

The genesis of the Llanrwst and Llanfair veinfields, North Wales: evidence from fluid inclusions and stable isotopes

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Abstract – The Llanrwst Pb–Zn veinfield occupies fractures in an Ordovician volcano-sedimentary sequence, with three separate mineralizing events (M_1 , M_2 and M_3). The Llanfair Pb–Zn–Cu veinfield consists of sporadic mineralization in Silurian sediments. Fluid inclusion data from both veinfields indicate mineralization took place from CaCl_2 -bearing brines, up to 26 wt% NaCl equivalent, between 125 and 190 °C with cooler (< 100 °C), more dilute fluids associated with later thrusting at Llanrwst. Sulphur at both veinfields was derived during the main phases of sulphide precipitation from the host rocks, with paragenetically late sulphides and sulphates deriving sulphur from ^{34}S -enriched surface waters. Carbon and oxygen isotopic data on vein carbonates shows that both deposits formed from waters that had undergone extensive water–rock interaction. Carbon was derived from at least two sources: marine carbonate dominated at Llanfair, whereas organic matter in the host rocks was more significant at Llanrwst. These data indicate that the veins formed from evolved brines which migrated along fault systems to the loci of deposition during a phase of extensional tectonics in late Devonian to Tournasian times.

1. Introduction

Several Lower Palaeozoic vein systems occur in Britain with broadly similar characteristics: Leadhills–Wenlockhead and Tyndrum in Scotland, the Vale of Newlands, Greenside and West Shropshire in England and Llanrwst, Plynlimon and the Dolgellau Gold Belt in Wales. These deposits are hosted in competent strata with sulphide mineralogies of galena + sphalerite + chalcopyrite + pyrite ± marcasite and associated carbonates + quartz ± baryte. The radiometric ages of these deposits show them to have formed in Devonian to Carboniferous times (Ineson & Mitchell, 1974*a,b*, 1975; Haggerty *et al.* 1995). It is believed that all these deposits share common genetic features, probably the extensional tectonic regime at the time of formation which facilitated fluid migration. The tectonic regime prevalent in the British Isles during Carboniferous time is considered a key factor in the formation of the synsedimentary base-metal deposits of Ireland (Russell, 1972, 1978; Boyce, Anderton & Russell, 1983).

Fluid inclusion and isotopic data on the Dolgellau Gold Belt (Bottrell *et al.* 1990) suggest a 300–320 °C, slightly saline fluid of metamorphic origin as the mineralizing agent. Fluid inclusion and stable isotope data on the Leadhills mineralization (Patrick & Russell, 1989; Samson & Banks, 1988) indicate a < 150 °C, highly saline (19–39 wt% NaCl equivalent) modified meteoric water as the mineralizing agent with sulphur derived from the surrounding shales. Base-metal mineralization at Tyndrum formed from moderately saline (approximately 15 wt% NaCl equivalent), relatively low-temperature

(140–200 °C) fluids, with sulphur supplied from the country rocks (Curtis *et al.* 1993). Sulphur isotope data (Patrick & Russell, 1989) suggest that the Vale of Newlands, Greenside, Plynlimon and West Shropshire veinfields derived sulphate-sulphur from seawater and/or sulphate-bearing ground waters, and sulphide-sulphur from the surrounding country rocks. Vein genesis models include circulating meteoric waters for Leadhills (Samson & Banks, 1988), hydrostatic migration of fluids from developing Carboniferous basins for the Vale of Newlands, Greenside, Plynlimon and West Shropshire (Patrick & Russell, 1989; Patrick & Howell, 1991) and metamorphic fluid expulsion for the Dolgellau Gold Belt (Bottrell *et al.* 1990) and Plynlimon (Phillips, 1972, 1983). A model of post-tectonic Lower Palaeozoic dewatering associated with Variscan crustal extension is proposed by Fitches (1987). These studies indicate that formation of Pb–Zn–Cu mineralized vein systems was widespread in the Lower Palaeozoic of Britain and that mineralization took place at different times over a period spanning the Devonian to Carboniferous (400–285 Ma).

Whilst many of the Lower Palaeozoic-hosted vein systems of Britain have received extensive study (see references above), the veinfields at Llanrwst and Llanfair have received little attention in recent times. They lie within the northern part of the Welsh Basin, a long-lived Lower Palaeozoic basin which formed in the late Precambrian and accumulated sediments and volcanic rocks until late Silurian time. During the Caledonian Orogeny, the basin was deformed and underwent very low- to low-grade metamorphism. These veinfields potentially contain information on the tectonic development of the Welsh Basin and the sources and migration of fluids following the Caledonian Orogeny. Stable isotope and fluid inclusion

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studies are powerful tools for the study of mineralized vein systems and can potentially elucidate the nature of mineralizing fluids, the sources of various components and the chemical reactions involved in mineral precipitation. In this paper sulphur, carbon and oxygen isotope ratios from vein minerals and microthermometric results from fluid inclusions are presented from these two vein systems. They are used to define the chemistry of the mineralizing fluid, temperature of mineral deposition and the sources of sulphur and carbon in the hydrothermal assemblages/rocks. Additionally, recent geochronological work on these veins (Haggerty *et al.* 1995) shows them to be approximately contemporaneous with Irish base-metal deposits, where Pb and Zn are thought to be sourced from underlying Lower Palaeozoic basement (Russell, 1978; LeHuray *et al.* 1987; Dixon, LeHuray & Rye, 1990), and we assess the significance of the data we present in the light of the new geochronological framework.

2. Geological setting

The Llanrwst veinfield (Fig. 1) occurs in Ordovician rocks to the west of the Conwy Valley Fault, a large crustal fracture active since Silurian times. The Llanfair veinfield is hosted in the Silurian sediments of the Denbigh Moors Basin, to the east of the fault with an underlying basement of Ordovician sediments and volcanic rocks. The geology and mineralogy of the Llanrwst veinfield was described in detail by Archer (1959), Marengwa (B. S. I. Marengwa, unpub. Ph.D. thesis, Univ. Leeds, 1973), Howells *et al.* (1978) and Haggerty (1995). The host volcano-sedimentary unit, the Crafnant Formation, consists of siltstone, shale, mudstone, calcareous sandstone, tuff and tuffite. Overlying these are the black Llanrhwychyn Slates and calcareous clastics of the Grinwllm Slates. Sulphide minerals occur in the host rocks in a variety of forms. In the black shales, tuffites and siltstones pyrite is present as fine-grained disseminations forming up to 9 wt % of the rock, with pyrite cubes locally up to a few centimetres in diameter. The pyrite is believed to be diagenetic in origin, forming during bacterial activity, as indicated by framboidal textures in places. In the late Ordovician, these strata were intruded by dolerite sills and stocks. Mineralization comprises a series of Pb–Zn veins, with three main trends corresponding to various periods of mineralization, N–S (M_1), ENE–WSW (M_2) and ESE–WNW (M_3), with the veins becoming progressively more Pb-rich with time. Wall rock alteration consists predominantly of sericitization and silicification with minor pyritization. At some localities the wall rocks are bleached due to the removal of organic carbon. After mineralization the veinfield experienced a period of thrusting and associated quartz veining. The veins were mined for Pb and Zn, containing in the order of 100 000 t of metal, with an atomic Pb:Zn value of 0.3, calculated from mine production records (Archer, 1959). The Llanfair veinfield consists of several areas of

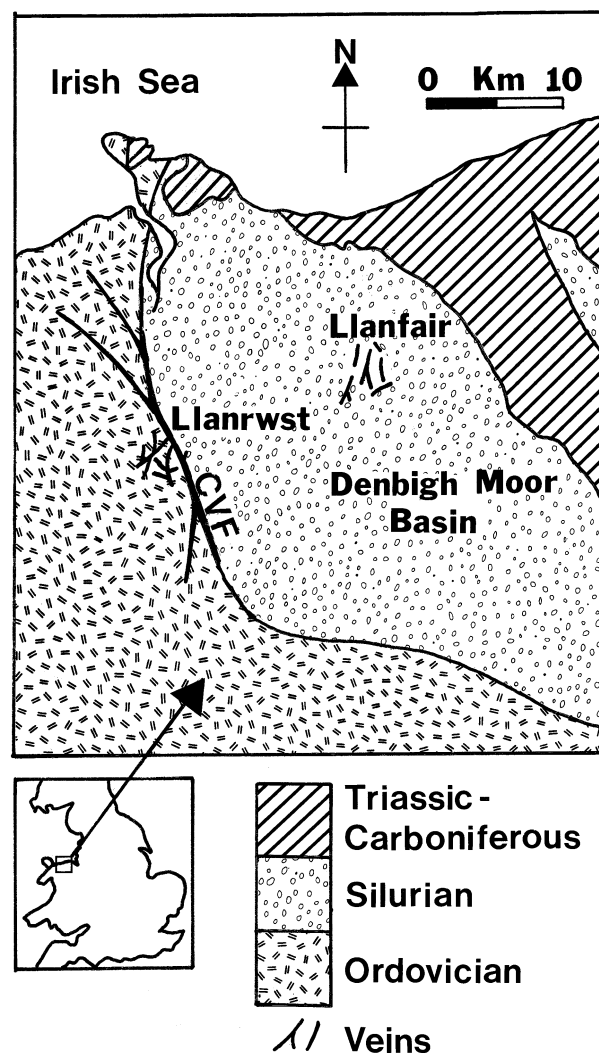


Figure 1. Location and simplified geology of the Llanrwst and Llanfair veinfields. CVF – Conwy Valley Fault.

localized Cu–Pb–Zn–Ba vein mineralization associated with north–south faults in Silurian clastic sediments (Fig. 1). The host lithologies are mudstones, siltstones, minor black limestones and subordinate sandstones, with numerous disturbed beds composed of any or all of these lithologies. Wall rock alteration consists of sericitization, with local clay-rich gouges, minor silicification and carbonatization.

The timing of mineralization has been determined by K–Ar and Rb–Sr dating of altered wall rock material (Haggerty *et al.* 1995). At Llanrwst, the M_1 and M_2 veins formed during middle Devonian to Tournasian times (386–359 Ma), with remobilization and/or renewed fluid injection forming the M_3 veins in Viséan to Wesphalian times (336–307 Ma). The Llanfair veins are broadly coeval with the Llanrwst mineralization, forming in late Devonian to Tournasian times (370–353 Ma). At the time of mineralization the region formed the northern part of St George's Land, with the sea transgressing slowly south during Carboniferous time, covering the region in the Chadian to Asbian period (350–336 Ma).

3. Vein mineralogy

The Llanrwst veinfield comprises veins and vein breccias predominantly developed in the more competent strata of the volcano-sedimentary sequence. Galena, sphalerite, pyrite and marcasite are the main sulphide minerals, with associated calcite, dolomite, quartz and ankerite. Textural evidence and microscopic investigation during this study of the mineralization indicates the veins are polyphase with the following paragenesis:

Pre-sulphide. Milky quartz and trace ankerite showing several phases of brecciation and cementation associated with the major phase of fault activity. The quartz has two phases: an early thin zone of very fine-grained quartz surrounding brecciated wall rock, indicative of a quench texture, and later coarse, subhedral quartz infilling voids. In some veins this assemblage is the only mineralization present, forming zones up to 1.5 m wide.

Sulphide. The main sulphide minerals are galena + sphalerite + pyrite + marcasite ± trace chalcopyrite in a calcite + dolomite + quartz matrix. The sulphide phase of mineralization often shows crustiform banding with galena, then Fe-rich sphalerite, then Fe-poor sphalerite. The sphalerite commonly shows microscopic banding due to fluctuations in FeS content.

Post-sulphide. The carbonate minerals, calcite, dolomite and ankerite were precipitated, with stringers of marcasite and trace chalcopyrite. In the north of the veinfield, brecciation during this phase shows continued fault activity. A small amount of late-stage dolomite and quartz infills voids and fractures.

Late-mineral thrusting. Milky quartz, with minor areas of smoky quartz, infilling low-angle thrusts which cut mineralized veins.

The primary vein mineralization at Llanfair exhibits similar mineralogy and paragenesis. Pre-sulphide brecciation is common with dolomite, quartz and minor calcite cementing rock fragments. The sulphide phase involves the precipitation of both fine-grained and coarsely crystalline sulphides (chalcopyrite, sphalerite, galena, pyrite) with quartz, dolomite, calcite, malachite and pink baryte. The sphalerite ranges from Fe-poor to Fe-rich 'black jack', with microscopic banding common. The post-sulphide assemblage contains dolomite, calcite, witherite and white baryte.

4. Methodology

4.a. Fluid inclusion analysis

The nature of the mineralizing fluids was determined by microthermometric analysis of fluid inclusions (Shepherd, Rankin & Alderton, 1985) on a Linkam TH600 stage. The majority of fluid inclusions were small (<5 µm) and unusable. Only five samples from Llanrwst and two samples from Llanfair contained workable fluid inclusions, and so may not be representative of the whole population (Table 1). Data were collected on the larger inclusions present, up to 50 µm in size. Petrographically it is not

Table 1. The nature of fluid inclusion samples from the Llanrwst and Llanfair veinfields

Sample	Grid. ref. (SH Sheet)	Mine	Paragenetic position	Mineral
<i>Llanrwst</i>				
C25	8080 5825	Cilcenus	M ₁ Pre-sulphide	Quartz
P88	7868 5978	Parc	M ₁ Sulphide	Quartz
P88	7868 5978	Parc	M ₁ Sulphide	Calcite
P11	7824 5982	Parc	M ₂ Post-sulphide	Dolomite
PA29	7938 5762	Pen-y-Allt	M ₃ Late-mineralization	Quartz
<i>Llanfair</i>				
BR9	9474 7150	Ty'n-y-ddol	Sulphide	Quartz
BR2	9474 7150	Ty'n-y-ddol	Post-sulphide	Calcite

certain whether inclusions were primary or secondary, although obvious secondary inclusions, in arrays on healed fractures, were avoided and measurements made on isolated inclusions. Salinities were derived by determination of melting points of solid phases produced during supercooling of inclusions to below -100 °C. First melting is difficult to observe and may not be noticed until a temperature above the true eutectic point. In all samples melting of only one phase was observed after first melting and was presumed to be ice. Salinities of inclusions were determined using $T_{m_{ice}}$ measurements, standardized to wt% NaCl equivalent using the conversion factors of Hall, Sterner & Bodnar (1988). Homogenization always occurred from liquid plus vapour to liquid. Examination of the vapour phase of inclusions at low temperature yielded no phase changes which might indicate the presence of CO₂, CH₄ or organic gases. Estimated measurement accuracies are $\pm 2^\circ\text{C } T_{first\ melt}$, $\pm 0.5^\circ\text{C } T_{m_{ice}}$ and $\pm 0.5^\circ\text{C } T_h$.

4.b. Sulphur isotope analysis

Vein sulphide and sulphate samples were obtained from as wide a paragenetic spread as possible and extracted from specimens by drilling and their purity checked where necessary by XRD. Rock samples were collected from the stratigraphic units containing significant pyrite. Sulphur was extracted from the rock powders for isotopic analysis using a chromous chloride digestion and recovered as CuS (Newton *et al.* 1995). Samples were quantitatively converted to SO₂ using the methods of Robinson & Kusakabe (1975) for sulphides and Halas, Shakur & Krouse (1982) for sulphates, and purified by standard vacuum-line separation techniques. Isotopic ratios were measured on a VG Sira 10 mass spectrometer and have accuracy and reproducibility at the 1σ level (determined by replicate analyses of standards) of $\pm 0.2\%$.

4.c. Carbon isotope analysis

Powdered samples of organic carbon-bearing host and altered wall rocks were treated with 6M HCl for 24 hours to remove any carbonate phases and recovered on a quartz microfibre filter. An aliquot containing 1 mg of carbon was combusted using the procedure of Bottrell *et al.*

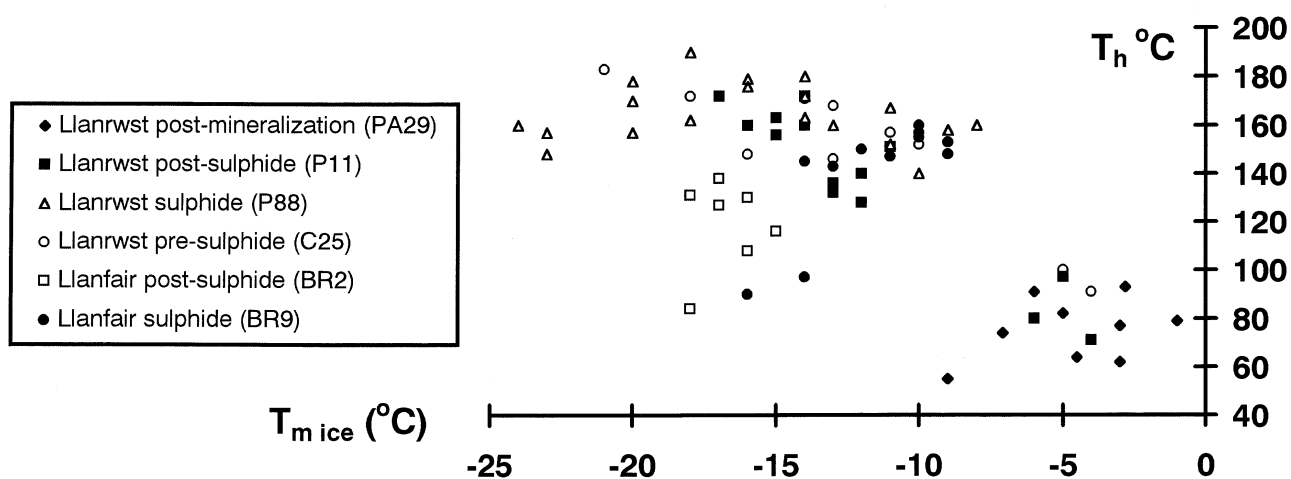


Figure 2. A plot of liquid-vapour homogenization temperature (T_h) versus final ice-melting temperature ($T_{m_{ice}}$).

(1991). Carbonate samples were drilled from hand specimens and their purity checked where necessary by XRD techniques. Samples and standards were reacted with 100% H_3PO_4 at $25 \pm 0.2^\circ C$ for 24 hours in the cases of calcite and witherite, and at $50 \pm 0.2^\circ C$ for 48 hours in the cases of ankerite and dolomite (McCrea, 1950). Carbon and oxygen isotopic ratios of CO_2 were measured on a VG Sira 10 mass spectrometer with analytical errors (1σ) for isotopic analysis of oxygen and carbon being 0.2‰ and 0.1‰, respectively. The data are reported relative to PDB for carbon and SMOW for oxygen.

5. Microthermometric results

The most common type of inclusions observed were liquid-vapour (LV) inclusions of Type I (Nash, 1976), which were present in all samples (Table 1). In the Llanrwst post-sulphide dolomite sample (P11) a few planar arrays of liquid only (L-type) were detected, but were too small for microthermometric analysis. The temperature of fluid inclusion homogenization (T_h) to a liquid phase ranged between 64 and 189°C in the Llanrwst veinfield and from 97 to 162°C in the Llanfair veinfield (Fig. 2), with homogenization temperatures commonly ranging widely within an individual sample. Some of the liquid-only inclusions were produced by necking-down, but others appear unmodified, suggesting entrapment at $< 70^\circ C$.

The four samples from Llanrwst (Table 1) are from different paragenetic stages; pre-sulphide, sulphide and post-sulphide samples have broadly similar T_h ranging from 72 to 189°C. Inclusions in quartz from a late-mineralization thrust (PA29) have a mean T_h of 77°C, distinctly lower than the mean of the fluids in the mineralized veins. Trapping of this late-mineralization fluid in secondary inclusions may account for the lower T_h ($< 100^\circ C$) recorded in some mineralization samples. The liquid-only inclusions in P11 are also considered to be secondary in origin, representing late-mineralization fluid flow.

Final ice melting temperatures ($T_{m_{ice}}$) range from -1 to -24°C at Llanrwst and from -9 to -18°C at Llanfair,

indicating a wide range of salinities from 2 to 26 wt% NaCl equivalent. Figure 3 shows the variation of salinity with paragenesis. Llanrwst pre-sulphide, sulphide and post-sulphide fluids lie between 6 and 26 wt% NaCl equivalent, and late-mineralization fluids are less saline. In the Llanfair veinfield the mineralizing fluids have

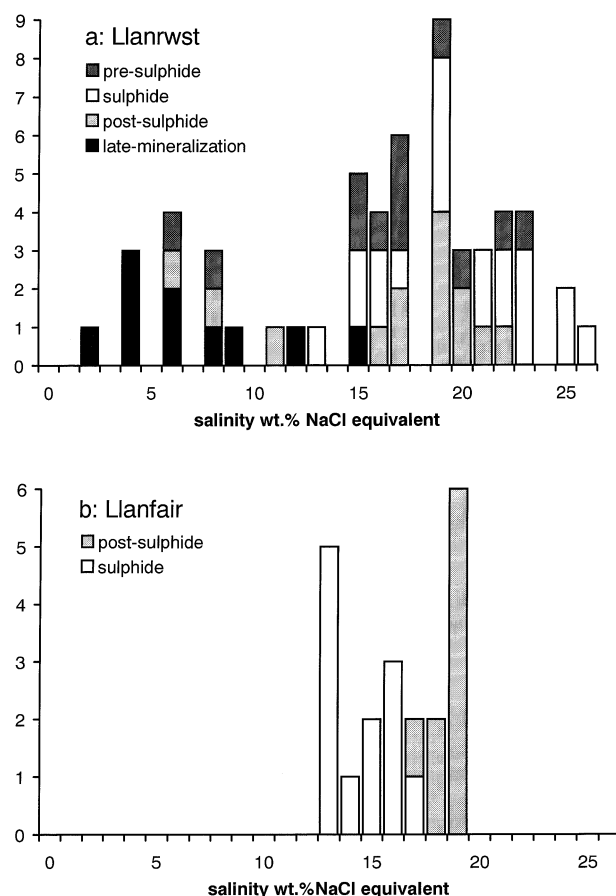


Figure 3. Histograms of fluid inclusion salinities (wt% NaCl equivalent) from (a) the Llanrwst veinfield and (b) the Llanfair veinfield. Salinities were calculated from final ice-melting temperatures ($T_{m_{ice}}$) using the correction factor of Hall, Sterner & Bodnar (1988).

similar salinities to the Llanrwst fluids, but higher salinities are observed in the post-sulphide phase at Llanfair. Temperatures of first melting in inclusions from Llanrwst range from -26 to -55 °C; most of these values are below the lowest metastable eutectic point for the NaCl–H₂O system (-28 °C) and indicate the presence of other salts in solution such as CaCl₂ and/or MgCl₂. The late-mineralization samples have $T_{\text{first melt}}$ near or slightly below -52 °C, with significant liquid present at -50 °C. Since -52 °C is the melting temperature of calcium chloride hydrate CaCl₂·6H₂O, we interpret these observations to indicate significant concentrations of CaCl₂ though the Ca/Na ratio is poorly constrained. The appearance of liquid below -52 °C in some inclusions in the late-mineralization samples suggests that other salts (MgCl₂ and/or FeCl₂) are present. Inclusions from the Llanfair veinfield have $T_{\text{first melt}}$ values between -29 and -41 °C, which we take to indicate that this fluid also had a significant CaCl₂ content, but lower Ca/Na ratio.

The mineralizing fluid at Llanrwst was a highly saline brine with a significant CaCl₂ content. A later lower salinity fluid is recorded by late-mineralization thrusting and by late-stage secondary inclusions in the mineralized veins. At Llanfair, the mineralizing fluid was of similar salinity and also contained significant CaCl₂, but here an increase in salinity from sulphide (15 wt % NaCl equivalent) to post-sulphide phases (20 wt % NaCl equivalent) is observed.

6. Sulphur isotope results

6.a. Host rocks

Sulphur-isotope compositions of thirteen Llanrwst host rocks are presented in Table 2 and Figure 4, and fall between -5.7 ‰ and $+1.3$ ‰. The sedimentary pyrite $\delta^{34}\text{S}$ values range from -5.7 ‰ to $+0.6$ ‰. In some host rocks, sulphur is present as small blebs (<4 mm) of pyrrhotite which has a $\delta^{34}\text{S}$ value of $+0.9$ ‰. Two exceptional ³⁴S-enriched samples ($+23.9$ ‰ and $+19.6$ ‰) are from minor pyrite veins and segregations in the black shales. These probably developed as the result of sulphur remobilization and ³²S loss during regional metamorphism. Some dolerite bodies in the veinfield contain primary magmatic sulphides with an assemblage of pyrite–pyrrhotite–chalcopyrite. The dolerite contains up to 0.6 wt % S, with $\delta^{34}\text{S}$ values of $+1.1$ ‰ and $+1.3$ ‰. The Llanrwst host rocks are therefore considered to be a reservoir of reduced sulphur with $\delta^{34}\text{S}$ around zero (-6 ‰ to $+2$ ‰), and remobilized sulphide $\delta^{34}\text{S}$ extending up to $+24$ ‰.

No sulphur isotopic data are available for the host rocks of the Llanfair veinfield as no sulphur-bearing (>0.05wt % S) rocks were encountered during field investigation.

6. b. Vein sulphides and sulphates

Forty-three Llanrwst vein sulphides were analysed to determine their S-isotope compositions (Table 3, Fig. 4). More than 80 % of sulphide samples have a restricted

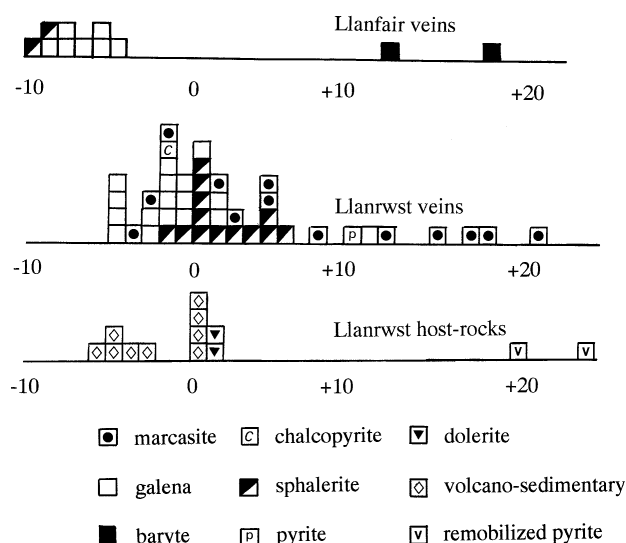


Figure 4. A histogram of $\delta^{34}\text{S}$ data from the Llanrwst and Llanfair veinfields, using data presented in Tables 2, 3 and 4.

range of ³⁴S between -5 ‰ and $+6$ ‰, while some post-sulphide marcassite samples have more positive $\delta^{34}\text{S}$ values up to $+21.9$ ‰. Galena samples range in $\delta^{34}\text{S}$ from -5.0 ‰ to $+2.0$ ‰, with one sample at $+10.8$ ‰, sphalerites range from -1.8 ‰ to $+5.1$ ‰, post-sulphide marcassite values range from -3.8 ‰ and $+21.9$ ‰, and two ore pyrite analyses gave $\delta^{34}\text{S}$ values of -1.1 ‰ and $+9.7$ ‰ (Fig. 4). The general ³⁴S-enrichment of the sphalerite relative to galena may indicate equilibrium isotopic fractionation between these minerals and the mineralizing fluid.

The sulphur-isotopic compositions of nine sulphide phase sulphides and two post-sulphide sulphates from the Llanfair veinfield were determined (Table 4, Fig. 4). The sulphide phase sulphides have $\delta^{34}\text{S}$ between -9.1 ‰ to -4.8 ‰. Two post-sulphide baryte samples had $\delta^{34}\text{S}$ values of $+11.4$ ‰ and $+17.5$ ‰. The mean sulphide $\delta^{34}\text{S}$ value is -7.2 ‰, with only minor variations in $\delta^{34}\text{S}$ between the mines despite a spatial separation of several kilometres.

Table 2. Llanrwst veinfield host rock $\delta^{34}\text{S}$ data

Sample	Grid ref. (SH sheet)	Stratigraphic unit	Description	S wt %	$\delta^{34}\text{S}$
D3	7854 6021	Metadolerite	Extraction	0.5	+1.1
D2	7809 5837	Metadolerite	Extraction	0.6	+1.3*
G1	7954 5810	Grinwllm Slates	Pyrite cube		-5.7
L4	7944 5785	Llanrhychwyn Slate	Extraction	3.8	-2.1
L1	7643 5996	Llanrhychwyn Slate	Extraction	1.1	-4.6
L6	8115 5830	Llanrhychwyn Slate	Extraction	0.5	+0.6*
L7	7965 5774	Llanrhychwyn Slate	Extraction	1.2	-3.3
L8	7965 5774	Llanrhychwyn Slate	Vein pyrite		+19.6
L8	7965 5774	Llanrhychwyn Slate	Vein pyrite		+23.2
UC5	7885 5963	CF tuffite	Extraction	0.4	+0.4*
MC2	7868 5997	CF black shale	Extraction	1.5	+0.5*
MC3	7650 6205	CF siltstone	Extraction	0.7	+0.9
MC7	7782 5927	CF black shale	Extraction	1.4	-4.3

CF = Crafnant Formation.

* Mean of two isotopic analyses. Analytical errors: extractions ± 0.4 ‰ (2σ), physically separated sulphides ± 0.2 ‰ (2σ). Whole-rock sulphur contents were determined by gas chromatography using a Carlo Erba 1106 Elemental Analyser.

Table 3. Llanrwst vein sulphide $\delta^{34}\text{S}$ data

Mine, sample	Grid ref. (SH sheet)	Mineral	Paragenetic position	$\delta^{34}\text{S}$	$\delta^{34}\text{S}_{\text{HS-fluid}}$
<i>Cilceus</i>					
C15-A *	8080 5825	Gn	M ₁ Sulphide	+1.1	+3.0
C15-B *	8080 5825	Gn	M ₁ Sulphide	-1.7	+0.2
C18	8080 5825	Gn	M ₁ Sulphide	-2.9	-1.0
C21-A *	8087 5820	Sp	M ₁ Sulphide	+3.4	+1.5
C21-B	8087 5820	Sp	M ₁ Sulphide	+1.3	-0.6
C25 *	8087 5820	Sp	M ₁ Sulphide	+0.7	-1.2
<i>Cyffty</i>					
Cy 474 *	7716 5881	Gn	M ₂ Sulphide	+10.8	+12.7
Cy 490	7716 5881	Sp	M ₂ Sulphide	+0.8	-1.1
<i>Hafna</i>					
H1	7794 6017	Gn	M ₂ Sulphide	-0.1	+1.8
H1-I	7794 6017	Gn	M ₂ Sulphide	-1.7	+0.2
H1	7794 6017	Marc	M ₂ Post-sulphide	+4.6	+1.4
H1-A	7794 6017	Marc	M ₂ Post-sulphide	+4.4	+1.2
<i>New Pandora</i>					
N10-B *	7670 6025	Gn	M ₁ Sulphide	-5.0	-3.1
180-B *	7670 6025	Gn	M ₁ Sulphide	-4.6	-2.7
N11	7644 5963	Sp	M ₁ Sulphide	+2.2	+0.3
N125-E	7642 5984	Sp	M ₁ Sulphide	+0.8	-1.1
N2	7670 6025	Marc	M ₃ Post-sulphide	+16.1	+12.9
NP9	7670 6025	Marc	M ₃ Post-sulphide	+2.4	-0.8
N11 *	7644 5963	Marc	M ₁ Post-sulphide	+21.9	+18.7
N11-C	7644 5963	Marc	M ₁ Sulphide	-3.8	-7.0
182 early	7680 6020	Marc	M ₃ Post-sulphide	+14.0	+10.8
182 late *	7680 6020	Marc	M ₃ Post-sulphide	+17.5	+14.3
<i>Klondyke</i>					
K2	7660 6179	Gn	M ₁ Sulphide	-1.8	+0.1
K3	7660 6179	Gn	M ₁ Sulphide	-2.2	-0.3
K23	7655 6188	Gn	M ₁ Sulphide	-0.7	+1.2
K15	7655 6188	Py	M ₁ Sulphide	9.7	+6.5
K	7655 6188	Marc	M ₁ Post-sulphide	11.2	+8.0
K16	7655 6188	Marc	M ₁ Post-sulphide	-1.1	-4.3
<i>Parc</i>					
P11	7824 5982	Gn	M ₂ Sulphide	+0.3	+2.2
P12 *	7820 5979	Gn	M ₂ Sulphide	+1.2	+3.1
P12 *	7820 5979	Sp	M ₂ Sulphide	+4.1	+2.2
P1-A	7870 5970	Sp	M ₁ Sulphide	-1.8	-3.7
P1-B	7870 5970	Sp	M ₁ Sulphide	+0.1	-1.8
150-A	7851 5990	Sp	M ₂ Sulphide	-0.3	-1.6
150-C *	7851 5990	Sp	M ₂ Sulphide	+0.8	-1.1
NMW-72	7885 5974	Marc	M ₂ Post-sulphide	+7.2	+4.0
<i>Pen-y-Allt</i>					
PA2 *	7938 5762	Cp	M ₃ Sulphide	-1.1	-2.3
PA2 *	7938 5762	Gn	M ₃ Sulphide	-4.2	-2.3
PA8-F	7975 5762	Gn	M ₃ Sulphide	-4.3	-2.4
PA8-F-A	7975 5762	Gn	M ₃ Sulphide	-0.3	+1.6
PA8-J	7975 5762	Gn	M ₃ Sulphide	+1.4	+3.3
26	7975 5762	Sp	M ₃ Sulphide	+4.3	+2.4
26-C	7975 5762	Sp	M ₃ Sulphide	+5.1	+3.2

Gn = galena, Sp = sphalerite, Marc = marcasite, Py = pyrite and Cp = chalcopyrite.

* Mean value of two analyses. Analytical errors: $\pm 0.2\%$ (2σ). $\delta^{34}\text{S}_{\text{HS-fluid}}$ values were calculated presuming a fluid temperature of 190 °C, using the fractionation factors of Kiyosu (1973) and Kajiwarra & Krouse (1971).

7. Carbon and oxygen isotope results

7.a. Host rocks

Ten black slate host-rock samples from the Llanrwst veinfield have organic carbon $\delta^{13}\text{C}$ values which group closely, ranging from -26.8 ‰ to -29.4 ‰ (Table 5), typical of sedimentary organic carbon. The black slate host rocks are thus a source of isotopically light reduced carbon.

Table 4. Llanfair vein mineral $\delta^{34}\text{S}$ data

Mine, sample	Grid ref. (SH sheet)	Mineral	Paragenetic position	$\delta^{34}\text{S}$	$\delta^{34}\text{S}_{\text{HS-fluid}}$
<i>Dyffryn Adel</i>					
DYA 1	9507 6697	Cp	Sulphide	-5.5	-7.2
DYA 2	9507 6697	Cp	Sulphide	-4.8	-6.5
<i>Llanfair</i>					
NMW 1	936 705	Sp	Sulphide	-8.7	-11.2
NMW 2	936 705	Sp	Sulphide	-9.1	-11.6
NMW 3	936 705	Cp	Sulphide	-5.9	-7.6
NMW 4 *	936 705	Ba	Post-sulphide	+11.4	
LL-1 *	9363 7017	Ba	Post-sulphide	+17.5	
<i>Ty'n-y-ddol</i>					
BR1 *	9474 7150	Gn	Sulphide	-7.5	-5.6
BR1-4	9474 7150	Gn	Sulphide	-8.1	-6.2
BR2-4	9474 7150	Gn	Sulphide	-6.9	-5.0
BR14	9474 7150	Gn	Sulphide	-7.9	-6.1

Gn = galena, Sp = sphalerite, Cp = chalcopyrite and Ba = baryte;

* Mean value of two analyses. Analytical errors: sulphide = $\pm 0.2\%$ (2σ), sulphate = $\pm 0.2\%$ (2σ). $\delta^{34}\text{S}_{\text{HS-fluid}}$ values were calculated presuming a fluid temperature of 160 °C, using the fractionation factors of Kiyosu (1973) and Kajiwarra & Krouse (1971).

Table 5. Organic carbon $\delta^{13}\text{C}$ values for black slate samples from the Llanrwst veinfield

Sample	Grid ref. (SH sheet)	Stratigraphic position	Organic carbon (wt %)	$\delta^{13}\text{C}_{\text{(PDB)}}$
<i>Host rocks</i>				
Aber A	7964 5777	Llanrhydwyn Slate	6.1	-29.4
C16	8115 5830	Llanrhydwyn Slate	0.8	-29.3
N8	7643 5996	Llanrhydwyn Slate	2.1	-28.8
Llan A	7800 5931	Crafnant Formation	3.8	-28.2
L1 110	7805 5933	Crafnant Formation	4.2	-28.0
P92	7880 5867	Crafnant Formation	3.7	-28.0
Cy 468	7727 5891	Crafnant Formation	1.4	-26.8
<i>Altered wall rocks</i>				
180-B	7670 6025	Llanrhydwyn Slate	3.4	-28.5
A24	7937 5810	Crafnant Formation	2.6	-29.3
Klon 504	7618 6107	Crafnant Formation	3.6	-28.0

All $\delta^{13}\text{C}$ values are the mean of two separate determinations. Analytical error: $\pm 0.1\%$.

7.b. Vein carbonates

Carbon and oxygen isotopic compositions of thirty-nine carbonate samples from the Llanrwst veins (ankerite, dolomite and calcite) are reported in Table 6. $\delta^{13}\text{C}$ values of the carbonates range from -12.5 ‰ to -8.6 ‰, with a mean value of -10.0 ‰ and $\delta^{18}\text{O}$ ranges from +17.1 ‰ to +25.1 ‰. Figure 5 shows the variation of carbonate isotopic compositions with paragenesis. There was a small progressive depletion in ^{13}C as mineralization progressed (mean M₁ $\delta^{13}\text{C}$ value is -9.7 ‰, mean M₃ $\delta^{13}\text{C}$ value is -11.2 ‰). However, the $\delta^{13}\text{C}$ values show relatively large short term isotopic variations, which reflect mixing of carbon from different sources, large temperature differences or very substantial changes in the fluid chemistry (see Section 8.c).

There was also a general decrease in $\delta^{18}\text{O}$ values during ore deposition. M₁ pre-sulphide ankerite values have a mean $\delta^{18}\text{O}$ value of +24.3 ‰, decreasing over time to an M₃ post-sulphide calcite $\delta^{18}\text{O}$ value of +19.8 ‰ (Fig. 5).

Table 6. $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values for vein carbonates from the Llanrwst veinfield

Mine, sample	Grid ref. (SH sheet)	Paragenetic position	Mineral	$\delta^{13}\text{C}$ (PDB)	$\delta^{18}\text{O}$ (SMOW)
<i>Cilcenus</i>					
C1	8080 5825	M ₁ Pre-sulphide	Ankerite	-9.0	24.0
C41	8087 5820	M ₁ Pre-sulphide	Ankerite	-8.6	25.1
C42	8087 5820	M ₁ Pre-sulphide	Ankerite	-8.8	24.6
C43	8087 5820	M ₁ Pre-sulphide	Ankerite	-9.1	23.5
<i>Klondyke</i>					
K23	7655 6188	M ₁ Post-sulphide	Calcite	-10.1	19.2
K27	7655 6188	M ₁ Post-sulphide	Calcite	-9.0	21.6
K28	7655 6188	M ₁ Post-sulphide	Calcite	-9.4	22.1
K56	7655 6188	M ₁ Post-sulphide	Calcite	-8.7	23.8
<i>New Pandora</i>					
NP4	7670 6025	M ₁ Sulphide	Calcite	-11.9	19.8
NP9	7670 6025	M ₁ Post-sulphide	Calcite	-10.9	20.3
180-1	7670 6025	M ₁ Pre-sulphide	Dolomite	-9.6	22.2
180-2	7670 6025	M ₁ Late pre-sulphide	Dolomite	-9.0	21.7
180-3	7670 6025	M ₁ Sulphide	Dolomite	-9.2	22.2
180-4	7670 6025	M ₁ Post-sulphide	Dolomite	-11.0	20.3
180-5	7670 6025	M ₁ Post-sulphide	Calcite	-11.5	18.9
N186	7680 6020	M ₃ Post-sulphide	Calcite	-10.9	19.8
N187	7680 6020	M ₃ Post-sulphide	Dolomite	-9.8	21.5
<i>Parc</i>					
P88	7868 5978	M ₁ Post-sulphide	Dolomite	-9.3	20.8
P12	7820 5979	M ₂ Post-sulphide	Calcite	-11.9	18.0
P14	7872 5955	M ₂ Post-sulphide	Calcite	-10.8	18.7
P14-B	7872 5955	M ₂ Post-sulphide	Calcite	-10.8	18.7
NMW-72	7885 5974	M ₂ Post-sulphide	Calcite	-11.8	17.9
P11-B	7824 5982	M ₂ late-sulphide	Dolomite	-8.8	21.4
P11-I centre	7824 5982	M ₂ Post-sulphide	Dolomite	-8.7	21.0
P11-I 5mm	7824 5982	M ₂ Post-sulphide	Dolomite	-8.7	21.7
P11-I 10mm	7824 5982	M ₂ Post-sulphide	Dolomite	-9.1	21.2
P11-I 15mm	7824 5982	M ₂ Post-sulphide	Dolomite	-8.8	21.8
P11-I 20mm	7824 5982	M ₂ Post-sulphide	Dolomite	-8.7	21.8
P11-I rim	7824 5982	M ₂ Post-sulphide	Dolomite	-9.1	21.6
P11-25	7824 5982	M ₂ Post-sulphide	Dolomite	-9.4	20.3
P11C	7824 5982	M ₂ Post-sulphide	Dolomite	-9.4	21.7
P11C-7	7824 5982	M ₂ Post-sulphide	Dolomite	-10.5	18.0
P11C-8	7824 5982	M ₂ Post-sulphide	Dolomite	-9.2	21.1
<i>Pen-y-Allt</i>					
PA2-1	7938 5762	M ₃ Sulphide	Calcite	-9.9	19.2
PA2-2	7938 5762	M ₃ Post-sulphide	Calcite	-10.0	19.1
PA3-F	7975 5762	M ₃ Sulphide	Calcite	-12.1	19.4
PA11-A	7975 5762	M ₃ Post-sulphide	Calcite	-12.3	17.1
PA11-B	7975 5762	M ₃ Post-sulphide	Calcite	-12.5	17.4
PA11-C	7975 5762	M ₃ Post-sulphide	Calcite	-11.8	18.0

Analytical errors: $\delta^{13}\text{C} \pm 0.2\text{‰}$, $\delta^{18}\text{O} \pm 0.1\text{‰}$.

Imposed on this general decrease in $\delta^{18}\text{O}$ values are minor short term variations with a magnitude of $\pm 2.5\text{‰}$.

A traverse across a single post-sulphide dolomite crystal from M₂ mineralization at Parc mine (Table 6, P11-I), shows only small variations in $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ during the period of individual crystal growth. The dolomite crystal appears homogeneous under cathodoluminescence and is chemically homogeneous as shown by ICP-AES analysis, but distinctly zoned with respect to Sr-isotopes (Haggerty *et al.* 1995). $\delta^{13}\text{C}$ values within the dolomite crystal range from -8.7‰ to -9.1‰ and $\delta^{18}\text{O}$ values range from $+21.2\text{‰}$ to $+21.8\text{‰}$ (Table 6). These variations are analytically significant, but reflect only minor changes in the chemistry and/or temperature of the mineralizing fluid during crystal precipitation.

Twelve carbonate samples (dolomite, calcite and

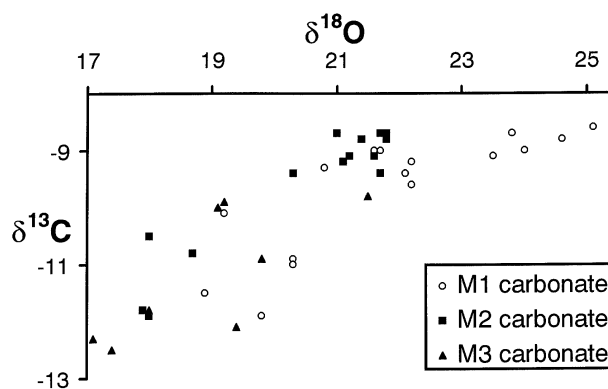


Figure 5. A plot of $\delta^{18}\text{O}$ versus $\delta^{13}\text{C}$ for the Llanrwst vein carbonates; data is presented in Table 6.

witherite) from the Llanfair veinfield were analysed (Table 7). $\delta^{13}\text{C}$ shows greater variations than at Llanrwst, ranging from -1.8‰ to -12.8‰ with a contrasting steady increase in $\delta^{13}\text{C}$ values with time. $\delta^{18}\text{O}$ values in the veinfield vary from $+15.5\text{‰}$ to $+26.3\text{‰}$, but show no simple correlation with paragenetic position (Fig. 6). Two calcite samples from the same hand specimen (BR2-1 and BR2-2), have $\delta^{13}\text{C}$ of -12.8‰ and -9.2‰ and $\delta^{18}\text{O}$ of $+15.5\text{‰}$ and $+25.1\text{‰}$, almost equal to the $\delta^{18}\text{O}$ range of the whole veinfield.

8. Discussion

8.a. Temperature of mineral deposition

In the Llanrwst veinfield the main stages of veining have homogenization temperatures between 140 and 190°C , while late-mineralization thrusts have inclusions which homogenized at $< 100\text{°C}$. In the Llanfair veinfield, inclusion homogenization temperatures decrease from sulphide to post-sulphide phases, falling from a maximum of 190 to 80°C . In general homogenization temperatures

Table 7. $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values for vein carbonates from the Llanfair veinfield

Mine, sample	Grid ref. (SH sheet)	Paragenetic position	Mineral	$\delta^{13}\text{C}$ (PDB)	$\delta^{18}\text{O}$ (SMOW)
<i>Nant-y-Plwm</i>					
S3	9277 6622	Post-sulphide	Dolomite	-3.4	24.2
S6	9277 6622	Post-sulphide	Dolomite	-3.3	23.4
S8	9277 6622	Sulphide	Dolomite	-6.9	22.9
S8	9277 6622	Sulphide	Calcite	-6.0	22.5
S9	9277 6622	Sulphide	Calcite	-7.3	24.7
S10	9277 6622	Pre-sulphide	Dolomite	-10.4	18.6
<i>Llanfair</i>					
LF 2	9363 7017	Pre-sulphide	Dolomite	-11.7	19.7
LF 4	9363 7017	Post-sulphide	Dolomite	-1.8	26.3
<i>Ty'n-y-ddol</i>					
BR2-1	9474 7150	Sulphide	Calcite	-12.8	15.5
BR2-2	9474 7150	Sulphide	Calcite	-9.2	25.1
NMW-Ba 1	9474 7150	Post-sulphide	Witherite	-2.5	16.6
NMW-Ba 2	9474 7150	Post-sulphide	Witherite	-3.0	16.7

Analytical errors: $\delta^{13}\text{C} \pm 0.2\text{‰}$, $\delta^{18}\text{O} \pm 0.1\text{‰}$.

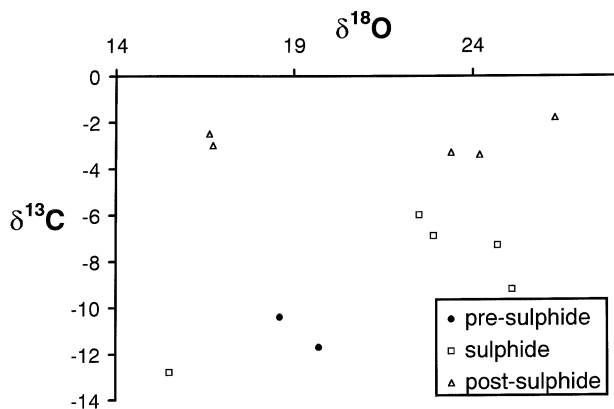


Figure 6. A plot of $\delta^{18}\text{O}$ versus $\delta^{13}\text{C}$ for the Llanfair vein carbonates; data is presented in Table 7.

underestimate the true trapping temperature of the fluid. However, isochores for aqueous brines are relatively steep in P - T space (that is, relatively large pressures necessitate relatively small temperature corrections).

Two specimens contain sulphide mineral pairs of the same paragenetic stage in close spatial association (though there is no definite textural evidence of co-genetic growth). Galena and sphalerite from sample P12 ($\Delta_{\text{sp-gn}} = 2.9\text{‰}$) give an isotopic equilibrium temperature of $235 \pm 30\text{ °C}$ (Kiyosu, 1973) and galena and chalcopyrite from sample PA2 ($\Delta_{\text{cp-gn}} = 3.1\text{‰}$) give an equilibrium temperature of $185 \pm 20\text{ °C}$ (Kajiwara & Krouse, 1971). These isotopic equilibrium temperatures are within error/slightly above the temperatures indicated by fluid inclusion data uncorrected for pressure effects (125 – 190 °C) and this agreement suggests that they reflect equilibrium precipitation of these minerals. Assuming $T_h = 190\text{ °C}$ for the Llanrwst mineralizing fluids, the highest temperature for sulphide mineral pairs would imply a maximum isochore pressure correction of under 1 km hydrostatic or *c.* 100 m lithostatic. Mineralization took place at temperatures close to the fluid inclusion homogenization temperatures and at relatively shallow depths, as is characteristic of epithermal vein systems of this type.

8.b. Sulphur sources

In modern hydrothermal systems only a small proportion of the sulphur present is precipitated at the site of deposition, thus any mass balance effect of removing sulphur from solution is minimal (Ohmoto & Rye, 1979). In such a situation, sulphur is present in the fluid in excess relative to the metals and the $\delta^{34}\text{S}$ of the fluid may be approximated by correcting the $\delta^{34}\text{S}$ values of the sulphide mineral to that of HS^- (the dominant reduced sulphur species in a relatively high pH environment, as indicated by the presence of carbonate in the vein/wall-rock mineral assemblage). The fractionation factors of Friedman & O'Neil (1977) were used and a temperature of 190 °C assumed for the isotopic correction of the Llanrwst data and 160 °C for the Llanfair data.

In the Llanrwst veinfield the $\delta^{34}\text{S}_{\text{HS}^-}$ of the fluid ranged between -7.0‰ and $+12.7\text{‰}$ during the main phase of sulphide deposition, and from -4.3‰ to $+18.7\text{‰}$ in the late phase. The Llanrwst host rocks provided a reservoir of reduced sulphur with a typical $\delta^{34}\text{S}$ range from -6‰ to $+2\text{‰}$ with some values extending to $+24\text{‰}$. Circulation of fluids through the host rocks could leach sulphur, with $\delta^{34}\text{S}$ values in the range observed in the vein sulphides associated with the sulphide phase of mineralization. Thus the host rocks are interpreted to be the major source of sulphur to the mineralizing fluid during the main sulphide phase, in a comparable fashion to that described by Anderson *et al.* (1989) for similar vein deposits in Ireland and southern Scotland.

However, the fluid apparently became generally ^{34}S -enriched as mineralization progressed, with paragenetically late marcasites having $\delta^{34}\text{S}$ values up to $+22\text{‰}$. This cannot be explained by depletion of ^{32}S in the fluid by the precipitation of galena and sphalerite prior to precipitation of ^{34}S -enriched post-sulphide marcasite. It is possible that these marcasites could have been precipitated from the same sulphur-bearing fluid as the main phase sulphides. A decrease in fluid temperature between sulphide and post-sulphide phases would increase the fractionation factor between the HS^- bearing fluid and marcasite, from $+3.3\text{‰}$ at 190 °C to $+4.3\text{‰}$ at 100 °C , but is unable to explain completely the ^{34}S -enrichment of these marcasites, though changing temperature coupled with major changes in fluid chemistry might. Alternatively, these marcasites may be related to the addition of ^{34}S -enriched sulphur derived from surface waters, possibly seawater or an evaporitically-concentrated groundwater (see Section 8.c and Haggerty *et al.* 1995) which entered during the waning stages of mineralization when the hydrothermal system collapsed.

In the Llanfair veinfield the calculated $\delta^{34}\text{S}_{\text{HS}^-}$ of the mineralizing fluid ranges from -12‰ to -5‰ (Table 4). Post-sulphide phase barites have compositions of $+11.4$ and $+17.5\text{‰}$, which would yield isotopic equilibrium temperatures of $\sim 400\text{ °C}$ and 250 °C , respectively (Sakai, 1968), if in equilibrium with the fluid dissolved bisulphide. These temperatures are higher than those from microthermometry and sulphide mineral pairs (see Section 8.a) and indicate that the sulphate sulphur was derived from a different source to the sulphide. We consider that the most probable source for this ^{34}S -enriched sulphate was ultimately a surface-derived water, there being two strong possibilities. First, at the time of mineralization Llanfair was situated on the northern shore of St George's Land (Leeder, 1987) making Lower Carboniferous seawater, with a $\delta^{34}\text{S}$ range of $+14\text{‰}$ to $+22\text{‰}$ (Claypool *et al.* 1980), a possible sulphate source. Baryte $\delta^{34}\text{S}$ values from Silvermines, Ireland, which is believed to have derived the bulk of its sulphur from Carboniferous seawater have $\delta^{34}\text{S}$ values as low as $+14\text{‰}$, with the lighter values reflecting a contribution from minor oxidation of sulphide (Boyce, Colman & Russell, 1983). A second possible source would be

evaporitically-concentrated groundwaters; at the southern tropical palaeolatitude of the time and a maritime setting, St Georges Land could have had surface and groundwaters with high salt concentrations derived from evaporitic concentration of sea-salt spray, similar to those in Western Australia today. Such waters evolve to gypsum saturation and have sulphate with ^{34}S similar to seawater, which could account for the baryte sulphur isotopic compositions at Llanfair and the calcic solute compositions observed. The underlying sedimentary rocks at Llanfair probably provided the isotopically lighter, reduced sulphur during the sulphide phase. It is possible that the evolution to ^{34}S -enriched compositions in the post-sulphide phase of both veinfields is related to a surface water influx into the hydrothermal system at a late stage, with bulk reduction of sulphate to sulphide occurring at Llanrwst (see Equation 1, Section 8.c).

8.c. Carbon sources

The vein carbonates in the Llanrwst veinfield have a restricted $\delta^{13}\text{C}$ range, from -12.5‰ to -8.6‰ . Black slates hosting some of the mineral veins contain organic carbon with $\delta^{13}\text{C}$ values ranging from -26.8‰ to -29.4‰ , and the Ordovician volcano-sedimentary sequence contains calcareous units with marine-derived carbonates, which are assumed to have $\delta^{13}\text{C}$ values of around 0‰ (Faure, 1986). At a mineralization temperature of 125 to 190°C as suggested by geothermometry (see Section 8.a), dissolved inorganic carbon (DIC) in isotopic equilibrium with the black slates would have $\delta^{13}\text{C}$ values of -9.3‰ to -14.9‰ and calcite precipitated would have similar values (Bottinga, 1969). Thus the graphite-bearing black slates could have provided a high proportion of the carbon in the mineralizing fluid, and this hypothesis is supported by the bleaching of wall rocks and removal of carbon at some localities. Small differences of a few permil might be expected due to local changes in fluid chemistry and temperature during carbonate precipitation (Ohmoto & Rye, 1979). Also, if a large fraction of the organic carbon were oxidized to produce DIC, or oxidation took place under non-equilibrium conditions, much lighter DIC could result. Some vein carbonate $\delta^{13}\text{C}$ values are heavier than -9.3‰ and may indicate that additional carbon was derived from isotopically heavier marine-derived carbonate present in the calcareous units, and to a lesser extent in the black slates themselves.

The local bleaching of organic-rich wall rocks requires an oxidizing agent (since carbonate is abundant and there is no evidence for reduced carbon species in the fluid inclusions), and possibly occurred via a reaction similar to



The stoichiometry of the exact reaction will depend on the nature of the organic matter involved, here assumed to be saturated aliphatic hydrocarbon. The DIC liberated from this reaction would be ^{13}C -depleted. If ^{34}S -enriched

sulphate was introduced into the system late in the paragenetic sequence (as suggested in Section 8.b) this reaction would explain both the trend to more ^{13}C -depleted carbonate later in the paragenesis at Llanrwst and the presence of late ^{34}S -enriched post-sulphide marcasite. The most likely source of ^{34}S -enriched sulphate would be surface-derived waters.

The carbon isotope data on hydrothermal carbonates in the Llanfair veins show a $\delta^{13}\text{C}$ range from -1.8‰ to -12.8‰ (Fig. 6). This scale of isotopic variation cannot be explained by local variations in the chemistry and temperature of the ore fluid during carbonate precipitation (Ohmoto & Rye, 1979) and most probably reflects variations in the mixing of at least two distinct carbon sources in the mineralizing fluid. The isotopically light end member (with a $\delta^{13}\text{C}$ value around or below -13‰) maybe derived from organic material in the host rocks and mixed with marine derived carbonate (assumed to have a typical marine carbonate $\delta^{13}\text{C}$ value of around 0‰ (Faure, 1986)) from the thin black limestone beds that host some of the Llanfair mineralization.

8.d. Mineralizing fluid sources

Fluid inclusion data indicate that the fluids responsible for the main phase of mineralization at both Llanrwst and Llanfair were highly saline calcic brines, up to 26 wt % NaCl equivalent. If the temperature of precipitation is known, the oxygen isotopic compositions of the carbonate minerals may be used to calculate the equilibrium isotopic compositions of the waters from which they precipitated (Northrop & Clayton, 1966; O'Neil, Clayton & Mayeda, 1969).

Oxygen isotope data on the Llanrwst veinfield carbonates ranges from $+25.1\text{‰}$ to $+17.1\text{‰}$. Using a mineralization temperature of 190°C (see Section 8.a) gives a range of fluid $\delta^{18}\text{O}$ from $+4\text{‰}$ to $+14\text{‰}$. These $\delta^{18}\text{O}$ values are within the range of $\delta^{18}\text{O}$ values for highly evolved basinal brines and metamorphic fluids (values from $+4\text{‰}$ to $+25\text{‰}$: Taylor, 1974; White, Barnes & O'Neil, 1973). Hence the hydrothermal solutions underwent significant fluid-rock interaction and isotopic exchange prior to mineral deposition. The mineralizing fluid $\delta^{18}\text{O}$ values are slightly too heavy to be related to formation waters or primary magmatic fluids. The decrease in $\delta^{18}\text{O}$ values during mineralization can be explained either by keeping the $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ the same and increasing the temperature in the later mineralization (Fig. 7), or, if temperature remained constant, by decreasing the $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ values. An evolution to less ^{18}O -enriched water compositions as mineralization progressed is consistent with the hypothesis of a greater role for a less-evolved surface-derived water advanced previously in Sections 8.b and 8.c.

Oxygen isotope data from the gangue carbonates in the Llanfair veins range in $\delta^{18}\text{O}$ from $+15.5\text{‰}$ to $+26.3\text{‰}$, and calculated $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ values at 160°C vary between $+3\text{‰}$ and $+14\text{‰}$, essentially the same range as at Llanrwst, implying a similar source.

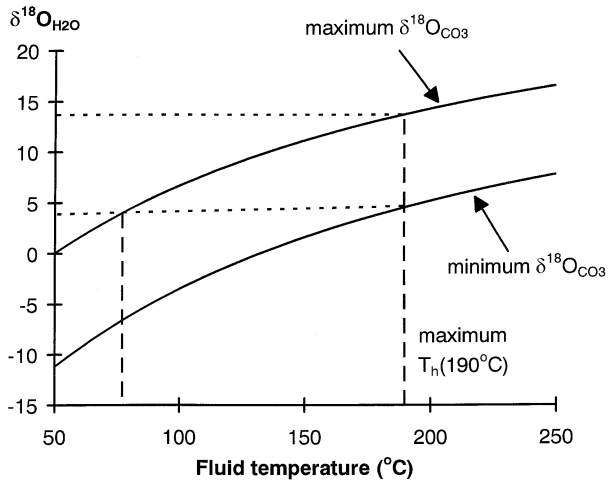


Figure 7. Variability of $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ of aqueous fluid with temperature, calculated for the range of vein carbonate data in Table 6 using the equations of Northrop & Clayton (1966) and O'Neil, Clayton & Mayeda (1969). The range of carbonate ^{18}O compositions observed would correspond to a range of aqueous fluid ^{18}O from 4 to 14 ‰_{SMOW} at the presumed mineralization temperature of 190 °C, or to precipitation over a temperature range of 190 to 77 °C if fluid ^{18}O remained constant at 4 ‰_{SMOW}.

9. Models for genesis of the Llanrwst and Llanfair veins

The isotopic and fluid inclusion data reported here confirm the link between the Llanrwst and Llanfair vein systems. Both deposits formed from waters with similar ranges of $\delta^{18}\text{O}$, indicative of evolved waters, but a component of surface-derived waters could have been involved to give the range of $\delta^{18}\text{O}$ observed. The timing of mineralization makes a metamorphic fluid unlikely, as peak metamorphism was reached in middle Devonian times, prior to mineralization. Most of the metamorphic fluids would have been released prior to or during the peak metamorphic event, with little fluid remaining in the rocks. Any residual water would probably have been consumed during retrograde metamorphic reactions. The temperature and composition of the fluids are most consistent with highly evolved brines, and Pb-isotope data show that the mineralizing agents at both Llanrwst and Llanfair interacted extensively with the underlying Lower Palaeozoic sequence (Haggerty, Cliff & Bottrell, 1996). A possible fluid would be a highly evolved, deeply penetrating surface-derived water or a formation water.

In both deposits, the majority of sulphur and carbon appears to have been derived from the local host rocks. The greater abundance of sulphur and organic carbon at Llanrwst probably caused the more extensive sulphide precipitation in those veins. Sulphate from surface waters appears to have been important in the later stages in both deposits, appearing as ^{34}S -enriched baryte at Llanfair. The more reduced conditions imposed by organic carbon-rich host rocks at Llanrwst caused reduction of this sulphate to produce ^{34}S -enriched post-sulphide marcasite and released $\delta^{13}\text{C}$ -depleted carbon to the mineralizing fluid. At Llanfair, sea-water (or a surface-derived water

dominated by sea-salts) may have provided the Sr in paragenetically late minerals which was not available from the host rocks (Haggerty *et al.* 1995). At Llanrwst there is a general progression to more radiogenic Sr-isotopic compositions with time (Haggerty *et al.* 1995), which would appear to militate against late involvement of sea-water. However, post-sulphide calcite (in the same paragenetic position as ^{34}S -enriched marcasite) has almost the least radiogenic Sr in the veinfield ($^{87}\text{Sr} / ^{86}\text{Sr} = 0.7098$, Haggerty *et al.* 1995) and water ^{18}O may have decreased during later stages of mineralization. These factors point to a greater involvement of a less-evolved surface-derived water as the ultimate source of the ^{34}S -enriched sulphur. This may have been sea-water, but an evaporitically concentrated brine might better explain the relatively high salinities and Ca contents and high ^{18}O of the mineralizing fluids. The earlier stages of mineralization must have been accomplished after such a fluid had interacted significantly with the basement rocks, acquiring radiogenic Sr, Pb, increased ^{18}O and a sulphur content dominated by interaction with reduced sulphur in the rocks. The later stages of mineralization appear to have involved a fluid with the same ultimate source but which had undergone much less interaction with the basement rocks. ^{18}O decreases at Llanrwst and Sr is less radiogenic; sulphur is present as sulphate at Llanfair and there is a shift from locally-derived sulphur to reduced surface-derived sulphate in the sulphide at Llanrwst.

The period of mineralization was one of prevailing extensional tectonics (Boyce, Anderton & Russell, 1983; Leeder, 1987). Fitches (1987) suggests that some of the mineral occurrences in the Welsh Basin (Plynlimon and West Shropshire) formed in fractures initiated during strain relaxation after regional deformation, with a common east–northeast to east–southeast trend, in the early Carboniferous and related to Viséan tectonism. The M_2 veins at Llanrwst have a east–northeast trend and the later M_3 veins a east–southeast trend. An extensional tectonic regime would encourage downward water migration, and reactivated Caledonian faults would have provided high permeability zones for fluid flow. Thus a surface-derived brine could have penetrated to depth and interacted with the Lower Palaeozoic basement while mineralization occurred where fluid flow was focused along faults into favourable environments. The Llanrwst deposit is intimately associated with the Conwy Valley Fault, occurring in splays from the main fault system, and the Llanfair veinfield is related to north–south faults, which correspond to faults in the Vale of Clwyd graben.

The Llanrwst and Llanfair veinfields are broadly coeval with the carbonate-hosted stratiform base-metal deposits of central Ireland, which are thought to have formed in response to Dinantian tensional tectonics (Boyce, Anderton & Russell, 1983). The Irish base-metal deposits formed from fluids which had interacted extensively with the underlying basement, as the main-stage fluids at Llanrwst and Llanfair had, so the Llanrwst and Llanfair vein systems may be analogous to the pathways

in the basement followed by ascending fluids during the formation of the Irish base-metal deposits.

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