchange occurs with the surrounding rock. The

401 water from depth is mixed with cold water in the shallow region, with a mixing ratio with cold
402 water of 64%–68%.

403 **5.4 Groundwater circulation**

404 Genie Mountain is located in the karst area of the gorge in the eastern plateau of the Qinghai–
405 Xizang Plateau. The existence of the Jinshajiang River structural belt has aggravated the complexity
406 of the hydrogeological structure. Groundwater circulation can be divided into four types (Figs 12
407 and 13).

408 Type I: Water is supplied from modern atmospheric precipitation or snow/ice melting on the half
409 slope or near the top of Genie Mountain. The water enters the epikarst system, the direction of
410 runoff is mainly affected by topography, and the water is discharged near the excretion base level,
411 with short runoff distance, shallow circulation depth, and a rapid circulation rate. Two examples of
412 these karst springs are A20 in the eastern group and G09 in the Huolong group.

413 Type II: At the top of Genie Mountain, this groundwater is replenished from modern atmospheric
414 precipitation or ice and snow melt water. Groundwater enters the karst system that extends along the
415 regional structure or secondary structures. The direction of runoff is controlled by the structures,
416 which mostly extend NNW or NE. During the process of runoff, the groundwater mixes with some
417 older groundwater. Discharge occurs near the junction of the structure or the discharge datum. The
418 runoff distance is generally ≥ 10 km, the circulation depth is great, and the circulation rate is fast.
419 The groundwater mainly dissolves carbonate rocks, and is affected little by evaporation. The runoff
420 and discharge of this type of groundwater are obviously controlled by structure, and this type
421 represents the main circulation type of karst water in the area.

422 Type III: Atmospheric precipitation and melted ice and snow replenish the lakes and moraines on
423 the top of Genie Mountain, experience evaporation and leaching, and then enter the karst water

424 system. The direction of runoff is controlled by the main fault of the Jinshajiang River, which
 425 strikes approximately NNE. In the process of runoff, the water also mixes with groundwater over 60
 426 years old and is discharged at the junction of the fractures near the mouth of the Huolong gully. The
 427 horizontal runoff distance is ≥ 15 km, the circulation depth is large, and the circulation rate is fast.
 428 This water type is strongly influenced by leaching and evaporation.
 429 Type IV: Geothermal water circulation. Atmospheric precipitation and melted ice and snow enter
 430 the Chalo–Songduo Fault belt through karst channels or fissures at various levels, and are heated by
 431 deep geothermal sources at a depth range of approximately 3300–3700 m. Under the action of deep
 432 dynamics, the water flows along the branch faults and interacts with other waters during ascent.
 433 Mixing with shallow cold water takes place. The runoff depth is large, the groundwater age is more
 434 than 60 yr, and the circulation rate is slow.

436

437 **Fig. 12. Plot of the relationship of TDS and SO_4^{2-} versus tritium in groundwater. I-groundwater recharged**
 438 **by modern precipitation, with rapid circulation; II-groundwater recharged by a mix of modern and more**
 439 **than 60-year-old precipitation, with long circulation; III- groundwater recharged by a mix of modern and**
 440 **more than 60-year-old precipitation, with evaporation and filtration and long circulation; IV-groundwater**
 441 **recharged by precipitation and melt water, influenced by deep thermal geological processes.**

442

443

444 **Fig. 13. Generalized model for the groundwater circulation of Genie Mountain. 1 type I; 2 type II; 3 type**

445 **III; 4 type IV; 5 boundary of flow system; 6 flow line; 7 fault.**

446 **6. Conclusions**

447 Genie Mountain is located in the Hengduan Mountains region of China, a tectonically active area.

448 The marked tectonic activity and complex tectonic system have shaped the complex karst aquifer

449 structure in this area. As a result of the high mountain and valley topography, with a difference in

450 altitude between the mountain peak and the valley in the study area of more than 2000 m,

451 transportation and research is extremely difficult. In the present study, hydrochemical and isotopic

452 methods are applied to understand the groundwater recharge source, runoff process, and

453 hydrochemical evolution of Genie Mountain. In total, 18 groundwater samples, 23 surface-water

454 samples, and 1 snow sample were collected in July and August 2019.

455 Genie Mountain's karst groundwater is mainly derived from atmospheric precipitation and melted

456 ice and snow. The groundwater is mainly recharged by local water circulation and is supplemented

457 by water vapor from the Middle East, the Indian Ocean, and the Western Pacific. Marked isotopic

458 depletion occurs. Groundwater recharge areas are mostly located in high mountains above 4500 m,

459 and the direction of runoff is mostly controlled by the Jinshajiang Fault, with drainage areas at the

460 intersection of multiple faults.

461 On the basis of the hydrochemistry, isotopes, and the location of the excretion zone, karst water is

462 divided into five groups: the northern, Huolong, eastern, and Gangtonglong groups and thermal

463 springs. Groundwater mainly dissolves carbonate rocks during runoff. The levels of Na^+ and SO_4^{2-}

464 in karst water of the Huolong group are markedly higher than in other groups. Through the analysis

465 of water chemical indicators, we conclude that the source of Na^+ and SO_4^{2-} is dissolution of

466 mirabilite. We infer from this result that the karst water replenishment area of the Huolong group is

467 an arid evaporative environment, and the groundwater experiences slow flow.

468 The karst groundwater cycle in Genie Mountain is complex and can be divided into three levels and
469 four types. The first level is the circulation of epikarst groundwater, in which circulation is rapid,
470 water–rock interactions are limited, and the groundwater is of Ca-HCO_3 type. Level two is the
471 structure-controlled deep karst groundwater cycle, which can be divided into two types. The first
472 type is Huolong group karst groundwater, for which the recharge area is located on the planation
473 surface of Genie Mountain. Groundwater interacts with evaporites and is mostly $\text{Na-SO}_4\cdot\text{HCO}_3$
474 type with TDS value ≥ 1000 mg/L. Modern precipitation and older groundwater become mixed in
475 circulation. The other type is karst water flowing along structural runoff, which is $\text{Ca}\cdot\text{Mg-HCO}_3$
476 type. The circulation distance is generally more than 10 km, and this will also mix with older
477 groundwater. The TDS value is generally ≤ 400 mg/L. The third level is thermal springs heated by a
478 deep heat source, for which the circulation rate is slow.

479 In areas where it is difficult to conduct direct investigations, such as alpine and gorge areas, analysis
480 of complex groundwater cycle processes and the combined use of water chemistry and isotopes can
481 effectively extract key information from water samples and provide explanations about the
482 evolution of hydrochemistry. In future research, additional new isotopic methods can be included to
483 further improve the accuracy of circulation data.

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