Supplementary Information

Routine determination of inorganic arsenic speciation in precipitates from acid mine drainage using orthophosphoric acid extraction followed by HPLC-ICP-MS

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1. SYNTHESIS OF AS(III)- AND AS(V)-SORBED SCHWERTMANNITE

Prior to As sorption, schwertmannite was synthesized according to Barham (1997). A solution of FeSO₄ (0.1 M) was adjusted to pH 2.5 with H₂SO₄ in an anaerobic chamber. The solution was then removed from the anaerobic chamber and oxidized using an excess of H₂O₂ while stirring and heating at 70 °C. After 2 hours, the solid phase was recovered by centrifugation and dried under vacuum. Sorption of As(III) or As(V) onto synthetic schwertmannite was performed under anoxic conditions by adding appropriate amounts of a solution of As(III) 0.1 M (NaAsO₂) or As(V) 0.1 M (Na₂HAsO₄ • 7H₂O) to obtain solid containing ratio of 0.05 As/Fe (mol/mol) according to Maillot et al. (2013). Solids were then centrifuged and dried under vacuum in the anaerobic chamber.

Reference

Barham R. J. (1997) Schwertmannite: a unique mineral, contains a replaceable ligand, transforms to jarosite, hematite, and/or basic iron sulfate. J. Mater. Res. 12(10), 2751–2758.

2. DETERMINATION OF TOTAL ARSENIC AND IRON CONCENTRATIONS

Total As and Fe concentrations were determined using an aqua regia digestion followed by ICP-MS analysis. Digestion of solid samples was carried out in a class 10,000 clean room. All material was acidcleaned before use. About 0.1 g of milled sample was digested in PTFE reactor on hot plate using (1) 3 mL of 35% H₂O₂ during 16 h at room temperature followed by 24 h at 95 °C and (2) a 1:3 mL concentrated HNO₃–HCl mixture (aqua regia) during 24 h at 95 °C. Samples were allowed to cool to room temperature and evaporated to dryness at 65 °C between the two steps and at the end of the procedure. Then, samples were brought to 30 mL using 3 mL HNO₃ and double deionized water. Finally, samples were filtered to remove possible residues using a polypropylene syringe and a 0.22 μ m cellulose acetate syringe filter previously rinsed with 10% v/v HNO₃. Method blank and certified reference material digestion (Stream sediments LGC6189 from United Kingdom Accreditation Service) were performed.

Total As and Fe concentrations were determined after an adequate dilution using an ICP-MS, iCAP Q (ThermoFisher Scientific) equipped with KED (Kinetic Energy Discrimination Technology). A $10 \ \mu g \ L^{-1}$ Ge solution in 1% HNO₃ (v/v) was injected on-line as internal standard. The quality of analytical methods was checked by analysing international certified reference waters (SLRS-5, NIST1643e); results ranged within 10% relative to the certified values. Analytical error (relative standard deviation) was better than 5%. Finally, accuracy was within 8% of the As certified value for the sediment reference material (LGC6189) and the procedural blank represents less than 0.1% of As and Fe concentration measured in samples.

3. <u>COMPARISON OF EXTRACTION METHODS</u>

3.1. Experimental section

In a first stage, in addition to the 1 M H₃PO₄ extraction method describes in section 2.4.a of the main paper (hereafter referred to as "protocol D"), the three following extraction protocols have been tested using 100 mg of samples. For that, F5 and F7 samples were selected because they contain both As(III) and As(V) species (As(III)/ Σ As of 53 and 41%, respectively) and As is associated with crystallized phases from which As may be more difficult to extract than from amorphous phases.

Protocol A- Extraction with 15 mL of 1 M H₃PO₄ (VWR Chemicals, analytical grade, 85%) in an acid-cleaned Pyrex tube. The sample was maintained at 60 W during 10 min using a microwave system (Discover SP-D Plus, CEM®) (Rahman et al., 2009).

Protocol B- Extraction with 15 mL of 1 M H₃PO₄ (VWR Chemicals, analytical grade, 85%) + 0.5 M ascorbic acid (Sigma-Aldrich, 99.7-100.5 %) in an acid-cleaned Pyrex tube. The sample was maintained at 60 W during 10 min using a microwave system (Discover SP-D Plus, CEM®) (Giral et al., 2010).

Protocol C- Extraction with 2 mL of 4 M HCl (Merck, Suprapur, 30%) + 10% acetic acid (VWR Chemicals, analytical grade, 100%) in a polypropylene tube. The sample was heated at 95 °C during 1 h on a hot plate (Huang and Kretzschmar, 2010).

After the extraction step, samples were allowed to cool to room temperature and were filtered using a polypropylene syringe and a cellulose acetate syringe filter (0.22 μ m). The first drops of the filtered extract were not kept allowing the syringe filter to be rinsed out. Extracts were diluted (10,000-fold for method A and B and 100,000-fold for method C) with an acid acetic-EDTA solution (1% v/v) and analysed by HPLC-ICP-MS as described in the section 2.4.b of the main paper.

References

- Giral, M., Zagury, G.J., Deschênes, L., Blouin, J.-P., 2010. Comparison of four extraction procedures to assess arsenate and arsenite species in contaminated soils. Environ. Pollut. 158, 1890–1898. doi:10.1016/j.envpol.2009.10.041
- Huang, J.H., Kretzschmar, R., 2010. Sequential extraction method for speciation of arsenate and arsenite in mineral soils. Anal. Chem. 82, 5534–5540. doi:10.1021/ac100415b
- Rahman, M.M., Chen, Z., Naidu, R., 2009. Extraction of arsenic species in soils using microwave-assisted extraction detected by ion chromatography coupled to inductively coupled plasma mass spectrometry. Environ. Geochem. Health 31 Suppl 1,93–102. doi:10.1007/s10653-008-9227-0

3.2. Results

Arsenic was almost completely extracted (Figure S2a) whatever the extraction method used, with extraction yield averaging $77 \pm 3\%$ for F7 and $100 \pm 7\%$ for F5 samples.

Similar proportions of As(III), expressed as a percentage of total As (As(III)/ Σ As), were obtained using the extraction methods A, C and D for both samples (As(III)/ Σ As = 46 ± 1% for F7 sample and As(III)/ Σ As = 41 ± 1% for F5 sample, Figure S2b). In contrast, the procedure B (1 M H₃PO₄ + 0.5 M ascorbic acid under microwaves) gave a higher As(III) proportion in F7 sample, with As(III)/ Σ As ratio of 89%, which implied either reduction of As(V) into As(III) during this procedure or As(III) oxidation with the other protocols. The latter assumption was inconsistent considering XANES data and suggest that a reduction of As(V) occurred during the extraction step. An As(III)/ Σ As ratio of 86% was obtained for F7 sample spiked with As(V) standard before applying the extraction procedure B confirming that As(V) was partially reduced during the extraction step.

On the basis of these tests, the method B was not tested further. Moreover, method D was preferred to the methods A and C. Indeed, H₃PO₄ concentration up to 0.3 M did not disturb chromatographic separation of As(III) and As(V) species (Gallardo et al., 2001), allowing a minimal 2000-times dilution factor for orthophosphoric acid extracts to be analysed, which remains compatible with the analysis of lower concentrated samples (see the section 3.3 of the main paper for details). Conversely, high chloride concentration in HCl extracts may generate polyatomic interferences during HPLC-ICP-MS analysis (Rahman et al., 2009). Finally, standard hot plate heating in procedure D was preferred to microwave-assisted extraction in procedure A for its easiest and cheapest implementation.

4. <u>ARSENIC SPECIATION BY ORTHOPHOSPHORIC ACID EXTRACTION AND HPLC-ICP-MS</u> <u>ANALYSIS: UNCERTAINTY CALCULATION</u>

The reproducibility of the orthophosphoric acid extraction method was determined through measuring replicate AMD-precipitate extracts for selected field samples (F5, F6 and F7) and laboratory samples (1A-G4 and 2A-G3) (Table S1). The relative standard deviations (RSDs) ranged from 1 to 6% for As(III) concentration and from 2 to 8% for As(V) concentration.

Total As concentrations (Σ As) and As(III) proportions (As(III)/ Σ As) were calculated according to equations 1 and 2, respectively. The uncertainties of total As concentrations and As(III) proportions were assessed from an error propagation calculation on the basis of the standard deviation (σ) and average values obtained for As(III) and As(V) concentrations (equations 3 and 4, respectively). The relative standard deviations (RSDs) were 2-6% for total As concentration and 3-11% for As(III) proportion (Table S1).

Equation 1: $\Sigma As = As(III) + As(V)$

Equation 2: $\frac{As(III)}{\Sigma As} = \left(\frac{As(III)}{As(III) + As(V)}\right)$

Equation 3: $\sigma[\Sigma As] = \sigma[As(III)] + \sigma[As(V)]$

Equation 4: $\sigma\left[\frac{As(III)}{\Sigma As}\right] = \left[\left(\frac{\sigma[As(III)]}{As(III)_{avg}}\right) + \left(\frac{\sigma[\Sigma As]}{\Sigma As_{avg}}\right)\right] \times \left(\frac{As(III)}{\Sigma As}\right)_{avg}$

Table S1: As(III) and As(V) concentrations measured in replicate extracts and corresponding total As concentration (Σ As) and As(III) proportion (As(III)/ Σ As ratio).

	As(III) (mg g ⁻¹)	$s(III) (mg g^{-1}) As(V) (mg g^{-1}) \Sigma As (mg$		g-1) As(III)/ΣAs (%)		
F5 sample						
#1	60	90	149	40		
#2	61	91	152	40		
#3	57	79	136	42		
#4	59	79	138	43		
#5	58	79	137	42		
Average	59	84	142	41		
Standard deviation	2	6	8	4		
RSD (%)	3	8	6	9		
F6 sample						
#1	89	47	136	65		
#2	85	46	131	65		
#3	87	48	135	65		
Average	87	47	134	65		
Standard deviation	2	1	3	3		
RSD (%)	2	2	2	4		
F7 sample						
#1	63	66	129	49		
#2	56	70	126	45		
#3	58	72	130	45		
Average	59	69	128	46		
Standard deviation	3	3	7	5		
RSD (%)	6	4	5	11		
1A-G4 sample						
#1	15	66	82	19		
#2	16	65	82	20		
#3	16	65	81	20		
#4	17	61	77	22		
Average	16	64	80	20		
Standard deviation	1	2	3	2		
RSD (%)	4	4	4	8		
2A-G3 sample						
#1	35	63	98	35		
#2	35	60	94	37		
#3	35	60	96	37		
#4	35	60	95	37		
Average	35	61	96	36		
Standard deviation	0	2	2	1		
RSD (%)	1	3	2	3		

	Total arsenic concentration (mg g ⁻¹)				Arsenic(III) proportion (%)				
Sample	Total digestion		Orthophosphoric acid extraction		XANES		Orthophosphoric acid extraction		
	Average	SD	Average	SD	Average	3SD	Average	SD	
AMD-precip	oitates (field s	amples)						
F1 (S32F00) ^a	220 ^b	18	220	12	7	3	6	1	
F2 (unpubl.)	120 ^b	10	124	7	14	3	11	1	
F3 (S30F00) ^a	210 ^b	17	232	13	58	3	48	5	
F4 (Cs12) ^a	240 ^b	19	267	15	72	3	59	6	
F5	145	12	142	8	53	5	41	4	
F6	138	11	134	3	72	6	65	3	
F7	157	13	128	7	41	5	46	5	
AMD-precipitates (laboratory samples)									
0-G1	76	6	87	5	40	3	37	4	
0-G2	66	5	64	4	71	3	63	7	
1A-G4	84	7	80	3	16	2	20	2	
1B-G1	83	7	76	4	22	2	25	3	
1B-G2	81	6	79	4	25	2	31	3	
2A-G1	75	6	71	4	46	2	53	6	
2A-G2	68	5	62	4	54	2	65	7	
2A-G3	95	8	96	2	31	2	36	1	
2A-G4	70	6	68	4	50	2	56	6	
3A-G1	97	8	89	5	66	2	65	7	
3A-G2	79	6	76	4	76	2	75	8	
3A-G3	71	6	69	4	80	2	80	9	
3A-G4	73	6	64	4	80	2	78	9	
3B-G1	72	6	70	4	77	2	77	9	
3B-G2	62	5	59	3	80	2	81	9	
3B-G3	59	5	42	2	78	2	78	9	
3B-G4			54	3	74	2	73	8	
Synthetic As(III)-/As(V)-schwertmannite mixtures									
100/0 ^c	48	4	46	3	100	0	99	11	
90/10 ^c	45	4	45	3	88	2	85	9	
50/50 ^c	37	3	40	2	43	2	41	5	
10/90 ^c	32	3	38	2	8	2	7	1	
0/100 ^c	31	2	36	2	0	0	0	0	

Table S2: Total arsenic concentration and As(III) proportion determined by total digestion–ICP-MS and XANES analysis and by orthophosphoric acid extraction–HPLC-ICP-MS.

^a Sample reference in Morin et al. (2003)

^b Data obtained by electron microprobe analysis (Morin et al. 2003)

^c Percentage of As(III)-Schwertmannite/As(V)-Schwertmannite



Figure S1: XANES spectra of reference compounds used for linear combination fitting procedure applied to experimental XANES spectra of AMD samples.



Figure S2: a) Sum of As(III) and As(V) concentrations (Σ As in mg g⁻¹) and b) proportion of As(III) (expressed as a percentage of total As: As(III)/ Σ As) determined in F5 and F7 samples using the four different extraction methods A, B, C and D; and comparison with (a) total digestion and (b) XANES data.



Figure S3: Examples of HPLC-chromatograms of As(III) and As(V) species obtained for selected samples (F6 and 0-G2) and calibration standard solutions (5 and 100 μ g L⁻¹) using an anion-exchange PRP-X100 column (250 x 4 mm) and ammonium phosphate buffer (pH 8.0, 30 mM).



Figure S4: X-Ray powder diffraction data obtained for selected AMD samples used in this study (F6, 0-G2, 90/10, 3A-G2). Each diffractogram is representative for a group of samples presented in the Table 1. Too stands for reflexions from Tooeleite, Ja for Jarosite, Qz for quartz, and Sw for schwertmannite.



Figure S5: Examples of LCF reconstruction of experimental XANES spectra using the reference compounds presented in Figure S1. LCF decomposition is given for four samples representative of the groups presented in Table 1 and whose diffractogram is presented Figure S4. Such decomposition allows the determination of As(III)/ Σ As ratios for the AMD samples considered in this study.