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Hydrochemical formation mechanism of mineral springs in Changbai Mountain, China

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• Author contributions

Jialin Li: Data curation, Formal analysis, Methodology, Software, Roles/Writing - original draft.

Jianmin Bian: Conceptualization, Funding acquisition, Project administration, Resources, Supervision.

Yihan Li: Investigation, Validation.

Yuxi Ma: Investigation, Visualization.

Yanmei Li: Writing - review &editing.

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•Ethics approval

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The author declares that they agree to participate

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ABSTRACT:

Changbai Mountain area in China is an important mineral water storage and development area. The hydrochemical composition of mineral water is the decisive factor for mineral-water quality. Therefore, it is necessary to study the hydrochemical characteristics and genesis of mineral water in Changbai Mountain area. Considering the integrity of basin and groundwater system, the study area was classified into three areas where mineral springs are densely distributed. For these areas, according to the mineral water parameter contents, the springs are further classified into single-type (metasilicic acid) mineral spring and compound mineral spring. By examining 74 mineral water samples collected from 2018 to 2020, the characteristics and formation mechanism of the hydrochemical components of the spring water were analyzed by mathematical statistics, model construction, cluster analysis, and principal component analysis. The results show that the formation of single-type mineral spring is controlled by rock weathering; compound mineral springs are the product of CO_2-rich, weakly acidic, confined hot groundwater with high salinity and its mixing with shallow groundwater as it rises along the fracture. Volcanic geological process greatly influence the formation of the hydrochemical components of mineral springs on the North slope of Changbai Mountain. The mineral springs on the Longgang Mountain are greatly affected by human activities. The results of cluster analysis only considering hydrochemical components are consistent with the classification of the areas with concentrated distributions of mineral springs as determined by hydrogeological and geomorphological studies. The results of this study are useful for understanding the distribution, hydrochemical characteristics, and formation mechanism of mineral springs in Changbai Mountain area of China and provide the theoretical basis for the protection and development of mineral spring water.

Keywords：

Hydrochemical formation mechanism; Cluster analysis；PCA ; Metasilicic-acid mineral springs；Changbai Mountain.

1. Introduction

Mineral water is special groundwater formed under special hydrogeological conditions. It contains a certain amount of minerals and some trace elements and is not polluted. It is a rare blue water resource. Mineral water generally has the characteristics of good oral feeling, fine water quality, and some minerals and trace elements needed by human body, and hence, it is favored by people for consumption. The Changbai Mountain in China is characterized by active geologic processes, and multiple stages of volcanic activities have resulted in the formation of basalt, trachyte, pumice, and other magmatic rocks here. These rocks constitute the lava platform and volcanic cone of Changbai Mountain and Longgang Mountain. The cracks and pores of volcanic rocks are very developed. The widely distributed volcanic eruptive clastic sediment favor the proliferation of forests and vegetation and promote the recharge of groundwater by meteoric water. These factors have created unique conditions for the formation and enrichment of mineral water in the Changbai Mountain area. During groundwater flow, hydrogeochemical interactions occur between groundwater and the surrounding rock and soil, dissolving some mineral components and trace elements in the volcanic rocks and forming abundant and high-quality mineral water resources. Mineral springs, mainly of the metasilicic-acid (H_2SiO_3) type, are distributed radially around the main peak of Changbai Mountain. At present, this area is an important mineral water source in China and is among the three major high-quality mineral water sources in the world, along with the Alps and Caucasus mountains.

Since mineral spring water is directly discharged groundwater, the research methods used for groundwater can be applied to study mineral spring water. Research on the hydrochemical characteristics and formation mechanism of mineral springs mainly involves the use of graphic analysis, descriptive statistics, and multivariate statistical methods; in addition, hydrogen and oxygen isotopes and a variety of radioisotopes are used to analyze the formation time and cycles of cold spring and hot spring (Prtoljan, Kapelj et al. 2012, Haklidir 2013). The characteristics, origins, and influencing factors of the hydrochemical components of mineral springs are analyzed based on the statistical analysis of hydrochemical data and isotope method (Kopylova, Lepokurova et al. 2011, Chelnokov, Bragin et al. 2018). The dissolution rules of mineral components and the hydrogeochemical formation mechanism of mineral water were explored using TOUGHREACT and PHREEQC simulators and by water–rock interaction experiments (Choi, Yun et al. 2014, Yan, Xiao et al. 2016). The conceptual model of the groundwater system was constructed by using the method of system science, and the groundwater system was characterized (Kulkarni, Deolankar et al. 2000, Dafny, Burg et al. 2006, Daniele, Taucare et al. 2020). The origins, dynamics, and influencing factors of mineral spring flow was studied by wavelet analysis (Gao, Bian et al. 2016). Multifactor statistical analysis and comprehensive evaluation methods were used to evaluate the quality of mineral water as daily life water (Leite, Stolberg et al. 2018). For mineral springs with industrial value and medical care value, the distribution of mineral springs, content and function of special components, and development and utilization were studied (Vinograd 2004). Considering the development and utilization value of mineral water resources, the hydrochemical characteristics, types, distribution, development, and utilization modes of mineral springs were studied (Barut, Erdogan et al. 2004, Corral, Galindo et al. 2014).

Research on mineral spring water in Changbai Mountain area began in the 1980s. The initial research focused on the distribution characteristics of mineral water resources and the qualitative analysis of mineral spring formation. At present, the experiments and models, simulation and other technical means, isotope and system science, hydrological analysis and other methods are used to study the whole process of mineral water formation and its quantity and quality (Yan, Xiao et al. 2014, Zhang, Liang et al. 2017). Although the mineral springs in Changbai Mountain area are distributed throughout the region, most of the springs are concentrated in certain small areas. In recent years, the development of mineral water resources has increased, and mineral water development has gained importance as a major industry. The mineral water in this area is developed by delimiting the protected areas where mineral springs are concentrated and establishing a mineral water industry base to realize the centralized development of mineral water in the protected areas. Within a given area with a high density of mineral springs, the springs are interrelated in terms of water quantity, water quality, and dynamics, all the springs within the given area is a unified whole. Because of the continuous increase in the development and utilization, problems such as reduction in water quantity and change in water quality have been observed in some springs. This will also affect other mineral springs and underground aquifers within the same spring-concentrated area. It is necessary to analyze and explore the hydrochemical characteristics and formation mechanism of mineral springs to provide a theoretical basis for protecting mineral water resources and ensuring sustainable development.

2. Study area

Changbai Mountain is the highest mountain range in Northeast Asia and is located at the border between China and Korea（Fig.1）. It is the largest volcanic mountain range in the humid areas of China. The volcanic geological process is active, and the lava and pyroclastic rocks ejected form a giant volcanic cone and basalt platform with the Tianchi caldera as the center. The total area of the basalt platform is 5500 km^2, and the average thickness is about 180 m. The climate of the study area is the East Asian monsoon climate with abundant rainfall and an annual average precipitation of more than 600 mm. Songhua River, Yalu River, and Tumen River originate in this region. The forest cover is more than 90%. The interception and absorption of rainwater by vegetation promotes the infiltration of rainwater. Groundwater is mainly supplied by atmospheric precipitation and converted to surface water and discharged into a low-lying valley. The main types of groundwater are basalt pore-fissure water, pore water in loose rock, karst-fissure water in carbonate rock, pore-fissure water in clastic rock, and fissure water in granite rock（Fig.1）. Basalt has the characteristics of pore development, good connectivity, and high silica content and is an ideal medium for groundwater storage and migration. Material exchange occurs between basalt and groundwater, forming abundant metasilicic-acid-type mineral water resources. Mineral springs are concentrated in the low basaltic platform of Longgang Mountain and basaltic plateau area of Changbai Mountain, forming a spring group. The low platform of the Longgang Mountain is located in the western part of the study area and has an altitude of 500–1200 m. In this platform, more than 170 craters were formed by the accumulation of basaltic trass. The Changbai Mountain basalt plateau is located under a giant volcanic cone, and around the volcanic cone, the altitude gradually decreases from a height of 1200 m to 600 m (the valley).

3. Data and methods

3.1 Sample collection and measurement

In all, 74 mineral water samples were collected in the months of July–October in 2018–2020（Fig.1）. The mineral water indexes were tested according to "Methods for examination of drinking natural mineral water" GB 8538-2016 (National Health Commission of the People's Republic of China. 2016). The sampling bottles were polyethylene bottles and glass bottles, which were washed with distilled water in advance. Before sampling, the sampling bottles were rinsed thoroughly with the spring water from the target sampling point thrice, and the pH value was measured on site. Subsequently, the water samples were sealed and labeled, stored at 4°C, and sent to the Testing Science Experimental Center of Jilin University and Jilin Provincial Institute of Geological Sciences for water chemistry testing.

The test items include HCO_3^-、Cl^-、SO_4^{2-}、Na^+、K^+、Ca^{2+}、Mg^{2+}、NO_3^-、F^-、TDS、TH、TFe、H_2SiO_3 , etc. Among them, Na^+ and K^+ were determined by FAAS; Ca^{2+} and Mg^{2+} were determined by EDTA disodium salt titration; HCO_3^- was determined by double-indicator; Cl^- was titrated with silver nitrate; SO_4^{2-}、NO_3^- and F^- were determined by ion chromatography; TDS determination by electronic balance by dry weight method; TH by EDTA disodium titration; TFe was determined by inductively coupled plasma mass spectrometry; H_2SiO_3 was determined by silicon molybdenum yellow spectrophotometry. Other trace elements such as Sr^{2+} and Li^+ were determined by FAAS.

3.2 Analytical methods

(1) The hydrochemical data were analyzed by mathematical statistics. The Piper trigram can be plotted using Grapher program. By distinguishing the types of mineral springs, the Gibbs diagram and the relation graph of Ca^{2+}/Na^+ and Mg^{2+}/Na^+,Ca^{2+}/Na^+ and HCO_3^-/Na^+（lithologic end element ratios diagram）were drawn to determine the dominant factors of hydrochemical formation. Based on the geophysical data and geological and hydrogeological conditions, the typical genetic diagram of a regional compound mineral spring was drawn; this diagram depicts the formation process of a series of compound mineral springs.

(2) Open-source software R was used for statistical calculation and mapping and principal component analysis (PCA). The histogram of the contribution rate and loading diagram were drawn. The steps in PCA include calculating the mean value and standard deviation, calculating the covariance matrix, calculating the covariance eigenvalues and eigenvectors, arranging the eigenvalues in the increasing order, retaining several larger vectors, and finally, transforming the data into the new space constructed by the eigenvectors.

The covariance matrix:

$$\mathrm{X} = \begin{pmatrix} x_{11} & x_{12} & \cdots & x_{1m} \\ x_{21} & x_{22} & \cdots & x_{2m} \\ \vdots & \vdots & \ddots & \vdots \\ x_{n1} & x_{n2} & \cdots & x_{nm} \end{pmatrix} = (x_1, x_2 \cdots x_m) \tag{1}$$

The covariance eigenvalues and eigenvectors:

$$\begin{cases} F_1 = a_{11}x_1 + a_{12}x_2 + \cdots + a_{1m}x_m \\ F_2 = a_{21}x_1 + a_{22}x_2 + \cdots + a_{2m}x_m \\ \cdots \\ F_m = a_{m1}x_1 + a_{m2}x_2 + \cdots + a_{mm}x_m \end{cases} \tag{2}$$

The larger matrix of K eigenvalues is obtained:

$$\begin{bmatrix} F_{11} & F_{21} & \cdots & F_{1k} \\ F_{12} & F_{22} & \cdots & F_{2k} \\ \vdots & \vdots & \ddots & \vdots \\ F_{n1} & F_{n2} & \cdots & F_{nk} \end{bmatrix} \tag{3}$$

(3) Cluster analysis is also called group analysis. The number of samples classified is unknown before analysis. According to the similarity degree, the samples are divided into several clusters, which are unaffected by other factors. Cluster

analysis can be classified into Q-type clustering for the research object itself and R-type clustering for variables and indicators of the research object. In this study, SPSS software was used for Q-type clustering analysis of hydrochemical data. The Euclidean distance was used to calculate the distance between different sample points. Ward algorithm was used to calculate the distance between clusters. Because the order of magnitude of different indicators is different, it is necessary to standardize the whole range 0–1 to obtain the cluster tree of mineral water chemistry.

Here, Euclidean distance is the absolute distance between two points in multidimensional space, and it is calculated as follows:

$$d_{ij} = \|x_i - x_j\| = \sqrt{\sum_{k=1}^{p}(x_{ik} - x_{jk})^2} \tag{4}$$

Ward algorithm is mainly based on the idea of variance analysis, and it requires that the sum of squares of deviation between the same clusters is as small as possible. The method involves merging two clusters of objects close to each other until all objects are merged. The calculation principle of this algorithm is as follows: First, all sample points are divided into m classes (P_1, P_2…P_m), where $P_n^{(m)}$ denotes the nth index in P_m, and the index number of P_m is k. Let $\overline{P^{(m)}}$ denote the center of gravity of P_m. Then, the sum of squares of deviation of each sample point is as follows:

$$S_m = \sum_{n=1}^{k}\left(P_n^{(m)} - \overline{P^{(m)}}\right)'\left(P_n^{(m)} - \overline{P^{m}}\right) \tag{5}$$

Then the intraclass sum of squares of deviation of m categories is as follows:

$$S = \sum_{m=1}^{m} S_m = \sum_{m=1}^{m}\sum_{n=1}^{k}\left(P_n^{(m)} - \overline{P^{(m)}}\right)'\left(P_n^{(m)} - \overline{P^{m}}\right) \tag{6}$$

If the order of magnitude of the variable index is different, it is necessary to transform the variable. The formula of standardized transformation for the full range 0–1 is as follows:

$$Z_{ij} = \frac{x_{ij} - \overline{x_j}}{s_j} \tag{7}$$

Where, $x_j = \frac{1}{n}\sum_{i=1}^{n} x_{ij}$ $s_j = \frac{1}{n-1}\sum_{i=1}^{n}\left(x_{ij} - \overline{x_j}\right)^2$

4. Results and discussion

4.1 Classification and hydrochemical characteristics of mineral springs

4.1.1 Classification of mineral springs

Water–rock interaction results in a type of dynamic, natural liquid mineral under the controls imposed by the rock medium and structure. This leads to a natural distribution of mineral water with fixed hydrochemical characteristics. The mineral springs in the study area have the characteristics of concentrated distribution in different hydrogeological and basin units. To analyze the similarity and differences in the chemical characteristics and hydrochemical origins of mineral water under the control of different hydrogeological and geomorphological conditions, digital elevation model (DEM) data were used. Using the hydrological analysis function of ArcGIS, the basin in the study area was extracted and divided. This process included the following steps: creating nondepression DEM; performing flow direction analysis and flow statistics; and defining the minimum surface runoff, river linking, grid river vectorization. By comprehensive consideration of basin division and mineral spring enrichment, three areas with a dense distribution of mineral springs were selected—the West Slope of Changbai Mountain (West slope), the North Slope of Changbai Mountain (North slope), and the Longgang Mountain (Longgang). Each of these areas is located in different hydrogeological and watershed units. The three areas form 26.55% of the research area, and contain 61 sampling points, accounting for 82.43% of the total number of sampling points（Fig.1）. The mineral springs within any one area are regarded as a group for classification analysis.

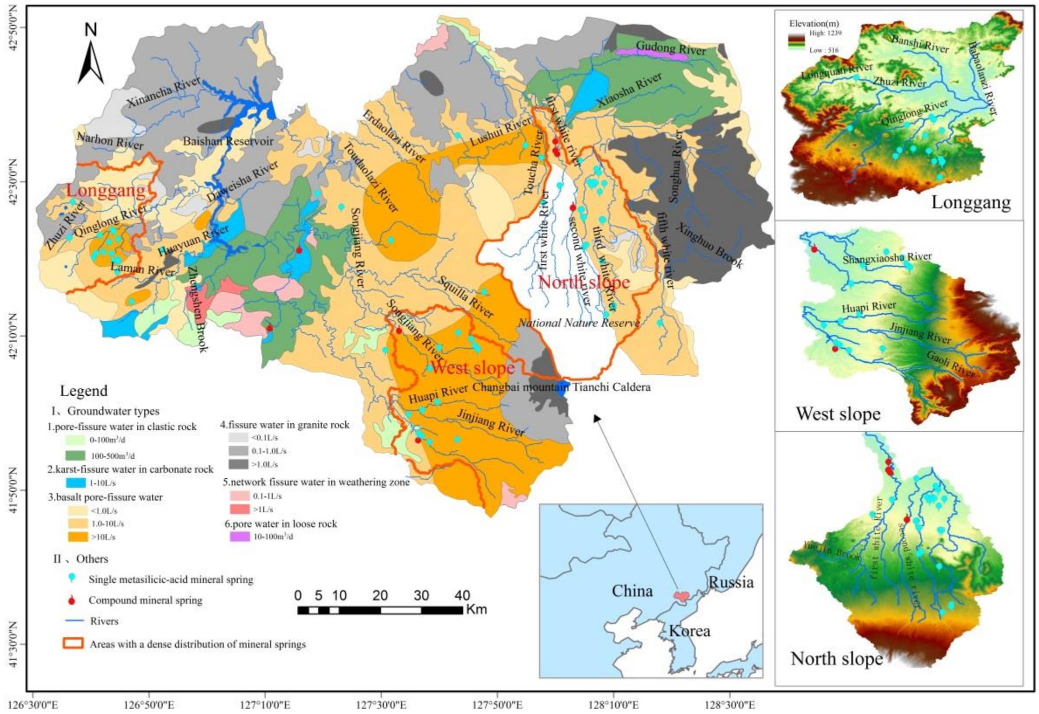


Fig.1. Hydrogeology conditions and sampling springs

Mineral spring water parameters include the contents of lithium, strontium, zinc, metasilicic, selenium, free carbon dioxide (CO_2), total dissolved solids (TDS), and the thresholds of the parameters are listed in Table 1. If only one parameter meets the standard of “Drinking natural mineral water” GB8537—2018 (National Health Commission of the People's Republic of China. 2018), the spring is a single-type mineral spring. If more than one parameter meets the standard, it is a compound mineral spring. Compound mineral springs are relatively rare in the study area, and their special components are listed in Table 2.

Table1. Drinking natural mineral water parameter and thresholds

Types	Parameter	Threshold
metasilicic	H_2SiO_3/（mg/L）	≥25.0（When the concentration is 25.0 mg/L-30.0 mg/L, the water temperature should be above 25 ℃）
lithium	Li /（mg/L）	≥0.20
strontium	Sr /（mg/L）	≥0.20（When the concentration is 0.20 mg/L-0.40 mg/L, the water temperature should be above）
zinc	Zn /（mg/L）	≥0.20
selenium	Se /（mg/L）	≥0.01
free carbon dioxide	CO_2/（mg/L）	≥250
total dissolved solids	TDS/（mg/L）	≥1000

Table2. Special components contents of compound mineral springs（all in mg/L）

Site	H_2SiO_3	CO_2	TDS	Li	Sr
I	77.55	--	1365.66	--	0.33
II	40.30	396.60	2646.72	0.64	1.48
III	40.00	308.00	2343.00	0.20	4.33
IV	56.47	305.56	1402.40	--	--
V	50.05	734.00	1371.00	--	0.45
VI	96.20	658.11	2029.68	--	--
VII	98.80	1188.00	1672.00	0.19	0.44
VIII	107.83	1056	1672.00	0.21	0.52

The special component contents of each mineral spring were analyzed. The results show that the H_2SiO_3, CO_2, and TDS of most of the compound mineral springs meet the quality standards of "Drinking natural mineral water" GB8537—2018, and the Li^+ and Sr^{2+} contents of some mineral springs meet the standards. Single metasilicic-acid mineral springs are widely distributed in the study area. All the single-type mineral springs in this study are of the metasilicic-acid type, and the average content of metasilicic-acid is 43.79 mg/L. There are great differences between compound mineral springs and single-type mineral springs in terms of their in hydrochemical characteristics. According to the types of mineral springs and the area with dense distributions of mineral springs, the mineral springs in the study area were classified into five categories—compound mineral springs were regarded as a separate category. The single-type mineral springs were subdivided into four categories according to their locations: the spring groups of (1) the west slope of Changbai Mountain (West slope springs,) (2) the north slope of Changbai Mountain (North slope springs), (3) Longgang Mountain (Longgang springs), and (4) other regional mineral springs. Mineral springs of category 1–4 are all single metasilicic-acid type. Based on the hydrochemical data of various types of mineral springs, the hydrochemical characteristics and genesis of different types and regions of mineral springs were analyzed and studied.

4.1.2 Hydrochemical types and component features

The minimum, maximum, average, and coefficient of variations of 14 hydrochemical indexes, such as K^+, Na^+, and H_2SiO_3 were calculated（Table.3）. The changes in the average contents of different hydrochemical indexes of all types of mineral springs show good consistency. Except for F and H_2SiO_3, the content of each component in the North slope springs is the lowest, and the TFe value of West slope springs is low. The hydrochemical characteristics of single-type mineral springs and compound mineral springs are quite different. The pH value of compound mineral springs is lower than that of the single-type mineral springs, and the F^- content is lower than that of the North slope springs; in comparison with the single-type mineral spring, the content of SO_4^{2-}, K^+ is 2–5 times, that of H_2SiO_3 is 1.5–1 times, the content of NO_3^- is one order of magnitude lower, and the content of other hydrochemical indexes is 1–2 orders of magnitude higher. The coefficient of variation of Longgang springs is relatively small except for NO_3^-, and the K^+, Na^+, Ca^{2+}, Mg^{2+}, Cl^-, HCO_3^-, TDS, TFe, and H_2SiO_3 are the lowest among all types of mineral springs. In addition to SO_4^{2-} and NO_3^-, the coefficient of variation of the West slope springs is relatively large, and the coefficients of variation of K^+, Na^+, Mg^{2+}, HCO_3^-, TDS, and pH are the largest among all types of mineral springs. The coefficients of variation of SO_4^{2-}, NO_3^-, TFe, H_2SiO_3, and F^- in compound mineral springs are the largest.

Table3. Minimum (min), maximum (max), median (Md), and Standard Deviation (CV) values of hydrochemical parameters in mineral springs of different types

Site	K^+	Na^+	Ca^{2+}	Mg^{2+}	Cl^-	SO_4^{2-}	HCO_3^-	NO_3^-	TDS	pH	TH	TFe	H_2SiO_3	F^-
West slope (n=16)														
Min	1.67	3.08	5.39	1.08	0.81	0.00	29.22	1.00	84.39	6.50	22.15	0.01	36.38	0.17
Max	15.19	66.25	24.39	16.76	7.25	8.92	300.78	8.08	484.93	7.85	199.00	0.38	84.64	0.79
Md	3.88	12.97	11.88	5.11	2.49	4.13	88.34	4.84	166.72	7.25	53.04	0.08	45.04	0.41
CV	1.01	1.19	0.44	0.93	0.66	0.50	0.85	0.39	0.66	0.06	0.81	1.21	0.30	0.47
North slope (n=23)														
Min	1.56	4.90	4.37	2.41	0.46	1.70	43.10	0.64	104.28	7.00	24.09	0.00	35.02	0.29
Max	3.60	15.60	18.53	22.14	4.91	7.66	184.91	10.00	294.44	7.89	137.45	0.26	59.13	1.34
Md	2.75	8.54	7.91	5.33	1.80	3.82	64.80	2.29	139.37	7.33	42.13	0.07	50.63	0.80
CV	0.18	0.28	0.47	0.73	0.63	0.43	0.42	0.81	0.27	0.03	0.53	1.10	0.12	0.32
Longgang (n=16)														
Min	2.42	5.76	10.98	5.96	1.76	4.26	70.12	1.87	142.50	6.67	62.06	0.01	30.46	0.07
Max	4.71	12.35	25.07	12.69	7.37	16.63	125.01	16.20	218.70	8.05	97.73	0.32	41.80	0.26
Md	3.79	9.43	15.81	9.20	3.29	7.83	104.42	4.84	180.24	7.58	78.74	0.11	36.49	0.16
CV	0.17	0.20	0.22	0.20	0.46	0.44	0.16	0.83	0.14	0.04	0.13	0.68	0.07	0.38
Others (n=11)														
Min	0.88	3.90	5.28	2.23	1.61	0.00	36.00	0.00	54.00	7.07	27.62	0.00	26.80	0.16
Max	6.50	15.85	22.76	22.10	13.49	8.88	216.99	5.00	322.24	8.15	145.97	0.29	63.01	0.36
Md	2.62	8.58	13.96	9.07	4.75	4.62	102.45	2.06	181.39	7.67	74.69	0.12	38.31	0.23
CV	0.67	0.45	0.42	0.80	0.97	0.53	0.61	0.83	0.47	0.05	0.56	0.79	0.25	0.22
Compound mineral springs (n=8)														
Min	6.53	43.75	98.08	48.77	5.89	0.00	678.13	0.00	1365.66	6.16	655.23	0.04	40.00	0.32
Max	25.68	214.05	181.61	152.36	42.60	46.06	1706.40	0.54	2646.72	6.98	903.65	3.30	107.83	1.50
Md	11.66	108.40	135.79	107.10	15.73	8.48	1239.34	0.12	1754.61	6.56	798.57	0.81	70.90	0.65

CV	0.48	0.50	0.24	0.33	0.75	1.69	0.24	1.54	0.24	0.04	0.09	1.50	0.37	0.62

Note: n is the number of samples, and the unit of each index (except pH value) is mg/L.

The Piper trilinear diagram of various mineral springs were drawn using Grapher, and their hydrochemical types were analyzed（Fig.2）. From the trilinear diagram, it can be seen that Ca^{2+} accounts for the largest proportion of cations in the North slope springs, and cations of other types of mineral springs are distributed in the mixed area, and there is no dominant cation. The distribution of anions of all types of mineral springs is concentrated, and HCO_3^- is the dominant anion. The hydrochemical types of all types of mineral springs are basically consistent, including the HCO_3-Ca type, HCO_3-Ca+Na type and HCO_3-Na type, among which HCO_3-Ca type accounts is the dominant type.

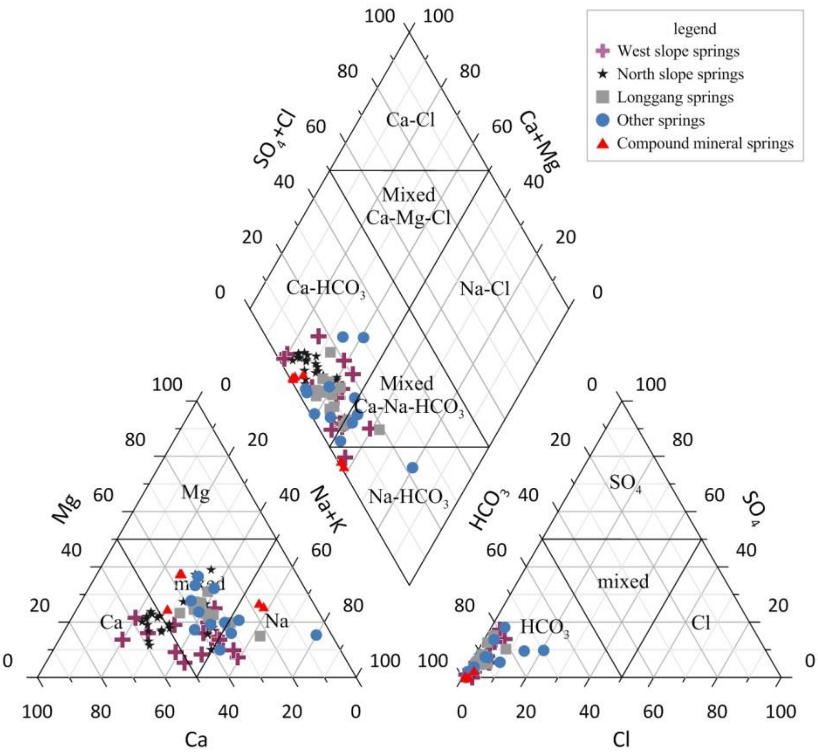


Fig.2. Piper trigram diagram of mineral water

4.2 Hydrochemical formation causes

There are differences and similarities in the characteristics of the hydrochemical components of different categories of mineral springs. This reflects the similarities and dissimilarities in the hydrochemical formation mechanisms of mineral water. The hydrochemical origins of various mineral springs were analyzed by using the Gibbs diagram and lithologic end element ratios diagram. The hydrochemical characteristics and genesis of single-type mineral springs and compound mineral springs are quite different. Different hydrogeochemical processes have different effects on the formation of single-type mineral water chemical components in different areas with high densities of springs. There are obvious differences in their hydrochemical components. By using PCA, cluster analysis, and other hydrochemical analysis methods, combined with regional geological and hydrogeological conditions, the hydrochemical genesis of mineral springs in each category was explored.

4.2.1 Controlling factors of hydrochemical formation

The Gibbs diagram is drawn based on the hydrochemical data of each mineral spring. According to the position of each spring in the Gibbs diagram, the main sources of the chemical components dissolved in water were analyzed, and the hydrochemical genesis of mineral springs was determined（Fig.3）. Most of the single-type mineral springs are located in the rock-weathering control area in the middle of Gibbs diagram, and rock weathering is the main factor determining the chemical composition of this type of mineral water. Meteoric water with very low mineral content leaches the surface soil and infiltrates the underground rock stratum. The groundwater flows through basalt and pyroclastic rock, and the mineral components in the weathered and broken rock are transferred to groundwater, forming the metasilicic-acid mineral water. Compound mineral springs are located in the evaporation zone and the periphery of the model. Because Changbai Mountain is a humid area, evaporation has little effect on the formation of mineral water. This type of mineral spring is not the product of evaporation and concentration, but it is affected by the special conditions during formation. The formation mechanism of hydrochemistry has changed, resulting in the atypical characteristics of hydrochemical components.

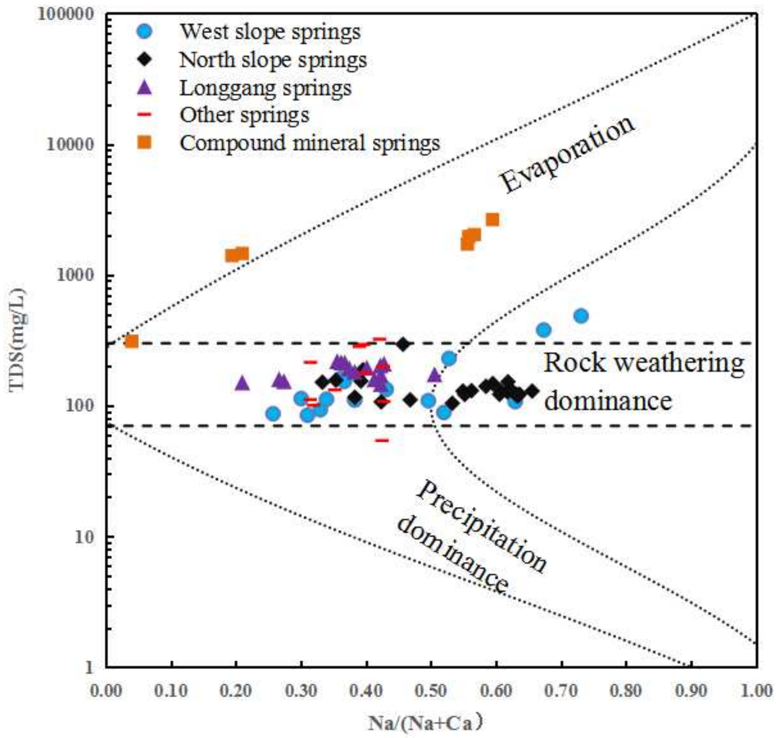
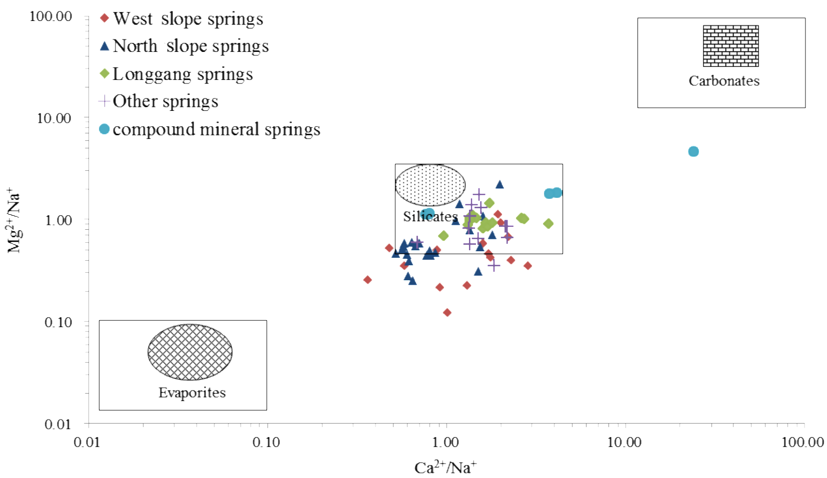
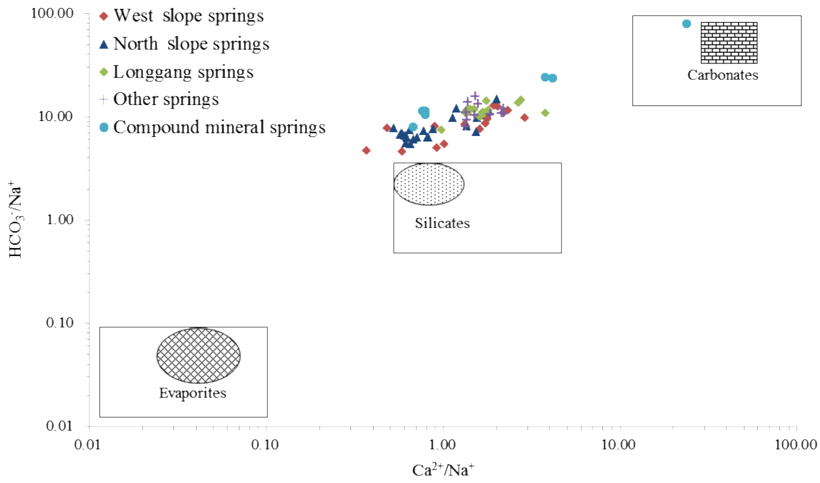


Fig.3. Gibbs diagram of springs

The lithologic end element ratios diagram (Fig. 4) for the mineral springs in the study area can be used to determine the rock types involved in water–rock interactions. Fig. 4 shows that the mineral springs mainly located in the silicate rock area and between the carbonate rock and silicate rock, and silicate rock is dominant. It shows that the hydrochemical components of mineral springs in Changbai Mountain are mainly controlled by silicate rocks and influenced by carbonate rocks. The influence of carbonate rocks on the West slope springs and the North slope springs is less than that of Longgang springs.



(a)



(b)

Fig.4. Lithologic end element ratios diagram of different springs

4.2.2 PCA of single-type mineral springs

The hydrochemical characteristics of mineral springs are controlled by the dominant hydrogeochemistry reactions, but the formation process of mineral springs is often affected by many factors. Different hydrogeochemistry reactions will produce different hydrochemical characteristics and components (Yang, Li et al. 2016, Ligavha-Mbelengwa and Gomo 2020). PCA can be used to judge the degree of influence of different hydrochemical actions in the process of mineral spring formation and the similarity and dissimilarity of each hydrochemical component source. PCA is a statistical analysis method that simplifies multiple indicators into a small number of comprehensive indicators. It uses a few variables to reflect the information of the original variables as much as possible to ensure that the loss of original information is small and the number of variables is as small as possible (Lourenço, Ribeiro et al. 2010, Huang, Sun et al. 2013). Using R, which integrates statistical analysis and graphic display, 13 hydrochemical indexes of single-type mineral spring in the study area were simplified and analyzed, and the histogram of factor contribution rate and double projection diagram of the load in PCA was drawn.

The factor contribution rate histogram can be used to help determine the optimal principal component. The abscissa represents the main component, and the ordinate represents the contribution rate. The first several principal components with larger contribution rates are the main components that should be selected. According to contribution rate of each factor the number of selected principal components is determined. The histogram of contribution rate is shown in Fig.5. The contribution rate of the first five principal components is relatively large, and the cumulative contribution rate is 85%. Selecting the first five principal components can comprehensively reflect most of the information of hydrochemical. The proportion of variance, cumulative proportion and rotation factor load matrix of single-type mineral springs are shown in Table4.

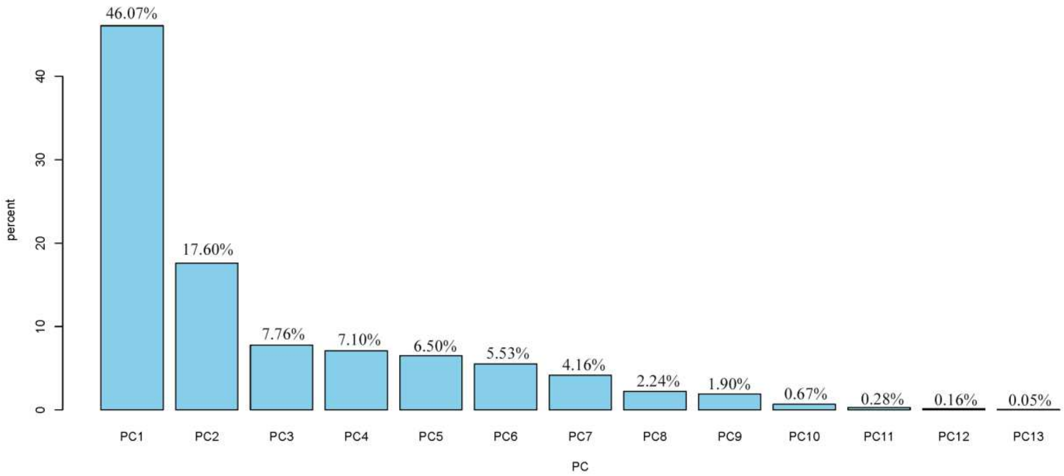


Fig.5. Histogram of contribution rate

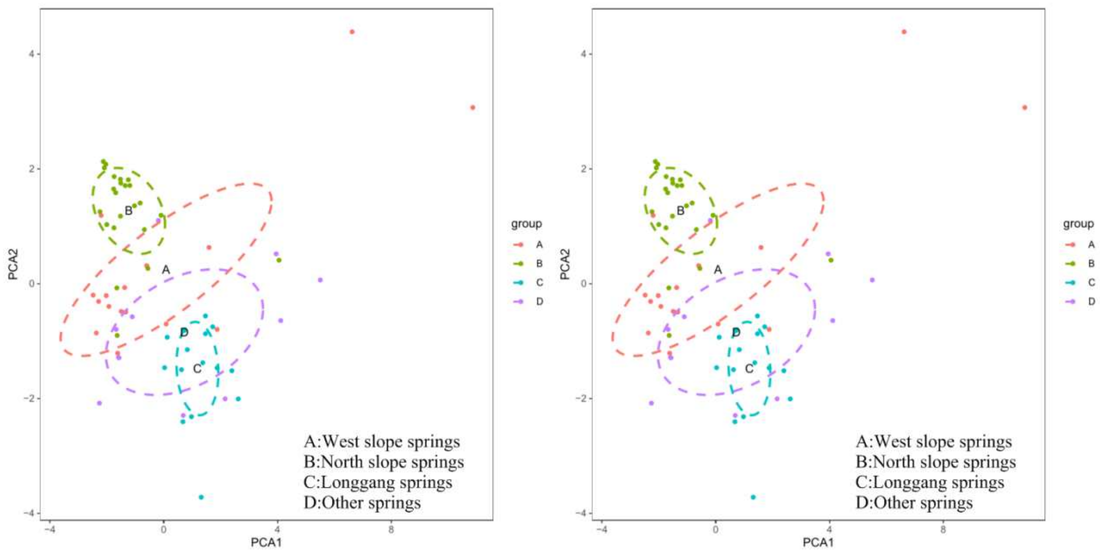
Table4. Rotation factor load matrix of PCA

Variables	PC1	PC2	PC3	PC4	PC5
K^+	**0.331**	0.242	0.049	-0.097	0.193
Na^+	**0.326**	0.246	0.011	-0.185	0.270
Ca^{2+}	**0.331**	-0.247	0.144	0.026	-0.108
Mg^{2+}	**0.353**	-0.020	-0.076	-0.038	-0.288
Cl^-	0.126	-0.265	-0.483	-0.012	**0.579**
SO_4^{2-}	0.047	-0.390	0.063	0.178	**0.509**
HCO_3^-	**0.399**	0.076	-0.046	-0.054	-0.134
NO_3^-	0.082	-0.235	**0.818**	-0.195	0.204
TDS	**0.398**	0.113	-0.022	-0.010	0.002
TH	**0.391**	-0.071	-0.043	-0.076	-0.103
TFe	0.166	-0.054	0.134	**0.903**	-0.073
H_2SiO_3	0.056	**0.557**	0.050	0.247	0.258
F^-	-0.155	**0.453**	0.200	0.014	0.242
Proportion of Variance	0.461	0.176	0.078	0.071	0.065
Cumulative Proportion	0.461	0.637	0.714	0.785	0.850

Table 4 shows that the contribution rate of the first factor is 46.1%, and it mainly comprises K^+, Na^+, Ca^{2+}, Mg^{2+}, HCO_3^-, TDS, and TH; it represent the process that mineral components in different types of rocks enter the groundwater, and various hydrochemical components of groundwater increase with the increase in the water–

rock interaction time. Because of the different types of rock and soil, the flow length and the mineral contents in rock and soil, the factor loads of the main components in the first factor are relatively small. The contribution rate of the second factor is 17.6%, and it mainly comprises H_2SiO_3 and F^- and represents the influence of volcanic activity and magmatic volatilization. In the volcanically active area, the release of F is closely related to deep magmatism and magma degassing. The solubility of silicate minerals increases with increase in temperature. In addition, the solubility of silicate minerals and the release capacity of F from rock and soil will also increase under weak alkaline conditions (Pachana, Zuddas et al. 2012, Sunkari, Abu et al. 2020). Hence, H_2SiO_3 and F^- are the main components in the second factor. The contribution rate of the third factor is 7.8%, and it mainly comprises NO_3^-. Human activities are the main source of nitrate, and hence, the third factor represents the impact of human activities (Singh, Rishi et al. 2020). The contribution rate of the fourth factor is 7.1%, and it is mainly TFe, representing the high background value of iron in the rock matrix of Northeast China and the characteristics of pyroxene in trachyte and pantellerite that erupted in Holocene and are rich in Fe and poor in Mg (Li, Fan et al. 2004). The contribution rate of the fifth factor is 6.5%, and it mainly comprises Cl^- and SO_4^{2-}, representing evaporation concentration.

PC1, PC2, and PC3 are the three factors that have the greatest impact on the chemical components of regional single-type mineral water. To analyze the influence degree of the three principal factors on springs located in different spring-concentrated areas, the double projection diagram of load in PCA of each area was drawn by using R（Fig.6）. Fig. 6 show that there is no significant difference in the influence degree of weathering-leaching processes (the first factor) and volcanic geology (the second factor) on the hydrochemical components of the West slope springs. Volcanic geology has a great influence on the formation of the hydrochemical components of the North slope springs, but less influence on the Longgang springs. This is attributed to the different active degrees of regional volcanic geology. The massive volcanic eruption time of Longgang Mountain Volcanic Group is about 150,000 years ago. At present, the volcanic geological activity has weakened. The northern slope of Changbai Mountain has a developed fault structure, which comprises a ring structure and radial structure closely related to the giant volcano. The North slope springs are greatly affected by geological volcanic activity (Liu, Chu et al. 2009). The nitrate produced by human activities (the third factor) has a relatively large impact on Longgang springs, but a relatively small impact on the springs in the other regions—this is consistent with the fact that there are relatively more human activities in Longgang mountain area.



(a) (b)

Fig.6. Projection diagram of load

4.2.3 Cluster analysis of single-type mineral springs

The Q-type cluster analysis of mineral water chemistry is a method to classify different types of samples according to the similarities and differences in hydrochemical components (Lambrakis, Antonakos et al. 2004, Ghesquière, Walter et al. 2015). Only according to the chemical composition of mineral water, all single-type mineral springs are regarded as a single type for Q-type cluster analysis. In the analysis, the selection of hydrochemical indexes is consistent with the PCA. A class comprises elements separated by a Euclidean distance less than 8; it is divided into four categories. Among these, cluster 1–2 and cluster 3–4 can be divided into two categories. On the whole, the content of hydrochemical components in cluster 3–4 is higher than that in cluster 1–2. The results of cluster analysis and the spatial distribution of mineral springs after clustering are shown in Fig.7, and the average contents of hydrochemical components of mineral springs in different clusters are listed in Table 5.

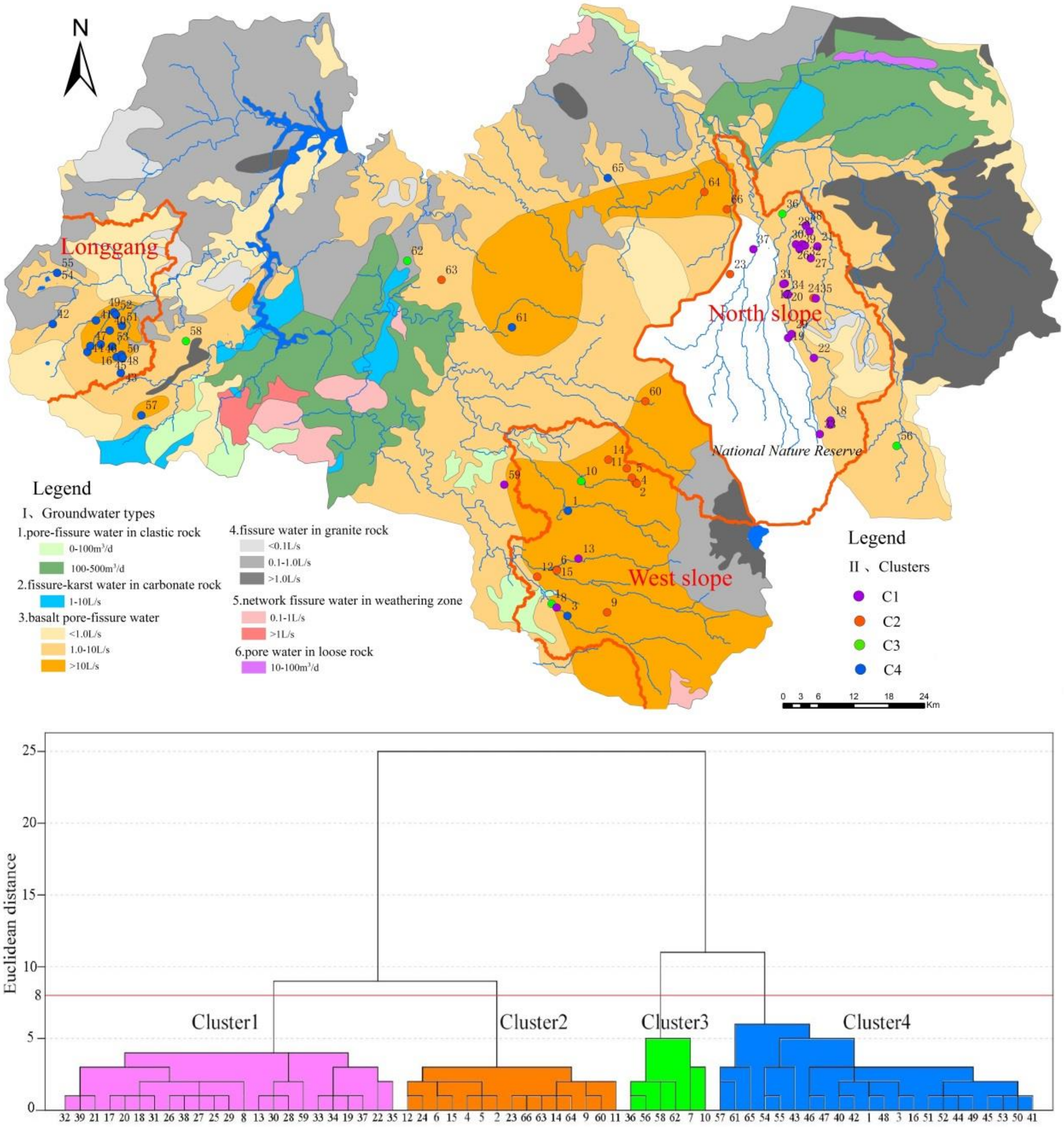


Fig.7. Cluster analysis results and their spatial distribution

Table5. Average contents of hydrochemical components in different clusters

cluster	n	K^+	Na^+	Ca^{2+}	Mg^{2+}	Cl^-	$SO4^{2-}$	HCO_3^-	NO_3^-	TDS	TH	TFe	H_2SiO_3	F^-
1	23	2.70	8.48	7.97	4.43	1.78	3.74	61.38	2.13	135.14	38.53	0.07	52.64	0.81
2	15	1.96	5.64	8.99	3.15	1.67	4.55	48.70	4.26	108.15	35.28	0.06	36.37	0.36
3	6	7.63	25.82	20.09	19.42	3.34	2.79	218.52	3.92	342.81	141.78	0.15	52.15	0.35
4	22	3.52	9.76	15.45	8.45	4.56	7.23	102.18	4.26	180.22	74.24	0.12	37.33	0.18

Note: n is the number of samples, and the unit of each index is mg/L.

Figure 7 and Table 5 show that the springs in cluster 1 are mainly located in the North slope springs area, along the second White River and third White River from south to north, and most of the mineral springs in the North slope belong to cluster 1. The results show that the mineral springs in the upper reaches have a good hydraulic connection with those in the lower reaches, which are supplied with the groundwater of the basalt platform in the south. The volcanic geological process (the second factor in PCA) has a greater impact on this cluster of mineral springs. Most of the springs in cluster 2 are located in the West slope springs area. Most of these springs are supplied by basalt pore-fissure water with a flow rate of more than 10 L/s and are located near the river. The contents of most hydrochemical components are low, while those of SO_4^{2-} and NO_3^- are relatively high, indicating that they are closely related to surface water. The springs in cluster 3 are scattered and few, and most of the components are present in relatively high contents. Some of the mineral springs are located in the bedrock area and the junction area between the basalt stratum and other types of strata, which are far from the supply area and concentrated areas of mineral springs. It shows that the flow path of this type of mineral spring is long, resulting in the inclusion of a large number of minerals from the rock and soil into groundwater. Most of the springs in cluster 4 are located in the Longgang springs area, and the distribution is relatively concentrated. Most of these springs are supplied by basalt pore-fissure water with a flow rate of more than 10 L/s. The contents of H_2SiO_3 and F^- are low, whereas those of Cl^-, $SO4^{2-}$, and NO_3^- are high. Human activities (the third factor in PCA) has a greater impact on this cluster. According to the topography, the area where Longgang springs are located is a valley surrounded by mountains on three sides. From the edge to the center of the valley, the amount of basalt pore-fissure water increased from less than 0.1 L/s to more than 10 L/s. It shows that the mineral spring classified as cluster 4 in Longgang mountain area is the atmospheric precipitation of the mountains around the valley that infiltrates into the ground, flows in the basalt under the action of topography, and is exposed at the bottom of the valley.

The results of cluster analysis show that the majority of North slope springs are in cluster 1; in the West slope springs, cluster 2 accounts for the majority, and all the Longgang springs are in cluster 4, which shows that the hydrochemical characteristics within a spring cluster are similar, and different spring clusters show relatively large differences. The result of cluster analysis is consistent with the division of the concentrated distribution area of mineral springs. Because the hydrochemical index is the only factor to be considered in cluster analysis, it shows that the hydrochemical composition of mineral water shows good consistency with the concentrated areas of mineral springs as determined by topography and landform. The division of the concentrated areas of mineral springs conforms to the basin conditions determined by topography and landform, as well as the hydrochemical characteristics of mineral springs.

4.2.4 Formation of compound mineral springs

In the Gibbs map, some compound mineral springs are located at the periphery of the model, which shows that their formation is affected by special conditions. Tectonization and volcanic activity are strong in the study area. The ring structure and radial structure closely related to the volcanic activity are distributed around the main peak of the Changbai Mountain. There are many deep faults extending north–south, north–east, and north–west. Most of the groundwater in the deep fault is supplied by surface water and underground hot water, thereby affecting the mineral water quality (Chen, Ai et al. 2019). In the process of magmatism and metamorphism, CO_2 is released, lowering the pH value of groundwater. In addition, the temperature in the deep underground is higher. These factors increase the strength of the water–rock interaction. The groundwater circulation time in the deep fault is long, and a large number of minerals in the rock enter into the groundwater, increasing the content of each component and the TDS in the groundwater. According to the statistical analysis of the annual variation in some mineral spring temperatures（Fig.8）, the annual variation of regional atmospheric temperature is large, and the annual variation of mineral springs temperature is small. The temperature of single-type mineral springs is between 6 and 9°C, and the temperature of compound mineral springs is higher than that of single-type mineral springs. The temperature difference between different compound mineral springs is also large. Through field observation, it can be seen that free CO_2 overflow occurs in the compound mineral spring, and travertine is attached to the spring mouth, and the rock surface has red iron oxide, and the pores are relatively developed（Fig.9）. The above analysis shows that the compound mineral spring is supplied by the underground hot water in the deep fault formed by geological volcanic activity, and the difference in hydrothermal cycle characteristics is the main reason for the temperature difference between different compound mineral springs.

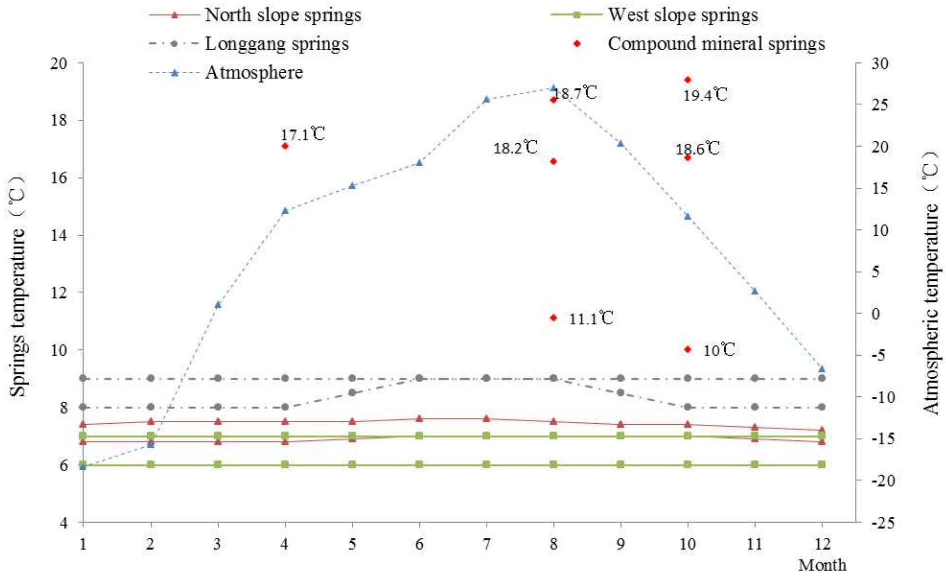


Fig.8. Annual variation of mineral spring temperature

Based on the regional geological structure conditions, a high TDS compound mineral spring near the north-south fault zone was selected. The mineral spring is located at Site IV (Table 2). Its genesis was analyzed. The spring is located in the second White River valley on the North slope of Changbai Mountain. Because of the volcanic geological process of Changbai Mountain, north–south zonal geothermal reservoirs are buried underground. The geothermal reservoirs include shallow geothermal reservoirs in the fracture zone under the basalt caprock and a deep geothermal reservoir formed by the development of karst and structural fractures in the marble. Regional magma and magma chamber provide a stable heat source for geothermal reservoirs. The genetic diagram was drawn according to the geothermal geological conditions（Fig.9）.

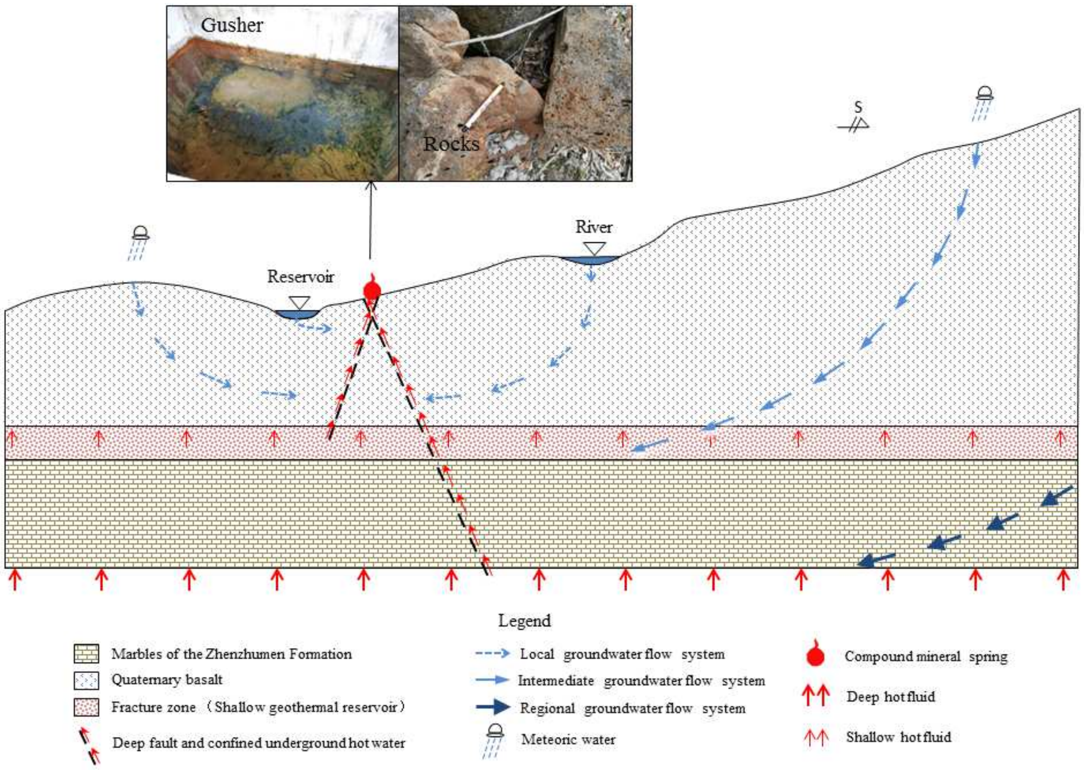


Fig.9. Genetic diagram of compound mineral spring

Figure 9 shows that there are local, intermediate, and regional groundwater flow systems in the region. Around the Changbai Mountain crater, radial and annular fractures are dense. Atmospheric precipitation and Tianchi lake water infiltrate into the rock fissures of high temperature and high pressure. Convection occurs under the action of temperature and pressure and rises along the marble fracture, forming a regional groundwater flow system from the main peak of Changbai mountain to the intersection of the fault structures in the river valley. The regional groundwater flow system is mainly affected by volcanic geology. The groundwater in the upper part of the basalt platform is recharged by precipitation and the surface runoff of the giant volcanic cone in the upstream. Under the control of topography, the groundwater flows downstream and accumulates in the basalt fracture zone, forming an intermediate groundwater flow system from the upper part of the basalt platform to the discharge area of the lower valley. The intermediate groundwater flow system is mainly controlled by topography and geological structural conditions. Mineral springs are located in the valley with a low terrain. Atmospheric precipitation infiltrates into the basalt and gathers in the valley under the action of gravity. There are rivers and reservoirs in the upstream and downstream of mineral spring. The water levels of surface water and reservoir are higher than the groundwater level; hence, they supply groundwater and form a local groundwater flow system. The local groundwater flow system is mainly controlled by the terrain conditions. The regional and intermediate groundwater flow through the geothermal reservoirs and is heated; it then rises along the fracture connected with the mineral springs and mixes with the local groundwater flow with a lower temperature to form compound mineral springs. According to the above analysis, a part of the compound mineral springs in the study area is the product of dilution and subsequent mixing of the confined groundwater formed under the high-temperature and high-pressure conditions in the deep fault with the shallow groundwater as the confined groundwater rises along the fracture.

5. Conclusions

There are single metasilicic-acid mineral springs and compound mineral springs in Changbai Mountain area. Most of the single-type mineral springs are distributed in three areas. According to the types and distribution of mineral springs, the springs can be classified into five types: West slope springs, North slope springs, Longgang springs, other regional mineral springs, and compound mineral springs. The average values of hydrochemical indexes of all types of mineral springs show good consistency, and the hydrochemical type is mainly the HCO_3-Ca type. The content of metasilicic-acid in all mineral springs meets the standard of "Drinking natural mineral water" GB8537—2018, and the content of most hydrochemical indexes of compound mineral springs is 1–2 orders of magnitude higher than that of single-type mineral springs.

Using the general and special methods to explore the hydrochemical origin of mineral springs, it is concluded that the formation of single metasilicic-acid mineral springs is controlled by rock weathering, and that silicate rock is the main medium in the water–rock interaction. The hydrochemical formation mechanism of the compound mineral spring is different and shows the characteristics of high temperature and high CO_2. The formation of compound mineral springs is affected by the deep geothermal reservoirs of high temperature and high pressure and long-term groundwater circulation. It is the mixed product of the deep acidic hot water rising along the fault and mixing with the shallow groundwater.

PCA was used to judge the source of hydrochemical components and the influence of each factor on the hydrochemical components of mineral springs in different regions. The first five principal factors representing 85% contribution rate were extracted. The results show that the water–rock interaction of groundwater, regional volcanic geological process caused by volcanic activity and magmatic volatilization, human activities, high background value of iron in the rock, and evaporation concentration are the main reasons for the formation of the chemical characteristics of mineral water, with the contribution rates of the factors are 46.1%, 17.6%, 7.8%, 7.1%, and 6.5%, respectively. Volcanic geological process has a great influence on the formation of the chemical components of mineral water on the North slope springs, and the Longgang springs are greatly affected by human activities.

Using cluster analysis, the samples are classified into four categories: the mineral springs in cluster 1 are mainly located in the North slope springs area, and the mineral springs in cluster 1 on the North slope springs are supplied by the same groundwater aquifer. Most of the mineral springs on the West slope springs are in cluster 2, which is closely related to surface water. Some of the springs in cluster 3 are scattered at the junction of different strata. Longgang springs are all in cluster 4 and are distributed at the bottom of the valley, where enrichment and concentrated exposure of meteoric water is observed. The cluster analysis shows that the clustering results of only considering hydrochemical components are consistent with the division of the concentrated distribution area of mineral springs.

All the analysis results show that there are great differences between compound mineral springs and single-type mineral springs in the study area in terms of the hydrochemical characteristics and genesis. The compound mineral spring is a mixture of the confined groundwater formed in deep fractures and shallow cold groundwater, and the single-type mineral spring originates from meteoric water leaching the basalt. Mineral springs are distributed over the whole study area and concentrated in specific areas. Different hydrogeological conditions and human activities have different impacts on the mineral springs in different regions, and there are obvious differences in their hydrochemical characteristics.

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Figures

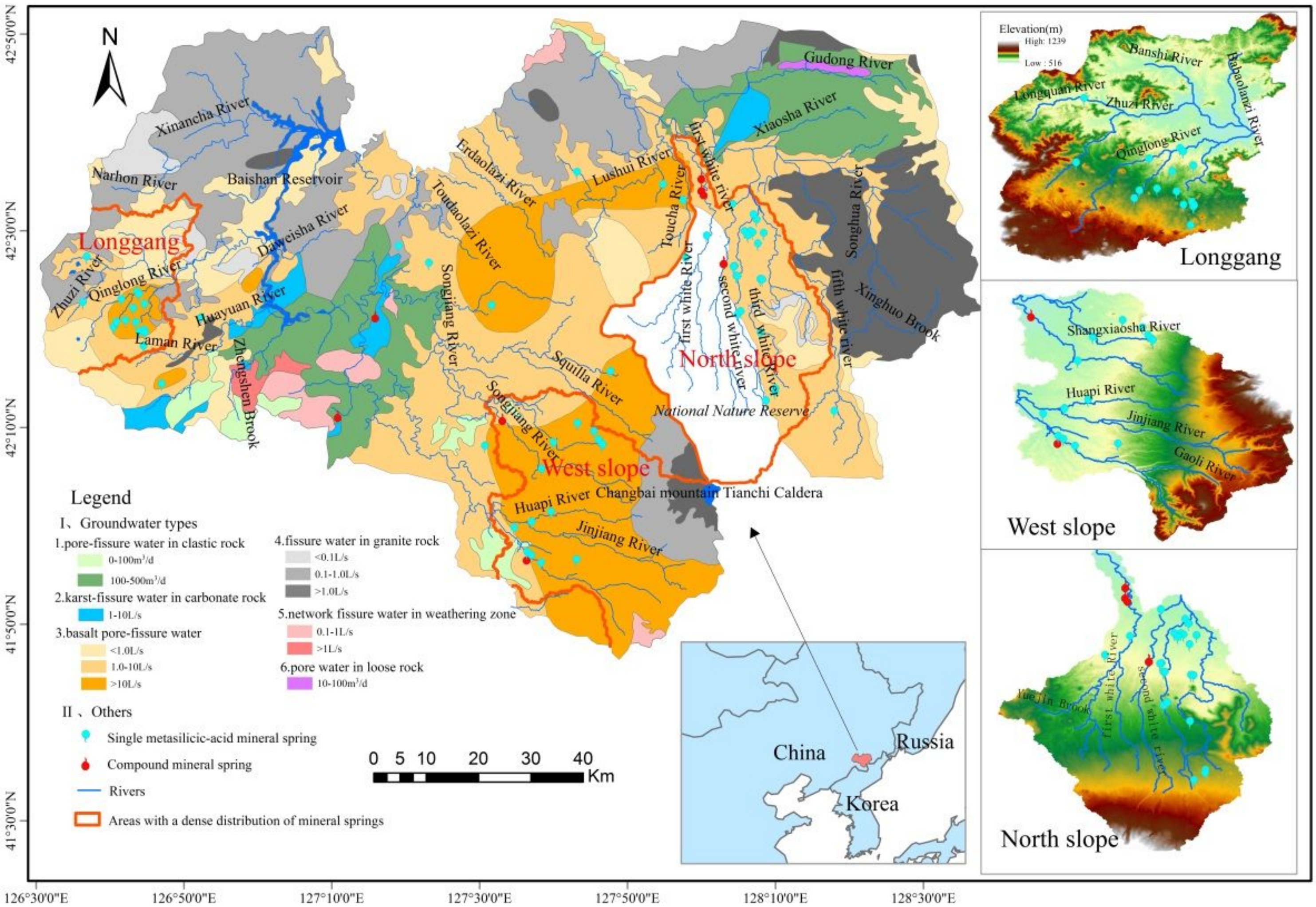

Figure 1

Hydrogeology conditions and sampling springs Note: The designations employed and the presentation of the material on this map do not imply the expression of any opinion whatsoever on the part of Research Square concerning the legal status of any country, territory, city or area or of its authorities, or concerning the delimitation of its frontiers or boundaries. This map has been provided by the authors.

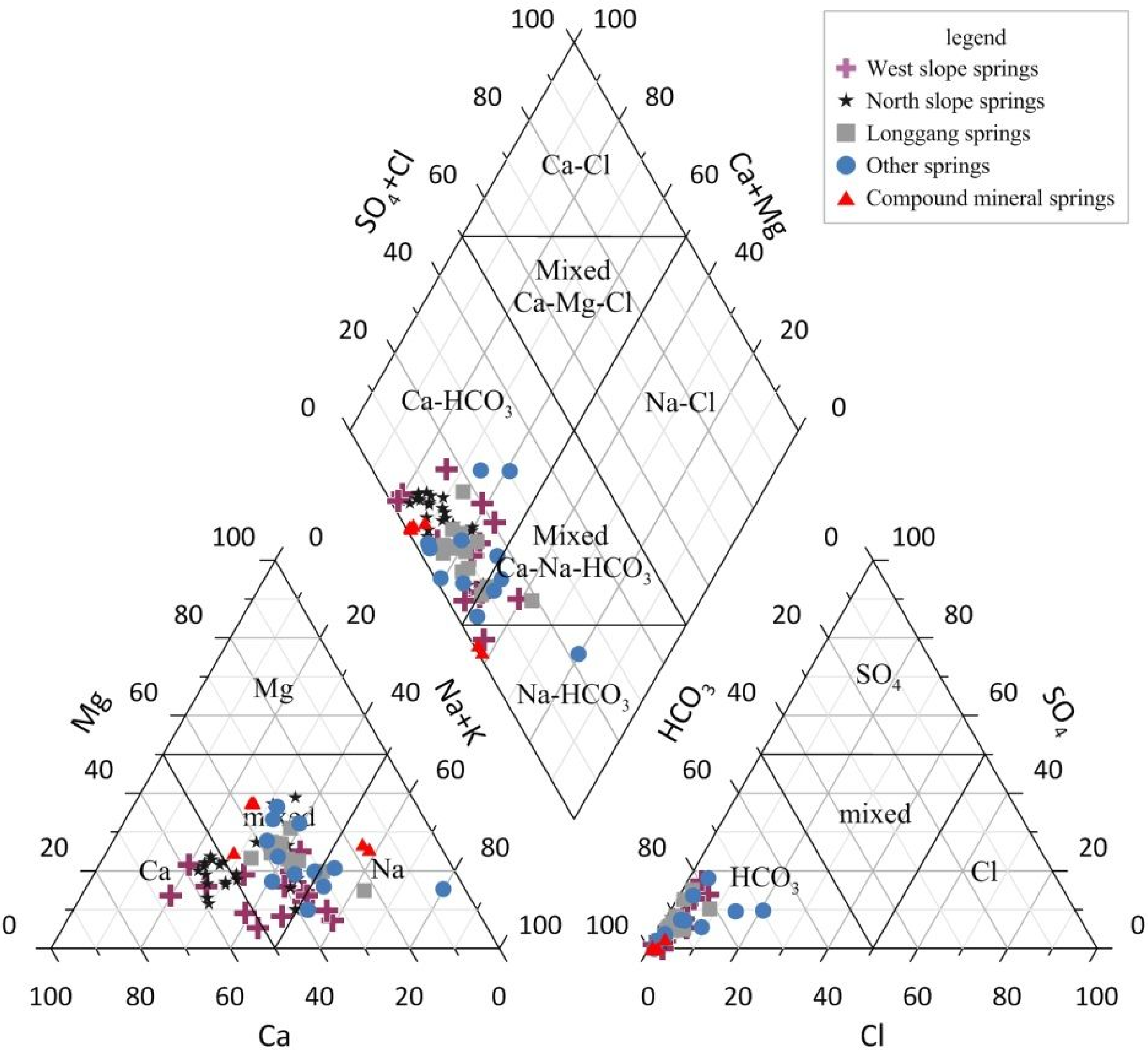

Figure 2

Piper trigram diagram of mineral water

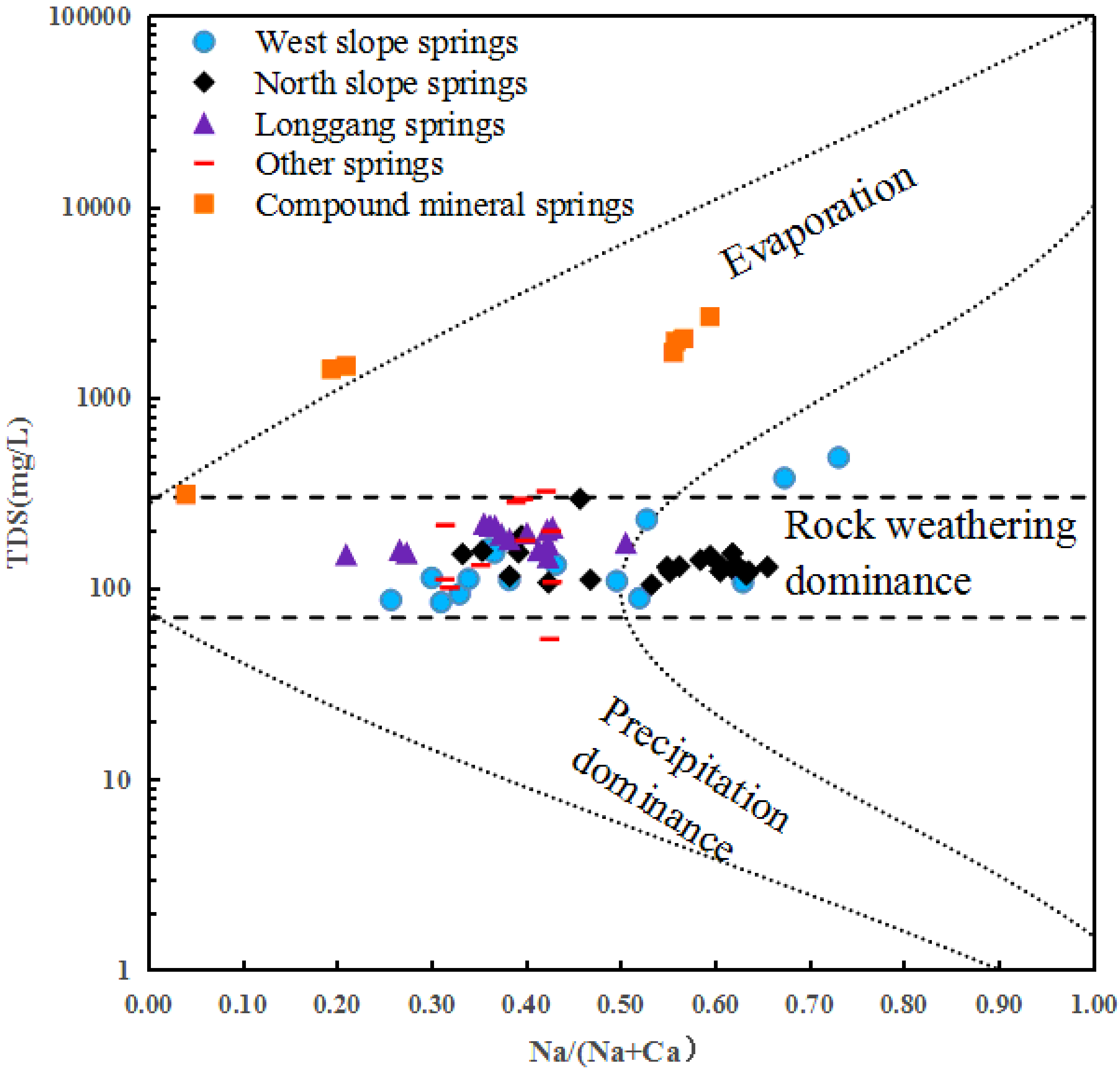

Figure 3

Gibbs diagram of springs

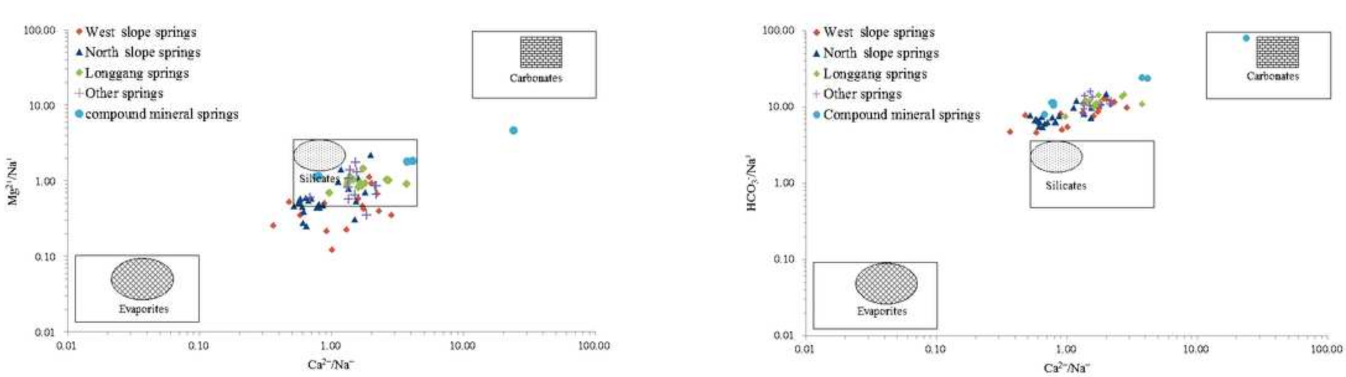

Figure 4

Lithologic end element ratios diagram of different springs

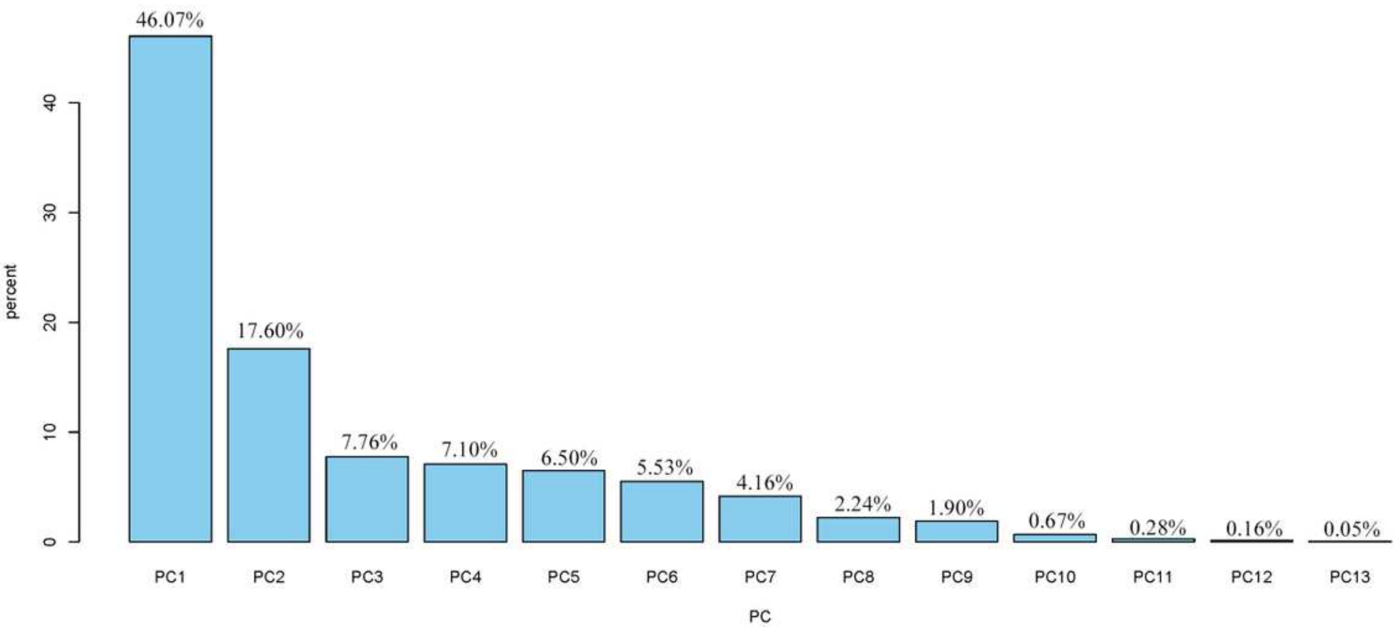

Figure 5

Histogram of contribution rate

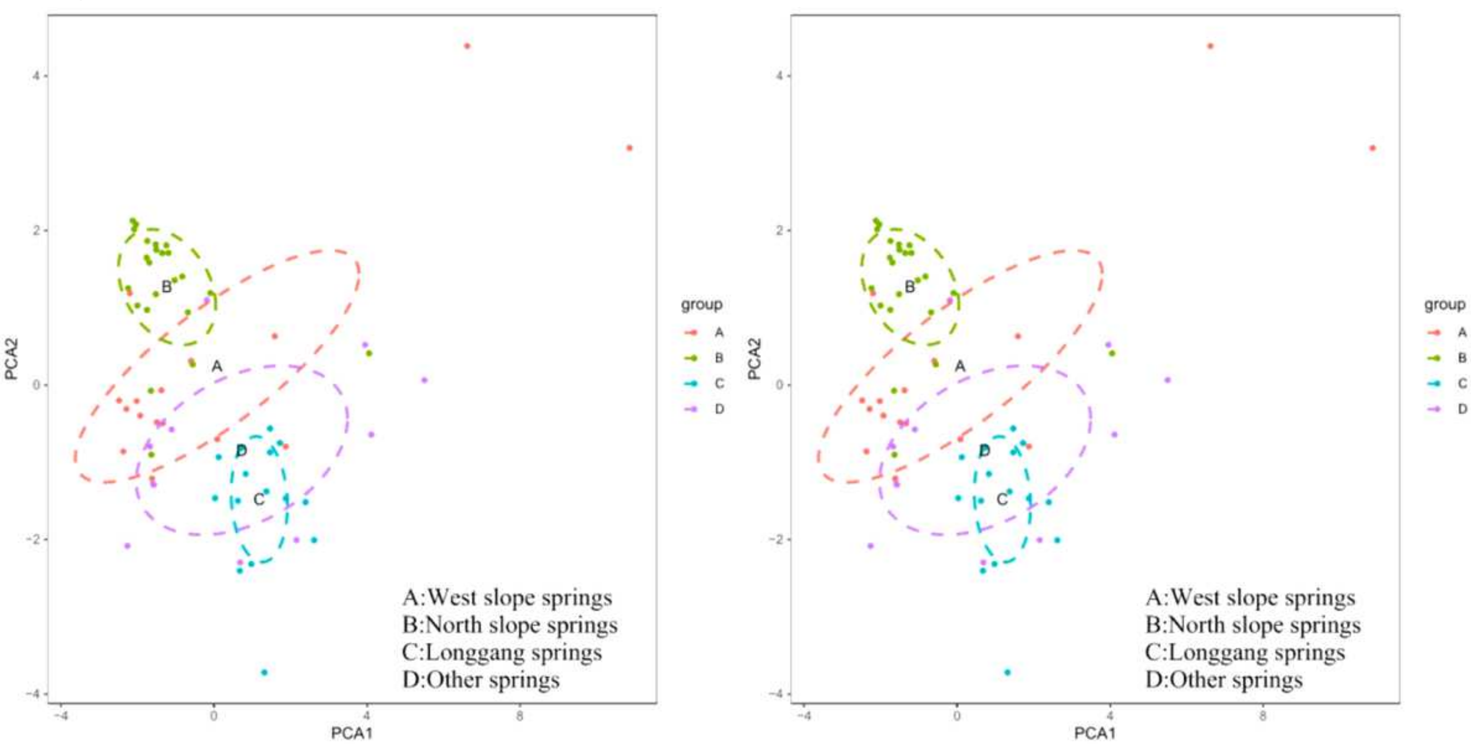

Figure 6

Projection diagram of load

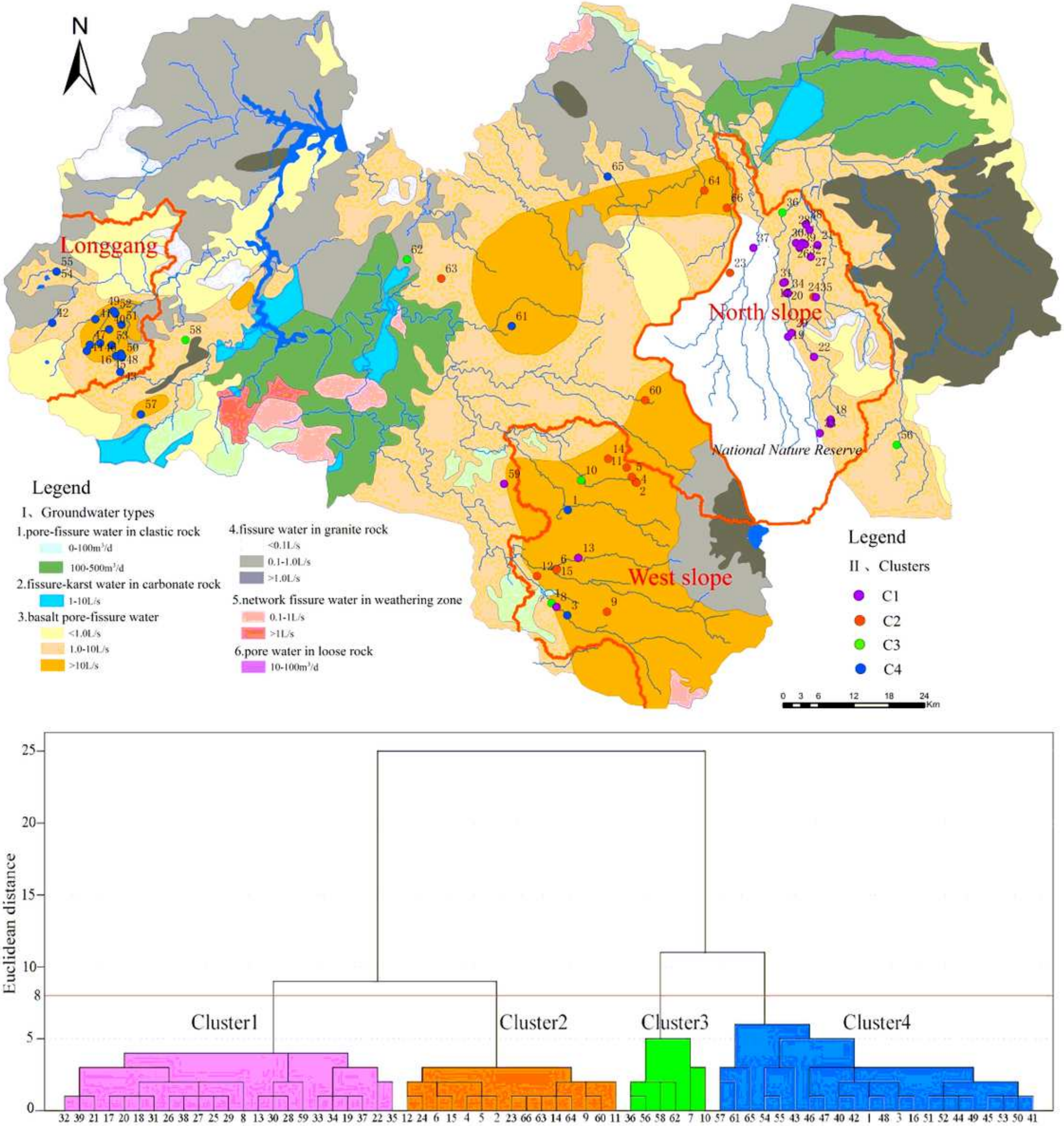

Figure 7

Cluster analysis results and their spatial distribution Note: The designations employed and the presentation of the material on this map do not imply the expression of any opinion whatsoever on the part of Research Square concerning the legal status of any country, territory, city or area or of its authorities, or concerning the delimitation of its frontiers or boundaries. This map has been provided by the authors.

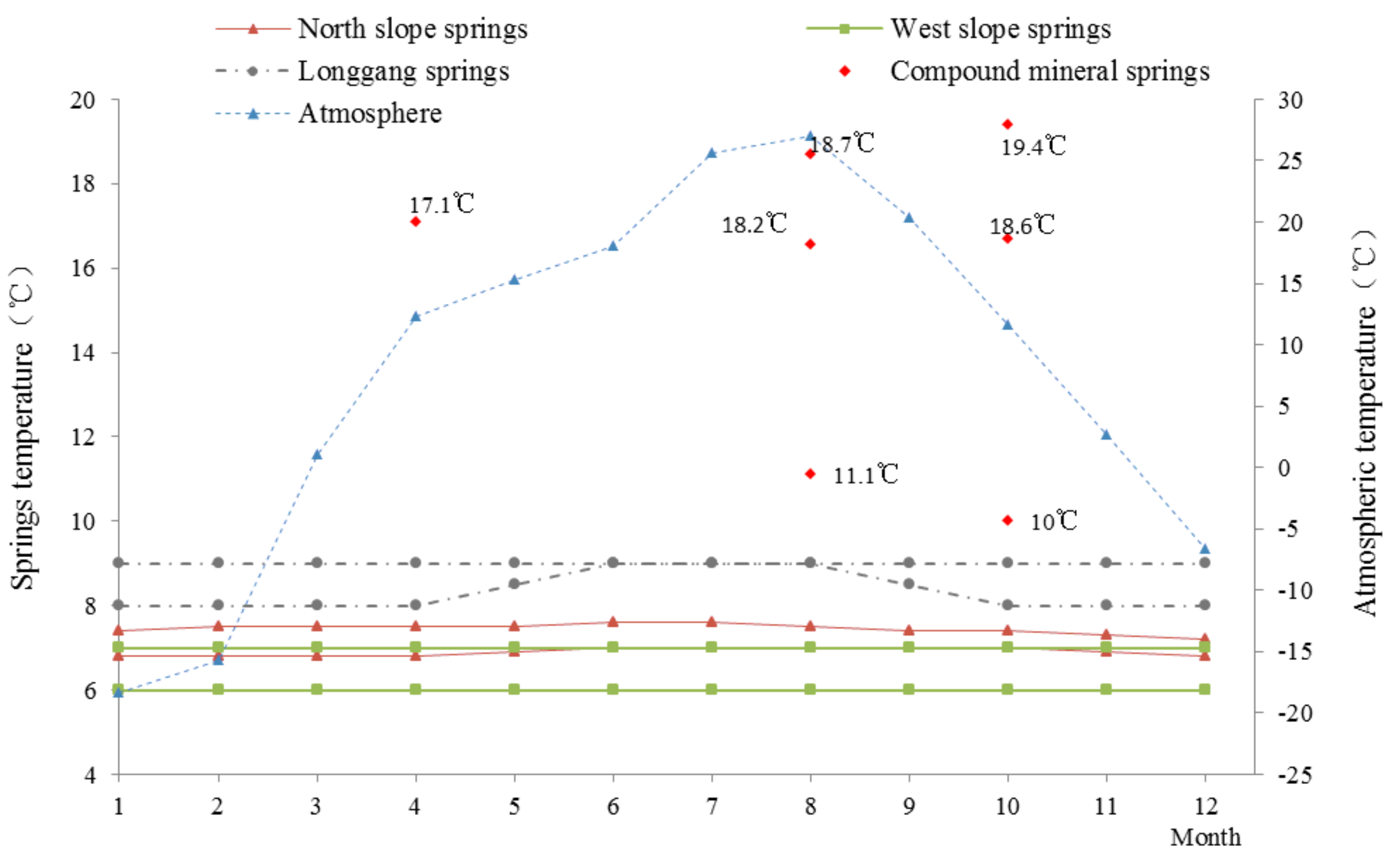

Figure 8

Annual variation of mineral spring temperature

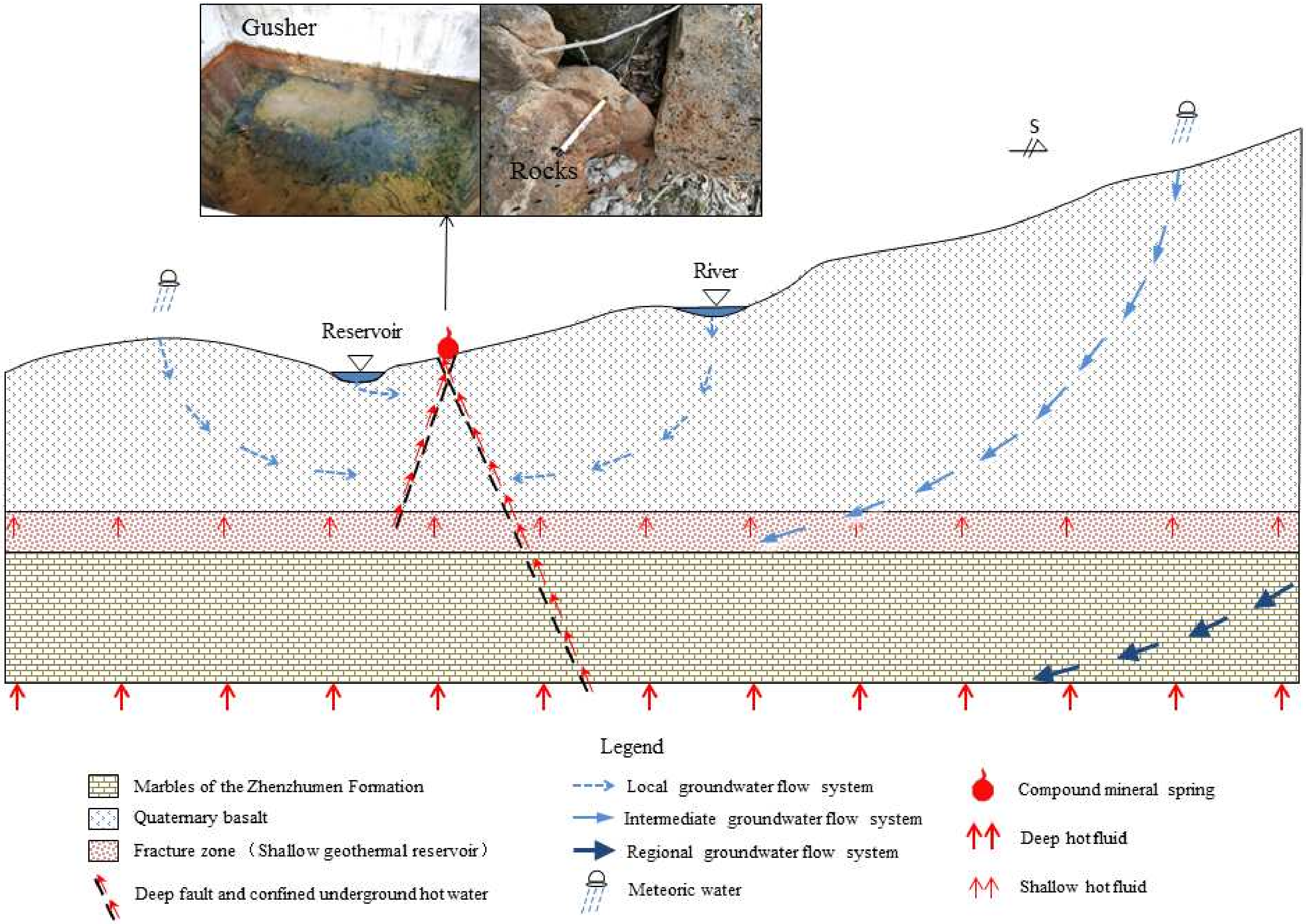

Figure 9

Genetic diagram of compound mineral spring