A new method for the characterisation and quantitative speciation of base metal smelter stack particulates

James M. Skeaff · Yves Thibault · David J. Hardy

Abstract Base metal smelters may be a source of particulates containing metals of environmental concern released to the atmosphere. Knowledge of the quantitative chemical speciation of particulate releases from base metal smelters will be of value in smelter emission fingerprinting, site-specific risk assessments, predictions of the behaviour of smelter stack particulates released to the environment and in resolving liability issues related to current and historic releases. Accordingly, we have developed an innovative approach comprising bulk chemical analysis, a leaching procedure, X-ray diffraction analysis and scanning electron microscopy/electron probe microanalysis characterisation in a step-wise apportioning procedure to derive the quantitative speciation of particulate samples from the stacks of three copper smelters designated as A, B and C. For the A smelter stack particulates, the major calculated percentages were 29 $CuSO_4$, 20 $ZnSO_4.H_2O$, 13 $(Cu_{0.94}Zn_{0.06})_2(AsO_4)(OH)$, 11 $PbSO_4$ and four As_2O_3. For the B smelter stack particulates, the primary calculated percentages were 20 $ZnSO_4.H_2O$, 20 $PbSO_4$, 12 $CuSO_4$ and nine As_2O_3. Finally, we calculated that the C smelter stack particulates mostly comprised 34 $ZnSO_4.H_2O$, 19 $(Cu_{0.84}Zn_{0.16})(AsO_3OH)$, 11 $PbSO_4$, 10 As_2O_3 and nine $Zn_3(AsO_4)_2$. Between 56% and 67% by weight of the smelter stack particulates, including the As, was soluble in water. For these and other operations, the data and approach may be useful in estimating metals partitioning among water, soil and sediment, as well as predictions of the effects of the stack particulates released to the environment.

J. M. Skeaff (✉) · Y. Thibault · D. J. Hardy
CANMET Mining and Mineral Sciences Laboratories,
555 Booth Street, Ottawa, K1A 0G1, Canada
e-mail: jskeaff@nrcan.gc.ca

Y. Thibault
e-mail: ythibaul@nrcan.gc.ca

D. J. Hardy
e-mail: dhardy@nrcan.gc.ca

Introduction

Smelting, converting and fire-refining of base metal concentrates can generate considerable volumes of gases which are usually passed through electrostatic precipitators to remove almost all of the entrained particulates. However, some particulates are inevitably released to the atmosphere.

Particulates may be formed during smelting and other pyrometallurgical operations chemically, by the vaporisation of solid or liquid chemicals followed by condensation, and mechanically, by physical breakdown of compounds into smaller particles (Samuelsson and Carlsson 2001).

Some base metal particulates can contain substances of environmental concern. For instance, Doyle et al. (2003) noted that aquatic and soil organisms close to copper and zinc smelters may incur adverse effects. In Canada, base metal smelters are required to prepare and implement comprehensive Pollution Prevention Plans and to publicly report on their conformance with an Environmental Code of Practice for Base Metals Smelters and Refineries (Environment Canada 2006). The requirement covers inorganic compounds of arsenic, cadmium, lead, mercury, certain compounds of nickel and particulate matter containing metals released from copper smelters and zinc plants (Canada Gazette 2006).

Moreover, Canada and 28 other countries have ratified the United Nations Economic Commission for Europe (UNECE) Convention on Long-Range Transboundary Air Pollution Protocol on Heavy Metals (UNECE 1998). The parties to the Convention are obligated to reduce their emissions of Cd, Hg and Pb from industrial sources (the non-ferrous metals and the iron and steel industries), combustion processes (power generation and road transport) and waste incineration to below their 1990 levels.

A typical copper smelter treats sulphide concentrates at elevated temperatures to produce a copper metal suitable for electro-refining (Biswas and Davenport 1994). In addition to Cu, Fe and S in the minerals chalcopyrite ($CuFeS_2$), chalcocite (Cu_2S), covellite (CuS), bornite (Cu_5FeS_4), the concentrates typically contain minor and trace quantities of Ag, As, Au, Cd, Co, Ni, Pb, Sb, Se and Zn residing in distinct phases or in solid solution in the copper-bearing matrices. Copper concentrates usually also contain various silicate minerals such as chlorite $((Mg,Fe)_3(Si,Al)_4O_{10}(OH)_2.(Mg,Fe)_3(OH)_6)$ and at least some from the feldspar group such as orthoclase $(K)AlSi_3O_8)$, microcline $(KAlSi_3O_8)$ and anorthoclase $((Na,K)AlSi_3O_8)$ (Dana and Ford 1958).

The copper concentrates are usually smelted at about $1200°C$ with fluxing materials such as CaO and SiO_2 to separate a liquid Cu–Fe–S phase known as a matte, with the viscosity of water, from a liquid oxide slag phase, with the viscosity of molasses that overlies the matte. The matte and slag phases are separated by gravity, with the slag being discarded and the matte proceeding to a conversion stage. In the converter, tonnage oxygen is blown into the matte with more fluxing materials to convert the S to SO_2, transfer the Fe to the converter slag with some of the Cu and many of the minor and trace elements, and yield an impure Cu liquid known as blister copper containing 0.03% or less S and 1% or less dissolved oxygen. In continuous converting processes, the SO_2 is also converted to sulphuric acid. The blister copper is fire-refined with either natural gas, ammonia or wood to remove the dissolved oxygen, and is then cast into anodes for electro-refining.

Some smelter emission characterisation studies have been reported in the literature. For instance, Samuelsson and Björkman (1998) applied bulk chemical analysis, X-ray diffraction (XRD) analysis and electron probe X-ray microanalysis (EPMA) to examine samples of particles from various stages in the converter gas stream of a copper smelter. Using XRD, they identified SiO_2, $CuFeS_2$, $Cu_{2-y}S$, Cu_5FeS_4, $PbSO_4$, $CuO.CuSO_4$ and FeS_2 in the samples. The variability in metal content could be quite substantial and depended on the sampling location. For instance, Cu in the particulates could vary between 0.2% and 66%, and the values for As between 0.25% and 12%. Since they reported their bulk chemical analyses in terms of the percentages of the elements Fe, Cu, Cd, Pb, As, Sn, Sb, Bi and S, the total percentages were less than 100%, and the speciation of the elements is unknown.

Using XRD and EPMA, Samuelsson and Carlsson (2001) examined the dusts from four locations in a copper smelting plant. They reported weight percentages of the elements Cu (2–20%), Fe (1–30%), Zn (6–33%), Pb (3–20%), Sb (0.05–1%), As (1–12%), S (2–12%), Sn (<0.01–2%) and SO_4 (4–23%), although in totals of less than 100% which might have been attained had they been able to assign speciation to the elements. From their microprobe analysis, they detected such

species as $CuFeS_2$, Cu_5FeS_4, K-feldspar, SiO_2, Fe–Cu oxide and small particles containing Zn, As, Pb, Cu, Fe, Si, K and Ca.

Using XRD, scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS) and Raman microspectroscopy, Sobanska et al. (1999) estimated individual particles of air pollution control particles from a lead smelter to comprise amounts of PbS, $PbSO_4$, $PbSO_4.PbO$, ZnS, ZnO, CdS and $CdSO_4$ in the range 15–60%. They also determined elemental compositions using bulk chemical analysis, obtaining close to 100% mass balances.

Ettler et al. (2005) used bulk chemical analysis, XRD analysis, SEM, transmission electron microscopy (TEM) and EPMA to identify the phases in four samples of particulate matter from the various stages of air pollution control in a lead smelter in the Czech Republic. The samples consisted of major amounts of such phases as quartz (SiO_2), anglesite ($PbSO_4$), cotunnite ($PbCl_2$), minor amounts of K-feldspar ($KAlSi_3O_8$), lanarkite ($PbO.PbSO_4$) and trace amounts of arsenolite (As_2O_3) and senarmontite (Sb_2O_3). From their bulk chemical analysis, they determined the concentrations of the elements in the four samples. While they qualitatively identified the sample phases, it might have been useful to quantify the amounts of each phase. Again, Ettler et al. (2008) used Rietveld XRD to quantitatively identify major amounts of $Na_2SO_4.NaCl.2PbSO_4$, $KCl.2PbCl_2$, NaCl and Na_2SO_4 in the crystalline fractions of two samples of lead smelter air-pollution-control residues.

Sánchez de la Campa et al. (2008) and Sánchez-Rodas et al. (2007) focused on arsenic speciation in PM2.5 and PM10 samples collected near a copper smelter. They found that As(V) was the predominant species, accounting for 79–84% of the total, with As(III) comprising the balance. Knowledge of the compounds associated with the arsenic, while of interest, was likely prevented by the practical difficulties in collecting samples in quantities sufficient for analysis. The practical difficulties in collecting sufficient sample quantities may have prevented a determination of the compounds associated with the arsenic.

Wong et al. (2006) determined the mass fractions of As, Cd, Cu, Ni, Pb, Se and Zn in mid-stack particulate samples and downstream plumes from a copper smelter. At 0.31–0.41 and 0.14–0.43 mass fractions, respectively, Pb and As were dominant elements in the mid-stack particulate samples, followed by Cu at 0.11–0.30 and Zn, 0.07–0.20. Working with very small sample sizes, they would have considerable difficulty in determining the speciation and compounds of As and the metals.

Beavington et al. (2004) measured the concentrations of trace elements Cr, Zn, Ag, Se, Cd, Sb, Au and Pb in the atmosphere near a copper smelter. Again, lack of sufficient sample may have prevented a determination of speciation and compounds.

In examining the electrostatic dust samples from a copper–nickel smelter, Barcan (2002) quantified several elements, such as As, Cu, Ni, Pb and Zn, and qualitatively identified phases such as pentlandite $(Fe,Ni)_9S_8$, pyrrhotite Fe_7S_8, As_2O_5, khyslevudite Ni_3S_2, PbO, ZnO, cuprite Cu_2O, tenorite CuO and silicates of Fe, As, Mg and Ca. A quantitative assessment of the identified phases would have been of interest.

Karczewska (1996) used sequential extraction to determine the distribution of eight metals including Cu, Pb and Zn in soil samples near a copper smelter. She found that 40–50% of the Cu and Pb were in the mobile and exchangeable fractions of strongly polluted sandy soils. However, the compounds with which the metals were associated remained unidentified.

Gieré et al. (2006) used TEM to identify the amorphous and crystalline phases in collected PM2.5 from a coal combustion station stack in which tires were experimentally combusted. The amorphous phases comprised silicates and sulphates of Al, K, Fe, Na and Zn. Among the crystalline phases were anglesite $PbSO_4$, gunningite $ZnSO_4.2H_2O$ and anhydrite $CaSO_4$. Of interest would have been the quantities of the amorphous and crystalline phases.

Thus, a limited amount of quantitative data on smelter particulates is available for elemental analyses, while speciation data tend to be qualitative or at best semi-quantitative. Analysis of smelter particulates to determine how they were formed and their chemical composition would be of considerable value in determining treatment

methods and in predicting environmental effects (Samuelsson and Björkman 1998).

The objective of this study was to develop quantitative chemical speciation of the stack particulates from three copper smelters, including a mass balance as close to 100% as possible. While we have applied it to stack particulate samples from copper smelters, the new method could equally be applied to stack particulates from any non-ferrous or ferrous smelting operation. By chemical speciation, we mean a characterisation of the compounds or dissolved species that comprise a solid or solution. The stack particulates may be considered as potential sources of metals released as compounds to the atmosphere.

Materials and methods

Samples of Smelter Stack Particulates   The samples of smelter stack particulates were from three copper smelters designated as A, B and C. The C smelter process consists of smelting copper concentrate in a Teniente converter and flash furnace followed by Peirce–Smith conversion and anodic furnace casting of blister copper. An electric furnace is used for slag cleaning. The A smelter process is similar to that for the C smelter, except that smelting is conducted in Teniente furnaces only and a tilting furnace is used for slag cleaning. The B smelter process is much the same as at the A smelter.

During continuous operation at all three smelters, the primary off-gases from the Teniente converters and Peirce–Smith converters pass through electrostatic precipitators and are combined and proceed to acid plants for conversion to H_2SO_4. However, following process interruption for routine maintenance, the converters and furnaces are returned to operational temperatures by heating with natural gas and, since they are unsuitable for acid plant treatment, these gases are diverted to the primary stack, which is cleared of particulates about once per month. The particulate samples under consideration here were removed from the interior walls of these primary stacks, from the A and C smelters in February, 2005, and from the B smelter in April, 2004. The samples may be

considered as surrogates for particulates released to the atmosphere aggregated over the period of about 1 month.

Bulk Chemical Analysis   We determined the total percentages of Al_2O_3, As, CaO, Cd, Cr_2O_3, Cu, Fe, K_2O, MgO, Na_2O, Ni, Pb, SiO_2, total S, SO_4, Sb, Se and Zn in the as-received (a-r) particulates by bulk chemical analysis. In Appendix 1, we have presented an overview of the analytical methods, limits of quantification (LOQs) and estimates of uncertainties in the analyses and in the quantitative speciation.

Leaching Procedure   To obtain an indication of their behaviour upon contact with aqueous media, the extent to which they contain soluble material, and whether the media would affect particulate reactivity, we also subjected the smelter particulates to leaching in three media: (1) the OECD (Organization for Economic Cooperation and Development) 203 aquatic ecotoxicity testing medium for fish and *Daphnia* (OECD 1992); (2) 18 MΩ deionised (d.i.) water and (3) RICH-95, a reference lake water obtained from Environment Canada's NWRI (National Water Research Institute). The compositions of the OECD 203 and the RICH-95 aqueous media are presented in Tables 1 and 2, respectively.

The leaching procedure was adapted from the UN Transformation/Dissolution Protocol for Metals and Sparingly Soluble Inorganic Metal compounds (United Nations 2009), that had been originally developed within the framework of the OECD (2001). The procedure consisted of agitating weighed quantities of a-r particulates in the leaching media at 200 rpm in the temperature range 22.4–25.3°C for 6 h, and filtering the resulting slurry through a 90-mm diameter 0.45-μm Acrodisc filter. We then acidified the filtrate to pH ~1 and analysed for total dissolved Al, As, Ca, Cd, Cr, Cu, Fe, K, Mg, Na, Ni, Pb, total S, SO_4, Sb, Se and Zn. We also thoroughly rinsed the residue, allowed it to air-dry and used bulk chemical analysis for Al_2O_3, As, CaO, Cd, Cr_2O_3, Cu, Fe, K_2O, MgO, Na_2O, Ni, Pb, total S, SO_4, Sb, Se and Zn. Ideally, a minimum of 5 g of post-leach residue should be available for bulk chemical analysis of the residues. A reasonable initial

Table 1 Composition of modified OECD 203 (ISO 6341) aqueous medium (no micronutrients)

Component	M.W.	mg/L	Mg^{2+}	Ca^{2+}	Cl^-	HCO_3^-	SO_4^{2-}	Na^+	K^+	mmol/L
$CaCl_2.2H_2O$	147.01	294.00		80.15	141.80					2.00
$MgSO_4.7H_2O$	246.47	123.25	12.15				48.04			0.50
$NaHCO_3$	84.01	64.75				47.03		17.72		0.77
KCl	74.55	5.75			2.73				3.02	0.077
Totals, mg/L			12.15	80.15	144.53	47.03	48.04	17.72	3.02	
mmol/L			0.50	2.00	4.08	0.771	0.50	0.771	0.077	
Hardness as $CaCO_3$, mg/L	250									

Reference: http://www.oecd.org/dataoecd/17/20/1948241.pdf; Calculated pH of medium when in equilibrium with air (0.038% CO_2) at 21.5°C: 8.00 (FactSage 6.2. 2009. www.factsage.com)

assumption is that about 50% of the smelter stack particulates will dissolve during leaching, so a minimum of 10 g of sample should be available for each leaching test. For 10 g weights, we prepared initial media volumes of 850 mL, and for the more ideal weights of 20 g, 1,800 mL, adjusting the final volumes to 1,000 and 2,000 mL, respectively, after filtration.

XRD We obtained XRD patterns of the a-r particulate samples and the leach residues using an automated 12 kW rotating anode Rigaku X-ray diffractometer, and achieved phase identification with the JADE version 9.0 interfaced with the Inorganic Crystal Structure Database and International Centre for Diffraction Data diffraction databases.

SEM/EPMA We further characterised the a-r particulate materials using a JEOL JXA 8900 electron microprobe that we used as an SEM and as an EPMA. We obtained backscattered electron (BSE) images and performed X-ray microanalyses by EDS and wavelength-dispersive (WDS) spectroscopy. Most of this microcharacterisation was done on pristine powder samples mounted

on conductive tape to reveal the morphology of the particulates in greater detail. Typically, on such rough surfaces, only qualitative EDS analyses can be achieved. Nevertheless, we also used WDS scans to resolve significant energy overlaps between some of the major elements (e.g. Pb M with S K; Pb L with As K and Zn K with Na K) and to confirm the presence of oxygen.

We also made polished mounts by embedding a portion of each particulate sample in epoxy. To prevent contact with water, we polished the mounts in alcohol and oil. Although the surface quality was not ideal, mainly due to the fine-grained nature of the materials, this approach allowed the quantitative analyses of some of the phases by WDS.

For the silicate analyses, the EPMA was operated with an accelerating voltage of 15 kV, a probe current of 5–10 nA and counting times of 10 to 30 s. Characteristic X-ray lines and standards used were: Si Kα (Orthoclase), Al Kα (Orthoclase), Fe Kα (Almandine), Cu Kα (Cu$_2$O), Zn Lα (ZnO), Pb Mα (PbSO$_4$), CaKα (Wollastonite), Na Kα (albite), K Kα (orthoclase), As Lα (FeAs2), S Kα (PbSO$_4$). An overlap correction was applied to account for the interference of Zn Lβ on Na Kα.

Table 2 Composition of RICH-95 National Water Research Institute certified reference Lake Water, Environment Canada

	Mg^{2+}	Ca^{2+}	Cl^-	SO_4^{2-}	Na^+	K^+	Dissolved carbon	
							Inorganic	Organic
Totals, mg/L	7.89	27.55	18.51	18.00	13.26	2.39	18.43	3.50
Mmol/L	0.32	0.69	0.52	0.19	0.58	0.06	1.53	0.29
Hardness as $CaCO_3$, mg/L	101							

Calculated pH of medium when in equilibrium with air (0.038% CO_2) at 21.5°C: 8.29 (FactSage 6.2. 2009. www.factsage.com)

An accelerating voltage of 20 kV with a probe current of 10 nA and counting times ranging from 20 to 30 s were used for the Cu oxides, sulphides and arsenates analyses. The characteristic X-ray lines and standards used were: Cu Kα (Cu$_2$O, CuS), Zn Kα (ZnO), As Lα (FeAs2), O Kα (Cu$_2$O). Potential O Kα and S Kα peak shift in the various phases were monitored and accounted for.

Quantitative speciation calculation Using a step-wise apportioning procedure, we developed the quantitative speciation of the particulate samples by assigning the metals and other analytes to specific phases and compounds on the basis of the results of the bulk chemical analyses, mass balances, XRD, and SEM/EPMA data. A worked example of the step-wise procedure is in Appendix 2. We have assigned the minor and trace metals such as Al, Fe, Sb and Si (but not Ag) to oxides since it is most unlikely that they would exist in the elemental state in the a-r particulates. Moreover, while we present the amounts of these oxides in percentages, they may not necessarily exist as separate and discrete phases, but may rather be associated as agglomerates with other minor and trace oxides or with the major phases.

Mass balance calculations Mass balances are important to ensure that we can provide an accounting of the amounts of a particular analyte in the a-r particulates against the corresponding amounts in the leach residue and leachate. A mass balance close to 100%, particularly for the major analytes, provides a validation of our quantitative speciation calculations and an assurance that we have accounted for most or all of the specified analyte between a-r particulates on the one hand and residues plus leachate on the other hand.

As per Appendix 2, the mass balance for any analyte is given by

mass balance

$$= 100 \times \frac{\dfrac{\text{moles leached}}{100 \text{ g sample}} + \dfrac{\text{moles in residue}}{100 \text{ g sample}}}{\dfrac{\text{moles in a-r particulates}}{100 \text{ g sample}}}. \quad (1)$$

Results and discussion

A smelter

Chemical composition of a-r particulates The bulk chemical analyses of Table 3 reveal that, in addition to SO$_4$ at 34.7%, the a-r A smelter particulate sample is dominated by Cu, Pb, As and Zn, in weight percentages of 20.5, 7.5, 6.6 and 6.6, respectively. We also detected trace and minor amounts of Cr, Ni, Se, Ag, Sb, Mg, C, Al, Ca, Si, Na, Fe and K in the range 0.0009% to 1.79%.

Leaching results and mass balances The percentage distributions of the analytes between the leachates from leaching with OECD 203, d.i. water and the RICH-95 medium and corresponding residues, as well as the mass balances for each analyte are also in Table 3. The distributions of the analytes As, Cu and SO$_4$ between the leachates and the residues indicate that averages of about 47%, 57% and 99%, respectively, dissolved during the leach tests. Almost all of the Pb reported to the residue. These distributions are supported by their mass balances being close to 100%. However, the mass balance for Zn was about 122%, so that the calculated ~110% level in the leachates is only a qualitative indication of a relatively high dissolution value. An average of about 65% of the total weights of the samples was leached.

The mass balances for the trace and minor components Ag, Al, Cd, Fe, K, Mg, Na, Ni, and Sb were all within 86–124%, so the distributions between leachate and residue can be considered credible, the more so because of the relatively low concentrations of each analyte. Even for the trace element Cr, the mass balances were between 104% and 135%. For Ca in the d.i. H$_2$O and RICH 95 lixiviants, the mass balances were 100% and 93%, respectively. However, subtracting the relatively high value of Ca in the OECD 203 lixiviant from the measured concentration in the OECD leachate reduced its mass balance to 79%. The mass balances in the range 32% to 38% for Se were the only ones to reflect the difficulty in obtaining ~100% values for minor or trace analytes.

Mineralogical analyses We used XRD and SEM/ EPMA characterisation to help assign the analytes

Table 3 Chemical analysis of A smelter stack particulates and percentage distributions of analytes between leachates and residues

A smelter as-received		Leached in								
		OECD 203			d.i. H_2O			RICH 95		
Analyte	wt.%	% Leached	% In residue	Mass balance, %	% Leached	% In residue	Mass balance, %	% Leached	% In residue	Mass balance, %
As	6.63	39.1	61.1	100	56.3	43.4	100	45.0	55.1	100
Cu	20.49	55.34	42.07	97	59.40	43.07	102	54.94	42.81	98
Zn	6.56	110	11	121	114	9.28	123	111	10.4	122
Ni	0.0039	51	46	97	53	57	111	51	47	98
Pb	7.49	0.0021	99.2	99	0.0043	97.0	97	0.0021	98.96	99
Cd	0.386	84.0	12.3	96	90.9	8.58	99	86.7	10.1	97
Se	0.009	4	31	35	8	30	38	4	28	32
Sb	0.16	2.0	108	110	6.0	103	109	4.3	103	107
Ag	0.024	0.47	94	95	0.12	92	93	0.11	96	97
Cr	0.0009	0.4	103	104	0.8	134	135	0.4	111	112
Fe	1.29	0.0536	91.8	92	1.14	85.4	86	0.125	89.8	90
C	0.19									
Al	0.193	2.08	120	122	13.5	105	119	8.63	113	121
Ca	0.577	72.9	6.09	79	94.3	5.27	100	87.1	5.41	93
Mg	0.185	89.0	10.4	99	114	10.0	124	97.7	10.4	108
K	1.79	97.5	5.59	103	97.9	5.10	103	97.5	5.60	103
Na	0.935	109	1.37	111	114	1.22	115	110	1.33	111
SO_4	34.71	98.84	9.731	109	97.49	10.06	108	100.84	9.879	111
Si	0.757									
Total	82.38	Initial wt., g:		10.0007	Initial wt., g:		10.0182	Initial wt., g:		10.0107
		Residue wt., g:		3.7242	Residue wt., g:		3.3527	Residue wt., g:		3.5795
		% Leached		62.76	% Leached		66.53	% Leached		64.24
Initial pH		7.89			4.94			7.86		
Final pH		4.02			3.65			3.86		

to specific phases/compounds. Whereas XRD is especially useful for identifying crystalline assemblages, SEM/EPMA allows the determination of the morphology and the chemical composition of the crystalline as well as potentially amorphous phases.

For the a-r A smelter stack particulates, the crystalline phases identified by XRD, Fig. 1a, are anglesite ($PbSO_4$), cuprite (Cu_2O), gunningite ($ZnSO_4.H_2O$), chalcocyanite ($CuSO_4$) and arsenolite (As_2O_3). Moreover, the background profile of the XRD pattern suggests the presence of amorphous material.

The SEM/EPMA characterisation of the a-r sample confirms the presence of most of the crystalline phases identified by XRD, and suggests that they all have near end-member compositions with no significant solid solutions. The Cu sulphate and Cu oxide grains typically occur in 5 to

10 μm diameter spheroids (Fig. 2a, b). The EDS spectra, shown in Fig. 3a, b, indicate that they are fairly pure phases. WDS analyses indicate a Cu_2O stoichiometry for the copper oxide (Table 4, Analysis #1), consistent with the XRD data. Anglesite is homogeneously distributed throughout the sample as fine, often ≤1 μm, discrete grains that appear very bright in BSE images (e.g. Fig. 2a, c) due to the high atomic number of Pb. EDS analysis suggests a pure $PbSO_4$ chemistry (Fig. 3c) Arsenolite occurs as well-formed octahedral crystals (Fig. 2d) consisting only of As and O (Fig. 3d). Crystalline Cu sulphide with dendritic overgrowths (Fig. 2e), in abundance too low to be detected by XRD, was observed, and WDS characterisation supports a Cu_2S formula. Copper arsenate grains with minor amounts of Zn, are also present. WDS analyses of a few larger grains indicate a composition close to olivenite,
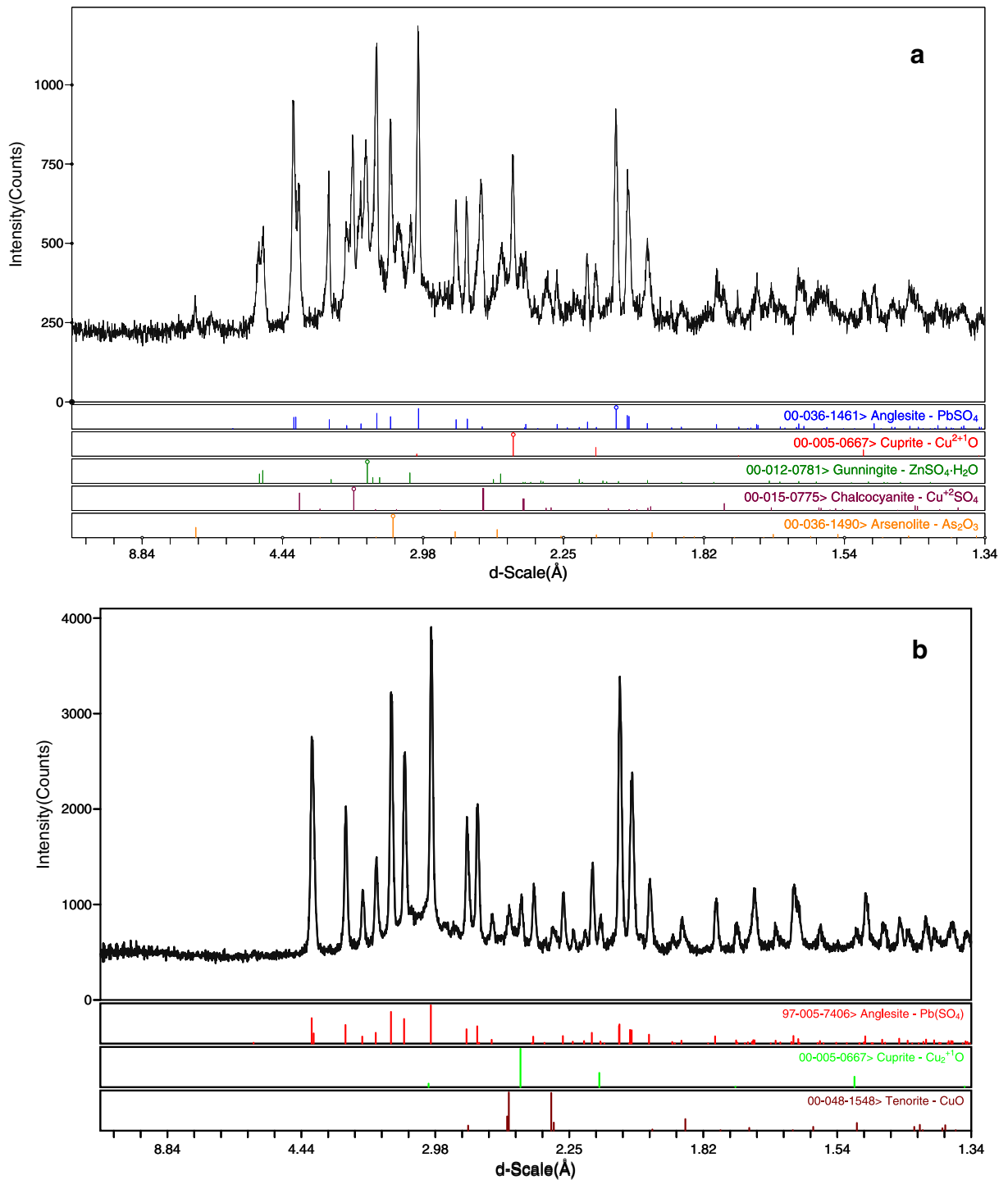
Fig. 1 XRD patterns of **a** the a-r A smelter stack particulates and **b** the residue from leaching of a sample of the A smelter stack particulates in OECD 203
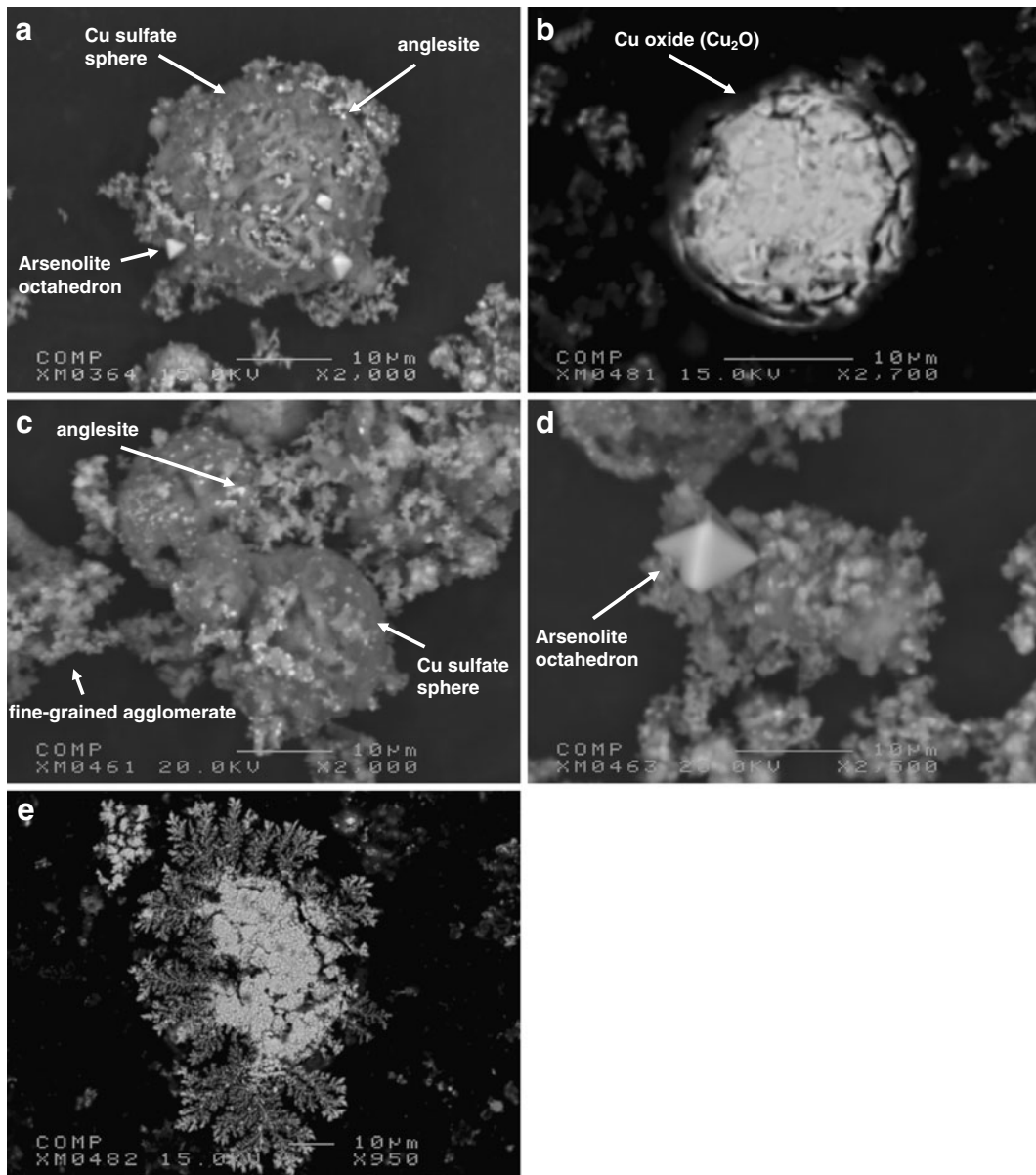
Fig. 2 BSE images of A smelter stack particulates: **a** Cu sulphate spheroid decorated with small arsenolite octahedra on a grain mount of the a-r material; **b** Cu₂O spheroid on a polished mount of the a-r material; **c** from a grain mount of the a-r sample, spheres of Cu sulphate and fine-grained agglomerate of sulphate material containing variable amounts of Zn, Cu, K, Na and As, both laced with small bright discrete grains of anglesite; **d** euhedral arsenolite octahedron attached to fine-grained agglomerate in a grain mount of the a-r material; **e** Cu₂S grain with dendritic overgrowths in a polished mount of the a-r material

$(Cu_xZn_{x-1})_2(AsO_4)(OH)$, with x at about 0.94 and with minor S substituting for As (Table 4, Analysis #3).

Additionally, phases of more complex compositions, some likely amorphous in nature, are present. In particular, we observed a very fine-grained agglomerate (Fig. 2c) whose composition determined by EDS suggests a sulphate with variable amounts of Zn, Cu, K, Na and As and minor levels of Si, Ca and Fe (Fig. 3e). The
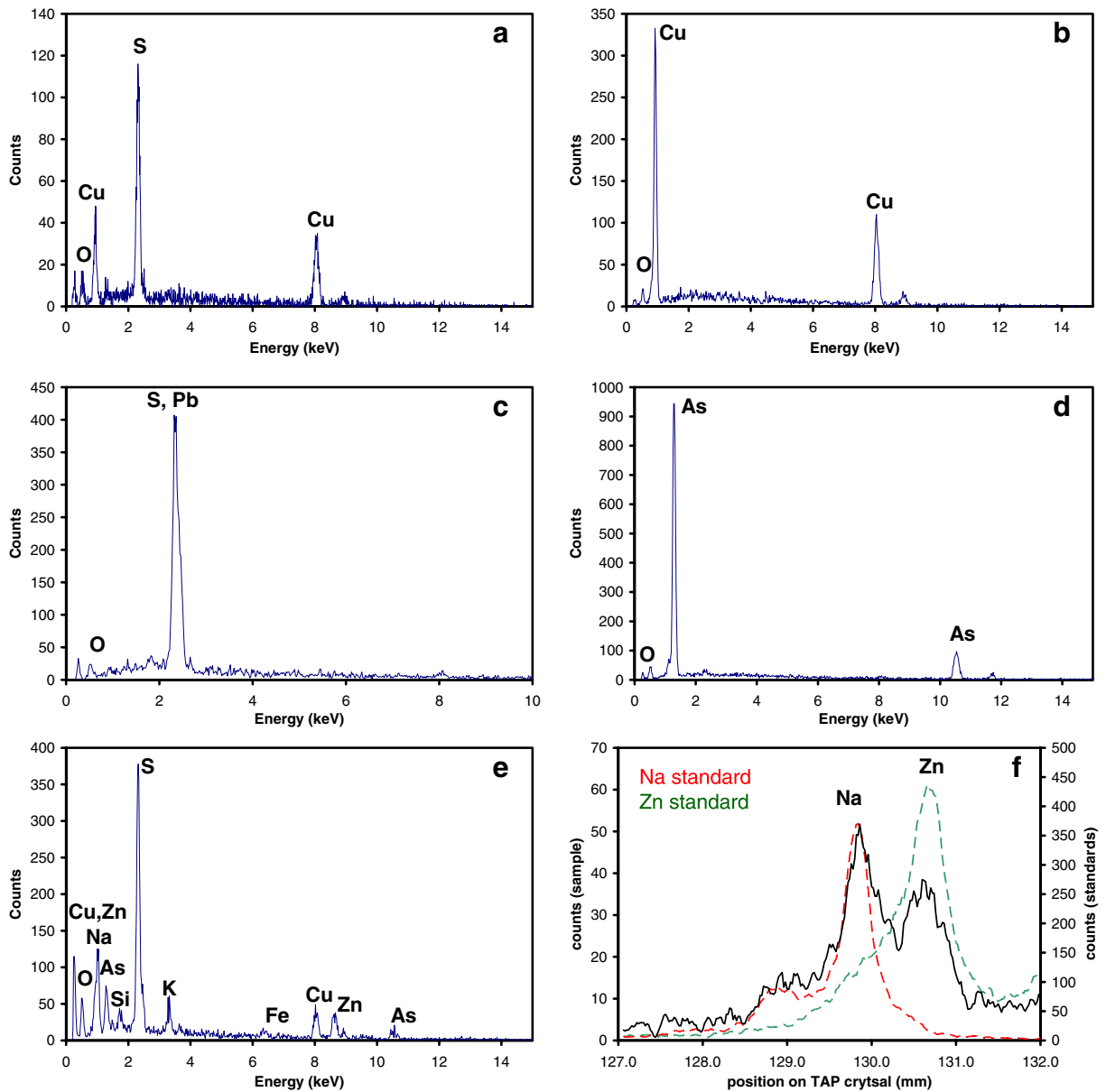
Fig. 3 EDS spectra obtained on grains of the A smelter stack particulates (note that EDS has Be window, so the response is poor for the low energy lines such as O): **a** Cu sulphate shown in Fig. 2a; **b** Cu oxide shown in Fig. 2b; **c** Anglesite shown in Fig. 2c; **d** Arsenolite shown in Fig. 2d; **e** fine-grained agglomerate shown in Fig. 2c; **f** WDS spectrum in the energy region for Na Kα and Zn Lα obtained with a thallium phthalate (TAP) diffracting crystal for the fine-grained agglomerate shown in Fig. 2c confirming the presence of Na

presence of Na, which strongly overlaps with Zn Lα in EDS, was revealed by a WDS scan (Fig. 3f). The fine-grained nature of this material prevents confirming if this represents one or

multiple phases, but there clearly appears to be a strong association, at least spatially, between Zn and the alkalis Na and K, in the form of fine-grained sulphate compounds, as per the calculated

Table 4 Chemical composition of representative Cu oxide, sulphide and arsenates observed in a-r particulate samples

	1 wt.%	(N = 9) S.D.	2 wt.%	(N = 10) S.D.	3 wt.%	(N = 5) S.D.	4 wt.%	(N = 4) S.D.	5 wt.%	(N = 3) S.D.
Cu	88.52	1.75	79.44	1.22	41.19	1.24	37.73	0.94	26.25	1.50
Zn					2.57	0.42	0.58	0.32	5.20	0.85
As					26.18	0.84	30.91	0.95	36.23	1.12
S			20.17	0.81	0.45	0.13	0.51	0.11	0.80	0.21
O	11.62	1.10			29.33	1.73	31.03	1.52	31.34	1.94
Total	100.14		99.61		99.71		100.76		99.82	
Formula based on										
	2 Cu		2 Cu		1 (As+S)		2 (As+S)		1 (As+S)	
Cu	2.000		2.000		1.783		2.772		0.812	
Zn					0.108		0.042		0.156	
Cu + Zn					1.891		2.813		0.969	
As					0.962		1.926		0.951	
S			1.007		0.038		0.074		0.049	
O	1.043				5.043		9.053		3.853	
Cu/(Cu+Zn)					0.94		0.99		0.84	
As/(As+S)					0.96		0.96		0.95	

The number of analyses (N) obtained for each phases is indicated together with the associated standard deviation (S.D.)

1: Cu oxide in a-r A sample; consistent with Cu_2O

2: Cu sulphide in a-r A sample; consistent with Cu_2S

3: Cu arsenate in a-r A sample; close to $(Cu_{0.94}Zn_{0.06})_2(AsO_4)(OH)$

4: Cu arsenate in a-r B sample; close to $(Cu_{0.98}Zn_{0.02})_3(AsO_4)_2.2H_2O$

5: Cu arsenate in a-r C sample; close to $(Cu_{0.84}Zn_{0.16.})(AsO_3OH)$

quantitative speciation. The presence of Zn sulphate in this agglomerate most likely represents gunningite, identified by XRD that cannot be resolved spatially with the SEM.

XRD analysis of the residue from leaching of the A smelter stack particulates in OECD 203 (Fig. 1b) reveals only the presence of anglesite and copper oxide, mainly cuprite, as crystalline phases. The lack of arsenolite in the XRD analysis is an indication of its ready solubility.

SEM/EPMA characterisation of a residue from leaching a sample of the A smelter particulates in d.i. water was also done. Grains of anglesite, copper oxide and copper arsenate were easily identified, thereby confirming their insoluble nature. Arsenolite grains and phases containing a significant amount of Zn and alkalis were not observed.

Quantitative speciation The step-wise apportioning procedure yields the following quantitative speciation for the a-r A smelter stack particulates,

as presented in Table 5, as well as a combined relative uncertainty (c.r.u.) for each compound as derived in Appendix 1:

- 29% $CuSO_4$ (chalcocyanite, phase confirmed by XRD);
- 20% $ZnSO_4.H_2O$ (gunningite, phase confirmed by XRD);
- 13% $(Cu_{0.94}Zn_{0.06})_2(AsO_4)(OH)$ (based on WDS analyses of Cu arsenate grains);
- 11% $PbSO_4$ (anglesite, phase confirmed by XRD);
- 4.1% As_2O_3 (arsenolite, phase confirmed by XRD);
- 3.9% K_2SO_4 (suggested by EDS data);
- 3.5% Cu_2O (cuprite, phase confirmed by XRD and WDS data);
- 3.3% Na_2SO_4 (suggested by EDS data);
- 1.6% Fe_2O_3;
- 1.6% SiO_2;

and about less than 0.5% of each of CdO, Al_2O_3, ZnO, Sb_2O_5, MgO, PbO, K_2O, Na_2O, Ag, NiO,

Table 5 Calculated compositions of components of C, A and B smelter stack particulates, %, based on recovered values, except for SiO_2 and C which are based on the a-r analyses

C

Component	Calculated average wt. %	SD	σ, %	c.r.u., %[a]
$ZnSO_4.H_2O$[b]	33.9	0.6	1.8	4
$(Cu_{0.839}Zn_{0.161})(AsO_3OH)$	19.4	2.4	12.4	2
$PbSO_4$[b]	10.8	0.7	6.5	1
As_2O_3[b]	10.4	0.6	6.0	1
$Zn_3(AsO_4)_2$[c]	9.0	0.8	8.5	1.0
ZnO	4.4	0.5	11.9	0.3
K_2O	2.7	0.2	8	0.2
$CuSO_4$	1.8	0.2	8	0.2
Fe_2O_3	1.1	0.1	11	0.1
Na_2O	0.8	0.0	1	0.1
PbO	0.8	0.3	35	0.0
CdO	0.7	0.03	4	0.1
SiO_2	0.4	0.0	0	0.0
Sb_2O_5	0.3	0.03	8	0.0
Al_2O_3	0.1	0.01	11	0.01
CaO	0.1	0.06	60	0.01
C	0.025	0.0	0	0.00
MgO	0.02	0.002	11	0.001
Ag	0.008	0.001	13	0.001
SeO_2	0.003	0.000	9	0.000
Cr_2O_3	6E-04	2E-04	26	5E-05
NiO	5E-04	2E-04	38	4E-05
Mass balances	97	7		

A

Component	Calculated average wt. %	SD	σ, %	c.r.u., %[a]
$CuSO_4$[b]	29	1	4	3
$ZnSO_4.H_2O$[b,c]	20	0	1	2
$(Cu_{0.943}Zn_{0.057})_2(AsO_4)(OH)$[b,c]	13	2	14	2
$PbSO_4$[b]	11	0	1	1
As_2O_3[b,c]	4.1	0.6	15	0.3
K_2SO_4	3.9	0.0	0	0.5
Cu_2O[b,c]	3.5	1.0	28	0.2
Na_2SO_4	3.4	0.3	9	0.5
Fe_2O_3	1.6	0.0	2	0.1
SiO_2	1.6	0.0	0	0.1
CaO	0.5	0.3	67	0.04
CdO	0.4	0.0	1	0.0
Al_2O_3	0.4	0.0	1	0.0
ZnO	0.4	0.0	3	0.0
Sb_2O_5	0.2	0.0	1	0.0
MgO	0.3	0.0	9	0.03
C	0.2	0.0	0	0.02
PbO	0.2	0.1	70	0.0
K_2O	0.1	0.0	4	0.01
Na_2O	0.02	0.00	5	0.00
Ag	0.02	0.00	2	0.00
NiO	0.005	0.000	6	0.000
SeO_2	0.004	0.000	7	0.000
Cr_2O_3	0.002	0.000	11	0.000
Mass balances	94	6		

B

Component	Calculated average wt. %	SD	σ, %
$ZnSO_4.H_2O$[b]	20	1	5
$PbSO_4$[b]	20	0	2
$CuSO_4$	12	0	2
As_2O_3[b]	8.7	0.4	5
K_2SO_4	6.1	0.0	0
SiO_2	5.2	0.0	0
Na_2SO_4	4.3	0.1	1
$(Cu_{0.985}Zn_{0.015})_3(AsO_4)_2.2H_2O$[b]	4.1	0.2	5
Fe_2O_3	2.4	0.0	1
CuO[c]	1.9	0.1	5
$CaSO_4$	1.9	0.2	8
ZnO	1.8	0.0	2
Sb_2O_5	0.5	0.0	2
CdO	0.4	0.0	0
PbO	0.4	0.0	9
K_2O	0.3	0.0	2
MgO	0.4	0.0	3
Al_2O_3	0.8	0.0	2
CaO	0.05	0.01	12
Na_2O	0.05	0.00	2
Ag	0.02	0.00	7
NiO	0.003	0.000	7
SeO_2	0.002	0.000	2
Cr_2O_3	0.001	0.000	27
Mass balances	91		

[a] Estimated combined relative uncertainty

[b] Detected by XRD

[c] Detected by SEM/EPMA

SeO_2 and Cr_2O_3. The sum of the calculated total is 93%, a reasonable result, considering the uncertainty in the phase compositions of some of the fine-grained amorphous material. Nonetheless, the calculation gives a good indication of the quantitative speciation of the A smelter stack particulates.

As per Table 3, the final pH values of the OECD 203, d.i. H_2O and RICH 95 leach media had declined to 4.02, 3.65 and 3.86, respectively, due most likely to the dissolution of the Cu and Zn sulphates and the establishment of the equilibrium:

$$H^+ + SO_4^{2-} = HSO_4^-, \qquad \text{(reaction 1)}$$

which introduces H^+ into solution, thereby decreasing its pH.

The observations support the conclusion that $CuSO_4$, $ZnSO_4$, K_2SO_4, Na_2SO_4 and most of the arsenolite will be soluble in aquatic media, whereas the Cu–Zn arsenate, anglesite and cuprite will be preserved in the residue.

B smelter

Chemical composition of a-r particulates The chemical analyses of Table 6 reveal that the B smelter stack particulates contain about 32% SO_4, 8% As, and 8% Zn, all comparable to those of the A material, but are significantly leaner in Cu (8%), and richer in Pb (14%) and SiO_2 (5%). Minor and trace amounts of Cr, Sb, Ag Mg, Cd, Al, Ca, Na Fe and K were found in the range 0.0011% to 2.92%. If C existed in the sample, it was below 0.01%.

Leaching results and mass balances In Table 6, the distributions of the analytes between leachates

Table 6 Chemical analysis of B smelter stack particulates, and percentage distributions of analytes between leachates and residues

| B smelter as-received		Leached in									
		OECD 203			d.i. H_2O			RICH 95			
Analyte	wt.%	% Leached	% In residue	Mass balance, %	% Leached	% In residue	Mass balance, %	% Leached	% In residue	Mass balance, %
As	7.99	68.6	32	101	69.0	30.6	100	64.6	36.7	101
Cu	7.88	60.0	39.9	100	61.4	35.5	97	59.1	39.7	99
Zn	7.81	98.1	19	117	98.6	18.1	117	98.0	19.0	117
Ni	0.0018	69	54	123	67	55	121	63	43	106
Pb	13.96	0.0034	98.09	98	0.011	96.56	97	0.0033	99.85	100
Cd	0.347	88.5	10.4	99	88.2	11.0	99	87.3	11.7	99
Se	0.009	4	15	19	4	14	18	4	15	19
Sb	0.32	2.5	107	109	2.7	103	105	2.9	104	107
Ag	0.0209	0.086	95	95	0.02	83	83	0.017	99	99
Cr	0.0011	4.5	70	74	5.3	116	121	4.0	63	67
Fe	1.98	6.92	78.0	85	7.74	74.9	83	6.17	79.3	85
C	<0.01									
Al	0.393	30.5	83.6	114	31.3	78.5	110	29.3	83.7	113
Ca	0.662	77.0	6.57	84	94.2	5.81	100	88.6	6.20	95
Mg	0.230	97.9	13.0	111	107	12.4	119	102	12.9	115
K	2.92	94.3	8.40	103	95.0	8.39	103	94.0	8.75	103
Na	1.27	108	3.20	111	110	3.12	113	108	3.27	111
SO_4	32.26	89.88	19.17	109	90.73	18.89	110	89.33	19.62	109
Si	2.42									
Total	80.48	Initial wt., g		20.0038	Initial wt., g		20.0075	Initial wt., g		20.0074
		Residue wt., g		8.5122	Residue wt., g		8.2147	Residue wt., g		8.7013
		% Leached		57	% Leached		59	% Leached		57
Initial pH		7.90			5.14			8.05			
Final pH		2.88			2.84			2.97			
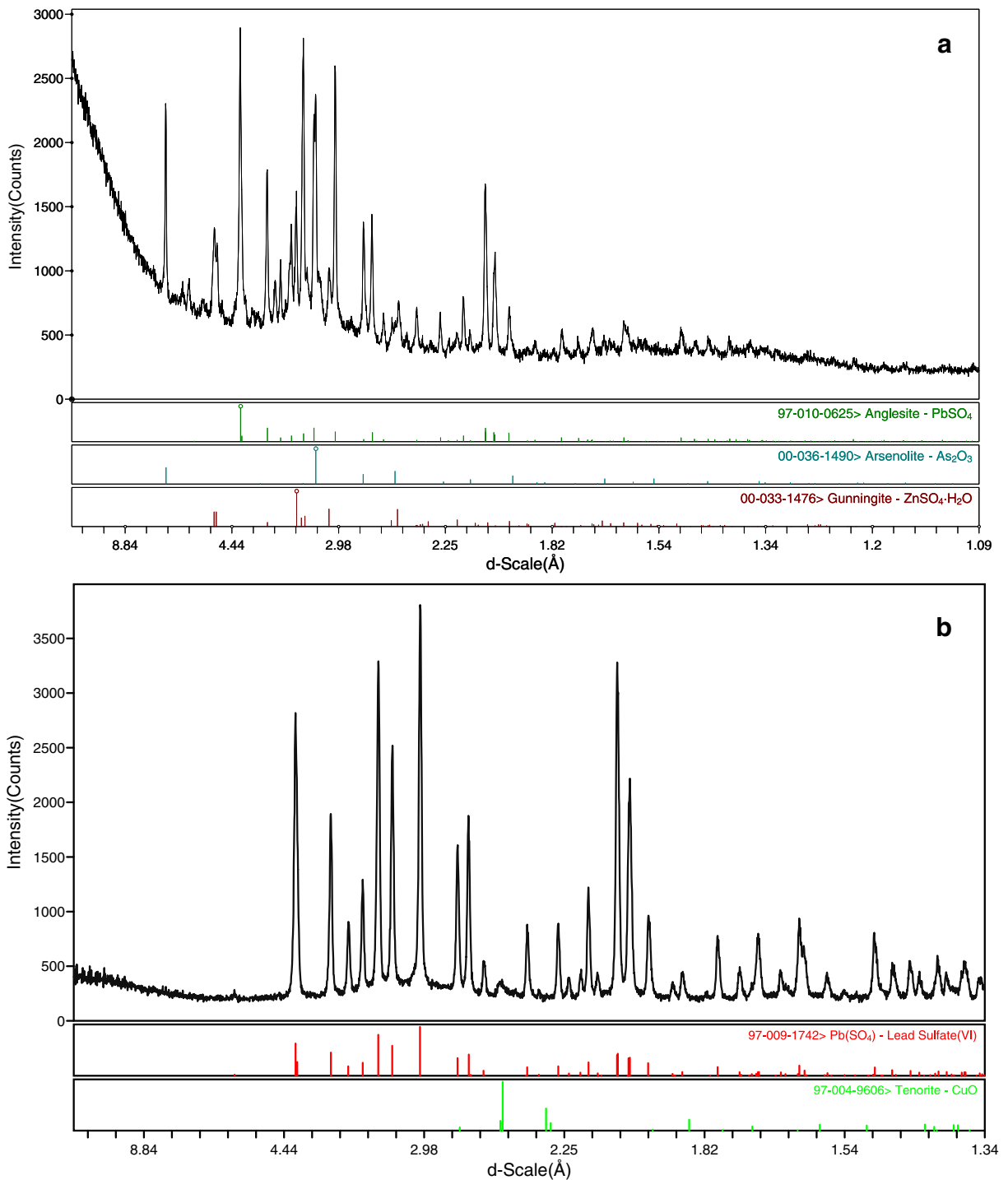
Fig. 4 XRD patterns of **a** the a-r B smelter stack particulates and **b** the residue from leaching of a sample of the B smelter stack particulates in OECD 203

and residues show that averages of about 67%, 60% and 90% of the As, Cu and SO$_4$, respectively, were leached, supported by mass balances of about 100% for As and Cu, and 109% for SO$_4$. As with the A smelter stack particulates, the calculated dissolution of Pb was less than 0.01%, supported by a Pb mass balance close to 100%. In contrast, on the basis of its concentrations in the leachates, Zn was almost 100% dissolved, although this value should be tempered by the 117% mass balance.

The distributions of the minor components Al$_2$O$_3$, Ag, Cd, Fe, Ni, Sb, Fe, K$_2$O and Na$_2$O between leachate and residue can be considered credible because their mass balances were all in the range 83–123%. However, those for Cr, CaO,

MgO and Se reflect the difficulty in obtaining accurate analytical data at low concentrations.

Mineralogical analyses The major crystalline phases identified by XRD in the a-r B smelter particulates are gunningite, anglesite, and arsenolite, with a background profile of the XRD pattern suggesting the presence of amorphous material (Fig. 4a).

BSE imaging such as Fig. 5a and EDS analyses confirm the presence of anglesite and arsenolite as discrete phases with relatively pure compositions. Additional phases that appear crystalline, based on their morphology, are Cu$_2$S (Fig. 5b), as well as Cu$_2$O and a copper arsenate (Fig. 5c). WDS analyses of a few copper arsenate grains indicate a
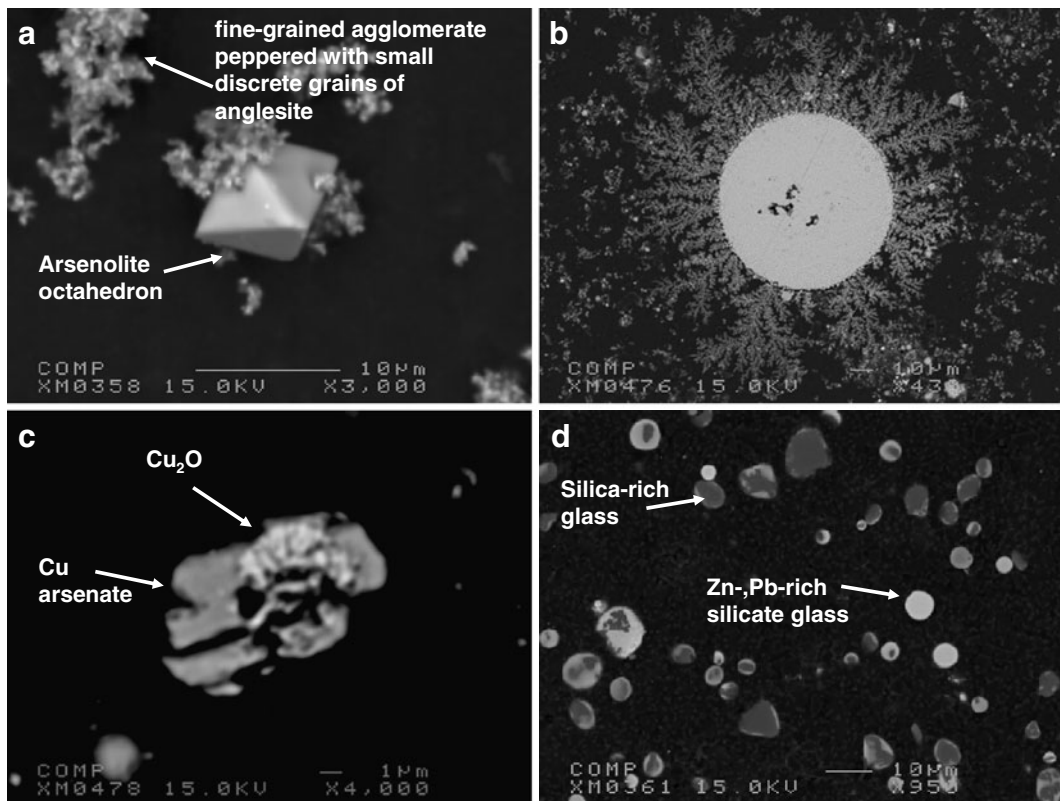

Fig. 5 BSE images of B smelter stack particulates: **a** euhedral crystal of arsenolite and fine-grained agglomerate laced with small bright grains of anglesite in a grain mount of the a-r material; **b** Cu$_2$S grain with dendritic overgrowths in a polished mount of the a-r material; **c** coexisting Cu$_2$O and Cu arsenate in polished mount of the a-r material; **d** glassy silicate spheres of various compositions in a polished mount of the a-r material
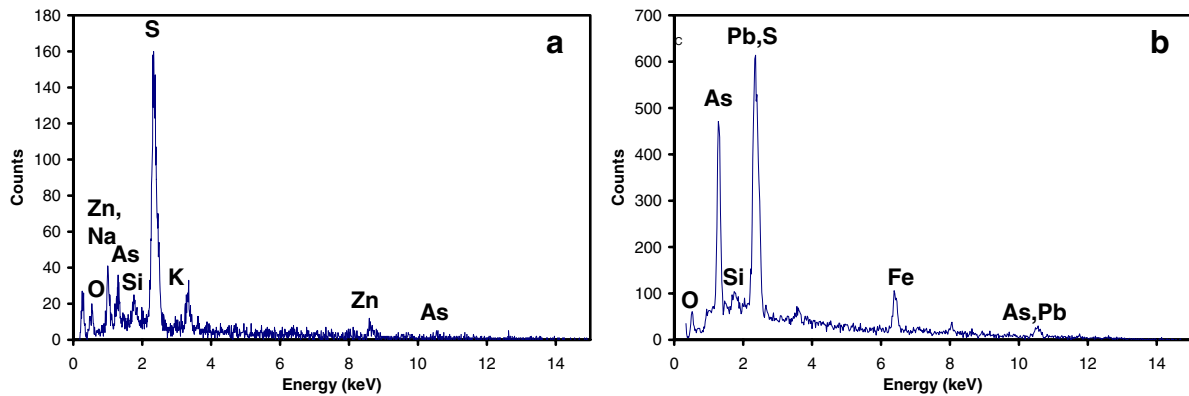
Fig. 6 EDS spectra obtained on grains of the B smelter stack particulates (note that EDS has Be window, so the response is poor for the low energy lines such as O):

a fine-grained agglomerate shown in Fig. 5a; **b** residual fine-grained agglomerate after leaching in d.i. water

stoichiometry close to $(Cu_xZn_{1-x})_3(AsO_4)_2 \cdot 2H_2O$, for which $x \approx 0.98$ and with a minor substitution of As by S (Table 4, Analysis #4).

It was not possible to obtain definitive identification of a gunningite phase with a simple $ZnSO_4 \cdot H_2O$ composition by SEM/EPMA characterisation. However, Zn can be found associated with S and O in fine-grained agglomerates that likely consist of multiple phases too small to be resolved with the spatial resolution of the instrument (Fig. 5a). EDS analysis obtained on this material revealed K and Na, with minor amounts of As, and Si associated with Zn, S and O (Fig. 6a).

Thus, as also observed in the A smelter stack sample, there seems to be a strong spatial association between Zn and the alkalis Na and K in the form of fine-grained sulphate compounds, although they may not necessarily all reside in one single phase.

The main amorphous component consists of glassy silicate spheres (Fig. 5d) of variable composition. Quantitative WDS analyses (Table 7) indicate that this glass represents a significant reservoir for PbO (up to 16.2 wt.%), ZnO (up to 30 wt.%), Na$_2$O (up to 1.8 wt.%), K$_2$O (up to 4.5 wt.%), and SiO$_2$ in the B particulate sample.

Table 7 Chemical composition of representative B smelter Zn–Pb-rich glassy silicate spheres

	Individual analyses						Average ($N = 15$)	
	wt.%	±	wt.%	±	wt.%	±	wt.%	S.D.
SiO$_2$	45.78	0.67	52.93	0.71	49.60	0.69	44.25	8.01
Al$_2$O$_3$	0.29	0.09	0.15	0.08	0.70	0.11	2.89	5.39
FeO	0.36	0.17	0.29	0.16	2.80	0.29	0.96	0.82
CuO	7.71	0.58	12.59	0.73	6.85	0.56	8.04	2.55
ZnO	30.02	1.08	18.94	0.89	21.20	0.92	25.18	6.40
PbO	10.34	1.04	9.88	1.02	13.55	1.18	11.56	3.49
CaO	0.04	0.07	0.04	0.07	0.09	0.07	0.09	0.10
Na$_2$O	1.35	0.20	1.35	0.23	1.46	0.23	1.15	0.36
K$_2$O	2.52	0.24	3.38	0.27	2.71	0.25	2.82	0.99
As$_2$O$_5$	0.25	0.21	0.34	0.22	0.25	0.21	2.19	3.27
SO$_3$	0.11	0.10	0.14	0.11	0.03	0.12	0.18	0.19
Total	98.77		100.03		99.25		99.31	

In addition to three representative individual analyses, the average of 15 analyses and the associated standard deviation (SD) are presented. The uncertainty (±) for the individual analyses represents 3σ based on counting statistics

The crystalline phases identified by XRD in the leach residue of the B smelter stack particulates in OECD 203 were anglesite and tenorite, CuO. The lack of detected gunningite and arsenolite suggests the high solubility of these phases.

SEM/EPMA was also used to characterise the residue from leaching of the B smelter stack particulates in d.i. water. Anglesite and the glassy silicate spheres, acting as a refractory reservoir for some of the Pb, Zn and alkalis, are both preserved. Finally, EDS analysis suggests that anglesite is sometimes intimately mixed with a Fe $(+/-$ Cu$)$ arsenate, most likely amorphous in nature (Fig. 6b).

Quantitative speciation The step-wise apportioning procedure yields this quantitative speciation for the B smelter stack particulates:

- 20% $ZnSO_4.H_2O$ (identified by XRD);
- 20% $PbSO_4$ (identified by XRD and EDS);
- 12% $CuSO_4$;
- 8.7% As_2O_3 (identified by XRD and EDS);
- 6.1% K_2SO_4 (suggested by EDS data);
- 5.2% SiO_2 (in silicate glass spheres, based on WDS data);
- 4.3% Na_2SO_4 (suggested by EDS data);
- 4.1% $(Cu_{0.98}Zn_{0.02})_3(AsO_4)_2.2H_2O$ (based on WDS data);
- 2.4% Fe_2O_3;
- 1.9% CuO (incorporated in silicate glass based on WDS data);
- 1.8% ZnO (incorporated in silicate glass based on WDS data);
- 1.4% $CaSO_4$.

The minor oxides, Al_2O_3, CaO, Fe_2O_3, and some of the K_2O, Na_2O, PbO and ZnO are most likely incorporated within the silicate glass which would account for their insoluble percentages. Sb_2O_5, CdO, Ag, NiO, SeO_2 and Cr_2O_3 are calculated

Table 8 Chemical analysis of C smelter stack particulates and distributions of analytes between leachates and residues

B smelter as-received		Leached in									
		OECD 203			d.i. H_2O			RICH 95			
Analyte	wt.%	% Leached	% In residue	Mass balance, %	% Leached	% In residue	Mass balance, %	% Leached	% In residue	Mass balance, %	
As	17.66	47.56	57.72	105	49.28	48.52	98	45.48	63.27	109	
Cu	5.68	12.8	89.2	102	13.7	75.9	90	11.1	103	114	
Zn	17.58	80.94	37.35	118	83.10	31.01	114	79.46	39.85	119	
Ni	0.0004	43	33	76	50	28	78	49	113	162	
Pb	8.28	0.0180	98.4	98	0.0162	88.0	88	0.0111	108.59	109	
Cd	0.603	52.3	46.3	99	52.2	41.9	94	46.8	56.7	104	
Se	0.0085	4.2	20	24	4.2	16	20	4.2	21	25	
Sb	0.208	2.89	114	116	2.74	98.3	101	2.82	120	123	
Ag	0.0063	0.21	116	117	0.056	107	107	0.056	145	145	
Cr	0.0006	0.6	62	62	0.6	52	52	0.6	94	95	
Fe	0.829	0.0286	92.9	93	0.00157	83.1	83	0.0203	108	108	
C	0.025										
Al	0.0773	0.767	68.6	69	0.486	54.4	55	0.788	69.5	70	
Ca	0.131				40.2	24.8	65	15.0	38.8	54	
Mg	0.0096				93.7	30.4	124				
K	2.25	100	4.73	105	99.5	4.35	104	100	5.41	106	
Na	0.554	101	2.73	103	104	2.45	106	100	3.54	104	
SO_4	22.36	86.17	15.71	102	84.70	14.00	99	87.20	16.37	104	
Si	0.196										
Total	77.35	Initial wt., g		20.0013	Initial wt., g		20.0008	Initial wt., g		20.0013	
		Residue wt., g		10.5480	Residue wt., g		8.8298	Residue wt., g		11.2819	
		% Leached		47	% Leached		56	% Leached		44	
Initial pH		7.95			4.76			7.88			
Final pH		4.16			4.14			4.23			

to be less than about 0.5% each. The sum of the calculated totals at 90% (Table 5) is somewhat low, partly related to uncertainty in the phase compositions of some of the fine-grained material, but nonetheless a good indication of the quantitative speciation of the B smelter stack particulates.
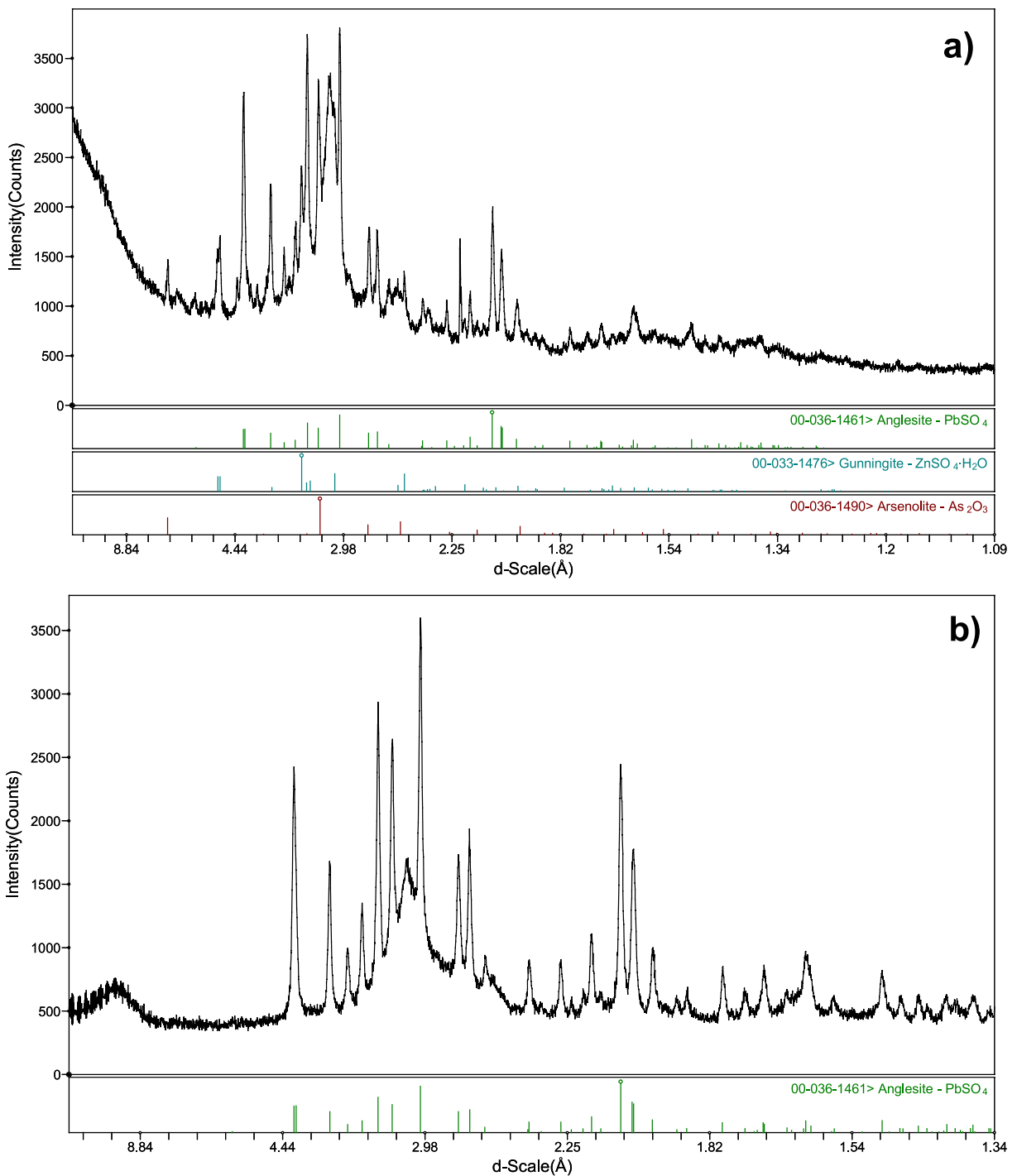

Fig. 7 XRD patterns of **a** the a-r C smelter stack particulates and **b** the residue from leaching a-r C smelter stack particulates in OECD 203
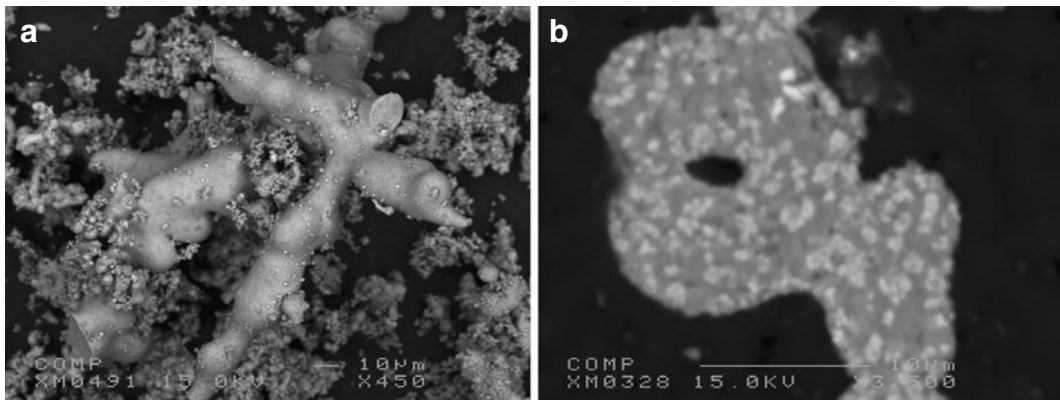
Fig. 8 BSE images of C smelter stack particulates: **a** arborescent structure in grain mount of a-r material; **b** cross-section of a branch of arborescent structure in a polished mount of the a-r material suggesting the presence of at least two phases
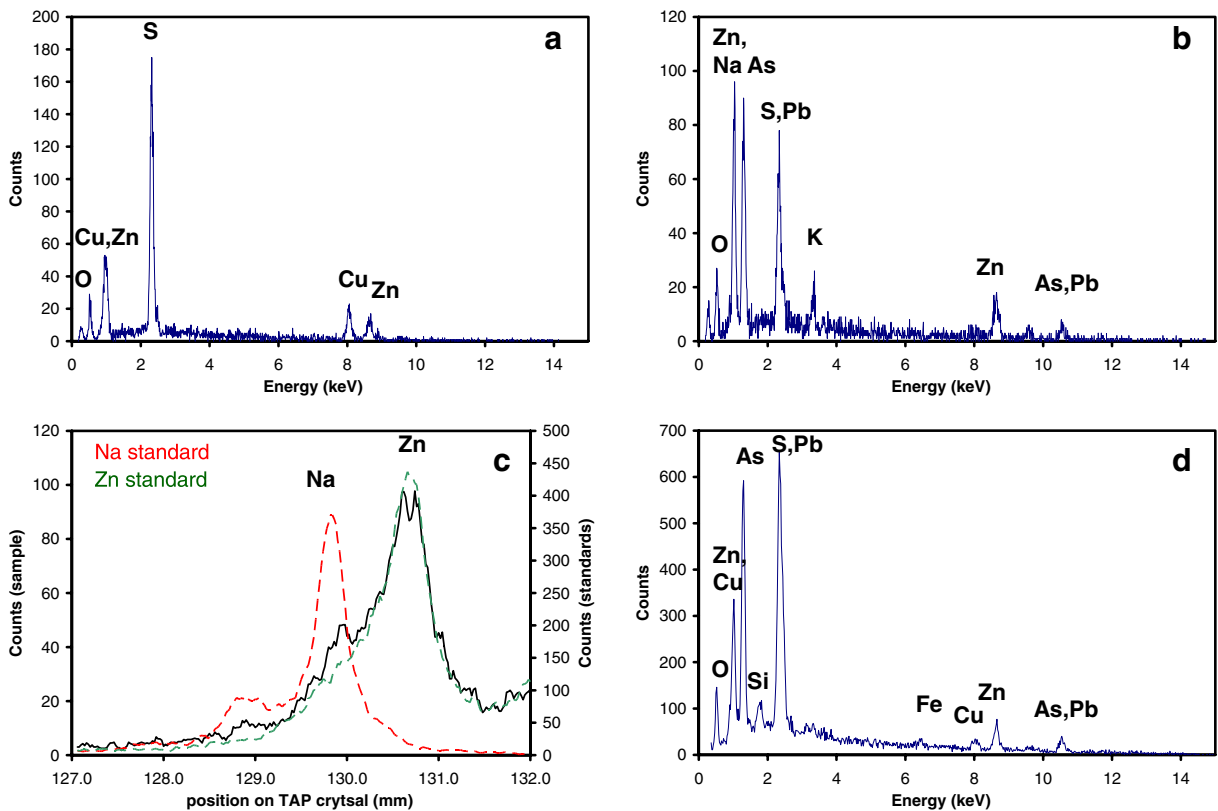

Fig. 9 EDS spectra obtained on grains from the C smelter stack particulates (note EDS has Be window, so the response is poor for the low energy lines such as O): **a** Cu–Zn sulphate; **b** arborescent structure shown in Fig. 8a, b; **c** WDS spectrum in the energy region for Na Kα and Zn Lα obtained with a TAP diffracting crystal for the arborescent structure shown in Fig. 8a confirming the presence of Na; **d** preserved arborescent structure in residue after leaching in d.i. water

In aquatic media, the gunningite, $CuSO_4$, K_2SO_4, Na_2SO_4 and most of the arsenolite should be soluble, whereas anglesite, copper sulphide, copper oxide, Cu–Zn arsenate and silicate glass would be insoluble.

C smelter

Chemical composition of a-r particulates The bulk chemical analyses of the a-r C smelter particulates are presented in Table 8. In comparison with the A and B particulate samples, the C material has significantly greater levels of As and Zn, 17.6% each, and a lesser amount of SO_4, 22.4%. Cu and Pb represent 5.7% and 8.3% respectively. The minor analytes Ni, Cr Ag, Se, Mg, C, Ca, Si, Sb, Cd, Al, Fe, Na and K occurred in the range 0.0004% to 2.25%.

Leaching results and mass balances The distributions of the analytes between the leachates and residues, as well as the mass balances for each analyte are also shown in Table 8. With values in the range 88% to 119%, the mass balance data for all three leaching media reveal that the components As, Cu, Pb, SO_4 and Zn are acceptably well-accounted for. The data of Table 8 also reveal that As, Cd, Cu, SO_4 and Zn dissolved to the extent of about 47%, 50%, 13%, 86% and 81%, respectively, while the dissolution of Pb was about 0.02%. The weight percentages of the samples leached over the 6 hr were 47, 56 and 44 for the OECD 203, d.i. water and RICH-95 lixiviants, respectively.

Of the minor components, the mass balances for Cd, Fe, K_2O, Na_2O and Sb lie in the range 83–123% and are also reasonable. However, those for Al_2O_3 and the trace elements Cr and Se suggest significant quantities for which we cannot calculate a reasonable distribution between leachate and residue. This result is not unexpected owing to their relatively low concentrations in the original sample, the leachates and the residues.

Mineralogical analyses Gunningite, anglesite and arsenolite are major crystalline phases identified by XRD, Fig. 7a. However, with the available databases, we could not identify one of the major peaks corresponding to a d-spacing of 3.11 Å.
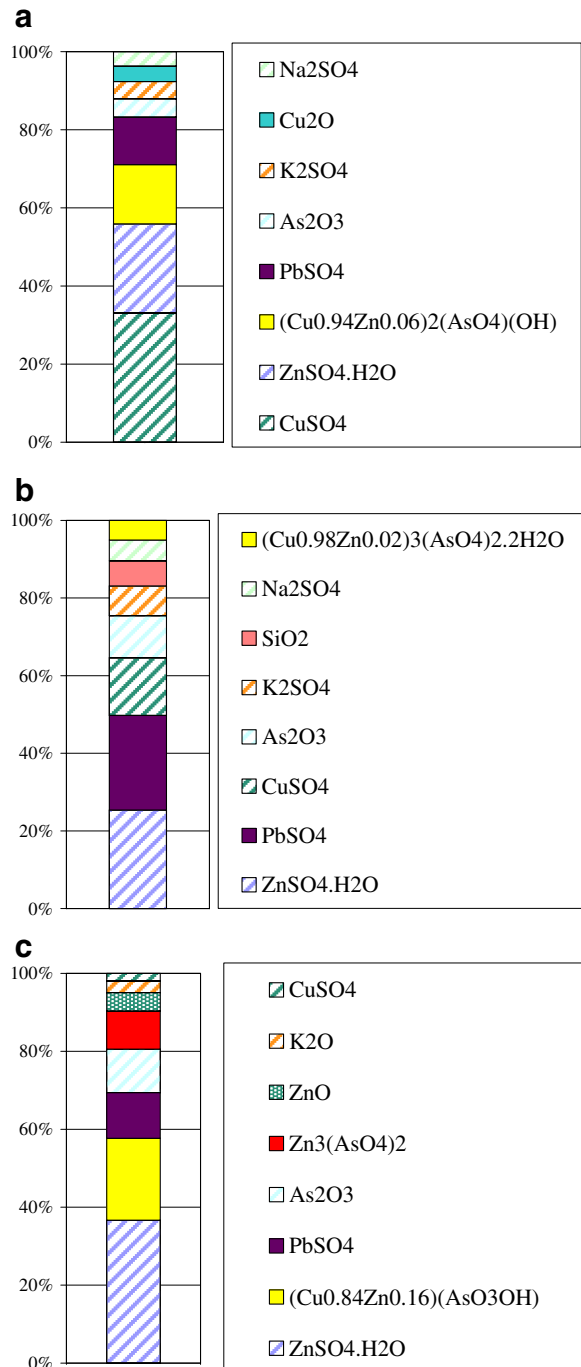
Fig. 10 Comparison of calculated compositions of smelter stack particulates. Commonalities and differences are discussed in the text. Note that, to enable this comparison, the percentages have been normalised to a 100% mass balance. Soluble and insoluble compounds are coded with *cross-hatched* and *solid bars*, respectively. In the case of ZnO for smelter C, about 50% is soluble

Once again, the background profile suggests the presence of a significant amount of amorphous material.

In addition to anglesite and arsenolite, a (Cu, Zn) arsenate was also identified by SEM/EPMA. Based on WDS analyses (e.g. Table 4, analysis #5), some of the grains exhibit a stoichiometry close to $(Cu_{0.84}Zn_{0.16})(AsO_3OH)$ with minor S substituting for As. It was not possible to isolate a pure hydrated zinc sulphate, gunningite. Nonetheless, a (Cu, Zn) sulphate is commonly observed, Fig. 9a.

Arborescent structures, Fig. 8a, that consist of at least two phases, Fig. 8b, are abundant. Although they could not be completely spatially resolved during EDS analysis, they appear to consist of a Pb-, S-, O-rich phase, most likely anglesite, and of a (Na,K)-bearing Zn arsenate (Fig. 9b, c). Considering the abundance of this material, this zinc arsenate may well represent the unidentified crystalline phase from the XRD.

In the XRD pattern of the residue from the OECD 203 leaching of the C smelter stack particulates (Fig. 7b), the only crystalline phase that could be identified was anglesite. However, the unidentified peak at d = 3.11 Å observed in the a-r sample is still present and could be zinc arsenate.

SEM/EPMA characterisation of a residue from leaching of the C smelter stack particulates in d.i. water clearly confirmed anglesite and copper arsenate as insoluble phases. Moreover, the characteristic arborescent structure is also preserved. EDS analyses suggest that it is a zinc arsenate of composition comparable to that in the a-r sample, with much lower levels of alkalis, Fig. 9d.

Quantitative speciation From the above data, the quantitative speciation calculated for the C smelter stack particulates is:

- 34% $ZnSO_4.H_2O$ (gunningite);
- 19% $(Cu_{0.84}Zn_{0.16})(AsO_3OH)$ (based on WDS data);
- 11% $PbSO_4$ (anglesite);
- 10% As_2O_3 (arsenolite)
- 9.0% $Zn_3(AsO_4)_2$ (assumed composition based on EDS data)
- 4.4% ZnO;

- 2.8% K_2O (possibly associated with Zn in an arsenate phase, based on EDS data);
- 1.8% $CuSO_4$;

and about 1% or less of each of Fe_2O_3, Na_2O, PbO, CdO, SiO_2, Sb_2O_5, CaO, Al_2O_3, C, Ag, MgO, SeO_2, Cr_2O_3 and NiO. The total of the calculated percentages of the components accounts for a quite reasonable 97% by weight of the a-r C smelter stack particulates, Table 5.

Gunningite, $CuSO_4$, and arsenolite appear soluble in the lixiviants, whereas the Cu and Zn arsenates and anglesite are preserved in the residue.

Conclusions

In examining particulates from three base metal smelter stacks as potential sources of metals released to the atmosphere, we observed in all samples rather complex phase assemblages with the presence of sulphates, arsenates and silicates whose abundances and compositions are strongly influenced by the bulk chemistry. Such distinct speciation will have important implications for the environment in terms of the distribution of some critical elements, such as As, between residue and solution during contact with aqueous media. As illustrated in Fig. 10, there were commonalities in composition among all three smelter stack particulates, which contained significant quantities—in the range 20–34%—of $ZnSO_4.H_2O$, although the C smelter particulates were the richest in this among all three. Again, the B particulates were the richest in insoluble $PbSO_4$ at 20%, compared to ~11% for the A and C particulates. For As_2O_3, most of which was soluble, the B and C particulates contained similar 9–10% levels, while the A particulates were about 4%. All three samples contained insoluble Cu–Zn arsenates in the order C (19%) > A (13%) > B (4%), while the C sample also contained 9% $Zn_3(AsO_4)_2$ for a total of 28% arsenates. At 29%, the A smelter particulates contained by far the greatest amount of the readily soluble $CuSO_4$, with the B and C samples containing 12% and only 2%, respectively.

Thus in general, the fate of Cu and Zn as sulphates and As_2O_3 in these smelter particulates would be dissolution and bioavailability in the

aquatic environment, while the arsenates and Pb as $PbSO_4$, which are relatively insoluble, would tend to be stable in aquatic media, soil or sediments. The data and approach may be useful in estimating water-soil-sediment partitioning and the environmental effects of the releases of these and other smelter stack particulates as well as in deriving site-specific risk assessments in general, including predictions of the behaviour of particulates released to the atmosphere, for these and other operations.

Appendix 1

Overview of analytical methods

In Table 9 of Appendix 1, we have listed the methods used to determine the percentages or concentrations of each analyte in each solid or solution. For the solid samples, CANMET-MMSL's Analytical Services Group (ASG) used four different methods of solids digestion followed by analysis of the resulting solutions. For Ag, Al, As, Pb, Sb, Se and Si in the a-r samples and for As and Sb in the residues, they used digestion in an *aqua regia* matrix in a sealed vessel within a CEM Microwave Digestion System Model MDS-81d, and then with appropriate dilution, analysed the resulting solutions using a Varian Vista RL ICP-AES. For Cd, Cr, Cu, Fe, K, Mg, Na, Ni and Zn in the a-r samples and for Ag, Al, Ca, Cd, Cr, Cu, Fe, K, Mg, Na, Ni, Pb, Se and Zn in the residues, they dissolved the samples in an HCl, HNO_3, $HClO_4$ and HF matrix, then evaporated the solution to a paste and dissolved it in dilute HNO_3, which they then analysed by ICP-AES. For Ca in the residues, they used fusion with $LiBO_2$ and then ICP-EAS analysis of the dissolved fusion product. For SO_4 in the a-r samples and in the residues, they dissolved the sulphate in a sodium carbonate solution and determined the dissolved SO_4 on a Dionex HPLC (high pressure liquid chromatograph). For S in the a-r samples, they used LECO furnace analysis.

For leach solution samples, they ran them undiluted or diluted by a factor of 10 and used

Table 9 Analytical methods and LOQs

	Ag	Al	As	Ca	Cd	Cr	Cu	Fe	K	Mg	Na	Ni	Pb	SO$_4$	Sb	Se	Si	Zn
Method for a-r particulates	1, 5	1, 5	1, 5	2, 5	3, 5	3, 5	3, 5	3, 5	3, 5	3, 5	3, 5	3, 5	1, 5	4, 6	1, 5	1, 5	1, 5	3, 5
ICP-AES LOQ, µg/L	0.8	7.9	40	1.3	1.5	2.6	3.9	1.8	143	0.1	4.2	7	30		42	176	5.7	6.6
[Me$_{min.}$]/LOQ	286	1.1	2000	147	5800	7	367	113	314	329	3313	1.6	25		38	0.2	7.6	246
HPLC LOQ, µg/L														200				
[SO$_{4min.}$]/LOQ														3370				
Method for residues	3, 5	3, 5	1, 5	3, 5	3, 5	3, 5	3, 5	3, 5	3, 5	3, 5	3, 5	3, 5	3, 5	4, 6	1, 5	3, 5		3, 5
ICP-AES LOQ, µg/L	0.8	3.4	86	11	2	1.9	1.6	0.9	5.8	16	52	12	33		37	159		16
[Me$_{min.}$]/LOQ	504	705	21	189	679	10	1070	4056	880	11	14	1.0	118		36	1.1		28
HPLC LOQ, µg/L														200				
[Me$_{min.}$]/LOQ														1460				
Method for leach solutions	5	5	5	5	5	5	5	5	5	5	5	5	5	7	5	5	5	5
ICP-AES LOQ, µg/L	0.7	4	20	4.1	1.7	0.7	1.4	2	14	15	47	13	32		21	72		7
[Me$_{min.}$]/LOQ	1.8	9.3	930	126	1865	6	4700	6	643	62	117	8	1.4		16			3575
HPLC LOQ, µg/L														200				
[Me$_{min.}$]/LOQ														8460				

1 microwave leaching, *2* metaborate fusion, *3* four-acid dissolution, *4* carbonate leaching, *5* ICP-AES, *6* HPLC for carbonate solutions, *7* HPLC

ICP-AES for all analytes except SO_4, for which they used the Dionex HPLC.

Throughout, they used reagent grade chemicals, trace metal grade acids and 18 MΩ deionised water. Operating under Certificate No. 004638, our ASG is in compliance with ISO 9002.

For each set of ICP-AES analyses, our ASG incorporated several QA/QC measures to verify initial instrument calibration and to monitor instrument stability. For every 10 samples, they analysed at least one duplicate sample, and for every 10 samples, they analysed one mid-range standard to check the stability of the ICP-AES instrumentation. After the initial calibration, they determined the LOQs by multiplying by 10 the average of the standard deviations of five measured calibration blanks. Typically, for the analyses of microwave digestion solutions of ~0.1 g of each of the three a-r smelter particulates plus one duplicate, they would run these undiluted and at 10 and 100 times dilution on the ICP-AES. In the same batch, preceding and interspersed among the digestion solutions, they would run five determinations of LOQ; between five (e.g., for minor elements such as Se) and 13 (e.g., for major elements such as Pb) multi-component standards comprising solid and solution Certified Reference Materials (CRMs) and spiked multi-component solutions; one 2% HNO_3 blank; and 10 rinses. They used a similar approach for the four-acid digestion solutions of ~0.25 g of both the a-r particulates and the leach residues, with as many as 17 solid and liquid standards for Cu in the a-r particulates and as few as five for Se in the residues.

LOQs

As with all ICP-AES instruments, the LOQs varied according to matrix and analyte. As per Table 9, for the major analytes As, Cu, Pb, SO_4 and Zn in the a-r particulates, the LOQs were 40, 3.9, 30, 200 and 6.5 μg/L, respectively. Also in Table 9, these LOQs were as low as 25 (for Pb), and as high as 3370 (for SO_4), times less than the lowest corresponding analyte concentrations in the digestion solutions. For the minor and trace elements, the LOQs varied between 0.1 μg/L (for Mg) and 176 μg/L (for Se), and were as low as 1.1

(for Al) and as high as 5800 (for Cd) times less than the lowest corresponding analyte concentrations in the digestion solutions, Se having been reported as below the LOQ.

For the major analytes As, Cu, Pb, SO_4 and Zn in the residues, the LOQs were 86, 1.6, 33, 200 and 16 μg/L, respectively, and were as low as 21 (for As), and as high as 1,460 times (for SO_4), less than the lowest corresponding analyte concentrations in the digestion solutions. For the minor and trace elements, the minimum and maximum LOQs were 0.8 and 159 μg/L, for Ag and Se, respectively. The LOQ for Ni was close to the lowest measured concentration in the digestion solution, but about 4,000 times less than the corresponding concentration for Fe.

The LOQs for As, Cu, Pb, SO_4 and Zn in the leach solutions were 20, 1.4, 32, 200 and 7 μg/L, respectively, and were between 1.4 (for Pb) and 8,460 (for SO_4) times less than the lowest corresponding analyte concentrations. The LOQs for the minor and trace elements lay between 0.7 (for Ag and Cr) and 72 (for Se) μg/L, and were between two (for Ag) and about 1,900 times (for Cd) less than the measured minimum concentrations.

The values of the LOQs for the major analytes were thus low enough to support the following estimates of uncertainties. When, as for some of the minor and trace analytes, the measured concentrations may be close to the LOQs, then the uncertainties will be greater.

Estimates of uncertainties in analyses

Solids

For analytes determined by digestion-ICP-AES, our ASG reported percentages in a-r solids and leach residues derived from dilutions (none at all, 10 or 100) of both microwave and four-acid digestion solutions in sequences in which the measured values for the standards and spikes best matched the known or certified values within a few percentage points. For instance, for Pb in the a-r samples, the concentrations of six solution standards lay in the range 99–102% of the known and certified values, and the measured values for a solid CRM fell in the 93–104% range of the standard 1.32% Pb (i.e., 1.24–1.37%). Then, the Pb concentrations

in the microwave digestion solutions at 100 times dilution for the solid CRM and for the a-r smelter samples lay in the range 0.148–1.407 mg/L, and for the solid CRM, the measured value of 1.37% Pb was 104% of the 1.32% Pb standard. For the duplicate samples of the a-r B smelter particulates, ASG found Pb values of 13.95% and 13.97%, for an average of 13.96% ± 0.01%. For the leach residues, ASG obtained 97% of the Pb in a solid CRM, and the duplicate analyses of the C smelter water leach residues were 16.50% and 17.18% for an average of 16.84% ± 0.02%. Taking the agreement between the measured and certified Pb values in the CRMs and the close agreement between the two sets of duplicate samples, we estimate that the c.r.u. in the concentration of Pb for the a-r particulates and the residues to be about 2%.

Using a similar approach for Cu in the a-r particulates, ASG found values of 7.63% and 8.12% Cu in the duplicate samples, i.e., within less than 1% of each other, for an average of 7.88% ± 0.04%. Moreover, their measured percentage Cu in a CRM was 100% of the certified value. The duplicates in the C smelter water-leach residues were 9.77% and 10.27% for an average of 10.02% ± 0.02%. Thus for Cu, we would estimate the c.r.u. to be about 1% in both the a-r particulates and the leach residues.

For As in the a-r particulates, the agreement between the nine measured and known solid and solution standards and spikes was 100.5% (σ = 6.6%; n = 9). On the other hand, the values for the duplicate samples of the a-r B smelter particulates were 7.92% and 8.06%, and within less than 1% of each other for an average of 7.99%. Moreover, the values of As in the duplicates of the C smelter residues from leaching in the RICH-95 medium were 19.81% and 19.65%, and also within less than 1% of each other. So we estimate the c.r.u. in As to be about 2% in both the a-r particulates and the leach residues.

For Zn in the a-r particulates, ASG's measured percentage Zn in a CRM was 98% of the certified value, and the duplicates for the C smelter particulates were 17.51% and 17.65%, yielding an average of 17.58% ± 0.07%. The values of Zn in the duplicate C smelter water-leach residues were 12.35% and 12.07% for an average of 12.21% ±

0.14%. For Zn, we would then estimate the c.r.u. to be about 1% in both the a-r particulates and the leach residues.

For the minor analytes Ag, Al, Ca, Cd, Cr, Fe, K, Mg, Na, Ni, Sb and Se, we estimate the relative uncertainties to be about 3% or less in both the a-r particulates and the leach residues.

For sulphate in the a-r particulates, the agreement between 10 measured and known solid and solution standards and spikes was 98.9% (σ = 6.8%; n = 10). The determinations of sulphate in duplicate samples of the a-r A smelter particulates were 34.41% and 35.01% for an average of 35.71% ± 0.30%. So we would estimate the c.r.u. to be 3% or less. For the leach residues, the agreement between nine measured and known solid and solution standards and spikes was 100.1% ($\sigma = 3.0; n = 9$), and duplicate samples resulted in 14.55% and 14.51% and an average of 14.53% ± 0.02%. Here, we would estimate the c.r.u. to be 2% or less.

Leach solutions

Our ASG used similar QA/QC methodology for the leach solutions determined by ICP-AES, which they ran both undiluted and diluted by a factor of 10. They used between four (e.g., for minor analytes such as Se) and seven (e.g., for major analytes such as Cu) standards comprising solution CRMs and spiked multi-component solutions. In the case of As, they used seven spikes and CRMs, which yielded 96.9% ($\sigma = 2\%; n = 7$) agreement between the measured and known values. For the major metal analytes As, Cu, Pb and Zn, the average percentage agreement between the measured and known values was 98.2% (σ = 1.7%; n = 4), and the minimum and maximum percentages were 92% and 105%. For the remaining 12 analytes, the average percentage agreement between the measured and known values was 100.4% (σ = 1.3%; n = 12), with the minimum and maximum percentages of 90% and 116%. Thus, we would estimate the c.r.u. in the solution determinations to be 2% or less.

For sulphate determinations, our ASG ran 12 standards and spikes, which yielded 101.0% (σ = 1.7%; n = 12) agreement between the measured and known concentrations. So we would estimate

the c.r.u. in the solution sulphate concentrations to be 2% or less.

Estimates of uncertainties in quantitative speciation

To estimate the uncertainties in the quantitative speciation of the a-r particulates, we have tabulated the estimated c.r.u. percentages for the analytes in the a-r particulates, residues and leachates, as well as their totals across the three media, in Table 10. For instance, the c.r.u. percentages for As in the a-r particulates, residues and leachates are 2, 2 and 2, respectively, for a total of 6%. To estimate the uncertainty in the percentage of a particular compound, we used the equation

$$c.r.u. = \text{calculated average wt\%}$$
$$\times \left[(c.r.u.)_i + (c.r.u.)_j + stdev \right] / 100$$

in which $(c.r.u.)_i$ and $(c.r.u)_j$ are the c.r.u. values for components i and j in the compound and stdev is the standard deviation in the calculated average wt.% from leaching in the three media. As an example, the c.r.u. for $ZnSO_4.H_2O$ in the C smelter particulates would be

$$34 \times [4 + 6 + 1]/100 = 4$$

so that the calculated average wt.% for $ZnSO_4.H_2O$ in the C smelter particulates lies between 30% and 38%. Similarly, that for $PbSO_4$ the A smelter particulates would lie between 10% and 12%. The c.r.u. for a compound with only one component analyte would be relatively

smaller, such as that for As_2O_3 in the B smelter particulates, which would be 0.6%, and the calculated average wt.% of As_2O_3 would lie between 8.1% and 9.3%.

Appendix 2

Table 11 below is a worked example of the derivation of the quantitative speciation of the C smelter stack particulates. Using bulk chemical analysis (space considerations allowing only for this example), we determined the percentages and concentrations of analytes in the a-r particulates, the leachate and the leach residue. We then used a step-wise procedure to apportion, on a molar basis, the analytes to the chemical species and compounds detected by XRD, SEM/EPMA, BSE, EDS and WDS characterisation. The calculated compositions are based on the components' values recovered from the leachate and leach residue.

Table 9 presents the results of leaching 20.00131 g of C smelter stack particulates in 1,800 mL of OECD 203, and then diluting the filtrate with d.i. water to 2,000 mL.

We have normalised the data to moles of component per 100 g of a-r smelter particulates. For a given component, we have calculated its percentage in the a-r particulates from its analyses in the leachate and the residue, and its mass balance as a percentage of the quotient of the molar quantity recovered in the leachate plus that in the residue divided by the molar quantity in the a-r particulates. Table 3 provides data on the weight percentages of the analytes in the a-r C smelter particulates, and the percentages of the leached and residue analytes, as well as the mass balances.

In this example, 0.0393 mol of Pb reported to the residue, which also contained 0.0366 mol of SO_4. From the XRD pattern of Fig. 2, we assign all 0.0366 mol of SO_4 in the residue to anglesite, $PbSO_4$, leaving 0.0028 mol of Pb, which we assign to PbO, likely associated with agglomerates, in the residue. Only 7.2×10^{-6} mol of Pb leached. Thus, we calculate that the a-r sample contained 11.09% $PbSO_4$ and 0.62% PbO. With 8.28% Pb in the a-r particulates, or 0.0400 mol Pb/100 g of sample, the Pb mass balance is $100(0.0393 + 7.2 \times 10^{-6})/0.0400 = 98 \%$.

Table 10 Estimated combined relative uncertainties in the concentrations of major, minor and trace analytes

Analyte	Estimated combined relative uncertainty (c.r.u.), %, in			Total c.r.u.
	a-r Particulates	Residues	Leachates	
As	2	2	2	6
Cu	1	1	2	4
Pb	2	2	2	6
SO$_4$	2	2	2	6
Zn	1	1	2	4
Minor and trace elements	3	3	2	8

Table 11 Worked example of derivation of quantitative characterisation of C smelter stack particulates

20.00131 g C Smelter a-r (as-received) sample leached in 1,800 mL OECD 203, then diluted to 2,000 mL

Component	Average wt %	Moles in a-r sample/100 g sample	Moles leached/100 g sample	Moles in residue/100 g sample	Moles in (residue plus leachate)/ 100 g sample	Mass balance, %	Calculated composition, %, based on recovered values	
Pb	8.28	0.0400	7.2E-06	0.0393	0.0393	98		
SO_4	22.36	0.2328	0.2006	0.0366	0.2371	102	as $PbSO_4$	11.09
bal Pb				0.0028			as PbO	0.62
bal SO_4		0.1928	0.2006	0.0000	0.1978			
Cu	5.68	0.0894	0.0115				as $CuSO_4$	1.83
bal SO_4			0.1891					
Zn	17.58	0.2689	0.2177					
bal SO_4			0.1891				as $ZnSO_4.H_2O$	33.93
bal Zn			0.0286					
bal SO_4			0.0000					
Zn			0.0286				as ZnO	2.32
As				0.1361				
Zn				0.1004	0.3181	118		
Cu				0.0798	0.0912	102		
Assign Cu to undissolved $(Cu_{0.839}Zn_{0.161})$ (AsO_3OH)				0.0951			$(Cu_{0.839}Zn_{0.161})$ (AsO_3OH)	19.37
Balance of As as As_2				0.0205			assigned to $Zn_3(AsO_4)_2$	9.71
Zn in $(Cu_{0.839}Zn_{0.161})$ (AsO_3OH)				0.0153				
Zn in Zn_3 $(AsO_4)_2$				0.0615				
				0.0768				
Balance of Zn				0.0236			assigned to ZnO	1.92
As	17.66	0.2357	0.1121				as As_2O_3	11.09
As total					0.2482	105		
K	2.25	0.058	0.0576	0.0027	0.0603	105	as K_2O	2.84
Na	0.554	0.024	0.0242	0.0007	0.0249	103	as Na_2O	0.77
Cd	0.603	0.0054	0.0028	0.0025	0.0053	99	as CdO	0.68
Fe	0.829	0.0148	4.2E-06	0.0138	0.0138	93	as Fe_2O_3	1.10
Si	0.196	0.0070					as SiO_2	0.42
Sb	0.208	0.0017	4.9E-05	0.0019	0.0020	116	as Sb_2O_5	0.32
Ca	0.131	0.0033	−0.0008	0.0014	0.0014	42	as CaO	0.18
Al	0.077	0.0029	2.2E-05	2.0E-03	0.0020	69	as Al_2O_3	0.10
C	0.025	0.0021					C	0.025
Mg	0.013	0.0005	−0.0004	0.0002	0.0002	41	as MgO	0.022
Ag	0.0063	5.8E-05	1.2E-07	6.8E-05	6.8E-05	117	Ag	0.007
Se	0.0085	0.00011	4.6E-06	2.1E-05	2.6E-05	24	as SeO_2	0.003
Cr	0.0006	1.15E-05	6.7E-08	7.1E-06	7.2E-06	62	as Cr_2O_3	5E-04
Ni	0.0004	6.8E-06	2.9E-06	2.2E-06	5.2E-06	76	as NiO	4E-04
								98.36

Moreover, in addition to the 0.0366 mol of SO_4 in the residue, 0.2006 mol of SO_4 reported to the leachate, for a total of 0.2371 mol, which compares favourably with the 0.2328 mol in the a-r stack particulates and yields a mass balance for SO_4 of 102%.

The a-r stack particulates also contained 5.68% Cu or 0.0894 mol. Of the 0.0115 mol of Cu in the filtrate, we assume that all was leached from the a-r stack particulates as the sulphate, yielding 1.83% $CuSO_4$ in the initial sample and leaving 0.1891 mol of unassigned dissolved SO_4.

We apportion the remaining 0.1891 mol of dissolved SO_4 to gunnigite, $ZnSO_4.H_2O$, as detected in the XRD pattern of Fig. 7, yielding 33.93%. This attribution has accounted for all the remaining dissolved SO_4, and leaves 0.0286 mol of dissolved Zn which we assign to ZnO, 2.32%.

With about 58%, 37% and 89% of the As, Zn and Cu unleached, respectively, the residue contained 19.33% (0.1361 mol) As, 12.45% (0.1004 mol) Zn and 9.61% (0.0798 mol) Cu.

From WDS analysis #5 of Table 4 and Fig. 9c, we assign the 0.0798 mol of undissolved Cu to $(Cu_{0.84}Zn_{0.16})(AsO_3OH)$, which yields 0.0951 mol of this Cu–Zn arsenate, or 19.37%. Since the $(Cu_{0.84}Zn_{0.16})(AsO_3OH)$ also contains 0.0951 mol of As, we are left with 0.0205 mol of As_2, all of which, from Fig. 9e indicating that Zn was associated with an arsenate, we assign to the insoluble $Zn_3(AsO_4)_2$ [A-1] at 9.71%. In the process, we have sequestered 0.0615 mol of Zn, leaving 0.0236 mol of Zn, which we assign in turn to ZnO.

Between the solution and residue, the Zn mass balance is $100(0.2177 + 3(0.0335))/0.2689 = 118\%$, somewhat greater than desirable, but nonetheless acceptable. The Cu mass balance is $100(0.0115 + 0.0798)/0.0894 = 102\%$, which is quite good.

Arsenolite is readily identified in Fig. 7. Moreover, since about 48% of the As in the a-r stack sample dissolved, we apportion this amount to the relatively soluble As_2O_3 [B-1], 11.09%, which with the 10.20% by weight of the a-r particulates as undissolved As associated with the arsenates, yields the mass balance for As of $100(0.1121 + 0.1361)/0.2357 = 105\%$, again quite good.

While they may not exist as discrete compounds, we assume that K and Na exist as oxides in some form and so have calculated the percentages of K_2O and Na_2O to be 2.84 and 0.77, respectively, with corresponding mass balances of 105 and 103%. The 0.42% SiO_2 is obtained from the percentage of Si in the a-r particulates.

We also assume that Cd, Fe, Sb, Se, Ni and Cr all exist as their respective oxides, so that their calculated weights in the a-r particulates vary between 4×10^{-4} and 1.1%. Because the differences between the measured concentrations of Ca and Mg in the OECD 203 leachate and those in the OECD medium were negative, we have simply converted the percentages of Ca and Mg in the a-r particulates to 0.18% CaO and 0.022% MgO. Moreover, we calculate Al_2O_3 to be 0.10% and Ag to be 0.007%. As might be anticipated with such low percentages, the mass balances vary between quite good as the 99% for Cd as CdO, the low of 24% for Se as SeO_2, and the high of 116% for Sb as Sb_2O_5.

The total mass balance for the C smelter stack particulates leached in the OECD 203 medium was 98.34%, which is close to the objective of achieving a 100% mass balance.

Other than the discrete compounds gunnigite, $ZnSO_4.H_2O$; anglesite, $PbSO_4$; and arsenolite, As_2O_3, the compounds for which we have presented calculated percentages in Table 11 were not detected by XRD. However, apportioning of the insoluble Cu and Zn to calculated amounts of Cu–Zn arsenate and Zn arsenate is consistent with the SEM/EPMA detection of Cu and Zn arsenates in the pristine smelter stack samples, and also accounts for the Cu and Zn in the leach residue. The compounds for which we have assigned quantitative speciation may exist in the amorphous and agglomerated material detected by XRD and SEM/EPMA characterisation, respectively.

We have followed the above general approach in developing the quantitative speciation of the a-r C smelter stack particulates from the d.i. water and RICH-95 leaching, as well as the A and B particulates.

Appendix 2 Reference

Godfrey, S.M., McAuliffe, C.A., Mackie, A.G. & Pritchard, R.G. (1998). Coordination chemistry and solution chemistry. In N.C. Norman (ed.), Chemistry of Arsenic, Antimony and Bismuth (pp 159–205). London: Blackie.

References

Barcan, V. (2002). Nature and origin of multicomponent aerial emissions of the copper-nickel smelter complex. *Environment International, 28*, 451–456.

Beavington, F., Cawse, P. A., & Wakenshaw, A. (2004). Comparative studies of atmospheric trace elements: Improvements in air quality near a copper smelter. *Science of the Total Environment, 332*, 39–49.

Biswas, A. K., & Davenport, W. G. (1994). *Extractive metallurgy of copper* (p. 305). New York: Elsevier.

Canada Gazette (2006). Vol. 140, no. 17, April 29, 2006. http://canadagazette.gc.ca/partI/2006/20060429/html/notice-e.html. Accessed July 24, 2008.

Dana, E. S., & Ford, W. E. (1958). *A textbook of mineralogy* (p. 535). New York: Wiley.

Doyle, P. J., Gutzman, D. W., Sheppard, M. I., Sheppard, S. C., Bird, G. A., & Hrebenyck, D. (2003). An ecological risk assessment of air emission of trace metals from copper and zinc production facilities. *Human and Ecological Risk Assessment, 9*(2), 607–636.

Environment Canada. (2006). http://www.ec.gc.ca/default.asp?lang=En&n=714D9AAE-1&news=12D55D41-87CA-4AB9-89AB-9D3D8520AA46. Accessed July 24, 2008.

Ettler, V., Johan, Z., Baronnet, A., Jankovský, F., Gilles, C., Mihaljeè, M., et al. (2005). Mineralogy of air-pollution-control residues from a secondary lead smelter: Environmental implications. *Environmental Science & Technology, 39*(23), 9309–9316.

Ettler, V., Šebek, O., Grygar, T., Klementová, M., Bezdièka, P., & Slaviková, H. (2008). Controls on metal leaching from secondary pb smelter air-pollution-control residues. *Environmental Science & Technology, 42*(21), 7878–7884.

Gieré, R., Blackford, M., & Smith, K. (2006). TEM study of PM2.5 emitted from coal and tire combustion in a thermal power station. *Environmental Science & Technology, 40*, 6235–6240.

Godfrey, S. M., McAuliffe, C. A., Mackie, A. G., & Pritchard, R. G. (1998). In N. C. Norman (Ed.), *Chemistry of arsenic, antimony and bismuth* (pp. 191–197). London: Blackie.

Karczewska, A. (1996). Metal species distribution in top- and sub-soil in an area affected by copper smelter emissions. *Applied Geochemistry, 11*, 35–42.

OECD (1992). OECD Guideline for Testing Chemicals. Fish, Acute Toxicity Test. http://www.oecd.org/dataoecd/17/20/1948241.pdf. Accessed, 2001.

OECD (2001). Harmonised Integrated Classification System for Human Health and Environmental Hazards of Chemical Substances and Mixtures. OECD Series on Testing and Assessment, Number 33. OECD Environment Directorate, Environment, Health and Safety Division, 2 rue André-Pascal, 75775 Paris Cedex 16, France. http://www.olis.oecd.org/olis/2001doc.nsf/LinkTo/NT00004D4E/$FILE/JT00111570.PDF. Accessed Feb. 14, 2007.

Samuelsson, C., & Björkman, B. (1998). Dust-forming mechanisms in the gas cleaning system after the copper converting process. *Scandinavian Journal of Metallurgy, 27*(2), 54–63.

Samuelsson, C., & Carlsson, G. (2001). Characterization of smelter dusts. *CIM Bulletin, 94*(1051), 111–115.

Sánchez de la Campa, A. M., de la Rosa, J. D., Sanchez-Rodas, D., Oliveira, V., Alastuey, A., Querol, X., et al. (2008). Arsenic speciation study of PM2.5 in an urban area near a copper smelter. *Atmospheric Environment, 42*, 6487–6495.

Sánchez-Rodas, D., Sánchez de la Campa, A. M., de la Rosa, J. D., Oliveira, V., Gomez-Ariza, J. L., Querol, X., et al. (2007). Arsenic speciation of atmospheric particulate matter (PM10) in an industrialised urban site in southwestern Spain. *Chemosphere, 66*, 1485–1493.

Sobanska, S., Ricq, N., Laboudigue, A., Guillermo, R., Brémard, C., Laureyns, J., et al. (1999). Microchemical investigations of dust emitted by a lead smelter. *Environmental Science & Technology, 33*(9), 1334–1339.

UNECE (United Nations Economic Commission for Europe) (1998). Convention on Long-range Transboundary Air Pollution (LRTAP) Protocol on Heavy Metals. http://www.unece.org/env/lrtap/hm_h1.htm. Accessed July 24, 2008.

United Nations (2009). Globally Harmonized System of Classification and Labelling of Chemicals, ST/SG/AC.10/30/Rev.3. http://www.unece.org/trans/danger/publi/ghs/ghs_rev03/03files_e.html. Accessed Apr. 21, 2010.

Wong, H. K. T., Banic, C. M., Robert, S., Nejedly, Z., & Campbell, J. L. (2006). In-stack and in-plume characterisation of particulate metals emitted from a copper smelter. *Geochemistry: Exploration, Environment, Analysis, 6*, 131–137.