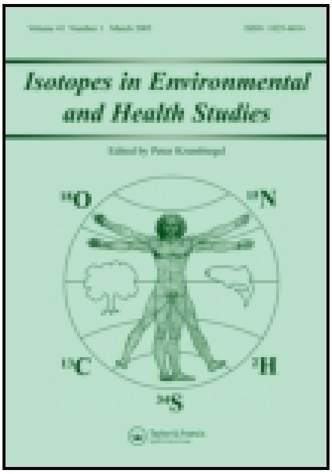
This article was downloaded by: [University of Birmingham]
On: 10 January 2015, At: 18:43
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Isotopes in Environmental and Health Studies
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gieh20

Lead and strontium isotopes as indicators for mixing processes of waters in the former mine 'Himmelfahrt Fundgrube', Freiberg (Germany)

Claudia Heidel [a], Marion Tichomirowa [a] & Jörg Matschullat [a]

[a] Institute of Mineralogy, Technische Universität Bergakademie Freiberg, Brennhausgasse 14, 09596, Freiberg, Germany

Published online: 27 Nov 2007.

To cite this article: Claudia Heidel, Marion Tichomirowa & Jörg Matschullat (2007) Lead and strontium isotopes as indicators for mixing processes of waters in the former mine 'Himmelfahrt Fundgrube', Freiberg (Germany), Isotopes in Environmental and Health Studies, 43:4, 339-354, DOI: 10.1080/10256010701701657

To link to this article: http://dx.doi.org/10.1080/10256010701701657

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms &

Isotopes in Environmental and Health Studies
Vol. 43, No. 4, December 2007, 339–354

Lead and strontium isotopes as indicators for mixing processes of waters in the former mine 'Himmelfahrt Fundgrube', Freiberg (Germany)[†]

CLAUDIA HEIDEL*, MARION TICHOMIROWA and JÖRG MATSCHULLAT

Institute of Mineralogy, Technische Universität Bergakademie Freiberg, Brennhausgasse 14,
09596 Freiberg, Germany

(Received 15 January 2007; in final form 21 September 2007)

To pinpoint the origin and mixing processes of mine waters, different mine water types from the polymetallic sulphide ore deposit 'Himmelfahrt Fundgrube' (Freiberg, Germany) were analysed by thermal ionisation mass spectrometry using lead and strontium isotope ratios.

Results show that the lead isotope composition of different mine waters results from a mixture of at least two sources: released lead from oxidised sulphide ores (mainly galena) and anthropogenic lead from groundwater. Furthermore, there are indications for an additional lead source. Strontium isotopes in mine waters identify at least three different sources: released strontium from weathered host rock (Grey Gneisses), released strontium from weathered gangue carbonates, and probably strontium from anthropogenic inputs. Contrary to former oxygen and sulphur isotope studies, strontium isotope compositions as well as hydrochemical parameters show the important role of gangue carbonates as an element source in mine waters.

Keywords: Mine water; Lead isotopes; Strontium isotopes; Sulphide oxidation

1. Introduction

Due to differences in the isotopic compositions of different minerals and atmospheric (anthropogenic) inputs, lead and strontium isotopes are a powerful tool for the identification of solute sources and mixing processes in waters [e.g. 1–13].

Lead may be released in mine waters due to sulphide weathering (especially galena) and is only partly fixed in secondary minerals (mainly anglesite) [14]. Therefore, lead isotopes can be used to distinguish ore-related lead from other solute sources. Due to host rock weathering, strontium isotopes likewise characterize solute sources of strontium and in case of several sources may help to understand water mixing processes. This is important in regions of acid

---

[†] Revised version of a paper presented at the 27th Annual Meeting of the German Association for Stable Isotope Research (GASIR), October, 4–6, 2006, Freiberg, Germany.

*Corresponding author. Tel.: +49-3731-392-656; Fax: +49-3731-393-129; Email: claudia.heidel@mineral.tu-freiberg.de

Isotopes in Environmental and Health Studies
ISSN 1025-6016 print/ISSN 1477-2639 online
http://www.tandf.co.uk/journals
DOI: 10.1080/10256010701701657

mine drainage, where continuous water and oxygen supply lead to the oxidation of remaining ores in abandoned sulphide mines. The polymetallic sulphide ore deposit ‘Himmelfahrt Fundgrube’ in Freiberg (Germany) is known to release acidic and trace metal-bearing mine waters that pollute surface waters via culverts [e.g. 14–16].

Oxygen and sulphur isotope studies in this mine have shown that sulphate in mine waters and culverts results from two major sources: groundwater and oxidized sulphide ores [17–20]. Lead and strontium isotope investigations in different mine waters accompanied by hydrochemical investigations can probably reveal additional sources and mixing processes; important to understand long-term changes in water chemistry of mine waters and drainage galleries. Without this knowledge it is almost impossible to predict the decrease of acid mine drainage for the next few decades or to propose attenuation methods.

2. Regional setting

The mining district ‘Himmelfahrt Fundgrube’ is located in the central part of the polymetallic sulphide ore deposit Freiberg, Saxony (Germany) – one of the largest ore lode deposits in Europe (figure 1). The ore lodes were formed when hydrothermal solutions penetrated into the Grey Gneiss dome (consisting mainly of plagioclase, quartz, mica) in two mineralization events: the Late Variscan (310–240 Ma) and the Post Variscan (140–60 Ma) [21]. The dominating Late Variscan mineralization event consists primarily of the quartz-polymetallic assemblage (qp assemblage). It mainly contains the sulphide minerals galena (PbS), pyrite (FeS_2), sphalerite (ZnS), and arsenopyrite (FeAsS), and mainly quartz and minor carbonates as gangue minerals. The Post Variscan mineralization event consists of the fluorite–barite–lead ore assemblage (fba assemblage) that contains mainly galena, sphalerite, and pyrite, and in addition to quartz also carbonates (calcite, dolomite, siderite, ankerite, rhodochrosite [14]), fluorite, and barite as gangue minerals [22].

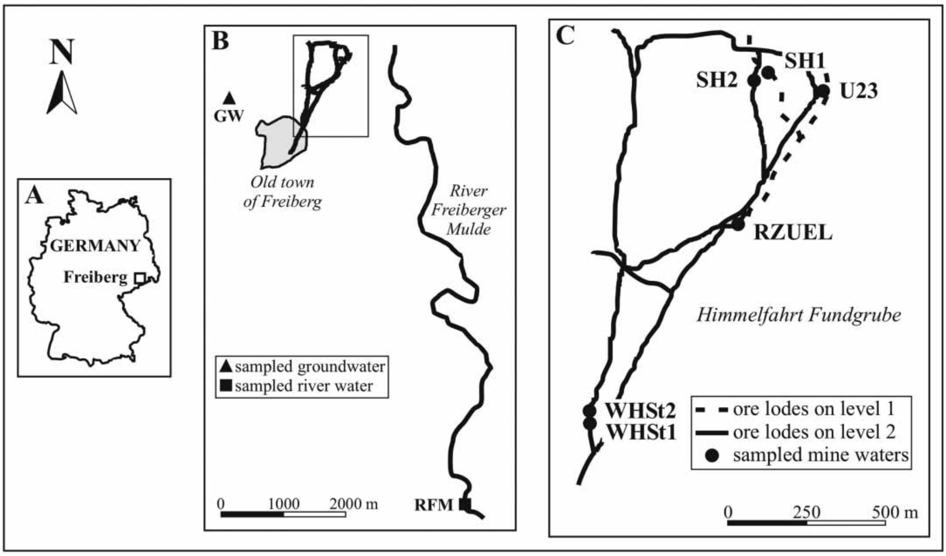


Figure 1. A: Location of the Freiberg region in Germany. B: More detailed map of the Freiberg region with sampling points of groundwater (GW) and river water (RFM) and the location of the ‘Himmelfahrt Fundgrube’ north-eastern of the old town of Freiberg. C: Detailed map of the ‘Himmelfahrt Fundgrube’ with sampling points of mine waters (pool water: WHSt1, WHSt2; flowing mine water: SH1, SH2; flooding water: RZUEL; drip water: U23) (compare figure 2).

The 'Himmelfahrt Fundgrube' was mined for silver, lead, copper, and zinc for more than 800 years until its closure in 1969. From 1969 to 1971, the mine was flooded to a depth of about 227 m below surface–the level of the deepest and most important drainage gallery, the 'Rothschönberger Stollen'.

Dispersed low-grade ores in altered host rock are being oxidized above the flooded part of the mine until today because of continuous water and air supply. Sulphide oxidation of the remaining ores forms pore waters with low pH values and high sulphate and trace metal contents [14–16]. (In this paper, the term 'pore water' is only used for pore waters that are affected by sulphide oxidation.) These pore waters drip gravitatively from the weathering matrix and accumulate on the bottom of mine levels in red-coloured pools. That is why this mine water type is called 'pool water' in the following.

Groundwater flows along mined and backfilled ore lodes towards the drainage galleries and mixes with pore waters formed by oxidation of Late Variscan (qp assemblage) or Post Variscan sulphide ores (fba assemblage). Groundwater that mixes with Late Variscan pore water was sampled where groundwater flows continuously and is, therefore, called 'flowing mine water' in the following.

In some places, the flow rate of groundwater is so low that the water only drips from fissures and does not flow continuously ('drip water'). The sampled drip water consists of groundwater and pore water from oxidised Post Variscan sulphide ores.

In the flooded part of the mine vertical streaming mineralized groundwater (approximately 2 m^3/min) mixes with horizontal streaming uncontaminated groundwater (approximately 2 m^3/min) [23] (figure 2). This mixture is called 'flooding water' in the following.

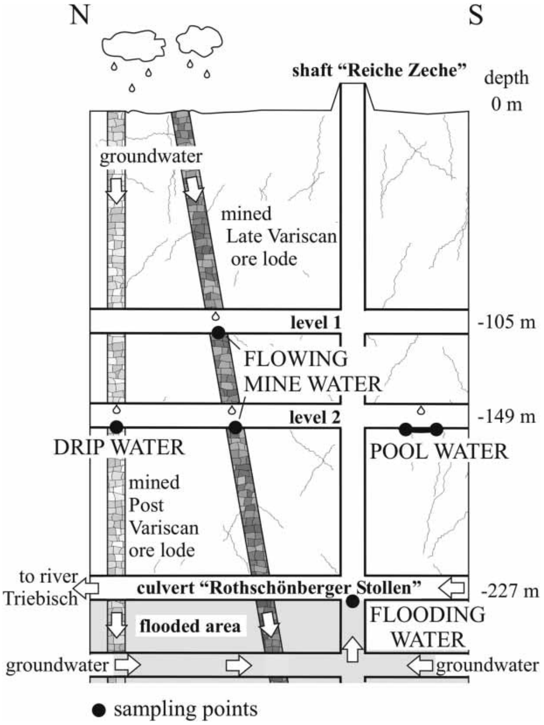


Figure 2. Profile through the mine 'Himmelfahrt Fundgrube' in Freiberg. Four major mine water types (pool water, flowing mine water, flooding water, drip water) are shown schematically.

3. Methods

3.1 *Sampling*

Four major mine water types were sampled in polypropylene bottles at six sampling points (figures 1C and 2) between December 2005 and March 2006.

Pore water formed by oxidation of Late Variscan sulphides (qp assemblage) was sampled as pool water (WHSt1, WHSt2) twice within the investigation period from a pool in the ore lode 'Wilhelm Stehender' (qp assemblage), 149 m below surface (level 2). The distance of the two sampling points was about 3 meters.

Groundwater that flows along the ore lode system 'Schwarzer Hirsch Stehender'(qp assemblage) was sampled as flowing mine water (SH1, SH2) ten times within the investigation period on two levels: 105 m below surface (level 1) and 149 m below surface (level 2). Both sampling points are hydraulically connected, as shown by tracer experiments with NaCl [24].

Sulphur isotope investigations of sulphate have shown that the drip water (U23) from level 2 consists of groundwater and pore water from the Post Variscan fba assemblage [19]. To prove this fact with lead and strontium isotopes, it was sampled once.

Flooding water (RZUEL) was sampled 227 m below surface, where water from the flooded area of the mine raises up in the shaft 'Reiche Zeche' until it leaves the mine via the drainage gallery 'Rothschönberger Stollen' into the river Triebisch. Flooding water was sampled ten times within four months.

To compare isotope compositions of mine waters with potential lead and strontium sources, galena and carbonate from the Freiberg mine, groundwater, and water from the river Freiberger Mulde were analysed. Galena (PbS) from the Late Variscan qp assemblage and from the Post Variscan fba assemblage were taken from archives. Furthermore, archival Late Variscan carbonate from the ore lode 'Gottlob Morgengang' (carbonate 1), from the ore lode 'Kirschbaum Stehender' (carbonate 2), and from the ore lode 'Christian/Erzengel Stehender' (carbonate 3) were analysed. Groundwater, which is not affected by the mine, was sampled in June 2007 from a monitoring well on the campus of the TU Bergakademie Freiberg (GWM 5, sampling depth: 15 m below surface). Surface water from the river Freiberger Mulde (RFM) was sampled twice (November 2006 and May 2007). The sampling point was located about 10 km upstream from the mine, where the river is not affected by mine waters (figure 1B).

3.2 *Sample preparation*

Water samples were dried at 130°C. The evaporated volume varied between 0.1 and 200 ml for lead and between 2 and 40 ml for strontium depending on the estimated concentrations. The residues were dissolved in 0.5 N HBr (1 ml) for lead analyses and in 2.5 N HCl (1 ml) for strontium analyses. About 50 mg of both galena samples were digested for 36 h in a HNO_3-HF-mixture (3 ml) at 110°C. They were then evaporated and redissolved in 6 N HCl (3 ml), evaporated again and redissolved in 0.5 N HBr (1 ml). About 20 mg of each carbonate sample were dissolved in 2 N HCl (1 ml) at 70°C. They were then evaporated and redissolved in 2.5 N HCl (1 ml).

Lead and strontium separation followed standard procedures of exchange chromatography. Lead was separated using an anion-exchange column with 200 µl Bio-Rad AG 1-X8 (100–200 mesh, chloride form). After washing and conditioning the column with H_2O, 6 N HCl, and 0.5 N HBr, lead was eluted with 6 N HCl [25]. The eluate was evaporated and redissolved in distilled water (5 µl). A portion of 3 µl was loaded onto a single rhenium filament using the silica gel technique [26].

Strontium was extracted by cation-exchange chromatography with about 4 ml Dowex 50WX8 (200–400 mesh) and 2.5 N HCl as eluent. After evaporation and solution of the residue in distilled water (10 μl), the sample was loaded onto a single tantal filament with 1 N H_3PO_4.

3.3 *Isotope analyses*

Lead and strontium isotope ratios were measured with the thermal ionization mass spectrometer Finnigan MAT 262. Relative errors ($2\sigma_M$) lie between 0.01 and 0.38 % for ^{206}Pb/^{204}Pb, between 0.01 and 0.37 % for ^{207}Pb/^{204}Pb, between 0.01 and 0.38 % for ^{208}Pb/^{204}Pb, and between 0.003 and 0.03 % for ^{87}Sr/^{86}Sr. Average lead isotope ratios of the NBS 981 standard ($n = 8$) in the period of analysis were 16.9129 ± 0.0017 (2σ) for ^{206}Pb/^{204}Pb, 15.4616 ± 0.0019 (2σ) for ^{207}Pb/^{204}Pb, and 36.646 ± 0.036 (2σ) for ^{208}Pb/^{204}Pb, slightly lower than the certified values (16.9405 ± 0.0015 for ^{206}Pb/^{204}Pb, 15.4963 ± 0.0016 for ^{207}Pb/^{204}Pb, and 36.7219 ± 0.0044 for ^{208}Pb/^{204}Pb [27]). Replicate analyses of the NBS 987 standard ($n = 26$) gave an average ^{87}Sr/^{86}Sr ratio of 0.710289 ± 0.000046 (2σ), slightly higher than the certified value of 0.71025 [28].

Compared to the analysed lead and strontium amounts, total procedural blanks were negligible (2.4 and 1 ng, respectively).

3.4 *Hydrochemical and chemical analyses*

pH values in waters were measured on site by a WTW pH 340 with a SenTix 41 sensor. Anion, cation, trace metal, and strontium concentrations were measured at the Geochemical-Analytical Laboratory of the Institute of Mineralogy, Freiberg. Bicarbonate was determined by acidic titration with 0.01 N H_2SO_4. Sulphate was measured by ion chromatograpy and calcium and magnesium were analysed by flame-AAS. Lead, strontium, iron, and zinc were measured by ICP-OES and ETA-AAS depending on the estimated concentrations. Precision for sulphate, cations, trace metals, and strontium was between 5 and 10 %.

4. Results

4.1 *Hydrochemical investigations*

Pool water (WHSt1, WHSt2) is characterized by low pH values (2.5) and extremely high sulphate, calcium, magnesium, iron, lead, and zinc concentrations (table 1 and 2). In contrast, strontium in pool water (115 μg/l) is not enriched.

Sulphate, cation, and trace metal concentrations of flowing mine water from level 1 (SH1) are relatively low. Flowing mine water from level 2 (SH2) has obviously higher sulphate, iron, lead, and zinc contents, but lower pH values and, thus, lower bicarbonate concentrations. Calcium and magnesium concentrations from level 1 and 2 agree within errors. Strontium concentrations in flowing mine waters are as high as in pool water and remain constant from level 1 to level 2 (mean = 120 μg/l).

Flooding water (RZUEL) shows a slightly acidic pH value (6.1), but high anion, cation, and trace metal concentrations. Drip water (U23) has a similar hydrochemical composition with a neutral pH value (7.2) and high anion and trace metal concentrations. Both flooding and drip water are distinct from other investigated mine waters by obviously higher strontium concentrations (660 and 220 μg/l, respectively). The lead concentration in drip water is remarkably

Table 1. Average (± standard deviation) pH values and ion concentrations of pool water, flowing mine water, flooding water, drip water, groundwater, and river water ($n = 10$ for SH1, SH2, and RZUEL; $n = 2$ for WHSt1, WHSt2, and RFM; and $n = 1$ for U23 and GW).

Sample	pH	SO_4^{2-} [mg/l]	HCO_3^- [mg/l]	Ca^{2+} [mg/l]	Mg^{2+} [mg/l]
Pool water					
WHSt1	2.5 ± 0.0	41000 ± 2000	0	460 ± 20	2300 ± 200
WHSt2	2.5 ± 0.0	40000 ± 2000	0	460 ± 30	2200 ± 200
Flowing mine water					
SH1	5.7 ± 0.2	96 ± 9	3.4 ± 0.3	32 ± 1	8.9 ± 0.4
SH2	3.9 ± 0.1	113 ± 17	0	33 ± 2	9.3 ± 0.6
Flooding water					
RZUEL	6.1 ± 0.0	830 ± 60	83.7 ± 1.7	240 ± 10	47 ± 3
Drip water					
U23	7.2	290	223	120	37
Groundwater					
GW	5.8	111	23.2	45	12
River water					
RFM	7.7 ± 0.3	37 ± 7	35.4 ± 1.2	20 ± 2.8	4.9 ± 0.4

Table 2. Average (± standard deviation) trace metal concentrations of pool water, flowing mine water, flooding water, drip water, groundwater and river water ($n = 10$ for SH1, SH2, and RZUEL; $n = 2$ for WHSt1, WHSt2, and RFM; and $n = 1$ for U23 and GW).

Sample	Fe [mg/l]	Pb [mg/l]	Sr [mg/l]	Zn [mg/l]
Pool water				
WHSt1	5000 ± 200	36 ± 1	0.120 ± 0.003	5700 ± 200
WHSt2	5000 ± 300	36 ± 1	0.110 ± 0.007	5800 ± 200
Flowing mine water				
SH1	0.039 ± 0.041	0.043 ± 0.015	0.120 ± 0.004	1.7 ± 0.1
SH2	0.500 ± 0.249	0.690 ± 0.260	0.120 ± 0.004	4.4 ± 1.4
Flooding water				
RZUEL	0.560 ± 0.040	0.013 ± 0.012	0.660 ± 0.011	12 ± 0.5
Drip water				
U23	1.3	0.003	0.220	1.2
Groundwater				
GW	0.159	0.012	0.171	0.102
River water				
RFM	0.169 ± 0.094	0.008 ± 0.002	0.101 ± 0.003	0.010 ± 0.003

low (3 μg/l) in comparison to other mine waters, but the iron concentration in drip water is more than double that of flowing mine water from the same level (SH2).

Uncontaminated groundwater has a slightly acidic pH value (5.8) and anion, cation, and trace metal concentrations that are about twice as high as those from a groundwater sampled in the region of Freiberg in 2002 [19]. The lead concentration in groundwater (12 μg/l) agrees with concentrations in flooding water, whereas the strontium concentration in groundwater is lower than those in flooding water and drip water, but higher than those in flowing mine water.

Water from the river Freiberger Mulde (RFM) is slightly alkaline (pH = 7.7). Despite higher pH value, the river water contains less bicarbonate than flooding water and drip water. Sulphate, calcium, magnesium, lead, strontium, and zinc concentrations are low in comparison to mine waters.

4.2 *Lead isotope investigations*

Ratios for pool water vary from 18.125 to 18.163 (^{206}Pb/^{204}Pb), from 15.606 to 15.659 (^{207}Pb/^{204}Pb), and from 38.286 to 38.465 (^{208}Pb/^{204}Pb). They are significantly higher (t-test, $\alpha = 0.01$) than lead ratios from flowing mine water, flooding water, and drip water. Differences between ratios from two different sampling points of pool water (WHSt1, WHSt2) are caused by incomplete mixing of the pool (table 3 and figure 3).

Galena from the Late Variscan qp assemblage has lower lead isotope ratios than that from the Post Variscan fba assemblage confirming previous results of lead isotope ratios in the

Table 3. Lead concentrations, flow rates, and lead isotope data of pool water, flowing mine water, flooding water, drip water, groundwater, river water, and galena (n.a. = not analysed).

Sample	Sampling date	Pb [μg/l]	Flow rate [l/min]	$^{206}\mathrm{Pb}/^{204}\mathrm{Pb} \pm 2\sigma_\mathrm{M}$	$^{207}\mathrm{Pb}/^{204}\mathrm{Pb} \pm 2\sigma_\mathrm{M}$	$^{208}\mathrm{Pb}/^{204}\mathrm{Pb} \pm 2\sigma_\mathrm{M}$
WHSt1	05/12/05	37000		18.163 ± 0.009	15.659 ± 0.009	38.465 ± 0.022
	06/02/06	35000		18.156 ± 0.006	15.652 ± 0.007	38.432 ± 0.023
WHSt2	05/12/05	34000		18.125 ± 0.008	15.606 ± 0.008	38.286 ± 0.019
	06/02/06	37000		18.142 ± 0.004	15.633 ± 0.003	38.370 ± 0.008
SH1	05/12/05	74	15.8	18.074 ± 0.047	15.556 ± 0.040	38.116 ± 0.102
	19/12/05	n.a.	60.0	18.062 ± 0.018	15.544 ± 0.015	38.075 ± 0.037
	09/01/06	41	74.4	18.098 ± 0.011	15.572 ± 0.009	38.151 ± 0.023
	23/01/06	48	36.0	18.107 ± 0.018	15.584 ± 0.016	38.179 ± 0.038
	30/01/06	45	43.6	18.063 ± 0.007	15.545 ± 0.006	38.086 ± 0.016
	06/02/06	47	35.2	18.061 ± 0.004	15.547 ± 0.003	38.093 ± 0.008
	20/02/06	44	100.0	18.041 ± 0.008	15.527 ± 0.007	38.036 ± 0.018
	27/02/06	39	144.9	18.062 ± 0.007	15.536 ± 0.006	38.064 ± 0.014
	13/03/06	11	120.0	18.069 ± 0.027	15.547 ± 0.015	38.099 ± 0.039
	20/03/06	36	122.8	18.066 ± 0.003	15.548 ± 0.003	38.094 ± 0.007
SH2	05/12/05	1300	13.2	18.054 ± 0.015	15.563 ± 0.011	38.157 ± 0.033
	19/12/05	500	35.0	18.049 ± 0.019	15.538 ± 0.016	38.055 ± 0.040
	09/01/06	600	44.6	18.058 ± 0.004	15.548 ± 0.004	38.081 ± 0.009
	23/01/06	800	26.5	18.064 ± 0.007	15.554 ± 0.006	38.095 ± 0.014
	30/01/06	810	33.4	18.059 ± 0.005	15.547 ± 0.007	38.089 ± 0.012
	06/02/06	870	25.9	18.057 ± 0.005	15.557 ± 0.003	38.104 ± 0.009
	20/02/06	500	54.3	18.032 ± 0.015	15.549 ± 0.007	38.073 ± 0.020
	27/02/06	510	63.3	18.055 ± 0.004	15.546 ± 0.003	38.078 ± 0.009
	13/03/06	440	60.0	18.059 ± 0.003	15.546 ± 0.002	38.073 ± 0.006
	20/03/06	540	70.1	18.057 ± 0.006	15.546 ± 0.005	38.098 ± 0.020
RZUEL	05/12/05	n.a.		18.088 ± 0.002	15.539 ± 0.002	38.079 ± 0.004
	19/12/05	10		18.158 ± 0.061	15.601 ± 0.053	38.186 ± 0.127
	09/01/06	10		18.109 ± 0.010	15.574 ± 0.008	38.190 ± 0.021
	23/01/06	11		18.092 ± 0.014	15.559 ± 0.011	38.162 ± 0.034
	30/01/06	12		18.090 ± 0.014	15.546 ± 0.012	38.110 ± 0.031
	06/02/06	10		18.053 ± 0.017	15.516 ± 0.018	38.028 ± 0.046
	20/02/06	7.5		18.094 ± 0.017	15.546 ± 0.015	38.095 ± 0.035
	27/02/06	8.6		18.105 ± 0.017	15.554 ± 0.015	38.117 ± 0.036
	13/03/06	47		18.105 ± 0.018	15.554 ± 0.016	38.135 ± 0.028
	20/03/06	8.8		18.110 ± 0.014	15.559 ± 0.012	38.134 ± 0.021
U23	06/02/06	3.0		18.035 ± 0.039	15.593 ± 0.035	37.786 ± 0.083
GW	08/06/07	12		18.033 ± 0.068	15.558 ± 0.057	37.940 ± 0.143
RFM	07/11/06	9.1		18.158 ± 0.009	15.565 ± 0.008	38.139 ± 0.019
Galena (qp)				18.147 ± 0.004	15.656 ± 0.005	38.433 ± 0.013
Galena (fba)				18.413 ± 0.011	15.668 ± 0.012	38.698 ± 0.038

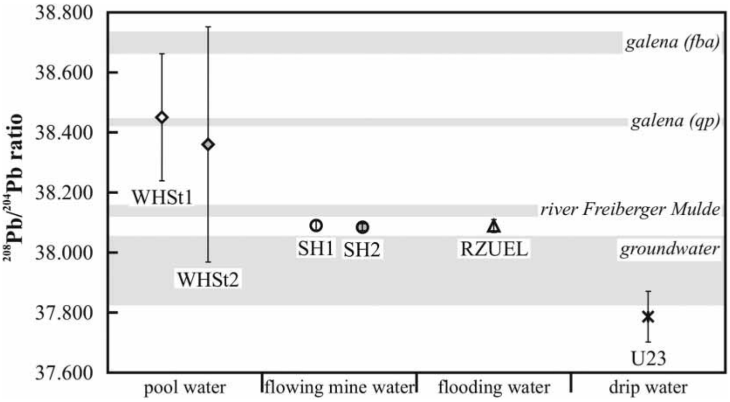


Figure 3. Weighted average ^{208}Pb/^{204}Pb ratios of mine waters ($n = 2$ for WHSt1 and WHSt2, $n = 10$ for SH1, SH2 and RZUEL, and $n = 1$ for U23). Grey shaded areas show ^{208}Pb/^{204}Pb ratios of galena from the quartz-polymetallic assemblage (qp) and fluor-baryte-lead ore assemblage (fba) and ^{208}Pb/^{204}Pb ratios of groundwater and river water according to table 3.

polymetallic sulphide ore deposit Freiberg [29, 30]. Ratios from galena (qp) correspond with pool water.

Flowing mine water from different levels (SH1, SH2) does not differ in its lead ratios (t-test, $\alpha = 0.01$). Lead isotope ratios range between 18.032 and 18.107 (^{206}Pb/^{204}Pb), between 15.525 and 15.584 (^{207}Pb/^{204}Pb), and between 38.036 and 38.179 (^{208}Pb/^{204}Pb). Lead fluxes clearly increase from level 1 to level 2, whereas flow rates at level 2 decline to about 63 % of the flow rates from level 1 (mean of ten measurements). All correlation coefficients between lead ratios and flow rates are smaller than 0.5 except for SH2 for ^{207}Pb/^{204}Pb (−0.61) and for ^{208}Pb/^{204}Pb (−0.55).

Flooding water (RZUEL) shows ^{206}Pb/^{204}Pb ratios from 18.053 to 18.158, ^{207}Pb/^{204}Pb ratios from 15.516 to 15.601, and ^{208}Pb/^{204}Pb ratios from 38.028 to 38.190, which cannot be distinguished from those of flowing mine water (t-test, $\alpha = 0.01$).

Lead ratios from drip water (U23) are lower (^{206}Pb/^{204}Pb = 18.035, ^{208}Pb/^{204}Pb = 37.786) and higher (^{207}Pb/^{204}Pb = 15.593) than those from flowing mine water and flooding water (t-test, $\alpha = 0.01$). Surprisingly, ratios from drip water do not agree with ratios from galena (fba) as has been expected from δ^{34}S values of sulphate [19]. Despite repeated measurements with larger sample volume, relative errors of lead isotope ratios in drip water are high in comparison to relative errors of other mine waters and galena samples (table 3).

Groundwater has lead isotope ratios (^{206}Pb/^{204}Pb = 18.033, ^{207}Pb/^{204}Pb = 15.558, ^{208}Pb/^{204}Pb = 37.940) which are significantly lower than those of pool water (t-test, $\alpha = 0.01$). Unfortunately, despite repeated measurements, relative errors of isotope ratios in groundwater are so high that it cannot be distinguished from flowing mine water, flooding water, and drip water (t-test, $\alpha = 0.01$).

Lead isotope ratios from the river Freiberger Mulde (RFM, ^{206}Pb/^{204}Pb = 18.158, ^{207}Pb/^{204}Pb = 15.565, ^{208}Pb/^{204}Pb = 38.139) differ significantly from mine waters (t-test, $\alpha = 0.01$)

4.3 *Strontium isotope investigations*

Pool water (WHSt1, WHSt2) shows an increase in ^{87}Sr/^{86}Sr ratios from December 2005 to February 2006 from 0.72244 to 0.72387 (WHSt1) and from 0.72224 to 0.72364 (WHSt2) (table 4 and figure 4). Furthermore, figure 4 shows that pool water has the highest strontium

Table 4. Strontium concentrations, flow rates, and strontium isotope data of pool water, flowing mine water, flooding water, drip water, groundwater, and river water.

Sample	Sampling date	Sr [µg/l]	Flow rate [l/min]	^{87}Sr/^{86}Sr $\pm 2\sigma_M$
WHSt1	05/12/05	110		0.72244 ± 0.00009
	06/02/06	120		0.72378 ± 0.00009
WHSt2	05/12/05	110		0.72224 ± 0.00013
	06/02/06	120		0.72364 ± 0.00019
SH1	05/12/05	130	15.8	0.71859 ± 0.00013
	19/12/05	130	60.0	0.71866 ± 0.00003
	09/01/06	120	74.4	0.71860 ± 0.00004
	23/01/06	120	36.0	0.71829 ± 0.00004
	30/01/06	130	43.6	0.71893 ± 0.00003
	06/02/06	120	35.2	0.71857 ± 0.00003
	20/02/06	120	100.0	0.71860 ± 0.00003
	27/02/06	120	144.9	0.71844 ± 0.00003
	13/03/06	120	120.0	0.71938 ± 0.00023
	20/03/06	120	122.8	0.71871 ± 0.00013
SH2	05/12/05	130	13.2	0.71856 ± 0.00008
	19/12/05	130	35.0	0.71859 ± 0.00012
	09/01/06	120	44.6	0.71895 ± 0.00003
	23/01/06	120	26.5	0.71858 ± 0.00003
	30/01/06	130	33.4	0.71879 ± 0.00003
	06/02/06	120	25.9	0.71859 ± 0.00003
	20/02/06	120	54.3	0.71852 ± 0.00005
	27/02/06	120	63.3	0.71863 ± 0.00005
	13/03/06	120	60.0	0.71852 ± 0.00003
	20/03/06	120	70.1	0.71855 ± 0.00003
RZUEL	05/12/05	640		0.71694 ± 0.00006
	19/12/05	650		0.71692 ± 0.00004
	09/01/06	670		0.71700 ± 0.00002
	23/01/06	650		0.71705 ± 0.00004
	30/01/06	680		0.71700 ± 0.00002
	06/02/06	660		0.71705 ± 0.00004
	20/02/06	670		0.71707 ± 0.00003
	27/02/06	640		0.71706 ± 0.00004
	13/03/06	670		0.71697 ± 0.00003
	20/03/06	660		0.71757 ± 0.00013
U23	06/02/06	220		0.71708 ± 0.00007
GW	08/06/07	171		0.71772 ± 0.00004
RFM	07/11/06	98		0.71538 ± 0.00004
	04/05/07	104		0.71650 ± 0.00004
Carbonate1				0.71010 ± 0.00010
Carbonate2				0.71268 ± 0.00018
Carbonate3				0.71563 ± 0.00007

ratios which differ significantly (t-test, $\alpha = 0.01$) from other mine waters, groundwater, and river water, but lie within ratios from Grey Gneisses [31].

Strontium isotope data of flowing mine water (SH1, SH2) from different levels do not differ (t-test, $\alpha = 0.01$) and vary between 0.71829 and 0.71938. Correlation coefficients between ^{87}Sr/^{86}Sr ratios and flow rates show that strontium ratios do not depend on flow rates ($r = 0.27$ for SH1 and $r = -0.10$ for SH2).

^{87}Sr/^{86}Sr ratios from flooding water (RZUEL) range from 0.71692 to 0.71757 and agree with ratios from drip water (U23, ^{87}Sr/^{86}Sr $= 0.71708$). Both mine waters are distinct from

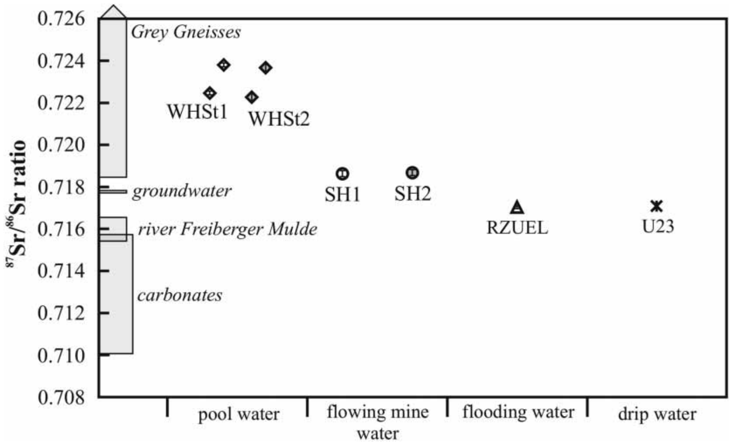


Figure 4. Average ^{87}Sr/^{86}Sr ratios of mine waters ($n = 2$ for WHSt1 and WHSt2, $n = 10$ for SH1, SH2 and RZUEL, and $n = 1$ for U23). Ratios from pool water are not averaged because of increasing ^{87}Sr/^{86}Sr ratios from 05/12/2005 (left point) to 06/02/2006 (right point). Grey shaded areas show ^{87}Sr/^{86}Sr ratios of Grey Gneisses [31], carbonates, groundwater, and river water according to table 4.

other investigated mine waters and groundwater (GW, ^{87}Sr/^{86}Sr = 0.71772) by significantly lower ratios (t-test, $\alpha = 0.01$).

The river Freiberger Mulde (RFM) (^{87}Sr/^{86}Sr = 0.71538 to 0.71650) and carbonates from the Freiberg mine (^{87}Sr/^{86}Sr = 0.71010 to 0.71563) have the lowest ^{87}Sr/^{86}Sr ratios.

5. Discussion

5.1 *Hydrochemical parameters*

Large ranges of trace metal concentrations (table 2) in streaming waters (flowing mine water, flooding water, and river water) are caused by varying flow rates. Low flow rates result in higher concentrations, whereas high flow rates result in lower concentrations because of dilution.

The hydrochemical composition of pool water (WHSt1, WHSt2) is controlled by ions and trace metals released by sulphide oxidation (proton, sulphate, iron, lead, zinc) and weathering of host rock (calcium, magnesium). The lead concentration is lower than iron and zinc concentrations because lead is partly fixed in anglesite soon after release by galena oxidation [14]. Strontium is not enriched in pool water because no strontium is released by oxidation of sulphide ores.

The adding of pore water from the qp assemblage into groundwater is shown by decreasing pH values and increasing fluxes of trace metals (iron, lead, zinc) in flowing mine water from level 1 (SH1) to level 2 (SH2) [14]. Strontium concentrations in water from level 1 and level 2 do not differ because strontium is not enriched in the added pool water. Consequently, the strontium fluxes decrease with the general decrease of flow rates from level 1 to level 2 (table 4).

Flooding water and drip water differ from other mine water types by higher pH values. Nevertheless, the sulphate concentrations in these waters point to sulphide oxidation, but pH values are buffered maybe by solution of carbonates that is indicated by high calcium and elevated magnesium and strontium concentrations. The groundwater is probably also influenced by carbonates, as shown by higher strontium concentrations in comparison to pool water and flowing mine water and moderate bicarbonate, calcium, and magnesium concentrations.

5.2 *Lead isotopes*

A plot of ^{208}Pb/^{204}Pb ratios *vs.* ^{206}Pb/^{204}Pb ratios (figure 5) shows that pool water and flowing mine waters lie on a mixing line, calculated by linear regression with WHSt1, WHSt2, SH1, and SH2 (coefficient of determination = 0.92). RZUEL and U23 were left out of the calculation because they are probably affected by a third source of lead as indicated by hydrochemical parameters, and because of the large measurement errors of drip water. None of the mine waters is obviously affected by oxidation of galena from the Post Variscan fba assemblage.

The mixing line's end member I consists of galena from the Late Variscan qp assemblage as the only or dominant lead source. Ratios of pool water (WHSt1, WHSt2) are similar to those from galena from the qp assemblage. It confirms our assumption that almost all lead in pool water originates from sulphide oxidation of Late Variscan ores. The lead isotope ratios differ from those of flowing mine water, flooding water, and drip water (figure 3). Therefore, these three mine water types should contain additional lead source(s).

The proposed end member II has lead isotope ratios similar to those from groundwater. Although the large measurement errors ($2\sigma_M$) do not allow a clear definition of this end member, anthropogenic lead is supposed to be the main lead source of groundwater. In figure 5, anthropogenic sources (soot from exhaust pipes and petrol additives of the company Novoctan of the former GDR [32]) comprise a large area which extends up to ^{206}Pb/^{204}Pb = 16.163 and ^{208}Pb/^{204}Pb = 36.015. Therefore, the trend towards lower isotope ratios may indicate an anthropogenic lead source in groundwater.

Furthermore, anthropogenic lead sources have been investigated in another study where lead isotopes in upper layers of forest soils were analysed [33]. Together with lead isotopes from the peat of an ombothrophic bog [34] they define a correlation line ($y = -0.930 + 0.853x$) in a plot of ^{208}Pb/^{206}Pb ratios *vs.* ^{207}Pb/^{206}Pb ratios [33]. This correlation line is called Standard European Lead Pollution (ESLP) and characterizes the average lead of the era of industrialization in Northern Europe [33]. A correlation line for petrol ($y = -0.886 + 0.830x$) plots to the right hand side of the ESLP. This indicates that the ESLP originates not only from petrol, but from geogenic sources, power plants, and cement factories [33]. Figure 6 shows our mixing line together with average lead isotope ratios of investigated water types. End member

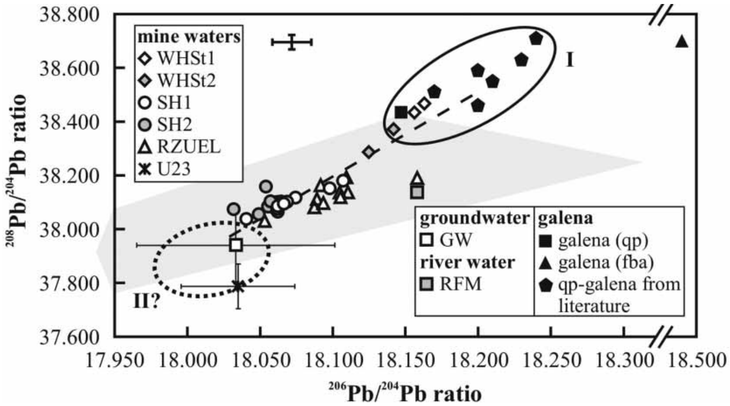


Figure 5. ^{208}Pb/^{204}Pb ratios *vs.* ^{206}Pb/^{204}Pb ratios of mine waters, groundwater, river water, and galena from the qp and fba assemblage (incl. lead isotope ratios from galena from [29]). The grey shaded area indicates the range of lead isotopes of anthropogenic sources with values up to ^{206}Pb/^{204}Pb = 16.163 and ^{208}Pb/^{204}Pb = 36.015 [32]. The error bar at the upper margin shows the average measurement error ($2\sigma_M$) of all samples. The error bars of U23 and GW are separately plotted because their measurement errors ($2\sigma_M$) are remarkable high in comparison to other waters. The end members I and II are discussed in the text.

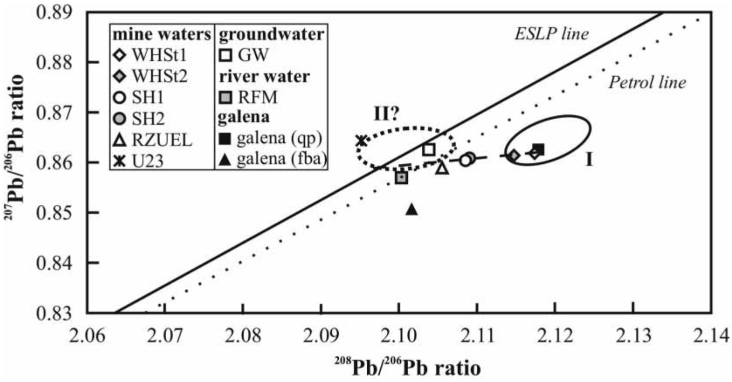


Figure 6. Average ^{207}Pb/^{206}Pb ratios *vs.* ^{208}Pb/^{206}Pb ratios of mine waters, groundwater, river water, and galena from the qp and fba assemblage. The dashed line represents the mixing line resulting from galena (qp), pool water, and flowing mine water. The European Standard Lead Pollution (ESLP) and petrol line [33] indicate anthropogenic lead sources.

II plots near the ESLP and petrol line and confirms our suggestion that lead in groundwater mainly represents anthropogenic sources.

The measurement errors ($2\sigma_M$) of drip water are also high in comparison to other mine waters. Nevertheless, lead isotope ratios from drip water show an unexpected result: they do not match ratios from galena (qp or fba), although it was suggested from sulphur and oxygen isotope ratios that this water is affected by weathering of fba ore assemblage [19]. Its high iron and zinc concentrations indicate that the water is affected by ore oxidation processes, but low lead concentrations point to an absence of galena in the weathered ore assemblage. Isotope ratios from drip water obviously do not agree with those from galena (fba), but they roughly agree with those from groundwater considering the large measurement errors of both waters. Therefore, we assume that lead in drip water originates mainly from groundwater as supported by its low lead concentration ($3\,\mu g/l$) that is even lower than in groundwater in the region of Freiberg ($12\,\mu g/l$). A minor portion of lead in drip water may originate from weathered carbonates, as indicated by a neutral pH value and high bicarbonate and elevated calcium concentrations (table 1).

In conclusion, the lead isotope composition of flowing mine water and flooding water is mainly controlled by two lead sources: lead from galena from residual ores and anthropogenic lead from groundwater. The amount of ^{206}Pb and ^{208}Pb decreases from end member I to end member II. Thus, the higher the contribution of lead from groundwater, the lower the lead isotope ratios in flowing mine water. But contrary to our assumption, lead isotope ratios of flowing mine water from level 1 do not differ from those from level 2, although water from level 2 is affected to greater degree by sulphide oxidation and consists to a greater portion of pore water from the qp assemblage, as indicated by a lower pH value and higher trace metal concentrations, including lead (table 1). We expected that the higher portion of pore water in flowing mine water from level 2 should lead to isotope ratios more similar to those from the Late Variscan qp assemblage but surprisingly results do not support our expectation.

Interestingly, flooding water has lead isotope ratios that cannot be distinguished from those of flowing mine waters by statistical tests (t-test, $\alpha = 0.01$), but shows hydrochemical parameters (almost neutral pH value, high bicarbonate and calcium concentrations) that point to an influence of lead from an additional source, probably weathered gangue carbonates. Lead isotope ratios of river water indicate that the low lead amount in the river Freiberger Mulde may also originate from carbonates.

5.3 *Strontium isotopes*

Three groups of mine waters can be distinguished on the base of their strontium isotope ratios: (a) pool water, (b) flowing mine water, and (c) flooding water and drip water (figure 4). A plot of reciprocal strontium concentrations vs. ^{87}Sr/^{86}Sr ratios (figure 7) shows that flooding water differs from drip water.

In figure 7, a triangle can be spanned by three possible end members: pool water (I), flooding water (II), and river water (III). The strontium isotope composition of pool water (end member I) lies within that of Grey Gneisses (the host rock of ore veins) and identifies these gneisses as the main strontium source of pool water. Depending on the content of mica and K-feldspar, ^{87}Sr/^{86}Sr ratios of the Grey Gneisses vary from 0.71841 to 0.73742 [31]. Weathering of these minerals is shown to occur at low pH values in the Freiberg mine leading to calcium, magnesium, and strontium release [14]. Strontium isotope ratios of pool water increased from the first to the second sampling campaign accompanied by an increase of its strontium concentration. This increase between two sampling campaigns could be caused by intensified weathering of mica and K-feldspar from Grey Gneisses due to interaction of pore water from the qp assemblage with low pH values (2.5 for WHSt1 and WHSt2) on these rocks, as indicated by higher calcium and magnesium concentrations.

Flooding water (end member II) and drip water are enriched in ^{86}Sr in comparison to other sampled mine waters. Thus, they should be influenced by an additional strontium source with lower isotope ratios. Both mine waters show (almost) neutral pH values (6.1 and 7.2 for RZUEL and U23, respectively) as well as high sulphate concentrations. These facts and the range of ^{87}Sr/^{86}Sr ratios of three carbonates from the Freiberg mine (0.71010 to 0.71563, see figure 4) indicate the presence of carbonates, able to buffer the pH values. The solution of carbonates releases large amounts of iron, calcium, magnesium, and strontium, leading to high concentrations of these elements in flooding and drip water (tables 1 and 2).

Strontium in the river Freiberger Mulde (end member III) does not originate from Grey Gneisses, the only host rock in the drainage area of the river, because Grey Gneisses show higher isotope ratios [31] than those from river water. Thus, strontium in river water should originate from an additional source, probably from anthropogenic inputs.

Strontium isotopes in flowing mine water, drip water, and groundwater can be interpreted as mixtures of these three sources (Grey Gneisses, carbonates, and probably anthropogenic inputs). ^{87}Sr/^{86}Sr ratios in flowing mine water are significantly lower than in pool water, although its strontium concentration is almost equal. Thus, strontium in flowing mine water

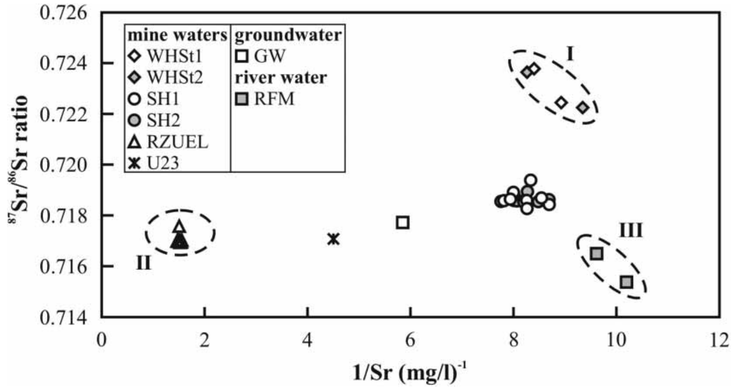


Figure 7. Measured individual ^{87}Sr/^{86}Sr ratios *vs.* reciprocal Sr concentration of mine waters. See text for the discussion of the end members I, II, and III.

partly originates from an additional source. Due to decreasing pH values accompanied by decreasing bicarbonate concentrations from level 1 to level 2 (table 1), the release of strontium from weathering of gangue carbonates can be denied. Therefore, strontium in flowing mine water probably originates from anthropogenic sources and weathered Grey Gneisses (figure 7).

Strontium in groundwater mainly originates from weathered carbonates and anthropogenic sources, whereas only a minor portion of strontium may originate from Grey Gneisses.

Judging from figure 7, the strontium isotope composition of drip water can be interpreted as a mix of strontium released from gangue carbonates and anthropogenic strontium in groundwater.

6. Conclusions

The four major mine water types in the polymetallic sulphide ore mine Freiberg were investigated by lead and strontium isotopes, where former studies with sulphur and oxygen isotopes established two major sulphate sources: oxidized sulphide ores and anthropogenic sulphate from groundwater [17–20].

The lead isotope composition can be interpreted as resulting from two major sources of lead in mine waters: (a) oxidation processes from remaining sulphide ores (mainly galena from the Late Variscan qp assemblage) and (b) anthropogenic sources. Furthermore, there are indications that lead in flooding water is released from an additional source, probably carbonates occurring as gangue minerals mainly in the Post Variscan fba assemblage and subordinately in the Late Variscan qp assemblage.

Strontium isotopes indicate at least three different strontium sources in mine waters: (a) released strontium from weathering of mica and K-feldspar of Grey Gneisses in sites of low pH values, (b) released strontium from gangue carbonates, and (c) strontium probably from anthropogenic sources brought with groundwater into the mine.

Strontium isotope compositions as well as hydrochemical parameters indicate a high contribution of elements released due to weathering of gangue carbonates in flooding mine water and to a lower degree in drip water. In contrast, flowing mine water which drains along a mined ore lode from the Late Variscan qp assemblage contains only a minor portion of elements released from gangue carbonates in agreement with its low bicarbonate, calcium, and magnesium concentrations and low pH values. Nonetheless, their lead isotope composition is not dominated by lead released from galena oxidation, but represents a mix of lead from groundwater and pore water from the qp assemblage.

Contrary to oxygen and sulphur isotopes [17–20], it is impossible to prove the increasing portion of sulphate formed due to sulphide oxidation processes along the flow path towards deeper mine levels with lead or strontium isotopes despite higher lead concentrations in sampling point SH2 compared to SH1. This means that the lead isotope composition of mine waters is controlled by that of galena only in case of very high lead concentrations like those in pool waters and that most lead in flowing mine waters originates from groundwater. The increase in sulphate concentrations and decrease of sulphur and oxygen isotopes of sulphate [17–20] along the flow path from SH1 to SH2 should therefore be explained by preferred oxidation of other sulphide minerals than galena (e.g., pyrite, sphalerite).

The application of lead and strontium isotopes on mine waters as well as hydrochemical investigations have shown the important role of gangue carbonates as a source of several elements of mine waters and revealed additional mixing processes which could not be identified by sulphur and oxygen isotopes alone.

Acknowledgements

We thank S. Mühlberg and A. Braun for supporting us with the lead isotope measurements and for analysing the strontium isotopes.

References

[1] T.D. Bullen, C. Kendall. Tracing of weathering reactions and water flowpaths: a multi-isotope approach. In *Isotope Tracers in Catchment Hydrology*, C. Kendall, J.J. McDonell (Eds), pp. 611–646, Elsevier, Amsterdam (1998).

[2] J.R. Bacon, D.C. Bain. Characterization of environmental water samples using strontium and lead stable isotope compositions. *Environ. Geochem. Health*, **17**, 39–49 (1995).

[3] D.I. Siegel, M.E. Bickford, S.E. Orrell. The use of strontium and lead isotopes to identify sources of water beneath the Fresh Kills landfill, Staten Island, New York, USA. *Appl. Geochem.*, **15**, 493–500 (2000).

[4] H. Zhang, D. Ma, X. Hu. Arsenic pollution in groundwater from Hetao Area, China. *Environ. Geol.*, **41**, 638–643 (2002).

[5] E. Petelet-Giraud, J.-M. Luck, D. Ben Othman, P. Negrel. Dynamic scheme of water circulation in karstic aquifers as constrained by Sr and Pb isotopes. Application to the Hérault watershed, Southern France. *Hydrogeol. J.*, **11**, 560–576 (2003).

[6] R.N. Toner, C.D. Frost, K.R. Chamberlain. Isotopic identification of natural vs. anthropogenic sources of Pb in Laramie basin groundwaters, Wyoming, USA. *Environ. Geol.*, **43**, 580–591 (2003).

[7] D.M. Allen, M.E. Lepitre. Use of Pb, ^{18}O, and ^{2}H isotopes in mining-related environmental studies. *Mine Water Environ.*, **23**, 119–132 (2004).

[8] I. Fernández, M. Olías, J.C. Cerón, J. De la Rosa. Application of lead stable isotopes to the Guadiamar Aquifer study after the mine tailings spill in Aznalcóllar (SW Spain). *Environ. Geol.*, **47**, 197–204 (2005).

[9] M.J. Duane, G. Pigozzi, C. Harris. Geochemistry of some deep gold mine waters from the western portion of the Witwatersrand Basin, South Africa. *J. Afr. Earth Sci.*, **24**(1/2), 105–123 (1997).

[10] P. Négrel, C. Fouillac, M. Brach. A strontium isotopic study of mineral and surface waters from the Cèzallier (Massif Central, France): implications for mixing processes in areas of disseminated emergences of mineral waters. *Chem. Geol.*, **135**, 89–101 (1997).

[11] P. Négrel, J. Casanova, J.-F. Aranyossy. Strontium isotope systematics used to decipher the origin of groundwaters sampled from granitoids: the Vienne Case France. *Chem. Geol.*, **177**, 287–308 (2001).

[12] B. Wiegand, M. Dietzel, U. Bielert, B. Groth, B.T. Hansen. ^{87}Sr/^{86}Sr-Verhältnisse als Tracer für geochemische Prozesse in einem Lockergesteinsaquifer (Liebenau, NW-Deutschland). *Acta Hydrochim. Hydrobiol.*, **29**(2–3), 139–152 (2001).

[13] S.K. Singh, A. Kumar, C. France-Lanord. Sr and ^{87}Sr/^{86}Sr in waters and sediments of the Brahmaputra river system: Silicate weathering, CO_2 consumption and Sr flux. *Chem. Geol.*, **234**, 308–320 (2006).

[14] D. Baacke. *Geochemisches Verhalten umweltrelevanter Elemente in stillgelegten Polysulfiderzgruben am Beispiel der Grube 'Himmelfahrt' in Freiberg,* Sachsen. PhD thesis, TU Bergakademie Freiberg (2001).

[15] M. Martin, P. Beuge, A. Kluge, T. Hoppe. Grubenwässer des Erzgebirges – Quelle von Schwermetallen in der Elbe. *Spektrum der Wissenschaft*, **5**, 102–107 (1994).

[16] F. Haubrich, D. Baacke, A. Kluge, A. Kindermann, C. Winkler. Sulfidverwitterung in aufgefahrenen Erzgängen. Ein Feld komplexer geochemisch-mineralogischer Forschung. In *Bergbau und Umwelt: Langfristige geochemische Einflüsse*, T. Wippermann (Ed.), pp. 57–66, Springer, Berlin (2000).

[17] F. Haubrich. *Schwefel- und Sauerstoffisotopen als Tracer für Wechselwirkungen zwischen Atmo-, Pedo-, Hydrosphäre und der Sulfiderzlagerstätte in der Region Freiberg*. PhD thesis, TU Bergakademie Freiberg (2001).

[18] F. Haubrich, M. Tichomirowa. Sulfur and oxygen isotope geochemistry of acid mine drainage – the polymetallic sulfide deposit 'Himmelfahrt Fundgrube' in Freiberg (Germany). *Isot. Environ. Health. Stud.*, **38**, 121–138 (2002).

[19] M. Junghans, M. Tichomirowa. Hydrocheochemical and stable isotope composition of mine waters in the non-flooded part of the Freiberg polymetallic sulfide mine – sulfate sources and mixing processes. Submitted to *Appl. Geochem.* (2007).

[20] M. Tichomirowa, F. Haubrich, M. Junghans, S. Pelkner. Schwefel- und Sauerstoffisotopen als Indikator für Herkunft und Mischungsprozesse in der Grube Himmelfahrt (Freiberg). In *Isotope und Tracer in der Wasserforschung*, D. Hebert, B. Merkel, C. Wolkersdorfer (Eds), pp. 91–93, Wissenschaftliche Mitteilungen des Instituts für Geologie 19, TU Bergakademie Freiberg (2002).

[21] M. Bayer. *Die Himmelfahrt Fundgrube – Ein Führer durch das Lehr und Besucherbergwerk der TU Bergakademie Freiberg*, TU Bergakademie Freiberg (1999).

[22] L. Baumann, E. Kuschka, T. Seifert. *Lagerstätten des Erzgebirges*, Enke im Thieme-Verlag, Stuttgart (2000).

[23] S. Kolitsch, M. Junghans, W. Klemm, T. Degner, D. Baacke. Hydrochemical monitoring (1970–2003), depth profile and flow measurements in partly flooded underground workings of the central polymetallic vein ore deposit of Freiberg/Germany. *Z. geol. Wiss.*, **33**, 51–80 (2005).

[24] D. Baacke, T. Degner. Hydrogeochemie, Wärmehaushalt und Strömung des Flutungswassers einer untertägigen Erzgrube. In *Bergbau und Umwelt: Langfristige geochemische Einflüsse*, T. Wippermann (Ed), pp. 163–174, Springer, Berlin (2000).

[25] G. Manhes, J.F. Minster, C.J. Allègre. Comparative uranium-thorium-lead and rubidium-strontium study of the Saint Sèverin amphoterite: consequences for early solar system chronology. *Earth Planet. Sci. Lett.*, **39**, 14 (1978).

[26] A.E. Cameron, D.H. Smith, R.L. Walker. Mass spectrometry of nanogram-size samples of lead. *Anal. Chem.*, **41**, 525–526 (1969).

[27] S.J.G. Galer, W. Abouchami. Practical application of lead triple spiking for correction of instrumental mass discrimination. *Mineral. Mag.*, **62A**, 491–492 (1998).

[28] G. Faure. *Origin of Igneous Rocks – The Isotopic Evidence*, Springer, Berlin (2001).

[29] J. Pilot, J. Legierski, H.J. Rösler. Pb- und S-Isotopenuntersuchungen an Freiberger und anderen Erzlagerstätten. *Geologie*, **1**, 41–55 (1970).

[30] F. Fiedler. Bleiisotopie und geochemische Untersuchungen kupferführender Polymetallsulfidlagerstätten im Erzgebirge, Granulitgebirge, Slavskovský Les und Vergleichsgebieten. Unpublished diploma thesis, TU Bergakademie Freiberg (2001).

[31] M. Tichomirowa. *Die Gneise des Erzgebirges – hochmetamorphe Äquivalente von neoproterozoisch-frühpaläozoischen Grauwacken und Granitoiden der Cadomiden*, Freiberger Forschungshefte C 495, TU Bergakademie Freiberg (2003).

[32] G. Bracke. *Bleiisotope als Tracer für Umweltbelastungen in der Uranbergbaufolgelandschaft Schlema-Alberoda/Sachsen*, Tübinger Geowissenschaftliche Arbeiten, Reihe E, Band 5, Shaker Verlag, Aachen (1998).

[33] U.K. Haack, H. Heinrichs, F.H. Gutsche, K. Plessow. The isotopic composition of anthropogenic Pb in soil profiles of Northern Germany: Evidence for pollutant Pb from a continent-wide mixing system. *Water Air Soil Pollut.*, **150**, 113–134 (2003).

[34] W. Shotyk, D. Weiss, J.D. Kramers, R. Frei, A.K. Cheburkin, M. Gloor, S. Reese. Geochemistry of the peat bog at Etang de la Gruère, Jura Mountains, Switzerland, and its record of atmospheric Pb and lithogenic trace metals (Sc, Ti, Y, Zr, and REE) since 12,370 ^{14}C yr BP. *Geochim. Cosmochim. Acta*, **65**, 2337–2360 (2001).