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阆中市思依镇水化学特征及其成因分析

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摘要:阆中市思依镇地区的水体主离子特征受该地区地质条件、地形地貌以及水文气象条件等因素影响,分析该地区的水化学离子特征对掌握地下水类型、成因以及水质情况具有重要作用。运用统计学、Piper 三线图、Gibbs 图、相关性分析、主离子比例关系和平衡分析等方法对阆中市思依镇河水和地下水水样中的主离子测试结果进行分析,表明河水和地下水水体阳离子中 Ca^2 和 Mg^2 占主要优势,阴离子中 HCO_3 占主要优势,水化学类型主要有 HCO_3 -Ca 型、 HCO_3 + SO_4 -Ca 型和 HCO_3 -Ca + Mg 型。水体离子主要受岩石风化作用过程中溶滤作用影响,并以方解石和白云石的溶解为主。

关键词:阆中市;地下水;水化学;主离子;化学成因

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Hydrochemical Characteristic and Reasoning Analysis in Siyi Town, Langzhong City

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Abstract: The characteristics of main ions in Siyi Town, Langzhong City was influenced by geological conditions, topography and hydrological and meteorological conditions and other factors. Here we analyzed the groundwater ions characteristics which will play an important role in mastering the groundwater types, chemical origin and water quality in this area. The testing data of main ions in river water and groundwater in this area were analyzed with statistics, Piper diagram, Gibbs figure, and correlation analysis, proportional relationship of main ions and equilibrium analysis method analysis. The results showed that Ca^{2+} and Mg^{2+} , and HCO_3^- dominant among cations and anions, respectively, and the hydrogeochemical types can be classified into HCO_3^- Ca type, HCO_3^- + SO_4^- Ca type and HCO_3^- Ca + Mg type. Main ions of all water are mainly affected by leaching effect in rock weathering process, which are dominantly dissolved from dolomite and calcite.

Key words: Langzhong City; groundwater; hydrochemistry; main ions; chemical origin

地下水的化学成分是水在循环过程中不断与周 围环境(大气、地表水、岩石)长期相互作用的结 果[1,2]. 地下水中的化学组分是地下水演化的直接 结果,可以帮助分析地下水的演变规律[3~5]. 研究 一个地区水体主离子特征,能够有效分析确定该区 水化学演化的控制因素,以及该区的水文地质及水 文地球化学发展历史. 影响一个地区的地下水的水 化学特征有众多因素,如气候、大气降雨、水文条 件、地质条件和人为因素等,其中起主导因素的是 地质因素. 朱秉启等[6]对塔克拉玛干沙漠南部地区 的河流以及沙区地下水进行分析,得出河水中溶解 物主要受岩石风化作用和蒸发结晶作用共同控制. 蒲焘等[7]对丽江盆地地表水和地下水的水化学成 分进行分析,得出水体无机离子主要来源于碳酸盐 的风化溶解,且其离子浓度受海拔影响较大,同时, 降雨对水体离子成分也有一定影响. 王鹏等[8] 通过 分析青藏高原地区淡水湖泊的水化学离子,得出该 区域水体的离子主要受硅酸盐岩的风化作用控制. 王晓曦等^[9]通过对滦河流域地下水以及河水进行研究,得出该地区地下水化学类型主要受溶滤作用控制,随着向下游含水介质颗粒变细,地下水径流变弱,蒸发作用、阳离子交替吸附作用逐渐增强,并最终代替溶滤作用.

思依镇地区的居民主要以浅表层地下水作为饮用水水源,由于地处农业区,地下水或多或少受到农业污染的影响.这一地区的水文地球化学特征还未有相关研究,本文利用水文地球化学基础理论与方法对思依镇地区浅层地下水以及河水水化学特征及其成因进行分析,以期为进一步研究该地区地下水

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水化学成分的影响、水质评价和是否需要重建水源 地提供基础信息.

1 研究区概况

研究区位于四川省阆中市思依镇的西边,距离阆中市约35 km(图1). 研究区属亚热带湿润季风气候,气候温和. 研究区年际年内降雨量分配不均,降雨主要集中在6~10月,年均降雨量1042.5 mm,年均蒸发量998.3 mm,平均相对湿度76. 研究区的主要河流桃花河、温家河大致呈南北走向,流经西河,最终注入嘉陵江.

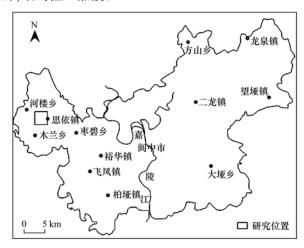


图 1 研究区地理位置

Fig. 1 Location of the study area

研究区属低山丘陵区, 地形大致呈"U"形分布——即东、西、南三方向上山体顶部到坡脚相对高差均在100 m以上, 中部和北部地势较低, 利于研究区的水体的汇集. 研究区最高地为西南部尖山子和东部棋盘山, 其海拔均高于700 m.

研究区地下水分为第四系孔隙水、红层砂-泥岩风化带孔隙水和砂岩-泥岩层间裂隙水.第四系孔隙水主要分布在研究区山体顶部、缓坡及各冲沟的第四系松散层覆盖物中;红层砂-泥岩风化带孔隙水主要分布在研究区山体砂岩、泥岩裸露风化带地区;红层砂-泥岩层间裂隙水是研究区地下水主要赋存形式,研究区含水层、隔水层相间存在,层间裂隙发育,为形成层间裂隙水提供有利条件,层间裂隙水以泉的形式出露地表.研究区地下水主要接受大气降雨补给,径流途径短,地下水水量呈现出季节性特点.

研究区地下水-地表水水力联系,表现在地下水 通过径流排泄于地表、地表水渗流补给地下水以及 地下水和河水之间的动态关系. 洪水期,部分降雨 经地表径流汇集河流,河水水位高于地下水位,河水 补给地下水;枯水期,降雨补给较少,地下水水位高 于河流水位,地下水补给河水.

2 研究方法

2.1 样品采集与测试

2013年12月,在阆中市思依镇进行河水和地下水水样采集,共采样53组,其中河水水样6组,浅层地下水47组.河水水样取自桃花河上中下游,地下水水样主要分布在研究区水系区域.取样工作由四川省核工业地质局二八二大队完成,采样时,在地形图上标出相应采样点的位置,河水水样编号H1~H6,地下水水样编号为1~47,采样点分布情况如图2所示.



图 2 采样点分布示意

Fig. 2 Distribution map of the water samples

样品水化学分析在四川省核工业辐射测试防护院进行. K^+ 、 Na^+ 采用原子吸收分光光度法测定; Ca^{2+} 、 Mg^{2+} 采用 EDTA 滴定法测定; Cl^- 采用硝酸盐滴定法; SO_4^{2-} 采用 EDTA-Ba 滴定法; HCO_3^- 采用盐酸滴定法.

2.2 数据分析方法

数据的统计处理及部分分析用 Microsoft Office 中的 Excel 电子表格软件完成,利用阴阳离子平衡 法检查样品数据的可靠性,并取电荷平衡误差 E < ±5%的水样数据为可靠数据.由计算结果显示,所有水样数据均为可靠.为了解研究区水化学特征及类型,绘制了 Piper 三线图,并对水化学参数进行 Spearman 相关性分析;为进一步研究该区水化学成因作了 Gibbs 图、离子比例相关性系数图,并进行水化学平衡分析.

3 结果与讨论

分别对河水和地下水水样数据各个指标做数理统计分析,由统计结果表 1 可知,研究区河水水样pH值的范围在 8.16~8.58,地下水水样pH值的范围在 7.47~8.52,整体上呈碱性. 河水水样中 TDS值在 183.73~415.13 $\text{mg} \cdot \text{L}^{-1}$,地下水水样中 TDS值的范围在 271.53~645.47 $\text{mg} \cdot \text{L}^{-1}$,河水和地下水 TDS的平均值均高于 300 $\text{mg} \cdot \text{L}^{-1}$,比一般大气降

水的矿化度(20~50 mg·L⁻¹)高,属于淡水.

河水和地下水水体中阳离子各组分含量整体为: $Ca^{2+}\gg Mg^{2+} > Na^{+}\gg K^{+}$,阴离子浓度表现为: $HCO_{3}^{-} > SO_{4}^{2-} > Cl^{-}$. 地下水阳离子平均值中, Ca^{2+} 含量占主要优势,是 Mg^{2+} 的 7. 54 倍,是 $Na^{+} + K^{+}$ 的 7. 14 倍;阴离子平均值中 HCO_{3}^{-} 占优势,分别为 SO_{4}^{2-} 和 Cl^{-} 的 4. 71 倍和 13. 13 倍.河水水样阳离子平均值中, Ca^{2+} 含量也占主要优势,分别是 Mg^{2+} 和 $Na^{+} + K^{+}$ 的 5. 84 倍和 5. 75 倍;阴离子平均值中 HCO_{3}^{-} 占优势,分别是 SO_{4}^{2-} 和 Cl^{-} 的 4. 43 倍和 11. 83 倍.

硬度($CaCO_3$) 的当量) 以钙镁的毫克当量总数乘以 50 计算, 地下水水样中硬度的范围在 120~272 $mg \cdot L^{-1}$, 平均值为 201 $mg \cdot L^{-1}$. 水的硬度类型划分:中软水为 75~150 $mg \cdot L^{-1}$, 微硬水为 150~300 $mg \cdot L^{-1}$, 地下水水样硬度超过 150 $mg \cdot L^{-1}$ 的水样占93.6%, 所以该区的地下水的硬度类型为微硬水.

表 1 水化学参数统计1)

Table 1	Statistics of h	vdrochemical	parameters of	groundwater	and river water
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分类	项目	pН	TDS	K +	Na +	Ca ^{2 +}	Mg^{2+}	Cl -	SO_4^2	HCO ₃
-	Min	7. 47	271. 53	0. 26	4. 70	65. 74	6. 66	1. 59	7. 70	108. 87
	Max	8. 52	645. 47	14. 2	69.60	193.72	26.00	85. 50	172. 90	580. 14
地下水	Mean	8. 16	468. 1	1.37	17. 03	131.48	17. 43	29.05	81.00	381. 51
	Std.	0. 27	88.31	2.49	12.43	29. 05	4. 12	19. 59	42. 26	87. 32
	Cv	0.03	0.18	1.36	0.61	0. 21	0. 22	0.63	0.50	0. 21
	Min	8. 16	183. 73	1. 13	5. 20	49. 47	6. 02	9. 33	3. 90	109. 12
	Max	8. 58	415. 13	4. 67	14.40	121.88	17. 86	29.00	151.00	388. 58
河水	Mean	8. 33	300. 28	2. 20	11.57	79. 19	13. 56	20. 21	53. 95	239. 19
	Std.	0.08	60. 26	0.48	2.37	16. 24	4. 11	6. 17	8. 65	62. 12
	Cv	0.01	0. 21	0. 22	0.20	0. 21	0.31	0. 28	0. 19	0. 26

¹⁾ Min 表示最小值; Max 表示最大值; Mean 表示均值; Std 表示标准偏差; Cv 表示变异系数; pH 无量纲,其余单位为 $mg \cdot L^{-1}$

3.1 水化学特征

3.1.1 水化学类型及其分布特征

研究区地下水水化学类型,按舒卡列夫分类方法,研究区地下水水化学类型整体上分为 HCO₃-Ca型、HCO₃-Ca型 和 HCO₃+SO₄-Ca型. HCO₃-Ca型广布研究区西部、北部、东北部以及南部天堡寨至白界山一带;HCO₃-Ca+Mg型分布在中东部至东南部绕棋盘山一带;HCO₃+SO₄-Ca型分布在西南尖山子省道公路陈家沟一带.

利用 Piper 三角图可以表明水体的主离子组成变化,体现水体化学特征. Piper 三线图以主要阳离子和阴离子的每毫升当量的百分数来表示^[10]. 根据研究区河水和地下水水化学数据,将河水和地下水水样绘制在 Piper 三线图中,如图 3.

由图 3 可以看出,河水水样中阳离子主要分布

在 Ca²⁺端,阴离子靠近于 HCO₃⁻端,分布较为集中. 地下水水样中阳离子也主要分布在 Ca²⁺端,阴离子主要靠近于 HCO₃⁻端,但分布较为分散,部分分布在 HCO₃⁻-SO₄²⁻线上,偏向 HCO₃⁻端。该地区地层中常见矿物有白云石、方解石等碳酸盐矿物分布,由此初步推测该区浅层地下水化学组分受碳酸盐溶滤作用控制.

3.1.2 水化学相关性分析

利用相关性分析,可以推测出水体各离子之间是否为相同来源. 研究区地下水-地表水水力联系紧密,将地下水和地表水水样合在一起进行相关性分析. 对所有水样的水化学参数进行 Spearson 相关系数计算,其计算结果如表 2. 从中可知, Ca^{2+} 与 K^+ 、 Ca^{2+} 与 HCO_3^- 、 Ca^{2+} 与 SO_4^{2-} 、 K^+ 与 SO_4^{2-} 、 Na^+ 与 HCO_3^- 相关性显著. Ca^{2+} 、 SO_4^{2-} 、 Na^+ 、

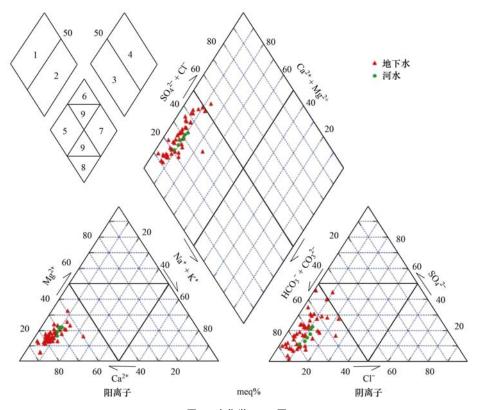


图 3 水化学 Piper 图

Fig. 3 Piper diagram of hydrochemical of groundwater and river water

 Mg^{2+} 与 TDS 相关性显著,其中 Ca^{2+} 与 TDS 相关性 系数达到 0.9. 此外,还有 Na^{+} 与 SO_4^{2-} 、 Na^{+} 与 Mg^{2+} 、 Ca^{2+} 与 Na^{+} 相关性较好.由于研究区地层中

矿物以方解石和白云石等矿物分布为主,据此,可以 推测水体的主要离子是由该地区的方解石、白云石 等碳酸盐经过风化溶解而来.

表 2 水化学参数相关系数矩阵1)

Table 2	Correlation	matrices	$of\ hydrochemical$	parameters

	K +	Na +	Ca ²⁺	Mg ^{2 +}	HCO ₃	Cl -	SO ₄ -	TDS
K +	1. 000 0							
Na +	0.0702	1.0000						
Ca ^{2 +}	-0.5005**	0. 388 0 * *	1.0000					
Mg^{2} +	-0.0705	0. 351 5 * *	-0.0270	1.0000				
HCO_3^-	0.047 5	0. 605 5 * *	0. 406 6 * *	0. 224 4	1.0000			
Cl -	-0.0663	0. 134 5	0. 246 3	0. 282 6 *	0.0886	1.0000		
SO_4^2	-0.4045**	0. 376 2 * *	0. 745 0 * *	0.0635	0. 197 9	-0.2696	1.0000	
TDS	-0.3715**	0. 567 1 * *	0. 926 7 * *	0. 622 11 * *	0. 514 8 * *	0. 437 1 * *	0. 650 9 * *	1. 000 0

1)*和**分别代表 0.05 和 0.01 显著水平

3.2 水化学成因分析

3.2.1 水化学类型形成作用讨论

将水样绘制在 Gibbs 图中,可以反映出研究区水化学类型的形成作用. Gibbs 根据世界河流、湖泊及主要海洋水分析,认为离子起源的自然控制因素分为岩石风化型、大气降雨控制型和蒸发-浓缩型^[11]. Gibbs 模型是分别以 $Na^+/(Na^+ + Ca^{2^+})$ 和 $Cl^-/(Cl^- + HCO_3^-)$ 为 X 轴, TDS 含量的对数为 Y 轴的两种关系图. 根据 Gibbs 图(图 4)的分布原

理可以知道,在图的右下角,即 $Na^+/(Na^+ + Ca^{2+})$ 比值或 $Cl^-/(Cl^- + HCO_3^-)$ 比值大于 0.5 且 TDS 含量较低时,反映该区域受大气降水影响明显;在图的中间靠左的位置,即 $Na^+/(Na^+ + Ca^{2+})$ 比值或 $Cl^-/(Cl^- + HCO_3^-)$ 比值小于 0.5 且 TDS 含量中等时,反映该区域受岩石组分对水体影响明显;在图的右上方,即 $Na^+/(Na^+ + Ca^{2+})$ 比值或 $Cl^-/(Cl^- + HCO_3^-)$ 比值较高(接近 1),且 TDS 含量较高时,反映出该区域水体特征受蒸发

结晶作用影响.

将研究区地下水和河水水样数据绘于 Gibbs 模型中,如图 4 所示. 由计算结果知道, TDS 含量对数在 $100 \sim 1~000$, $Na^+/(Na^+ + Ca^{2+})$ 的比值整体小于 0.3, $Cl^-/(Cl^- + HCO_3^-)$ 的比值整体小于 0.3. 研究

区所有水样落在 Gibbs 模型范围内,且主要分布在 Gibbs 模型的左端,且该地区年均降雨量与年均蒸 发量基本保持平衡,由此可知研究区水化学类型主 要受岩石风化作用控制,蒸发和沉淀作用微弱且远 离大气降雨.

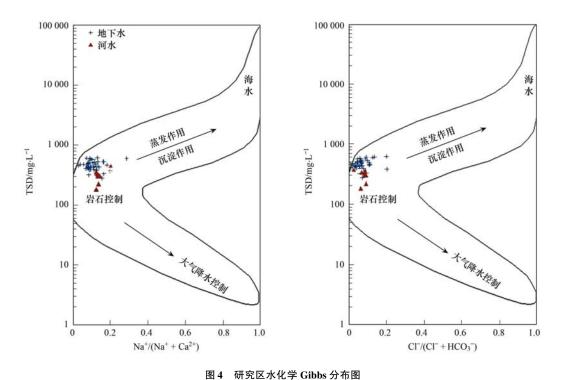


Fig. 4 Plot of the major ions within the Gibbs' model for water in study area

研究区存在的溶滤作用还可以用离子之间的比 值关系来反映. Cl^- 与 TDS 的比值如图 5(a) 所示, 河水中 Cl⁻/TDS 随 TDS 增长不变, 地下水中 Cl⁻/ TDS 随 TDS 变化主要表现在 TDS 增加,Cl⁻/TDS 值 不变或者 Cl-/TDS 值增加缓慢,表明地下水存在岩 盐溶解,受蒸发作用影响较小. 如图 5(b) 所示,由 $(K^+ + Na^+)$ 与 Cl^- 的比值关系图可以看出,地下水 大多数点位于 $(K^+ + Na^+)/Cl^- = 1$ 的附近,部分点分 布在 $(K^+ + Na^+)/Cl^- = 1$ 两边,表明该地区在发生岩 盐溶解的同时还发生着铝硅酸盐矿物等的溶解[9]. 研究区水中 Ca2+、Mg2+主要来自含钙和镁的碳酸盐 或铝硅酸盐的溶解,通过(Ca2+ + Mg2+)的当量浓度 与 $(HCO_3^- + SO_4^{2-})$ 当量浓度的比值关系,可推断其来 源[9,12,13],如图 5(c)所示,河水和地下水水样点主要 位于 $(Ca^{2+} + Mg^{2+})/(HCO_3^- + SO_4^{2-}) = 1$ 的附近,表 明该地区同时存在碳酸盐和铝硅酸盐矿物的溶解. $(SO_4^{2-} + Cl^-)$ 与 HCO_3^- 的关系图如图 5(d)所示,河 水水样点绝大多数位于 $(SO_4^2 + Cl^-)/HCO_3^- = 1$ 线 以下,且偏离较远,极少部分点位于该线的上方,暗示

碳酸盐岩为主要来源,蒸发盐岩的溶解微弱. 该地区地下水样中($Ca^{2+} + Mg^{2+}$)/($K^+ + Na^+$)的平均值为12.8,是世界平均值(2.2)的5.8倍,研究区河水水样中($Ca^{2+} + Mg^{2+}$)/($K^+ + Na^+$)的平均值为8.8,典型的以碳酸盐岩风化为主的印度河流域($Ca^{2+} + Mg^{2+}$)/($K^+ + Na^+$)为6.0^[9,14,15],因此,研究区地下水和河水($Ca^{2+} + Mg^{2+}$)与($K^+ + Na^+$)的比值均高于印度河流域的比值.

综上所述,阆中市思依镇水化学类型形成的主要作用是碳酸盐和铝硅酸盐矿物溶解作用,且碳酸盐的溶解作用明显,该地区属于碳酸盐岩地区.

3.2.2 水化学平衡分析

(1)CO, 分压

研究区属于碳酸盐岩地区,地下水化学类型主要受方解石和白云石两种矿物控制,系统中的 CO₂ 控制了这个两种矿物的溶解和沉淀. 该系统中存在的碳酸平衡反应:

$$\mathrm{CO_2} + \mathrm{H_2O} = \mathrm{H_2CO_3}$$
,
 $\left[\mathrm{H_2CO_3} \right] = K_\mathrm{H} \times p\mathrm{CO_2} \quad (K_\mathrm{H} \ \mathrm{\Delta} \ \mathrm{Henry} \ \mathrm{\Box{\Box{\Box{\Box{\tiny T}}}}} \ \mathrm{\Box{\Box{\Box{\tiny T}}}} \ \mathrm{\Box{\Box{\Box{\tiny T}}}} \ \mathrm{\Box{\Box{\Box{\tiny T}}} \ \mathrm{\Box{\Box{\Box{\tiny T}}}} \ \mathrm{\Box{\Box{\Box{\tiny T}}}} \ \mathrm{\Box{\Box{\Box{\tiny T}}} \ \mathrm{\Box{\Box{\Box{\tiny T}}}} \ \mathrm{\Box{\Box{\Box{\tiny T}}} \ \mathrm{\Box{\Box{\Box{\tiny T}}}} \ \mathrm{\Box{\Box{\Box{\tiny T}}}} \ \mathrm{\Box{\Box{\Box{\tiny T}}} \ \mathrm{\Box{\Box{\tiny T}}} \ \mathrm{\Box{\Box{\tiny T}} \ \mathrm{\Box{\Box{\tiny T}}} \ \mathrm{\Box{\tiny T}} \ \mathrm{\$

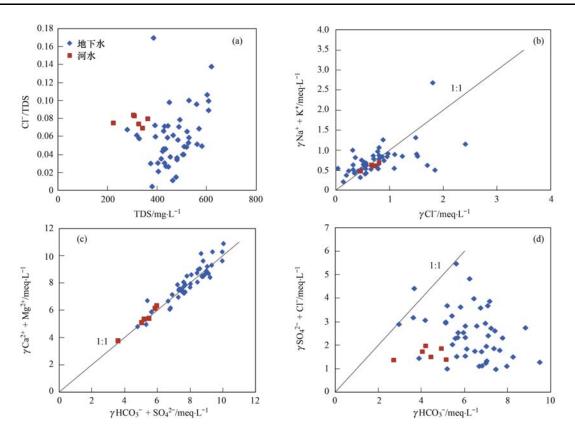


图 5 研究区水化学主离子比例关系图

Fig. 5 Relationship between the rate of the selected ions of water samples in study area

$$H_{2}CO_{3} = H^{+} + HCO_{3}^{-}, \quad K_{1} = \frac{[H^{+}][HCO_{3}^{-}]}{[H_{2}CO_{3}]},$$

$$[H_{2}CO_{3}] = \frac{[H^{+}][HCO_{3}^{-}]}{[K_{1}]}$$
(2)
$$HCO_{3}^{-} = H^{+} + CO_{3}^{2-}, \quad K_{2} = \frac{[H^{+}][CO_{3}^{2-}]}{[HCO_{3}^{-}]},$$

$$[HCO_{3}^{-}] = \frac{[H^{+}][CO_{3}^{2-}]}{[K_{2}]}$$
(3)

存在的方解石溶解平衡有:

$$CaCO_3 = Ca^{2+} + CO_3^{2-}, K_3 = [Ca^{2+}][CO_3^{2-}],$$

$$\left[\operatorname{CO}_{3}^{2-}\right] = \frac{K_{3}}{\left[\operatorname{Ca}^{2+}\right]} \tag{4}$$

整理所有式子,有:

$$pCO_{2} = \frac{K_{2} \times [Ca^{2+}][HCO_{3}^{-}]^{2}}{K_{H} \times K_{1} \times K_{3}}$$
 (5)

 Ca^{2+} 和 HCO_3^- 以 $mol \cdot L^{-1}$ 代人公式(5),求出研究区地下水各个水样 CO_2 分压,其结果统计如表 3 所示. 大气中的 pCO_2 为 $10^{-3.5} \times 100$ kPa,表 3 中 pCO_2 在($10^{-1} \sim 10^{-2}$) × 100 kPa 之间,均高于大气中的 pCO_3 值,地下水系统属于开系统.

表 3 地下水 pCO_2 分压计算结果 $^{1)} \times 100/kPa$

			Table 3 Calculat	tion results	of pCO_2 of groundy	vater × 100	/kPa		
编号	pCO ₂ 分压	编号	pCO ₂ 分压	编号	pCO ₂ 分压	编号	pCO_2 分压	编号	pCO ₂ 分压
1	0. 128	11	0. 280	21	0. 082	31	0.069	41	0.066
2	0.082	12	0. 085	22	0. 126	32	0. 183	42	0. 085
3	0. 179	13	0.097	23	0. 146	33	0. 140	43	0.012
4	0. 107	14	0.079	24	0. 036	34	0. 109	44	0. 138
5	0.087	15	0. 147	25	0.053	35	0.069	45	0. 134
6	0.099	16	0. 158	26	0. 119	36	0.067	46	0.019
7	0. 137	17	0. 206	27	0. 121	37	0.075	47	0.026
8	0. 127	18	0.060	28	0. 143	38	0. 124		
9	0. 338	19	0. 114	29	0. 146	39	0. 055		
10	0. 111	20	0. 102	30	0.052	40	0.020		

¹⁾ $\lg K_{\rm H} = -1.466^{\left[16,17\right]}$, $\lg K_{1} = -6.351^{\left[16,17\right]}$, $\lg K_{2} = -10.33^{\left[16,18\right]}$, $\lg K_{3} = -8.475^{\left[16,19\right]}$

(2)水化学碳酸平衡

水体离子之间以配位键的方式结合在一起的复杂缔合物称之为络合物,并影响水体的溶解组分^[16,20,21],因此,在计算地下水中溶解方解石和白云石的饱和指数时,需要考虑地下水中络合物.随着文献[22~24]对水体中络合物深入的研究,在饱和指数计算模型中,是否考虑络合物的存在对饱和指数的计算影响较大.

地下水中常量组分的主要离子对有以下 10 种: $CaSO_4^0$ 、 $MgSO_4^0$ 、 $NaSO_4^-$ 、 KSO_4^- 、 $CaHCO_3^+$ 、 $MgHCO_3^+$ 、 $NaHCO_3^0$ 、 $CaCO_3^0$ 、 $MgCO_3^0$ 和 $NaCO_3^-$. 根据饱和指数计算公式 SI = IAP/K,利用 Excel 先求得离子强度以及活度系数,然后计算各络合物的含量,将剩下的游离离子再次代入以上计算,进行迭代. 由于以 mSO_4^{2-} 前后两次计算值之差小于0.000 1 $mmol \cdot L^{-1}$ 来控制计算的迭代次数的稳定性差[25],以离子强度 I 的前后计算差值比 mSO_4^{2-} 更具稳定性,

本次采取离子强度 I 前后计算误差区间 ε 为 0. 01 ~ 0. 02, 取第 3 次迭代计算结果, 如表 4.

由表 4 可知,研究区的地下水水样中方解石饱和指数大部分大于 1,部分白云石饱和指数大于 1,处于饱和状态,而 1、2、5、6、11、46 和 47 号水样中方解石的饱和指数小于 1,表明水样中方解石处于非饱和状态. 其中 46 和 47 方解石的饱和指数较小,处于非饱和状态的主要原因是,该两处的岩石风化程度可能偏低,所受溶滤作用较弱,因此水中溶解的方解石较少. 1、2、5 和 6 属于排泄区,地下水以泉的形式出露地表,溶解于水中的CO₂ 逸出,pCO₂ 分压减小,部分络合物沉淀使得这些水体中离子含量减少,因此,饱和指数有所降低. 河水水样中 H1~H3 方解石溶解饱和,H1 的白云石溶解饱和. 且由数据可知,河水中方解石和白云石饱和指数随河流上中下游的变化呈递增变化.

表 4 方解石和白云石饱和指数计算结果1)

境

科

编号	SI_C	SI_D	编号	SI_C	SI_D	编号	SI_C	SI_D	编号	SI_C	SI _D
1	0. 32	0.04	15	1. 77	0. 74	29	2. 51	1.14	43	1. 25	0. 66
2	0.77	0. 20	16	2. 18	1.42	30	1.81	1.06	44	2. 85	2. 53
3	1. 17	0.33	17	2.44	1. 25	31	1. 57	0.73	45	2. 93	2. 08
4	1. 13	0.43	18	1. 97	1. 33	32	1. 26	0.33	46	0.31	0.07
5	0.30	0.03	19	1. 55	0.83	33	4. 02	4.60	47	0. 22	0.02
6	0.66	0.10	20	1.61	0.71	34	1.82	0.88	H1	1.61	1.08
7	1. 39	0. 67	21	1. 26	0.66	35	1. 43	0.60	H2	1. 26	0.68
8	1.38	0.18	22	1. 12	0.40	36	2. 78	2.79	НЗ	1. 10	0.45
9	1. 19	0.03	23	1. 23	0.44	37	2. 59	1.42	H4	0.96	0.40
10	1.65	1. 21	24	1. 14	0. 52	38	3.47	2.87	H5	0. 98	0.43
11	0.74	0.11	25	1. 26	0.70	39	1.60	1. 23	Н6	0.81	0. 21
12	1. 25	0.51	26	1. 12	0. 29	40	1. 12	0.70			
13	2.06	1. 10	27	2. 13	1. 08	41	1. 43	0.41			

Table 4 Saturation index of calcite and dolomite

1)1~47 为地下水,H1~H6 为河水; SIc 为方解石饱和指数,SIp 为自云石饱和指数

4 结论

- (1)总体上,研究区水体中 Ca^{2+} 、 Mg^{2+} 和 HCO_3^- 占主要优势. 地下水水化学类型分为 HCO_3 -Ca 型、 HCO_3 +SO₄-Ca 型和 HCO_3 -Ca + Mg 型,以 HCO_3 -Ca 型为主. 硬度以 $CaCO_3$ 的当量计算,属微硬水.
- (2)研究区水样化学组分全部落在 Gibbs 图的中间靠左端,该区的水化学组分主要受岩石风化作用影响,蒸发和沉淀作用微弱.
- (3)研究区水体水化学类型主要受溶滤作用控制.据方解石和白云石饱和指数计算结果,研究区

地下水中 Ca^{2+} 、 Mg^{2+} 主要来自方解石和白云石的溶解. 研究区地下水系统属于开系统,水体中 HCO_3^- 有两种来源:—是大气中的 CO_2 与地下水溶解后离解形成; 二是方解石和白云石遇水溶解形成. 同时,研究区还存在铝硅酸盐矿物(石英、长石、云母等)的溶解作用.

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