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NOTE

Germanium and precious metals (Ag–Au–Pt–Pd) at low temperature: the hematite–carbonate–selenide vein system of Tilkerode, Harz Mountains, Germany

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Abstract

At the historical Eskeborner Berg underground workings at Tilkerode (Eastern Harz Mountains, Germany), Fe was mined from a carbonate–hematite vein system that was locally enriched in selenide minerals. Clausthalite [PbSe] was the most abundant selenide mineral in a carbonate matrix with laths of specular hematite. To date, the selenide-bearing carbonate–hematite vein system at Tilkerode has not been geochemically investigated. Here, we present the first whole-rock chemical data for a wide suite of trace elements. The following metals are enriched relative to bulk continental crust (orders of magnitude in parentheses): Se ($>10^5$), Hg ($>10^4$), Ag and Pb (10^3), Au, Bi, Pt, Ge, Te, Pd and Cd (10^2). Samples from Tilkerode have up to 2640 ppm Ag, 338 ppm Ge, 1560 ppb Au, 970 ppb Pt and 365 ppb Pd, with Pt/Pd > 1, and a significant positive correlation of Ge vs. (Pd+Pt). The selenide mineralisation took place below 112 °C, the maximum temperature stability of umangite [Cu_3Se_2]. Our data indicate there is potential for prospecting Ge and precious metals in low-temperature vein systems.

Keywords Tilkerode · selenide minerals · whole rock data · germanium · palladium · platinum · gold

Introduction

Modern analytical techniques have allowed for accurate measurements for a variety of trace elements, some of which have been overlooked or underestimated in previous studies of mineral deposits. For example, the recent finding of Ge-rich chalcopyrite in sulfide–calcite veins suggests that the Kupferschiefer Cu–Ag deposits of southwest Poland have been underexplored for Ge resources (Foltyn et al. 2022). Selenide analogues of such veins occur in the Harz Mountains of Germany. One carbonate–hematite–selenide vein system occurs at Tilkerode (Fig. 1). Although Tilkerode is the type locality of some Pd-selenide minerals (Stanley et al. 2002; Ma et al. 2020), quantitative whole-rock data for Pd and other precious metals are lacking. Here, we report the first whole-rock chemical analyses for a suite of trace elements, including the precious metals Ag, Au, Pd and Pt, in samples of carbonate–hematite–selenide vein material from Tilkerode. Our samples not only have high contents of precious metals, but also hitherto unknown Ge enrichments, a finding that prompts reevaluation of the Harz (carbonate–hematite–selenide) vein systems as potential resources of Ge and precious metals.

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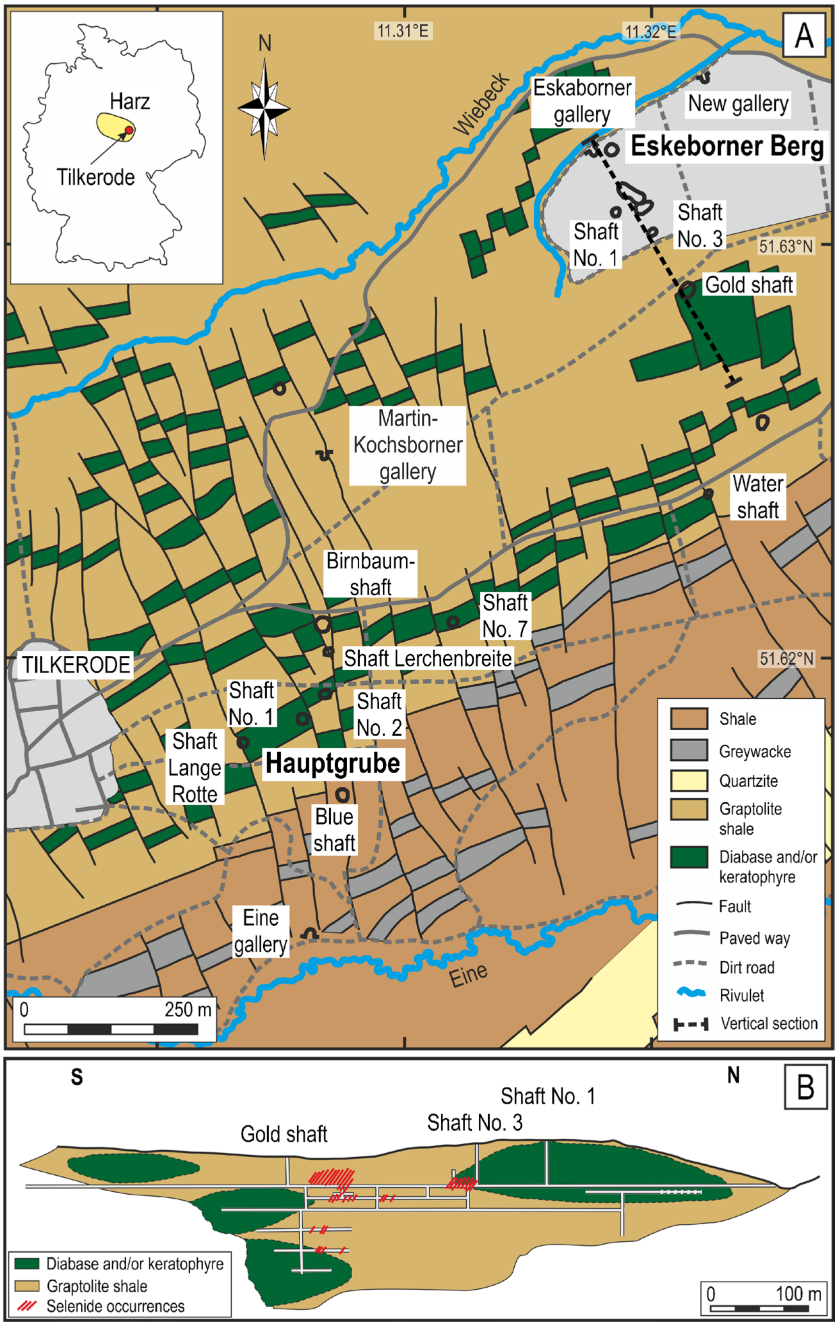

Fig. 1 **A** Geological map of the area around Tilkerode (modified after Tischendorf 1959). **B** Vertical cross section of the Eskeborner Berg showing the largest selenide shoots (modified after Tischendorf 1959)

Tilkerode and its geological setting

The historical Tilkerode mining area, comprising the underground workings known as 'Hauptgrube' and the 'Eskeborner Berg' in the Eastern Harz Mountains (Tischendorf 1959, and references therein), is a classical example of low-temperature hydrothermal, carbonate–hematite–selenide vein-type mineralisation (e.g., Simon et al. 1997). Tilkerode is the type locality of naumannite [Ag_2Se], eskebornite [$CuFeSe_2$], tischendorfite [$Pd_8Hg_3Se_9$] and tilkerodeite [Pd_2HgSe_3] (Ramdohr 1949; Tischendorf 1959; Stanley et al. 2002). In total, 18 selenide minerals have been reported from the Tilkerode selenide shoots or 'Selenid-Lager' (Ma et al. 2020), the most abundant of which are clausthalite [PbSe], tiemannite [HgSe] and naumannite [Ag_2Se] (Tischendorf 1959). Other low-temperature ('telethermal') hydrothermal occurrences of selenide minerals have also been documented in the Harz Mountains, for example from Bad Lauterberg, Clausthal, Lerbach, Sankt Andreasberg, Rieder (Gernrode), Sieber, Straßberg, Sülzhayn, Treseburg, Trogtal and Zorge (Tischendorf 1959; Keutsch et al. 2009; Cabral et al. 2012, 2015, 2017, 2018; Heider and Siemroth 2012; Heider 2014; Koch and Heider 2018; Heider et al. 2019, 2020, 2022).

Despite its reputation for selenide minerals, Tilkerode was mined for Fe. Mining of Fe ore was spatially related to carbonate–hematite veins, and began in the vicinity of the town of Tilkerode prior to 1762 at two sites, 'Einestollenrevier' (also known as 'Hauptgrube') and 'Eskeborner Berg' (Fig. 1). The first findings of selenide minerals likely date back to mid-1780s at Einestollenrevier, but, the first documented occurrence of selenide minerals was at Eskeborner Berg in 1825 (Tischendorf 1959). The discovery of minor native Au within shoots of selenide minerals, hereafter referred to as the shoots, led to an ephemeral flourish of mining activities. However, neither Fe nor Au was economic in the long term so that mining was suspended several times. The last exploration attempt was made in the 1950s, and only provided evidence for spatially restricted shoots of selenide minerals (Tischendorf 1959; Oelke 1973).

The shoots have on average 10 cm in width, with one shoot ('Selenfirste') of 35 m in vertical extension × 10 m in length. They are spatially related to a NNW–SSE-trending carbonate–hematite vein system of ~ 450 m in length, varying from ~ 0.05 to 8 m in width, with a vertical extension of > 63 m at the Einestollenrevier and of > 100 m at the Eskeborner Berg. These vertical extensions correspond to the deepest levels of underground workings (Tischendorf 1959). The shoots occur along or within carbonate–hematite veins or in the hydrothermally altered host rocks, i.e., reddened and/or bleached graptolite schist and keratophyre over the full vertical extension of the underground workings (Tischendorf 1959, and references therein). Generally, tectonically displaced blocks of Silurian black graptolite shale and of Devonian keratophyre and diabase of the Eastern Harz Silurian anticline ('Ostharzer Silursattel') host the carbonate–hematite vein system.

At least four different mineral-forming stages can be distinguished on the bases of carbonate minerals at Tilkerode. 'Carbonate I + II', consisting mostly of calcite, and disseminated hematite flakes make up approximately 98% of the carbonate–hematite vein system. This calcite–hematite mineralisation with minor quartz is followed by a mineral assemblage of selenide minerals, ankerite ('carbonate III'), subordinate quartz and clinochlore, with selenide minerals constituting at most 10% (in total ~ 120 kg of Se were historically mined; Tischendorf 1959). Most sulfide minerals and minor calcite ('carbonate IV') formed during late-stage overprinting on the selenide mineralisation.

The selenide mineralisation is restricted to pockets. Tischendorf (1959) interpreted this style of mineralisation to result from lateral leaching and mobilisation of metals and S from the host rock, a C-rich graptolite black shale, by neutral to weakly alkaline hydrothermal fluids with a high oxygen fugacity. Tischendorf's interpretation is in agreement with thermodynamic calculations by Simon et al. (1997). Importantly, the presence of umangite [Cu_3Se_2] constrains the temperature of selenide-mineral formation to < 112 °C (Simon et al. 1997, and references therein). In contrast, the paragenesis of selenide minerals and their fluid and metal sources are less well constrained. For example, the selenide minerals of the Harz Mountains have been considered older than the main-stage vein mineralisation of base metals and silver, probably from Permo-Triassic times (e.g., Kuschka and Franzke 1974; Stanley et al. 1990; Cabral et al. 2012), but Pb isotopic data are suggestive of an even younger age, possibly Triassic-Jurassic, for the selenide-mineral occurrences (Bielicki and Tischendorf 1991). A late-stage formation is compatible with new fluid-inclusion data for the main-stage vein mineralisation of base metals (de Graaf et al. 2020).

Sampling and methods

Nine whole-rock samples of selenide-bearing carbonate–hematite vein were taken for reconnaissance geochemical analyses from Tischendorf's vein-sample set, collected in the 1950s and currently stored at the 'Landesamt für Geologie und Bergwesen Sachsen-Anhalt'. Exact sampling locations within the Eskeborner Berg underground workings are documented for samples TK1 (barite vein), TK3 (southern adit, mid-sole), TK4 (southern winze) and TK7 (mid-sole to the south). Sample TK6 is from the 'Goldschacht' (gold shaft), and sample TK5 comes from a former selenide ore stockpile of the mine. The other samples cannot be assigned to specific sites of the Eskeborner Berg underground workings due to missing documentation. Half of the sample material was crushed and milled in the facilities of the Technische Universität Clausthal (TUC), and then sent to Activation Laboratories (Canada) for whole-rock geochemical analysis. Contamination during crushing and milling was strictly minimised by repeated, thorough cleaning of crusher and mill. The other half of the sample material was used for preparation of polished sections for ore microscopy. Major elements were determined by X-ray fluorescence after Li-borate fusion. Minor and trace elements were determined by inductively coupled plasma-mass spectrometry (ICP-MS), after 4-acid digestion ($HF–HNO_3–HClO_4–HCl$), instrumental neutron activation analysis and fire assay ICP–MS. Loss on ignition was obtained gravimetrically. Details for the bulk-rock analytical methods are provided in the electronic supplementary material (ESM). Reference materials and duplicates were also analysed for data quality and reproducibility. In addition, reconnaissance microanalyses of chalcopyrite for some trace elements were obtained in situ by laser–ablation–sector field–ICP–MS at the Karlsruhe Institute of Technology; analytical details are provided in the ESM.

Results

All samples contain selenide-mineral spots which are dark in hand samples and vary in size up to approximately 5 cm across. The selenide-mineral spots are surrounded by white and red carbonate gangue with fine-grained hematite (Fig. 2A). Clausthalite is the dominant selenide mineral in all samples. Massive clausthalite surrounds laths of specular hematite (Fig. 2B) of varied length (≤ 2 mm). Most hematite laths are arcuated, but show no preferential orientation. Clausthalite is intergrown with minor tiemannite (Fig. 2C) and encloses anhedral to euhedral quartz crystals, chlorite, rarely observed sphalerite, and minor anhedral chalcopyrite, which may contain anhedral to subhedral pyrite crystals of < 100 µm in length (Fig. 2D). Some chalcopyrite also occurs along clausthalite domains and in the carbonate mineral gangue. Locally, hematite is corroded and overgrown by late pyrite and marcasite (Fig. 2E). Clausthalite and hematite laths fill the interstices among carbonate-mineral rhombohedra (Fig. 2E), which are compositionally analogous to ankerite. The paragenesis of naumannite (Fig. 2B) and the Cu-selenide minerals berzelianite, eskebornite (Fig. 2F) and klockmannite are not clear. Native gold has not been identified by reflected-light microscopy in our samples.

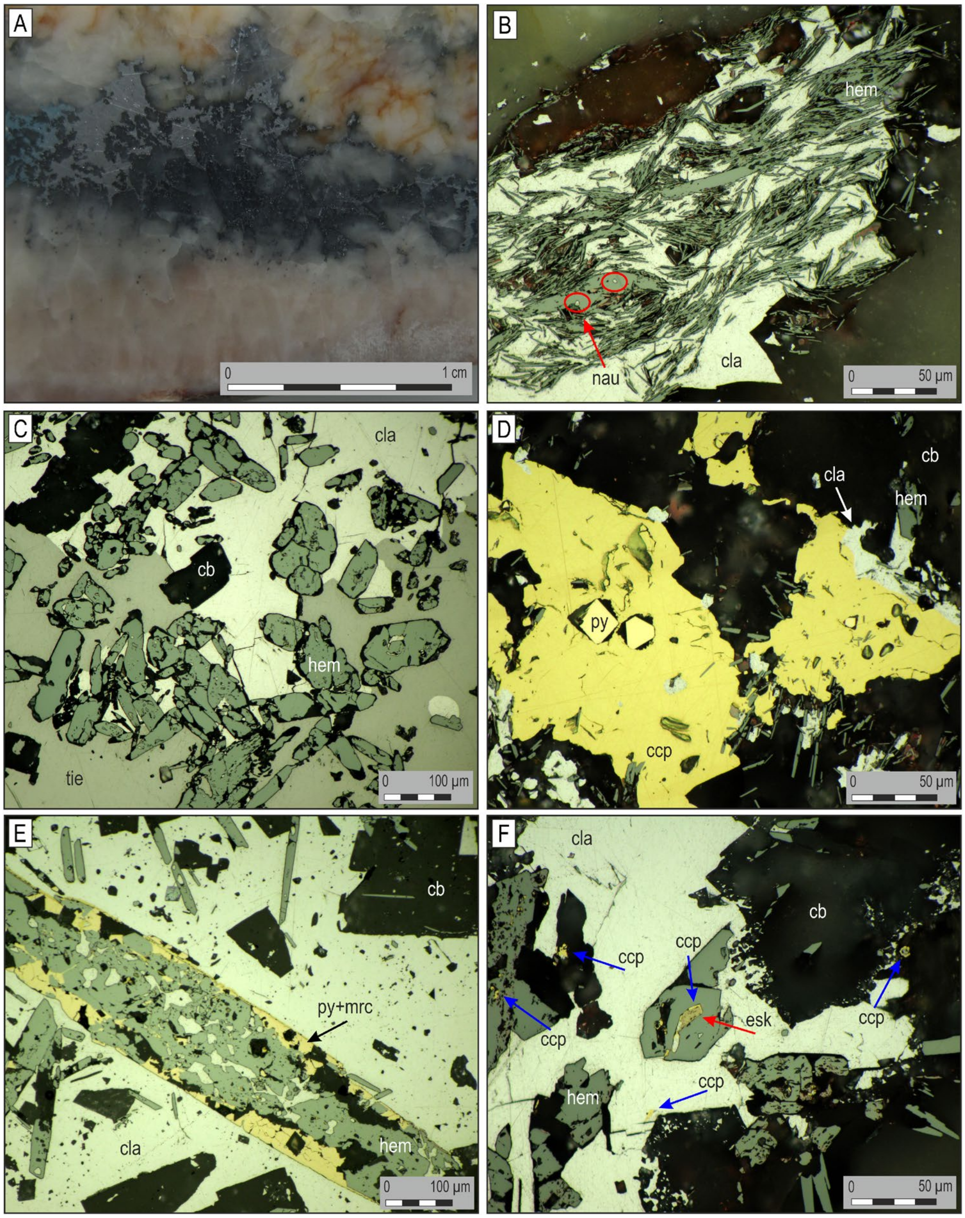

Fig. 2 **A** Photograph of a polished slab of sample TK-6, showing a grey to black pocket of selenide minerals and hematite, within a vein of carbonate minerals (white). **B-F** Photomicrographs taken under reflected light in oil immersion. **B** Specular hematite laths (grey) of varied size in massive clausthalite (white). Some hematite laths are arcuated. Naumannite occurs as tiny whitish inclusions in hematite (within red circles). **C** Clausthalite (white) intergrown with tiemannite (light grey, low relief), with hematite inclusions (dark grey, high relief). **D** Chalcopyrite (yellow) surrounding subhedral pyrite crystals (light yellow). **E** Pyrite and marcasite (light yellow; not distinguishable in photomicrograph) corroding a coarser lath of hematite (grey) within clausthalite (white). Carbonate rhombohedra appear black. **F** Eskebornite (pink; red arrow) and chalcopyrite (yellow; blue arrows) within hematite (grey) in a groundmass of clausthalite (white). Abbreviations: cb = carbonate minerals; cla – clausthalite; ccp = chalcopyrite; esk = eskebornite; hem = hematite; marcasite = mrc; nau = naumannite; py = pyrite; tie = tiemannite

The results of whole-rock geochemical analysis are reported in ESM Table 1. The samples are characterised by high contents of CaO (15.7–47.5%; av. 25.5%) and total Fe expressed as Fe_2O_3 (5.1–18.3%; av. 12.35%), and comparatively minor MgO (1.9–8.9%; av. 6.4%). The LOI values of our samples, which are in the range of 26.8 to 37.5%, are representative of carbonate-mineral contents. Most Se and Pb values are > 10,000 and > 5,000 ppm, respectively, which are the upper detection limits. Likewise, some Hg values are > 1,000 ppm. Silver (~ 1–2,640 ppm), Ge (~ 5–338 ppm), Cu (~ 7–264), and Zn (56–168 ppm) have average values of > 100 ppm. The precious metals Au (5–1,560 ppb), Pt (5–970 ppb), and Pd (2–365 ppb) show average values of 454, 282, and 138 ppb, respectively (Fig. 3A). There is no significant correlation of Pt and Pd, but there are relevant positive correlations of Pt and Au ($R^2 = 0.89$), Pt and Ag ($R^2 = 0.82$), Cu and Ge ($R^2 = 0.78$), (Pt + Pd) and Cu ($R^2 = 0.70$), (Pt + Pd) and Ge ($R^2 = 0.69$), and Pt and Ge ($R^2 = 0.62$), where R^2 is the coefficient of determination (Fig. 4). Using a threshold of statistical significance of 0.05, the p-values are as follows: Pt and Au ($p < 0.0001$), Pt and Ag ($p = 0.0003$), Cu and Ge ($p = 0.0007$), (Pt + Pd) and Cu ($p = 0.005$), (Pt + Pd) and Ge ($p = 0.006$), and Pt and Ge ($p = 0.007$). Due to the correlation between Cu and Ge, we performed reconnaissance in situ LA–SF–ICP–MS analyses of chalcopyrite. For all measurements ($n = 10$), Ge content is < 0.63 ppm (ESM Table 2).

Discussion

Samples from the selenide-mineral-bearing carbonate–hematite vein of Tilkerode are enriched in Se (> 10^5), Hg (> 10^4), Ag and Pb (> 10^3), Au, Bi, Cd, Ge, Te, Pd and Pt (10^2), relative to the bulk continental crust (Fig. 3B; Rudnick and Gao 2003). The selenide minerals clausthalite, tiemannite, and naumannite primarily host Pb, Hg, and Ag, respectively

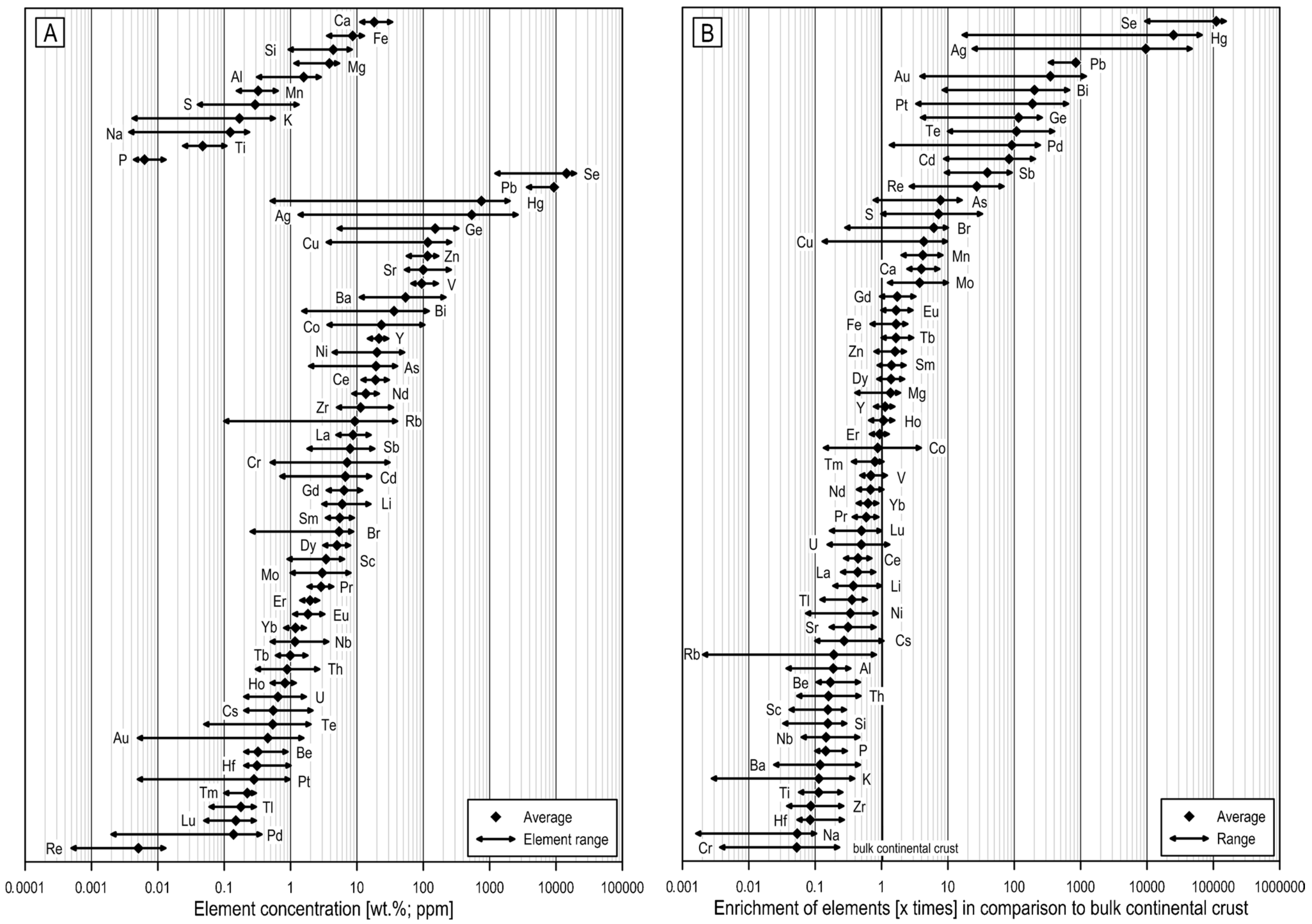

Fig. 3 **A** Element contents of whole-rock chemical analyses. Major-element contents are in wt.%, all other elements are in ppm. **B** Element enrichments compared to bulk continental crust (data from Rudnick and Gao 2003). **A**, **B** Values below the minimum limit of detection (MDL) are substituted with ½ MDL; values above the maximum limit of detection are doubled. Arrows reflect the total range of element contents in the samples. Diamonds represent average element contents

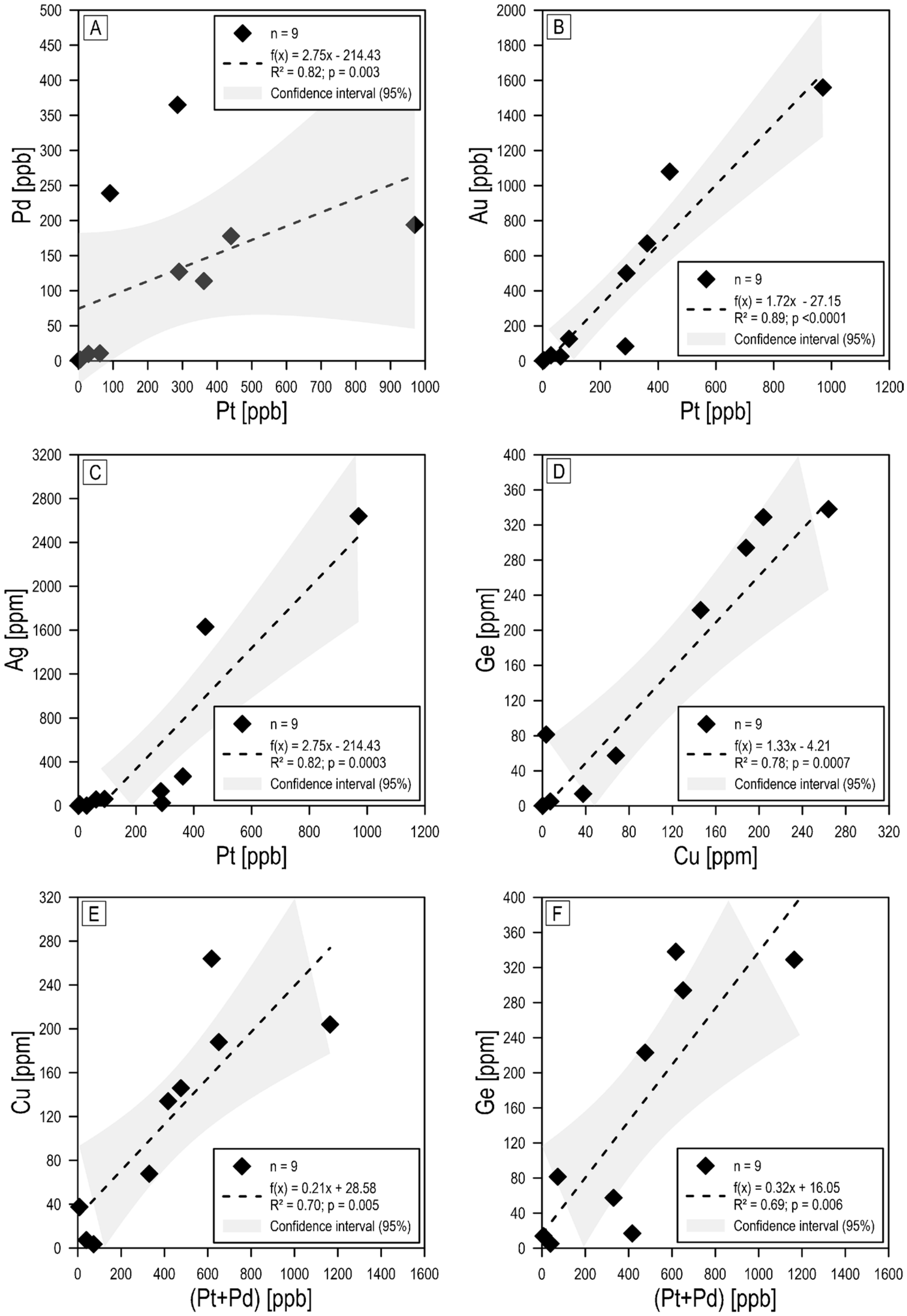

Fig. 4 **A** Variation plot of Pt and Pd. **B** Variation plot of Pt and Au. **C** Variation plot of Pt and Ag. **D** Variation plot of Cu and Ge. **E** Variation plot of (Pt + Pd) and Cu. **F** Variation plot of (Pt + Pd) and Ge

(Fig. 2B–D). Previous studies reported the presence of gold (Tischendorf 1959; Oelke 1973), Pd-selenide minerals (Stanley et al. 2002; Ma et al. 2020), and a Pt-selenide mineral (Ma et al. 2020). Therefore, enrichments of Au, Pt and Pd in samples from Tilkerode could be explained mineralogically (e.g., Tischendorf 1959), although we have not identified any of those minerals (Fig. 2). The origin of Ge enrichments remains elusive, however, because no Ge-selenide minerals have been discovered.

In nature, Ge enrichments are known in sulfide minerals, such as sphalerite and chalcopyrite, and in organic matter (e.g., Goldschmidt and Peters 1933; Ketris and Yudovich 2009; Melcher and Buchholz 2014). Germanium can be enriched in banded iron formations and in oxidised sulfide ore deposits with Ge contents of up to ≤ 7,000 ppm in hematite and ≤ 5310 ppm in goethite (Bernstein 1985; Höll et al. 2007), but most Ge is dispersed through silicate minerals due to Ge substitution for Si (Goldschmidt 1930;

Höll et al. 2007). Discrete Ge-sulfide minerals, such as argyrodite [Ag_8GeS_6], briartite [$Cu_2(Fe,Zn)GeS_4$], germanite [$Cu_{13}Fe_2Ge_2S_{16}$], and renierite [$(Cu,Zn)_{11}Fe_4(Ge,As)_2S_{16}$], are rare. They are only known from few deposits worldwide, including the high-grade, polymetallic, epigenetic, carbonate-hosted ('Kipushi-type') ore deposits (Höll et al. 2007). Average whole-rock Ge contents in low-temperature Kipushi-type ore deposits amount to several hundred ppm Ge (Höll et al. 2007), whereas average Ge contents in black shale and coal are in the range of < 1 to 3 ppm (Ketris and Yudovich 2009, Slack et al. 2004), but can locally attain values as high as 4,000–5,000 ppm (Goldschmidt 1930; Höll et al. 2007). Exceptionally, high Ge contents in Fe-poor sphalerite that formed in low-temperature epigenetic deposits can amount to 3,000 ppm (Bernstein 1985; Höll et al. 2007; Liu et al. 2023), delineating Mississippi Valley-type deposits as one of the most important hosts of Ge (Frenzel et al. 2014).

Given the positive correlations of Cu and Ge ($R^2 = 0.78$), (Pt + Pd) and Cu ($R^2 = 0.70$), and (Pt + Pd) and Ge ($R^2 = 0.69$; Fig. 2C), it is reasonable to assume that chalcopyrite is the primary host of Ge in our whole-rock samples. Nonetheless, our reconnaissance microanalytical study of chalcopyrite demonstrates that the Ge contents are low (< 1 ppm, ESM Table 2). As the total amount of Cu is relatively low (< 270 ppm) and the Ge contents are higher than Cu contents in 5 out of 9 samples, a coupled substitution into another mineral is possible, but remains speculative at present. In contrast, chalcopyrite from epigenetic sulfide–calcite veins in the Kupferschiefer deposits of SW Poland is exceptionally enriched in Ge, containing up to 4,800 ppm Ge (Foltyn et al. 2022), whereas Fe-poor sphalerite, the common Ge host in low-temperature environments, has ≤ 6.5 ppm Ge. In general, Ge contents in the Kupferschiefer are not well documented. Few data indicate Ge in the range of ~ 1 to 15 ppm (Höll et al. 2007; Melcher and Buchholz 2014; Foltyn et al. 2022, and references therein). Sphalerite is an accessory mineral in our samples, which have similar contents of Zn and Ge (ESM Table 1; Fig. 3), making sphalerite unlikely as the host mineral of Ge at Tilkerode.

Although the Ge-bearing mineral has not yet been identified at Tilkerode, we note that its Ge enrichment and that in the Kupferschiefer deposits have two features in common: an epigenetic carbonate-mineral vein overprint and a black-shale host rock (rich in organic matter). The latter implies that migrating hydrothermal fluids interacted with organic matter and sourced Ge from it. In this regard, Ge-bearing sulfide deposits are frequently associated spatially with organic-bearing sedimentary host rocks (Bernstein 1985; Jones 2021). A magmatic or igneous origin for the Ge enrichment is deemed unrealistic. Instead, a more likely origin seems to be attributable to sulfate-bearing, oxidised brines that originated from the overlying Zechstein evaporitic sediments, as proposed by Cabral et al. (2018) for vein selenide minerals at Clausthal, in the Harz mountains. Given that carbonates and evaporites are generally depleted in Ge concentrations compared to the crustal Ge abundance (Höll et al. 2007), Ge would have been sourced from organic matter by Zechstein-derived brines. Future fluid-inclusion studies of vein minerals from Tilkerode should elucidate the fluid origin. Future work should also focus on the Silurian black graptolite shale, the Ge contents of which are not yet known. A potential link between organic matter and Ge enrichment in the Tilkerode vein system could also be sought by Ge isotopes, which are sensitive to complexing processes with organic matter and/or sulfide compounds (Rouxel and Luais 2017).

At Tilkerode, hydrothermal fluids of low temperature, constrained by the presence of umangite, were also capable of transporting Au, Pt and Pd. These metals are also locally enriched in the Kupferschiefer deposits (Kucha and Przylowicz 1999; Piestrzyński et al. 2002). There is a tendency of elevated Ge contents to occur with Ag-rich minerals in sulfide ore deposits (Höll et al. 2007). Tilkerode also has Ag-rich minerals, but as selenide minerals. Germanium enrichments in environments with predominance of Se over S has, to our knowledge, gone unrecognized. It seems that Tilkerode is a Se-rich part of the broader fluid system that led to the formation of the Kupferschiefer Cu–Ag deposits in central Europe.

Conclusion

This study reports the finding of high contents of Ge, Au, Pt and Pd, and other metals in whole-rock samples from a historical deposit where hematite was mined for Fe. Tilkerode is just one of numerous (carbonate–hematite–selenide) vein-type deposits in the Harz Mountains, a former mining region of economical relevance, of which modern whole-rock chemical data for precious and critical metals are lacking. Our study provides evidence of a genetic link between Ge enrichment in a low-temperature hydrothermal carbonate–hematite vein system and a black-shale host rock (rich in organic matter). Tilkerode is likely a small-scale manifestation of a regional process involving fluid interaction with organic matter, from which Ge and other metals are likely sourced. This regional-scale process is substantiated by the high Ge contents that have recently been reported from the Kupferschiefer Cu–Ag deposits in central Europe. Our finding suggests that the carbonate–hematite vein systems of the Harz Mountains have the potential to be prospected for Ge and precious metals.

Supplementary Information The online version contains supplementary material available at https://doi.org/10.1007/s00126-023-01182-y.

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Authors' contribution All authors contributed to the study conception and design. Sampling was done by Stephanie Lohmeier, Alexandre Raphael Cabral and Bodo-Carlo Ehling. Material preparation was done by Stephanie Lohmeier. LA-SF-ICP-MS was performed by Armin Zeh. Data analysis was done by Stephanie Lohmeier, Alexandre Raphael Cabral and Armin Zeh. The first draft of the manuscript was written by Stephanie Lohmeier and Alexandre Raphael Cabral and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

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Declarations

Conflict of interest There is no conflict of interest to be declared.

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