1   Supporting Information

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3   Effects of soil composition and mineralogy on the bioaccessibility of arsenic

4   from tailings and soil in gold mine districts of Nova Scotia

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11   Number of pages: 11

12   Number of figures: 4

13   Number of tables: 2

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16   Note: Literature cited corresponds to numbered list in main document.

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Table S1. Description of selected samples[a].

Sample[b]	Field Description	Bulk[c] arsenic concentration (mg•kg^{-1})	Proportion < 150 µm (weight %)	XRD analysis[d] (< 150 µm)
Part I: 2005 Collection				
CAR1	broken grey-green hardpan	61,000	18	Qtz, Ms, **12Sc**, Pl, **6Kn**, Chl
CAR2	sulphide-rich silty tailings	250,000	14	**56Apy**, Qtz, **14Py**, Pl, Ms, Ch
CAR3	red-brown sandy tailings.	12,000	12	Qtz, Ms, Pl, Ch
CAR4	red-brown sandy tailings	6,700	12	Qtz, Ms, Pl, Ch, *Ank*
CAR5	red-brown tailings, hardpan flakes	48,000	16	Qtz, Pl, Ms, Ch
GD1	green, oxidized mill concentrate	190,000	30	**84Sc**, Ms, Qtz
GD2	grey tailings with hardpan chips	13,000	29	Qtz, Pl, Ms, Chl, **6Sc**
GD3	yellow-green broken hardpan	87,000	18	Qtz, Ms, **10Sc**, Pl, Chl
GD4	light grey-brown sandy tailings	14,000	7.0	Qtz, Ms, Pl, Chl
GD5	v. fine grained, green-grey tailings	5,400	61	Qtz, Ms, Chl, Pl, *Cal*
MG1	brown tailings with hardpan chips	40,000	11	Qtz, Ms, Pl, Chl, **6Sc**
MG2	brown sandy tailings over hardpan	17,000	9.0	Qtz, Ms, Chl, Vrm, Pl
MG3	fine grained, red-brown tailings	19,000	21	Qtz, Vrm, Ms, Chl, Pl, **6Phr**
MG4	grey silty tailings in wetland area	19,000	18	Qtz, Vrm, Ms, Chl, Pl, **2Apy**
MG6	orange-brown, B-horizon soil	210	16	Qtz, Ms, Pl, Chl
NB1	grey sandy tailings with silty layers	300	17	Qtz, Ms, *Cal*, Pl, Chl
NB3	grey sandy tailings, minor silty clay	630	25	Qtz, Ms, *Cal*, Pl, Chl
NB6A	brown-grey sandy tailings (0-15 cm)	460	16	Qtz, Ms, *Cal*, Pl, Chl
NB6B	red-brown sandy tailings (15-35 cm)	620	8.0	Qtz, Ms, Pl, Chl
NB6C	medium grey tailings (35-65 cm)	4,200	9.0	Qtz, Ms, *Cal*, **Apy**, Chl, Pl
NB7	light grey sandy tailings	300	23	Qtz, Ms, Pl, *Cal*, Chl
NB8	light grey clay-rich tailings	580	36	Qtz, Ms, *Cal*, Pl, Chl, **Apy**
NB10	red-brown sandy tailings	1,600	42	Qtz, Ms, Pl, **5Hem**, Chl
NB11A	red-brown sandy tailings	3,800	16	Qtz, Ms, **25Hem**, Pl, Chl
NB11B	sandy tailings, light green hardpan	5,300	22	Qtz, Ms, Pl, Chl, **3Hem**
NB12	light brown, B-horizon soil	4,200	11	Qtz, Ms, Pl, Chl, Rt
NB13	grey-brown, A/B-horizon soil	290	7.0	Qtz, Ms, Pl, Chl
OLD4	sandy, olive-brown tailings	21,000	19	Qtz, Ms, Pl, Chl, **4Jr**
WB1	grey sandy tailings, rusty lenses	29,000	13	Qtz, Ms, Chl, Pl

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Table S1. Continued.

Part II: 2006 Collection[e]:

Sample	Field Description	Bulk[c] arsenic concentration (mg•kg^{-1})	Proportion of < 150 μm (weight %)	XRD analysis (< 150 μm)
GD61	dark grey-brown sandy tailings	5,200	12	n/p[f]
GD62	grey-brown coarse sandy tailings	3,100	7.0	n/p
GD65	sandy tailings, hardpan chips	7,200	9.0	n/p
GD67	brown sandy tailings, hardpan chips	4,200	12	n/p
MG62	grey sandy tailings, hardpan chips	25,000	15	n/p
MG64	brown, fine sandy tailings on jump	14,000	26	n/p
MG67	grey-green sandy tailings on jump	9,100	22	n/p
MG68	green-brown sandy tailings on jump	9,200	28	n/p
MG614	sandy tailings & gravel on dirt road	1,000	16	n/p

[a]Visual characteristics, bulk arsenic concentration and grain size proportion (weight percentage of the < 150 μm particle size fraction in the bulk sample) are presented for samples collected in 2005 and 2006 (*3*).[b]Sample names are described in the main document. [c]From unsieved material.   [d]X-ray diffraction (XRD) analysis was performed on the < 150 μm particle size fraction of samples from the 2005 collection, and is reported in decreasing order of abundance based on semi-quantitative fitting of XRD patterns, including an approximate percent (based on summation of area under each peak, taking into account overlaps) for the arsenic-bearing phases, where detected (*24*). **Arsenic**-bearing minerals are indicated in bold. Calcium carbonate minerals are indicated in italics. Abbreviations: *Ank* = ankerite; Akg = akaganeite; Apy = arsenopyrite; *Cal* = calcite; Chl = chlorite; Hem = hematite; Jr = jarosite; Kn = kankite; Ms = muscovite; Phr = pharmacosiderite; Pl = plagioclase; Py = pyrite; Rt = rutile; Qtz = quartz; Sc = scorodite; Vrm = vermiculite. [e]Information on the 2006 collection is included in this table to complement Figure S2 (page S7). [g]XRD analysis was not performed (n/p) on the 2006 samples.

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Table S2: Results of quality control tests[a].

Medium	Measurement	Method	Experiment	n[b]	Range	Average
Blank[c]	Arsenic concentration	PBET P1, P2	All L:S	19	< 3 μg•L^{-1}	–
Spike recovery[d]	Arsenic recovery (%)	PBET P1, P2	L:S = 100:1	6	93–116%	98%
Standard solution[e]	Arsenic recovery (%)	Instrument	–	36	85–101%	93%
SRM NIST2710	Bioaccessible arsenic (%)	PBET P1	Control limits[f] (L:S = 100:1)	23	24–57%	40%
SRM NIST2710	Bioaccessible arsenic (%)	PBET P2	Control limits (L:S = 100:1)	37	23–49%	36%
SRM NIST2710	Bioaccessible arsenic (%)	PBET P1	L:S = 100:1	5	23–45%	39%
SRM NIST2710	Bioaccessible arsenic (%)	PBET P2	L:S = 100:1	5	31–38%	38%
SRM NIST2710	Bioaccessible arsenic (%)	PBET P1	All other L:S	9	31–51%	37%
SRM NIST2710	Bioaccessible arsenic (%)	PBET P2	All other L:S	9	33–62%	46%
Duplicate pairs	RPD[g], bioaccessible arsenic (%)	PBET P1, P2	All L:S	38	0.22–20%	7.2%

[a]Tests include blanks, duplicates and NIST 2710 as standard reference material (SRM) used in bioaccessibility extractions, as well as matrix spikes and a calibration check solution for ICP-MS analysis. Tests were performed on < 150 μm particle size fraction from samples described in the main document, except for the SRM, which is < 70 μm. All other abbreviations are described in the main document. [b]Number of replicates. [c]The detection limit on the ICP-MS instrument is 1 μg•L^{-1}, based on three standard deviations of eight replicate measurements of a standard solution; 14 of the 19 blanks returned numbers below the instrument detection limit. The limit of quantification for this series of tests is 3 μg•L^{-1}. [d]Spike recovery was calculated from the analysis of 100 ppb•L^{-1} potassium arsenate (KH_2AsO_4, Fluka reagent grade) in blank PBET solution added immediately before analysis. [e]Standard solutions used in the ICP-MS analysis include both 50 ppb and 750 ppb multi-element solutions (PlasmaCAL), prepared from a different source solution than the ICP-MS calibration solutions. [f]Control limits for SRM are average ± three standard deviations for all laboratory results recorded between 2001 and 2008. [g]Relative percent difference (RPD) is calculated as 100 • (result of primary sample – result of duplicate sample) • average^{-1}.
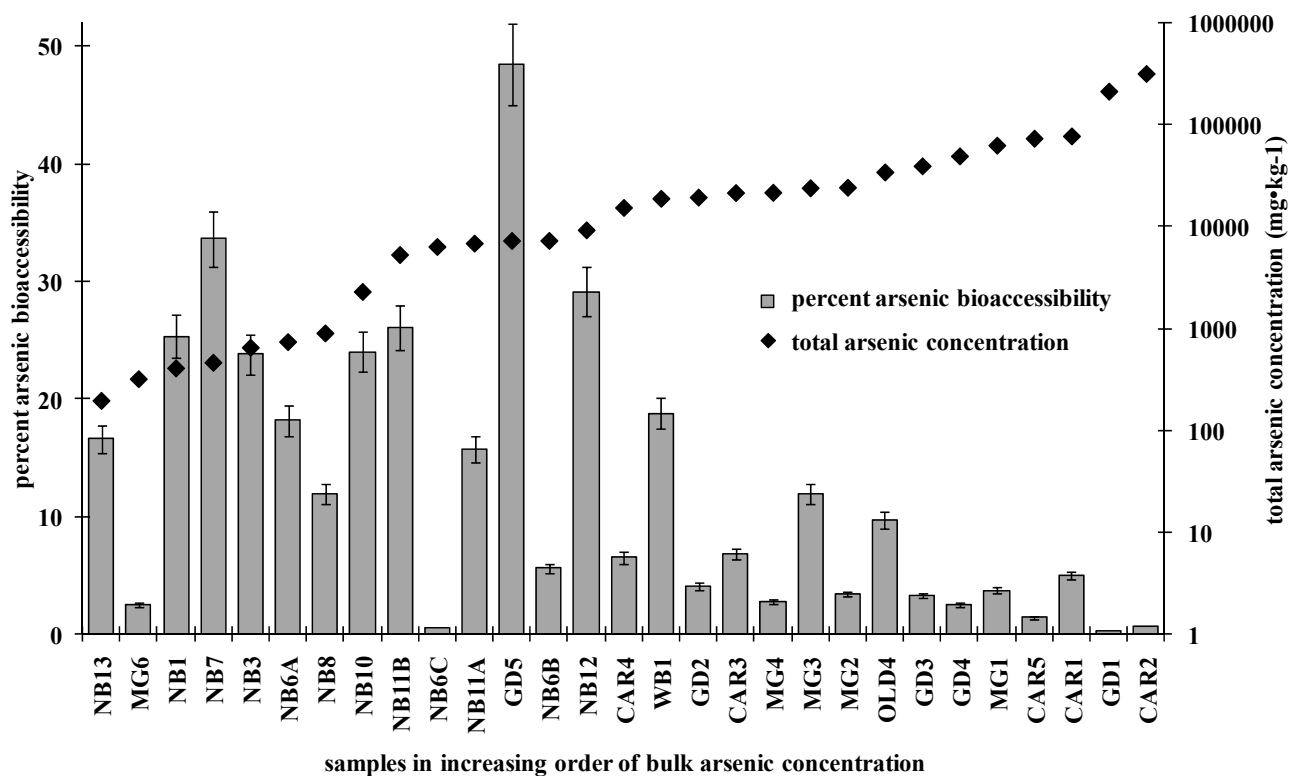
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Figure S1. Percent arsenic bioaccessibility and total arsenic concentration of samples collected in 2005 in Nova Scotia. The data illustrated in this figure is presented in Table 1 (main document). Results are for the < 150 μm particle size fraction. The percent arsenic bioaccessibility is chosen as the higher of either P1 (gastric phase) or P2 (gastric + intestinal phase), and is calculated as 100 • bioaccessible arsenic concentration • (total arsenic concentration)[-1].

Effect of Selected Particle Size. Bioaccessibility results may be affected by particle size, making the choice of particle size important in estimating arsenic bioaccessibility (*9, 16*).

Limited sample material from the 2005 collection (described in the main document) precluded its use in a particle size study. Instead, samples were selected from a 2006 collection (*3*). The 2006 sample set ($n = 27$) was assembled following a similar collection pattern as the samples collected in 2005 at the Goldenville and Montague sites. Nine samples (four from Goldenville and five from Montague) were selected for the particle size study, representing a range of arsenic concentrations and bioaccessibilities (Table S1). The requirement to sieve the bulk material to three particle size fractions (resulting in small subsample sizes) limited this series of bioaccessibility tests to the gastric phase (P1) only.

The extraction procedures used in the particle size study are the same as described in the main document, and the quality controls (9 duplicates, 6 blanks, 6 standard reference materials) met the criteria described in Table S2. For this series of tests, the relative percent difference (RPD) between duplicates ranged from 0.59 to 4.9% (average 4.3%). The percent arsenic bioaccessibility results were calculated with respect to total arsenic concentrations measured in each particle size fraction (Figure S2).
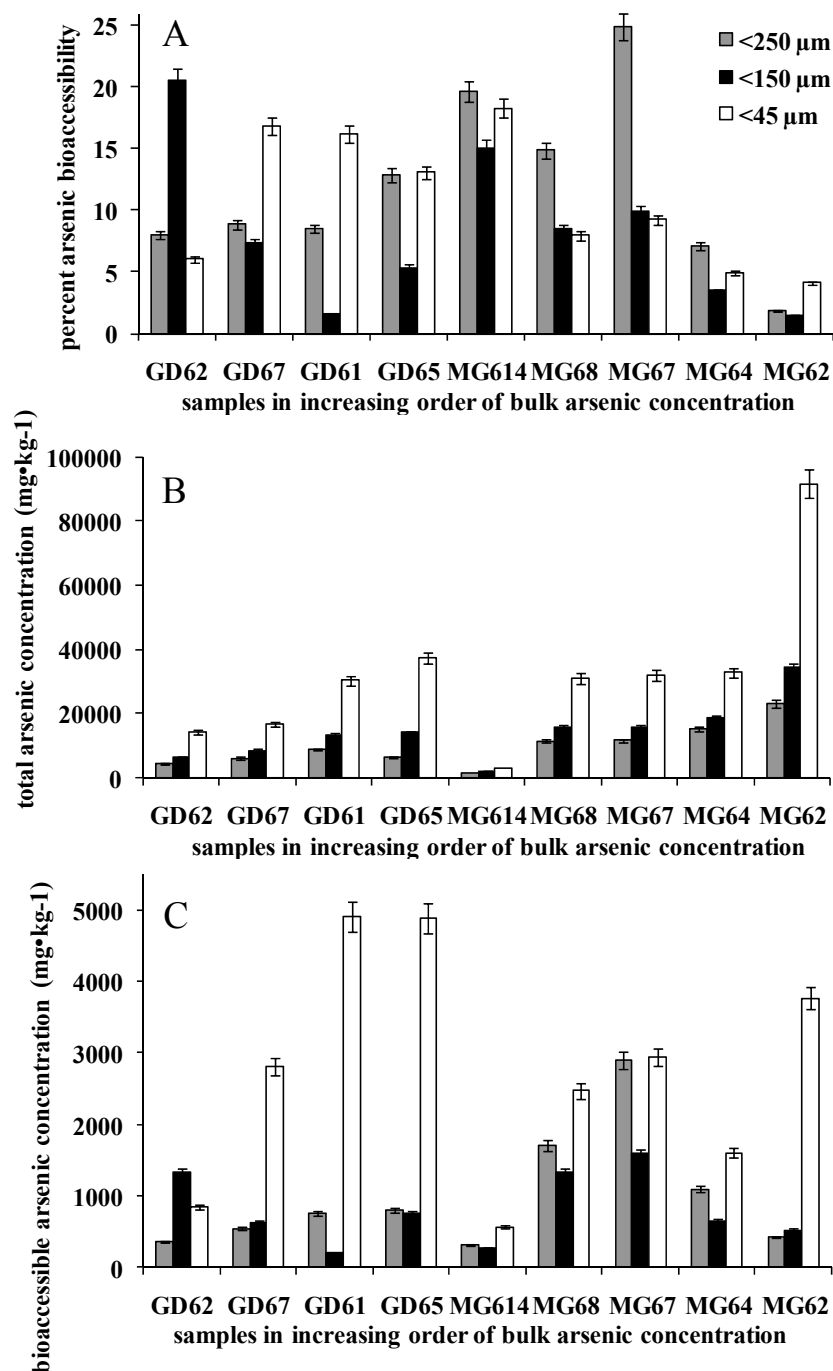
Figure S2. Bioaccessibility and concentration of arsenic in different particle size fractions. The percent arsenic bioaccessibility (Panel A), total arsenic concentration (Panel B), and bioaccessible arsenic concentration (Panel C) are shown for selected 2006 samples sieved to three particle size fractions (< 250 μm, < 150 μm and < 45 μm) tested by PBET in the gastric phase (P1) only. Error bars (± 4.3% for the bioaccessibility tests, and 5.0% for the total arsenic concentrations) represent the average of the relative percent difference between duplicates for this series of tests.

Principal Components Analysis (PCA). Bulk major and trace element concentrations (Ag, Al, As, Au, Ba, Bi, Ca, Ce, Co, Cr, Cs, Cu, Fe, Ga, Hg, K, La, Li, Mg, Mn, Mo, Na, Ni, P, Pb, Rb, S, Sb, Se, Sn, Te, Th, Ti, Tl, V, W, Y, Zn and Zr), inorganic (IC) and organic carbon (OC) concentrations, and arsenic bioaccessibility results (BiAc) obtained for the 29 samples collected in 2005 (for the < 150 μm particle size fraction) were placed in a 42×29 matrix. The PCA results are presented in two related maps (Figure S3: Maps A and B). The factor loadings, shown on Map A, express the influence of the original variables on each sample, which are spatially represented according to factor scores on Map B. SYSTAT^{TM} 10 was used to treat mean centered and scaled matrices, and each correlation matrix was generated with default Eigenvalues of 1.

The two first principal components (used to construct Figure S3) account for nearly 60% of the variance. Three main groups of samples were revealed when samples were plotted according to factor scores. Groups were labelled 1, 2 and 3 from top to bottom and generally include samples from the same location. Group 1 contains all the Montague samples, the Whiteburn sample, and four of the North Brookfield samples (NB11A, 11B, 12 and 13). Group 2 includes the rest of the North Brookfield samples and all of the Goldenville samples, except for GD1. Group 3 contains all of the Caribou samples except CAR2. Sample OLD4 stands outside of Group 1. The relative position of the three groups along the vertical axis may correlate with the loading positions of factors potassium and aluminum, which may reflect the proportion of muscovite (Figure S3, Map A) in these samples. With the exception of the two outliers (GD1 and CAR2 discussed below), samples have barium, caesium, rubidium and thallium concentrations (*3*) that systematically increase from site to site and correspond to the PCA distribution observed. Barium, caesium and rubidium are known to be common trace elements in micas. Thallium can also be present as it

exhibits similar geochemical behaviour to potassium. In addition, the OLD4 sample, which plots above all other samples on the PCA, contains the highest concentrations of barium, caesium, rubidium and thallium 3 to 9 times the mean of all samples (excluding GD1 and CAR2). Therefore, the geographical trend in the PCA data is likely due to variation in the trace element chemistry of mica minerals (*e.g.* muscovite) from location to location.

Samples CAR2 and GD1 stand apart from the groups and are closer to the arsenic loading position. These contain arsenic in concentrations nearly an order of magnitude higher than the average concentrations: CAR2 (310,000 mg•kg^{-1}, 31 wt%) and GD1 (210,000 mg•kg^{-1}, 21 wt%).

The division of the North Brookfield samples between Groups 1 and 2 (Figure S3, Map B) may be attributed to different ore treatments used at this location. Samples NB6B, NB6C, NB11A, NB11B and NB12 were collected near the former processing plant and contain > 4000 mg•kg^{-1} arsenic, although not all of these fall within the same Group (samples NB6B and NB6C are in Group 2, whereas the other three are in Group 1). This suggests that the PCA Groups may correspond to soil composition based on mining process history as well as the aforementioned similar geographical location.

The arsenic bioaccessibility results were compared with Groups 1, 2 and 3. Although the percent arsenic bioaccessibility is lower than the average of 13% for Group 3 (from 0.5 to 6.8%), the bioaccessibility results fluctuate within each Group. Results vary from 2.5 to 29% for Group 1, and from 0.40 to 49% for Group 2. The PCA analysis did not reveal groupings that correlate with either the bioaccessibility results or the detailed arsenic mineralogy information described in the

main document. For example, the five Montague samples tested display a wide range of arsenic mineralogy (as detailed in Table 2, main document), and the percent arsenic bioaccessibility varied from 2.5 to 12%; however, these samples were all found within Group 1 of the PCA analysis (Figure S3, Map B). Overall, no PCA groupings emerged to explain the arsenic bioaccessibility results (in terms of percentage or as a concentration) for the samples tested.

Figure S3: Principal components analysis. Elemental analysis and bioaccessibility tests results (mean centred and scaled) for the < 150 μm particle size fraction of the 29 samples from the 2005 collection were used in this principal components analysis. Groups identified by the numbers 1, 2 and 3, generally reflect sample location. The percent arsenic bioaccessibility varies within each Group: 2.5 to 29% for Group 1; 0.4 to 49% for Group 2; and 0.5 to 6.8% for Group 3. Factor loadings are presented in Map A, and factor scores for each sample in Map B. The one or two-letter code in Map A corresponds to element names, except: BiAc = arsenic bioaccessibility; OC = organic carbon; IC = inorganic carbon. Sample labels in Map B are described in the main document.
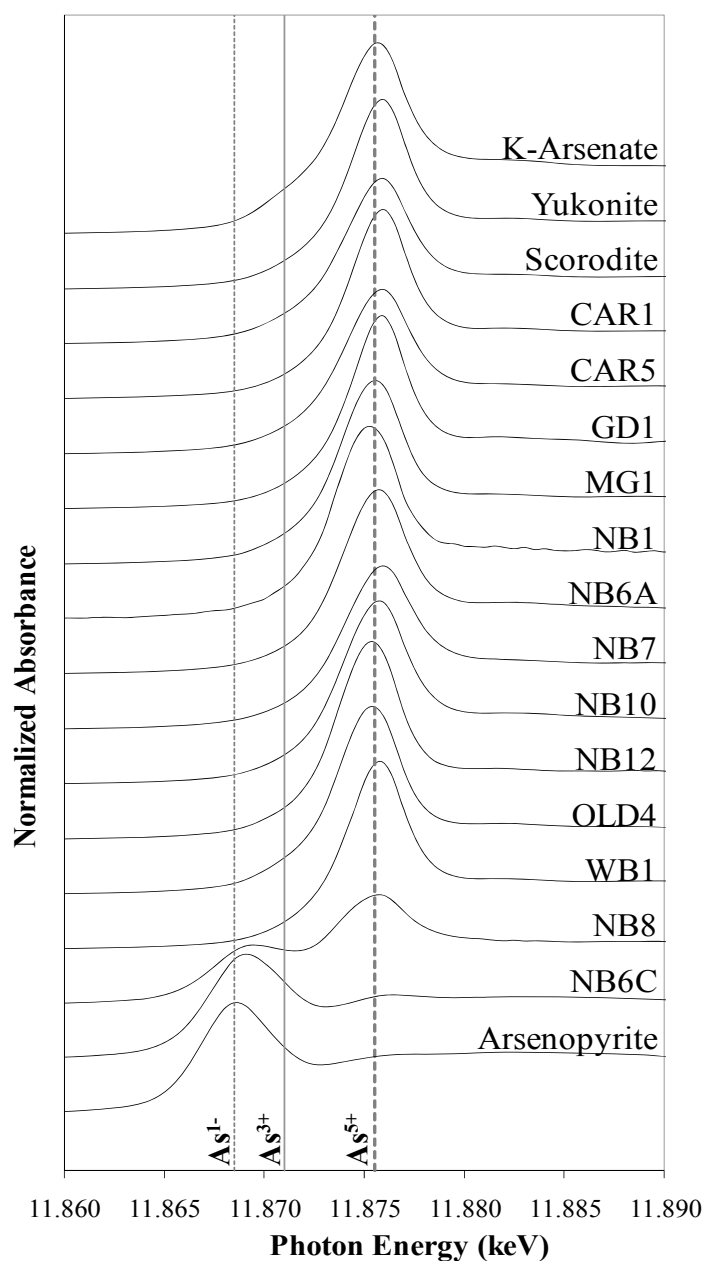
Figure S4. Normalized arsenic K-edge profiles of selected samples. Analysis of samples from the 2005 collection (described in the main document) and reference arsenic compounds: potassium arsenate (KH$_2$AsO$_4$, Fluka reagent grade); yukonite and scorodite (samples M990 and M6303 respectively, from Miller Museum, Queen's University); arsenopyrite, (FeAsS, Ninas de Panasqueira, Portugal (Ward's Natural Science)). The arsenic K-edge shifts to higher energies with increased oxidation state, as shown with the vertical lines plotted at peak position for three arsenic oxidation states (As^{1-}, As^{3+} and As^{5+}), based on the spectra of arsenopyrite (11,867.6 eV), arsenic trioxide (11,871.7 eV) and potassium arsenate (11,875.3 eV), respectively.