"Background" δ^{34}S values of Kupferschiefer sulphides in Poland: pyrite-marcasite nodules *

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Abstract. Regional "background" δ^{34}S values of pyrite-(marcasite) nodules throughout the Zechstein basin in Poland have been measured to help estimate the proportion of externally derived sulphur in the Kupferschiefer Cu-Ag ores. The δ^{34}S values of the 17 FeS$_2$ nodules measured range widely, from -25.2 to -51.9‰, similar to the previously published -28 to -43‰ range in disseminated pyrite in the Kupferschiefer. The wide variation cannot be attributed to pyrite versus marcasite mineralogy, amount of contained chalcopyrite or sphalerite, carbonate versus shale host rock, early versus late formation, percent of included calcite, or to size, shape, or texture. There is also no relation with proximity to the centres of copper mineralization in southwestern Poland where sulphides are typically isotopically heavier. The δ^{34}S values do, however, vary directly with percent of host-rock fragments included in the nodules. Repeat samples that were washed with acid or hot water show the same wide variation, indicating that contamination by sulphate sulphur in the host rock is not a factor. Neither is organic sulphur because of its small volume. Instead, the sulphur composition may be fundamentally controlled by the formation mechanism of the nodule, whereby ^{34}S-rich sulphide is preferentially concentrated, possibly replacing anhydrite lenses. Alternatively, a network of host rock inclusions might act as a more accessible conduit for later, ^{34}S-rich fluids to infiltrate the nodule and add to earlier, ^{34}S-poor pyrite.

In the ore deposits, higher δ^{34}S values of ore nodules suggest less indigenous sulphur in limestone than shale lithologies. An isotopic temperature of 61 °C from a chalcopyrite-galena pair agrees with other estimates of < 105 °C. Higher values in ore nodules/veinlets than in adjacent disseminations, and the calculated δ^{34}S$_{py}$ value from a pyrite-bornite mixture support the idea that metal-bearing ^{34}S-rich fluids penetrated the Kupferschiefer through a network of fractures.

Conflicting models of genesis for Kupferschiefer Cu-Ag ores remain unresolved despite extensive studies during the past few decades. The controversy hinges largely on the timing of ore formation relative to the host rock and the source of the ore-forming sulphur.

Although the origin is split between syngenetic and diagenetic camps, it is now generally agreed that the non-ferrous metals must have come from a source external to the seawater in which the Kupferschiefer was deposited – most likely the underlying Rotliegendes continental clastics (Marowsky 1969; Wedepohl 1971; Rydzewski 1976; Haranczyk 1986; Jowett et al. 1987a). However, two views still exist regarding the origin of the ore-forming sulphur. Syngenetic advocates suggest that all sulphur was bacteriogenic and that ore formation was essentially coeval with shale deposition – metals came from the Rotliegendes and other continental deposits either by erosion or from below during transgression of the Zechstein sea (Marowsky 1969; Wedepohl 1971; Haranczyk 1986). Alternatively, sulphur may instead have been introduced with the metal-bearing fluids from an external source during later diagensis and mixed with the indigenous, largely bacteriogenic supply (Jowett et al. in press).

The issue of sulphur source may be resolved by comparing the isotopic signatures of the indigenous pyrite with that of the ore sulphides. Although background values exist for East and West Germany (Rösler et al. 1968; Marowsky 1969), diagnostic isotope data from barren shales in Poland are still lacking. This paper is an outgrowth of the work of Roth (1989) and represents part of an ongoing study to establish background δ^{34}S values of pyrite and marcasite sulphur obtained from regionally distributed samples of the Kupferschiefer and Zechstein Limestone (Ca1) in Poland (Fig. 1). In particular, it focusses on pyrite and marcasite nodules and their place in the diagenetic history.

The Kupferschiefer horizon

General geology

The Kupferschiefer is a carbonaceous black shale or marl at the base of the Late Permian marine-evaporite Zech-
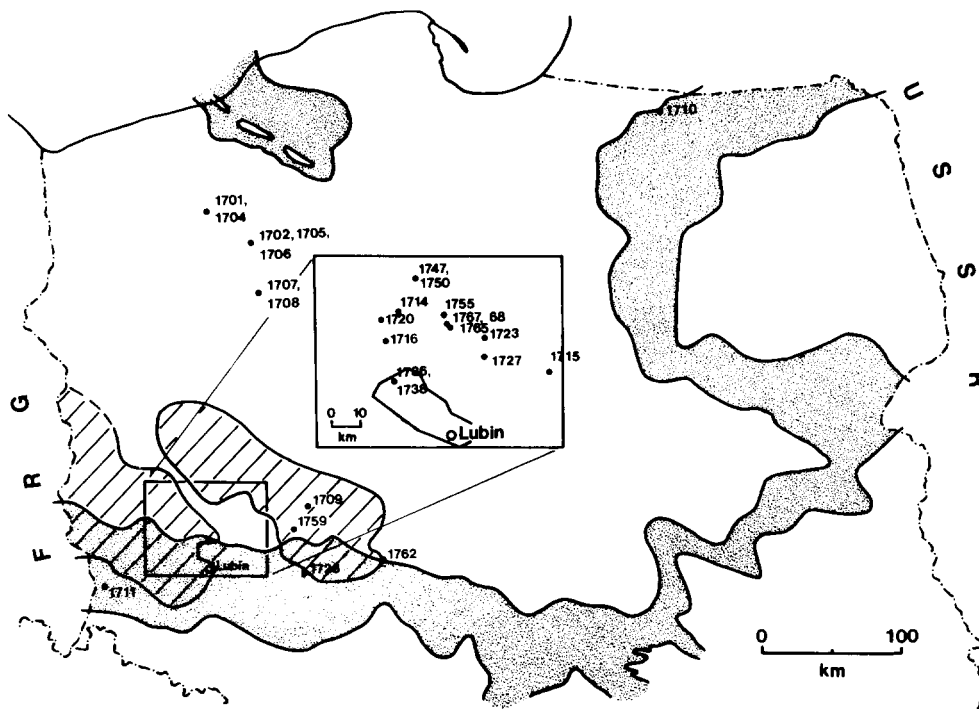

Fig. 1. Location map of Poland with samples used in this study. Inset is of Lubin ore district. Zechstein basin is outlined by stippled pattern which represents nearshore, lagoonal, and barrier environments. Interior of basin is the open-marine shelf sedimentation. Rote Fäule (hematite) and copper sulphide zones (striped areas in SW Poland) mark the centre of upwelling of oxidized, ore-forming fluids from the Rotliegendes redbeds

stein sequence (Fig. 2 a) and is typically gradational with the overlying Zechsteinkalk carbonate (Ca1) (Oszczepalski and Rydzewski 1987). The 80-cm thick unit covers the Early Permian Rotliegendes continental rift sequence of redbed sandstones and volcanics, the generally accepted source of the metals. Saline-lake conditions in the closed basins of the Rotliegendes allowed continental evaporites such as gypsum and rock salt to form (Brunstrom and Walmsley 1969). Natural gas (mainly CH_4) generated from Carboniferous coal beds (with the Kupferschiefer as a minor source) coexist with the ore deposits beneath the Zechstein seal (Peryt 1989). (For detailed reviews of the geologic and mineralogic framework of the Kupferschiefer and its ores, the reader is referred to Marowsky (1969), Rydzewski (1965, 1969, 1976), Wedepohl (1971), Oszczepalski (1986, 1989), Tomaszewski (1986a), Haranczyk (1986), and Jowett et al. (1987a).)

Depositional environment and original sulphur

The depositional environment of the Kupferschiefer is contentious and is considered to be one of two extremes: (1) deep-marine euxinic; or (2) shallow-marine euxinic or brackish-marine coal-swamp (a summary in Jowett et al. 1987a). Despite its narrow width, the unit can be divided into "more continental" lower and "more marine" upper parts (Tomaszewski 1986b). The preservation of abundant organic matter and the lack of benthonic fossils indicate that the environment was anoxic (Wedepohl 1971; Haranczyk 1986; Oszczepalski and Rydzewski 1987). Of importance to this paper is that the reducing environment preserved several types of sulphur: (1) bacteriogenic iron sulphide from seawater sulphate (Love 1962), (2) pyrite and marcasite nodules formed during diagenesis, (3) terrestrial-source organically bound sul-

phur, which is usually < 0.5% of the organic matter (Tissot and Welte 1984, p. 441), and (4) marine-source organically bound sulphur, often in significant amounts (> 1%, up to 6–7%). The diagenetic environment also affected original sulphur. Gypsum and anhydrite nodules formed in the basal Zechstein (Fig. 2 a) formed during the sabka environments of the upper Ca1 and the A1 (Peryt 1989) and may have contributed sulphur during late ore formation.

The ore deposits and sulphide-sulphur source

Rote Fäule and metal zoning

In East Germany and southwestern Poland, economic Kupferschiefer Cu-Ag mineralization crosscuts the stratigraphy at a low angle through the overlying carbonate, the shale, and the underlying sandstone (Fig. 2b) (Rydzewski 1976; Jowett et al. 1987a). Areas of intense sulphide mineralization surround zones of oxidation (Rote Fäule) in which the original organics and pyrite of the basal Zechstein have been oxidized and largely removed, leaving organic-poor, hematite-rich rock (Rentzsch 1974; Oszczepalski 1989). The Rote Fäule oxidation and thus the mineralization has been dated as mid-Triassic by paleomagnetic means (Jowett et al. 1987b), a late diagenetic timing supported by Püttmann and Gossel (1990).

The Rote Fäule zones have shallow dome shapes concave to underlying Rotliegendes redbeds, and are related to underlying basement highs and not to bounding faults or depositional margins (Jowett et al. 1987a). This geometry and the upward migration of the oxidized horizon suggests that the Rote Fäule and ore zones were formed by upwelling, oxidized fluids from the Rotliegendes redbeds during diagenesis (Rentzsch 1974; Jowett et al.
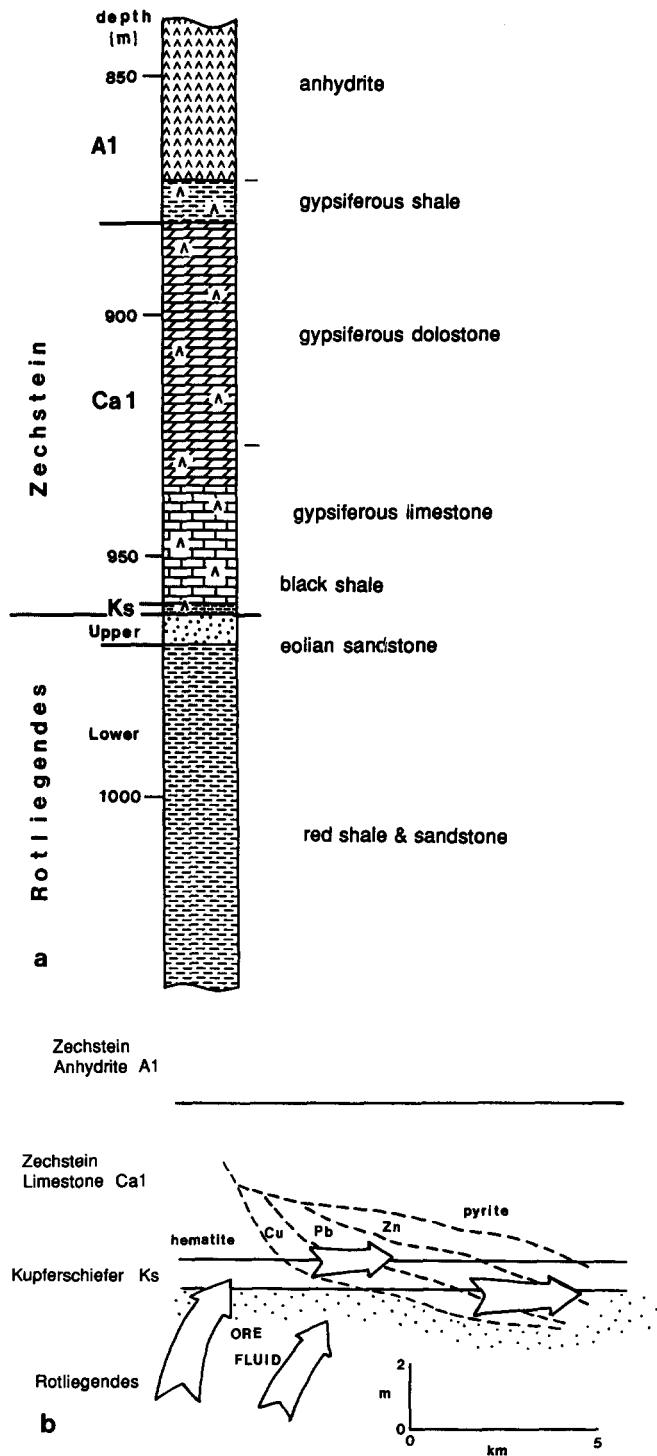
Fig. 2. a Lithologic section of the Permian sequence: example from the Koscielna Wies drill hole, North Sudetic Trough, SW Poland. The ore deposits occur in and adjacent to the Kupferschiefer (Ks) black shale horizon. b Schematic cross-section of the sulphide and oxide zones which indicate upwelling of oxidized ore-forming fluids from SO_4^{-2}-rich Rotliegendes redbeds to mix with the FeS_2-rich Kupferschiefer horizon

1987a) rather than from downward moving fluids as suggested by Davidson (1966).

The base metals are distinctly zoned laterally and vertically in successive belts of chalcocite, bornite, chalcopyrite, galena, and sphalerite around and above the Rote

Fäule (Fig. 2b), leaving a permanent record of the paleo-flow directions of the metal-, and likely sulphur-bearing solutions; i.e., upward to the Rote Fäule zone where the fluid has penetrated the shale and carbonate, then laterally basinward through the shale, carbonate, and sandstone, precipitating Cu-Pb-Zn sulphides along the way. No indigenous FeS_2 minerals remain in the high-grade chalcocite-bornite zones, but further out in the barren basin the dominant sulphides are pyrite and marcasite (Rydzewski 1969), likely the indigenous sulphides before ore formation.

Evidence of externally derived sulphur

Whereas the Rote Fäule and ore crosscut stratigraphy and depositional facies, pyrite is more facies-specific (Rydzewski 1969) suggesting that the Rote Fäule and ore zones are secondary alteration "imprints" on the original pyrite-rich basin. Sulphur isotopes of the ore zone in Poland (Jowett et al. in press) suggest that there was also an external source of sulphur (again probably from the Rotliegendes) superimposed on the original FeS_2 sulphur. The evidence used was that base-metal sulphides are ^{34}S-rich with respect to the presumed value of the precursor disseminated pyrite ($\delta^{34}S = -28$ to $-43‰$) found by Rösler et al. (1968) and Marowsky (1969) in East and West Germany. In addition, sulphides in veinlets are isotopically heavier than coeval sulphides disseminated in adjacent host rock, suggesting that ^{34}S-rich external sulphur, mixed with indigenous sulphur, infiltrated and mineralized the shale via a network of horizontal and vertical hydrofractures (Jowett et al. in press).

Potential sources of sulphur

In their preliminary work, Jowett et al. (in press) concluded that sulphur in the Kupferschiefer ore deposits could be a complex mixture of sulphur from various sources. Potential sources include: (1) direct replacement of indigenous pyrite and marcasite; (2) thermal degradation of S-bearing kerogen in the Kupferschiefer during hydrocarbon generation; (3) oxidation of S-bearing organic matter by oxidized ore fluids; (4) oxidation and hydrolysis of indigenous pyrite to SO_4^{-2} and H_2S; (5) thermochemical reduction of evaporite sulphate leached from the Rotliegendes; and (6) H_2S-rich hydrocarbon gases from underlying coalbearing beds considered to be the source of most Rotliegendes gases (Peryt 1989).

Because the original content of pyrite is high (3–4% by volume; Rydzewski 1969) and the volume of basal Zechstein oxidized to Rote Fäule is large, it is logical to suggest that most of the base-metal sulphur comes from indigenous pyrite and oxidized indigenous pyrite (sources 1 and 4 above). This premise is supported by the overall very negative $\delta^{34}S$ values in the ore zone. It is therefore necessary to establish the base $\delta^{34}S$ values of the indigenous pyrite in order to determine the source(s) of the ^{34}S-rich sulphur so evident in the ore veinlets and lenses (Jowett et al. in press).
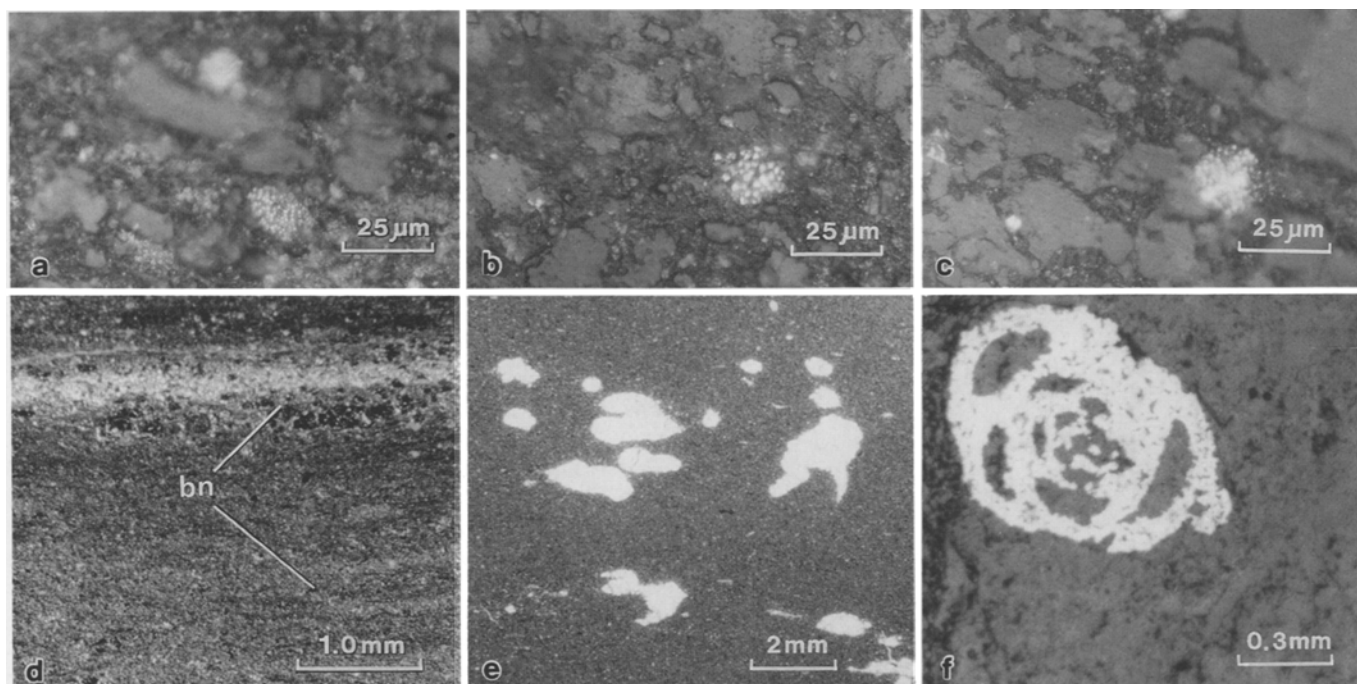
Fig. 3. a Framboidal pyrite in Kupferschiefer from Ksiazenice 1 (# 1762), 16 µm diameter $\partial^{34}S = -39.5\permil$. b Framboidal pyrite in Kupferschiefer from Wilkow 3 (# 1768), 18 µm diameter. The smaller framboid in the lower right corner is 5 microns across. $\partial^{34}S = -22.8\permil$. c Framboidal pyrite in Kupferschiefer from Grabkowo 1 (# 1759), 19 µm diameter. $\partial^{34}S = -40.6\permil$. d Horizontal bornite vein containing small grains of chalcocite in Kupfer-schiefer from Naratow (# 1723). Disseminated chalcocite-bornite is found in the shale away from the vein. $\partial^{34}S_{vein} = -30.8\permil$. $\partial^{34}S_{rock} = -35.7\permil$. e Pyrite nodules in Kupferschiefer from Grabkowo 1 (# 1759). $\partial^{34}S = -25.2\permil$. f Foraminifera replaced by chalcopyrite in the carbonate unit above the Kupferschiefer. From Czeszow (# 1725)

Petrography of the sulphide minerals

Sulphide mineralogy and textures of 76 polished sections provided by the Panstwowy Instytut Geologiczny were examined to aid in the selection of samples used in the sulphur isotope analyses.

Base-metal sulphides

Disseminations. Base-metal sulphides observed include chalcocite, bornite, chalcopyrite, covellite, galena, sphalerite, and minor digenite. They occur most often as fine, disseminated grains or as agglomerated lenses and streaks and compose 1-10% of the rock volume. In the Weissliegendes sandstone, sulphides fill the grain interstices and locally replace detrital grains and earlier carbonate cement.

Veinlets. Bornite, generally with chalcocite, and sphalerite with chalcopyrite form thin (0.1-2.0 mm) veinlets which are both concordant and discordant to the shale lamination (Fig. 3 d). Disseminated sulphides occur adjacent to the veinlets and tend to decrease in abundance outward from the veinlet.

Nodules. Base metal sulphides also occur locally as 3-20 mm nodules, e.g., #1711-Czerwona Woda; Fig. 4a, b), or may be massive like the galena in #1716-S394 from the Lubin ore district. Chalcopyrite and ga-lena locally replace detrital grains and foraminifera (#1725-Czeszow 6; Fig. 3f).

Pyrite and marcasite

Pyrite is the dominant "background" mineral in the Kupferschiefer away from base-metal mineralized zones, and is ubiquitous throughout the unit (Oszczepalski and Rydzewski 1987) except in very intensely mineralized zones. It occurs as nodules, finely disseminated subhedral grains, in veinlets, or as framboids and spheroids. Although isotope results of disseminated sulphides are not a focus of this paper, a brief description of their textures will help in understanding the relationship with the nodules and lenses.

Disseminations. "Disseminated" refers to small, subhedral to euhedral, randomly distributed grains, and is distinguished from "spheroidal" which refers to round grains of pyrite, generally 0.5-2.0 µm in size. Occasionally, larger spheroids (up to about 30 µm) are present. Clusters of small spheroids result in a "framboidal texture" (Fig. 3a-c), generally 5-30 µm across. Framboidal pyrite is characteristic of pyrite which formed early in the depositional history (Love 1962; Rydzewski 1969), and has been detected in several modern marine environments (Berner 1970, 1984; Goldhaber and Kaplan 1975; Boesen and Postma 1988).
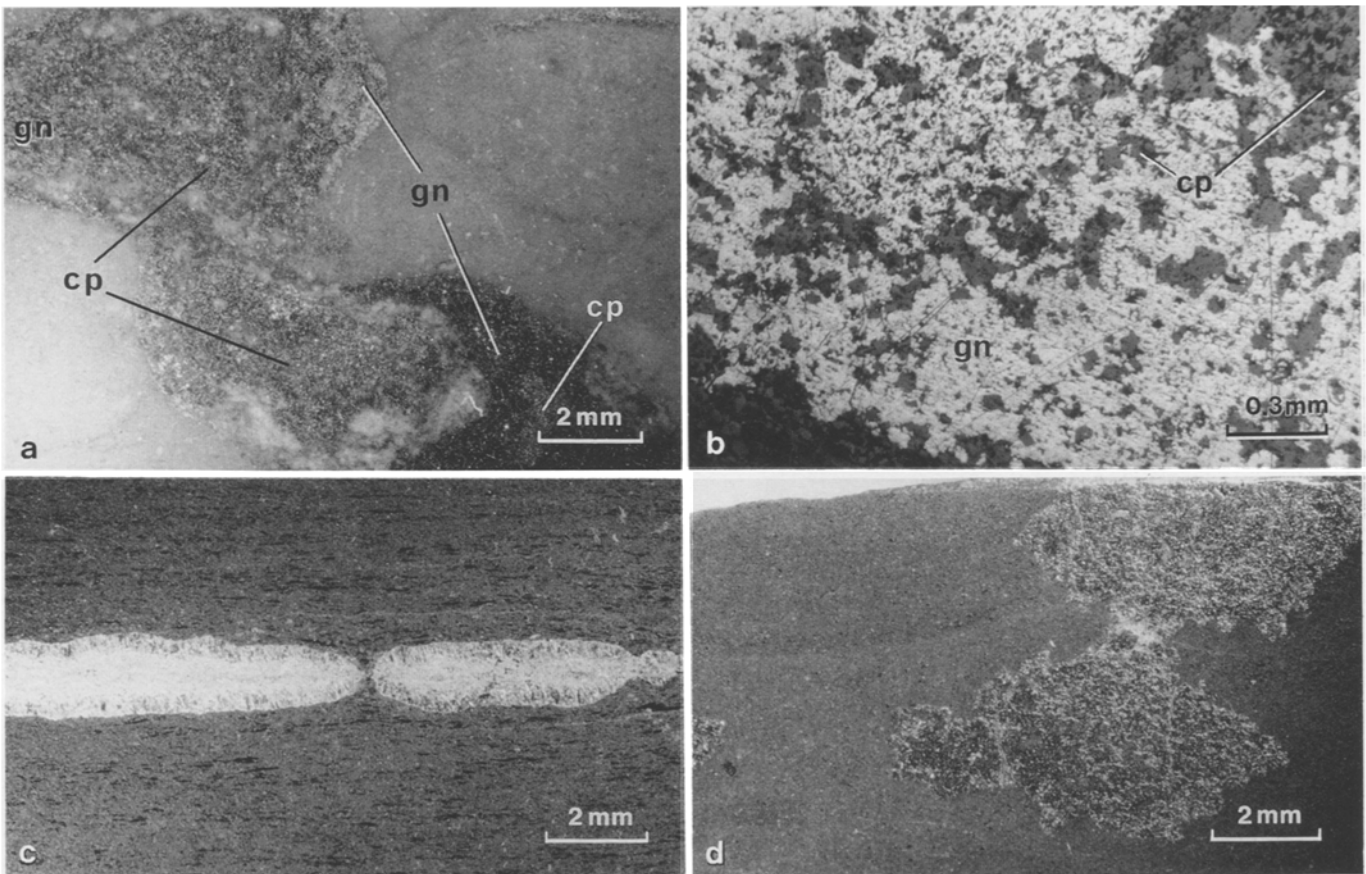
Fig. 4. a Galena (gn) and chalcopyrite (cp) nodule in the carbonate unit above the Kupferschiefer from Czerwona Woda (# 1711). $\partial^{34}S_{gn} = -21.1‰$. $\partial^{34}S_{cp} = -16.8‰$. This mineral pair yields a formation temperature of 94 °C or 61 °C if mixing is considered. b Close-up of nodule in (a). The lighter mineral is galena, the darker patches are chalcopyrite. c A nodule in the Kupferschiefer from Czaplinek IG1 (# 1701). The lathlike minerals on the rim of the nodule appear to be marcasite. The fine-grained material in the centre of the nodule is unidentified. $\partial^{34}S = -26.5‰$. d Pyrite nodule from the Kupferschiefer at Czaplinek IG2 (# 1706) which yielded a light $\partial^{34}S$ value of $-46.4‰$

Early formation of framboidal pyrite is supported by observations of pyrite spherules enclosed by, or imbedded within, later base-metal sulphides, usually bornite or chalcopyrite, a texture also observed by Rydzewski (1969). Locally, framboidal pyrite appears to be replaced by base-metal sulphides.

Nodules. Pyrite (cubic FeS_2) and its dimorph, marcasite (orthorhombic FeS_2), occur as 1–30 mm sized nodules in the shale, and locally in the sandstone. Marcasite is distinguished from pyrite by its whiter colour and distinctive elongate crystal habit. Its presence, usually mixed with pyrite, is confirmed by X-ray diffraction. Several nodules contain chalcopyrite or sphalerite, and one chalcopyrite nodule was sampled. The nodules are frequently elongate and parallel to the shale lamination (Fig. 4c), but are also irregular (Fig. 1 and Fig. 4d). Macroscopic pyrite nodules may be late diagenetic and not representative of the depositional or early diagenetic environment in which framboidal pyrite is formed (Bonnell and Anderson 1987).

Although the nodules appear solid in hand specimen, under microscopic examination, they are seen to contain substantial amounts of included host rock material and intergrown, possibly coeval, calcite (Table 1). The sul-

phides appear in cases to have simply infilled the interstices between the host rock grains. In some instances, framboidal pyrite is enclosed within the pyrite nodules (e.g., #1765-Wilkow 4) indicating that at least some of the nodules formed during alter diagenesis.

Sulphur isotopes of the sulphide minerals

Isotope fractionation processes

At low temperatures, sulphur isotopes fractionate very strongly between phases by bacterial activity (Ohmoto and Rye 1979). Bacteria preferentially reduce isotopically light (^{32}S-bearing) sulphate to sulphide, producing framboidal, bacteriogenic pyrite with the characteristic negative $\delta^{34}S$ values. Other fractionation processes (differential diffusion, preferential adsorption onto sediment grains, kinetics, etc.) are less important (Ohmoto and Rye 1979). Direct replacement of sulphides (e.g., chalcopyrite replacing pyrite by the addition of Cu alone) should not change the $\delta^{34}S$ value relative to the original sulphide (Ohmoto and Rye 1979).

Fractionation also occurs between different minerals which are in isotopic equilibrium with each other, and

Table 1. Descriptions and $\partial^{34}S$ values of FeS_2 nodules and lenses and one $CuFeS_2$ nodule in the Kupferschiefer black shale. py – pyrite; mc – marcasite; cp – chalcopyrite; sp – sphalerite; b – barite and s – pure sulphide preparation techniques; refer to figure 3 for relative ages

Sample	Mineralogy	Method	$\partial^{34}S$	L × W mm	Rel. Age	Host rock %	Calcite %
FeS$_2$							
1701.01	mc-py	b	−26.5	21 × 2	1	42	1
1702.03	py	s	−41.9	1 × 1		37	10
1704.01	py-mc	b	−39.5	20 × 5	5	44	0
1706.01	py	b	−46.4	4 × 2	2	8	12
1707.02	py(cp)	s	−30.9	12 × 3	5	18	38
1708.01	py	s	−46.4	9 × 5	3	7	22
1710.01	py	b	−26.9	5 × 2	5	49	5
1714.01	py(cp)	b	−38.5	4 × 2	2	37	8
1720.01	py(cp,sp)	s	−32.3	1 × 1		38	29
1727.01	py	s	−47.1	1.5 × 0.5	2	19	7
1747d.02	py	s	−39.7	3 × 0.5	2	43	9
1750.01	py(sp?)	s	−43.3	7 × 2.5	2	37	2
1750.02	py(sp)	b	−46.4	2 × 0.3	2	7	2
1755.01	py	s	−29.4	8 × 1	1	43	0
1759.01	py	b	−25.2	2.5 × 1	3	44	3
1765.01	py(cp,sp)	s	−51.9	7 × 5	5	12	31
1767.01	py(cp,sp)	s	−50.3	7 × 1	1	18	24
CuFeS$_2$							
1707.01	cp	s	−32.4	18 × 1.5	5	49	0

because the degree of fractionation is temperature-dependent, it can be used as a paleothermometer. In these cases, the $\delta^{34}S$ values will be such that pyrite > sphalerite > chalcopyrite > galena (Bachinski 1969).

Other factors controlling the isotopic signature

The supply of sulphate is important in determining final isotopic compositions under bacterial conditions (Schwarcz and Burnie 1973; Goldhaber and Kaplan 1975). Fractionation typically results in sulphide $\delta^{34}S$ values 40–60‰ lower than the seawater sulphate (Schwarcz and Burnie 1973). With a $\delta^{34}S$ value of Permian seawater sulphate of +11‰, the predicted background values for syngenetic sulphides should cluster betwen −29 and −49‰, which fits well with the main cluster of −28 to −43‰ found by Rösler et al. (1968) and Marowsky (1969) for disseminated Kupferschiefer pyrite.

Upon burial, the pore waters become isolated from the seawater, and as bacteria continually reduce the ^{32}S isotope preferentially, $\delta^{34}S$ values of both residual sulphate and sulphides become progressively higher. The expected increase in sulphide $\delta^{34}S$ values with depth are found in recent anoxic sediments (Schwarcz and Burnie 1973; Chanton et al. 1987) and later-formed nodules are typically heavier than presumably earlier disseminated pyrite (Bonnell and Anderson 1987 and this study). An alternate explanation would be that ^{34}S-rich sulphur was introduced to the Kupferschiefer from external sources during diagenesis, as suggested by Jowett et al. (in press) for the Lubin ore deposits.

If, however, the nodules have values similar to the framboidal pyrite, we can expect either that they were formed during early diagenesis, still within the influence

Table 2. Description and $\partial^{34}S$ values of base-metal sulphide nodules and lenses from the Kupferschiefer shale (Ks) and the Zechstein limestone carbonate (Ca1). cc – chalcocite; bn – bornite; cp – chalcopyrite; gn – galena; sp – sphalerite; py – pyrite; nod – nodule; diss – disseminated; mass – massive; vein – veinlet; b – barite and s – pure sulphide preparation

Sample	$\partial^{34}S$	Mineralogy	Type	Method	Host
1705.01	−33.9	cp-(bn)	diss	b	Ks
1711.01	−21.1	gn-((cp))	nod	s	Ca1
1711.02	−16.8	cp-((gn))	nod	s	Ca1
1716.01	−23.7	gn	mass	s	Ca1
1723.01	−30.8	bn-cc	vein	s	Ks
1723.02	−35.7	bn-cc	diss	b	Ks
1736.01	−34.2	cc	diss	b	Ks
1738.01	−31.3	cc	diss	b	Ks
1759.02	−40.6	py	diss	b	Ks

of seawater, or alternatively, that the nodule may contain a significant amount of framboidal pyrite.

$\delta^{34}S$ values in the Polish Kupferschiefer

Sampling, preparation, and analysis

A total of 22 samples were analyzed for $\delta^{34}S$. Most were taken from the Ks shale and the Ca1 carbonate, with one sample from the underlying sandstone-shale contact. Nodules and veinlets which could be drilled out as pure sulphide were reacted directly with cupric oxide to form SO_2 gas for analysis (Fritz et al. 1974) (method 's' in Tables 1 and 2). For disseminated sulphides, monominer-alic areas were identified and removed together with the rock matrix using a microdrill or were sliced off and crushed in a mortar. The sulphides were then oxidized to

sulphate using the nitric acid-bromine oxidation method (summarized in Drimmie 1988) and precipitated as barium sulphate by the addition of barium chloride. The $BaSO_4$ was then converted to SO_2 gas by reaction with vanadium pentaoxide and silica (Yanagisawa and Sakai 1983) and analyzed in the mass spectrometer (method 'b' in Tables 1 and 2).

Pyrite and marcasite nodules

The $\delta^{34}S$ values of 17 nodules and lenses measured fall in a broad range between -25.2 and $-51.9‰$ (Table 1). (The $\delta^{34}S$ value of the $CuFeS_2$ nodule also falls within this range.) The wide range cannot be explained on the basis of nodule composition since neither the $\delta^{34}S$ values of the two marcasite-rich nodules (-26.5 and $-39.6‰$) nor the chalcopyrite- and sphalerite-bearing nodules are distinctive. Neither is there any distinction between FeS_2 nodules in carbonate versus shale host rock, nor on size, shape, or texture of the nodule. There is no systematic change is isotope signature with proximity to the Lubin mines in southwest Poland which would otherwise suggest a general influence of ore-forming solutions.

Because $\delta^{34}S$ values may vary as pore fluids mature with diagenesis (Chanton et al. 1987), an attempt was made to correlate $\delta^{34}S$ values with relative ages of the nodules. Ages were estimated using host rock lamination: laminations wrapped around the nodule indicate substantial compaction and an early diagenetic timing (Fig. 5a), whereas laminations transecting the nodule indicate a later, post-compaction formation (Fig. 5c). However, there is no correlation between relative age and $\delta^{34}S$ value (Fig. 6), suggesting that the sulphur source remained equally variable through diagenesis.

Substantial host rock inclusions and calcite intergrowths exist in the FeS_2 nodules; up to 50% host rock and 40% calcite determined by point-counting. Although there is no correlation between $\delta^{34}S$ values and calcite intergrowths (Fig. 7a), there is a strong correlation with host rock inclusions (Fig. 7b). Because the sulphides were drilled and burned directly without chemical preparation, contamination by sulphate sulphur in the rock is a possible explanation. Ten nodules were re-sampled and either boiled in distilled water to remove sulphate or heated in dilute HCl solution to remove sulphate and calcite. This leaching treatment did not change the linear relationship seen in Fig. 7b, indicating that contamination is not a factor. Even assuming generous amounts of organically bound sulphur (50% host rock, 10% organics which contain 10% sulphur with $\delta^{34}S = 10‰$), organic sulphur is quantitatively insufficient to affect the isotopic composition of a nodule.

The relationship between $\delta^{34}S$ and host rock inclusions may indicate either: (1) that isotopic fractionation is somehow controlled by the mechanism that formed the nodules and that ^{34}S-rich sulphide was preferentially concentrated in the inclusions or in the nodule; (2) that inclusion-rich nodules are replacing anhydrite nodules with isotopically heavy sulphur; or (3) that the inclusions formed a interconnected latticework which allowed later,
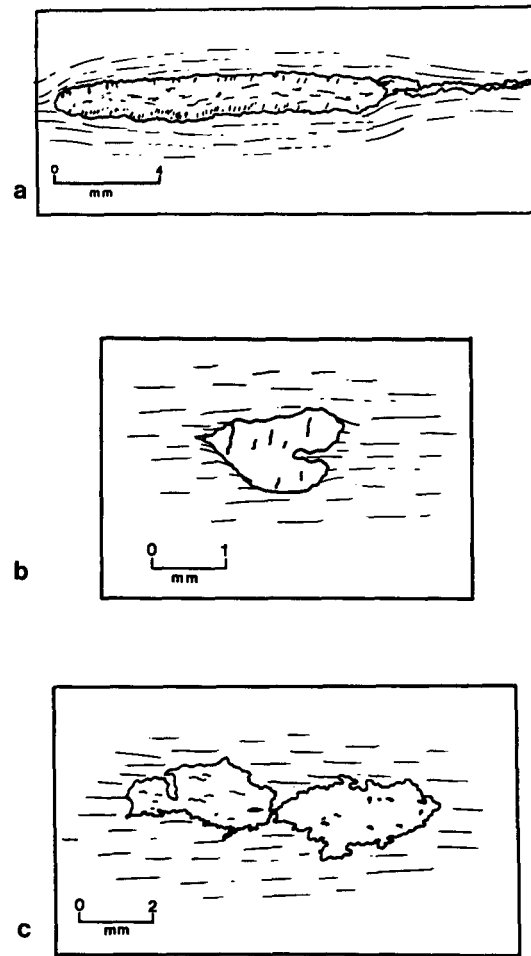

Fig. 5a–c. Nodules are categorized according to relative age based on the amount of compaction which occurred since formation: (a) early – all laminations wrap around nodule; (b) middle – some laminations wrap around, some pass through; and (c) late – all laminations pass through the nodule
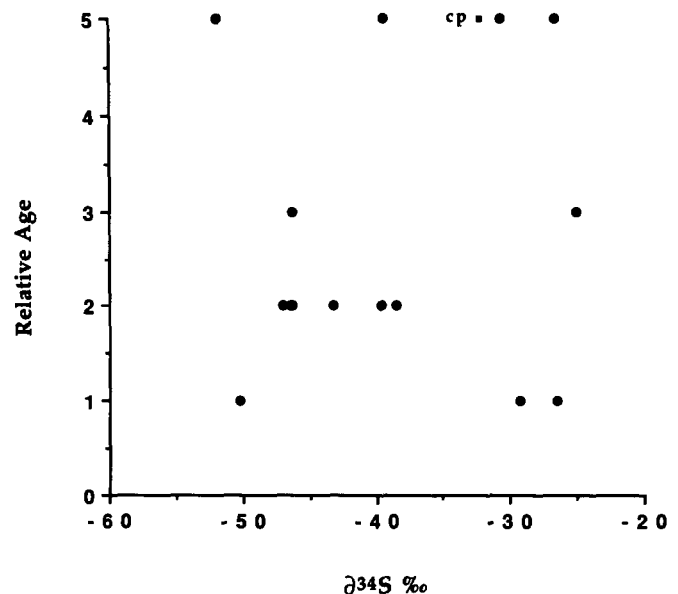

Fig. 6. No correlation exists between the $\delta^{34}S$ values of nodules and the relative age of the nodules based on compaction criteria. 1 – early; 5 – late (see Fig. 5)
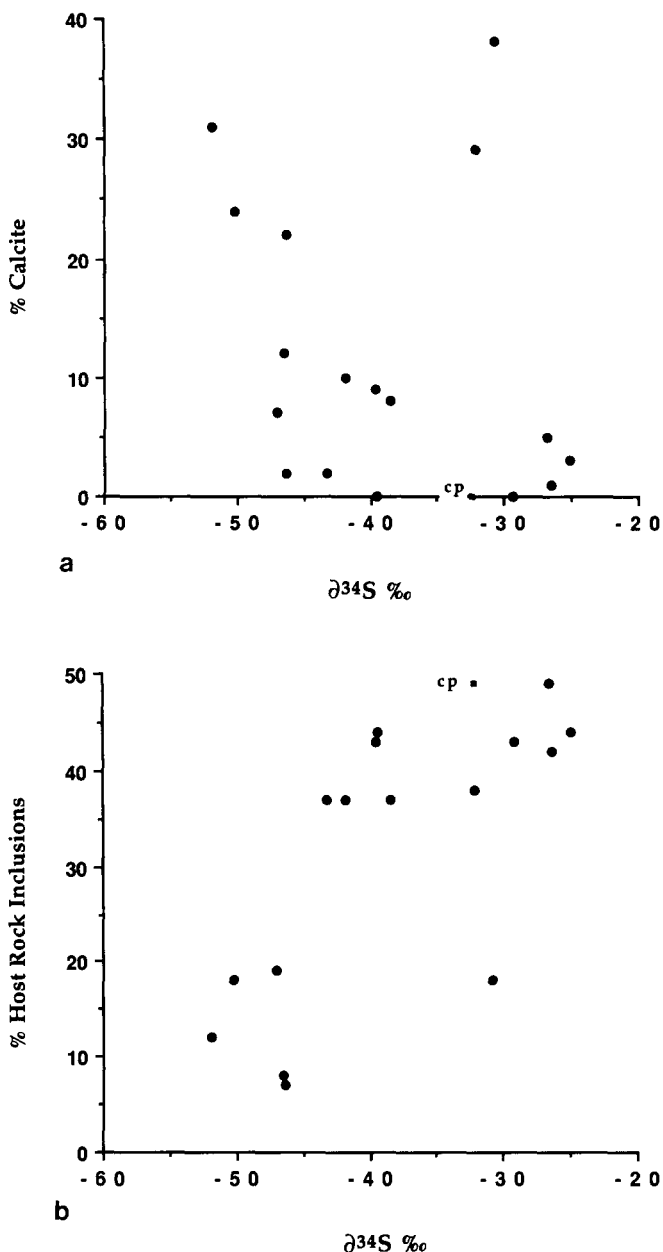
Fig. 7. a No correlation exists between $\partial^{34}S$ values of FeS_2 nodules and calcite inclusions contained in the nodules, determined by point-counting. b There is, however, a positive correlation with the proportion of host-rock inclusions incorporation in the nodules. This relation is not due to contamination by sulphate, but it is not clear what mechanism is responsible. It might be due to fractionation of ^{34}S-rich sulphur into the inclusions or nodule by some means during nodule formation, or the inclusions may have acted as an easy access route for later ^{34}S-rich fluids to infiltrate the nodule and replace the earlier FeS_2

^{34}S-rich fluids more complete access to the nodule interior, consequently replacing more of the earlier, ^{34}S-poor sulphide.

Base-metal nodules and veinlets

There is a marked difference between base-metal nodules in the Kupferschiefer (-30.8, -32.4‰) and those in the Zechstein Limestone (-16.8, -21.1, -23.7‰) (Tables 1 and 2), perhaps reflecting less indigenous pyrite (^{34}S-poor) in the limestome (thus a higher proportion of externally derived, ^{34}S-rich sulphur) compared to pyrite-rich Kupferschiefer.

Disseminated copper sulphides

The $\delta^{34}S$ values of four disseminated chalcocite, bornite and chalcopyrite samples from the Kupferschiefer ore horizon (Table 2) fall between -31.3 and -35.7‰, similar to the -32.0 to -35.5‰ range found by Jowett et al. (in press). Base-metal nodules and veinlets (-16.8 to -32‰) are significantly richer in ^{34}S than base-metal disseminations (-31.3 to -35.7‰), again suggesting that the disseminated sulphides contain a higher proportion of indigenous pyrite sulphur.

Isotopic mass balance and sulphur mixing

Comparison of bornite-(chalcocite) in a veinlet and adjacent disseminated bornite-(chalcocite) (#1723 Naratow 1; Fig. 3d) showed that the $\delta^{34}S$ of the vein material is 4.9‰ heavier than the disseminated sulphides, indicating a more ^{34}S-rich source for the veinlet material. Using similar observations, Jowett et al. (in press) suggested that the metalliferous fluids introduced ^{34}S-rich sulphur into the Kupferschiefer, using the fractures as their main conduits, and infiltrated the adjacent host rock to mix with indigenous pyrite. With this model, $\delta^{34}S$ values should decrease progressively away from the ore veinlets, as observed. Successive mineral zones parallel to the veinlets also support the idea of ore-fluid infiltration from the veinlets, with copper-rich minerals forming next to the veinlets and copper-poor minerals further away.

A simple mass-balance exercise was carried out on sample #1723 to test this infiltration-mixing hypothesis. Detailed point-counting showed that sample #1723.02 contained 7.5% (vol.) microscopic framboidal pyrite and 6.8% disseminated (but macroscopic) bornite-(chalcocite). Together the sulphides have a $\delta^{34}S$ value of -35.7‰. If we assume that the 4 sulphur atoms in the disseminated bornite were derived from the same sulphur source as veinlet #1723.01 ($\delta^{34}S = -30.8$‰) and there was minimal replacement of the framboids (none was seen), the calculated value for the 2 sulphurs in the indigenous pyrite is ~ -38‰, a very reasonable number for pyrite (Marowsky 1969; Haranczyk 1986). These calculations support the idea that the ore-bearing fluids, carrying ^{34}S-rich sulphur, traversed the Kupferschiefer shale through a network of open fractures and infiltrated adjacent shale as suggested above.

Sulphide minerals pairs and paleotemperatures

A nodule of intergrown, presumably coeval, chalcopyrite and galena from the Ca1 carbonate unit (#1711-Czerwona Woda; Fig. 4a, b) was carefully drilled to separate

chalcopyrite (with ~5% PbS) from galena (~10% $CuFeS_2$). The $\delta^{34}S$ values of the calcopyrite and galena separates are −16.8‰ and −21.1‰, respectively, yielding a formation temperature of 94 °C (Table 10-1 in Ohmoto and Rye 1979) assuming isotopic equilibrium. The $\delta^{34}S$ values recalculated using the chalcopyrite-galena mixtures (0.90−0.10 and 0.95−0.05) are −16.6‰ and −21.8‰, respectively, yielding a temperature of 61 °C. One mineral pair obtained by Jowett et al. (in press) indicated temperatures for a bornite-chalcopyrite veinlet to be 60−90 °C calibrated from Spar Lake fluid-inclusion temperatures (T. S. Hayes, pers. comm. 1989). These temperatures are reasonable for diagenetic deposits like this and fit in with the temperatures of <105 °C suggested by the orthorhombic (rather than the higher-temperature hexagonal) crystallography of veinlet chalcocite from the Lubin deposit (unpublished XRD data of E. C. Jowett 1989).

Nodular versus framboidal pyrite

In sample #1759-Grabkowo 1, the $\delta^{34}S$ value of the pyrite nodule (−25.2‰) is 15.4‰ heavier than adjacent framboidal pyrite (−40.6‰) (Tables 1 and 2). Similar results were obtained by Bonnell and Anderson (1987) who concluded that the disseminated pyrite probably formed during early diagenesis and the complex isotopic composition of the nodules may be explained by fluctuating sulphate supply and redox conditions during later diagenesis.

References

Bachinski, D.J.: Bond strength and sulphur isotopic fractionation in co-existing sulfides. Econ. Geol. 64:56−65 (1969)

Berner, R.A.: Sedimentary pyrite formation. Am. J. Sci. 268:1−23 (1970)

Berner, R.A.: Sedimentary pyrite formation: an update. Geochim. Cosmoch. Acta 48:605−615 (1984)

Boesen, C., Postma, D.: Pyrite formation in anoxic environments of the Baltic. Am. J. Sci. 288:575−603 (1988)

Bonnell, L.M., Anderson, T.F.: Sulfur isotopic variations in nodular and disseminated pyrite: Hole 603B. In: Initial Reports of the Deep Sea Drilling Project, v. 93(2), p. 1257−1262 (1987)

Brunstrom, R.G.W., Walmsley, P.J.: Permian evaporites in North Sea Basin. Am. Assoc. Petrol. Geol. Bull. 53:870−883 (1969)

Chanton, J.P., Martens, C.S., Goldhaber, M.B.: Biogeochemical cycling in an organic-rich coastal marine basin. 8. A sulphur isotopic budget balanced by differential diffusion across the sediment-water interface. Geoch. Cosmoch. Acta 51:1201−1208 (1987)

Davidson, C.F.: Some genetic relationships between ore deposits and evaporites. Trans. Inst. Min. Metall. 75:B216−225 (1966)

Drimmie, R.J.: Standard laboratory Methods. University of Waterloo, Isotope Lab Internal Report (1988)

Fritz, P., Drimmie, R.J., Nowicki, V.K.: Preparation of sulphur dioxide for mass spectrometer analyses by combustion of sulfides with copper oxide. Analy. Chem. 46:164−166 (1974)

Goldhaber, M.B., Kaplan, I.R.: Controls and consequences of sulfate reduction rates in recent marine sediments. Soil Sci. 119:42−55 (1975)

Haranczyk, C.: Zechstein copper-bearing shales in Poland: lagoonal environments and the sapropel model of genesis. In: Geology and Metallogeny of Copper Deposits, G.H. Friedrich et al., Eds., 461−476 (1986)

Jowett, E.C., Rydzewski, A., Jowett, R.J.: The Kupferschiefer Cu-Ag ore deposits in Poland: a re-appraisal of evidence of their origin and presentation of a new genetic model. Can. J. Earth Sci. 24:2016−2037 (1987a)

Jowett, E.C., Pearce, G.W., Rydzewski, A.: A mid-Triassic paleomagnetic age of the Kupferschiefer mineralization in Poland, based on a revised apparent polar wander path for Europe and Russia: Jour. Geophys. Res. B-92:581−498 (1987b)

Jowett, E.C., Rye, R.O., Rydzewski, A., Oszczepalski, S.: Isotopic evidence for the addition of sulphur during formation of the Kupferschiefer ore deposits in Poland. In: International Symposium Zechstein 1987, K.-C. Käding, J. Kulick, G. Richter-Bernburg, B. Schröder, Eds. Zentralbl. Geol. Paläont. I 1991 (in press)

Love, L.G.: Biogenic primary sulphide of the Permian Kupferschiefer and Marl Slate. Econ. Geol. 57:350−366 (1962)

Marowsky, G.: Schwefel-, Kohlenstoff-, und Sauerstoff-, Isotopenuntersuchungen am Kupferschiefer als Beitrag zur genetischen Deutung. Contr. Mineral. Petrol. 22:290−334 (1969)

Ohmoto, H., Rye, R.O.: Isotopes of sulphur and carbon. In: Geochemistry of Hydrothermal Ore Deposits, H.L. Barnes, Ed. pp. 509−567. New York: Wiley 1979

Oszczepalski, S.: On Zechstein copper shale lithofacies and paleoenvironments in SW Poland. In: The English Zechstein and Related Topics, G.M. Harwood, D.B. Smith, Eds. Geol. Soc. Lond. Spec. Publ. 22:171−182 (1986)

Oszczepalski, S.: Kupferschiefer in southwestern Poland: sedimentary environments, metal zoning, and ore controls. In: Sediment-Hosted Stratiform Copper Deposits, R.W. Boyle, A.C. Brown, E.C. Jowett, R.V. Kirkham, Eds. Geol. Assoc. Can. Spec. Paper 36, 571−600 (1989)

Oszczepalski, S., Rydzewski, A.: Paleogeography and sedimentary model of the Kupferschiefer in Poland. In: The Zechstein Facies in Europe, T.M. Peryt, Ed., pp. 189−205. Lectures Notes in Earth Sci. 10, Berlin-Heidelberg-New York: Springer 1987

Peryt, T.M.: Basal Zechstein in southwestern Poland: sedimentation, diagenesis, and gas accumulation. In: Sediment-Hosted Stratiform Copper Deposits, R.W. Boyle, A.C. Brown, E.C. Jowett, R.V. Kirkham, Eds. Geol. Assoc. Can. Spec. Paper 36, 601−625 (1989)

Püttmann, W., Gossel, W.: The Permian Kupferschiefer of southwest Poland: a geochemical trap for migrating, metal-bearing solutions. Appl. Geochem. 5:227−235 (1990)

Rentzsch, J.: The Kupferschiefer in comparison with the deposits of the Zambian Copperbelt. In: Gisements stratiformes et provinces cuprifères, P. Bartholomé, Ed. Soc. géol. Belg., 395−418 (1974)

Rösler, H.J., Pilot, J., Harzer, D., Krüger, P.: Isotopengeochemische Untersuchungen (O,S,C) an Salinar- und Sapropelsedimenten Mitteleuropas. 23rd IGC Proc. 6, 89−100 (1968)

Roth, T.: Sulphur Isotope Studies in the Polish Kupferschiefer. 67 p. Hon. B.Sc. Thesis, University of Waterloo, Canada (1989)

Rydzewski, A.: Die Petrographie and die Vererzung der Zechsteinsedimente in der Vorsudetischen Monoklinale und der Periklinale von Zary (V.R. Polen). In: Kupferschiefer und „Rote Fäule". Freib. Forsch. C193:157−167 (1965)

Rydzewski, A.: Occurrence and genesis of pyrite in the Zechstein rocks of the Fore-Sudetic Monocline (Polish). Kwart. Geol. 13:811–820 (1969)

Rydzewski, A.: Genesis of the Lower Zechstein polymetallic mineralization (Polish). Prz. Geol. 24:176–181 (1976)

Schwarcz, H.P., Burnie, S.W.: Influence of sedimentary environments on sulfur isotope ratios: a review. Mineral. Deposita 8:264–277 (1973)

Tissot, B.P., Welte, D.H.: Petroleum Formation and Occurrence (2nd Ed.). 699 p., Berlin-Heidelberg-New York: Springer 1984

Tomaszewski, J.B.: Comments on the genesis and structure of the copper-polymetallic ore deposit of the Foresudetic Monocline, SW Poland. In: The English Zechstein and Related Topics, G.M. Harwood, D.B. Smith, Eds. Geol. Soc. Lond. Spec. Publ. 22, 183–194 (1986a)

Tomaszewski, J.B.: Sedimentary environments of the lowest Zechstein sediments in the Lubin Region, SW Poland. In: The English Zechstein and Related Topics, G.M. Harwood, D.B. Smith, Eds. Geol. Soc. Lond. Spec. Publ. 22, 195–201 (1986b)

Wedepohl, K.H.: "Kupferschiefer" as a prototype of syngenetic sedimentary ore deposits. Soc. Mining Geol. Jap., IMA-IAGOD Spec. Issue 3, 263–273 (1971)

Yanagisawa, F., Sakai, H.: Thermal decomposition of barium sulfate-vanadium pentaoxide-silica glass mixtures for preparation of sulfur dioxide in sulfur isotope ratio measurements. Analy. Chem. 55:985–987 (1983)