

许耿, 肖方景, 崔小梅, 等. 西藏羊八井高温地热水砷和氟浓度及来源探析[J]. 岩矿测试, 2024, 43(3): 487–500. DOI: [10.15898/j.ykcs.202310260168](https://doi.org/10.15898/j.ykcs.202310260168).

XU Geng, XIAO Fangjing, CUI Xiaomei, et al. Concentrations and Sources of Arsenic and Fluoride in High-Temperature Geothermal Water from Yangbajing, Xizang[J]. Rock and Mineral Analysis, 2024, 43(3): 487–500. DOI: [10.15898/j.ykcs.202310260168](https://doi.org/10.15898/j.ykcs.202310260168).

西藏羊八井高温地热水砷和氟浓度及来源探析

许耿, 肖方景, 崔小梅, 布多*, 张强英*

(西藏大学生态环境学院, 西藏 拉萨 850000)

摘要: 砷(As)和氟(F)是西藏羊八井高温地热流体中两种典型的高浓度有害元素,通过地热开发可以进一步促进与加速地热源 As 和 F 向地表或近地表环境释放,导致地表水和土壤环境污染。如何从 As 和 F 浓度分布特征联系水化学特征从而揭示水体 As 和 F 的富集规律,对丰富和认识西藏地区水环境中 As 和 F 的环境地球化学行为具有重要意义。本文结合野外调查现场测定了水体常规理化指标,包括水温、pH 值、电导率(EC)、总溶解固体(TDS)和盐度(SAL),采用原子荧光光谱法和 X 射线荧光光谱法分别测定水体和土壤样品中的 As 浓度,离子选择性电极法测定水体和土壤样品中的 F 浓度,评价 As 和 F 超标风险,探析其富集机制。结果表明:水化学类型为 Na-HCO₃·Cl 型,水体 Na⁺浓度高达 445.5mg/L, Ca²⁺浓度低至 3.31mg/L,水体 pH 在 7.87~9.42 之间,富钠贫钙高 pH 是羊八井地热水和温泉水最主要的水化学特征。受水汽蒸发浓缩影响,温泉水 As 和 F 浓度高于地热水,两元素浓度最高分别达 6.50mg/L 和 17.89mg/L。地热废水的不当处理存在水体和土壤 As 和 F 暴露风险,地热水和温泉水 As 和 F 浓度显著高于《地热资源评价方法》(DZ40—85)对有害成分规定的最高允许排放浓度(总砷为 0.50mg/L,氟化物为 10mg/L)。而土壤中总 As 浓度为 79.50~99.08mg/kg, F 浓度为 1162.70~1285.10mg/kg,显著高于西藏土壤背景值。地热水体和地表土壤 As 和 F 富集主要为水-岩浸溶相互作用,独特的水化学特征为水体 As 和 F 浸取溶出提供了有利条件。

关键词: 羊八井地热水; 砷; 氟; 原子荧光光谱法; X 射线荧光光谱法; 水-岩相互作用

要点:

- (1) 富钠贫钙高 pH 是羊八井地热水和温泉水最主要的水化学特征。
- (2) 受水汽蒸发浓缩影响,温泉水 As 和 F 浓度高于地热水,As 和 F 浓度最高分别达 6.50mg/L 和 17.89mg/L,水期变化趋势呈现枯水期>平水期>丰水期。
- (3) 地热水和地表土壤 As 和 F 来源主要为水-岩浸溶相互作用,独特的水化学特征为水体 As 和 F 离子浸取溶出提供了有利条件。

中图分类号: P618.64; P641.12

文献标识码: A

西藏处于典型的喜马拉雅地热带,是中国高温地热流体分布最密集的地区,其地热资源居中国第一^[1],境内共有 709 个地热带活动区,其中有 131 个地热系统温度高于 150℃,8 处地热层温度高

于 200℃^[2]。位于境内的羊八井地热站是中国最大的地热发电站,也是中国所有热液系统中测得的储层温度最高的地热田^[3],其日开采汽水总量约为 12000t^[2]。砷(As)和氟(F)是西藏羊八井高温地热

收稿日期: 2023-10-26; 修回日期: 2024-01-06; 接受日期: 2024-05-08

基金项目: 国家自然科学基金项目(22266032); 第二次青藏高原综合科学考察研究项目(2019QZKK0603); 西藏自治区科技厅中央引导地方科技发展资金项目(XZ202202YD0016C); 中央支持地方高校改革发展计划项目([2023]1 号)

第一作者: 许耿, 硕士研究生, 主要从事水污染及其控制技术研究。E-mail: xgydsa@163.com。

通信作者: 布多, 博士, 教授, 主要从事环境化学与环境生态学研究。E-mail: phudor@vip.163.com。

通信作者: 张强英, 博士, 副教授, 主要从事地热水水质调查、水污染及其控制技术研究。

E-mail: zhangqiangying@utibet.edu.cn。

流体中两种典型的高浓度有害元素,通过地热开发可以进一步促进或加速地热源 As 和 F 向地表或近地表环境释放,从而威胁附近水土生态环境。因此,调查 As 和 F 浓度水平与水体水化学特征从而揭示水体 As 和 F 的富集规律,对丰富和认识西藏地区水环境中 As 和 F 的环境地球化学行为具有重要意义。

关于羊八井地热水的水化学特征、水热蚀变和水体胶体粒子特征已开展前期研究^[4-6]。研究表明,羊八井地热田热水水化学类型为 Na-Cl 型,大部分地热水为中性偏碱性,pH 值在 6.70~9.60 之间,浅层热水主要来源于深层热水与地表水(冰川雪山融水和大气降水)的混合^[7-8]。地表水补给来源于念青唐古拉山海拔 4400~5800m 的雪山融水^[8],融雪水渗入地下后由底层岩浆热源加热,由于热水密度低于融雪水,加热后的热水能自然地流向地表。相比水化学研究,羊八井地热储层流体中 As 和 F 浓度特征、地热源 As 和 F 引起的水土环境影响是地热利用过程中关注的热点环境问题^[9-12]。郭清海等^[13]报道了羊八井地热流体 As 和 F 浓度分别高达 5.70mg/L 和 19.60mg/L,远高于西藏其他地区^[14-15],由于地热开发,输入地热邻近河流堆龙曲中主要的污染物为 As 和 F。魏晓阳等^[11]研究表明地热邻近河流堆龙曲中检出了高浓度 F(0.41~1.31mg/L)。在 As 和 F 来源及富集机制方面,氟化物浓度受到氟石(CaF_2)溶解度限制,其浓度与水化学类型密切相关,表现为 F 元素在 Na-Cl 或 Na-Cl- SO_4 等 Na 型水中富集程度常高于 Na-Ca- HCO_3 或 Ca- HCO_3 等 Ca 型水体^[15],因此羊八井高温地热水氟化物浓度高达 19.60mg/L^[13]。同时,弱碱性 pH 水体也为 As 和 F 的富集提供了有利条件^[16]。羊八井地热流体中 As 主要来自岩浆脱气^[17],As 的富集与岩浆流体的浸取和地幔侵入高砷岩浆热源有关^[18],也就是说,决定岩浆热液流体中 As 浓度高低最关键的因素是岩浆流体的地质成因及其化学成分。综上所述,羊八井高温地热水中 As 和 F 的来源及富集机制主要有两方面:①深部地热流体的升流混合作用;②补给水向下渗流过程中与含 As 和 F 硅酸盐矿物的溶滤作用,因此地下水体中 As 和 F 往往表现为共生性^[19-20]。尽管研究者在羊八井地热水中 As 和 F 的浓度特征及其来源方面有了前期研究基础,但仍需要深入分析地热源 As 和 F 浓度年变化趋势、水环境演变规律和水土环境生态风险。

本文在前期研究的基础上,于 2021—2022 年对西藏羊八井地热田进行了三期的地热水、温泉水和

土壤样品采集,分析羊八井热田水化学常规理化指标、水化学类型、阴阳离子组成,揭示地热水、温泉水和土壤样品中 As 和 F 浓度变化特征,剖析地热水和温泉水 As 和 F 的来源与富集机制,评价了水体和地表土壤超标风险情况,研究成果为羊八井地区地热的持续合理利用提供科学依据。

1 研究区域地理位置概况

西藏羊八井地热发电站位于西藏自治区拉萨市西北约 90km 的当雄县羊八井镇,海拔约 4300m。羊八井地层主要由第四系沉积物和基岩风化壳组成,第四系沉积物主要为冲洪积砂砾石层和冰碛砂砾层,而基岩风化壳则主要由花岗岩风化而成。羊八井气候寒冷干燥,年平均气温在 2.5℃ 左右,年降水量在 500mm 左右^[2]。由于空气稀薄,太阳辐射强,日照时间长,全年无霜期短,羊八井热田是中国目前已知的热储温度最高的地热田,其深部热储平均温度为 252℃,最高记录热储温度达 329.8℃^[2],地表出露温度为 68~84℃^[21]。羊八井地热发电厂是中国建设的第一座最大的、海拔最高的地热试验田,也是当今世界迄今为止唯一利用中温浅层热储资源发电的电厂。地热站的建设为西藏地区的经济发展和社会稳定发挥了举足轻重的作用。羊八井地热站地势平坦,海拔 7000m 以上的念青唐古拉山屹立于地热站西北,东南方向为海拔 6000m 以上的唐山,终年覆盖有大量冰川,是地表径流的重要补给,地势上具有西北高、东南低的特点^[22]。羊八井地热发电站和周边地理分布格局如图 1 所示。

青藏公路将热田分为南北两区,北区分布有二电厂和国家地质公园,南区分布有一电厂,一电厂紧邻藏布曲。羊八井镇因地热资源丰富而闻名,镇内分布有规模宏大的喷泉、沸泉、涌射泉、热泉和热水湖等。在羊八井镇格达乡建设有规模仅次于羊八井地热站的羊易地热站。羊八井地热温泉洗浴已成为重要的旅游胜地,目前建成“蓝色天国”温泉旅游区。地热站于 2019 年进入休采期,休采期间“蓝色天国”温泉旅游区对外开放,钻井口仍有地热水流出,在地热休采期间,其水环境影响仍不容忽视。

2 实验部分

2.1 样品采集

根据资料显示和现场勘察,三次采样分别于 2021 年 6 月(丰水期)、2021 年 11 月(平水期)和 2022 年 4 月(枯水期)在羊八井地热发电站钻井口、

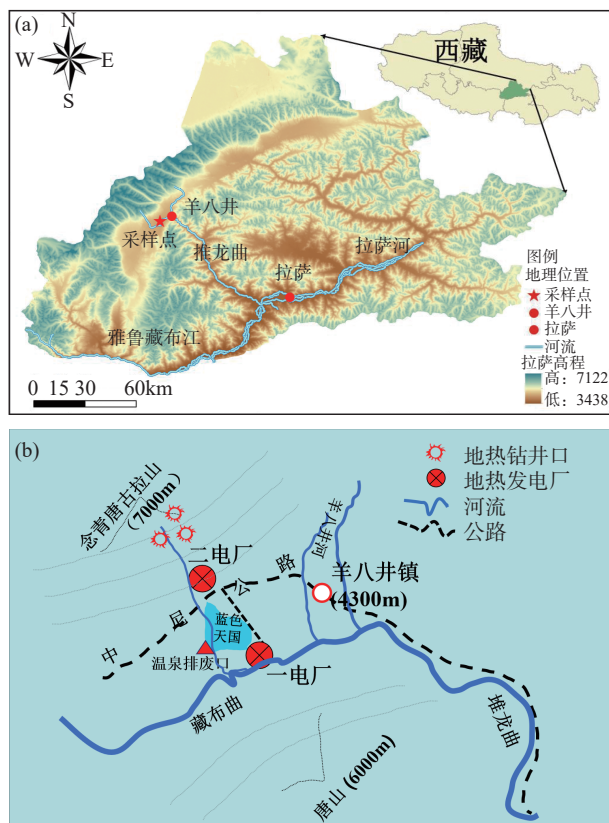


图1 羊八井地热发电站位置(a)及周围分布格局(b)

Fig. 1 Geographical location (a) and surrounding distribution pattern (b) of Yangbajing geothermal power plant.

温泉水口共设2个采样点,水样采集依照《水和废水监测分析方法》(GB/T 8538—2008)进行。现场采集2份平行水样约1L,测定常规指标,包括pH值、电导率(EC)、总溶解固体(TDS)和盐度(SAL)。测定方法是将优特PCS Testr 35型便携式多参数测量仪电极深入水面下10cm处^[23],待显示数字稳定后进行读数记录。地热水和温泉水出露温度采用水银温度计现场测定。

土壤样品全部采集于温泉排废口,使用铁锹采集温泉水淋滤的土壤约2kg,沥水冷却后装于塑料密封袋中保存,土壤样品带回实验室自然风干,过100目筛保存备用。水样带回实验室自然冷却,一份经0.45μm滤膜过滤后,加入优级纯硝酸5mL酸化并保存在0~4℃冰箱中备用,用于As和其他元素分析;另一份水样过滤后用于F离子和其他阴离子分析。

2.2 分析仪器

原子荧光光谱仪(AFS-9330型,AFS-8300型,北京吉天仪器有限公司)、高精度X射线荧光光谱仪(HD Rocksand型,美国XOS公司)、离子选择性电极(F090 ION 700型,美国Thermo Eutech公司)、

电感耦合等离子体发射光谱仪(Optima 5300 DV型,美国PerkinElmer公司)、电感耦合等离子体质谱仪(ELAN DRC-e型,美国PerkinElmer公司)和离子色谱仪(IC, ICS-1000型,美国Dionex公司)用于目标物测定。

2.3 样品分析方法

(1) 水体和土壤中总As浓度采用原子荧光光谱法(AFS)和高精度X射线荧光光谱法(XRF)测定。水体总As浓度测定方法:地热水和温泉水逐级稀释200倍后,在9mL稀释后的待测水样中加入1mL 5%(硫脲+抗坏血酸)溶液,30℃恒温水浴反应30min,标准曲线的不同浓度点采用上述相同的操作进行,反应结束后进行总As浓度测定。土壤总As浓度测定方法:XRF测定土壤总As时,先用仪器自带能量校准样品(A750)进行能量校正,使用标准品(GBW07310)对仪器主要参数进行实验调试,以消除或减少元素间干扰,提高仪器准确度。

(2) F离子浓度采用离子选择性电极法测定。土壤中总F浓度的测定方法:依据《土壤质量 氟化物的测定 离子选择电极法》(GB/T 22104—2008)。具体流程:称取0.20g土壤样品于坩埚中,加入2g氢氧化钠,高温550℃条件下熔融煅烧,煅烧后采用热水浸取并定容至100mL,测定前加入适量盐酸中和到pH为5~6,采用氟电极测定F离子浓度。10mL样品中加入1mL总离子强度调节缓冲溶液(TISAB)并以掩蔽溶液中Fe³⁺和Al³⁺干扰。水体中总F浓度的测定与土壤中F的浸取液测定方法相同。

(3) 水体中元素Ca、K、Na、Mg、Fe、Al和Mn采用电感耦合等离子体发射光谱法(ICP-OES)测定;Zn、Cr、Co、Ni、Mn、Cu和Cd等元素采用电感耦合等离子体质谱法(ICP-MS)测定,用浓度为10.00μg/L的Ba、Be、Ce、Co、In的调谐液优化仪器检测条件,使仪器灵敏度、氧化物离子产率、双电荷离子产率等各项指标达到测定要求。ICP-MS/OES元素分析采用在线加入内标物(In/Rh)的方法降低基体干扰。水体Se、Hg和Sb通过原子荧光光谱仪测定。地热水和温泉水中阳离子(K⁺、Na⁺、Ca²⁺和Mg²⁺)和阴离子(Cl⁻和NO₃⁻)采用离子色谱法(IC)测定,CO₃²⁻和HCO₃⁻采用容量法测定。水体阴阳离子IC分析和元素ICP-MS/OES分析是委托具有权威资质的第三方测试平台(西藏自治区地质矿产勘查开发局中心实验室)完成,样品测定值均为3次平行测定的平均值扣除空白后的结果,标准偏差小于5%。

目标物的分析方法和测定条件及检出限如表1所示。

表 1 样品分析及测定条件

Table 1 Sample analysis methods and measurement conditions.

样品类型和元素	分析方法	检出限	RSD	仪器测定条件
水体 As、Hg、Sb、Se	AFS	As: 0.0096μg/L Hg: 0.0017μg/L Sb: 0.01μg/L Se: 0.01μg/L	<5%	(1) 还原剂: 0.5% (m/m) NaOH+2% (m/m) KBH ₄ (2) 载液: 5% (V/V) 盐酸 (3) 载气 (Ar) 流速 0.4L/min
土壤 As	XRF	1mg/kg	<5%	分析线 Kβ; 能量 11.72keV; 电压 50kV; 分析时间 300s; 滤光片 Ag
土壤和水体 F	ISE	定量下限 0.09mg/L	<5%	10mL 样品+1mL 总离子强度调节缓冲溶液 (TISAB)
水体 Ca ²⁺ 、K ⁺ 、Na ⁺ 、Mg ²⁺ 、Cl ⁻ 、NO ₃ ⁻	IC	Ca ²⁺ : 0.011mg/L K ⁺ : 0.02mg/L Na ⁺ : 0.005mg/L Mg ²⁺ : 0.013mg/L Cl ⁻ : 0.032mg/L NO ₃ ⁻ : 0.054mg/L	<5%	(1) EGC-III 淋洗液自动发生器; DS6 型电导检测器 阳离子测定条件: CSRS 300-4 mm 阳离子抑制器; CS12A 型分离柱 (4mm×250mm); 淋洗液 20mmol/L 硫酸; 流速 1mL/min; 进样体积 500μL (2) 阴离子测定条件: ASRS 300-4 mm 阴离子抑制器; Ion Pac AS19 型分离柱 (4mm×250mm); 淋洗液: 30mmol/L KOH; 流速 1mL/min; 进样体积 500μL
水体 CO ₃ ²⁻ 、HCO ₃ ⁻	容量法	—	<1%	5% 酚酞-乙醇指示剂; 1% 溴酚蓝指示剂; 双指示剂滴定分析法
水体 Ca、K、Na、Mg、Fe、Al、Mn	ICP-OES	Ca: 0.003mg/L K: 0.06mg/L Na: 0.02mg/L Mg: 0.02mg/L Fe: 0.002mg/L Al: 0.03mg/L Mn: 0.005mg/L	<5%	(1) 射频功率 1250W; 等离子体气 (Ar) 流速 15L/min; 辅助气 (Ar) 流速 0.2L/min; 雾化器气体 (Ar) 流速 0.75L/min; 样品提升量 1.5L/min; 观测方式: 垂直; 冲洗时间 30s; 积分时间 5s; 重复测定 3 次 (2) 最佳波长选择: Ca 317.933nm、K 766.49nm、Na 588.995nm、Mg 285.213nm、Fe 238.204nm、Al 396.153nm、Mn 285.213nm
水体 V、Be、Zn、Cr、Co、Ni、Mn、Pb、Mo、Ti、Cu、Ba、Cd	ICP-MS	Zn、Cr、Be、Co、Ni、Mn、Cu、Cd: 1 ~ 10ng/L; Mo、Pb、Ba、Ti、V: 0.1 ~ 1ng/L	<5%	(1) 射频功率 1150W; 等离子体气 (Ar) 流速 17 L/min; 辅助气 (Ar) 流速 1.2 L/min; 载气 (Ar) 流速 1.06 L/min; 扫描模式为跳峰; 重复测定 3 次 (2) m/z: ⁵¹ V、 ⁹ Be、 ⁶⁶ Zn、 ⁵² Cr、 ⁵⁹ Co、 ⁶⁰ Ni、 ⁵⁵ Mn、 ²⁰⁸ Pb、 ⁹⁸ Mo、 ⁴⁸ Ti、 ⁶³ Cu、 ¹¹⁵ Ba、 ¹¹¹ Cd

2.4 测试数据质量控制

水体总 As 和 F 浓度测定结果采用加标回收率的方法进行了准确性验证, 结果如表 2 所示, 水体总 As 的回收率在 103.00% ~ 114.80%, F 的加标回收率在 98.20% ~ 99.90%。F 的测定较 As 更准确, 主要

是 F 离子选择性电极法测定浓度为 mg/L 水平, 而原子荧光光谱法测定总 As 浓度在 μg/L 水平, 因而 F 的测定准确度更高。总体而言, As 和 F 的加标回收率结果都在理论范围 (80% ~ 120%), 表明测定方法可靠。在土壤总 As 和 F 含量测定中, 采用国家一级

表 2 水体和土壤中 As 和 F 浓度测定准确性验证

Table 2 The accuracy of measuring As and F concentrations in water and soil samples.

样品类型	元素	加标值 (mg/L)	测定值 (mg/L)	回收率 (%)
地热水	As	0	3.16±0.10	—
		3	6.25±0.12	103.0±2.69
	F	0	15.91±0.24	—
		15	30.65±0.47	98.2±3.16
温泉水	As	0	4.18±0.07	—
		4	8.78±0.12	114.8±2.98
	F	0	17.67±0.23	—
		20	37.65±0.15	99.9±0.75
土壤样品	元素	标准值 (mg/kg)	测定值 (mg/kg)	回收率 (%)
沉积物 GBW07310	As	25±3.0	28.4±0.85	113.5±3.40
	F	149±25	138.0±16.57	92.6±11.10

标准物质的方法对分析方法准确度进行了检验。选择了沉积物标准品 GBW07310 作为分析样品, 在相同分析方法下进行测定, 总 As 和 F 的回收率分别为 113.5% 和 92.6%, 总 As 和 F 的测定值与标准值吻合, 综上所述, 方法的准确性良好, 数据可靠。

3 结果与讨论

3.1 水体水化学类型

地热水主要用于电热发电厂发电, 而温泉水主要用于蓝色天国洗浴中心。水质常规理化参数如表 3 所示, 钻井口地热水出露温度在 76~78℃ 之间, 出露温度随季节性变化差异较小。温泉水水温在 28.30~41.40℃, 温泉洗浴水入口温度为 41.40℃, 温泉利用后, 随着冷却水和生活水的共排放, 温度会降低, 排废温度在 28.30~29.60℃。温泉水 pH 范围在 7.87~9.42 之间, 入口 pH 值更高, 排废口 pH 值低, 地热水 pH 在 8.95~9.15 之间。温泉水和地热水的电导变化范围在 1670~1882μS/cm 之间, TDS 值在 1126~1340mg/L 之间, 盐度在 914~983mg/L 之间, 水质变化基本呈现枯水期>平水期>丰水期的趋势。

以平水期地热水和温泉水样品为代表, 测定了 8 个阴阳离子浓度, 结果如表 4 所示, 水体中阳离子 Na⁺占主导, 温泉水中的阴离子 HCO₃⁻和 SO₄²⁻占主导, 而地热水中阴离子 Cl⁻和 HCO₃⁻占主导。此外, 阴阳离子平衡和相对误差也列入表 4 中, 地热水阴阳离子平衡相对误差小于 5%, 表明分析数据可靠。在温泉水中, 阴阳离子平衡相对误差较高, 最高达 13.15%, 因为温泉水 Na⁺占比较高, Cl⁻占比太低, 导致阴阳离子平衡失调, 从而导致相对误差偏高。

采用 Origin 9.2 软件绘制了水体水化学 Piper 三线图, 如图 2 所示, Piper 三线图左侧三角形体现了主要阳离子的比例, 右侧三角形体现了主要阴离子的比例, 中间菱形体现了主要阴阳离子情况。数据点往高占比区域分布, 表明水化学类型主要为高占比区域类型。地热水数据点集中分布在低 Ca²⁺、高 K⁺+Na⁺占比方向, 占阳离子总量的 80% 以上, 而地热水中 Na⁺浓度占 K⁺+Na⁺总浓度的 87.50%~97.70%, 因此阳离子主要以 Na⁺为主导。水体 Na⁺浓度高达 445.5mg/L, Ca²⁺浓度低至 3.31mg/L。在右下角的主要阴离子分布图中, 阴离子主要分布在低 Cl⁻和高 CO₃²⁻+HCO₃⁻占比方向, 而地热水中 HCO₃⁻的浓度占

表 3 水质常规理化参数

Table 3 Conventional physicochemical parameters of the water quality.

采样时间	水期	样品类型	采样位置	水温 (℃)	pH	电导 (μS/cm)	TDS (mg/L)	盐度 (mg/L)
2021 年 6 月	丰水期	温泉水	温泉洗浴入口	41.4	9.42	1690	1180	914
		地热水	电站钻井口	76.0	9.15	1699	1220	952
2021 年 11 月	平水期	温泉水	温泉洗浴排废口	29.6	7.87	1882	1340	956
		地热水	电站钻井口	78.0	8.95	1670	1213	935
2022 年 4 月	枯水期	温泉水	温泉洗浴排废口	28.3	7.93	1783	1238	974
		地热水	电站钻井口	77.5	9.14	1678	1126	983

表 4 地热水和温泉水中主要阴阳离子浓度

Table 4 Concentrations of major anion and cation ions in the geothermal and hot spring waters.

样品类型	阳离子浓度 (mg/L)				阴离子浓度 (mg/L)				阳离子当量浓度 (mmol/L)	阴离子当量浓度 (mmol/L)	相对误差 (%)
	Ca ²⁺	Mg ²⁺	K ⁺	Na ⁺	Cl ⁻	SO ₄ ²⁻	CO ₃ ²⁻	HCO ₃ ⁻			
地热水 (钻井口) 一电厂	6.66	0.20	35.19	445.5	331.6	16.79	85.95	546.4	20.63	21.53	2.13
地热水 (废井口) 二电厂	3.31	0.013	3.42	147.2	59.26	26.30	14.51	260.1	6.66	6.97	2.28
温泉水洗浴 (入口)	38.23	10.86	15.91	183.4	72.46	99.9	4.84	262.3	11.19	8.59	13.15
温泉水洗浴 (排废)	31.45	5.66	47.02	328.5	91.60	229	ND	428.9	17.53	14.38	9.85

注: “ND”为未检出。

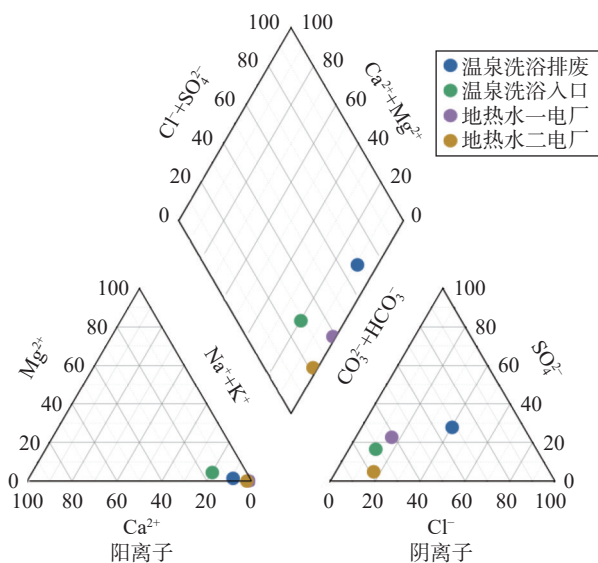


图2 水体水化学成分 Piper 三线图

Fig. 2 Piper three-line diagram of the hydrochemical composition of water samples.

$\text{CO}_3^{2-}+\text{HCO}_3^-$ 总浓度的 86.50% ~ 100%, 因此阴离子主要以 HCO_3^- 为主导。此外地热水 Cl^- 占比最高达 60%, 综上所述, 地热水水化学类型为 $\text{Na-HCO}_3\cdot\text{Cl}$, 与文献 [10] 报道一致。

3.2 水体砷和氟浓度

高温地热水中 As 的来源主要为岩浆脱气, 表现

为深层地热水中总 As 浓度 (5.70mg/L) 大于浅层地热水 (2.99mg/L) [24]。此外, As 的浓度还会受到水体 pH 值影响, 在碱性条件下硫代砷酸盐浓度占比高达 83% [25]。羊八井地热水和温泉水总 As 浓度如图 3a 所示, 钻井口地热水浓度在 3.16 ~ 3.56mg/L 之间, 平均值为 3.32mg/L, 几乎不随水期的变化而变化。地热水总 As 浓度与张庆等 [10] 报道的羊八井地热水中总 As 浓度 (3.54 ~ 3.56mg/L) 一致。同时, 对比了位于同一流域上游的羊易电站地热水中总 As 浓度, 羊八井地热水中总 As 浓度高于羊易电站 (2.24 ~ 2.30mg/L), 这主要是地热区岩浆背景不同。相比钻井口地热水, 温泉水总 As 浓度在 4.18 ~ 6.50mg/L, 浓度更高。地热水中 F 离子浓度如图 3b 所示, 羊八井钻井口地热水 F 离子浓度在 15.90 ~ 16.20mg/L, 几乎不随水期的变化而变化, 远高于西藏日多温泉中 F 离子浓度 (6.20mg/L)。同时, 对比了同一流域上游的羊易电站地热水中 F 离子浓度, 羊八井地热水中 F 离子浓度显著 ($P < 0.01$) 高于羊易电站钻井口 (12.63mg/L) 和羊易电站喷射泉 (5.19mg/L)。显著 ($P < 0.01$) 高于其他地区地热水 (1.00 ~ 12.70mg/L) [26-27], 与文献 [28-29] 报道的 F 离子浓度 (17.00 ~ 18.90mg/L) 相当, 低于美国黄石公园报道的热泉氟化物浓度 (31.60mg/L) [30]。地热水总 F 离

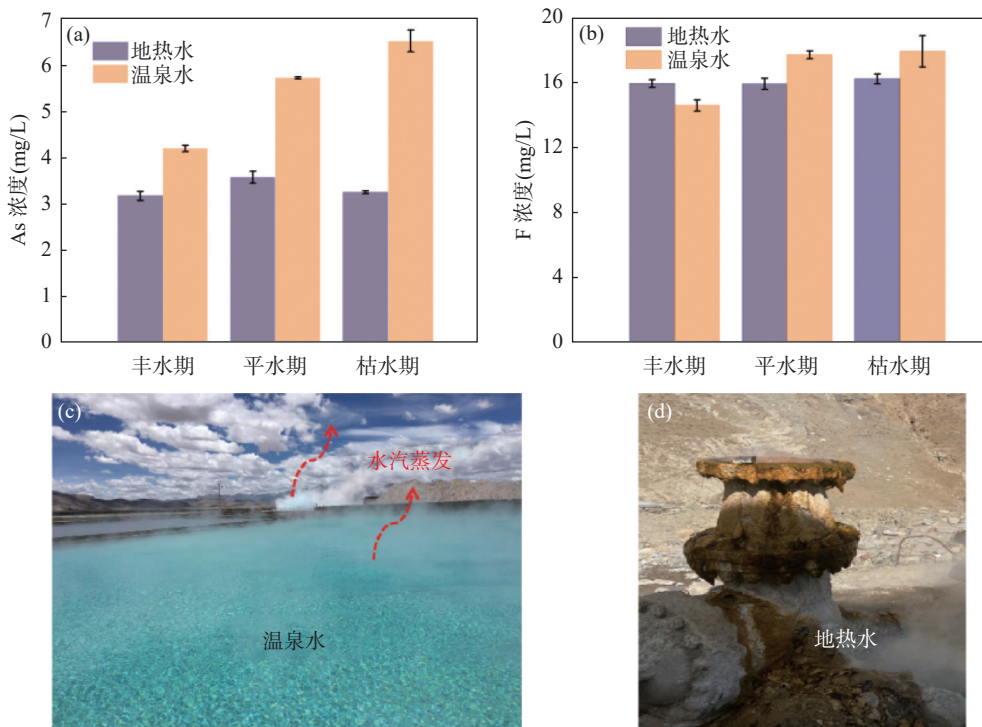


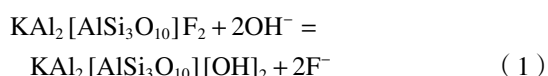
图3 水体中总 As(a) 和 F 浓度 (b), 温泉水水汽蒸发 (c) 和地热钻井口 (d) 照片

Fig. 3 The concentrations of total As (a) and F (b) in water samples, and pictures of hot spring (c) and geothermal water (d).

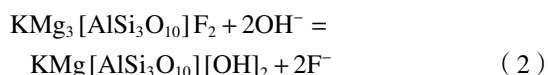
子浓度与2012年报道的羊八井地热水(18.00~18.90mg/L)和羊易电站地热水(19.20mg/L)^[24]相比,F离子浓度呈下降趋势。与As的分布规律一致,温泉洗浴水中总F离子浓度更高,在14.56~17.89mg/L,这是因为受水气蒸发浓缩影响(图3c),温泉水中As和F的浓度高于地热水。地热水来源于钻井口,水汽未发生分离或分离较少(图3d),因而浓度低于温泉水。温泉水中As和F浓度呈现枯水期>平水期>丰水期,这与季节蒸发量大小一致。地热水和温泉水As和F浓度显著高于《地热资源评价方法》(DZ40—85)对有害成分规定的最高允许排放浓度(总As为0.50mg/L,氟化物为10mg/L),地热废水的不当处理存在As和F的暴露风险。

As和F是高温地热水中典型的高浓度有害元素,主要来源于深层岩浆。通常,一些羟基矿物如白云母和黑云母常与F离子发生离子交换,当地下水为碱性时交换作用更容易发生,OH⁻能取代含F矿物质中的F离子,增加了地热水中F离子浓度,其基本过程存在如下反应^[31]:

白云母:



黑云母:



羊八井浅层地热流体,pH值为8.95~9.15,偏碱性的水体为As和F溶出提供了有利条件。此外,水体中F离子浓度受氟石(CaF₂)溶解度限制,Ca²⁺浓度越低,溶液中F离子浓度就会越高,而地热水中Ca²⁺浓度低至3.31mg/L,低浓度Ca²⁺是地热流体中F离子浓度富集的另一有利条件。

3.3 土壤砷和氟浓度

图4a为温泉排废口废水淋滤的土壤样品总As浓度。如图所示,枯水期和平水期总As浓度变化差异不大,总As浓度在97.60~99.08mg/kg之间,显著($P<0.01$)大于丰水期浓度(79.50mg/kg)。丰水期土壤浓度较低,可能是河水受雨水补给,周边泥沙冲刷,稀释了土壤中总As的量,使其浓度偏低。土壤中总As浓度随季节性变化差异不大。与西藏土壤总As背景值(18.70mg/kg)相比^[32],地热区的总As浓度显著高于背景值($P<0.01$),是背景值的4.25~5.31倍,表明地热区土壤浓度处于高As污染风险。与济南温泉水尾水土壤中As浓度相比(15.45μg/kg)^[33],羊八井地热区As浓度约高出3个数量级。与污染的寨上金矿矿区河流沉积物中As浓度(55~189mg/kg)相当^[34]。

土壤母质是土壤中氟化物的基本来源。土壤中总F浓度如图4b所示,总F浓度在1162.70~1285.10mg/kg之间,三次采样的平均值为1237.40mg/kg。表现为丰水期、平水期浓度大于枯水期,土壤总F浓度随季节变化差异不大。与西藏土壤总F背景值(542mg/kg)相比^[32],温泉淋滤的土壤总F浓度显著高于背景值,是背景值的2.28倍。与全国土壤F背景值(453mg/kg)以及世界土壤F中位值(200mg/kg)相比^[35],温泉淋滤的土壤氟化物显著偏高($P<0.01$)。与云南省洱源县高氟温泉点附近土壤总F浓度相比(630.48~1000.27mg/kg)^[36],其浓度也处于居高水平,其来源主要受高氟温泉水的冲刷、沉降和土壤吸附。水溶性的氟化物会对周边地下水和生物体产生富集影响,从而造成氟威胁。因此,对温泉水淋洗过的土壤样品进行了可溶态氟离子测定,土壤可溶态氟离子浓度在3.47~9.37mg/kg之间,表明温泉淋洗后的土壤可溶态氟浓度占比较高。

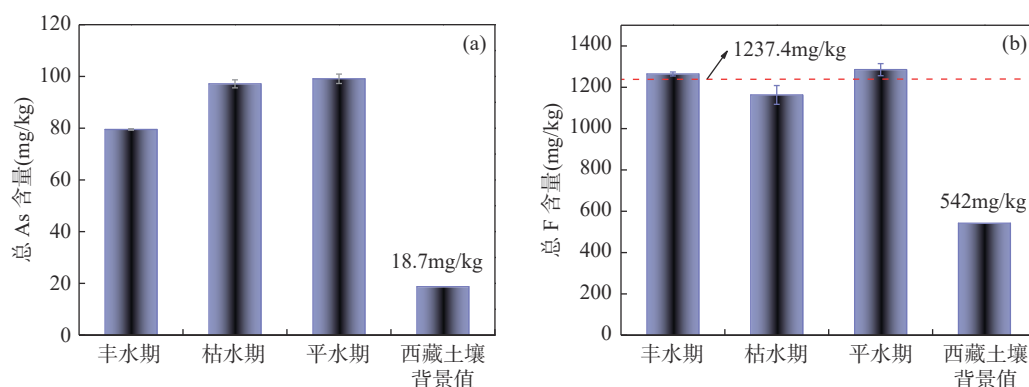


图4 土壤中总As浓度(a)和总F浓度(b)

Fig. 4 The concentrations of total As (a) and F (b) in the soil samples.

3.4 水体中金属离子浓度

以平水期为代表,测定了地热水和温泉水样品中的元素组成。结果如表 5 所示,地热水常量组成主要为 Na 和 K;而温泉水中 Na 离子占主导,其次为 Ca。通常,F 离子浓度受氟石 (CaF₂) 溶解积 (K_{sp}) 约束,Ca 离子浓度越低,溶液中 F 离子浓度就会越高,地热水和温泉水中 Ca 离子浓度在 6.36 ~ 35.74mg/L 之间,低浓度 Ca 离子为 F 离子富集提供有利条件。

此外,地热流体 F 离子溶解还会受到多因素的影响,如温度、pH、配体、共存离子等,使得 F 离子浓度分布出现反常。温泉水检出 10.20mg/L 的 Mg 离子,而在地热水却几乎未检出,Mn 离子也出现了相同的规律。考虑到 Mg 和 Mn 两元素主要存在于母质矿石中,猜测温泉水与地表母质岩石中的 Mg 和 Mn 氧化物发生了交换。其他金属如 Be、Cr、Pb、Sb 和 Mo 等组分的浓度分布几乎没有显著差异。

表 5 地热水和温泉水中金属元素浓度

Table 5 The metal element concentrations in geothermal and hot spring waters.

样品类型	金属元素浓度 (mg/L)										
	Ca	K	Mg	Na	Fe	V	Be	Mn	Cr	Pb	Sb
温泉水	35.74	15.46	10.20	195.4	0.091	0.009	0.002	0.14	0.035	0.0002	0.014
地热水	6.36	36.63	<0.013	456.5	0.047	0.013	0.005	0.012	0.049	0.0002	0.027
样品类型	Mo	Cd	Ti	Se	Zn	Cu	Ni	Co	Ba	Hg	
温泉水	0.035	0.0002	0.018	ND	0.002	0.0008	0.0032	0.00013	0.16	<0.0004	
地热水	0.070	0.0001	0.025	ND	0.003	0.0014	0.0029	0.00003	0.090	<0.0004	

注:“ND”表示未检出。

4 结论

本文结合野外调查和室内分析对西藏羊八井地热区的地热水和温泉水水样开展了水化学、As 和 F 浓度调查,阐明了水体水化学类型及 As 和 F 浓度变化趋势,揭示了水体 As 和 F 的来源及富集机制,评价了水体和土壤 As 和 F 超标情况和生态风险,具体结论如下:①富 Na 贫 Ca 高 pH 是羊八井地热水和温泉水最主要的水化学特征,为 As 和 F 离子溶出富集提供了有利条件;②地热废水的不当处理存在 As 和 F 的暴露风险,受水汽蒸发浓缩影响,温泉水 As

和 F 风险相比地热水更高;③水体 As 和 F 来源主要为水-岩浸溶相互作用,温泉淋滤促进了地表土壤 As 和 F 的富集,导致土壤总 As 和总 F 浓度均显著高于西藏土壤背景值。

本文丰富了西藏地区水环境中的 As 和 F 来源探析及环境地球化学行为,为地热水持续合理开发利用和水土环境风险评价提供依据。需要进一步完善覆盖地热流经区堆龙曲流域地表水、地下水 As 和 F 生态风险评价,加强环境监测预警。其次,需要关注温泉洗浴中 As 和 F 暴露风险。

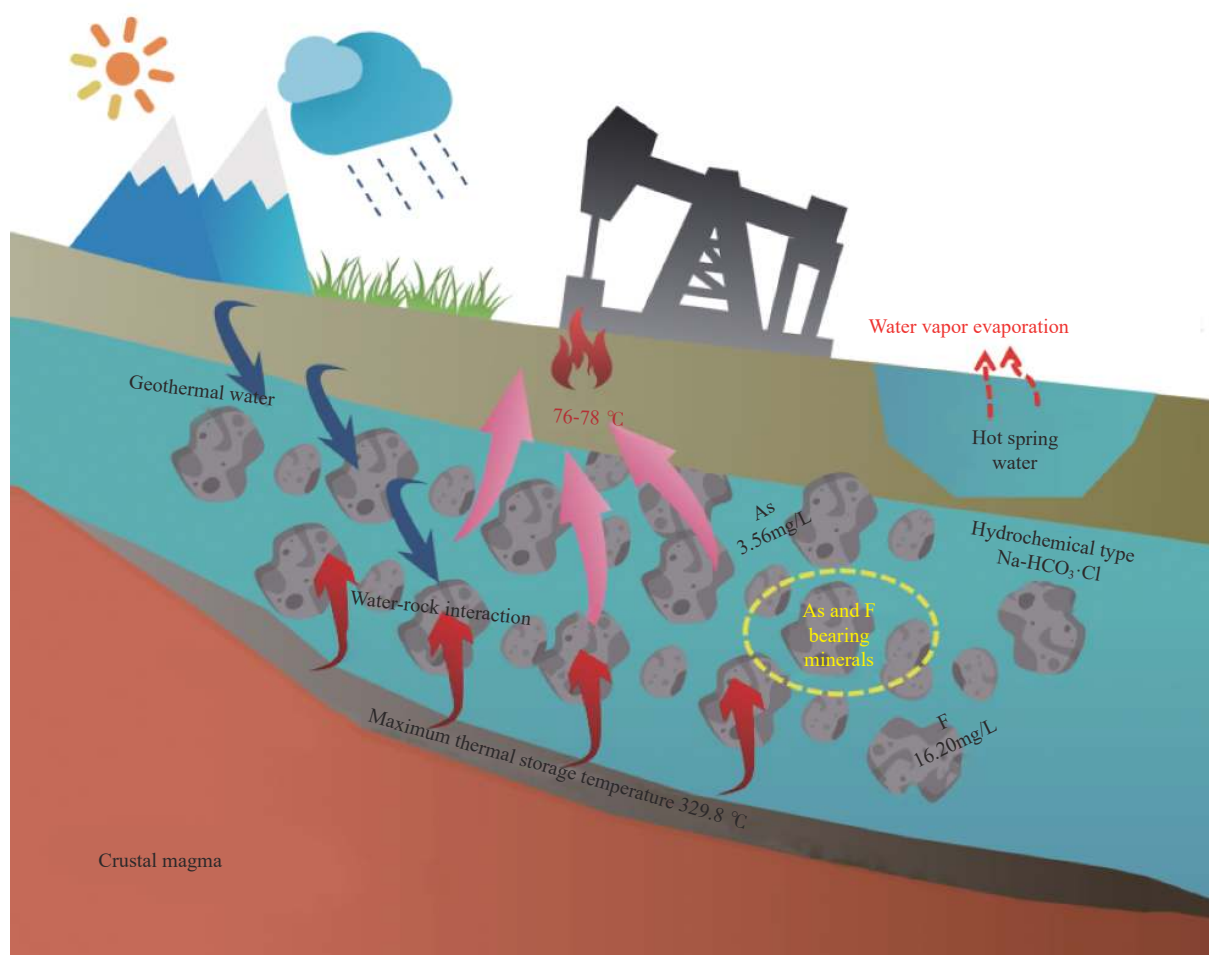
Concentrations and Sources of Arsenic and Fluoride in High-Temperature Geothermal Water from Yangbajing, Xizang

XU Geng, XIAO Fangjing, CUI Xiaomei, BU Duo*, ZHANG Qiangying*

(College of Ecological Environment, Tibet University, Lhasa 850000, China)

HIGHLIGHTS

- (1) Rich in Na, poor in Ca, and high pH are the main hydrochemical characteristics of Yangbajing geothermal and hot spring water.
- (2) Affected by water vapor evaporation, the concentrations of As and F in hot spring water reached 6.50mg/L and 17.89mg/L, respectively, showing a trend of dry season>normal season>flood season.
- (3) The main sources of As and F in geothermal water and surface soil are water-rock leaching interaction, and the unique hydrochemical characteristics provide favourable conditions for the leaching of As and F.



ABSTRACT: Arsenic (As) and fluoride (F) are two typical harmful elements with high concentrations in Yangbajing high-temperature geothermal water, and the release of As and F from geothermal sources to the surface or near-surface environment can be further promoted and accelerated through geothermal development, causing surface water and soil environmental pollution. To understand the enrichment mechanism of As and F in the

geothermal water body, hydrochemical characteristics as well as the concentrations of As and F were investigated by water quality analyzer, atomic fluorescence spectrometry, X-ray fluorescence spectrometry, and ion selective electrode method. The results indicate that the main sources of As and F in geothermal water and surface soil are water-rock leaching interaction. Unique hydrochemical characteristics ($\text{Na-HCO}_3\cdot\text{Cl}$) with high concentration Na^+ (reach to 445.5mg/L), poor in Ca^{2+} (as low as 3.31mg/L), and high pH (7.87–9.42) provided a favourable condition for the leaching of As and F in water. Affected by water vapor evaporation, the concentrations of As and F in hot spring water were higher than those in geothermal water and reached 6.50mg/L and 17.89mg/L, respectively. Notably, the total concentrations of As and F in waters were significantly higher than the maximum allowable emission concentrations for harmful components (0.5mg/L for As, and 10mg/L for F) in the *Geothermal Resources Assessment Method* (DZ40—85). Moreover, the concentrations of total As and F in the soils were 79.50–99.08mg/kg and 1162.70–1285.10mg/kg, respectively, significantly higher than the background values in Xizang soil. The BRIEF REPORT is available for this paper at <http://www.ykcs.ac.cn/en/article/doi/10.15898/j.ykcs.202310260168>.

KEY WORDS: Yangbajing geothermal water; arsenic; fluoride; atomic fluorescence spectrometry; X-ray fluorescence spectrometry; water-rock interaction

BRIEF REPORT

Significance: It is of great significance to study the concentration characteristics and sources of As and F to understand the environmental geochemical behavior of As and F in the geothermal system and their impact on the surrounding water and soil environment. Xizang Plateau is the region of China where high-temperature hydrothermal systems are intensively distributed, and the distribution of heat flow in the Xizang Plateau ranks first in China^[1]. The Yangbajing Geothermal Power Plant is the highest and largest geothermal power plant in China, setting a record for the highest reservoir temperature in China^[3]. The release of As and F can cause surface water and soil environmental pollution. Although researchers have made preliminary research on the concentration of these two typical harmful elements in geothermal fluids and their impact on the surrounding water environment^[9-12], it is still necessary to conduct in-depth analysis of the annual variation trend of As and F concentrations in a geothermal system, the contribution of hydrochemical characteristics to the enrichment of As and F, and the ecological risks of the surrounding soil and water environment caused by As and F leakage. On the basis of previous studies, we investigated the As and F concentrations of geothermal water, hot spring water and soil samples in the Yangbajing geothermal field, analyzed the hydrochemical characteristics of the water bodies, identified the source and enrichment mechanism of As and F in a geothermal system, and evaluated the ecological risks of As and F in water bodies and surface soils.

Methods: Three periods of field collection of geothermal water, hot spring water and soil samples were carried out in the Yangbajing geothermal field in Xizang from 2021 to 2022. Conventional physicochemical parameters were measured on site, including pH value, conductivity (EC), total dissolved solids (TDS), salinity (SAL), and temperature. The indoor analysis used atomic fluorescence spectrometer and X-ray fluorescence spectrometer to determine the concentration of total As in water and soil, respectively. The F concentration was measured using the ion selective electrode method. The pollution of As and F in water samples and soils was evaluated by comparing with the allowable maximum emission values of harmful elements in the standard and specified soil background values, respectively.

Data and Results: (1) The main hydrochemical characteristics. The conventional physicochemical parameters of water quality are shown in Table 3. The pH value of geothermal fluids is between 7.87 and 9.42. Geothermal fluids have a complex matrix, with conductivity, TDS, and salinity ranging from 1670–1882 $\mu\text{S}/\text{cm}$, 1126–1340mg/L, and 914–983mg/L, respectively. The changes in water quality physicochemical parameters generally show a trend of dry

season>normal season>high season. The analysis of the concentration composition of eight major anions and cations shows that cation Na^+ dominates in water, anions HCO_3^- and SO_4^{2-} dominate in hot spring water, and anions Cl^- and HCO_3^- dominate in geothermal water. As the result of the Fig.E.1(a), the hydrochemical type of geothermal water is $\text{Na-HCO}_3\cdot\text{Cl}$, consistent with literature^[10]. Rich Na, poor Ca, and high pH are the main hydrochemical characteristics of Yangbajing geothermal and hot spring water.

(2) Concentration levels of As and F in geothermal fluids and ecological risk assessment. The total As and

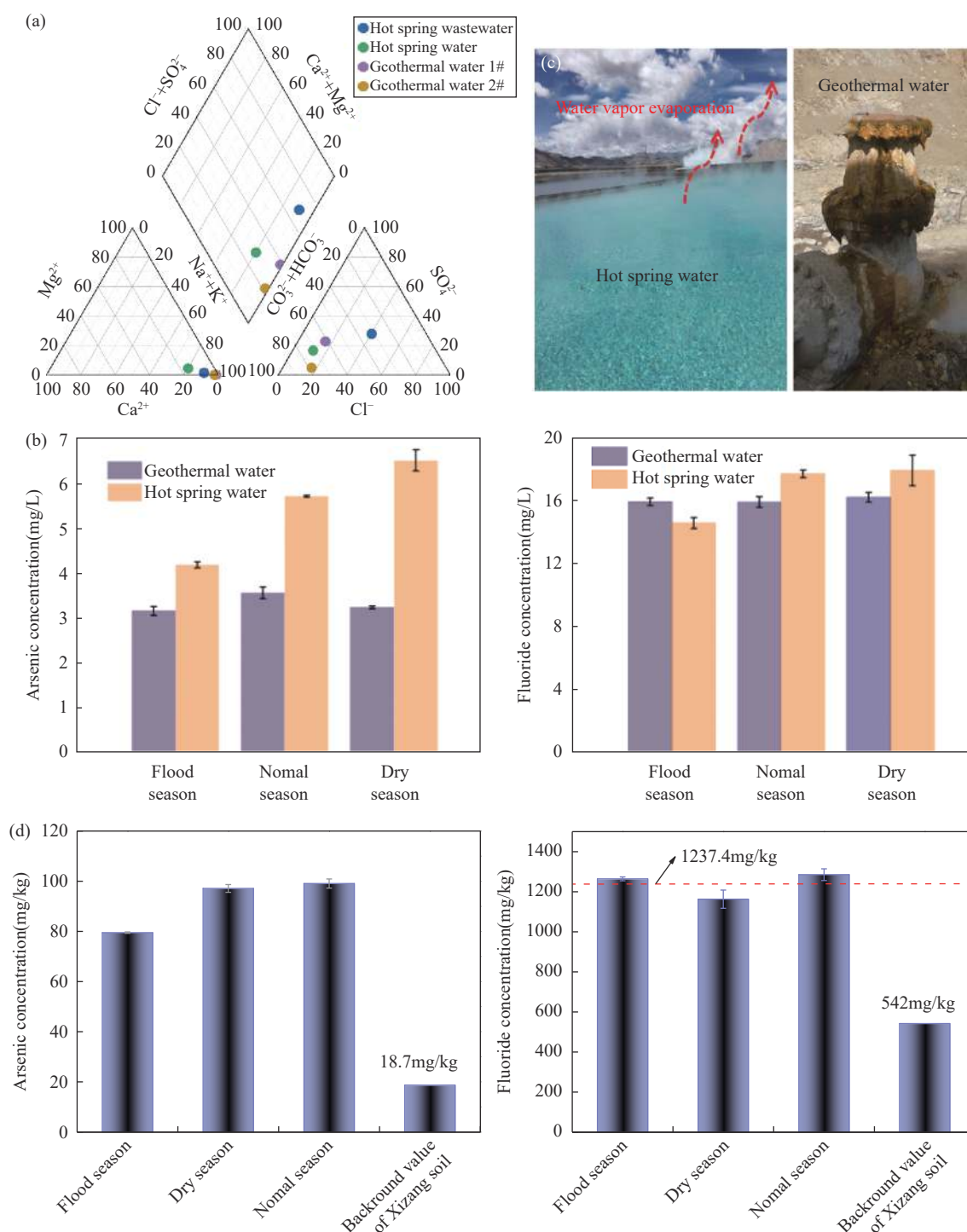


Fig. E.1 Hydrochemical composition of water sample (a), the concentrations of total As and F in water sample (b), pictures of hot spring and geothermal water (c), and the concentrations of total As and F in the soils (d).

F concentrations of Yangbajing geothermal water and hot spring water are shown in Fig.E.1(b). The concentrations of total As and F in geothermal water are 3.16–6.50mg/L and 15.90–17.89mg/L, respectively, which hardly changes with the change of water period. The total As concentration in geothermal water is consistent with the total As concentration in Yangbajing geothermal water reported by Zhang et al.^[10] (3.54–3.56mg/L). The F concentration of geothermal water shows a decreasing trend compared to the reported Yangbajing geothermal water (18.0–18.9mg/L) and Yangyi hydropower station geothermal water (19.2mg/L)^[24]. As shown in Fig.E.1(c), influenced by the evaporation of water, the total concentration of As (4.18–6.50mg/L) and F (14.56–17.89mg/L) in hot spring water are higher than those in geothermal water. The concentration of As and F shows a trend of dry season>normal season>flood season. Notably, the total concentration of As and F in waters are significantly ($P<0.01$) higher than the maximum allowable emission concentrations for harmful components (0.5mg/L for As, and 10mg/L for F) in the *Geothermal Resources Assessment Method* (DZ40—85). Improper treatment of geothermal wastewater may pose exposure risks to As and F in the surrounding environment.

(3) Concentration levels of As and F in soils and ecological risk assessment. Fig.E.1(d) shows the total As and F concentrations of soil samples leached from the wastewater at the hot spring discharge outlet. There is no significant difference in the total As concentration between the dry season and the normal season. The total As concentration ranges from 97.6 to 99.08mg/kg, which is significantly higher ($P<0.01$) than the concentration during the flood season (79.5mg/kg). The total F concentration ranges from 1162.7 to 1285.1mg/kg, showing no significant variation with the seasons. Compared with the background values of total As (18.7mg/kg) and F (542mg/kg) in Xizang soil^[32], the total As and F concentrations in the geothermal area are significantly higher than the background values ($P<0.01$), which are 4.25–5.31 and 2.28 times of the background values respectively. The results show that the soil in the geothermal area is at risk of high As and F pollution.

(4) The main sources of As and F in geothermal water and surface soil are water-rock leaching interaction, and the unique hydrochemical characteristics provide favourable conditions for the leaching of As and F. Rock leaching in the geothermal reservoir is the main resource of As and F enrichment in geothermal water. The geothermal fluids in Yangbajing have a pH value of 7.87–9.42. In addition, some hydroxyl minerals such as muscovite and biotite often undergo ion exchange with F. If the groundwater is alkaline, the exchange is more likely to occur. OH^- can replace F in fluorinated minerals, increasing the concentration of F in geothermal water. It is known that the concentration of F in a water system is restricted by the solubility of fluorite. The alkaline environment caused by the hydrolysis of minerals due to water-rock interaction has a significant impact on the dissolution of fluoride, and the alkaline environment with high concentrations of Na^+ and low concentrations of Ca^{2+} is an important reason for the formation of high fluoride. Additionally, low sulfide concentrations (as low as 16.79mg/L) further promote high arsenic geothermal water. It is worth noting that the geothermal water in Xizang has high sodium (up to 445.5mg/L), low sulfur (16.79–26.3mg/L), low calcium (3.31–6.66mg/L), and weakly alkaline (8.95–9.15), providing better convenient conditions for the dissolution of high As and F in Yangbajing geothermal fluids.

参考文献

- [1] Wang G L, Zhang W, Ma F, et al. Overview on hydrothermal and hot dry rock researches in China[J]. *China Geology*, 2018, 1(2): 273–285.
- [2] 多吉. 典型高温地热系统——羊八井热田基本特征[J]. *中国工程科学*, 2003(1): 42–47.
- [3] 陈卫营, 薛国强, 赵平, 等. 西藏羊八井地热田 SOTEM 探测及热储结构分析[J]. *地球物理学报*, 2023, 66(11): 4805–4816.
- [4] Duo J. The basic characteristics of the Yangbajing geothermal field—A typical high temperature geothermal system[J]. *Strategic Study of CAE*, 2003(1): 42–47.
- [5] Chen W Y, Xue G Q, Zhao P, et al. SOTEM exploration and reservoir structure analysis of Yangbajing geothermal field, Xizang[J]. *Chinese Journal of*

- Geophysics, 2023, 66(11): 4805–4816.
- [4] Wang X, Wang G, Gan H, et al. Genetic mechanisms of sinter deposit zones in the Yangyi geothermal field, Tibet: Evidence from the hydrochemistry of geothermal fluid[J]. *Geothermics*, 2022, 103: 102408.
- [5] 胡志华, 高洪雷, 万汉平, 等. 西藏羊八井地热田水热蚀变的时空演化特征[J]. *地质论评*, 2022, 68(1): 359–374.
- Hu Z H, Gao H L, Wan H P, et al. Temporal and spatial evolution of hydrothermal alteration in the Yangbajing Geothermal Field, Xizang (Tibet)[J]. *Geological Review*, 2022, 68(1): 359–374.
- [6] 刘高令, 姜贞贞, 刘高博, 等. 西藏地区羊八井地热水中胶体粒子分析与表征[J]. *岩矿测试*, 2023, 42(6): 1156–1164.
- Liu G L, Jiang Z Z, Liu G B, et al. Analysis and characterization of colloidal particles in Yangbajing geothermal water, Tibet[J]. *Rock and Mineral Analysis*, 2023, 42(6): 1156–1164.
- [7] 赵平, 金建, 张海政, 等. 西藏羊八井地热田热水的化学组成[J]. *地质科学*, 1998(1): 62–73.
- Zhao P, Jin J, Zhang H Z, et al. Chemical composition of thermal water in the Yangbajing geothermal field, Tibet[J]. *Scientia Geologica Sinica*, 1998(1): 62–73.
- [8] 孙红丽, 马峰, 蔺文静, 等. 西藏高温地热田地球化学特征及地热温标应用[J]. *地质科技情报*, 2015, 34(3): 171–177.
- Sun H L, Ma F, Lin W J, et al. Geochemical characteristics and geothermometer application in high-temperature geothermal field in Tibet[J]. *Geological Science and Technology Information*, 2015, 34(3): 171–177.
- [9] 刘勇, 王阳, 布多, 等. 羊八井地热水中金属特征分析及对周边环境的影响[J]. *西藏科技*, 2014(9): 22–24.
- Liu Y, Wang Y, Bu D, et al. Characterization of metals in geothermal water from Yangbajing and their impact on the surrounding environment[J]. *Tibet Science and Technology*, 2014(9): 22–24.
- [10] 张庆, 谭红兵, 渠涛, 等. 西藏地热水中典型有害元素对河流水质的影响[J]. *水资源保护*, 2014, 30(4): 23–29.
- Zhang Q, Tan H B, Qu T, et al. Impacts of typical harmful elements in geothermal water on river water quality in Tibet[J]. *Water Resources Protection*, 2014, 30(4): 23–29.
- [11] 魏晓阳, 郭清海, 袁建飞, 等. 高温地热流体来源氟在环境中的分布特征——以西藏羊八井热田为例[J]. *东华理工大学学报(自然科学版)*, 2009, 32(1): 38–44.
- Wei X Y, Guo Q H, Yuan J F, et al. Environmental migration and transformation of fluoride from high-temperature geothermal fluid: A case study at Yangbajing, Tibet, China[J]. *Journal of East China Institute of Technology*, 2009, 32(1): 38–44.
- [12] 郭清海, 叶露, 魏晓阳, 等. 富砷地热废水排放的水环境效应——以西藏羊八井热田为例[J]. *环境科学与技术*, 2009, 32(9): 116–119, 128.
- Guo Q H, Ye L, Wei X Y, et al. Water-environmental effects induced by discharging geothermal wastewater with high as levels: A case study at Yangbajing in Tibet[J]. *Environmental Science & Technology*, 2009, 32(9): 116–119, 128.
- [13] Guo Q H, Wang Y X, Liu W. Major hydrogeochemical processes in the two reservoirs of the Yangbajing geothermal field, Tibet, China[J]. *Journal of Volcanology and Geothermal Research*, 2007, 166(3): 255–268.
- [14] Zheng T, Deng Y, Lin H, et al. Hydrogeochemical controls on As and B enrichment in the aqueous environment from the Western Tibetan Plateau: A case study from the Singe Tsangpo River Basin[J]. *Science of the Total Environment*, 2022, 817: 152978.
- [15] 孙红丽, 马峰, 刘昭, 等. 西藏高温地热显示区氟分布及富集特征[J]. *中国环境科学*, 2015, 35(1): 251–259.
- Sun H L, Ma F, Liu Z, et al. The distribution and enrichment characteristics of fluoride in geothermal active area in Tibet[J]. *China Environmental Science*, 2015, 35(1): 251–259.
- [16] Li S, Wang M, Yang Q, et al. Enrichment of arsenic in surface water, stream sediments and soils in Tibet[J]. *Journal of Geochemical Exploration*, 2013, 135: 104–116.
- [17] Guo Q, He T, Wu Q, et al. Constraints of major ions and arsenic on the geological genesis of geothermal water: Insight from a comparison between Xiong'an and Yangbajing, two hydrothermal systems in China[J]. *Applied Geochemistry*, 2020, 117: 104589.
- [18] Guo Q H, Planer-Friedrich B, Liu M L, et al. Magmatic fluid input explaining the geochemical anomaly of very high arsenic in some Southern Tibetan geothermal waters[J]. *Chemical Geology*, 2019, 513: 32–43.
- [19] Qiao W, Cao W, Gao Z, et al. Contrasting behaviors of groundwater arsenic and fluoride in the lower reaches of the Yellow River Basin, China: Geochemical and modeling evidences[J]. *Science of the Total Environment*, 2022, 851: 158134.
- [20] 王妍妍, 曹文庚, 潘登, 等. 豫北平原地下水高砷和高氟分布规律与成因[J]. *岩矿测试*, 2022, 41(6):

- 1095–1109.
- Wang Y Y, Cao W G, Pan D, et al. Distribution and origin of high arsenic and fluoride in groundwater of the North Henan Plain[J]. *Rock and Mineral Analysis*, 2022, 41(6): 1095–1109.
- [21] 孙明露. 西藏羊八井地区地热资源水化学特征与成因机制研究[D]. 拉萨: 西藏大学, 2023.
- Sun M L. Hydrochemical characteristics and genetic mechanism of geothermal resource in the Yangbajing area, Tibet[D]. Lhasa: Tibet University, 2023.
- [22] 马丹, 鲍新华, 张大勇, 等. 拉萨河羊八井剖面水化学特征及水质评价[J]. *科学技术与工程*, 2018, 18(15): 190–195.
- Ma D, Bao X H, Zhang D Y, et al. Hydro-chemical characteristics and water quality evaluation of the Yangbajing section in the Lhasa River Basin[J]. *Science Technology and Engineering*, 2018, 18(15): 190–195.
- [23] 布多, 李明礼, 许祖银, 等. 西藏拉萨河流域巴嘎雪湿地水化学特征[J]. *中国环境科学*, 2016, 36(3): 793–797.
- Bu D, Li M L, Xu Z Y, et al. Study on aquatic chemistry characteristics of Bagaxue wetland in Lhasa River Basin, Tibet[J]. *China Environmental Science*, 2016, 36(3): 793–797.
- [24] Guo Q. Hydrogeochemistry of high-temperature geothermal systems in China: A review[J]. *Applied Geochemistry*, 2012, 27(10): 1887–1898.
- [25] Planer-Friedrich B, London J, Mccleskey R B, et al. Thioarsenates in geothermal waters of Yellowstone National Park: Determination, preservation, and geochemical importance[J]. *Environmental Science and Technology*, 2007, 41(15): 5245–5251.
- [26] Yoshizuka K, Nishihama S, Sato H. Analytical survey of arsenic in geothermal waters from sites in Kyushu, Japan, and a method for removing arsenic using magnetite[J]. *Environmental Geochemistry and Health*, 2010, 32(4): 297–302.
- [27] Kundu N, Panigrahi M K, Sharma S P, et al. Delineation of fluoride contaminated groundwater around a hot spring in Nayagarh, Orissa, India using geochemical and resistivity studies[J]. *Environmental Geology*, 2002, 43(1-2): 228–235.
- [28] Birkle P, Merkle B. Environmental impact by spill of geothermal fluids at the geothermal field of Los Azufres, Michoacan, Mexico[J]. *Water Air and Soil Pollution*, 2000, 124(3-4): 371–410.
- [29] Sracek O, Wanke H, Ndakunda N N, et al. Geochemistry and fluoride levels of geothermal springs in Namibia[J]. *Journal of Geochemical Exploration*, 2015, 148: 96–104.
- [30] Stefánsson A, Arnórsson S. Feldspar saturation state in natural waters[J]. *Geochimica et Cosmochimica Acta*, 2000, 64(15): 2567–2584.
- [31] Gherardi F, Panichi C, Gonfiantini R, et al. Isotope systematics of C-bearing gas compounds in the geothermal fluids of Larderello, Italy[J]. *Geothermics*, 2005, 34(4): 442–470.
- [32] 张晓平. 西藏土壤环境背景值的研究[J]. *地理科学*, 1994(1): 49–55.
- Zhang X P. A study on the background values of soil environment in Tibet[J]. *Geoscience*, 1994(1): 49–55.
- [33] 陈刚. 岩溶型地热尾水排放对周边环境的影响[J]. *化工矿产地质*, 2021, 43(2): 144–149.
- Chen G. Influence of karst geothermal tail water discharge on peripheral environment[J]. *Geology of Chemical Minerals*, 2021, 43(2): 144–149.
- [34] 冯卫卫, 罗锡明, 刘丹丹. 寨上金矿矿区河流沉积物中砷的形态分析[J]. *生态环境学报*, 2011, 20(4): 659–662.
- Feng W W, Luo X M, Liu D D. Speciation of arsenic in sediment of the river around Zhaishang goldmine[J]. *Ecology and Environmental Sciences*, 2011, 20(4): 659–662.
- [35] 刘丹青, 朱梦杰, 汤琳. 上海市土壤氟含量风险管控限值探讨[J]. *中国环境监测*, 2021, 37(4): 128–134.
- Liu D Q, Zhu M J, Tang L. Discussion on risk control limits of soil fluorine content in Shanghai[J]. *Environmental Monitoring in China*, 2021, 37(4): 128–134.
- [36] 杨惠. 云南省洱源县高氟温泉水中氟的来源及其对周围环境影响分析[D]. 昆明: 云南师范大学, 2015.
- Yang H. Analysis of the source of fluorine in high-fluorine hot spring water and its impact on the surrounding environment in Eryuan County, Yunnan Province[D]. Kunming: Yunnan Normal University, 2015.