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FIELD STUDY METHODS IN KARST GEOCHEMISTRY AND SOME EXAMPLES

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1 INTRODUCTION

Introducing geochemical methods into karstology makes not only the branch of science substantial in content, but also some problems solved effectively by use of quantitative analysis. The problems of studying carbon, water and calcium cycle of karst system are that this system is extremely sensitive to environment and the major selected elements which exist in karst water system are very active. The elements will change quickly when they separate from this system. The real circumstance can not be reflected correctly if we only make indoor normal analysis by collecting some samples[1]. Therefore, in the past few years, many difficult problems were solved better by use of a series of field karst geochemical measure and research methods for tracing the carbon, water and calcium cycles, which is a breakthrough in karst study.

2 THEORITICAL BASIS

The general equation of carbonate rock dissolution or deposition is as follows:

$$MCO_3(s) + CO_2(g) + H_2O(l) = M^{2+} + 2HCO_3^-$$

From this equation, it can be calculated easily when 1000 kg carbonate rock dissolve or deposit, 440 kg CO_2 is released or consumed. Karstification takes place in $CO_2-H_2O-MCO_3$ three-phase nonequilibrium open system[2]. The meaning of the open system is when carbonate rock dissolves, CO_2 can get supply from the air constantly, and when carbonate rock deposits, CO_2 is released from this system and return to air circle. CO_2 has a certain solubility in water and its solution is slightly acid. The concentration of CO_2 dissolving in water changes when water is stirred or water temperature varies. This process brings about a change in pH value and as a result, the dissolution or deposition of carbonate rock take place. So the $CO_2-H_2O-MCO_3$ system is in a dynamic condition transferring to a equilibrium one. This process is shown in Fig. 1.

3 FIELD RESEARCH METHODS

In order to research karstification from the viewpoint of hydrochemistry, some major and relatively stable hydrochemical elements which are included in the karst water system should be selected and observed. These elements are HCO_3^-, pH, concentration of CO_2 in gas and liquid phase, temperature of water and conductivity which can synthetically reflect the characteristics of karst water. Besides these internal indexes, the external factors should also be monitored. They are climate, geological, geographical and hydrological conditions, and dissolution or deposition of carbonate rock.

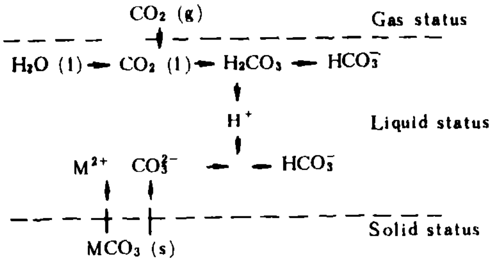

Fig. 1 $CO_2-H_2O-MCO_3$ **three-phase nonequilibrium open system**

3.1 Measurement of Water pH

In natural karst water, the process of water pH formation can be expressed in following dynamic equation:

$$CO_2 + H_2O + H_2CO_3 \longrightarrow 2H^+ + 2HCO_3^-$$

This balanced system is influenced by many factors, such as agitation of water, CO_2 gas release, changes in temperature, dissolution or deposition of carbonate rock, etc.. The pH values of water samples will change quickly if samples separate from karst water system. So a pH-meter which is high in precision (0.01 pH unit) and easy to operate and carry is required, if we want to describe the change law of karst geological system. In order to ensure the accuracy of data, the pH-meter must be calibrated before operation. The steps of calibration are as follows. (a) Put a pH electrode into the standard solution with a pH value of 6.86, adjust "STANDARD" key to make the meter show 6.86, and then fix this key, take out the electrode, clean and dry it. (b) Put the electrode into the standard solution with a pH value of 9.18, adjust "SLOPE" key to make the meter show 9.18. The two steps above are repeated once again to test whether the meter is OK. Fig. 2 shows how the slope affects the reading, i.e. the larger the slope is, the larger the reading is, when the pH of water is higher than that of the standard solution; the case is on the contrary, when the pH value of water is lower than that of the standard solution.

3.2 Measurement of the Concentration of Gaseous CO_2 in Soil

The concentration of gaseous CO_2 in karst soil directly affects the partial pressure of CO_2

(P_{CO_2}) dissolving in water. The equilibrium relation of $H_2CO_3-HCO_3^--CO_3^{2-}$ in carbonate system is a main factor for the pH value of karst water, and the process of CO_2 dissolution or release is coincident with that of carbonate rock dissolution or deposition. Thus it can be seen that CO_2 acts as a motive power which drives the $CO_2-H_2O-MCO_3$ nonequilibrium system to change. The concentration of CO_2 gas in soil is commonly measured by use of GASTEC-CO_2 detector. The procedure in measurement is described as follows. (a) Drill a hole of a required depth in the ground with a drill rod (15 mm in diameter), put a rubber tube with a tester on its end into the bottom of the hole, another end of this rubber tube is connected with a gas pump. (b) Pump 100 ml soil air and take out the tester three minutes later. We can get the reading when the veagent colour changes from white to purple. In order to raise measurement precision, a suitable tester should be selected according to the characteristics of soil structure. Usually, we measure the CO_2 content in A layer (20 cm deep) where vegetation grows well, and in B layer (50 cm deep) of soil as well. The karstification is accompanied with CO_2 cycle which is in the atmosphere, biosphere, hydrosphere and lithosphere. Some samples are collected to analyze their $\delta^{13}C$ so that we can know from where CO_2 comes and where it goes.

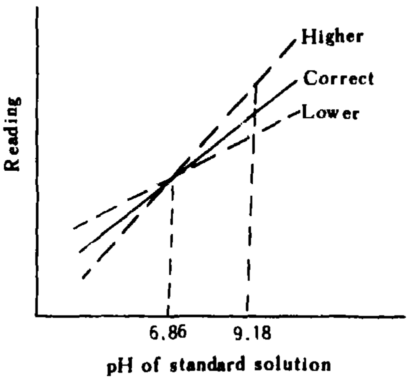

Fig. 2 The influence of slope on reading

3.3 Measurement of HCO_3^- of Water

In general, karst water pH values are between 6.0 and 9.0. It is shown in Fig. 1 that HCO_3^- is a superior content in the three-phase nonequilibrium system of karst water. HCO_3^- is a comprehensive index reflecting the characteristics of karst system. As the pH value, the HCO_3^- changes easily too and can be measured by acid-alkali titration. Get 10 ml water sample, take methyl-yellow as indicator and HCl (0.05 N) as titrant, by the end of titrantion the colour of solution changes from light yellow to light red. Note down the volume of hydrochloric acid consumed. According to equivalent law, we can calculate the concentration of HCO_3^-.

3.4 Limestone Corrosion Rate Observation

The purpose of this test is to observe the corrosion rate of carbonate rock under different climate conditions. In order to make a comparison of the observed data with each other, all samples are prepared in same size and laid according to special requirement. The sample is 4 cm in diameter, about 0.3 cm in thickness and 9~16 g in weight. After being cleaned, dried and weighed, the samples were laid on 150 cm (above the ground surface), 0 cm (on the ground surface), —20 cm and —50 cm (below the ground surface). One year later, take all samples out, clean, dry and weigh them, and the loss or increment of unit weight in a year can be calculated. Meanwhile, the annual precipitation and average air temperature is required to be measured.

3.5 Other Field Observation Items

Besides all above mentioned, some other items are also required to be described, such as the position and elevation of the observation point, observation date, temperature of water, discharge of spring, etc..

4 SOME EXAMPLES

The Guilin karst geological experimental site is located in the east-southern part of the city, the juncture of peak cluster-karst depression and peak forest-karst plain. The field measurement was carried out for an integrated karst hydrogeological system. The spring S_{31} (154 m a. s. l.) is a main output of this system. The recharge area is about 1.0 km², the water temperature varies in the range of 18.0℃ to 20.0℃. The spring S_{25} is an epikarst one, 330 m a. s. l. , with a recharge area of about 0.1 km² and the range of water temperature variation of 11.2℃ to 22.4℃ . Tab. 1 lists the observation results of the two springs during 1993~1994. Fig. 3 shows the corresponding changes in CO_2 concentration of soil gas, pH value and HCO_3^- of water.

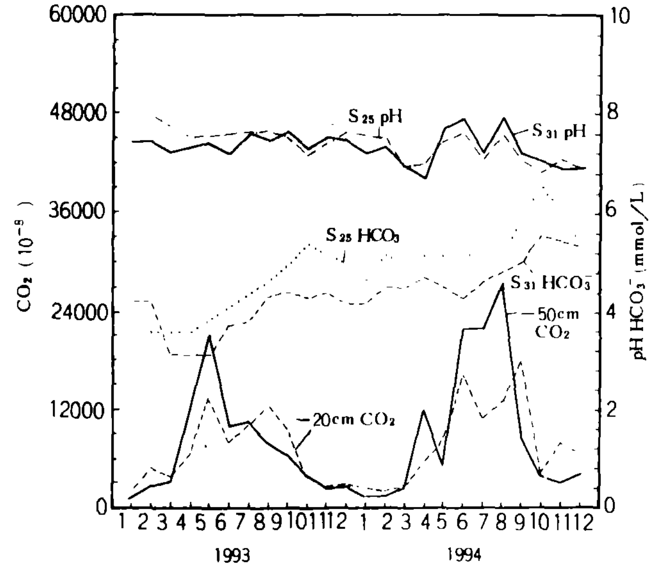

Fig. 3 The corresponding changes in soil CO_2, pH and HCO_3^- of water in two measured points

It can be seen from these results that there is a regularity for the change in the concentration of soil CO_2 gas.

(1) In the period from January to April and from September to December, the CO_2 concentration in 20 cm depth is less than that in 50 cm depth. It turns out contrary in the period from May to August of the same year, when a top value appears. The change in CO_2 concentration is related to the photosynthesis of vegetation and the distribution of precipitation. In the first four months of year, the vegetation is coming to grow. From May to August, it is growing very luxuriantly, whereas from September to December, it is beginning to turn yellow. Over 80 percent of precipitation occur in the period from May to August. Abundant rainfall is advantageous for vegetation to grow. So it's certain that the CO_2 concentration of soil A layer (20 cm deep) where roots grow well is higher than that of soil B layer (50 cm deep). In addition, we have found that the CO_2 coming from soil has a $\delta^{13}C$ value of -20.66 ‰, which is in the range from -18 ‰ to -28 ‰. The data indicate that the CO_2 belongs to biogenetic.

Tab. 1 Observation results

Date	Spring	T (℃)	pH	HCO_3^- (mmol/l)	Spring	T (℃)	pH	HCO_3^- (mmol/l)	$CO_2(10^{-6})$ at−20cm	$CO_2(10^{-6})$ at−50cm
19930112	S_{35}	—	—	—	S_{31}	18.60	—	4.20	1200	1800
19940121	S_{35}	11.20	7.54	4.60	S_{31}	19.20	7.19	4.17	1350	2300
19930216	S_{35}	19.20	7.94	3.56	S_{31}	19.70	7.42	4.20	2500	4700
19940217	S_{35}	15.50	7.49	5.13	S_{31}	19.60	7.32	4.50	1400	2050
19930317	S_{35}	—	—	—	S_{31}	19.20	7.20	3.14	3000	3800
19940309	S_{35}	17.20	6.92	4.92	S_{31}	19.70	6.92	4.49	2400	2500
19930420	S_{35}	18.40	7.48	3.56	S_{31}	19.20	7.29	3.10	11500	6500
19940411	S_{35}	18.60	6.96	5.13	S_{31}	19.30	6.69	4.70	12000	5500
19930520	S_{35}	—	—	—	S_{31}	19.20	7.38	3.14	21000	13500
19940519	S_{35}	18.00	7.42	5.13	S_{31}	18.00	7.71	4.50	5300	8000
19930622	S_{35}	—	—	—	S_{31}	18.00	7.17	3.70	10000	8000
19940623	S_{35}	18.20	7.60	5.03	S_{31}	19.20	7.90	4.28	22000	16000
19930706	S_{35}	—	—	—	S_{31}	18.50	7.59	3.79	21000	14500
19940707	S_{35}	18.80	7.07	5.45	S_{31}	19.80	7.22	4.60	22000	11000
19930802	S_{35}	19.30	7.64	4.60	S_{31}	19.50	7.48	4.06	10800	10500
19940813	S_{35}	18.60	7.58	5.13	S_{31}	19.20	7.93	4.81	27500	13000
19930921	S_{35}	21.00	7.48	4.92	S_{31}	19.90	7.64	4.38	6500	9550
19940913	S_{35}	22.40	7.06	5.99	S_{31}	20.00	7.19	5.02	9000	18000
19931021	S_{35}	21.40	7.13	5.35	S_{31}	19.80	7.28	4.28	3800	3600
19941021	S_{35}	20.00	6.82	6.52	S_{31}	19.90	7.04	5.56	3850	4000
19941124	S_{35}	19.50	7.08	6.09	S_{31}	20.00	6.90	5.45	3100	8000
19931228	S_{35}	17.30	7.60	5.02	S_{31}	19.60	7.42	4.17	2500	2700
19941222	S_{35}	17.90	6.99	6.63	S_{31}	19.70	6.91	5.35	4100	6800

(2) As the change in CO_2 concentration, the HCO_3^- of the two springs has an increasing tendency from 1993 to 1994. Generally, the HCO_3^- of epikarst spring is more than that of vadose spring. All these indicate the following two facts. (a) Karstification intensity changes along with seasons. Karstification will be strengthened in the seasons with plentiful rainfall, higher humidity and higher soil gaseous CO_2 concentration. On the contrary, karstification will be weakened. (b) Karstification has different intensities in different positions. There is a high HCO_3^- concentration in epikarst spring water (such as S_{25}) because the rain water which is low in pH value and of high aggressiveness comes into contact with carbonate rocks directly, or it flows in a short distance in soil. This kind of water is very favourable for carbonate rocks to dissolve. As to vadose spring, such as S_{31}, the circumstance is otherwise. Rainwater is regulated hydrochemically when it flows in epikarst. Part of CO_2 gas escapes and is consumed. The aggressive ability of water is weakened greatly, even tufa will deposit at some advantageous position, the HCO_3^- concentration of this kind of water is relatively low. Otherwise, as shown in Fig. 3, the increase in the HCO_3^- of the two springs may be attributable to the climatic change.

5 CONCLUSIONS

As one of the most active elements, CO_2 can vary along with seasons and is a motive force which drives other hydrochemical elements to change. Master these field research methods correctly to measure main hydrochemical elements synchronously is the basis for studying karstification.

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岩溶地球化学的野外研究方法及观测实例*

何师意

摘 要

本文阐述了捕捉一些碳、水、钙循环踪迹的野外岩溶地球化学研究方法。它们是以碳酸盐岩溶解的开放系统的三相平衡理论为依据的。述及的野外观测项目和内容包括：现场测定水的pH值的意义及实际操作步骤；现场测定岩溶水中重碳酸根离子含量及其岩溶意义；土壤CO_2气体浓度的测定；石灰岩溶蚀观测试验，包括试样的制作、安放及数据的获得；岩溶作用的环境因素的配套观测，主要包括地质、气候、水文及植被因素等。文章最后以桂林岩溶地质试验场的野外观测为实例，进一步阐明上述方法的具体应用，并对该区实际观测资料作了分析，得到的结论是：CO_2作为系统最活跃的因素之一，不仅本身具季节性变化，而且直接影响水的pH值及碳酸盐岩的溶解和沉淀过程。将各种指标配套研究发现：水的pH值与水中的HCO_3^-呈负相关；表层岩溶带泉水的硬度普遍高于包气带泉水的硬度；植被发育情况和年降雨量，在一定程度上可从水化学的年变化规律中反映出来。

关键词 岩溶地球化学 水化学 野外研究方法 观测实例

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