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海相钾盐矿床溶滤卤水找钾指标体系：以川东北天星桥构造寒武系深部地下卤水为例

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摘 要：长期工作成果显示我国现阶段常用的找钾指标Br×10³/Cl值偏低．创新性地应用"以古验古"的溶滤实验与地质统计法厘清了海相蒸发盐盆地找钾指标体系，充分考虑了不同地质年代海水成分的变化，也可克服"将今论古"应用于现代海水在等温等压条件下实验数据的不足．通过对世界上典型钾盐矿床的石盐、含钾石盐及钾盐（含光卤石）进行溶滤实验，并结合前人海水及海相卤水的蒸发实验成果，总结了海相钾盐矿床溶滤卤水找钾指标体系：Br×10³/Cl、K×10³/Cl、K/Br重量比及nNa/nCl、nMg/nCl摩尔浓度比等．以天星桥构造寒武系深部地下卤水为例，分析其Br×10³/Cl、K×10³/Cl、K/Br重量比及nNa/nCl、nMg/nCl等找钾指标与δD、δ¹⁸O特征，认为天星桥构造寒武系深部地下卤水的水化学特征与溶滤卤水一致，与沉积卤水有较大差异，其δD、δ¹⁸O投点均靠近大气降水线．因此，综合分析认为该区卤水属于溶滤卤水，且有溶解含钾石盐甚至是溶解钾盐的可能性．该成果对评价研究区地下卤水钾资源具有重要意义，也为在该区寻找寒武纪固体钾盐矿提供了新依据．

关键词：深部地下卤水；卤水成因；找钾指标体系；川东北；天星桥构造；寒武系．

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Index System for Potassium Prospecting in Marine Potash Deposits: A Case Study of Cambrian Deep Brine from Tianxingqiao Structure of Northeast Sichuan in China

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Abstract: Through summary of long-term work, it is found that the value of Br×10^3/Cl, which is commonly used, is low. In this paper, it innovatively clarifies the index system for potassium prospecting of marine evaporative basin by using the "ancient test" leaching experiment and geological statistics method. This method fully considers the changes of seawater composition in different geological years and can also overcome the insufficiency of data for applying modern seawater under isothermal and pressure conditions. Through the leaching experiment of rock salt, potassium-bearing salt and potassium salt (including carnallite) of the typical potash deposits in the world, and combining the previous evaporation experiment results of sea water and marine brine, the index system for potassium prospecting in mineral deposit: Br×10^3/Cl, K×10^3/Cl, K/Br, *n*Na/*n*Cl, *n*Mg/*n*Cl, is summarized. This study aims to trace the origin of the brine which is Cambrian deep brine from Tianxingqiao structure of Northeast Sichuan Basin by analyzing its hydrochemical characteristics (weight ratios of Br×10^3/Cl, K×10^3/Cl and K/Br, and molar ratios of *n*Na/*n*Cl and *n*Mg/*n*Cl). The results show that the hydrochemical characteristics and δD and δ^{18}O values of the brine from Tianxingqiao are similar to those of the brine from dissolution and that of the salt precipitates, but have distinct difference from that of the primary brine. Therefore, it is believed the formation brine from Tianxingqiao is sourced from meteoric water and the brine salinity come from saliferous strata, which might come from the dissolution of halite beds or even the sylvinite beds. This finding is in contrast to the previous studies which held that the brine is primary brine. This study provides new and important information for searching potash deposits in this area.

Key words: deep brine; brine origin; index system for potassium prospecting; Northeast Sichuan Basin; Tianxingqiao structure; Cambrian.

0　引言

盐类沉积周围多见三种成因卤水:(1)由母卤或沉积卤水形成(原生沉积水)(王东升,1989;周训,1993);(2)由溶解含盐矿层形成(溶滤卤水)(王东升,1989;单慧媚等,2013;周训等,2014);(3)混合变质型或深源补给型卤水(汪蕴璞,1984;黄思静和曾允孚,1997;林耀庭等,1997).不同类型卤水的离子组成存在很大差异,找钾指标也大不相同,所以在运用水化学找钾工作中首要任务就是区分卤水成因.目前常用的指示溶滤卤水成因的水化学指标为Br×10^3/Cl、K×10^3/Cl与K×10^3/∑盐系数等.目前常用的溶滤石盐、含钾石盐和钾盐的溶滤卤水Br×10^3/Cl指标多沿用前人的成果,分别为0.1~0.3、0.3~0.5和>0.5(石油化学工业部化学矿山局,1977;云南省地质局第十六地质队,1978),在四川盆地、江汉盆地等岩盐钻孔资料显示与实际有一定的差距,上述指标并未达到钾盐沉积阶段.因此,目前的找钾指标Br×10^3/Cl值偏低.

本文通过模拟钾盐矿等在天然环境下的溶解,对世界典型海相钾盐矿床的石盐、含钾石盐及钾盐(含光卤石)等进行溶滤分析,总结了适合于海相钾盐溶滤卤水矿床的找钾指标体系:Br×10^3/Cl、K×10^3/Cl、K/Br重量比及*n*Na/*n*Cl、*n*Mg/*n*Cl摩尔浓度比等,并以天星桥构造寒武系深部地下卤水为例研究其卤水成因,为寒武系找钾工作和钾等资源的综合利用提供科学依据.

1　区域地质背景

四川盆地卤水资源丰富,分布广泛,矿化度高,含有较高的钾、锂、溴、硼等资源,具有较高的利用价值.主要含卤层有埃迪卡拉系、寒武系及三叠系(林耀庭,2009;王淑丽和郑绵平,2014).四川盆地不同含盐次盆地及不同含水层的卤水成因不同,前人已做过较多研究(王东升,1988;Zhou and Li,1992;林耀庭和熊淑君,1996;林耀庭等,1997;Zhou *et al.*,1997;李亚文等,1998;Yan *et al.*,2013).如川中武胜县龙女寺构造三叠系地下卤水主要有两种成因:一种是碎屑岩储卤层的Cl-Na-Ca型卤水,其成因是以陆相为主的同生沉积水;另一种是碳酸盐岩储卤层的Cl-Na型卤水,其来源于海相同生沉积残余卤水(周训,1993).川东北巫溪县大宁河三叠系盐泉水为大气降水溶解含盐地层的溶滤卤水(周训等,2014).关于寒武系深部地下卤水的研究相对较少,尤其是天星桥构造地下卤水成因问题未见报道,前人仅因其矿化度、K^+、Br^-及Br×10^3/Cl偏高等将其定义为沉积卤水(原卤),没有详细论证卤水的成因类型.因此,结合当前我国多个盐盆地的高品质卤水、钾盐短缺形势,有必要对卤水成因及钾盐找矿前景进行重新论证.

川东北地区寒武系发育,沉积厚度较大,岩性以白云岩为主夹膏盐岩、局部见砂岩夹膏质白云岩,含膏盐岩层位主要是中寒武统覃家庙组.本区共钻遇膏盐岩钻井8口,分别为建深1井、利1井、鱼

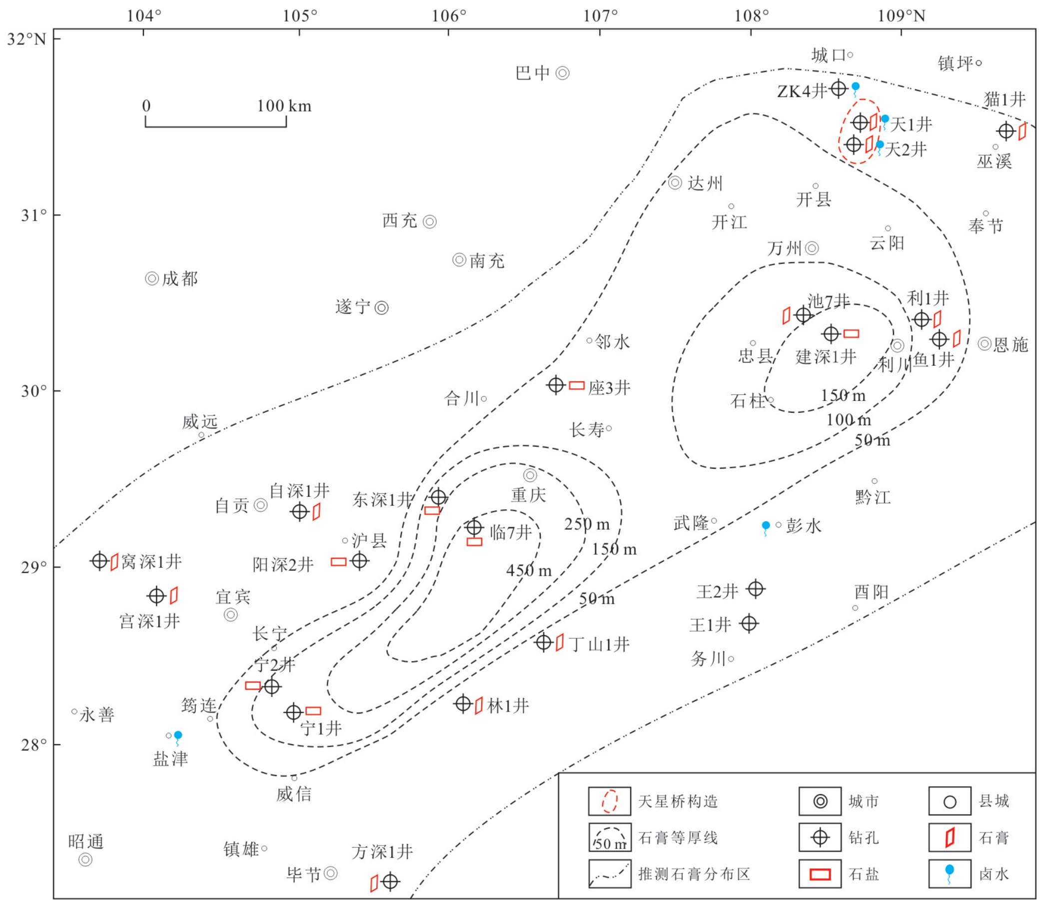

图1　四川盆地寒武系膏盐岩及卤水钻孔分布

Fig.1　Distribution of wells encountering Cambrian gypsum and salt rock and brine in Sichuan Basin

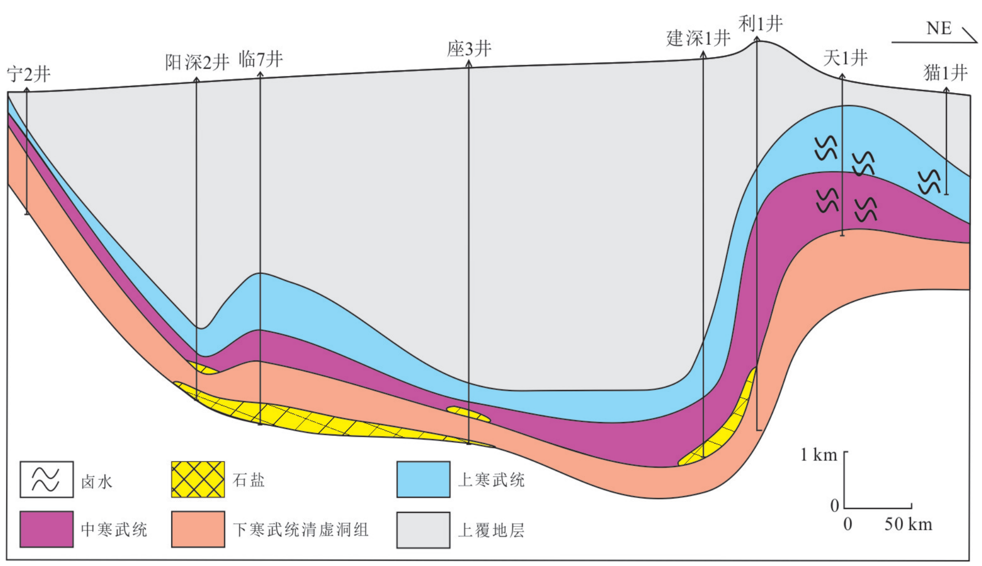

图2　四川盆地寒武系主要含盐层位剖面示意图

Fig. 2　Diagrammatic cross-section of main Cambrian salt-bearing strata in Sichuan Basin

1井、池7井、五科1井、天1井、天2井与猫1井，在城口明通镇(ZK1-4井)、巫溪田坝镇(天1井、天2井)、忠县(猫1井)及彭水地区(老郁井)均发现高矿化度卤水(图1，图2).巫溪县天星桥构造位于四川盆地东北缘，古生界十分发育，为一套厚2 000余米的泥岩和碳酸盐岩交互组成的海相地层.天星桥构造是

表1 世界主要海相钾盐矿床石盐、含钾石盐与钾石盐(含光卤石)溶滤分析结果

Table 1 Chemical compositions of halite, sylvinite and sylvite in marine potassium deposit of the world

地点	样品号	岩性	矿化度 (g/L)	K^+ (g/L)	Na^+ (g/L)	Ca^{2+} (g/L)	Mg^{2+} (g/L)	Cl^- (g/L)	SO_4^{2-} (g/L)	Br^- (mg/L)	Li^+ (mg/L)	B_2O_3 (mg/L)	Br×10^3/Cl	K×10^3/Cl	K×10^3/盐	K/Br	nNa/nCl	nMg/nCl
中国	my6#-12	石盐	48.5	0.14	18.6	0.07	<0.01	29.7	0.16	22.9	<0.1	6.92	0.77	4.71	2.89	6.11	0.97	-
中国	my6#-13	含钾石盐	59.8	0.61	22.9	0.01	<0.01	36.2	<0.03	37.3	<0.1	5.47	0.59	16.85	10.21	28.50	0.98	-
中国	my6#-5	钾石盐(含光卤石)	44.3	6.50	10.2	0.05	1.41	27.4	0.04	21.4	<0.1	4.32	3.60	237.20	146.70	65.92	0.57	0.076
加拿大	jnd-2	含钾石盐	48.4	0.87	16.4	0.55	0.02	27.4	0.84	9.9	<0.1	9.88	0.36	31.75	17.99	88.24	0.92	0.001
加拿大	jnd-1	含钾石盐	58.6	1.68	22.0	0.13	0.01	34.8	0.30	16.2	<0.1	7.67	0.47	48.28	28.67	103.70	0.98	0.000
加拿大	jnd-3	钾石盐	57.7	9.20	13.5	0.18	0.02	31.0	0.40	31.2	<0.1	9.59	1.01	296.77	159.50	294.87	0.67	0.001
老挝	lw-67	石盐	62.4	0.05	23.2	0.08	0.02	35.9	0.18	25.1	<0.1	11.0	0.70	1.39	0.80	1.99	1.00	0.001
老挝	lw-71	钾盐(含光卤石)	46.8	3.68	11.8	0.05	1.86	28.0	0.05	128.0	<0.1	8.87	4.57	131.43	78.64	28.75	0.65	0.098
老挝	lw-79	钾盐(含光卤石)	49.7	7.91	9.7	0.03	2.03	28.8	<0.03	162.0	<0.1	14.7	5.63	274.65	159.12	48.83	0.52	0.104
德国	K7	石盐	65.5	0.08	23.0	0.02	0.01	36.1	0.03	21.8	<0.1	5.22	0.60	2.08	1.15	3.44	0.98	0.000
德国	K4	含钾石盐	63.2	1.05	21.4	0.23	0.29	34.2	1.63	28.6	<0.1	4.93	0.84	30.70	16.62	36.71	0.97	0.013
德国	K9	钾石盐	46.3	15.30	5.3	1.02	0.01	24.5	2.34	178.0	0.11	3.98	7.27	624.4	330.40	85.96	0.33	0.001

呈北西西向延伸的高陡背斜，长113 km、宽5.5 km，构造高点出露上寒武统，由高孔隙度的含膏盐碳酸盐岩地层组成，富含高矿化度的地下卤水．天星桥构造目前共有两口井钻遇寒武系卤水：天1井与天2井．天1井井深3 094 m，166.5～2 250 m共有6个储卤层，总厚415.1 m，主要产卤层为第五、第六层，井深分别为1 790～1 839 m、2 250～2 287 m. 天2井井深2 538 m，852～2 275 m有4个储卤层，主要产卤层为第二、第四层，井深分别为1 700～1 824 m、2 275～2 395 m. 据原地矿部第二地质大队估算，卤水资源量为(6 000～7 000)×10^4 m^3(四川矿产储量委员会办公室，1992. 巫溪县天星桥构造寒武系卤水资源论证报告). 川东北天星桥构造寒武系深部地下卤水矿化度较高，其K^+、Br^-含量最高分别可达4.6 g/L和886 mg/L(埋深1 000 m以下的卤水矿化度高，其各离子组分也相对较高)，可进行综合开发利用(王淑丽等，2012；Wang *et al.*，2013).

2 采样与测试方法

2.1 卤水采样

2012年8月通过重新打开天2井密封的井口对其取样．经测量天2井内卤水液面在井口以下150 m左右，使用定深取样器对天2井内深度160～360 m(套管下至400 m)采样4件(表1中13～16号样品，取样深度分别为160 m、200 m、260 m和360 m)，先使用取出的卤水对样品瓶反复清洗3次，然后将卤水装满样品瓶(容量为500 mL)，密封保存放于室内阴凉处，并尽快寄回实验室保存．取样时记录气温、水温、盐度与密度等信息并贴于样品瓶，取样时气温在38 ℃左右，水温基本稳定在21 ℃，卤水盐度与密度作为实验室分析矿化度的辅助信息与分析结果一致，本文不再列具体数值．

2.2 测试方法

针对目前划分海相溶滤卤水与沉积卤水的常用系数存在一定差异的问题，笔者专门选取了世界典型海相沉积钾盐矿床的石盐、含钾石盐与钾石盐(含光卤石)等共计12个样品进行溶滤实验(表1)，与前人蒸发实验对比研究天星桥构造地下卤水成因．样品选自德国蔡希斯坦钾盐矿床、加拿大萨斯喀彻温钾盐矿床、老挝万象钾盐矿床、中国云南勐野井钾盐矿床．将样品溶于蒸馏水中，溶解至矿化度为60 g/L左右，分取部分液体酸化稀释至一定倍数后进行检测．该分析在中国地质科学院国家地质实验测试中心完成．Ca^{2+}、K^+、Mg^{2+}、Na^+、Li^+、SO_4^{2-}、Br^-、B_2O_3由全谱直读光谱仪(ICP-AES)电感耦合等离子体原子发射光谱法分析，型号是IRIS，由美国TJA公司制造；取pH<2的硝酸酸化水样，

表2 天星桥构造寒武系深部地下卤水化学组成

Table 2 Chemical compositions of Cambrian brine of Well Tian1 and Well Tian2

井名	序号	采样时间	矿化度(g/L)	采样层位或深度(m)	pH	离子含量(mg/L)								重量比				摩尔浓度比		数据来源
						K^+	Na^+	Ca^{2+}	Mg^{2+}	Cl^-	SO_4^{2-}	Br^-	B_2O_3	Br×10^3/Cl	K×10^3/Cl	K×10^3/盐	K/Br	nNa/nCl	nMg/nCl	
天1井	1	1990-11	281.22	$\in_2$	6.91	3 100	94 120	9 813	1 692	171 765	583	573.12	215.83	3.34	18.05	11.02	5.41	0.85	0.015	1972-1993年生产分析数据
	2	1993-05	285.67	$\in_2$	/	3 550	97 700	8 310	1 360	171 200	2 320	465.00	486.56	2.72	20.74	12.43	7.63	0.88	0.012	
	3	1987-05	134.22	$\in_3$	7.83	684	48 612	2 076	521	76 630	5 455	75.62	100.99	0.99	8.93	5.10	9.05	0.98	0.010	
	4	1972-10	220.36	/	/	2 599	72 112	5 865	1 082	136 659	1 310	334.67	/	2.45	19.01	11.79	7.76	0.81	0.012	
	5	1987-08	134.50	/	7.39	669	48 659	2 086	531	76 726	5 415	75.58	92.38	0.99	8.72	4.97	8.85	0.98	0.010	
	6	1988-05	142.31	/	7.32	707	51 626	2 183	493	81 481	5 462	81.91	92.82	1.01	8.67	4.96	8.62	0.98	0.009	
	7	1988-12	119.26	$\in_3$	8.30	636	43 371	2 044	481	72 109	419	65.66	95.73	0.91	8.83	5.34	9.69	0.93	0.010	
天2井	8	1972-10	293.02	/	/	4 151	96 002	9 434	1541	179 830	877	532.81	/	2.96	23.08	14.17	7.79	0.82	0.013	
	9	1993-05	218.80	/	/	2 000	78 830	3 860	640	129 700	3 150	211.00	327.05	1.63	15.42	9.14	9.48	0.94	0.007	
	10	1990-10	234.29	$\in_3$	7.42	1 850	83 748	4 658	863	140 261	2 374	250.63	139.65	1.79	13.19	7.90	7.38	0.92	0.009	
	11	1989-07	261.92	/	5.80	2 375	92 826	5 678	1 175	157 970	1 290	315.00	327.05	1.99	15.03	9.07	7.54	0.91	0.011	
	12	1988-12	317.20	/	5.70	4 578	105 210	10 655	1 847	189 215	3 948	885.94	226.26	4.68	24.19	14.43	5.17	0.86	0.014	
	13	2012-08	119.66	160	/	1 134	41 848	2 246	345	71 699	2 173	120.00	93.14	1.67	15.82	9.48	9.45	0.90	0.007	本文
	14	2012-08	177.05	200	/	1 678	61 487	3 141	570	106 629	3 268	120.00	159.12	1.13	15.73	9.47	13.98	0.89	0.008	
	15	2012-08	184.88	260	/	1 734	66 931	3 574	608	108 468	3 309	88.00	170.76	0.81	15.99	9.38	19.71	0.95	0.008	
	16	2012-08	167.11	360	/	1 549	58 846	3 615	557	99 276	3 029	80.00	159.12	0.81	15.61	9.27	19.37	0.91	0.008	

注:"/"表示未分析该项;卤水矿化度随埋藏深度的加深逐渐增大.本文采集样品为井中的混合水,只能代表采样时水在井中的位置.

表3 川东北寒武系深部地下卤水盐泉氢氧同位素组成

Table 3 Isotopic analysis of subsurface brine and salt spring in Northeast Sichuan Basin

序号	采样时间	样品名称	出露方式	含卤层位	δD (H_2O) [‰ vs. SMOW]	$\delta^{18}O$ (H_2O) [‰ vs. SMOW]
1	2012-08	天2井	地下卤水	寒武系	−81.8	−11.7
2	2012-08	天2井	地下卤水	寒武系	−92.9	−14.3
3	2012-08	天2井	地下卤水	寒武系	−93.5	−12.0
4	2012-08	天2井	地下卤水	寒武系	−97.3	−14.8
5	2012-03	ZK_4-1	盐泉	寒武系	−84.9	−13.2
6	2012-08	ZK_4-2	盐泉	寒武系	−87.4	−13.9

使用电感耦合等离子光谱仪测定,对试样在电感耦合等离子体焰炬中受到高温激发所发射出的特征谱线进行定量分析,分析精度<±5%.Cl^-由银量滴定法测定,吸取试样于三角瓶中,加入铬酸钾溶液10滴,在不断振荡下慢慢滴入硝酸银标准溶液至出现稳定的淡桔黄色即为终点,精度<±5%.

本次共收集1972−1993年生产分析数据12件(表2中1~12号样品),13~16号样品是笔者于2012年8月对天2井重新开井取水的分析数据,分析方法同上.

本文共采集川东北地区寒武系深部地下卤水、寒武系出露盐泉水、三叠系石盐溶解卤水和三叠系地表盐泉水等6件卤水样品(表3),分析川东北地区卤水氢氧同位素组成,用于讨论与验证天星桥构造地下卤水成因.其中1~4样品是2012年所取的巫溪县田坝镇天2井寒武系深部地下卤水;5~6号样品为城口县明通镇寒武系出露盐泉水.测试方法采用高纯氦气(99.999%)对Flash EA元素分析仪进行冲洗,排除空气,以降低H_2及CO本底.当Flash EA元素分析仪的炉温升高到1 380 ℃、本底降到50 mV以下时,开始样品测试.水在装有玻璃碳的陶瓷管里与过量的C发生还原反应,生成供测试用

的H_2及CO气体；H_2及CO在高纯氦气流的带动下，经过色谱柱分离后分别进入质谱MAT253进行分析．测量结果以SMOW为标准，记为δD_{V-SMOW}及$\delta^{18}O_{V-SMOW}$，分析精度分别优于±1‰及±0.2‰．

3　结果与讨论

3.1　本次溶滤实验获得的指标体系

现阶段中国常用于判别溶滤卤水的$Br\times10^3/Cl$值为：溶滤石盐一般为0.1～0.4，溶滤含钾石盐为0.4～0.5，溶滤钾盐时一般大于0.5（林传律，1994；林耀庭，1994，2009；张兆广，2009）；沉积卤水在蒸发浓缩阶段达到石盐沉积时的$Br\times10^3/Cl$值一般大于4.7，钾镁盐沉积阶段大于15（Valyashko，1956）．对比国外部分海相盐岩盆地，海相岩盐的溶滤卤水$Br\times10^3/Cl$为0.06～0.76；晚前寒武纪Amadeus盆地溶滤石盐的$Br\times10^3/Cl$为0.20～0.35；绿河建造溶滤石盐的$Br\times10^3/Cl$为0.02～0.30（Herrmann，1972）．Alcalá and Custodio（2008）研究指出溶滤石盐、光卤石、钾石盐的$Br\times10^3/Cl$分别为0.34～0.64、3.98～5.31、6.37～7.96．笔者根据前期研究和矿山实际调研，发现目前中国较常用的判别溶滤卤水的$Br\times10^3/Cl$值偏低．

陈郁华（1983）对黄海海水进行了25℃恒温蒸发实验，根据实验结果将黄海海水不同浓缩阶段析出矿物的溶滤卤水的$Br\times10^3/Cl$、$K\times10^3/Cl$及K/Br重量比与nNa/nCl及nMg/nCl摩尔浓度比等进行分析，得出溶滤石盐-泻利盐、钾石盐-光卤石和水氯镁石的$Br\times10^3/Cl$分别为0.18～0.56、2.36～8.17和17.03，均远远高于目前常用溶滤卤水的钾盐找矿指标；溶滤石盐-泻利盐、钾石盐、光卤石和水氯镁石的nNa/nCl可分别达到1、0.57、0.2和0. McCaffrey（1987）对巴哈马英纳加岛海相卤水进行了蒸发实验，认为沉积卤水蒸发浓缩至40.4～78.8倍时（石盐晚期及钾镁盐沉积阶段）的$Br\times10^3/Cl$值均大于13，且随浓缩程度的增大，从13.19升高至21.85；nNa/nCl值逐渐从0.45降至0.07；nMg/nCl从0.39升高至0.55．国内外海相卤水的蒸发实验对比结果表明我国现阶段使用的$Br\times10^3/Cl$找钾指标确实偏低．

因此，本文开展了溶滤实验并进行统计分析，得出海相固体钾盐沉积矿床与溶滤卤水的找钾指标（表1）：溶滤石盐岩的$Br\times10^3/Cl$为0～0.8，该值随浓缩程度的增加而增大，溶滤含钾石盐岩为0.4～1.0，溶滤钾盐岩的$Br\times10^3/Cl>1$，且随着钾离子含量的增高而增大，最大超过7，其中加拿大钾盐矿床的$Br\times10^3/Cl$相对较低；溶滤石盐岩的$K\times10^3/Cl<5$，含钾石盐岩为5.0～50，溶滤钾盐岩的$K\times10^3/Cl>50$；溶滤石盐岩的K/Br<5.8，最低可达1.99，当溶解含钾石盐时K/Br增大，并且随着钾离子含量的增加而增大，溶滤含钾石盐岩及钾盐岩的K/Br>5.8；溶解石盐岩的nNa/nCl为0.97～1，溶解含钾石盐岩为0.92～0.97，溶解钾盐岩时小于0.92；溶解石盐岩、含钾石盐岩、钾盐岩的nMg/nCl一般小于0.01，均小于海水（0.13），溶解含光卤石钾盐岩的nMg/nCl>0.01，最大为0.104，小于原始海水．

3.2　天星桥构造寒武系深部地下卤水的成因判别

3.2.1　溴氯与钾氯重量比　溴在钾盐矿物中富集是由于溴离子半径（1.96Å）和电负性（2.8）与氯离子半径（1.81Å）和电负性（3.0）相近，溴以类质同像的形式替换矿物中的氯．海水蒸发、浓缩、盐类矿物结晶时，水溶液中溴的浓度逐渐增加，沉积石盐层中溴含量也逐渐增加．溴与石盐、钾盐等矿物关系密切，是找钾的重要指标（Valyashko，1956；Herrmann，1972，1980；Herrmann *et al.*，1973；McCaffrey *et al.*，1987；Fontes and Matray，1993；Smith *et al.*，1995；Kloppmann *et al.*，2001；Rahimpour-Bonab and Alijani，2003；Kovalevych *et al.*，2006；Gupta *et al.*，2012；García-Veigas *et al.*，2013；牛新生等，2014）．因此，盐类矿物中溴含量的高低可代表盐湖卤水浓缩淡化程度（许效松和吴嘉陵，1983；渠洁瑜等，1984；Walter *et al.*，1990；林耀庭，1995；Bottomley *et al.*，1999；Jensen *et al.*，2006；程怀德等，2008；Gupta *et al.*，2012；李洪普等，2014；Sun *et al.*，2019；Shang *et al.*，2020；Yu *et al.*，2021）．

$Br\times10^3/Cl$值对卤水成因具有很好的指示性，能够较好地区分溶滤卤水和沉积卤水（Stueber and Walter，1991；Fontes *et al.*，1993；Edmunds，1996；Eastoe *et al.*，2001；Gleeson *et al.*，2001；Freeman，2007；Shouakar-Stash *et al.*，2007；Alcalá and Custodio，2008；张西营等，2010；Boschetti *et al.*，2011；Richard *et al.*，2011；Skrzypek *et al.*，2013；Zarei *et al.*，2013）．除此之外，溴氯系数（重量比或摩尔浓度比）应用广泛，可用于辨别现代

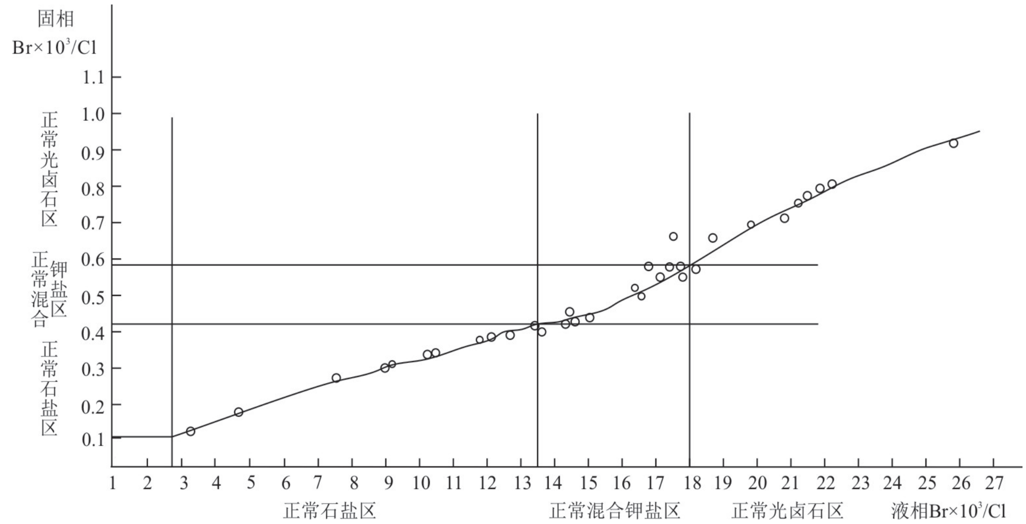

图 3 海水浓缩时固相石盐溴氯系数与液相卤水溴氯系数(据 Valyashko,1956)

Fig. 3 Br×10³/Cl of the halite and brine for the seawater in different concentration stages (from Valyashko,1956)

地下水与结晶岩深层水(Davis *et al.*, 2004),也可判断地下水的盐度和高溴氯系数的影响因素,如降雨或其他有机过程等(Davis *et al.*, 1998; Hudak, 2003; Alcalá and Custodio, 2008; Katz *et al.*, 2011).原始海水的 Br×10³/Cl 值为 3.4(Stueber and Walter, 1991; Kloppmann *et al.*, 2001).一般情况下,溶滤岩盐及含钾氯化物的 Br×10³/Cl 值都小于原始海水,而蒸发浓缩的沉积卤水的 Br×10³/Cl 值一般要大于原始海水. Braitsch 研究认为 Br×10³/Cl 值在石盐、含钾石盐、含光卤石钾石盐、钾石盐和光卤石沉积阶段分别为 0.11、0.28、0.41、3.62 和 5.24,与 Valyashk 研究结果相近(Valyashko, 1956;Braitsch, 1971;图 3).

天星桥构造寒武系深部地下卤水矿化度一般为 120~300 g/L,大部分为 180~300 g/L,Br×10³/Cl 值偏高,一般为 1~3,最大可达 4.68;K×10³/Cl 值一般为 10~20. 图 3 表明,若天星桥构造地层水为沉积卤水,则该卤水应该处于石盐早期沉积阶段,但其矿化度及 K^+、Br^- 含量远超出石盐早期沉积阶段;若为石盐晚期或正常混合钾盐的沉积阶段,则卤水的 Br×10³/Cl 应该大于 10. 结合该区卤水高矿化度及其 Br×10³/Cl 值,笔者认为天星桥构造地下卤水为溶滤卤水,且应该达到了溶滤含钾石盐的指标,个别样品(如序号 1、2、8、12)甚至可能达到溶滤钾盐的指标,符合溶滤实验所得的含钾石盐及钾盐的指标.

3.2.2 钾溴重量比 K/Br 值对于分析含钾沉积卤水和溶滤卤水的成因较为敏感. 不同地区的海水 K/Br 稍有不同,一般为 5.4~5.8(肖章棋, 1982).海水在蒸发浓缩过程中,钾盐逐渐从卤水中析出,而溴在卤水中的含量越来越富集. 因此,沉积卤水的 K/Br 值随着海水蒸发浓缩程度的升高而降低,到共结点时为 0.1~0.2,原生沉积卤水的 K/Br 在正常情况下不可能大于原始海水(5.4~5.8);相反,在溶滤含钾石盐或钾镁盐时卤水的 K/Br 一般大于 5.8(肖章棋, 1982). 根据海水蒸发过程中 K/Br 随 Cl^- 含量变化的规律曲线,K/Br 值在曲线下方时为沉积卤水,在曲线上方时则为溶滤卤水(石油化学工业部化学矿山局,1977).

将天 1 井与天 2 井卤水样品投点于 K/Br 值随 Cl^- 含量变化曲线上,16 个样品的 K/Br 值均分布于曲线上方(图 4a),表明该卤水为溶滤卤水. 天 1 井与天 2 井卤水的 K/Br 为 5.17~12.14,一般为 7.5~9.0,仅有 12 号样品小于 5.4;结合研究区卤水的高矿化度与高 K^+ 含量(4.58 g/L),认为该卤水可能为溶滤含钾石盐、甚至是钾石盐卤水.

3.2.3 钠氯摩尔浓度 卤水 *n*Na/*n*Cl 值是反映卤水蒸发浓缩及岩盐溶解淋滤作用的重要指标(Fontes and Matray, 1993; Chan *et al.*, 2002; 韩佳君等, 2013; Khaska *et al.*, 2013). 原始海水的 *n*Na/*n*Cl 基本为 0.85~0.87. 随着海水的逐步浓缩,*n*Na/*n*Cl 逐渐降低,直至共结点时 *n*Na/*n*Cl 可降至 0.04. 溶滤岩盐卤水的 *n*Na/*n*Cl 一般大于原始海水的初始值,可接近 1(Kesler *et al.*, 1996). 只有在溶滤钾盐时该值才比较低,含钾量越高,该值越小,最低可降至 0.3(李廷伟等,2006). 因

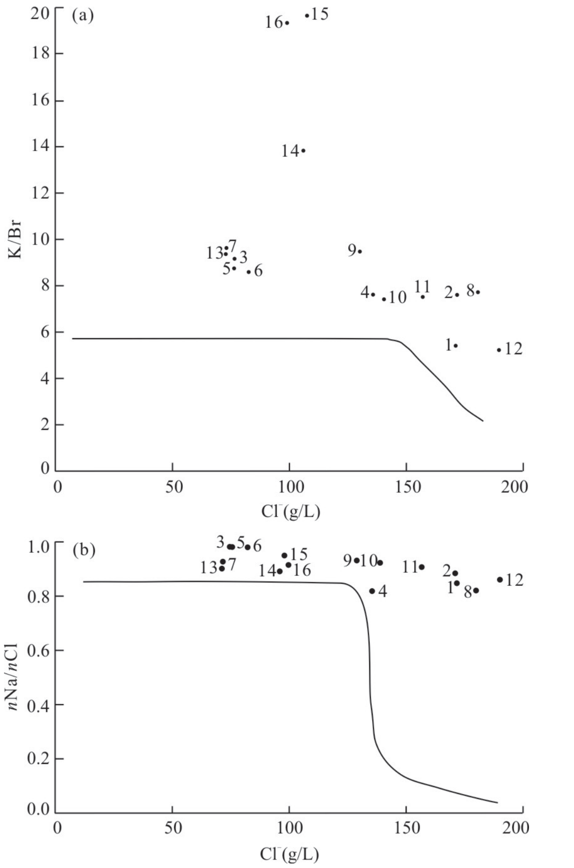

图4　天星桥构造寒武系深部地下卤水 K/Br(a)和 nNa/nCl(b)分布

Fig. 4　The change of K/Br with Cl^- (a) and nNa/nCl with Cl^- (b) of the seawater in different concentration stages

此,根据海水浓缩时 nNa/nCl 随 Cl^- 含量变化的规律曲线,曲线上方表示溶滤卤水,下方为沉积卤水(石油化学工业部化学矿山局, 1977).

天 1 井与天 2 井卤水的 nNa/nCl 为 0.81～0.98,一般为 0.88～0.95,仅有个别样品小于原始海水值(0.85);将天 1 井与天 2 井卤水的 nNa/nCl 值投点于图 4b,均分布于曲线上方,表明研究区卤水符合溶滤卤水的特征.

3.2.4　镁氯摩尔浓度　卤水 nMg/nCl 值对分析其是原生沉积卤水还是溶滤卤水具有指导意义.原始海水的 nMg/nCl 值为 0.13,随海水的不断蒸发浓缩,镁在溶液中不断聚集,nMg/nCl 也越来越高,浓缩至共结点时可达 0.97,所以沉积卤水的 nMg/nCl 应大于 0.13,而溶滤卤水的 nMg/nCl 一般小于 0.13,只有当溶滤光卤石时可略有增大.天星桥构造地层水的 nMg/nCl 均较小,最大仅为 0.015,均远小于原始海水值(0.13),表明天星桥构造寒武系深部地下卤水为溶滤卤水.

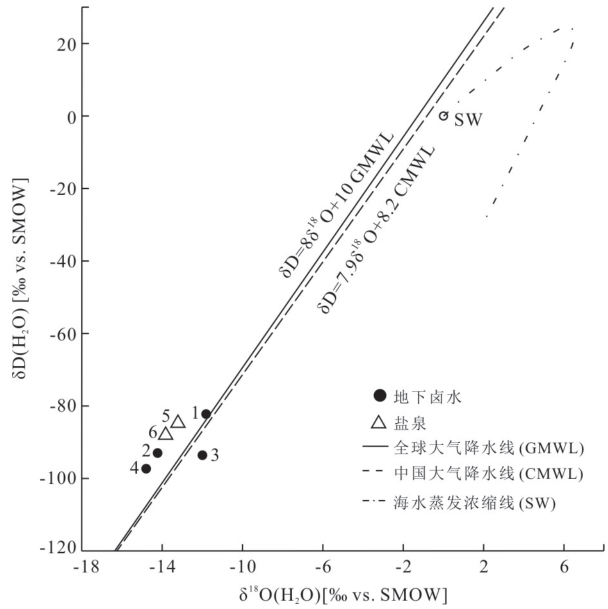

图5　川东北地下卤水与盐泉的氢氧同位素关系

Fig. 5　Relation between δD and $δ^{18}O$ of of formation brine and salt spring in Northeast Sichuan Basin

3.3　氢氧同位素分析卤水成因

水的 δD、$δ^{18}O$ 可用于有效判断地下水的成因(Matray and Fontes, 1990; Wittrup and Kyser, 1990; Fontes and Matray, 1993; Cai *et al.*, 2001; Xie *et al.*, 2012; Khaska *et al.*, 2013).本次采集的 6 个卤水样品的 δD 值为 −97.3‰～−81.8‰,$δ^{18}O$ 值为 −14.8‰～−11.7‰(表 3).所有卤水样品的 δD、$δ^{18}O$ 值投点(图 5)均靠近全球大气降水线(GMWL δD=8$δ^{18}O$+10; Craig, 1961)和中国大气降水线(CMWL δD=7.9 $δ^{18}O$+8.2;郑淑蕙等, 1983),明显偏离海水蒸发浓缩过程中的 δD、$δ^{18}O$ 关系曲线(Yager *et al.*, 2007);说明天星桥构造寒武系深部地下卤水为溶滤卤水,其水来源于大气降水,而非原生沉积卤水.

4　结论

(1)根据世界典型的4个海相钾盐矿床的石盐、含钾石盐及钾盐(含光卤石)样品的溶滤实验,结合国内外海水及海相卤水的蒸发实验,提出溶滤石盐的 Br×10^3/Cl 可达 0.1～0.7;溶滤含钾石盐时为 0.4～0.8;溶滤钾石盐时 Br×10^3/Cl 较高,一般大于 1.溶滤石盐岩的 K/Br<5.8,溶滤含钾石盐岩及钾盐岩时大于 5.8;溶解石盐岩的 nNa/nCl 为 0.97～1,溶解含钾石盐岩的 nNa/nCl 为 0.92～0.97,溶解钾盐岩的小于 0.92;溶解石盐岩、溶解含钾石盐岩、溶

解钾盐岩的 nMg/nCl均小于0.01,其中溶解含光卤石钾盐岩的 nMg/nCl>0.01. 该成果也可以应用于其他海相蒸发盐盆地的钾盐找矿工作.

(2)根据天星桥构造寒武系深部地下卤水的离子组分及其水化学系数特征,包括Br×10^3/Cl、K×10^3/Cl、K/Br重量比和 nNa/nCl、nMg/nCl摩尔浓度比,结合本文溶滤实验及国内外前人蒸发实验成果,认为天星桥构造寒武系深部地下卤水为溶滤卤水,其盐度为溶解含盐地层盐类,甚至可能溶解了含钾石盐及钾盐;该认识为在该区寻找固体钾盐矿床提供了新的依据.

(3)川东北地下卤水、石盐溶解卤水与地表盐泉水等6个卤水样品的δD、δ^{18}O分析结果表明天星桥构造寒武系深部地下卤水与盐泉水特征相似,均靠近全球大气降水线,由此认为天星桥构造寒武系深部地下卤水为溶滤卤水,其水来源于大气降水,盐度来源于含盐地层.

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