Effect of weathering product assemblages on Pb bioaccessibility in mine waste: implications for risk management.

Barbara Palumbo-Roe • Joanna Wragg • Mark Cave • Doris Wagner

B. Palumbo-Roe (✉) • J. Wragg • M. R. Cave • D. Wagner

British Geological Survey, Keyworth Nottingham, NG12 5GG, UK

e-mail: bpal@bgs.ac.uk

(✉) **Corresponding author:**

Barbara Palumbo-Roe

e-mail: bpal@bgs.ac.uk

Abstract

General assessments of orebody types and associated mine wastes with regards to their environmental signature and human health hazards are needed to help managing present and historical mine waste facilities.

Bioaccessibility tests and mineralogical analysis were carried out on mine waste from a systematic sampling of mine sites from the Central Wales orefield, UK.

The bioaccessible Pb widely ranged from 270 to 20300 mg/kg (mean 7250 mg/kg; median 4890 mg/kg) and the bioaccessible fraction from 4.53 % to >100 % (mean 33.2 %; median 32.2 %), with significant (p=0.001) differences among the mine sites. This implies sensitivity of bioaccessibility to site-specific conditions and suggests caution in the use of models to assess human health impacts generalised on the basis of the mineral deposit type. Mineralogical similarities of the oxidation products of primary galena provided a better control over the observed Pb bioaccessibility range. The higher Pb bioaccessibility (%) was related to samples containing cerussite, irrespective of the presence of other Pb minerals in the mineral assemblage; lower Pb bioaccessibility resulted where anglesite was the main Pb mineral phase and cerussite was absent.

A solubility diagram for the various Pb minerals in the waste was derived using PHREEQC model and the experimental Pb concentration measured in the simulated gastric solution compared with the equilibrium modelling results. For samples containing cerussite, the model well predicted the soluble Pb concentrations measured in the experimental simulated gastric solution, indicative of the carbonate mineral phase control on the Pb in solution for these samples and little kinetic control on the dissolution of cerussite. On the contrary, most mine waste samples containing dominant anglesite and or plumbojarosite (no cerussite) had lower solution Pb values, falling at or below the anglesite and plumbojarosite solubility equilibrium concentrations, implying kinetic or textural factors hindering the dissolution.

INTRODUCTION

International guidelines and European directives emphasise the importance of reducing the long-term environmental impact of mining by a more regulated and rigorous management of the extractive industry waste after mine closures. The Directive 2006/21/EC of the European Parliament and of the Council on the management of waste from the extractive industries (The Mining Waste Directive) (European Commission 2006) requires Member States to maintain an inventory of closed and abandoned mining waste facilities that are causing serious environmental impacts or have the potential to cause such an impact, with the ultimate aim to use this knowledge for planning effective remediation measures at national scales. The Directive requires these inventories to be based on risk assessment methods, i.e. based on the Hazard-Pathway-Receptor framework. Therefore, hazard source characterisation is an important part of this assessment.

The environmental signatures of mine waste associated with different metalliferous mineral deposits are highly variable. Nevertheless, some general observations have been drawn according to 'Geoenvironmental Models of Mineral Deposits' (Plumlee and Nash, 1995; Seal and Foley, 2002), which provide information about natural geochemical variations associated with a particular deposit type, and its mining effluents and wastes. The pyrite contents of ore and the carbonate contents of ore / host rock principally determine the pH and contaminant content of mine waters, seepage from mine waste piles and tailings. Similar general assessments of orebody types and associated mine wastes with regards to the potential human health hazards are needed to help assessing and managing present and historical mine waste facilities.

One of the main risks to human health posed by unvegetated tailings heaps is through ingestion and inhalation of mine waste contaminated material. Lead is among the elements of greatest concerns due to its toxicity. Studies on the relation between elevated Pb contents in soils and blood Pb concentrations in mining impacted communities have been reported (Cotter-Howells and Thorton, 1991, Heyworth., et al 1981, Steele et al., 1990). *In vitro* methodologies have been developed and applied to simulate exposure to soil borne/mining related contaminants via the human ingestion and inhalation pathways (Oomen et al., 2002; Bennet et al., 2007; Drexler and Brattin, 2007; Beak et al., 2008; Guney et al., 2010; Denys et al., 2012) to provide an estimate of exposure. Such methodologies have included dynamic and batch based systems, which operate at human body temperature (37ºC) utilising simulated body fluids, residence times and average masses of ingested or inhaled material for the receptors considered in a given conceptual model (e.g. children). In general, simulated ingestion systems consist of one, two or three phases corresponding to the mouth at near neutral pH, a stomach phase at acidic pH (c. 1.2-2.5) and a small intestine phase respectively (c. pH 6.5 -7.0). Sample collection for further analysis generally arises from the stomach and/or the small intestine phases, where applicable. In contrast, fewer studies have been carried out to simulate exposure to inhalation of such contaminants and in most cases the simulant used is predominantly Gamble's fluid (or variants of), a simulant of lung surfactant fluid with a pH of 7.3 (Wragg and Klinck, 2007; Berlinger et al., 2008; Okorie et al., 2012).

As literature related to bioaccessibility methods and their correlation to in vivo (animal) studies becomes available, there is a growing body of evidence to support the rationale that 100% of the total amount of contaminant present is not available to be taken up via a specific exposure route, indicating the importance of

such data in human health risk assessment (e.g. Van de Wiele et al., 2007; Wragg et al. 2011; Appleton et al., 2012; Denys et al., 2012).

When assessing the Pb toxicity and bioaccessibility in Pb-rich mine waste and mine contaminated soils, it is critical to know the form of Pb and its solubility at the conditions of the gastrointestinal (GI) tract. The observed lower bioaccessibility of Pb from mining sites compared to urban sites has been related to mineral solubility and kinetic factors (Ruby et al. 1992). Ruby et al. (1999) reported that Pb mineral bioaccessibility (defined as the solubility of soil metal in simulated stomach and intestinal solutions), assessed by an in-vitro physiologically-based extraction test (PBET), increases in the order: galena (PbS) <pyromorphite $Pb_5(PO_4)_3Cl$, <Fe-Pb oxides<plumbojarosite $(PbFe_6(SO_4)_4(OH)_{12})$ <Mn-Pb oxides<Pb oxides<cerussite $(PbCO_3)$. Dissolution kinetics (directly related to particle size) during the limited residence time in the stomach (<2 h) must also be considered when assessing the availability of Pb from an ingested Pb-bearing mineral or soil. In addition, other geochemical factors including the degree of encapsulation and the nature of the alteration rinds are critical parameter controlling mineral dissolution (Davis et al. 1992).

This study applies mineralogical and geochemical data to assess the bioaccessibility of Pb from various mine wastes from abandoned mines typical of the Lower Palaeozoic Pb-Zn shale-hosted mineralisation in central Wales in UK. The aim was to determine the relative importance of ore mineralogy and site-specific geochemistry in affecting Pb bioaccessibility in the mine waste and to establish if a characteristic bioaccessibility range could be constrained and a common pattern drawn for the study mining area. This would be valuable for a first screening of abandoned mining areas for human health risk assessment.

MATERIAL AND METHODS

Site setting

The main host rocks to the mineralisation in central Wales are Silurian mudstones and greywackes deposited in a thick series of sediments in the Welsh Basin (Raybould, 1974). The mineralisation occurs as narrow veins of quartz and sulphides, up to 2 m wide, within wider zones of faulting up to 30 m across. The veins are commonly brecciated with angular to rounded fragments of sulphides, quartz and country rock within the whole fault zone. The main ore minerals were galena and sphalerite, with quartz as the main gangue mineral, while ankerite is abundant only locally. Pyrite in small amounts commonly accompanied the mineralisation.

The study was conducted in the catchment of the River Ystwyth (Figure 1), one of the main rivers of central Wales with a long history of pollution originating in metalliferous mining (Jones, 1922).

Sampling methods

Nine mines were visited over two field campaigns from August to September 2007 (Quigley et al., 2012). Aerial photos, historic and Ordnance Survey maps were used in conjunction with visual inspection to identify suitable mine waste sites and the areal extent of each site. The predominant waste types were identified at each site and thirty trowel sub-samples (approximately 250 ml each) were taken from the surface material (upper 15 cm) at roughly equally spaced intervals over the extent of each waste type area to give 7 to 8 litres of material in total.

All sub-samples were then combined in a polypropylene bucket in situ, mixed and sieved through a 2mm sieve, producing a total of 42 samples.

In the environmental management of old mining sites it is important to recognise that the heaps are not homogeneous in either composition or permeability. Changes due to geological and economic factors in the grade and types of ores mined during the nineteenth century gave rise to highly variable ore production, affecting the characteristics of the produced tailings in terms of particle size, permeability, secondary mineral formation and concentration of heavy metals. Despite this likely vertical variability of mine waste spoils, it was chosen to sample only the surface material, as more representative of the hazard posed to potential receptors like livestock and people, via erosion, windblown dust and the dermal contact-ingestion pathways.

Sample site descriptions are given in Table 1. Across the sites the majority of mine waste dump material was present as very coarse/ coarse sand (Cwmystwyth, Glog Fawr and Glog Fach, Grogwynion, Level Fawr and Wemyss) or poorly sorted sand (Frongoch, Graiggoch), where the <250 μm fraction normally comprises less than 35 wt% of the bulk material in the samples. The tailings lagoons at Frongoch and Logaulas are predominantly fine sand, silt and clay.

Analytical methods

A suite of total elemental concentrations (Al, As, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, S, Se, Sr, V and Zn) in the <2mm and <250μm air-dried fraction materials was determined by mixed acid (HF, HNO_3 and $HClO_4^-$) digest following the procedure described by Thompson and Walsh (1983).

The pH of each sample was analysed at a ratio of 1:2.5 in 0.01M $CaCl_2$. The organic matter content was estimated by measuring the weight loss (LOI) after heating to a temperature of 450 °C.

Mineralogical analysis

Quantitative mineralogical characterisation of the waste samples was carried out using X-Ray Diffraction (XRD). The XRD analysis was carried out using a PANalytical X'Pert Pro series diffractometer equipped with a cobalt-target tube, X'Celerator detector and operated at 45kV and 40mA. The samples were scanned from 4.5-85°2θ at 2.76°2θ/minute. Diffraction data were initially analysed using PANalytical X'Pert Highscore Plus Version 2.2a software coupled to the latest version of the International Centre for Diffraction Data (ICDD) database.

Following identification of the mineral species present in the samples, mineral quantification was achieved using the Rietveld refinement technique (e.g. Snyder and Bish, 1989) using PANalytical Highscore Plus software. This method avoids the need to produce synthetic mixtures and involves the least squares fitting of measured to calculated XRD profiles using a crystal structure databank. Errors for the quoted mineral concentrations are typically ±2.5% for concentrations >60 wt%, ±5% for concentrations between 60 and 30 wt%, ±10% for concentrations between 30 and 10 wt%, ±20% for concentrations between 10 and 3 wt% and ±40% for concentrations <3 wt% (Hillier et al., 2001). Where a phase was detected but its concentration was indicated to be below 0.5%, it is assigned a value of <0.5%, since the error associated with quantification at such low levels becomes too large.

Scanning Electron Microscopy (SEM) was carried out on a selection of samples. For the identification of anglesite the presence of the S-K line within the Pb-M series of peaks was verified using the deconvolution and

peak reconstruction procedures used in the INCA software and by examining the resulting fit indices for the S-K and Pb-M lines.

Bioaccessibility extraction and analysis

The bioaccessible Pb content of the soil samples was determined using a physiologically based extraction test (PBET), based on that first described by Ruby et al., (1996) and modified for practical application by the BGS (Wragg and Cave, 2003). The *in vitro* system was a two stage extraction, simulating the chemical environment of the human gastro-intestinal (GI) system, incorporating simulated stomach and small intestine fluids at human body temperature (37ºC), fasted state residence times, a solid to liquid ratio of 1:100 and pHs of 2.5 and 7.0 in the two GI compartments, respectively. Sample size fraction for the bioaccessibility testing is <250µm, as this is considered to be the optimum size to adhere to children's hands. Modifications to, and application of the BGS PBET have been fully described by several workers including Palumbo-Roe et al., (2005), Wragg et al., (2007).

Total element and Bioaccessible Pb determinations

The total element concentrations in the mixed acid digests and the bioaccessible Pb concentrations in the *in vitro* solutions were determined by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES). Full details of the analysis method in relation to digested soils and bioaccessibility extracts have been previously described (Palumbo-Roe et al., 2005).

QA/QC

Within each analytical run a minimum of one digestion blank, one sample duplicate, one standard reference material (SRM) was digested and analysed per twenty unknown samples. The SRM used was the National Institute of Standards & Technology (NIST) Montana soil 2711. All reagents used in the digestion/extraction and subsequent analysis were of AristaR® grade or equivalent.

The average repeatability for the total digestion, for all elements was <5% (n=10), with the exception of Al (6.5%), K (11%) and Mo (7.2%). Lead bioaccessibility repeatability, reported as % relative standard deviation (RSD) was 10% (n = 5). All blank digestions were reported as less than the method limit of detection LoD (LoD$_{Pb}$ 0.010 mg/l). Average recovery of the SRM NIST 2711 after the total digestion procedure, across all elements determined, was $101 \pm 23\%$.

Statistical analysis

Analysis of variance (ANOVA) was carried out in R® and Box & Whisker plots produced using Minitab® 15.

RESULTS AND DISCUSSION

Pb mineralogy

The main mineral phases were identified by XRD analysis (Table 2).

The bulk of the mine waste is composed of quartz, feldspar, illite and chlorite. Minor quantities of dolomite and/or calcite were measured at Cwmystwyth, Glog Fawr and Glog Fach, Grogwynion and Logaulas. The

principal Pb minerals include cerussite, plumbojarosite and anglesite (PbSO$_4$) and minor galena. Cerussite is reported to be more abundant than anglesite in most of the supergene Pb mineralisation in Central Wales (Mason, 2004). Cerussite was indeed found to be the dominant Pb mineral at Grogwynion, Level Fawr and Logaulas mines, with the latter also containing minor amounts of anglesite. Figure 2 shows the occurrence of cerussite as a cement phase holding together composite grains including fragments of silicates and as a surficial coating on galena. Both cerussite and anglesite were detectable in Glog Fawr and Glog Fach samples, while cerussite, plumbojarosite and anglesite in variable proportions were identified at Cwmystwyth mine. A different Pb mineral assemblage dominated by anglesite (Figure 3) with subordinate plumbojarosite was found in samples from Frongoch, Graiggoch and Wemyss. Pyromorphite is also described as commonly occurring in mine dumps of Central Wales, the source of phosphate in solution being the apatite and phosphatic concretions typical of turbidite wallrocks accross the Central Wales orefield (Mason, 2004). However, pyromorphite was not detected in our samples by XRD. Only traces of pyrite were observed, although not for all sites.

Total Pb concentrations

The total Pb concentration in the <2 mm fraction ranged from 480 to 68790 mg/kg (mean 20800 mg/kg; median 11700 mg/kg). Total Pb concentrations in the <250μm fraction ranged from 450 to 131200 mg/kg (mean 28800 mg/kg; median 22000 mg/kg) (Table 3), indicating that the smaller size fraction was enriched in Pb relative to the bulk waste material.

The mine waste samples exhibited low organic matter content (median 1.63 %) and pH values ranging from 3.79 to 7.37 (Table 3).

Bioaccessible Pb concentrations

Absorption of available potentially harmful elements occurs in the small intestine of the GI tract and the PBET method generates samples for analysis for both the stomach and intestine compartments (Table 3). The higher pH and increased concentration of a number of enzymes used to simulate intestinal phase of bioaccessibility tests leads to the complexation and precipitation of Pb from solution (Grøn and Andersen, 2003), resulting in lower bioaccessibility values and poorer reproducibility of results (Wragg et al., 2011). In a similar manner to Appleton et al., (2012) the bioaccessibility values from the stomach phase of the PBET have been chosen for all data interpretation, as this phase is considered to provide a more conservative estimate of risk (Farmer et al., 2011). Lead bioaccessibility has been reported as an actual bioaccessible concentration (mg/kg) and as a fraction of the total Pb concentration in the sample (%) and referred to as the bioaccessible fraction (BAF). The bioaccessible Pb ranged from 270 to 20300 mg/kg (mean 7250 mg/kg; median 4890 mg/kg) (Table 3). The bioaccessible fraction of Pb (% Pb-BAF) varied considerably from 4.53 % to >100 % (mean 33.21 %; median 32.24 %) (Figure 4).

ANOVA showed that the bioaccessible Pb and the bioaccessible Pb fraction means were significantly (p=0.001) different among the mine sites. This implies sensitivity of bioaccessibility to site-specific conditions and suggests caution in the use of generalised models to assess human health impacts, based on the mineral deposit type.

Relationships between solid-phases and Pb in the simulated gastric solution

Figure 5 shows a lack of correlation between total Pb concentrations and bioaccessible Pb. However, some distinct features observed when grouping the samples by mineralogy may reflect the presence of at least two distinct bioaccessibility pools. To aid the interpretation of the mineralogical controls, four categories were defined in Figure 5, based on the presence of anglesite and/or cerussite, the other Pb mineral phases either being almost ubiquitous (i.e. galena) or in traces (e.g. plumbojarosite). Higher bioaccessible Pb fractions are related to samples where cerussite occurred in the Pb mineral assemblage, irrespective of other Pb mineral presence (e.g. anglesite) (Pb-BAF median value 40%; range 20 - <100%). Lower Pb bioaccessibility (median 11%, range 5-30%) resulted where anglesite was the main Pb mineral phase and cerussite was absent. Indeed, it was observed that the highest median values of bioaccessible fraction were found at Grogwynion, Logaulas and Glog Fawr and Glog Fach mine sites, containing cerussite as the main Pb mineral phase, while the lowest values at Frongoch and Graiggoch where anglesite was dominant. Wemyss and Cwmystwyth showed intermediate values of Pb bioaccessibility.

In order to substantiate these observations, the equilibrium geochemical model PHREEQC (Parkhurst and Appello, 1999) with the WATEQ4f database (Ball and Nordstrom, 1991) was used to evaluate the Pb mineral solubilities in HCl at pH 2.5 and T= 37° C of the simulated gastric solution, and the predicted concentrations were compared with values measured in the PBET gastric solutions. The solid phase components considered were anglesite, cerussite, galena, Cl-pyromorphite and plumbojarosite (solubility product for plumbojarosite from Chapman et al., 1983). Lead concentrations in solution were modelled i) at saturation conditions and ii) limited by the available mass of solid material. The available mass of each Pb mineral at a S:L ratio of 1:100, simulating the PBET experimental conditions, was calculated on the basis of the mineralogical analysis.

The model results are shown in Figure 6. Although the gastric solutions remained below the saturation in cerussite, the total Pb in solution for samples containing cerussite matched the predicted soluble Pb concentrations constrained by the amount of cerussite present in those samples (0.5 to 4 %), indicative of the mineral phase control on the Pb in solution and little kinetic control on the dissolution of cerussite. This corroborates previous studies (USEPA, 1999) confirming that, in the case of mine waste with presence of relatively small amounts of cerussite alteration products of the primary Pb ore minerals, Pb is immediately available upon ingestion, greatly increasing the bioaccessibility of the ingested material. Most samples containing dominant anglesite and or plumbojarosite (no cerussite) had lower solution Pb values, falling at or below the anglesite and plumbojarosite solubility equilibrium concentrations. For those samples with soluble Pb lower than values constrained by the available 0.5% anglesite, it is plausible to suggest kinetic or textural factors hindering the dissolution, as demonstrated by Ruby et al., (1992). A value of 815 mg/l soluble Pb in the PBET gastric solution associated with the mine tailings from Frongoch mine, containing dominant anglesite and no cerussite, may indicate the contribution of a significant additional bioaccessible Pb fraction, probably as an adsorbed fraction.

Conclusion

This study presents the Pb bioaccessibility of mine wastes from a systematic sampling of the lead mineralisation in Central Wales, UK. By focusing on the potential human health impact posed by mine wastes, this study

complements the assessments of the environmental impact of abandoned mine waste facilities on watercourse receptors, available in the UK literature.

Despite being derived from a single orefield , the mine waste bioaccessible Pb fraction varied significantly among the mine sites (from 5% to >100%), indicating, for these sites, the inadequacy of using a single value when considering the fraction of Pb assumed to be bioaccessible for human health risk assessment.

Mineralogical analysis by XRD has proved an effective tool to provide a first screening level of Pb bioaccessibility with the higher Pb bioaccessibility related to samples where cerussite is present in the Pb mineral assemblage, regardless of the presence of other Pb minerals (Pb-BAF median value 40%; range 20 - <100%). Lower Pb bioaccessibility resulted where anglesite was the main Pb mineral phase and cerussite was absent.

The PHREEQC batch-equilibrium model predicted the experimental soluble Pb concentrations measured in the simulated gastric solution of the PBET test in samples containing cerussite. Lead concentrations in the gastric solution lower than equilibrium values constrained by the available 0.5% anglesite highlight the importance of kinetic or textural factors hindering dissolution of this mineral phase.

The application of mineralogical data would be a valuable screening technique of abandoned lead mine sites for human health risk assessment. Uncertainty, due to the contribution of Pb-adsorbed fraction (not resolved by the XRD analysis), to the metal bioaccessibility remains. Iron oxide analysis and particle size measurements, together with leaching tests can be integrated to improve the assessment of Pb solid-speciation. However, mineralogical data cannot be used to replace bioaccessibility testing which provides the definitive data required for human health risk assessments.

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Table 1- Mine sites and mine waste sample locations.

Mine	Sample Code	Location Description	Easting	Northing
Cwmystwyth				
	6017	Cwmystwyth upper western tip	280081	274467
	6018	Cwmystwyth lower western tip	280159	274482
	6019	Cwmystwyth river shingle	280460	274520
	6020	Cwmystwyth lower-middle tip	280343	274555
	6021	Cwmystwyth upper-middle tip	280472	274639
	6022	Cwmystwyth eastern tip	280532	274676
Frongoch				
	WLS7	Frongoch tailings lagoon	272250	274210
	WLS8	Frongoch southern tailings tip	272314	274405
Glog Fawr and Glog Fach				
	6011	Glog Fach Mine	274722	270909
	6012	Glog Fawr Mine western tip	274597	270871
	6013	Glog Fawr Mine (old level)	274697	270529
	6014	Tip east of Glog Fawr	275002	270765
	6015	Glog Fawr northern tip	274907	270998
	6016	Tip north of Glog Fawr	275143	271050
Graiggoch				
	5009	Graiggoch western slope	270301	274039
	5010	Graiggoch darker tailings tips	270444	274055
	5011	Graiggoch lighter tailings tip	270460	274146
	5012	Graiggoch upper/eastern slime pit	270441	274207
	5013	Graiggoch lower/western slime pit	270377	274211
	5015	Graiggoch tip area adjacent to stream	270327	274211
Grogwynion				
	6001	Grogwynion Upper Craig Goch	270754	272234
	6002	Grogwynion Lower Craig Goch	270782	272098
	6003	Flood plain at base of Craig Goch	270708	271968
	GWS100	Grogwynion southern dump	271462	272050
	GWS101	Grogwynion southern dump	271463	272073
	GWS102	Grogwynion southern dump	271393	272068
Level Fawr				
	6005	Level Fawr tip	273840	272179
Logaulas				
	6006 to 6010	Logaulas tailings lagoon	274391	271850
Wemyss				
	5001	Wemyss partly vegetated area	271883	274357
	5002	Wemyss tip (base)	271541	274052
	5003	Wemyss tip (0.5 - 1 m above base)	271594	274139
	5004	Wemyss tip 4	271526	274291
	5005	Wemyss tip 3 top area	271380	274262
	5006	Wemyss tip 3 lower area	271296	274233
	5007	Wemyss tip 2	271217	274227
	5008	Wemyss tip 1	270868	274255

Table 2 - Mineralogical composition of mine waste samples

	Mineralogy (%)												
	albite	anglesite	calcite	cerrussite	chlorite	dolomite	galena	'mica'	plumbo-jarosite	pyrite	quartz	rutile	sphalerite
Cwmystwyth													
6017	5.4	nd	nd	nd	15.4	nd	nd	25.4	0.7	nd	51.7	1.1	<0.5
6018	4.3	nd	nd	nd	10.7	nd	nd	21.5	0.8	<0.5	61.3	1	<0.5
6019	5.4	nd	nd	nd	13	nd	nd	24.7	nd	nd	54.9	1.1	0.9
6020	4.9	nd	nd	<0.5	7.8	5.7	<0.5	17.6	nd	nd	62.1	0.8	0.8
6021	5	nd	nd	nd	15.9	nd	nd	27.6	nd	nd	50.2	1.1	<0.5
6022	5	2.1	nd	<0.5	11.9	nd	<0.5	26.3	nd	nd	53	1	<0.5
Frongoch													
WLS7	2.1	17.6	nd	nd	9.2	nd	<0.5	10.3	nd	nd	59.1	nd	0.9
WLS8	3.9	nd	nd	nd	7.3	nd	nd	5.1	3	nd	80.7	nd	nd
Glog Fawr /Glog Fach													
6011	5.7	1	<0.5	1.1	17.8	0.9	<0.5	25.8	nd	nd	45.9	1.3	nd
6012	7.2	nd	2.6	0.6	16.8	2.5	<0.5	21.9	nd	<0.5	46.7	1	nd
6013	5.1	nd	nd	<0.5	20.1	<0.5	<0.5	27.8	nd	nd	45	1.3	nd
6014	8.1	0.9	nd	0.6	20.4	0.6	1.1	28.3	nd	<0.5	38.4	1.2	nd
6015	4	0.8	nd	0.7	19.3	nd	<0.5	29.3	nd	nd	44.3	1.4	nd
6016	2.6	1	nd	<0.5	18.5	nd	<0.5	24.8	nd	nd	51.2	1.4	nd
Graiggoch													
5009	4.1	7.1	nd	nd	14	nd	nd	22.1	nd	nd	51.3	1.4	nd
5010	4.1	0.5	nd	nd	15.2	nd	nd	20.1	nd	nd	59	1.1	<0.5
5011	3	4	nd	nd	8.9	nd	<0.5	14.2	<0.5	nd	68.3	0.8	<0.5
5012	3	1.2	nd	nd	10.5	nd	nd	13.6	nd	nd	70.9	0.7	nd
5013	3	2	nd	nd	9.6	nd	nd	14.7	nd	nd	69.9	0.8	nd
5015	5.8	nd	nd	nd	17.3	nd	nd	22.5	nd	nd	53.2	1.2	nd
Grogwynion													
6001	4.8	nd	nd	nd	18.7	nd	nd	33.3	<0.5	nd	41	1.9	nd
6002	5.6	nd	nd	nd	20.7	nd	nd	28.4	<0.5	nd	43.2	1.8	nd
6003	8.2	nd	nd	nd	17.5	nd	nd	24.3	nd	0.6	48.2	1.2	nd
GWS100	6.4	nd	0.6	5.9	21.2	<0.5	nd	16.6	nd	nd	48.8	nd	nd
GWS101	7.4	nd	0.8	<0.5	22.1	0.9	<0.5	19.4	nd	nd	49.4	nd	nd
GWS102	6	nd	nd	4.3	21.5	nd	<0.5	17.6	nd	nd	50.6	nd	nd
Level Fawr													
6005	8.2	nd	nd	1.4	15.5	nd	0.7	23.6	nd	<0.5	48.9	0.9	<0.5
Logaulas													
6006	6	1.2	<0.5	3.2	20.2	1.3	nd	22.2	nd	nd	44.3	1.1	nd
6007	6.9	1.2	<0.5	2.3	20.2	1.1	nd	23.2	nd	nd	43.5	1.1	nd
6008	6.9	0.8	0.6	2.6	20.3	1.4	nd	23.8	nd	nd	42.3	1.3	nd
6009	7.1	0.8	<0.5	2.2	19.5	1.1	nd	23.7	nd	nd	44	1.1	nd
6010	6.3	0.6	0.6	1.9	16.3	1.3	1.2	22.9	nd	<0.5	48.1	0.9	nd
Wemyss													
5001	3.3	2.6	nd	nd	12	nd	nd	20.6	nd	nd	60.2	1.3	nd
5002 -1	6.2	nd	nd	nd	19.3	nd	nd	31.9	<0.5	nd	40.3	1.9	nd
5002 -2	7.6	nd	nd	nd	19.6	nd	nd	26.9	nd	nd	44.4	1.5	nd
5002 -3	7.5	nd	nd	nd	16.3	nd	nd	28.1	nd	nd	46.5	1.6	nd
5003	2.7	nd	nd	nd	9.4	nd	nd	13.5	<0.5	nd	73.3	0.8	nd
5004	4.1	9.7	nd	nd	7.5	nd	<0.5	15.1	nd	nd	62.2	0.9	<0.5
5005	2.8	7.3	nd	nd	6.9	nd	<0.5	12.3	nd	nd	69.6	0.8	<0.5
5006	2.9	nd	nd	nd	16.8	nd	nd	23.5	<0.5	nd	55	1.4	nd
5007	1.6	0.9	nd	nd	6.5	nd	nd	8.6	<0.5	nd	81.4	0.6	<0.5
5008	3.5	0.6	nd	nd	10.4	nd	nd	15.2	nd	nd	69.2	0.9	<0.5

Table 3 – LOI, pH, Total Pb, Bioaccessible Pb (stomach, intestine 1, intestine 2) and BFA

|	LOI (%)	pH$_{Ca2Cl}$	Total Pb < 250μm (mg/kg)	Bioaccessible Pb $_{Stomach}$ (mg/kg)	Bioaccessible Pb $_{Intestine\,1}$ (mg/kg)	Bioaccessible Pb $_{Intestine\,2}$ (mg/kg)	BFA (%)
Cwmystwyth							
6017	1.36	3.79	3999	640	189	108	16.00
6018	1.58	3.97	14237	2196	567	537	15.43
6019	1.80	4.39	12312	1708	2116	2122	13.88
6020	0.79	6.02	22835	4465	814	706	19.55
6021	1.30	4.46	4054	1629	588	499	40.18
6022	1.63	5.22	32282	10719	738	236	33.21
Frongoch							
WLS7	0.38	4.48	80648	3655	1862	1102	4.53
WLS8	0.79	3.98	4293	589	270	228	13.72
Glog Fawr /Glog Fach							
6011	2.73	5.74	40969	16539	4071	2820	40.37
6012	0.55	7.19	36403	13643	3210	166	37.48
6013	0.65	6.80	11720	5280	1839	244	45.05
6014	1.95	5.66	35633	13925	161	372	39.08
6015	3.32	4.82	33462	10479	350	1496	31.32
6016	2.28	4.68	36803	7248	142	1859	19.69
Graiggoch							
5009	4.38	4.04	53922	4759	3892	3864	8.83
5010	1.24	4.55	8957	2688	1043	989	30.01
5011	0.89	4.90	76458	5015	578	1050	6.56
5012	1.03	4.24	19252	2119	1312	1307	11.01
5013	0.72	4.30	21126	3016	1114	1070	14.28
5015	1.16	4.83	3526	1830	758	720	51.88
Grogwynion							
6001	2.27	4.42	9412	4718	1718	1546	50.13
6002	3.12	4.81	12664	6329	2126	1319	49.98
6003	1.07	4.77	1272	599	196	163	47.04
GWS100	1.18	7.37	47667	20332	186	759	42.65
GWS101	1.29	6.58	29334	19787	1347	3179	67.45
GWS102	0.66	6.20	6090	7497	2139	837	123.1
Level Fawr							
6005	1.67	6.03	72119	16348	3944	3404	22.67
Logaulas							
6006	3.59	6.10	43363	19848	3487	4413	45.77
6007	2.58	6.02	34613	16302	4541	3959	47.10
6008	2.57	6.15	42090	18557	3738	3805	44.09
6009	2.21	6.25	30938	16155	3917	3731	52.22
6010	6.63	6.69	45886	15641	5731	5309	34.09
Wemyss							
5001	3.24	4.19	32427	5377	2818	2831	16.58
5002 -1	1.25	4.97	451	272	104	94.4	60.19
5002 -2	1.49	4.07	878	622	382	362	70.87
5002 -3	22.4	4.22	1964	310	338	332	15.80
5003	0.49	4.06	10622	2708	1275	1231	25.50
5004	7.15	4.16	131227	8333	3938	3720	6.35
5005	6.11	3.83	68803	5032	2548	2381	7.31
5006	1.35	4.35	6068	2012	659	584	33.15
5007	0.51	4.02	17207	3012	1045	982	17.50
5008	1.16	4.10	10941	2529	1122	1051	23.12
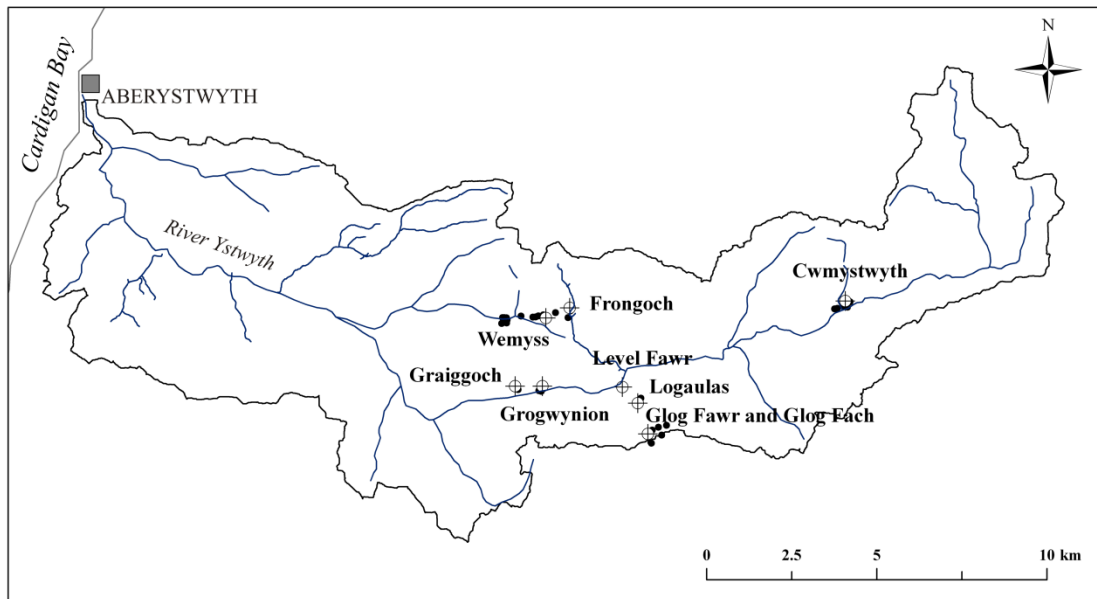
Figure 1 – Map of the River Ystwyth catchment with location of the mine sites (crossed circles) and sampling points (black circles).
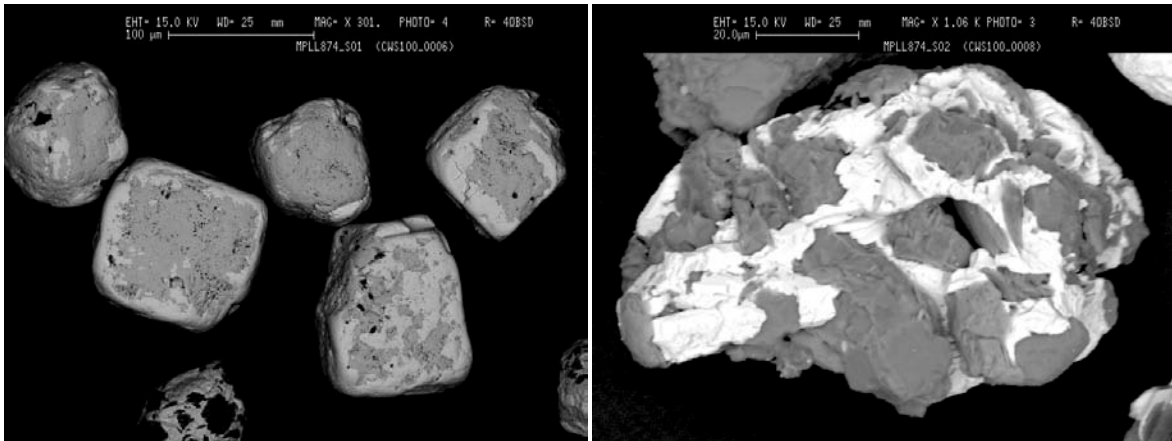
Figure 2 – BSEM images from Grogwynion mine waste sample. Left: single grains of galena (brighter grey material) with cubic habit, coated by fine-grained cerussite (darker-grey). Right: composite grain comprising fragments of quartz and feldspar (dark greys) cemented by cerussite (light grey).
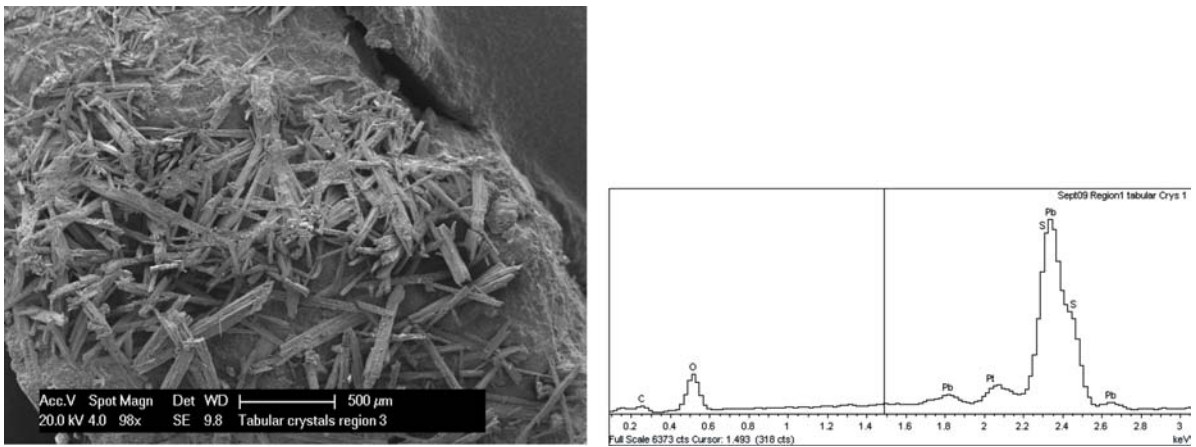

Figure 3 – SEM image and EDX spectrum of surface encrustations of acicular well-formed crystals on mine waste from Frongoch (Note: the EDX spectrum shows the S-K line overlapped by the Pb-M line). The small Pt peak is due to a thin coating of conductive Pt metal applied to the sample prior to SEM examination.
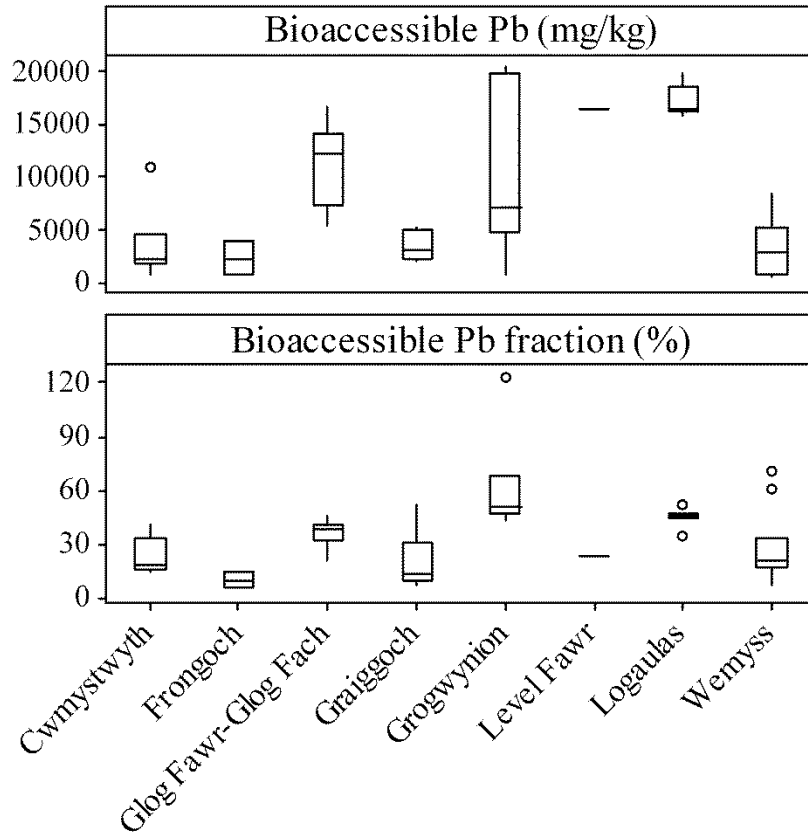
Figure 4 – Boxplots of bioaccessible Pb (mg/kg) and bioaccessible Pb fraction (%) across the mine sites.
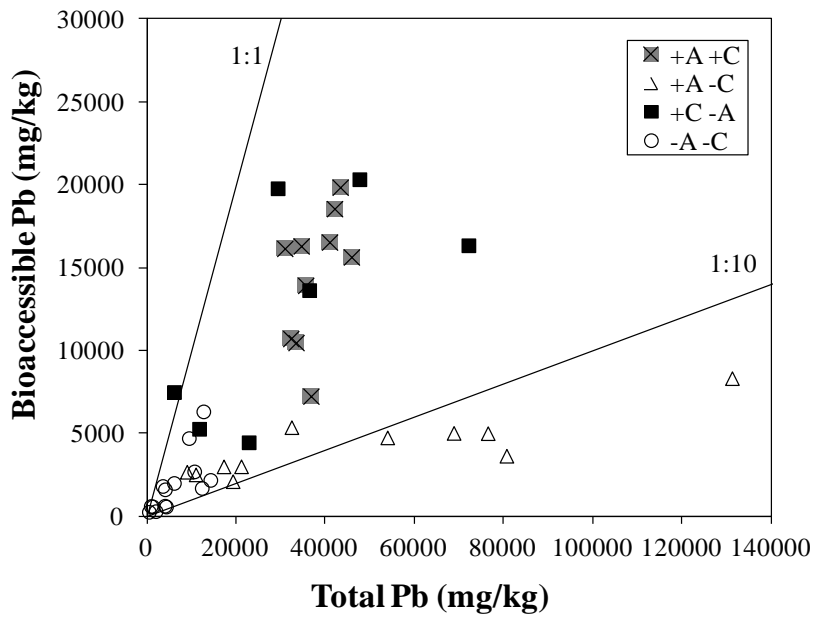
Figure 5 – Total Pb (mg/kg) versus Bioaccessible Pb (mg/kg). Groups: +A +C: Mineral assemblage contains anglesite and cerussite; +A -C: anglesite, no cerussite; +C -A: cerussite, no anglesite; -A -C: no anglesite, no cerussite.
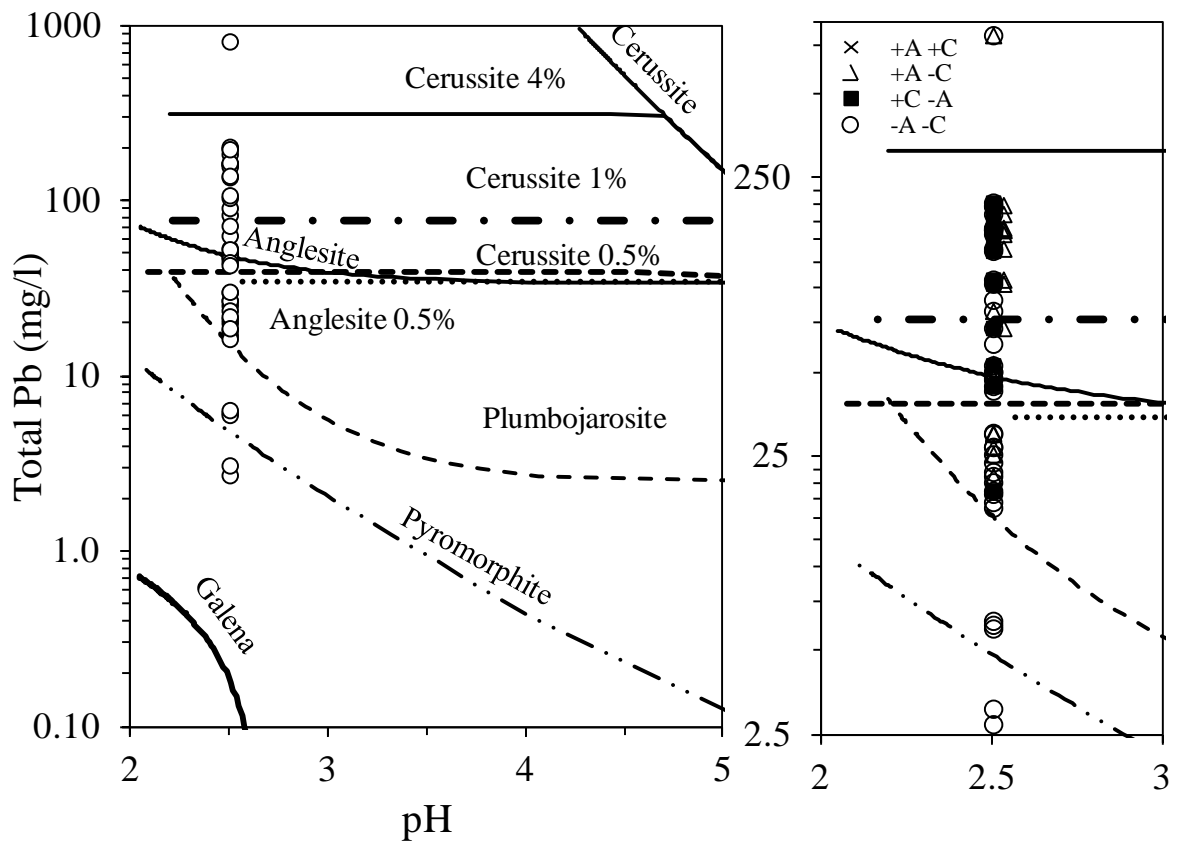
Figure 6 – Left: measured Pb concentrations in experimental gastric solution (circle symbols) (pH: 2.5) compared with the solubility of various Pb minerals as a function of pH, T= 37°C, in HCl. Right: detail of the distribution of Pb concentrations grouped by the mineralogy (categories as per Figure 5).