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Formation of stratiform sulfide mineralizations in the Lower Muschelkalk (Middle Triassic) of Southwestern Germany and Northern Switzerland: constraints from sulfur isotope data

by *Beda A. Hofmann*¹ and *Kurt v. Gehlen*²

Abstract

Stratiform, disseminated Pb-Zn-Cu-As sulfide mineralizations occur in biotitic carbonates, siltstones and shales of the shallow-marine Lower Muschelkalk east and south of the Schwarzwald (Black Forest). To clarify the conditions of formation, variations of sulfur isotope ratios of sulfides and sulfates were investigated. A high variability of sulfide $\delta^{34}\text{S}$, the presence of sulfates with $\delta^{34}\text{S}$ more positive than in possible source evaporites, and a slightly positive correlation of $\delta^{34}\text{S}$ of galenite and sphalerite with the intensity of mineralization indicate that sulfides were formed by in-situ sulfate reduction during late diagenesis. The scatter of sulfide $\delta^{34}\text{S}$ values and sulfide-sulfate fractionations of up to 46‰ indicate that sulfate reduction was microbially mediated although thermochemical sulfate reduction cannot be ruled out in the absence of precise data on the temperature history of the Lower Muschelkalk and of the timing of sulfide mineral formation.

Keywords: sulfur isotopes, Pb-Zn-Cu-As mineralization, diagenesis, Triassic, Muschelkalk, sulfate reduction, Germany, Switzerland.

Zusammenfassung

Zur Klärung der Genese von stratiformen Pb-Zn-Cu-As-Sulfid-Mineralisationen in biotitischen Karbonathorizonten, Silt- und Tonsteinen des Unteren Muschelkalks (Mittlere Trias) in Südwestdeutschland und in der Nordschweiz wurden an Sulfiden und Sulfaten Schwefelisotopenmessungen durchgeführt. Eine hohe Variabilität von $\delta^{34}\text{S}$ in Sulfiden, gegenüber Evaporiten an ^{34}S angereicherte Sulfate sowie eine positive Korrelation zwischen der Intensität der Mineralisation und den $\delta^{34}\text{S}$ -Werten von Galenit und Sphalerit deuten darauf hin, dass die Sulfide durch intraformationale, spätdiagenetische Sulfatreduktion gebildet wurden. Die Variabilität der $\delta^{34}\text{S}$ -Werte sowie Sulfid-Sulfat-Fraktionierungen von bis zu 46‰ sprechen für mikrobielle Sulfatreduktion. Thermochemische Sulfatreduktion kann jedoch angesichts der Unsicherheiten in der Temperaturgeschichte des Unteren Muschelkalkes und im Alter der Sulfidbildung nicht ausgeschlossen werden.

Introduction

The Middle Triassic Lower Muschelkalk of Southwest Germany and Northern Switzerland is a 50 to 80 m thick, marine sequence dominated by grey to black shales with interbedded biotitic carbonates and siltstones (SCHWARZ, 1975; HOFMANN, 1985). Shales contain up to 1.3% organic carbon. Carbonates are partially dolomitized, with dolo-

mitization increasing from top to base and from south to north. The Muschelkalk is underlain by the Lower Triassic Buntsandstein, a clastic continental redbed sequence, and overlain by the evaporitic Middle Muschelkalk, comprising shale, dolomite, anhydrite/gypsum and locally halite.

Disseminated sulfides of Pb, Zn, Cu and As commonly occur in the Lower Muschelkalk of Northern Switzerland and Southwest Germany

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(SCHALCH, 1873, HOFMANN, 1980, 1989; see Fig. 1). Within the stratigraphic sequence from the Carboniferous to the Tertiary, the Lower Muschelkalk shows by far the most intense and laterally most widespread mineralizations in the area un-

der consideration (HOFMANN, 1989). The ore mineral assemblage comprises galenite, sphalerite, chalcopyrite, pyrite, marcasite, native arsenic, bornite, tennantite, bismuthinite, bravoite, covellite, luzonite and realgar. Two major types of ga-

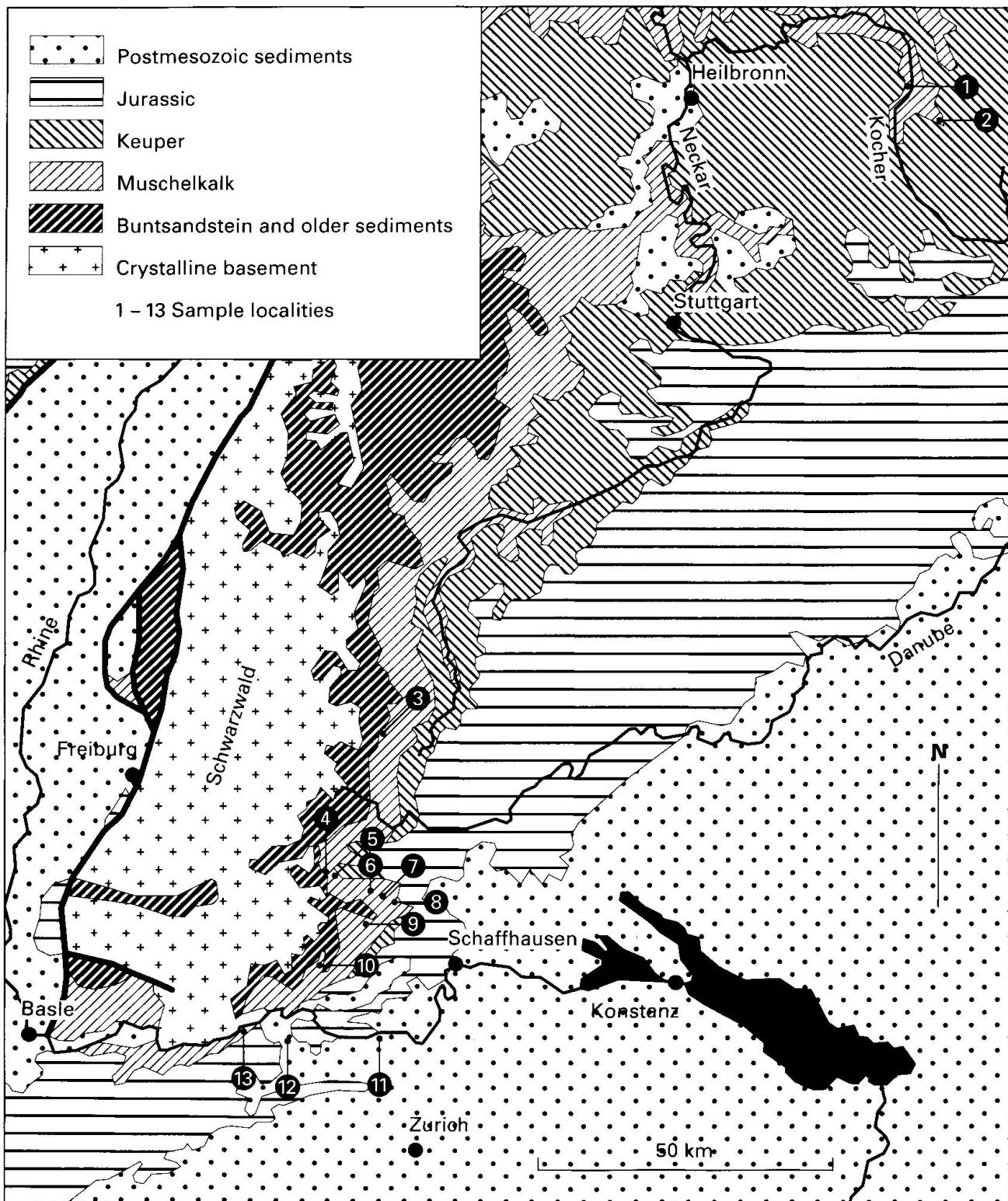


Fig. 1 Simplified geological map with sample localities. Locality numbers refer to table 1.

len, sphalerite and tennantite can be distinguished: Type I is spongy with $\geq 50\%$ inclusions of host minerals. Sphalerite of type I is Fe-poor ($\leq 0.5\%$) but partially Cd-rich (up to 1.3% Cd). Type II is free of inclusions, partially idiomorphic and represents open-space fillings. Sphalerite of type II contains up to 3% of either Cd or Fe, but

never both. Textural evidence indicates that type I minerals are older than type II minerals.

The most intense mineralizations are bound to ≤ 50 cm thick, biotitic carbonate horizons and to a lesser extent to siltstones. In these horizons, ore minerals are found as irregular disseminations and filling secondary porosity created by dissolu-

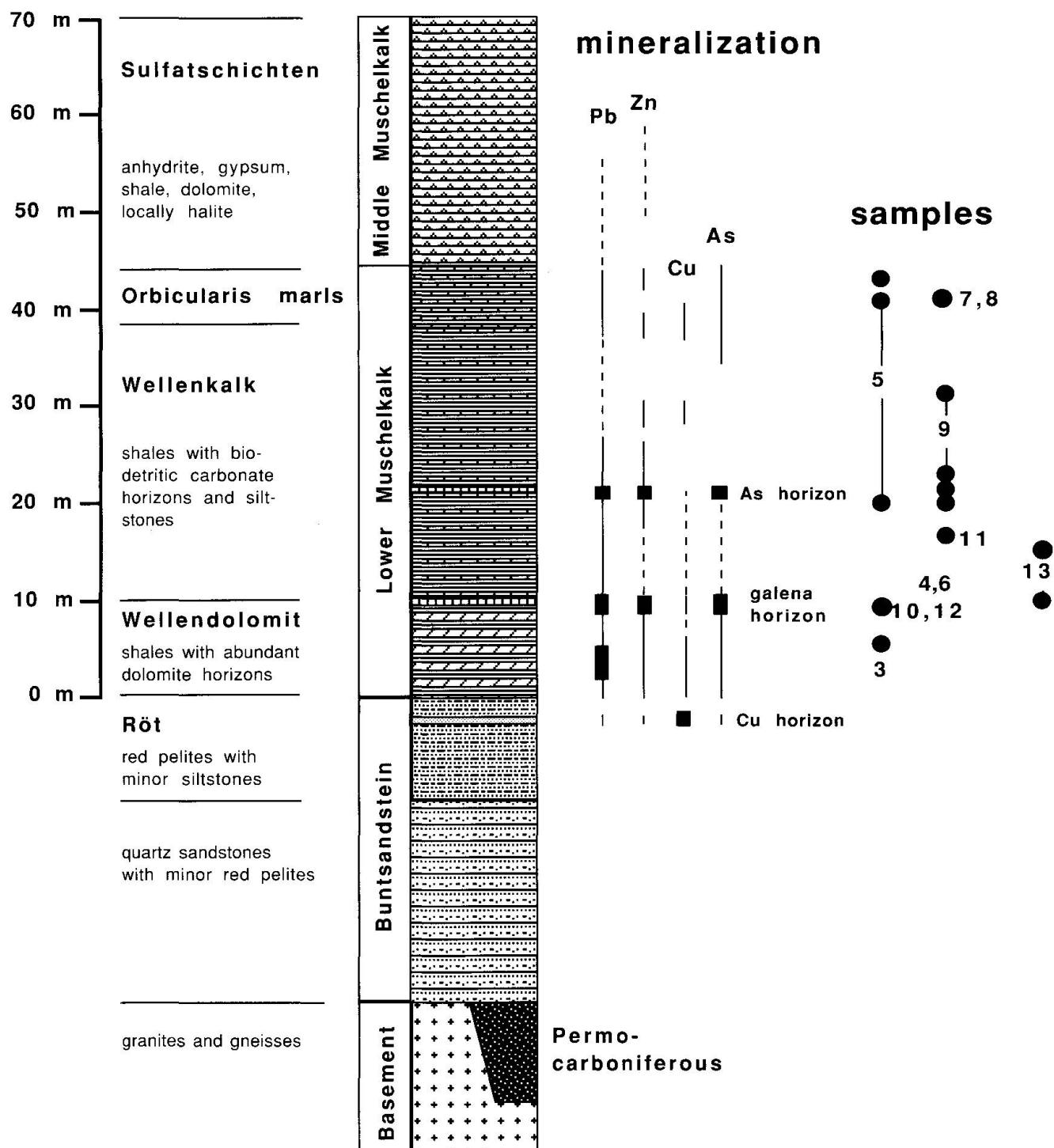


Fig. 2 Simplified stratigraphic column showing mineralized horizons and stratigraphic position of sample localities. Locality numbers refer to table 1.

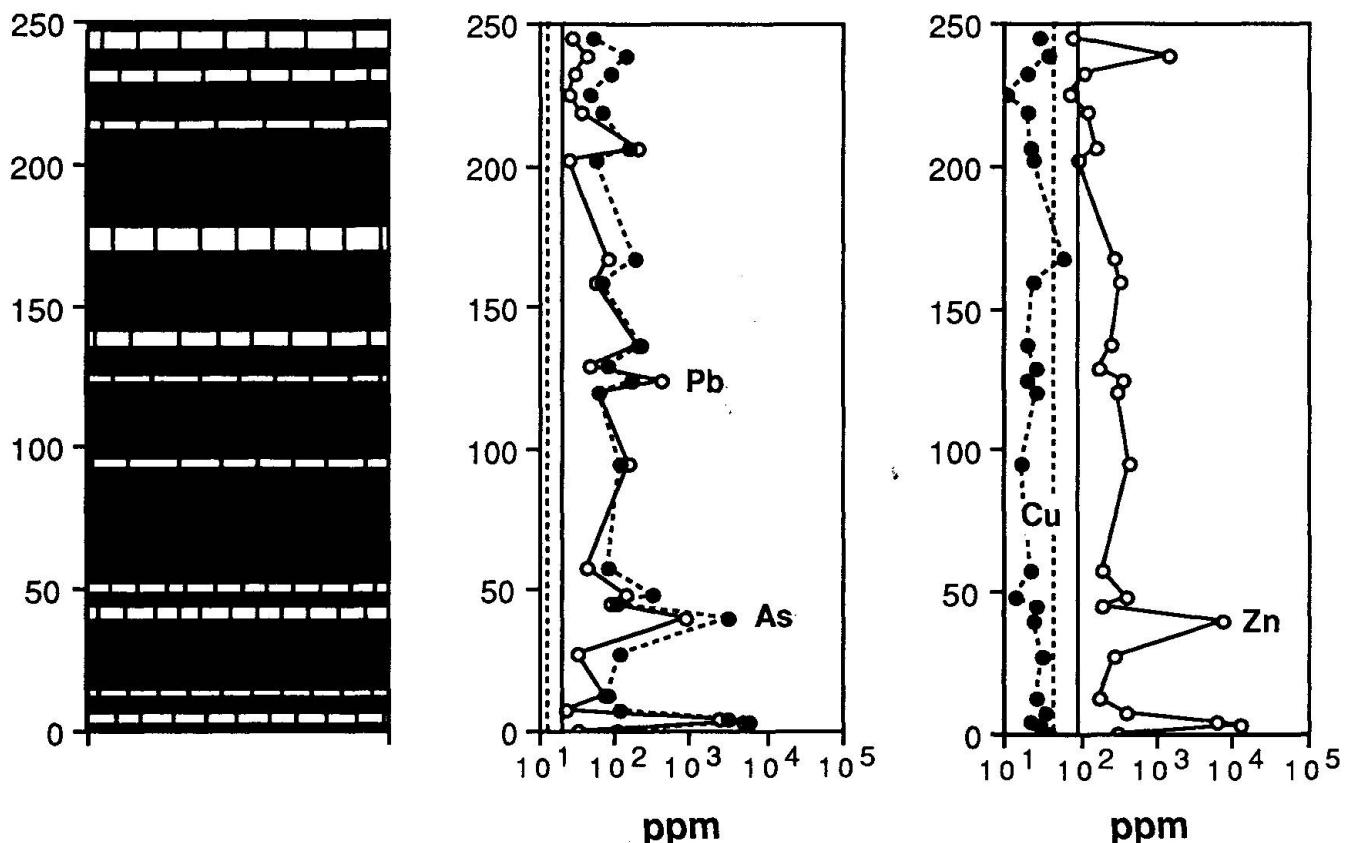


Fig. 3 Typical mineralized profile (250 cm vertical extent) in the Lower Muschelkalk As horizon (lowermost carbonate bed) and enclosing shales in the Upper Wutach Valley (locality 5). Left column: simplified lithology consisting of thin carbonate beds in shale. Right columns: contents of Pb, As, Cu and Zn. Vertical lines (dashed and continuous) are average shale values after TUREKIAN and WEDEPOHL (1961): Pb 20 ppm, As 13 ppm, Cu 45 ppm, Zn 95 ppm. Data from HOFMANN (1985).

tion of fossil fragments. Some of these mineralized horizons, also known as "Bleiglanzbänke", can be traced over areas of up to 2000 km² with Pb concentrations of 0.1 to 3% across a thickness of 5 to 20 cm, thus representing significant geochemical anomalies. Although the highest concentrations of Pb, Zn, Cu and As are found in carbonate horizons, the shales that dominate the sequence also display anomalous concentrations of Pb, Zn and As but not of Cu. Ore minerals in the shales are present as partial replacements of early diagenetic pyrite, as irregular grains and as highly deformed cuboctahedric galenites ("gallenite dollars"). Figure 2 shows the vertical distribution of mineralized horizons in the Lower Muschelkalk. A typical mineralized profile is shown in figure 3. The carbonate affinity of the mineralizations is also demonstrated in figure 4, from which it is evident that Pb and As values > 100 ppm and Zn values > 500 ppm pertain to carbonate rich samples.

The mineralization in carbonate horizons is probably due to diagenetic remobilization of elements from adjoining shales that were enriched in these metals as a result of syngenetic processes

(HOFMANN, 1985, 1989). The time of sulfide crystallization is unknown but it certainly occurred after partial lithification and is at least partially contemporaneous with dolomitization. Late diagenetic sulfide mineral precipitation occurred from a saline fluid that also introduced sulfate into the Lower Muschelkalk as indicated by the presence of late diagenetic sulfates associated with sulfides. An increase of pH₂S during ore mineral crystallization is indicated by decreasing Fe contents in the younger layers of strongly zoned sphalerites (HOFMANN, 1989).

The burial and temperature history of the mineralized strata of the Lower Muschelkalk is not very well constrained. The maximum overburden during the Tertiary can be estimated as 700 to 1000 m in the Wutach area east of the Black Forest and up to 2000 m in Northern Switzerland. The fact that the less deeply buried mineralizations in the Wutach area are very similar to those in Northern Switzerland could be an indication that mineralization occurred prior to maximum burial in the Tertiary, as long as the depth of burial was 1 km or less. Modelling of vitrinite

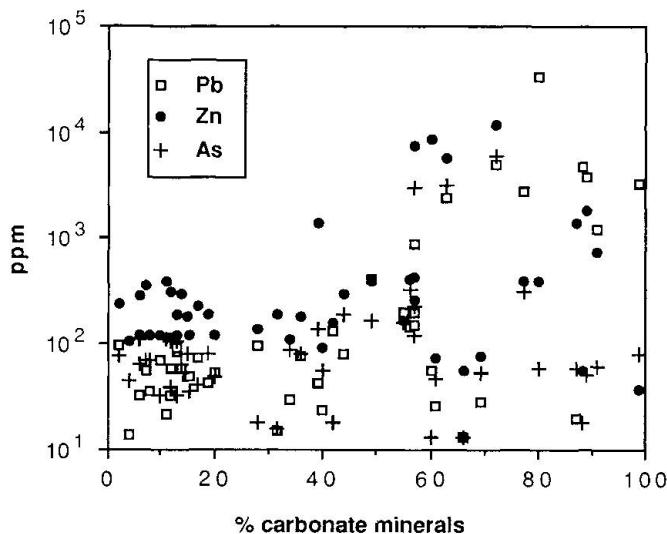


Fig. 4 Plot of Pb, Zn and As concentrations versus carbonate content (calcite + dolomite) for samples of the Lower Muschelkalk. Data from HOFMANN (1985).

reflectance and fluid inclusion data from deep boreholes in Northern Switzerland indicate geothermal gradients ranging from 37 °/km during the Mesozoic (WOLF and HAGEMANN, 1987) to 60 °/km during the Miocene (MULLIS, 1987). Present-day geothermal gradients in the area range from 30 to 60 °/km, the former value being more typical (RYBACH et al., 1987). Considering all uncertainties and assuming a depth of burial of 1 to 2 km and a mean annual surface temperature of 20 °C in the Mesozoic and Tertiary, formation temperatures in the Lower Muschelkalk might have ranged from 50 to 140 °C during mineralization. Adding to the uncertainty, a regional thermal event of Mesozoic age is indicated by radiometric dating of minerals from hydrothermal veins in the Schwarzwald (e.g. MERTZ, 1987) and Northern Switzerland (PETERS et al., 1989).

Comparable mineralizations in Triassic rocks in Europe are known from the Muschelkalk and Keuper of Southern Germany (BROCKAMP, 1973; SCHWEIZER, 1979; SCHMID, 1981), East Germany (KÜHN, 1976, 1991), Northern Germany (MEMPEL, 1962), the Netherlands (HOFMANN, 1985) and East Greenland (THOMASSEN et al., 1982). A possible relation to sandstone-hosted Pb-Zn mineralizations is indicated by the occurrence of Cu-Pb-Zn mineralizations in the Buntsandstein below the Muschelkalk in Northern Switzerland (HOFMANN, 1989).

Distinctly different, partly economic Pb-Zn mineralizations of the Mississippi-Valley and Alpine-type are also common in the Triassic of Central Europe, especially in Upper Silesia, Poland (GALKIEWICZ, 1967; GRUSZCZYK, 1967) and the

Eastern Alps (MAUCHER and SCHNEIDER, 1967). Alpine-type mineralizations exhibit light sulfur isotopes indicating bacterial sulfate reduction in a system at least partially open to the ocean (SCHROLL et al., 1983).

The origin of the mineralizations described here is directly related to the origin of the sulfide sulfur. We therefore investigated the sulfur isotopic composition of a variety of sulfide minerals and associated sulfates. Possible sulfur sources include late diagenetic bacterial sulfate reduction (BSR), late diagenetic thermochemical sulfate reduction (TSR), maturation of S-rich organic compounds during late diagenesis, remobilization of sulfides from early diagenetic sulfides in the shales, and introduction of sulfides from an extraformational source.

Samples and methods

The provenance of the investigated samples is shown in table 1 and figure 1. Samples are both from outcrops and from drillcores (No. 11, 12). Sulfides and baryte were separated from carbonate rocks by treatment with dilute hydrochloric acid leaving the sulfides largely unattacked. Sulfides from shales were mechanically isolated by repeated drying and dispersion in water. Sulfide concentrates were further purified by sieving, panning, hand picking and magnetic separation (chalcopyrite-pyrite). The analyzed sulfide mineral fractions were at least 99% pure with two exceptions noted in table 1.

Sulfur isotope ratios were measured in the laboratory of Prof. J. Hoefs in Göttingen using standard methods explained elsewhere (e.g. RICKE, 1964). All results are presented in the per mil notation relative to the Cañon Diablo troilite standard (CDT).

Results

Results are presented in table 1 where samples from the same locality are grouped together. Also presented are data for sulfide minerals from the Lower Muschelkalk of the Böttstein drillhole taken from PEARSON et al. (1991). These samples were originally separated by one of us (B.A.H.) using the same methods as for the present study. The samples (Fig. 5) show a large spread in $\delta^{34}\text{S}$ values, ranging from -36 to -1.8‰ for sulfides and from -2.1 to +24.6‰ for sulfates. With the exception of two clearly early diagenetic pyrites (-36.0, -33.0‰), the sulfides range from -23.7 to -1.8‰ (mean $-13.1 \pm 6.5\text{‰}$).

Tab. 1 Sample localities and sulfur isotope data (compare Figs 1 and 2)

		$\delta^{34}\text{S}$
1) Braunsbach, Kocher Valley		
dolomite	early diagenetic pyrite chalcopyrite	-35.99 -13.01
2) Eberthal N Dörrenzimmern		
micritic limestone	sphalerite	-13.29
3) Clay pit N Villingen		
coarsely crystalline dolomite	tennantite	-19.50
4) E Schattenmühle, Wutach Valley		
coarsely crystalline dolomite (galena horizon)	galena	-12.44
5) Obere Dietfurt, Wutach Valley		
"As horizon" (+ 0 m)	galena (+ native As) sphalerite	-12.25 -17.59
biotitic limestone, mu3 (+ 22 m) (fissure minerals)	barite	+24.43
marl (+ 24 m)	galena early diagenetic pyrite sphalerite band	-21.92 -7.60 -13.85
6) Lausheim		
coarsely crystalline dolomite (galena layer)	galena	-1.76
7) NW Grimmelshofen		
biotitic limestone, Orbicularis marls (fissure minerals)	galena barite	-22.02 +18.07
8) Weiltunnel, Grimmelshofen		
limestone, Orbicularis marls	galena sphalerite barite	-8.66 -5.64 +15.85
9) Stühlingen, Wutach Valley		
"As horizon" (+ 0 m)	galena (+ native As) sphalerite early diagenetic pyrite anhydrite in vug galena ("galena-dollars") galena barite	-21.50 -18.12 -18.99 +24.60 -23.73 -1.94 +0.94
biotitic limestone (+ 0.4 m) shale (+ 1 m) Spiriferina bed (+ 10 m)		
10) Ühlingen		
biotitic limestone (galena horizon)	galena	-9.63
11) Weiach drillhole, 966.6 m		
siltstone	sphalerite	-4.31
12) Böttstein drillhole, 301.0 m (PEARSON et al., 1991)		
biotitic limestone (galena horizon)	galena sphalerite early diagenetic pyrite	-8.27 -7.73 -33.05
13) Etzgen		
biotitic limestone (galena horizon)	galena	-11.42
biotitic limestone (+ 4 m)	galena sphalerite barite	-17.92 -14.79 -2.11

The sulfates form three groups: Two baryte samples are close to $\delta^{34}\text{S} = 0\text{\textperthousand}$, two are slightly lighter than or close to the typical European

Muschelkalk sulfate values of +17 to +21‰ (PILOT et al., 1972; PEARSON et al., 1991), and two are significantly heavier than Muschelkalk sulfate

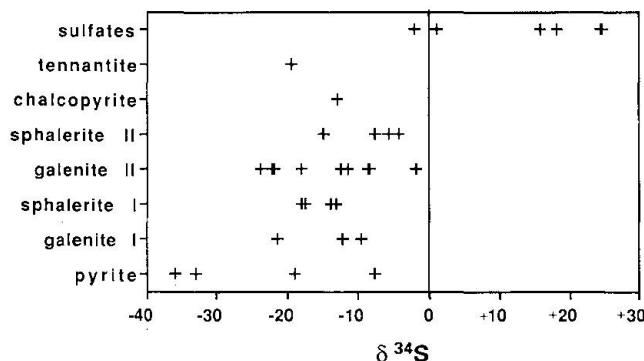


Fig. 5 Plot of $\delta^{34}\text{S}$ values for individual minerals from the Lower Muschelkalk.

(+24.4, +24.6‰). Two possibly cogenetic pairs of galenite and baryte were analyzed. These two pairs yielded baryte-galenite $\delta^{34}\text{S}$ fractionations of 40 and 46‰, respectively. In another occurrence of baryte plus galena, the two minerals are most probably not cogenetic.

Sulfur isotopes of the spongy type I sphalerites tend to be slightly lighter than type II sphalerites (Fig. 5), type I averaging $\delta^{34}\text{S} = -15.7 \pm 2.5\text{‰}$ and type II $-8.1 \pm 4.7\text{‰}$.

The $\delta^{34}\text{S}$ values of galenites and sphalerites seem to be slightly positively correlated ($r = +0.45$) with the total sulfide content (Fig. 6): More strongly mineralized samples seem to be characterized by heavier sulfur.

Of five sphalerite-galena pairs, three pairs yield a PbS which is $3.18 \pm 0.18\text{‰}$ lighter than ZnS, in one pair PbS is 0.54‰ lighter than ZnS. Only in one case, ZnS is lighter than PbS by 5.3‰. Assuming equilibrium fractionation, the three

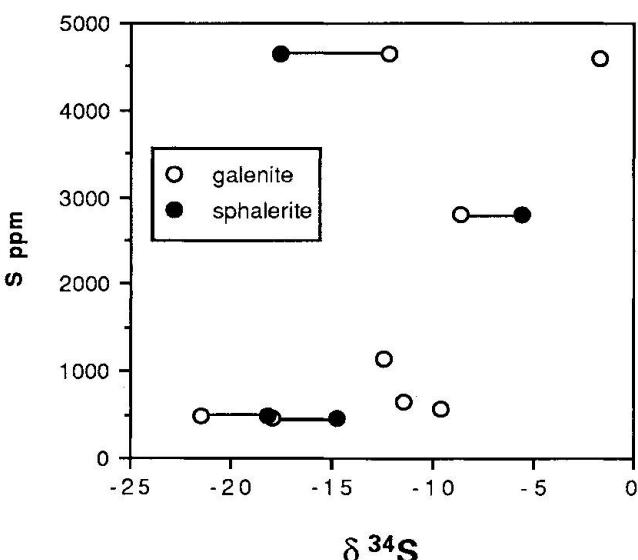


Fig. 6 Plot of $\delta^{34}\text{S}$ of galenite and sphalerite versus sulfide sulfur concentration.

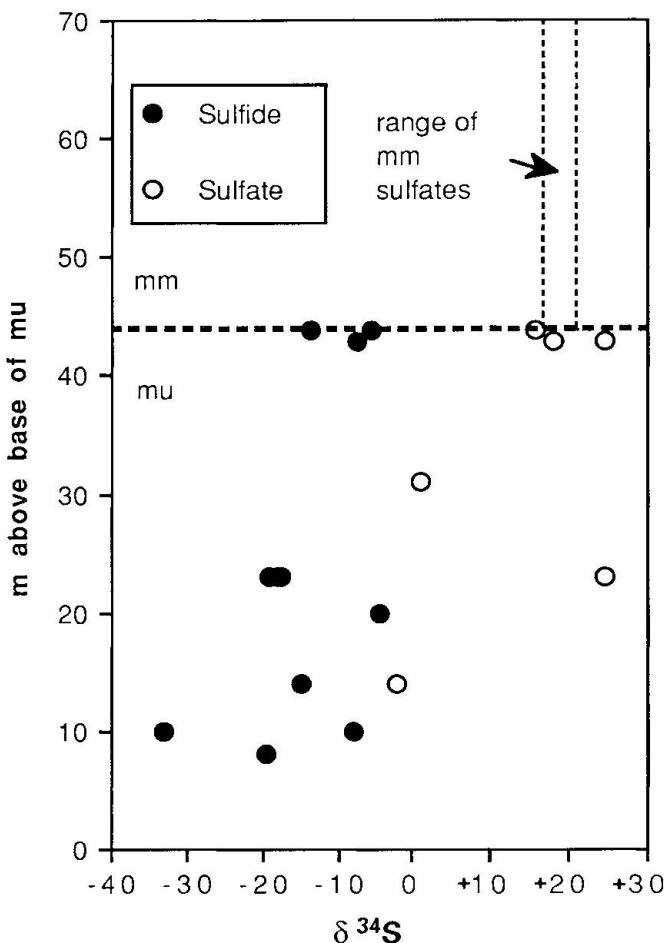


Fig. 7 Plot of $\delta^{34}\text{S}$ -values of minerals versus stratigraphic position in the Lower (mu) and Middle (mm) Muschelkalk.

similar pairs would yield a temperature of $200 \pm 30^\circ\text{C}$ (Fig. 47 in FRIEDMAN and O'NEIL, 1977).

There is no obvious dependence of sulfide $\delta^{34}\text{S}$ on stratigraphic position (Fig. 7). The sulfates, however, show a much larger variation in the Lower Muschelkalk than the narrow range of sulfate $\delta^{34}\text{S}$ known for European Middle Muschelkalk sulfates.

Our data are similar to $\delta^{34}\text{S}$ values from other mineralizations in the Triassic of Germany (v. GEHLEN and NIELSEN, 1985 a, b). Typical is the large spread of sulfide $\delta^{34}\text{S}$ values from about -40 to 0‰.

Interpretation

Two samples of early diagenetic pyrite are the isotopically lightest sulfides, consistent with an early diagenetic origin in a system partially open to sea water. The bulk of sulfides, however, was not formed under the same conditions. A late

diagenetic origin is indicated by textural evidence. Even if the $\delta^{34}\text{S}$ values of early diagenetic pyrite (Fig. 5) are disregarded, a large spread of 25‰ for the sulfides is obvious (even for one locality, e.g. 9). This spread is inconsistent with a derivation of the sulfide sulfur from an extraformational source, from remobilized early diagenetic sulfides or from the thermodegradation of sulfur-rich organic matter. In these cases, sulfide sulfur would be expected to be isotopically much more homogeneous. The isotopic inhomogeneity indicates that sulfide was formed by intraformational reduction of dissolved sulfate in a partially closed system. Sulfide sulfur then reacted with low concentrations of metal ions to form the various sulfides.

Sulfide formation by in-situ sulfate reduction is also supported by the presence of anhydrite and barite with $\delta^{34}\text{S}$ values of up to +24.6‰ which is at least 3.6‰ heavier than Muschelkalk sulfate and indicates Rayleigh-type isotope fractionation in a partially closed system. A positive correlation of $\delta^{34}\text{S}$ with intensity of mineralization would indicate more complete sulfate reduction led to higher degrees of mineralization. The most likely source of sulfates in the Lower Muschelkalk is the overlying Middle and Upper Muschelkalk with sulfate- $\delta^{34}\text{S}$ of +17.7 to +19.7‰ (PEARSON et al., 1991). An introduction of sulfates from the Buntsandstein (sulfate- $\delta^{34}\text{S}$ of +18 to +29‰, PEARSON et al., 1991) seems less likely because of the small amount of evaporites in the Buntsandstein.

The presence of sulfates with slightly elevated $\delta^{34}\text{S}$ values compared to source evaporites suggests that only a comparatively small portion of the available sulfate was reduced. Assuming a closed system in which an initial sulfate with $\delta^{34}\text{S}$ of +18.7‰ was partially reduced to diagenetic sulfides with an average $\delta^{34}\text{S}$ of $-13.1 \pm 6.5\text{‰}$ ($n = 23$), and assuming a value of +24.5‰ to be typical of the residual bulk sulfate after reduction was completed, about 15% of the initial sulfate must have been reduced to sulfide. Mineralized horizons typically contain 0.27% Pb and 0.19% Zn (HOFMANN, 1989), resulting in the presence of 0.135% sulfide S. If this corresponds to 15% of total sulfate sulfur, 0.9% sulfate S (in bulk rock) is needed to account for the sulfides present in mineralized horizons. Assuming 10% porosity during mineralization and a fluid with about 900 ppm sulfate S, typical of deep Upper Muschelkalk waters (PEARSON et al., 1991), about 270 flushings of the rock porosity are needed. If a diffusive supply of sulfate or sulfide from pelitic sediments is assumed and 5% of the stratigraphic column is assumed to be mineralized, still 9 flushings of the

whole sequence are needed. This indicates that the system certainly was not entirely closed during late diagenesis. Another possible sulfate source would be syngenetic sulfates in the Lower Muschelkalk but these were only observed in the topmost part of the Lower Muschelkalk, the *Orbicularis* marls (GEYER and GWINNER, 1991).

Late diagenetic sulfate reduction can be either bacteriogenic (BSR) or thermochemical (TSR). Both BSR (v. GEHLEN and NIELSEN, 1985 a, b; SASSEN et al., 1989) and TSR (KROUSE et al., 1988; POWELL and MACQUEEN, 1984) are known to be important in the generation of sediment-hosted sulfides. Temperature regimes for BSR and TSR are still debated (MACHEL and BURTON, 1991, TRUDINGER et al., 1985). Generally it is assumed that BSR can occur at temperatures up to at least 80 °C and TSR at temperatures as low as 90 °C if preexisting H_2S is present as a catalyst (ORR, 1982). It is also unclear whether a gap exists between the temperature regimes of BSR and TSR or whether the two regimes are overlapping (MACHEL and BURTON, 1991). As the temperature during mineralization in the Lower Muschelkalk is estimated at 50 to 140 °C (see introduction), both BSR and TSR are possible.

In cases where thermochemical sulfate reduction is demonstrably responsible for sulfide formation, only moderate sulfate-sulfide sulfur isotope fractionation was observed (KROUSE et al., 1988; HEYDARI and MOORE, 1989; POWELL and MACQUEEN, 1984). The large fractionation of 40 and 46‰ observed in coexisting and cogenetic sulfate-sulfide pairs in the Lower Muschelkalk are generally considered as typical of BSR. BSR also best explains the large variations of $\delta^{34}\text{S}$ values. However, in the case of a similar, but heavier range of sulfur isotope values (-5.4 to +19.9‰) for late diagenetic sphalerites from Lower Palaeozoic carbonates of Quebec, TASSÉ and SCHRIJVER (1989) interpreted large sulfide-sulfate fractionations of up to 39.4‰ as a result of TSR and equilibrium isotope fractionation at 130 °C over long time periods.

The three PbS-ZnS pairs for which application of sulfur isotope thermometry leads to temperature estimates of about 200 °C are no proof of such a high temperature during sulfide precipitation but of isotopic disequilibrium because this temperature is inconsistent with evidence from vitrinite reflectance data indicating a maximum temperature close to 100 °C at 2000 m depth (WOLF and HAGEMANN, 1987).

In the case of BSR as well as TSR, the limitation of sulfate reduction most probably is due to the limited availability of organic reductants. The incomplete sulfate reduction in the Lower

Muschelkalk contrasts with the almost complete, closed system bacterial sulfate reduction in the Pb-Zn deposits of Wiesloch and Upper Silesia, Poland, as indicated by the heavy $\delta^{34}\text{S}$ of sulfides (v. GEHLEN and NIELSEN, 1969, 1985b).

While the $\delta^{34}\text{S}$ values of 4 sulfate samples can be interpreted as slightly modified sulfates similar to those of the Middle Muschelkalk, the two samples close to 0‰ must be explained by secondary sulfide oxidation. This sulfide oxidation may have occurred much later than the sulfide mineralization and could have been caused by the infiltration of oxygenated surface waters.

Evidence for recent bacterial sulfate reduction in deep strata in Northern Switzerland is obtained from H_2S -rich formation waters in the Upper Muschelkalk of the Schafisheim drillhole with 2850 ppm sulfate ($\delta^{34}\text{S} = +26\text{‰}$) and 740–950 ppm H_2S ($\delta^{34}\text{S} = +4.4\text{‰}$) at a temperature of 58 °C (PEARSON et al., 1991).

Conclusions

$\delta^{34}\text{S}$ values of sulfides from Pb-Zn-Cu-As mineralizations in Middle Triassic Lower Muschelkalk sediments are consistent with an origin due to late diagenetic intraformational sulfate reduction by bacterial and/or thermochemical processes which acted on infiltrated sulfate-rich brines from the overlying evaporitic Middle Muschelkalk at depths of burial of < 1 to 2 km.

Acknowledgements

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