

Pb-isotope evidence on the origin of the West Shropshire orefield, England

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Abstract – Pb-isotope data on ore galenas from the West Shropshire orefield show a significant spread of $^{206}\text{Pb}/^{204}\text{Pb}$ values, with minor variation in $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ ratios. These indicate that lead was derived from multiple sources, some of them uranium-enriched and incompletely mixed prior to ore deposition. Four possible mineralizing agents are considered: circulating sea-water, metamorphic waters, basinal brines and convecting formation waters. Pb-isotope data exclude a circulating sea-water origin for the mineralization, and best support a convecting formation water mineralizing agent. A model involving a single fluid tapping multiple lead sources is proposed to explain the observed Pb-isotope variation.

1. Geology and mineralization

The West Shropshire orefield, while being of minor economic importance, is geologically significant in terms of understanding the origins of Lower Palaeozoic-hosted base-metal mineralization within the British Isles. Incomplete mining records show production from the area between 1845 and 1944 exceeded 240 000 t of lead concentrate, 19 400 t of zinc concentrate and 307 000 t of baryte. The geology and mineralogy of the West Shropshire orefield have been described in detail by Smith (1922) and Dines (1959), with possible ore genesis models proposed by Patrick & Bowell (1991). The West Shropshire orefield lies on the eastern margin of the extensive Welsh Basin which formed in a back-arc setting during early Palaeozoic time and contains a volcano-sedimentary sequence several kilometres thick. The sedimentary pile contains predominantly marine clastic sediments, with minor carbonates in the southeast, which were deposited in a series of basins orientated roughly northeast–southwest. Associated with the sediments are thick sequences of volcanic rocks, predominantly of Ordovician age. The whole basin experienced deformation and low-grade metamorphism in the late Silurian to mid-Devonian as part of the Caledonian Orogeny.

The orefield consists of a series of lead–zinc–copper-bearing veins and vein breccias hosted within Ordovician strata of the Shelve Inlier and late Precambrian rocks of the Longmynd (Fig. 1). The oldest rocks in the area belong to the Uriconian Volcanic Complex, which contains andesites, dacites and rhyolites intruded by quartz-porphyry stocks and dolerite dykes (Greig *et al.* 1968). The partially coeval sedimentary Longmyndian Supergroup consists of shales, mudstones, grits and conglomerates, with a total thickness of 6500 m (Pauley, 1991). The Cambrian strata west of the Pontesford Fault

are composed mainly of shales and carry no mineralization (Dines, 1959). The Ordovician of the Shelve Inlier hosts the bulk of the mineralization, with the main lithologies being shales and sandstones, interbedded volcanic rocks and dolerite intrusions (Dines, 1959).

The Shelve Inlier (Fig. 2) is the surface expression of the Pontesford Lineament, an anticlinal structure which developed during the late Ordovician inversion of the Welsh Basin. The Pontesford Fault is believed to be an extension of the Church Stretton Fault System, a key structural element in the regional geology (Woodcock, 1984; Smith, 1987). Both structural features have played an important role in the geological evolution of the region from the late Ordovician to Triassic (Woodcock, 1984). The Shelve Inlier is unconformably overlain by Silurian and Carboniferous sediments, with the extensive Permo-Triassic Cheshire basin lying to the northeast (Fig. 2).

In the Precambrian rocks, which lie to the east of the Pontesford Fault, baryte and minor copper mineralization occur in predominantly east–west orientated veins, whereas to the west, east–west and northwest trending veins in the Ordovician strata contain the main lead–zinc mineralization and associated baryte. The mineralization occurs as veins and vein breccias hosted preferentially in the more competent strata. The vein mineralogy consists of galena and sphalerite as the principal metal sulphides with calcite, quartz, baryte and witherite. Mineral zoning of the veins occurs at some localities with sphalerite and quartz at depth, and galena and baryte at higher levels (Dines, 1959). Concentrations of chalcopyrite and pyrite occur at depth in the Precambrian hosted veins (Smith, 1922) and at Roman Gravels to the west of the Pontesford Fault.

The mineral paragenesis has been described by Patrick & Bowell (1991) as (1) quartz with minor pyrite; (2) brown sphalerite; (3) colour-banded sphalerite with

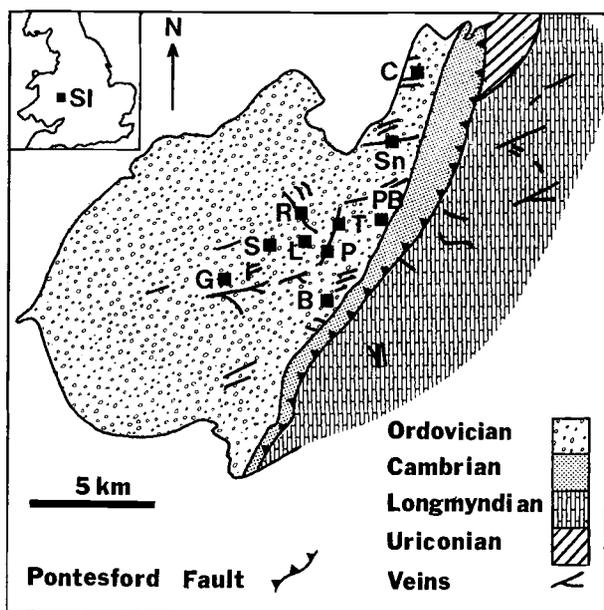


Figure 1. Location and simplified geology of the Shelve Inlier showing the key mines of the West Shropshire orefield (after Dines, 1959). SI = Shelve Inlier; B = Bog; C = Callow Hill; G = Grit; L = Ladywell; P = Pennerley; PB = Perkins Beach; R = Roman Gravels; S = Shelve; Sn = Snailbeach; T = Tankerville.

calcite and quartz; (4) galena, calcite and quartz; (5) light brown sphalerite; (6) galena, chalcopryite and baryte; (7) baryte. Fluid inclusion data suggest that the mineralizing fluid was a highly saline NaCl-CaCl_2 brine containing 16–30 wt% CaCl_2 equivalent, with a temperature of between 100 and 180 °C. A trend over the period of emplacement, from higher temperature and lower salinity to lower temperature and higher salinity fluids, is recognized by Patrick & Bowell (1991). This is similar to the trends detected in Ireland, at Silvermines (Samson & Russell, 1987) and Tynagh (Banks & Russell, 1992). Fluid inclusion homogenization temperatures (T_h) of 180 °C are relatively high for Mississippi valley-type (MVT) deposits, which typically have T_h values of 70–150 °C. The relatively high T_h values detected in the West Shropshire orefield suggest that basinal brines were not the sole mineralizing agents, as these rarely obtain temperatures over 150 °C (Bethke, 1986). Known fault movements and intrusives define the age of mineralization between the early Devonian and Westphalian (Smith, 1922; Dines, 1959). K–Ar data from Ineson & Mitchell (1975) on hydrothermal alteration clay assemblages, corrected to the Steiger & Jäger (1977) decay constant, indicate an age of 360 ± 8 Ma (late Devonian–early Tournaisian), with age data ranging from 380–330 Ma (mid-Devonian to Namurian).

2. Pb-isotope measurements

Samples of galena were collected from mine dumps and provenanced museum specimens. After dissolution in HCl and conversion to the nitrate, lead was separated in

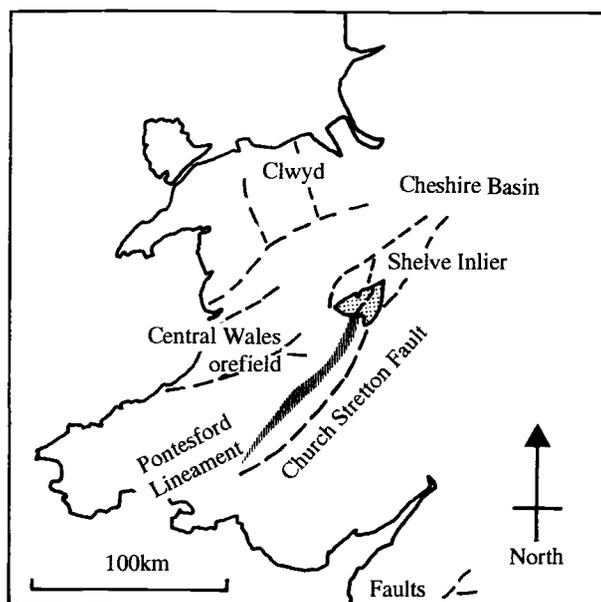


Figure 2. Key features of the Welsh basin and region surrounding the Shelve Inlier.

the pure state by anodic deposition (Arden & Gale, 1974). Pure lead samples in the nitrate form were loaded on to rhenium filaments for thermal ionization mass spectrometry using the standard silica-gel/phosphoric acid activator. Isotopic analysis was carried out in static mode using a VG Isotech 38-54M double-focusing mass spectrometer, at a filament temperature of about 1250 °C as determined by an optical pyrometer. Pb-isotope ratios were normalized in terms of the mean ratios obtained for many repeat analyses of the NIST SRM 981 standard. Blank values were under 0.8 ng. Repeat analyses of this standard established the analytical errors (2σ) as better than $\pm 0.09\%$ for the ratio $^{206}\text{Pb}/^{204}\text{Pb}$, $\pm 0.1\%$ for the ratio $^{207}\text{Pb}/^{204}\text{Pb}$ and $\pm 0.13\%$ for the ratio $^{208}\text{Pb}/^{204}\text{Pb}$. The correlation coefficient between $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{206}\text{Pb}/^{204}\text{Pb}$ is 0.998, and between $^{208}\text{Pb}/^{204}\text{Pb}$ and $^{206}\text{Pb}/^{204}\text{Pb}$ is 0.994. These combined errors produce Cumming–Richards (1975) model age errors of ± 55 Ma.

The measurements are listed in Table 1 and presented in Figures 3 and 4. The Pb-isotope data from the galenas show a significant spread in the $^{206}\text{Pb}/^{204}\text{Pb}$ ratio and minor variations in the $^{208}\text{Pb}/^{204}\text{Pb}$ and $^{207}\text{Pb}/^{204}\text{Pb}$ ratios. The $^{206}\text{Pb}/^{204}\text{Pb}$ values range from 18.094 to 18.518 (a spread of 2.29%), the $^{207}\text{Pb}/^{204}\text{Pb}$ values from 15.632 to 15.736 (0.67%) and the $^{208}\text{Pb}/^{204}\text{Pb}$ from 38.294 to 38.702 (1.07%). There is slight $^{206}\text{Pb}/^{204}\text{Pb}$ zonation within the orefield with the highest values associated with the Snailbeach and Tankerville mines.

3. Discussion of the Pb-isotope data

The spread of $^{206}\text{Pb}/^{204}\text{Pb}$ data suggest either lead derived from multiple sources during a relatively short period of geological time or extracted from a single source at various times. Both the field evidence and K–Ar isotopic

age data (Ineson & Mitchell, 1975) suggest that mineralization took place as a single, short-lived event in the late Devonian to early Tournaisian. If this is correct, then the lead must have been derived from a variety of sources, each with a different range of U/Pb and Th/Pb compositions.

The fact that the data lie close to or within error of the Cumming-Richards growth curves implies that the metal sources were well mixed and composed of multi-cycled sediments, with no significant lead derived from isotopically depleted basement (Fletcher, Swainbank & Colman, 1993). However, model ages calculated from the Cumming-Richards model (1975) range from 199 Ma to 502 Ma, a much more extensive range than the corrected K-Ar age data of Ineson & Mitchell (1975) (380 to 330 Ma). In this context it is noteworthy that epigenetic mineralization hosted within sedimentary/volcanic sequences similar to those of West Shropshire, that do not meet all the requirements outlined in the lead evolution models, often give erroneous model ages, reflecting complex lead evolutionary histories (Gulson, 1986, p. 155).

Fletcher, Swainbank & Colman (1993) studied several base-metal deposits in Wales using Pb-isotope measurements, concluding that two major mineralizing events occurred, the first at between 390 and 330 Ma and the second at between 240 and 200 Ma. In both cases the metal sources were believed to be the underlying, isotopically homogeneous, Lower Palaeozoic rocks, with the Pb-isotope composition of individual deposits reflecting their geological ages. The proposed first phase of mineralization (390–330 Ma) is represented by the Central Wales orefield (Fig. 2), which shares many characteristics with the West Shropshire orefield. Clearly, in comparison to the Fletcher, Swainbank & Colman (1993) data, the West Shropshire values do not give

reasonable model ages and are highly variable, extending beyond the range so far reported for the whole Welsh region. It is possible that the Welsh deposits and West Shropshire orefield shared common sources, but the lead in the Welsh deposits was homogenized to a higher degree prior to ore deposition.

Pb-isotopic studies on the United States Mississippi Valley-type districts have shown them to contain distinctly radiogenic lead, with $^{206}\text{Pb}/^{204}\text{Pb}$ values commonly > 20, reaching 24 in the Upper Mississippi mining district (Hart, Shimizu & Sverjensky, 1981; Crocetti, Holland & McKenna, 1988). Often the mineral districts show isotopic zonation with systematic increases in Pb-isotopic compositions across orefields, a feature believed to reflect the movement of fluids through the district and the importance of different sources, particularly the underlying basement rocks (Spirakis & Heyl, 1995). Pb-isotopic data on the Pine Point Mississippi Valley-type district of northwest Canada show uniform values across the orefield with realistic model ages (Cumming, Kyle & Sangster, 1990). This indicates that radiogenic lead may not be typical of Mississippi Valley-type deposits, but a reflection of the data bias towards studies on classic deposits within the United States.

The spread of $^{206}\text{Pb}/^{204}\text{Pb}$ data from West Shropshire suggests that more than one metal source was tapped during mineralization. Possible metal sources are: (a) the Lower Palaeozoic pile, (b) shale-rich sedimentary basins and (c) the underlying Uriconian basement. Fletcher, Swainbank & Colman (1993) suggest that the thick Lower Palaeozoic pile of the Welsh Basin was the source for most of the Welsh ore deposits, with the variation of Pb-isotope ratios for the most part being attributed to the age of mineralization. In the case of West Shropshire the higher variability of the data implies that the Lower

Table 1. Galena Pb-isotope data from the West Shropshire orefield, England

Mine	Grid Reference	$^{206}\text{Pb}/^{204}\text{Pb}$	$^{207}\text{Pb}/^{204}\text{Pb}$	$^{208}\text{Pb}/^{204}\text{Pb}$	Model Ages (Ma)
Snailbeach	SJ 375 022	18.506	15.685	38.682	227
Snailbeach	SJ 374 022	18.347	15.643	38.387	279
Snailbeach	SJ 374 022	18.483	15.650	38.554	199
Bog	SO 356 978	18.191	15.657	38.326	394
Callow Hill	SJ 388 049	18.094	15.701	38.358	502
Grit	SO 319 978	18.103	15.687	38.335	477
Ladywell	SO 329 993	18.296	15.649	38.365	309
Pennerley	SO 352 988	18.333	15.689	38.493	337
Perkins Beach	SO 366 998	18.285	15.632	38.310	307
Roman Gravels	SO 334 998	18.278	15.646	38.362	326
Roman Gravels	SO 335 999	18.275	15.645	38.350	327
Shelve*	SO 330 991	18.310	15.684	38.572	340
Shelve*	SO 330 991	18.411	15.736	38.584	338
Shelve*	SO 330 991	18.175	15.665	38.307	413
Shelve*	SO 330 991	18.342	15.675	38.294	316
Shelve*	SO 330 991	18.413	15.704	38.468	302
Shelve*	SO 330 991	18.374	15.647	38.444	265
Shelve*	SO 330 991	18.462	15.652	38.578	214
Tankerville	SO 355 995	18.518	15.698	38.702	228

* Data provided by Dr Ian Swainbank of the British Geological Survey. Model ages calculated using Cumming & Richards (1975).

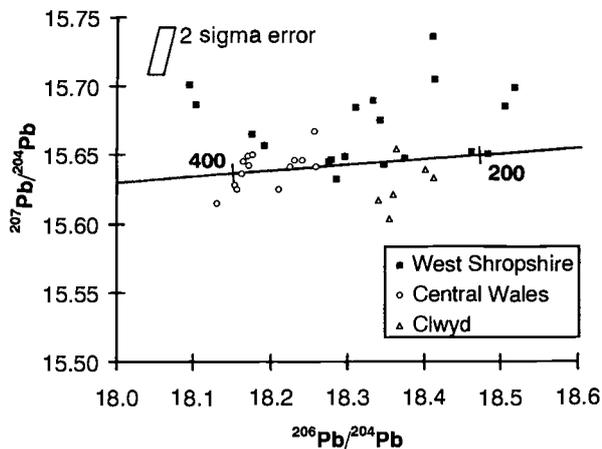


Figure 3. A plot of $^{207}\text{Pb}/^{204}\text{Pb}$ versus $^{206}\text{Pb}/^{204}\text{Pb}$, showing the isotopic composition of galenas from the West Shropshire orefield, using data from Table 1. The growth curve is that of Cumming & Richards (1975). Model ages are marked.

Palaeozoic pile was not the sole source, however, it may have been a major component. The expulsion of metal-rich fluids from subsiding shale-rich sedimentary basins has been proposed as the metal sources for the British Pennine mineralization by Halliday *et al.* (1990). However, in the case of West Shropshire, no suitable shale-rich basins are known at the time of mineralization. Spirakis & Heyl (1995) suggest that in the Upper Mississippi mining district, basinal brines started thermal convection through the underlying Precambrian granitic basement when fracturing released stored heat from within the uranium- and thorium-enriched granites. The West Shropshire orefield is underlain by Precambrian Uronian volcanic and intrusive rocks, which may have acted in a similar fashion to the basement of the Upper Mississippi mining district.

4. Ore genesis models and possible mineralizing agents

Patrick & Howell (1991) discuss three possible ore genesis models: circulating sea-water, metamorphic fluid expulsion and basinal dewatering. They point out that, although sea-water and metamorphic waters are potential mineralizing agents, the fluid inclusion data are not supportive. The Pb-isotope data presented here are unable to discriminate between the proposed models, but do allow conclusions to be drawn about their relative probabilities.

4.a. Circulating sea-water

Sea-water is a potential mineralizing fluid and Russell, Solomon & Walsh (1981) suggest that the mineralizing fluid in the broadly coeval Irish base-metal deposits, was largely downward-penetrating sea-water that became heated and rose up faults at the margins of subsiding basins. At the time of mineralization, the Shelve area lay on the northern margin of the St George's landmass. There is no evidence that the Shelve area was submerged

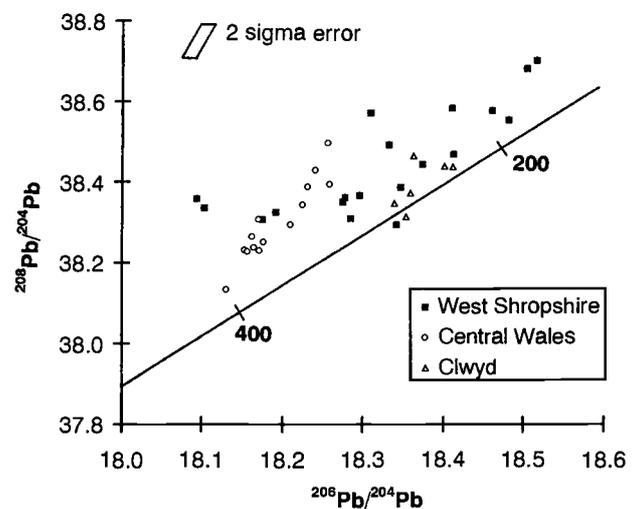


Figure 4. A plot of $^{208}\text{Pb}/^{204}\text{Pb}$ versus $^{206}\text{Pb}/^{204}\text{Pb}$, showing the isotopic composition of galenas from the West Shropshire orefield, using data from Table 1. The growth curve is that of Cumming & Richards (1975). Model ages are marked.

during the late Devonian–early Carboniferous, although Dinantian marine sediments crop out some 30 km to the north and east.

Although it has been compared with Irish deposits, the Pb-isotope data for the West Shropshire orefield varies significantly, a feature which does not occur in Ireland. O'Keefe (1986), LeHuray *et al.* (1987) and Dixon, LeHuray & Rye (1990) have shown that individual Irish base-metal deposits have very restricted Pb-isotope variations as a result of lead homogenization in the hydrothermal cells prior to ore deposition. The Irish base-metal deposits show a marked linear trend in Pb-isotope values, from non-radiogenic ($^{206}\text{Pb}/^{204}\text{Pb} = 17.75$) values in the northwest to more radiogenic values in the southeast ($^{206}\text{Pb}/^{204}\text{Pb} = 18.40$). This trend is attributed to a non-radiogenic lead component being derived from the Precambrian high-grade metamorphic basement of the north and radiogenic lead being scavenged from the Lower Palaeozoic basement of the south (Dixon, LeHuray & Rye, 1990). In the larger deposits, for example, Navan, the hydrothermal cells expand to scavenge metals from progressively deeper parts of the crust producing increased dispersion and less radiogenic Pb-isotope compositions in stratigraphically higher ore lenses (Mills *et al.* 1987). The complete Pb-isotope signature for the Irish base-metal deposits lies significantly below the Cumming-Richards growth curve and is unradiogenic relative to the West Shropshire data. The Pb-isotope data presented here does not therefore support a circulating sea-water model.

4.b. Metamorphic fluid expulsion

Attention has been drawn to similarities between the West Shropshire mineralization and that of Central Wales, where base-metal veins also occupy fractures in

large anticlinal structures. The Central Wales orefield has been dated using K–Ar methods by Ineson & Mitchell (1975) to the early Carboniferous (361 ± 8 Ma), with a data range from early Devonian (395 Ma) to Viséan (337 Ma). Phillips (1972, 1983) postulates that the mineralizing fluids responsible for the Central Wales mineralization were metamorphic pore waters released during normal shear fracturing at a depth of 6–8 km. However, the involvement of metamorphic fluids in the West Shropshire mineralization is doubtful in view of the K–Ar dates which suggest that ore deposition took place after the low-grade metamorphism of the Welsh Basin (Patrick & Bowell, 1991). Despite this, the situation remains ambiguous as the accuracy of K–Ar dating on hydrothermal alteration clay assemblages is known to be questionable as a result of Ar loss subsequent to clay formation and contamination by older non-alteration clay minerals (Hamilton, Kelley & Fallick, 1989). The exact timing of peak metamorphism of the Welsh Basin is still a matter of debate, with Bevins & Robertson (1988) proposing an Emsian (390–386 Ma) age and Soper, Webb & Woodcock (1987) and Woodcock (1987) suggesting a period from Eifelian to Givetian (386–377 Ma).

4.c. Basinal brines

The fluid inclusion data from West Shropshire suggest fluid characteristics very similar to those detected in MVT deposits, which are CaCl_2 –NaCl brines, >20 wt % NaCl equivalent, with T_h values of 70 °C to 150 °C (Patrick & Bowell, 1991). Pb-isotope data from Mississippi Valley-type mineralization show many deposits have highly variable compositions. The Upper Mississippi Valley Mining District, USA, has a $^{206}\text{Pb}/^{204}\text{Pb}$ range of 22 % (Heyl, Landis & Zartman, 1974) and a single galena cube, just 10 mm across, a $^{206}\text{Pb}/^{204}\text{Pb}$ range of 5.7 % (Deloule, Allegre & Doe, 1986). The source of the fluids responsible for Mississippi Valley-type deposits is still a matter of debate, although generally they are considered to be intrinsically related to adjacent sedimentary basins. Four main models have been proposed to explain the role of basinal brines: (I) overpressuring of basinal sediments through rapid sedimentation (Cathles & Smith, 1983) or hydrocarbon generation (Eisenlohr *et al.* 1994); (II) regional tilting and/or topographically driven flow (Bethke, 1986; Garven *et al.* 1993); (III) basinal compression and thrusting (Oliver, 1986); (IV) convection through the underlying basement (Bjørlykke, Sangster & Fehn, 1991; Spirakis & Heyl, 1995). The possibility of a similar sedimentary basin-related genesis for the West Shropshire orefield was considered by Patrick & Bowell (1991). Although they considered the West Shropshire orefield to have many features suggestive of a basinal brine source, no suitable subsiding shale-rich basins could be identified at the time of mineralization in the late Devonian to early Tournaisian.

If lead were derived from the sediments of a subsiding shale-rich basin, variable Pb-isotope ratios would be

expected as a result of the incomplete mixing of lead from various sources prior to deposition. In this situation there is a single fluid source tapping multiple lead sources. Fluids and lead are expelled from different portions of rock at slightly different times as diagenesis is a diachronous process in sedimentary sequences, with each rock portion having a slightly different isotopic composition. In this situation there is a single (basinal) fluid source that varies isotopically over relatively short time periods due to different rock layers entering and leaving the pressure and temperature conditions required for fluid and lead expulsion. Even within single rock units lead may be released from a variety of mineral sites depending on the chemical and physical conditions. For example, as a shale undergoes burial and diagenesis, lead may be released from clay adsorption sites, the clay lattice during recrystallization and by the decomposition of potassium feldspar. In this situation a single rock type can contain several isotopically different lead sources. Such a mechanism could account for the Pb-isotope variations detected in the West Shropshire galena samples and Mississippi Valley-type deposits.

4.d. Convecting formation waters

The West Shropshire orefield may be the product of convecting formation waters, interacting with the underlying Precambrian basement, producing the variations in Pb-isotopic composition and detected fluid inclusion T_h values. Radioactive heat from solidified high heat-producing granites has been shown to be capable of generating convection cells of sufficient magnitude to form uranium deposits and possibly strata-bound lead–zinc deposits (Bjørlykke, Sangster & Fehn, 1991). Spirakis & Heyl (1995) argue that the fracturing of uranium- and thorium-enriched granites within the basement changes the way heat is lost from conduction to convection, sending a pulse of pent-up heat into the overlying rocks. The resulting fracture permeability allows heat to be lost rapidly, initiating convection in overlying fluids. Doe, Stuckless & Delevaux (1983) found that the Conway Granite, New Hampshire, which contains 15 ppm uranium and 57 ppm thorium produced thermal anomalies of more than 100 °C above ambient in the overlying rocks. In the case of West Shropshire the ambient temperature was under 55 °C, presuming a burial depth of under 1 km (Patrick & Bowell, 1991), an estimated geothermal gradient of 35 °C km⁻¹ and a surface temperature of 20 °C. The West Shropshire basement contains quartz-porphyry intrusions which could have supplied metals and heat to the overlying fluids, producing the T_h values detected in the mineral veins.

5. Conclusions

The highly variable nature of the Pb-isotope data for the West Shropshire orefield excludes the possibility that the mineralizing fluid was circulating sea-water. This would

have homogenized the lead in the surrounding country rocks producing deposits with constrained Pb-isotope values (O'Keefe, 1986; LeHuray *et al.* 1987; Dixon, LeHuray & Doe, 1990). The Pb-isotope data best fit a model in which there was a single fluid source that varied isotopically over relatively short periods of time as lead was tapped from multiple sources. A mineralizing agent composed of convecting formation waters is consistent with the isotope values detected and the fluid inclusion temperatures reported by Patrick & Bowell (1991). Future study should concentrate on the timing of mineralization and the application of strontium and stable isotopic techniques to investigate the fluid sources.

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