Chapter 18

Acid Mine Drainage in Wales and Influence of Ochre Precipitation on Water Chemistry

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A long history of metalliferous mining has left Wales with a legacy of abandoned mines and attendant spoil tips which are continuing sources of environmental contamination. Several of these old mines in the ore fields of mid and north Wales are sources of highly polluted acid drainage resulting from the oxidative weathering of pyrite and marcasite (FeS_2). The acid mine drainage which contains elevated levels of many elements, including Al, Fe, Cu, Zn, As, Cd and the SO_4 anion, is characterized by red-brown precipitates of ochre on stream beds and in lakes intercepting the drainage. Precipitation of the ochre has a marked influence on the chemistry of these acid waters with many elements concentrated in the ochre. The precipitation of Pb and Ba is controlled by the SO_4^{2-} content of the waters whereas elements such as As, Mo, Sn and Tl appear to be coprecipitated or adsorbed by the hydrated iron oxide. The degree of precipitation of Al, Mn, Fe, Cu, Zn and Cd is controlled by pH; lower acidity and higher pH favor precipitation.

Wales has a long history of metalliferous mining, ores having been extracted since at least Roman times with the industry at its peak during the eighteenth and nineteenth centuries. The extensive ore fields of mid and north Wales were mainly Pb, Zn and Cu producers with Ag also being extracted from the PbS ore. Barium, Mn and Fe were produced in some areas whereas Au mines were important in the Dolgellau gold belt (1) and are a continuing source of interest.

Although some metal mining interest has persisted to the present day, most mines had ceased operation by the 1920s and many abandoned mines and spoil tips scar the old ore fields. During the peak period of mining, techniques of ore extraction were very inefficient and there was little environmental control of the operations. Many of the old mines occurred in fault-controlled river valleys and as a result many river systems were badly polluted and were devoid of fish and insect life (2-4). In addition,

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flood-plain soils were contaminated and are found to contain high levels of heavy metals (5,6).

Cessation of much of the metalliferous-mining operations in the early part of this century has seen a marked improvement of river water quality but old mine workings and spoil heaps are continuing sources of pollution (7). Several of the mines intersected lodes containing pyrite and marcasite (FeS_2) and, as a result of the oxidative weathering of these minerals, some of the abandoned mines and associated spoil heaps have acidic drainage waters. These acid waters are characterized by hydrated iron oxide precipitation resulting in red-brown drainage channels and tip areas.

In this paper we consider the chemistry of some of these acid waters and their attendant ochres. In addition, some consideration is given to the role of ochre precipitation as a control on the chemistry of the pollutant drainage.

The Study Areas

The specific study sites are marked on Figure 1. The Cwmrheidol and Y Fan mines are typical of the mid Wales ore field, working ENE-trending lodes within Lower Paleozoic sediments. Both mines were worked primarily for lead and zinc, however, the Y Fan mine also produced some barite. While the Cwmrheidol deposit contains abundant pyrite and marcasite, the Y Fan deposit contains only subordinate amounts (8). Both mines, with extensive underground workings drained by adits driven in from valley sides, were abandoned early this century and have been continuing sources of significant pollution (9,10). Drainage channels from both mines are coated with rust-colored ochre, this being particularly so at Cwmrheidol where the stream draining the mine is known locally as "the red stream."

Gwynfynedd mine which was originally worked as a lead mine became a gold producer in the mid 19th century. Situated at the northern end of the Dolgellau Gold Belt (1), it produced 40,000 ounces of gold between 1888 and 1916 (11). Closed in 1938, it re-opened during the 1980s and was abandoned again in 1989. The mineralization within this mine occurs in veins cutting Lower Paleozoic sediments and intrusive rocks and consists of the sulfides pyrite, arsenopyrite, chalcopyrite, galena and sphalerite with gold occurring rarely in the veins. Mining at Gwynfynedd was from a series of shafts, open cuts and adits the lowest of which also serves as a drainage conduit. The mine drainage is characterized by ochre precipitation.

Level Goch in Snowdonia, north Wales, was one of several copper mines in that area. Little is known of its history but it is thought to have been mined more than 200 years ago (12). The geology of the area is comprised of Lower Paleozoic sedimentary and volcanic rocks. The old adit is drained by an ochreous stream.

Parys Mountain is known to have been mined by the Romans but the peak of extraction was during the late 18th and the 19th centuries when it was a major copper producer (13); mining ceased in 1911 (14). Although chiefly worked for copper, the deposit is polymetallic and there is current interest in the area for Pb, Zn and Cu mining (14). The mineralization includes chalcopyrite, sphalerite, galena and arsenopyrite but according to Pointon and Ixer (15) it is dominated by pyrite; these workers also list Bi sulphosalts and barite as occurring. The deposit is intimately

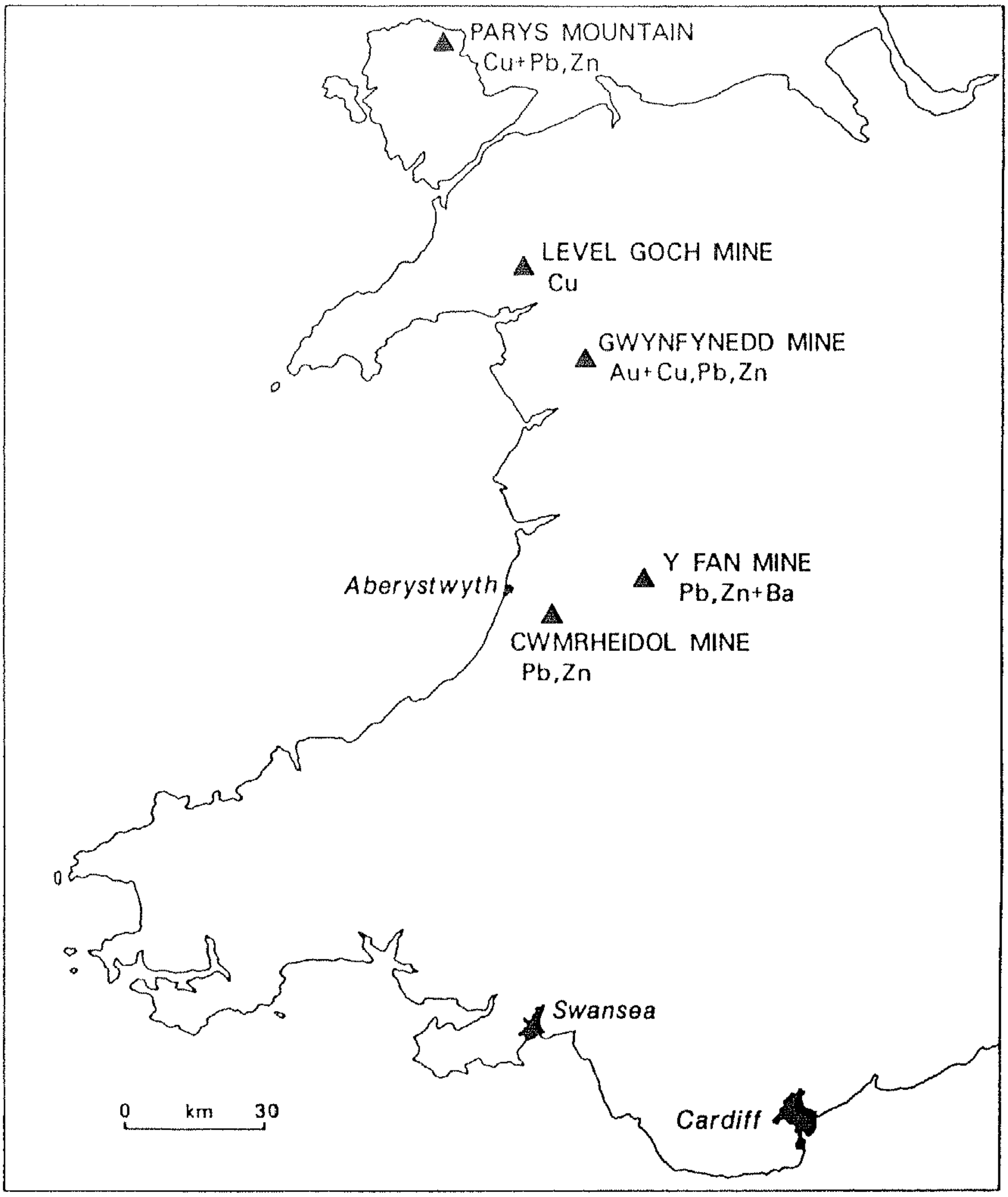

Figure 1. Wales with sampling sites marked.

associated with mid-Ordovician rhyolitic volcanism and is overlain by Silurian shales (16); it has been described as a Kuroko-type massive sulfide deposit (17).

Much of the drainage of the surface workings at Parys Mountain flows into the old pits and other hollows creating a series of lakes with brown-colored waters. In addition, the area had several ochre settling ponds during its working life and these also intercept surface and subsurface drainage (Figure 2).

Methodology

Water samples were collected in acid-washed polypropylene bottles and refrigerated until analyzed. Analyses were performed within 48 h of collection. Samples were filtered through a 0.45 μm filter but were not acidified. Initial results from both acidified and non-acidified samples were found to be identical when analyses were performed within 48 h of collection so it was deemed unnecessary to acidify all other samples.

Mine drainage was sampled several times over periods of from several months to more than a year during 1990 to 1992. Results quoted are mean values for all of these replicates.

Lake waters were sampled twice during the summer of 1992. Samples were collected from the surface, bottom and mid-level depths; the samples were analyzed independently.

Ochre samples were collected by gently removing surface material (generally to 1 cm depth). The samples were dried at a temperature of 40°C and disaggregated in an agate pestle and mortar. Samples were prepared for analysis with a variety of acids (40 ml) involving extraction of 500 mg of duplicate samples with:

1. Concentrated HCl
2. Concentrated HNO_3
3. A 4:1 mixture of concentrated HNO_3 and $HClO_4$

Sample extractions 1 and 2 gave results which were identical within analytical error for all elements other than Fe, HCl giving the more consistent results. Method 3 gave lower results for several metals including Pb and As. Therefore, for this work analyses were performed on duplicate samples leached with HCl.

Analyses were performed using a VG Instruments inductively coupled plasma - mass spectrometer (ICP-MS). The analytical technique used was based on a single calibration method using indium as the internal standard (18). In addition two 10 g samples of ochre powder were mixed with 1 ml of 1000 ng g^{-1} indium solution, dried, reground and bricketted before being analyzed by laser ablation ICP-MS, using artificial standards made from analytical grade chemicals (see 19,20). Results obtained by this method gave values which agree closely with HCl solution analysis.

Results and Discussion

Some representative analyses of acid mine drainage waters and ochres are presented in Tables I, II, and III. Results in Table I are for mine drainage waters and associated ochres from mid and north Wales and Table II for drainage samples from the mine and tip areas of Parys Mountain. Table II presents data for waters and ochreous precipitates

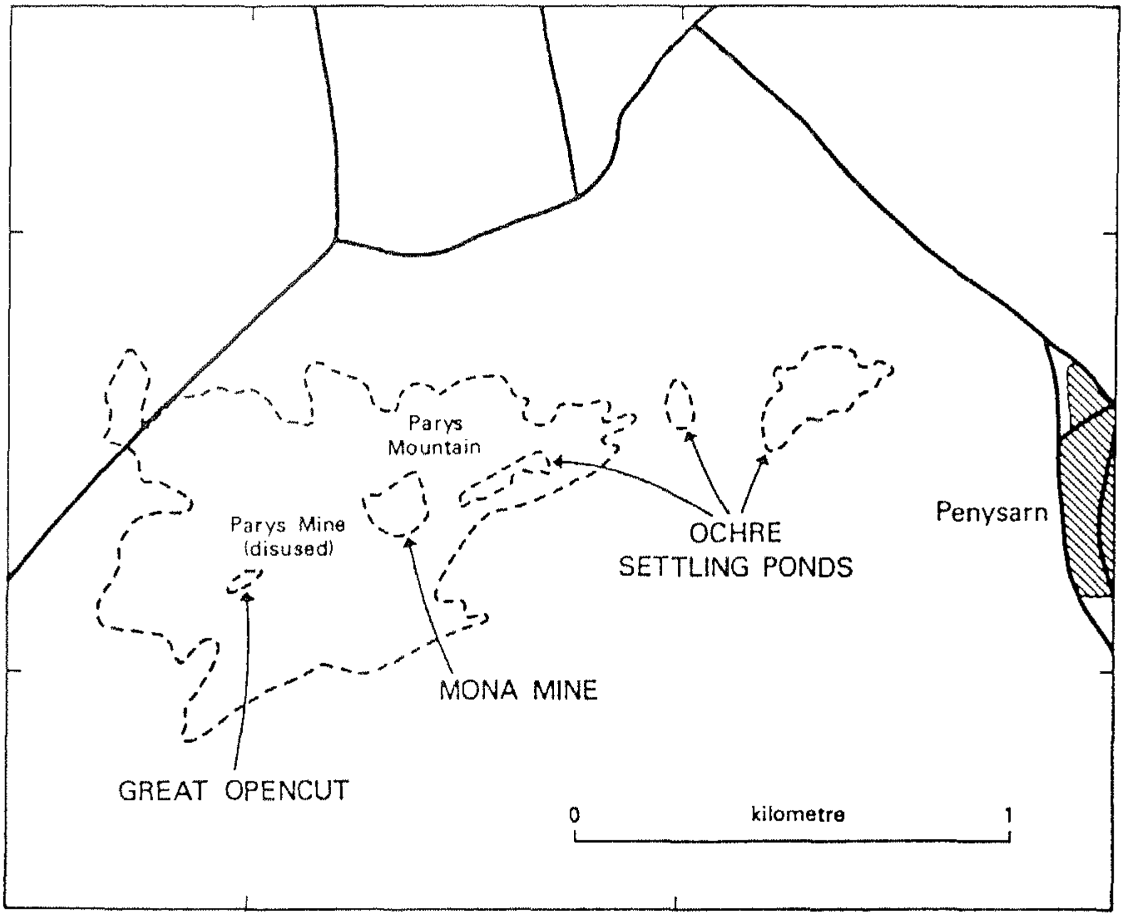

Figure 2. The Parys Mountain minesite.

Table I. Chemistry of mine water and ochre

	Cwmrheidol mine		*Gwynfynedd mine*		*Y Fan mine*	
	Water (mg/l)	Ochre (mg/kg)	Water (mg/l)	Ochre (mg/kg)	Water (mg/l)	Ochre (mg/kg)
pH (units)	2.9		3.5		5.0	
SO_4	850		280		285	
Li	0.014	8.7	0.028	4.1	0.22	4.0
Mg	25.6	2140	8.03	450	10.3	712
Al	14.2	14000	0.77	3840	1.05	6890
Ca	32.2	117	27.1	700	77.3	519
Mn	2.50	688	5.26	267	0.92	184
Fe	36.2	26.7%	21.0	40.9%	0.68	20.9%
Co	0.14	10	0.034	52	0.043	8
Ni	0.76	22	0.057	120	0.073	14
Cu	0.063	44	0.12	527	0.13	1520
Zn	53.3	764	3.79	608	64.5	24600
As	0.014	13	0.13	102	0.16	44
Cd	0.071	2.4	0.009	3.0	0.42	160
Sb	0.001	14	0.009	6.0	0.001	110
Ba	0.004	52	0.005	3.3	0.116	28
Pb	0.017	127	0.033	891	1.28	76900
Bi	0.002	0.3	0.003	0.3	0.005	110

Table II. Chemistry of typical acid lake water and ochre from Parys Mountain

	Lake, Great Opencut		*Lake, Mona mine*		*Ochre settling ponds*	
	Water (mg/l)	Ochre (mg/kg)	Water (mg/l)	Ochre (mg/kg)	Water (mg/l)	Ochre (mg/kg)
pH (units)	2.3		2.4		2.5	
SO_4	5200		4100		3800	
Li	0.97	4.0	1.2	2.7	2.1	2.3
Mg	59.6	183	68.2	88	155	187
Al	108	794	91.2	432	174	514
Ca	21.6	143	10.9	3460	45.0	74
Mn	4.80	13	17.5	20	23.0	100
Fe	1300	14.4%	783	13.3%	934	359%
Co	0.38	15	0.37	6.0	0.63	16
Ni	0.16	3.0	0.38	30	0.30	67
Cu	69.6	1790	57.3	1910	74.4	636
Zn	54.0	247	47.6	246	82.2	314
As	0.77	667	0.16	1510	0.20	623
Mo	0.005	56	nd	29	nd	14
Ag	nd	17	nd	29	nd	3.0
Cd	0.118	0.9	0.098	1.0	0.17	1.3
Sn	nd	44	nd	24	nd	31
Sb	0.002	53	0.004	59	0.001	48
Ba	nd	22.0	nd	3.0	nd	7.0
Hg	nd	6.0	nd	10	nd	2.6
Tl	0.006	17	0.001	26	0.005	6.0
Pb	0.53	24300	0.056	80300	0.11	6450
Bi	0.001	275	nd	172	nd	16
U	0.009	0.4	0.006	0.5	0.010	0.2

nd = not detected (detection limits = .001 mg/l for water; .001 mg/kg for ochres)

Table III. Chemistry of some waters flowing into Parys Mountain lakes

	1 (mg/l)	2 (mg/l)	3 (mg/l)	4 (mg/l)
pH	2.1	2.7	2.2	2.0
SO_4	7200	480	4800	7400
Li	0.33	0.038	0.05	0.28
Mg	41	9.7	6.9	31
Al	48.3	19.7	27.8	60.1
Ca	51.6	16.4	0.7	5.0
Mn	1.6	0.70	1.6	7.1
Fe	1070	13.5	649	1290
Co	0.40	0.043	0.34	0.54
Ni	0.08	0.025	0.32	0.14
Cu	60.7	48.0	71.2	108
Zn	52.7	26.7	66.8	45.6
As	2.6	0.004	0.60	2.9
Mo	0.035	nd	0.034	0.029
Ag	nd	0.001	nd	nd
Cd	0.129	0.058	0.120	0.080
Sn	nd	nd	nd	nd
Sb	0.013	nd	0.010	0.008
Ba	0.003	0.011	0.002	0.003
Hg	nd	nd	nd	nd
Tl	0.024	0.011	0.002	0.012
Pb	0.508	1.64	0.466	0.325
Bi	0.010	0.001	0.004	0.007
U	0.016	0.002	0.017	0.217

nd = not detected (detection limits = 0.001 mg/l) from the lakes and pools which intersect the surface and subsurface drainage of Parys Mountain.

Water chemistry. There are obvious differences in the pH values of the different waters. The highest values recorded were for the Y Fan mine where only minor FeS_2 is associated with the mineralization, whereas the lowest pH values are recorded for Parys Mountain where there is ubiquitous pyrite and arsenopyrite. Generally, the pH values are reflected in the SO_4^{2-} contents of the waters; Parys Mountain samples contain up to 7400 mg/l and those of Y Fan contain only 285 mg/l.

As would be expected the Al content of the waters reflects the acidity, with the content ranging from 1.05 and 0.77 mg/l in the Y Fan and Gwynfynedd waters (pH 5.0 and 3.5 respectively) to 60.1 mg/l in a sample draining Parys Mountain (pH 2.0). Iron contents of the waters also reflect the acidity ranging from 0.68 mg/l at Y Fan to 1970 mg/l in a sample from Parys Mountain. Magnesium while being more variable is generally present in higher concentrations in the more acidic waters.

The Pb content of the waters would seem to be roughly reflecting the levels of the SO_4^{2-} anion. At Y Fan where that anion is relatively low the highest level of Pb is recorded (5.07 mg/l), similarly at Parys Mountain the highest Pb level (1.64 mg/l) is found in a sample with only 480 mg/l of sulfate. The low lead contents of high SO_4 waters suggests solubility control by $PbSO_4$ and the precipitation of $PbSO_4$ due to the common ion effect. A similar pattern emerges for Ba but the highest value is recorded for Y Fan where the mineral barite occurs.

From sample K_{sp} calculations it is apparent that the Y Fan water together with some of the Parys Mountain waters contain more Pb and Ba than would be expected from the SO_4^{2-} content. While samples were filtered through a 0.45 μm filter it is possible that solid $PbSO_4$ and $BaSO_4$ could exist in a very fine form that passes through this filter.

For several metals analyzed in the present study the content of the drainage waters reflects the source. Thus at Cwmrheidol, where there is little copper mineralization, low levels of that element occur in the drainage waters. At Parys Mountain, a copper mine, very large copper concentrations are recorded in the waters. Similarly, the variable levels of Ca are likely to reflect the amounts of calcite gangue.

The relatively high levels of U and Mo recorded for surface runoff at Parys Mountain probably reflect the presence of these elements within the deposit of Silurian black shales. Such shales occurring in other parts of north Wales are enriched in these elements (21; R. Fuge, unpublished data).

There are some marked differences in the chemistry of the lake waters and surface runoff at Parys Mountain. Aluminum is considerably higher in the lake waters than in the runoff; the same is true for Mg, Mn and possibly Ca. However, Pb, Bi, Tl, Ba, Sb, Mo and As are generally lower in the lake and pool waters. The relative enrichment of Al, Mg, Mn and Ca in the lake waters is possibly due to evaporation where these elements are held in solution due to the relatively high acidity. It is perhaps pertinent to note that the alkali metal Li is also much enriched in the lake waters (range 0.97 to 2.1 mg/l) relative to surface runoff (range 0.038 to 0.33 mg/l); in addition this element is almost totally absent from the ochreous precipitates (maximum value 4 mg/kg). The group of elements which are lower in concentration in the lake water are possibly lost from the standing waters by mineral precipitation (see following sections).

The smaller lakes of Parys Mountain are generally about 0.5 to 1 m in depth. To assess if any stratification occurs samples were collected from the top, bottom and mid depth of each lake. Only Pb exhibited any difference in concentration. It was slightly elevated in bottom waters of 3 of the lakes by about 10 to 20%. Similar elevated values for lead were found in deeper waters from the Great Opencut pit.

During the course of this work, samples of mine drainage were analyzed on a monthly basis for more than one year. From this work it is apparent that there are large variations in composition through time with, generally, highest values recorded for the winter months. For example, in Gwynfynedd outfall Zn ranges from 0.4 to more than 14 mg/l (20).

Ochre chemistry. The Fe content of the ochreous sediments is somewhat variable, ranging from more than 40% to 13.3%. Dry ochre from disused ochre settling pits was found to contain between 38 and 42% Fe. Of the ore metals, Cu is highly concentrated in the Parys Mountain ochres whereas Zn and Cd tend to be somewhat richer in the ochres from the Pb-Zn mines.

Several elements are strongly enriched in the ochres, including As, Mo, Ag, Sn, Sb, Ba, Hg, Tl, Bi and Pb. Whereas highest values of most of these elements were found in the Parys Mountain samples the highest level of Sb was found at Y Fan. The highest Mo content found was for the Level Goch mine where values of up to 240 mg/kg were recorded along with 42 mg/kg of W, which was undetected in any other samples. Aluminum is enriched in the ochres; the highest concentration detected was 1.4% in the Cwmrheidol samples. The Parys Mountain samples are lower in aluminum than are those from the adit drainage waters. Magnesium and Mn are also considerably more enriched in the adit ochres than in the ochreous lake sediments of Parys Mountain.

Relationship of water and ochre chemistry. A comparison of water and ochre chemistry shows that, in general, As, Mo, Ag, Sn, Sb, Ba, Hg, Tl, Pb and Bi are strongly concentrated into the solid phase (see Figure 3). In the case of Ba and Pb, the very high levels of the sulfate anion in the acid waters together with the low solubilities of the respective sulfates would suggest that these are the major controlling factors resulting in precipitation. Certainly in the waters, the highest levels of Ba and Pb are generally found where SO_4 contents are lowest (see earlier section).

In the case of the elements other than Pb and Ba that are enriched in the solid phase, it is likely that coprecipitation and adsorption by hydrated oxides of iron are responsible for their concentration in the ochreous precipitates. The adsorption and coprecipitation of metals by hydrated Fe oxides has long been known to be of importance in explaining soil and water geochemistry (22). Several workers have suggested that the adsorption of heavy metals and As by precipitating hydrated iron oxides is a major controlling influence on the mine drainage (23-25). The strong enrichment of As and Mo in ochres has been demonstrated by several workers (24,26,27). However, the high levels of Ag in the ochres would seem to contradict the findings of other workers (28).

Although the present data for elements such as As, Mo and Bi suggest that scavenging by hydrated Fe oxides is unaffected by pH variations in waters, several of the elements appear to show differing degrees of scavenging in differing pH regimes.

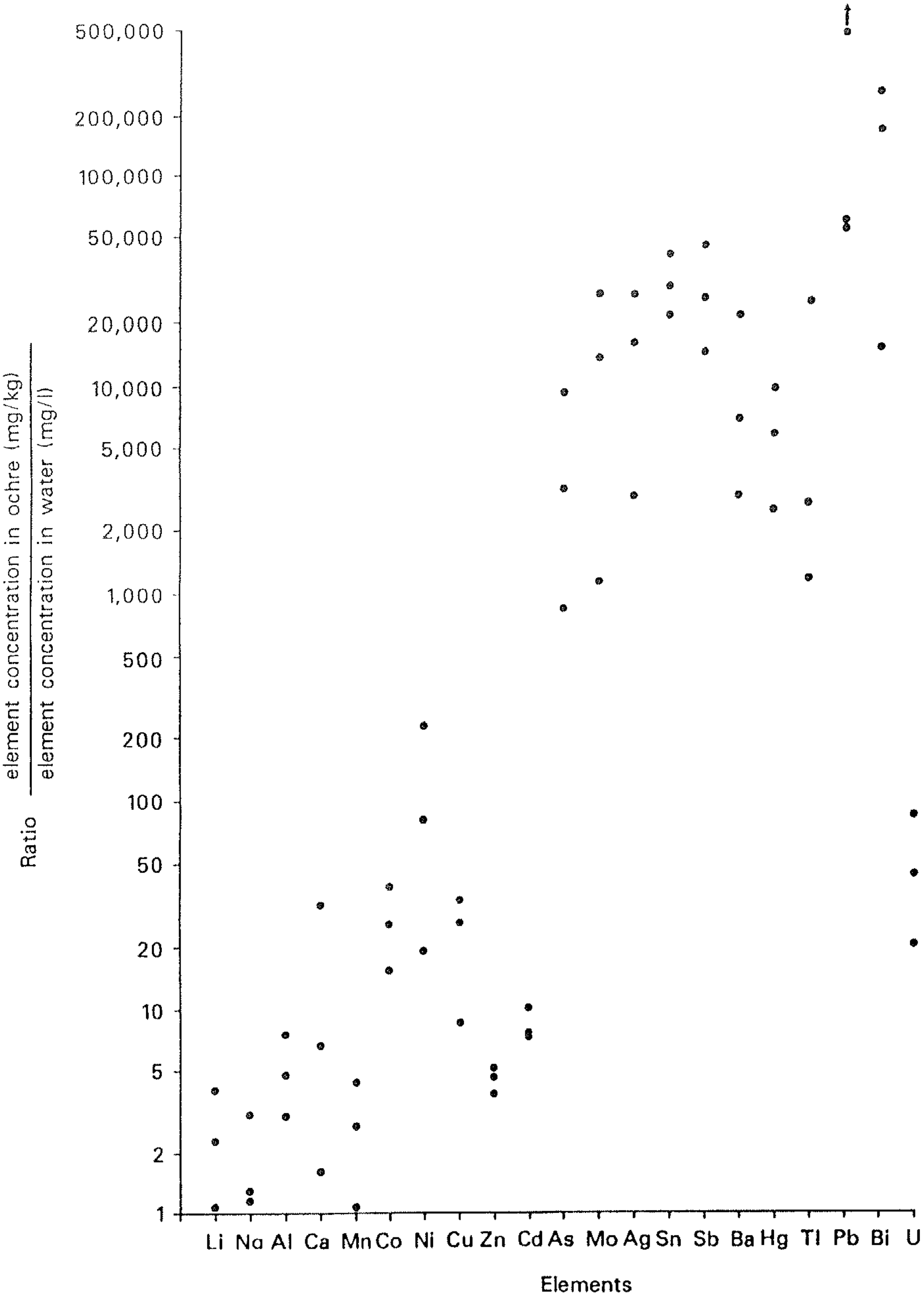

Figure 3. Relationship of ochre and water chemistry in Parys Mountain lakes.

Table IV lists concentration factors for ochres relative to the corresponding water, together with the pH of the waters. The pH ranges from 5 to 2; from Table IV it is apparent that with decreasing pH the concentration factors for Fe, Cu, Zn and Cd decrease markedly. Thus the greatest relative concentrations of all 4 of these elements is in the Y Fan mine ochres while the lowest is found in the Parys Mountain ochres. For Mg and Mn there is not a correlation with decreasing pH but both are strongly enriched in ochres from the less acidic adit drainage. The results strongly suggest that the pH of the metal-rich ochre-precipitating solutions has a dramatic effect on the degree of scavenging of some metals by hydrated iron oxide.

The increased adsorption of Zn and Cu by Fe oxyhydroxide in higher pH waters has been previously demonstrated for the acid mine drainage impacted River Carnon, Cornwall, England (29). It is possible that the degree of adsorption of Zn, Cu and Cd is controlled by the nature and structure of the ochreous precipitate, as this has been found to vary with pH (30,31).

The relative behavior of Zn and Cd is of interest as they are generally considered to be geochemically similar and highly mobile (25). However, it has been suggested that ochreous mine waters have relatively high Zn/Cd ratios compared to those which are non-ochreous (32). It is apparent from Table IV that the relative concentration of Cd to Zn in the ochres compared to the waters is 1 for Y Fan but ranges from 0.4 to 0.6 for all of the other samples considered. Thus it seems likely that in near-neutral waters Cd and Zn are adsorbed to a similar degree into the ochres whereas in waters of pH 3.5 and below Cd is preferentially adsorbed.

For Co and Ni there appears to be little effect of pH on scavenging; the degree of enrichment in ochre varies from locality to locality.

The relative enrichment of U in the Parys Mountain ochres suggests this element is being adsorbed by the hydrated Fe oxides. However, the degree of adsorption is relatively small which is possibly due to the low pH of the Parys Mountain waters making U generally soluble (33).

The precipitation of Al from acid mine drainage due to increasing pH has been demonstrated by several workers (24,34). Although Nordstrom (34) has suggested that Al tends to precipitate as amorphous or poorly crystalline $Al(OH)_3$ at a pH of 4.6 and above, the data in the present study would suggest that appreciable precipitation occurs at lower pH (see Table IV). The relatively high levels of Al in the ochres from the low-pH waters suggest precipitation in some other phase. In this context it is of interest that Tardy and Nahon (35) showed that Al could substitute for Fe in hydrous Fe oxides in soils.

Conclusions

1. The composition of mine drainage waters in Wales is strongly influenced by pH with highest concentrations of Mg, Al and Fe occurring in the most acid waters. The SO_4 anion is enriched in the most acid waters and, from simple calculation of the K_{sp} for $BaSO_4$ and $PbSO_4$, it is probable that this anion exerts a major controlling influence on the solubility of Ba and Pb which consequently become enriched in the precipitated ochres.

Table IV. Concentration factors for selected elements in ochre

Locality[1]	1	2	3	4	5	6
pH	5.0	3.5	2.9	2.5	2.4	2.3
	Concentration factor[2]					
Mg	69	56	87	1.2	1.3	3.1
Al	6660	4990	985	3.0	4.7	7.4
Mn	200	51	275	4.3	1.1	2.7
Fe	307000	19500	7380	384	169	111
Cu	11500	4390	700	8.5	33	26
Zn	382	160	14	3.8	5.2	4.6
Cd	381	333	34	7.6	10	7.6

[1] Localities: 1 = Y Fan mine; 2 = Gwynfynedd mine; 3 = Cwmrheidol mine; 4, 5, 6 = Parys Mountain.

[2] Concentration factor = concentration of element in ochre (mg/kg) / concentration in water (mg/l).

2. The ochres are also strongly enriched in As, Mo, Ag, Sn, Sb, Hg, Tl and Bi, probably by coprecipitation and/or adsorption by the hydrated Fe oxides.

3. The degree of precipitation of Fe, Cu, Zn and Cd is controlled by pH; ochres precipitated from the most acid waters show less relative enrichment in Cu, Zn and Cd than those from higher pH waters.

4. Aluminum precipitates in response to high pH levels and is relatively enriched in ochres from moderate- to high-pH waters.

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