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Alteration zones around Kupferschiefer-type base metal mineralization in West Germany

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Abstract. Several occurrences of red-colored rocks, which represent an unusual species within the lower Zechstein sediments as well as siderite ribbons and kaolinization have been reported from the West German lower Zechstein sequence. The red-colored rocks had been classified into two types, i.e., the stratiform red layers (SRL) and the Rote Fäule (RF). With regard to the gray beds, both types are characterized by enrichments and depletions of certain elements. As a result, ore-related Rote Fäule could be distinguished from insignificant stratiform red layers. Whereas Rote Fäule, which represents the alteration zone around diagenetic Kupferschiefer-type deposits, is chiefly characterized by apparent red coloring and enrichment in sulfate S, both the siderite ribbons and kaolinization of feldspars refer to formation of Cu-As sulfides and arsenides due to a hydrothermal, epigenetic process. Formation under more oxidizing, synsedimentary conditions is presumed for the stratiform red layers.

Kupferschiefer-type base metal deposits are hosted within the lower Zechstein gray beds and are always accompanied by red-colored rocks, referred to as "Rote Fäule" [red rotten (barren) rocks] by miners in the old days.

In contrast to the common suggestion that all those red rocks, which have been more or less frequently observed in the West German lower Zechstein, represent ore-controlling Rote Fäule, within the Spessart-Rhön area red layers have been detected which show no spatial relationship to the distribution of the mineralization (Fig. 1).

On the other hand from the southern part of the Richelsdorf mining district, where mining ceased in the mid 1950s, due to observation and recognition of characteristic zonation pattern Rote Fäule has been identified within the Weissliegend sandstone, the Kupferschiefer black shale, and the Zechsteinkalk (Zechstein limestone) (Schmidt et al. 1986).

With respect to the importance of Rote Fäule delineation for exploration purposes, investigations have been principally focused on the discrimination between Rote Fäule (RF) and stratiform red layers (SRL), which were of doubtful provenance.

Further significant features like kaolinization and siderite ribbons are subjects of a forthcoming research project and are just briefly mentioned here.

Analytical Methods

Samples have been analyzed using XRF (SiO_2, Al_2O_3, TiO_2, MgO, CaO, Na_2O, K_2O, MnO, P_2O_5, Rb, Sr, Y, Zr, Nb, Ba), AAS (Cu, Pb, Zn, Ni, Co), ICP (As, Se, V), INAA (Cr, Th, U), DC (S, C_{org}), and TP (Fe^{2+}, SO_4^{2-}) at Robertson Research Int. Ltd., Wales. Thin sections and polished sections were prepared at the Institut für Mineralogie und Lagerstättenlehre, RWTH Aachen.

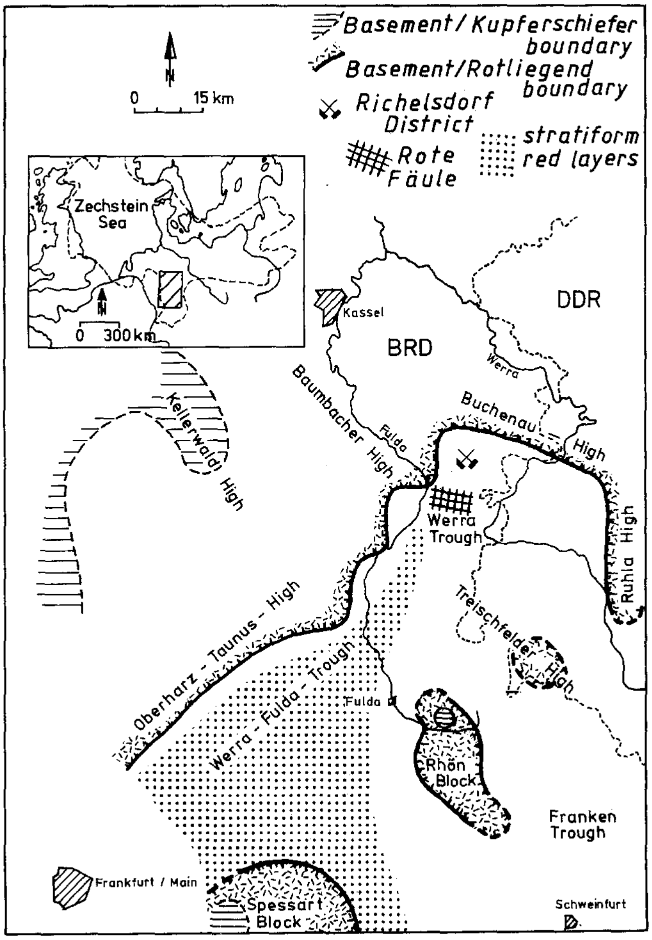

Fig. 1. Lower Zechstein paleogeography of the Werra-Fulda basin

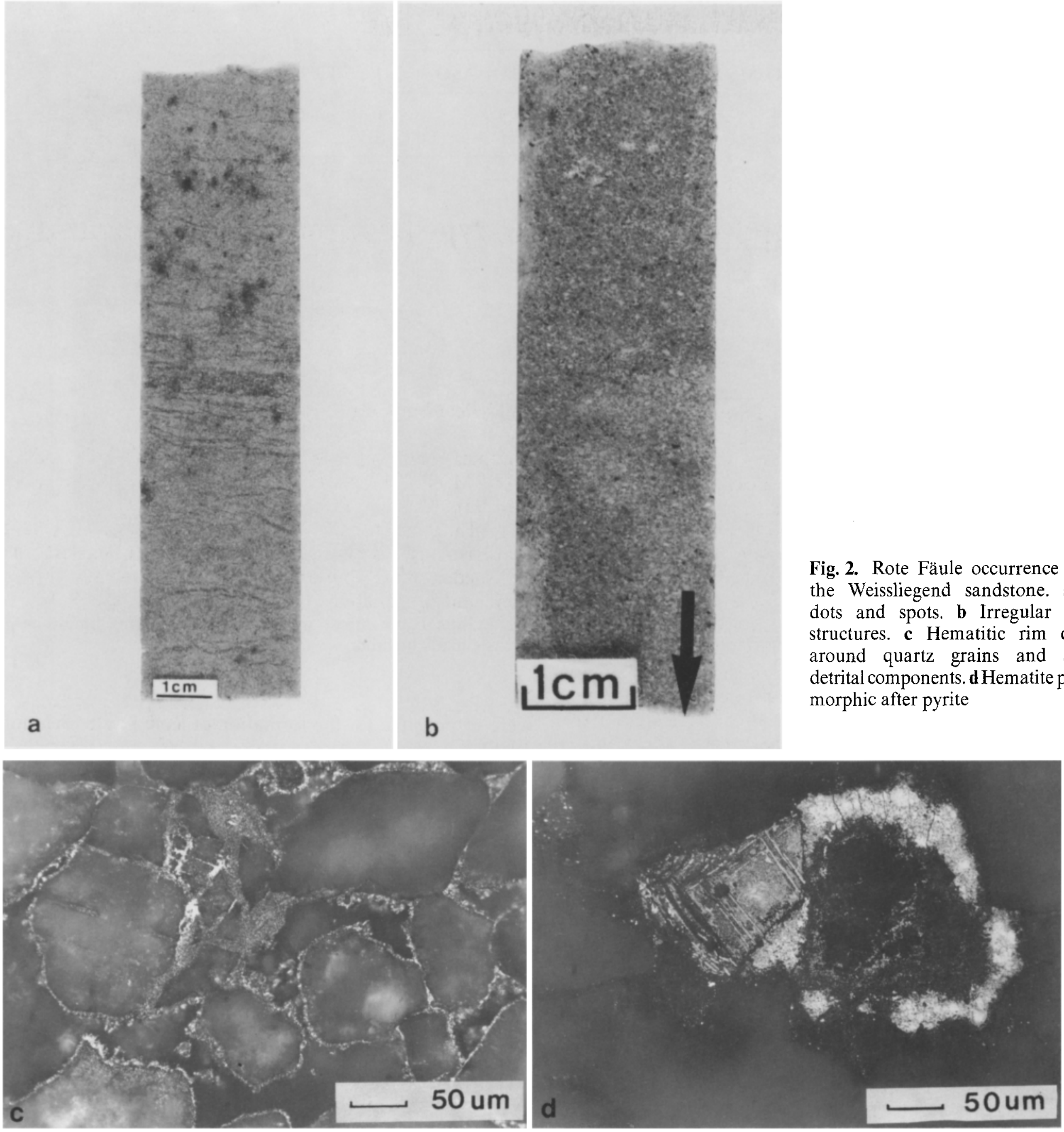

Fig. 2. Rote Fäule occurrence within the Weissliegend sandstone. **a** Red dots and spots. **b** Irregular cloudy structures. **c** Hematitic rim cement around quartz grains and among detrital components. **d** Hematite pseudomorphic after pyrite

Rote Fäule within the Weissliegend

Gray- to beige-colored, middle- to fine-grained sandstones with predominantly calcic matrix represent the typical rocks which form the footwall of the Kupferschiefer horizon.

Red dots, spots, or cloudy structures due to hematite and limonite filling the intergranular spaces or forming rims around the quartz grains, mark typical Rote Fäule occurrences (Fig. 2). According to Rydzewski (1978) the replacement of euhedral pyrite by limonite and hematite is one of the most apparent features of Rote Fäule, pointing to a diagenetic formation. Rote Fäule supporting matrix consists mainly of a calcite-anhydrite admixture bearing various amounts of disseminated Fe hydroxide particles. Minor amounts of pyrite, chalcopyrite, covellite, bornite, chalcocite, digenite, and loellingite have been observed among abundant oxides like anatase and rutile; graphite, which represents the end member of organic matter which had undergone coalification, had also been noticed within the Rote Fäule.

Multielement analyses yielded a significant depletion in chalcophilic elements, like Cu, Pb, Zn, and As, as well as in Co, coupled with an enrichment in sulfate S compared to the average Weissliegend gray beds (Fig. 3).

Taking some element ratios into account as well, which might portray typical geochemical trends within the environment of generation, Rote Fäule is characterized by

Table 1. Characteristic element ratios for Weissliegend gray beds and Weissliegend-hosted Rote Fäule

	K_2O/Na_2O	CaO/MgO	Fe_2O_3/MnO	SiO_2/Al_2O_3	Fe^{3+}/Fe^{2+}
Gray beds	4.7	13.9	7.3	4.9	0.6
Rote Fäule	1.9	7.6	4.8	8.1	1.5

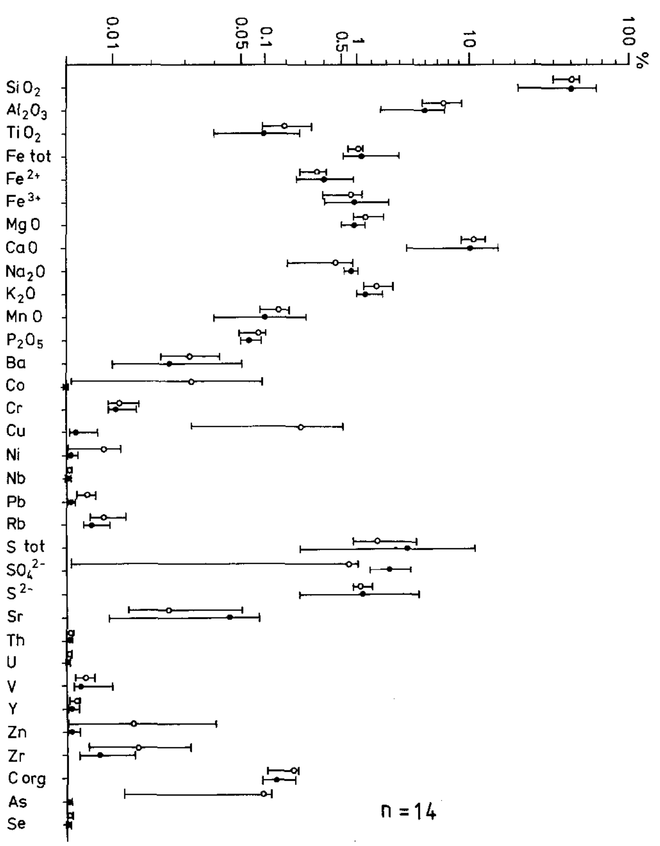

Fig. 3. a Multielement plot of major- and trace-element contents (wt%) for Weissliegend gray beds (open circles) and Rote Fäule within the Weissliegend (full circles)

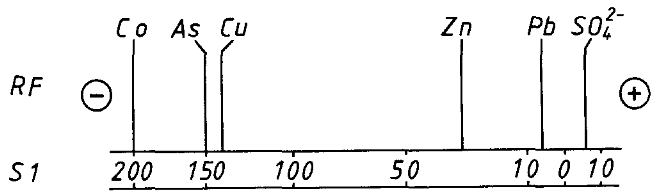

Fig. 3. b Enrichment-depletion factors of significant elements for Weissliegend gray beds (S1) vs Rote Fäule (RF)

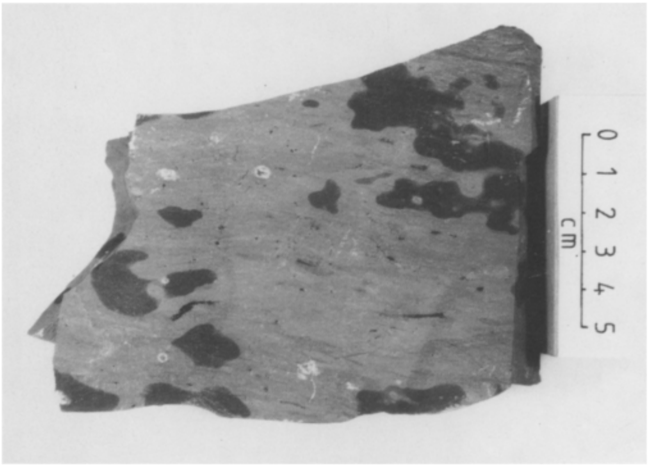

Fig. 4. Rote Fäule shreds within anhydrite-bearing limestone of Zechsteinkalk member

higher SiO_2/Al_2O_3 and Fe^{3+}/Fe^{2+} ratios in combination with lower K_2O/Na_2O, CaO/MgO, and Fe_2O_3/MnO ratios (Table 1). The increasing SiO_2 content could be explained by the paleogeographic position, where Rote Fäule is located mainly within sandbars of the Weissliegend. Higher ferric iron/ferrous iron ratios and lower iron/manganese ratios both point to a more oxic environment than within the gray beds.

The abundance of sulfate S associated with lower potassium/sodium and calcium/mangnesium ratios gives rise to the assumption, that alkaline, oxidizing solutions were responsible for the formation of Rote Fäule (Schmidt 1985).

Intergrowths between hematite and digenite, which have been observed at the Rote Fäule margin, point to an environment of formation with a pH of 7–8 (Tischendorf and Ungethüm 1965).

Predominance of ferric iron and abundant sulfate S are the most significant features for Rote Fäule alteration within the Weissliegend. In accordance with Speczik (personal communication) so-called "invisible Rote Fäule" represents another type of more subtle alteration zone. Geochemical features are similar to Rote Fäule, but due to lacking absolute ferric iron content, red stainings did not develop.

Rote Fäule and stratiform red layers within the Zechsteinkalk

The Zechsteinkalk forms the hanging wall of the Kupferschiefer horizon and consists of calcite- and dolomite-bearing limestones, marlstones, and packstones. Two types of red-colored rocks have been observed, both distinct in mineralogical and geochemical pattern.

Rote Fäule has irregular shape, often spatially associated with copper sulfides and anhydrite nodules (Fig. 4). In particular, chalcocite, bornite, and digenite hieken occur surrounded by Fe hydroxides and hematite (Fig. 6).

Compared to the gray-colored limestones, taken from the direct vicinity to exclude facies changes within the host sediment, Rote Fäule is enriched in sulfate S and CaO in contrast to the depletion in MgO and Cr (Fig. 5). (Enrichment and depletion refer only to those cases where mean values of RF and SRL, which range both within very

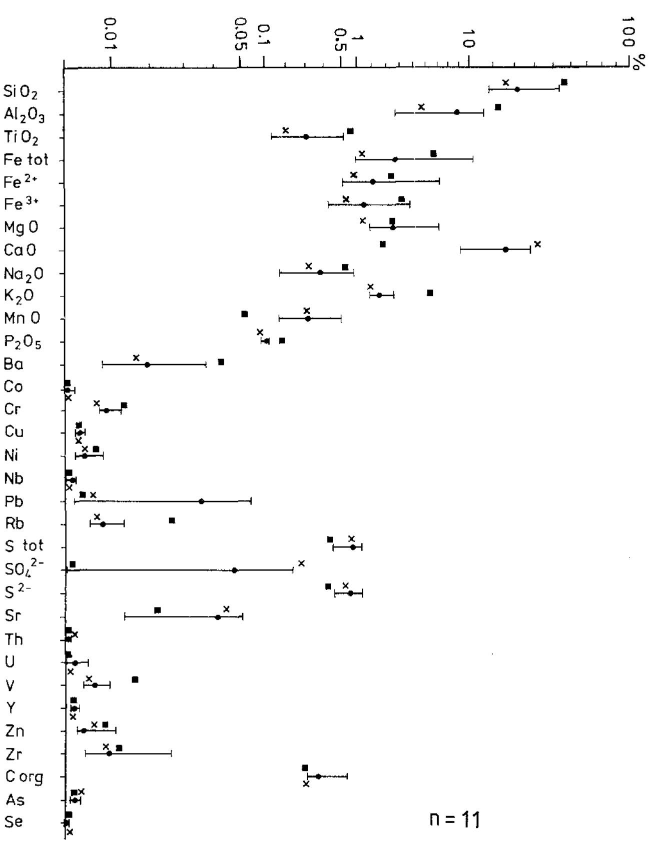

Fig. 5. a Multielement plot of major- and trace-element contents (wt%) for Zechsteinkalk gray beds (circles), Rote Fäule (crosses), and stratiform red layers (squares)

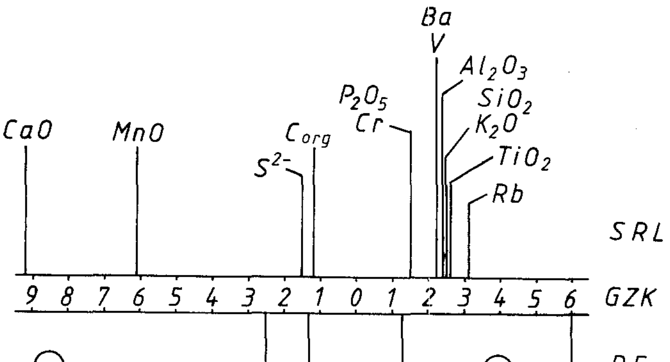

Fig. 5. b Enrichment-depletion factors of significant elements for stratiform red layers (SRL) and Rote Fäule (RF) vs Zechsteinkalk gray beds (GZK)

narrow limits of ± 10%, stay clearly outside the standard deviation of gray bed values.)

Based on calculations of some interesting element ratios K_2O/Na_2O and Fe_2O_3/MnO ratios are lower within the Rote Fäule, whereas CaO/MgO ratios appears to be higher than for the gray beds (Table 2).

In contrast to common suggestions, Zechsteinkalk-hosted Rote Fäule is characterized by a predominance of ferrous iron; evidence for the existence of hematite is only occasionally given.

The stratiform red layers, which range in thickness from several millimeters up to 1 m, display random distribution within the sedimentary pile. Obviously, they are concentrated within alternating beds of argillaceous marl and marlstones, particularly within the more argillaceous portions (Fig. 7). Microtexures show graded bedding and very fine lamination caused by intercalation of quartz, clay, and carbonate.

In contrast to the irregular-shaped Rote Fäule, no sulfides have been found within the SRL. With regard to the argillaceous marl-bearing gray beds an enrichment in Cr, Ba, V, Rb, P_2O_5, Al_2O_3, SiO_2, K_2O, and TiO_2 has been reported from the SRL coupled with depletion in C_{org}, sulfide S, MnO, and CaO. Focusing on certain element ratios in a similar way as it had been done for the RF, higher K_2O/Na_2O, Fe_2O_3/MnO, and Fe^{3+}/Fe^{2+} coupled with lower CaO/MgO and SiO_2/Al_2O_3 ratios were ascertained for the SRL. In comparing RF and SRL, a remarkable difference in absolute enrichment and depletion as well as opposing trends in the element ratios were found (Fig. 5 b).

Due to the relationship between Rote Fäule and high-grade mineralization a diagenetic formation had been presumed by several authors (e.g., Rentzsch 1974; Rydzewski 1978; Schmidt 1985; Jowett 1986). In contrast to the recently given explanation of the SRL in terms of Rote Fäule (Schumacher et al. 1984; Kulick et al. 1984), due to lacking ore-controlling characteristics and based on the different geochemical and mineralogical fingerprints a reinterpretation has to be made.

Features similar to the SRL like abundant hematite, enrichment in PO_4 and depletion in Mn had recently been reported by Franke and Paul (1982) from red layers embedded in siltstones and claystones of Devonian age. In accordance with the suggestion of Franke and Paul a critical content of ferric iron is required to cause reddening of the sediments. In most cases the depositional environment bears significant amounts of organic matter which caused reduction of the ferric iron. Preservation of hematite could be explained either by oxidizing conditions due to supply of fresh water, coupled with dilution of C_{org} content by increasing influx of terrigeneous debris, mainly quartz

Table 2. Characteristic element ratios for Zechsteinkalk gray beds, Zechsteinkalk-hosted Rote Fäule, and stratiform red layers (SRL)

	K_2O/Na_2O	CaO/MgO	Fe_2O_3/MnO	SiO_2/Al_2O_3	Fe^{3+}/Fe^{2+}
SRL	9.7	0.9	124.5	2.5	1.7
Gray beds	8.7	10.5	14.6	4.2	0.9
Rote Fäule	4.9	19.9	5.1	4.9	0.7

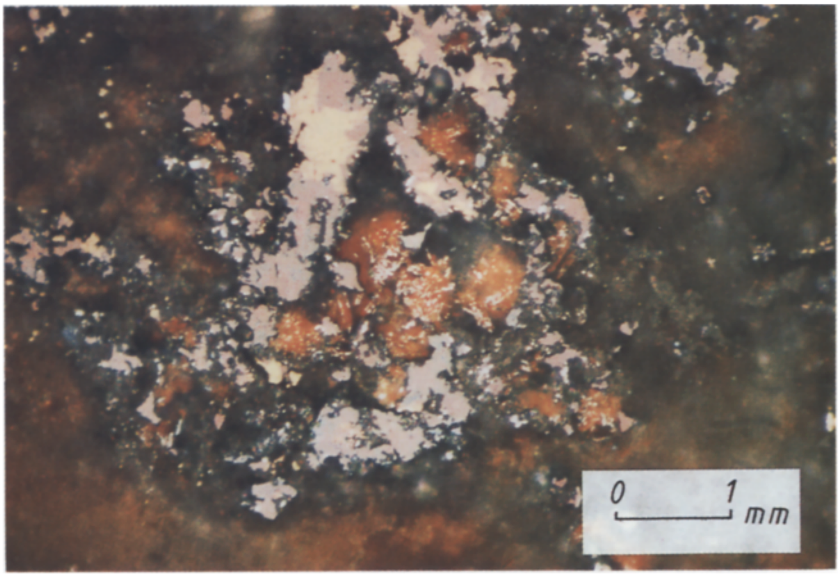

Fig. 6. Hematite/chalcocite-bornite intergrowth as a characteristic feature for Zechsteinkalk-hosted Rote Fäule

Fig. 7. Stratiform red layer within the Zechsteinkalk unit

and clay, or by oligothrophic conditions lacking organic matter like in deep-water sediments.

With reference to the enrichment in SiO_2 and Al_2O_3 associated with the depletion in CaO, C_{org}, and sulfide S a synsedimentary formation of SRL under more oxic conditions seems most likely, probably supported by short-range element migration as a result of very early diagenetic processes.

Siderite ribbons and kaolinization

In addition to the previously described SRL and RF which could be more or less related to syndiagenetic processes, further alteration patterns have been observed which occur in the vicinity of so-called structure-bound mineralization (Schmidt and Friedrich, in press).

Siderite ribbons appear just within the Zechsteinkalk of the Spessart-Rhön area supported by a matrix bearing various amounts of quartz, calcite, dolomite, and clay. In contrast to the SRL there seems to be no restriction of siderite ribbons to certain rock types within the Zechsteinkalk unit; an almost similar quantity of siderite has been reported regardless of the host rock composition, indicating an allochemical nature of the iron content.

From the same area abundant kaolinization of feldspars has been found within the Weissliegend sandstones and in the Kupferschiefer horizon. Narrow kaolin peaks ascertained by XRF were able to be traced back to a very well arranged crystal latice, which refers almost to a hydrothermal influence.

According to Friedrich et al. (1984) Kupferschiefer mineralization of the Spessart-Rhön area is governed by Cu-As sulfides and arsenides, generated during Saxonian tectonism.

Even today outgassing of CO_2 which is used for economic purposes, occurs mainly along major fault structures. With reference to these features around the structure-bound Cu-As sulfide and arsenide mineralization there appears to be evidence for an affiliation of both siderite ribbons and kaolinization to hydrothermal activities.

Concluding remarks

It has been shown that at least two out of four apparently distinct features observed within the lower Zechstein rock sequence can be referred to as alteration pattern.

Rote Fäule displays a clear response to high-grade mineralization, representing the oxidized side of the redox boundary, whereas kaolinization of feldspars is connected with the formation of Cu-As sulfide and arsenide assemblages.

Generation of siderite ribbons by the same hydrothermal process seems likely, but also the possibility of a diagenetic formation could be considered, which was independent of mineralization. For the generation of SRL a development due to more oxic conditions as a result of slackened subsidence seems to be the most convincing explanation.

Nevertheless, Rote Fäule and SRL are not similar, neither in composition nor in mode of operation, and could be distinguished by application of mineralogy and geochemistry.

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