



## The new critical metals database “HTMET”: High tech trace element characteristics of sulphides from base metal provinces in the Variscan basement and adjacent sedimentary rocks in Germany

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**Abstract:** High tech (HT) trace elements such as germanium, gallium and indium gain rising importance in the development of innovative technologies. The database “HTMET” forms the first nationwide metal-ore database for Germany, created to visualise HT metal characteristics of base metal ores from important mining districts. Mineralogical and geochemical investigations on 478 samples and ore concentrates from 109 Pb-Zn-Cu occurrences were carried out using analytical methods with high spatial resolution and bulk sample methods. The database provides aggregated data based on 17,000 geochemical data sets, compiled information on regional infrastructure and environmental risks as well as data on innovative raw material-efficient processing techniques. Evaluation of combined data provides interactive maps revealing new potentials for specific HT metals in Germany.

Differences in regional distribution of these trace elements and dependency of their concentration levels in the ore on the genetic deposit type became apparent. Sphalerite from the sediment-hosted massive sulphide (SHMS) deposit “Rammelsberg” and skarn deposits in the Erzgebirge contain elevated indium contents (median 14–119 ppm), whereas the SHMS deposit “Meggen” is poor in HT metals. Germanium forms the predominant HT trace element in colloform sphalerite of Mississippi-Valley-Type (MVT) deposits (median 29–147 ppm); in contrast, crystalline sphalerite is low in germanium in this deposit type. Sphalerite in all hydrothermal vein deposits shares a distinct enrichment in gallium (median 6–81 ppm); however, germanium and indium concentrations vary significantly depending on the metal source and fluid conditions. The Ruhrgebiet and the Schwarzwald ore veins show an enrichment in germanium (median 55–73 ppm), whilst vein sphalerite from the Erzgebirge is specialised in indium (median 33 ppm). The data demonstrate that the HT trace element inventory of the studied base metal sulphides is not only a function of the genetic ore deposit type, but is also triggered by locally variable geology such as source rock and fluid composition and organic content of the rock. Gallium seems to derive from adjacent lithologies, whereas indium and germanium may have more distant sources.

**Kurzfassung:** Durch die fortschreitende Verbreitung und Weiterentwicklung von modernen Technologien erlangen die sogenannten hochtechnologierelevanten (HT) Spurenelemente Germanium, Gallium und Indium steigende Bedeutung. Die „HTMET“-Datenbank ist das erste deutschlandweite Metallerg-Kataster, welches die HT-Metall-, „Spezialisierung“ wichtiger Buntmetall-Bergbaudistrikte reflektiert. An 478 Erzproben und -konzentraten aus 109 Pb-Zn-Cu-Vorkommen wurden mittels hochortsaufgelösten Punktanalysen und nasschemischen Gesamterzmessungen mineralogische und geochemische Untersuchungen durchgeführt. Die Datenbank beinhaltet aggregierte Daten von 17.000 geochemischen Datensätzen, Informationen zur regionaler Infrastruktur und möglichen Umweltrisiken, sowie Ergebnisse aus innovativen, rohstoffeffizienten Aufbereitungsversuchen. Unter Verwendung aller Ergebnisse können interaktive Karten zu neuen HT-Metall-Rohstoffpotenzialen erzeugt werden.

Hinsichtlich der regionalen Verteilung der HT-Spurenmetalle zeigen sich Abhängigkeiten der Gehalte im Erz zum genetischen Lagerstättentyp. Sphalerit aus der SEDEX-Lagerstätte „Rammelsberg“ sowie aus Skarn-Lagerstätten des Erzgebirges beinhaltet erhöhte Indium-Gehalte (Median 14–119 ppm). Im Gegensatz dazu zeigt Sphalerit aus der SEDEX-Lagerstätte „Meggen“ nur sehr geringe HT-Spurenmetallgehalte. Germanium ist in „Schalenblenden“ aus MVT-Lagerstätten das vorherrschende HT-Spurenelement (Median 29–147 ppm). Allerdings ist kristalliner Sphalerit aus diesen Vorkommen durch geringe Germanium-Gehalte charakterisiert. Sphalerit aus allen untersuchten hydrothermalen Ganglagerstätten ist durch moderate bis hohe Gallium-Konzentrationen (Median 6–81 ppm) gekennzeichnet. Die Germanium- und Indium-Gehalte

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variieren dagegen signifikant, abhängig von der Metallquelle sowie den Fluideigenschaften. Ganglagerstätten aus dem Ruhrgebiet und dem Schwarzwald beinhalten Sphalerit mit erhöhten Germanium-Gehalten (Median 55–73 ppm), während Sphalerit aus Gängen des Erzgebirges durch erhöhte Indium-Konzentrationen (Median 33 ppm) charakterisiert ist.

Die Ergebnisse dieser Arbeit zeigen, dass die HT-Spurenelementgehalte in den Buntmetallsulfiden nicht ausschließlich vom genetischen Lagerstättentyp abhängig sind. Auch die lokal variierenden geologischen Bedingungen, wie beispielsweise die Ausgangsgesteine, Fluidbedingungen sowie das Vorhandensein von organischer Materie, haben einen bedeutenden Einfluss auf die Spurenelementanreicherungen. Im Gegensatz zu den eher lokalen Quellen für Gallium sind für Indium und Germanium in den untersuchten Systemen auch weiter entfernte Reservoirs als Quelle zu diskutieren.

**Keywords:** germanium, gallium, indium, sphalerite, database, Germany, hydrothermal veins, MVT, SHMS, skarn, deposits, economic geology

**Schlüsselwörter:** Germanium, Gallium, Indium, Sphalerit, Datenbank, Deutschland, hydrothermale Gänge, MVT, SEDEX, Skarn, Lagerstätten, Rohstoffgeologie

## 1. Introduction

Mining on non-ferrous metals has a long history in Germany's ore districts. Early prospecting work and mining on lead and silver ores during the Roman period and the Middle Ages, is assumed (Geurts et al. 2004; Werner & Dennert 2004). Mining of base metals in Germany discontinued in the late 20<sup>th</sup> century due to decreasing ore grades and low commodity prices (Stedingk 2012). Result of the complete stop of activities in this field is an overall under exploration of the important mining districts in Germany in terms of modern geochemical analysis.

Today, the steadily rising demand for metals worldwide and the advancing development of modern technologies place new demands on the exploration and production of raw materials. Elements for high tech applications (HT elements) such as germanium (Ge), gallium (Ga) and indium (In) gain rising importance. These critical raw materials frequently occur at trace levels incorporated in base metal sulphides such as sphalerite and chalcopyrite, or as small mineral inclusions of, for example, roquesite, gallite or germanite (Cook et al. 2009).

Currently, Ge is economically the most important of the HT trace elements studied here and can be enriched in sphalerite with concentrations up to 3000 ppm (Bernstein 1985; Cook et al. 2009; Belissont et al. 2014). Owing to its characteristics as semiconductor element and its infrared transmission properties, the main applications are in infrared optics, fibre optic cables, catalysts and solar applications (Melcher & Buchholz 2013; Marscheider-Weidemann et al. 2016). Gallium is incorporated in sphalerite with concentrations up to thousands of ppm (Cook et al. 2009; Marscheider-Weidemann et al. 2016). It is used as a semiconductor element in the electronics industry (e.g. LEDs, solar applications) and is commonly extracted from bauxite ores. However, its occurrence and incorporation in sulphides are less well investigated. Indium is preferentially used in various thin-film applications such as transparent electrodes for displays and semiconductor layers in solar applications (Marscheider-Weidemann et al. 2016). Sphalerite hosts up to thousands of ppm of In in several ore deposits worldwide (Schwarz-Schampera & Herzig 2002; Seifert & Sandmann 2006).

Despite the enormous interest in these elements worldwide, there are no systematic studies on HT trace elements in German ore districts available so far. Furthermore, the reliability of the sparse trace element data from times of active base metal mining in Germany is insufficient also due to outdated analytical methods used in the past. However, the fact that In was extracted from the sediment-hosted massive sulphide (SHMS) deposit “Rammelsberg” (Harz) from 1948–1964 as a by-product (mine closure in 1988), indicates elevated contents of this trace element in some of its ore types (Mehner 1993). Potentials of base metal ores in Germany for HT trace elements were also suggested in some recent studies. Skarn deposits from the Erzgebirge yielded elevated In contents (Seifert & Sandmann 2006). Mostly moderate concentrations of Ge and Ga were measured in a few sphalerite samples from a small number of hydrothermal vein deposits in Germany and a Mississippi-Valley-Type (MVT) deposit in the Odenwald region (e.g. Möller & Dulski 1993; Werner et al. 2002; Pfaff et al. 2011). Finally, studies on base metal deposits in the EU and worldwide indicate a dependency of enrichment of the HT trace elements on the genetic deposit type and also on the formation temperature (Cook et al. 2009; Ye et al. 2011; Frenzel et al. 2016).

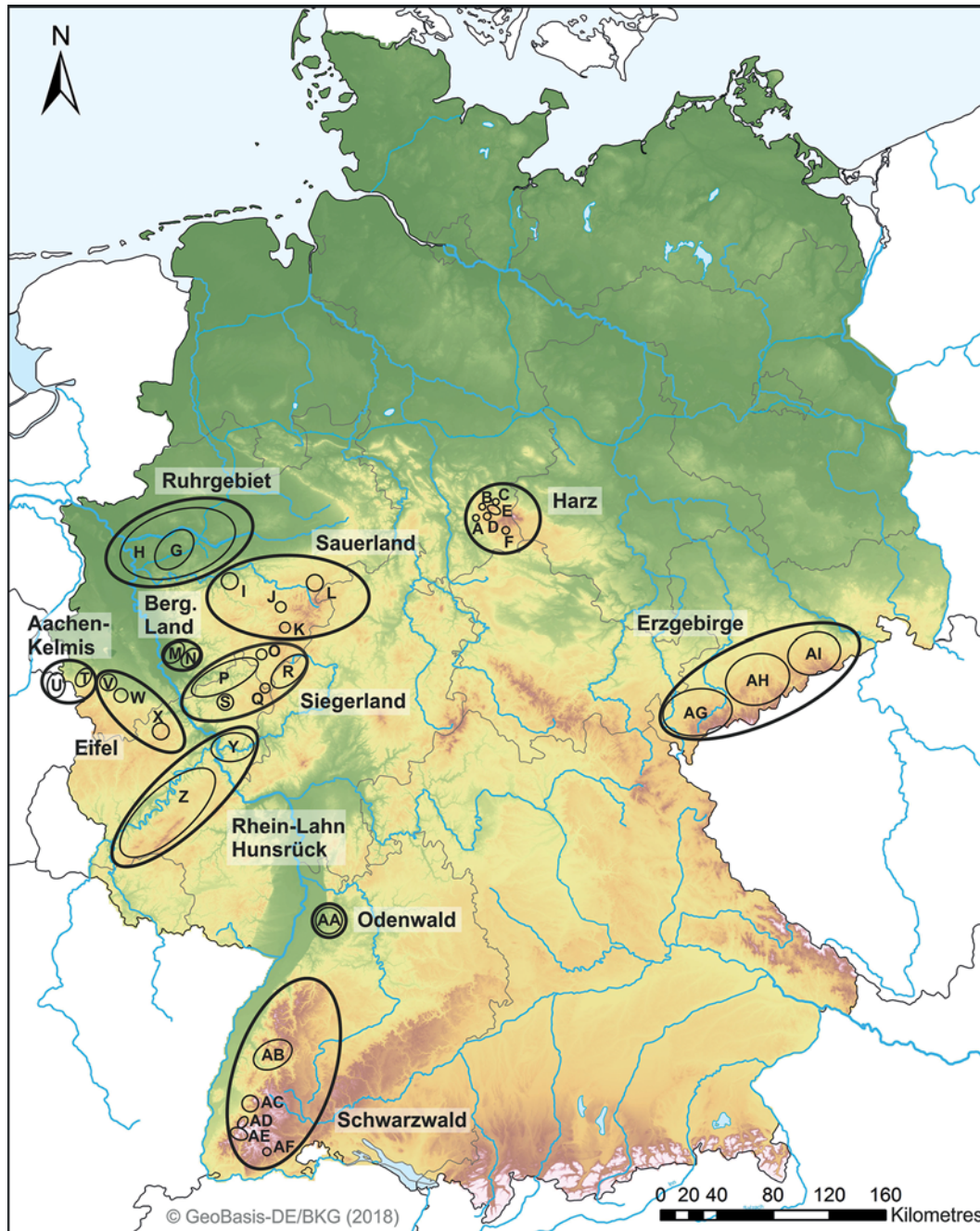
The overall objective of the present study was the evaluation of raw material potentials for Ge-, Ga- and In-extraction as important by-products of mining in Germany's base metal mining districts. Geochemical data for ore samples from the adjacent EU region Plombières in Belgium are added for scientific comparison. The main focus of the work is to provide active support for future exploration activities. Therefore, a high tech metal-oriented database was set up summarising state-of-the-art data on ore mineralogy and chemistry (primary indicators), historic mining site-related infrastructural (secondary) indicators and mineral processing-related (tertiary) indicators. The produced mineralogical and geochemical data sets for ore samples from eleven important mining districts of Germany, e.g. data from “micro-energy-disperse X-ray fluorescence microscopy” ( $\mu$ -EDXRF), “laser ablation inductively coupled plasma mass spectrometry” (LA-ICP-MS) and “electron micro probe analyser” (EMPA), are also scientifically interpreted with focus on trace element concentration and distribution characteristics in base metal deposits of different genetic

types. Results are discussed to reveal a possible influence of the geological framework on observed regional enrichment or depletion of HT trace metals in the base metal ores.

## 2. Geology and sampling

Fig. 1 illustrates the locations of the investigated eleven base metal mining districts in Germany and Belgium. These districts were subdivided into 35 clusters of deposits (A–AI) in

terms of geographical and geological aspects (Table 1). In this study, five genetic base metal deposit types are distinguished: (a) Sediment-hosted massive sulphide deposits (SHMS), (b) skarn deposits (SKARN), (c) hydrothermal vein deposits (VEIN), (d) carbonate-hosted Mississippi-Valley-Type deposits (MVT), and (e) disseminated ore deposits (DISSEM). Although regional differences in the geological framework of the deposits are obvious, all mining districts are located in the Variscan mountain belt that was mainly formed in the Devonian and Carboniferous due to the colli-



**Fig. 1:** Geomorphological map of Germany showing the locations of the eleven ore districts and 35 clusters of deposits (A-AI) included in the HTMET database (see also Table 1 for further details).

**Table 1:** List of clusters (A–AI), deposit types and mineral paragenesis, as well as numbers of investigated locations and samples included in the HTMET database. <sup>1</sup>Hand specimen and industrial ore concentrates; <sup>2</sup>“calamine” ore was not analysed; <sup>3</sup>Belgium.

Ore district	Cluster	Locations	Deposit type	Mineral paragenesis	No. of samples <sup>1</sup>
<b>1 Harz</b>					
A	Grund ore mine	1	VEIN	quartz-calcite-siderite veins; Pb-Zn(-Cu) ore	44
B	Lautenthal	1	VEIN	quartz and calcite veins; Zn-Pb-Cu ore	35
C	Rammelsberg	1	SHMS	polymetallic Zn-Cu-Fe-Pb ore; barite	14
D	Clausthal-Zellerfeld	5	VEIN	quartz and calcite veins; Pb-Zn(-Cu) ore	14
E	Bockswiese	4	VEIN	quartz-carbonate veins; Zn-Pb-Cu ore	8
F	St. Andreasberg	3	VEIN	quartz-calcite veins; Zn-Pb ore / barite veins; Zn-Cu ore	6
<b>2 Ruhrgebiet</b>					
G	Core zone	7	VEIN	quartz-barite-carbonate veins; Pb-Zn(-Cu) ore; hard coal	30
H	Marginal zone	4	VEIN	quartz-barite-carbonate veins; Pb-Zn(-Cu) ore; hard coal	4
<b>3 Sauerland</b>					
I	Iserlohn	1	VEIN	carbonate hosted Pb-Zn ore	4
J	Ramsbeck	1	VEIN	quartz veins; Pb-Zn ore	11
K	Meggen	1	SHMS	polymetallic Fe-Pb-Zn ore; barite	10
L	Brilon <sup>2</sup>			Pb-Zn ore (“calamine”)	
<b>4 Bergisches Land</b>					
M	Bensberg Pb-Zn area	7	VEIN	quartz(-carbonate) veins; Pb-Zn(-Cu) ore	25
N	Bergisch Pb-Zn area	4	VEIN	quartz-carbonate veins; Pb-Zn(-Cu) ore	9
<b>5 Siegerland</b>					
O	Müsen	1	VEIN	siderite-quartz veins; Cu-Zn-Pb ore	2
P	Siegen	7	VEIN	siderite-quartz veins; Pb-Zn-Cu(-Ni) ore	12
Q	Burbach	1	VEIN	siderite-quartz-veins; Pb-Zn-Ni-Co ore	4
R	Lahn-Dill	2	VEIN	siderite veins; Pb-Zn ore / quartz veins; Pb-Sb-Cu ore	4
S	Hamm (Sieg)	1	VEIN	siderite veins; Pb-Zn ore	2
<b>6 Aachen-Kelmis</b>					
T	Aachen-Stolberg	2	MVT	carbonate hosted Pb-Zn(-Fe) ore	10
U	Plombières-Kelmis <sup>3</sup>	9	MVT	carbonate hosted Pb-Zn(-Fe) ore	25
<b>7 Eifel</b>					
V	Maubach	1	DISSEM	dissiminated Pb(-Zn-Cu) ore	2
W	Mechernich	1	DISSEM	dissiminated Pb(-Zn) ore	1
X	Adenau	1	VEIN	siderite-quartz veins; Pb-Zn ore	1
<b>8 Rhein-Lahn-Hunsrück</b>					
Y	Rhein-Lahn	12	VEIN	quartz-siderite veins; Pb-Zn-Cu ore	39
Z	Hunsrück	7	VEIN	quartz-carbonate veins; Pb-Zn-Cu ore	26
<b>9 Odenwald</b>					
AA	Odenwald	1	MVT	carbonate hosted Pb-Zn(-Fe) ore	9
<b>10 Schwarzwald</b>					
AB	Kinzigtal	3	VEIN	fluorite-barite veins; Pb-Zn-Cu(-Ag) ore	10
AC	Glottertal-Suggental	4	VEIN	barite veins; Pb-Zn-Cu ore / quartz-siderite veins; Zn-Pb-Cu ore	4
AD	Schauinsland	2	VEIN	quartz-barite-carbonate veins; Zn-Pb ore	33
AE	Münstertal	7	VEIN	quartz-barite veins; Pb-Zn ore / fluorite-barite veins; Zn-Pb (-Cu) ore; fluorite veins; Ag-As-Sb ore	25
AF	St. Blasien	1	VEIN	fluorite-barite veins; Zn-Pb-Cu ore	4

Table 1: cont.

Ore district	Cluster	Locations	Deposit type	Mineral paragenesis	No. of samples <sup>1</sup>
<b>11</b>	<b>Erzgebirge</b>				
AG	Western part	8	SKARN	Fe-Zn ore / Zn-Cu ore / Sn-Zn-Cu ore and magnetite	18
		1	VEIN	quartz veins; Sn ore	1
AH	Central part	1	SKARN	Sn ore	13
		2	MVT	carbonate hosted Pb-Zn ore	5
		1	VEIN	quartz veins; Pb-Zn-Sn-As ore / carbonate-quartz veins; Zn-Pb-Sb ore	8
AI	Eastern part	2	SKARN	Fe ore / magnetite and Zn-Cu ore	4

sion of Laurussia and Gondwana during the formation of Pangaea. As the majority of the deposits selected for investigation are not accessible anymore, most of the samples were taken from geological collections of the Federal Institute for Geosciences and Natural Resources (BGR), associated partners and private mineral collectors. Sampling campaigns in mining museums, like the “Lautenthal’s Glück” mine (Harz) and several abandoned mines in the Schwarzwald district have been realised thanks to active support by local state geological surveys and museum operators. If present, differences in the sampled ore type and the ore appearance (e.g. grain-sizes of sulphides or associated gangue minerals) were considered during sampling.

### 3. Methods

#### 3.1 Analytical methods

##### 3.1.1 $\mu$ -EDXRF

Energy dispersive X-ray fluorescence spectrometry maps ( $\mu$ -EDXRF) were carried out using the M4 Tornado by Bruker to obtain an overview on the textural properties and the mineral proportions of larger cut rock slices (max. 16 x 20 cm). The X-ray beam of the Rh-tube is focused on the sample surface with a 51° angle and approx. 17  $\mu$ m diameter in spot size at 17.48 keV. Mapping of the samples with maximum excitation (tube: 50 kV, 600  $\mu$ A), 2 ms measuring time per spot and step ranges between 20 to 50  $\mu$ m leads to spatially resolved analytical data, with elements heavier than Na measurable under low vacuum conditions (Flude et al. 2017). Mineral distribution maps were obtained by supervised classification using the “Spectral Angle Mapper” algorithm (Nikonow & Rammlmair 2017). An endmember database for base metal sulphides and associated minerals in the above deposit types was created. Unclassified areas (mostly silicates) were assigned to the host rock. Mixed analysis and boundary effects, as well as diffraction effects for the interpretation of the mineral distribution maps were considered during manual spectrum interpretation and endmember definition (Nikonow & Rammlmair 2016). This method provides

a link between micro-scale geochemistry data and macro-scale ore outcrops and rock specimen. Based on the  $\mu$ -EDXRF results smaller pieces (3 x 3 cm) from the original rock slices were cut and prepared as polished sections, which were used as samples for LA-ICP-MS and EMPA analysis (details see below).

##### 3.1.2 LA-ICP-MS

The quantitative analysis of major, minor and trace elements in sphalerite and chalcopyrite was conducted in-situ by a PlasmaQuant Elite quadrupole ICP-MS by Analytik Jena coupled to a 213 nm laser ablation system (LSX-213 G2+ by CETAC Technologies). The laser system was adjusted to ablate round 40  $\mu$ m spots using a fluence of 8 J/cm<sup>2</sup> at 20 Hz for 15 s. Prior to each ablated spot a gas blank was monitored for 15 s. On each sample (polished sections, see above) 30 to 60 spots on sphalerite and chalcopyrite were analysed. Helium was used as the carrier gas (0.4 l/min). Cool, auxiliary and sample gas flows of the ICP-MS were adjusted to 9.0, 1.35 and 1.04 l Ar/min, respectively. The isotopes <sup>34</sup>S, <sup>44</sup>Ca, <sup>51</sup>V, <sup>52</sup>Cr, <sup>55</sup>Mn, <sup>56,57</sup>Fe, <sup>59</sup>Co, <sup>60</sup>Ni, <sup>63,65</sup>Cu, <sup>66</sup>Zn, <sup>71</sup>Ga, <sup>74</sup>Ge, <sup>75</sup>As, <sup>77,78,82</sup>Se, <sup>83</sup>Kr, <sup>95</sup>Mo, <sup>107</sup>Ag, <sup>111</sup>Cd, <sup>115</sup>In, <sup>117,118</sup>Sn, <sup>121</sup>Sb, <sup>126</sup>Te, <sup>137</sup>Ba, <sup>205</sup>Tl and <sup>208</sup>Pb were monitored by the ICP-MS using a dwell time of 10 ms for each isotope. In the analytical sessions, the sphalerite reference material MUL-ZnS-1 (Onuk et al. 2017) and the polymetallic reference material MASS-01 (Danyushevsky et al. 2011) were ablated several times. Element concentrations in sphalerite were quantified using MUL-ZnS-1 as an external calibration material and MASS-01 as reference material for quality control (Wilson et al. 2002; Yuan et al. 2012). Element concentrations in chalcopyrite were quantified using MASS-01 as an external calibration material. Raw data were exported and processed with a data-handling software tool (Gäbler et al. 2011). A calibration strategy based on ablation yield correction factors (Liu et al. 2008) was used, in which the sum of all cations was normalised to the stoichiometric content of Zn in sphalerite (67.00 wt.%) and the stoichiometric content of Cu and Fe in chalcopyrite (65.06 wt.%). This calibration strategy eliminates the need for additional element analysis at each spot for internal standardisation by an independent

method (e.g. by EMPA) and enables the analysis of a higher number of samples (Danyushevsky et al. 2011).

Isobaric interference needs to be considered when analysing trace elements in sphalerite by LA-ICP-MS (Cook et al. 2009; Danyushevsky et al. 2011; Belissont et al. 2014). The interference of  $^{115}\text{Sn}$  on  $^{115}\text{In}$  was corrected using  $^{117}\text{Sn}$ . The isotope  $^{74}\text{Ge}$  was used for determination of the Ge concentration because this isotope shows least isobaric interference caused by other relevant ions and the highest natural abundance of all Ge isotopes. Although no collision cell was used, a large influence of  $^{40}\text{Ar}^{34}\text{S}$  on  $^{74}\text{Ge}$  intensities can be excluded due to the record of Ge concentrations below the detection limit for many laser spots in sphalerite and chalcopyrite. A typical analytical uncertainty for laser ablation of no more than 20–30 % is expected for the analysed element concentrations (Cook et al. 2009; Danyushevsky et al. 2011). Single spots with clear indications of mixed mineral analyses involving underlying minerals or mineral inclusions (ragged spectrum) were excluded.

The average detection limits of LA-ICP-MS analysis are 1 ppm for Ga, 2 ppm for Ge and 0.1 ppm for In. The reliability of the used analytical method was verified by re-measurement of selected samples with a larger number of laser spots and by comparative measurements at the Montanuniversität Leoben (Austria), where a quantification method based on sulphur concentrations as internal standard was applied. Exemplary, the concentrations of the major elements were also compared with electron microprobe data for several samples. However, box plot diagrams indicate that the natural variability of trace element concentrations in sphalerite covers several orders of magnitudes and is as such much larger than the analytical uncertainty. Nevertheless, measurement of a given sample is reproducible and distinct differences between samples can be illustrated by their populations within box plot diagrams.

### 3.1.3 EMPA

Fine-grained samples and sphalerite grains containing intense chalcopyrite disease could not be analysed by LA-ICP-MS due to the selected spot size of 40  $\mu\text{m}$ . These samples were measured by a Jeol JXA-8530F Hyperprobe (FEG-EMPA) where smaller spot sizes of about 1–2  $\mu\text{m}$  are applied. The analytical setup was similar to that used by Goldmann et al. (2018). The quantitative analysis of the ma-

ior, minor and trace element compositions of sphalerite and chalcopyrite grains were conducted by single spot analyses using wavelength-dispersive spectrometry with an acceleration voltage of 20 kV and a beam current of 80 nA. Major elements were analysed for 8–40 s applying ZnS as reference material for Zn and S,  $\text{CuFeS}_2$  for Cu and  $\text{FeS}$  for Fe using their respective  $K\alpha$  X-ray lines. Minor and some trace element signals were counted for 60–120 s using a PET crystal for In- $L\alpha$  and a LIF crystal for Ge- $K\alpha$  and Ga- $K\alpha$ . For calibration, GaAs as well as pure metals (In and Ge) were used as reference materials. The limits of detection for Ge (30 ppm), Ga (23 ppm) and In (24 ppm) are much higher compared to those of the LA-ICP-MS method.

### 3.1.4 Bulk ore geochemistry

In order to estimate the trace element compositions of different ore types in the base metal deposits and occurrences and to cross-check the results of the mineral chemistry determinations by LA-ICP-MS, geochemical bulk sample analysis was conducted. Per location and ore type up to 100 g of sample material knocked off several hand specimen was crushed and enriched to 25–100 wt.% sulphide content by hand picking, resulting in Zn-, Cu- or mixed-“sample concentrates”. The quantitative determination of major, minor and trace elements was carried out in the laboratories of Actlabs (Canada) using the analytical packages “Ultratrace 3” (INAA + 4-acid digestion/ICP-OES/ICP-MS), “Ultratrace 7” (peroxide fusion – ICP and ICP/MS) and “Code 8-Peroxide-ICP-OES”. Precision and accuracy are ensured by blank runs, in-house control, duplicate analysis and a suite of internationally certified standards. Furthermore, industrial concentrates deriving from the historic ore processing plants were analysed by ICP-OES (aqua regia digestion) at TU Clausthal (IFAD Institute). Sulphur was measured by use of an infrared cell here and Ge concentrations were analysed by use of multistep digestion (nitric acid) to avoid Ge loss.

## 3.2 Definition of ore types and data handling

According to the mineralogical compositions of the ores, seven major ore types were defined based on the sulphide mineral proportions as estimated by  $\mu$ -EDXRF maps (Table

**Table 2:** Ore types in studied base metal samples based on  $\mu$ -EDXRF mineral distribution maps; the types are independent of the genetic deposit type; proportions are in wt.% and are referred to sulphide contents.

Ore type	Definition
sphalerite-dominated	sphalerite >90 wt.%
sphalerite-galena	sphalerite + galena >90 wt.%, sphalerite < 90 wt.% and galena <90 wt.%
sphalerite-chalcopyrite	sphalerite + chalcopyrite >90 wt.%, sphalerite <90 wt.% and chalcopyrite <90 wt.%
sphalerite-galena-chalcopyrite	sphalerite + galena >25 wt.% and chalcopyrite >25 wt.%
chalcopyrite-dominated	chalcopyrite >90 wt.%
galena-dominated	galena >90 wt.%, sphalerite-bearing
fahlore-bearing/-dominated	occurrence of larger amounts of fahlore, chalcopyrite-bearing

2). This classification is independent of the genetic deposit type. As literature data (e.g. Cook et al. 2009) and first studies have shown that sphalerite and chalcopyrite form the major carriers of the HT trace metals in base metal sulphide ores, the mineralogical and geochemical work of this project mainly focused on these minerals. The mineral chemistry data (LA-ICP-MS, EMPA) stored in the database consist of aggregated data for each deposit further subdivided into the separated ore types (see Figure 3b). These aggregated data describe the obtained distributions of element concentrations within each ore type of each deposit. The 25<sup>th</sup>, 50<sup>th</sup> (median) and 75<sup>th</sup> percentiles, as well as an average value (calculated arithmetic mean), are used. Data for sphalerite and chalcopyrite are given separately. The underlying numbers of samples, analysed single spots, and the applied analytical technique are given for each distribution as well.

## 4. Results and discussion

### 4.1 High tech trace element database “HTMET”

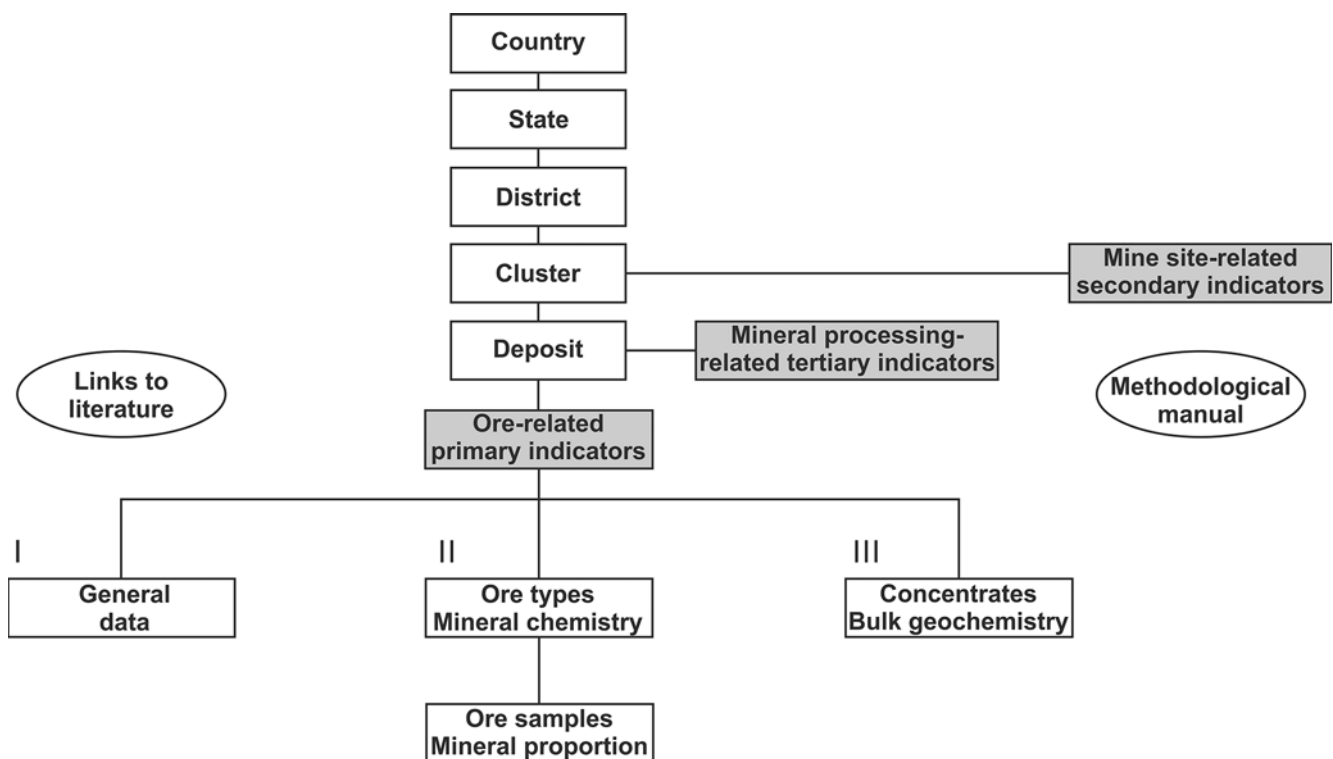
#### 4.1.1 Database structure

The aim of the HTMET database is to conveniently manage the extensive and complex data stock and to enable the evaluation of raw material potentials for the above mentioned 35

clusters of base metal deposits as a fundamental basis for future exploration activities. Therefore, a relational database was set up to store and handle mineralogical and geochemical data (ore-related primary indicators) as well as mine site-related secondary and mineral processing-related tertiary indicators. For the purpose of data access and visualisation a graphical user interface including a multicriterial evaluation tool has been developed as a front end to the database.

A python-based importer software reads all data and converts it from MS Excel to PostgreSQL format. The data is stored normalised in the database and PostgreSQL. Postgis is used to support GIS-based queries. The design is data driven, which means that additional data types can easily be added to the database, mostly without the need to change the database scheme. Fine-grained access rights are implemented to support federal state-based access. Each individual deposit, which can be selected either by a search function or from a list of deposits, is unambiguously allocated to a cluster, district, federal state and country (Fig. 2). Primary indicators are included for most deposits and contain:

(1) General data such as the genetic ore deposit type, a short description of the mineral paragenesis and the mining history as well as associated gangue minerals (barite, fluorite and calcite) and other raw materials, possibly harmful minerals (marcasite and arsenopyrite), an image of a typical ore sample, the exact geographical location of the mine site and links to further literature.



**Fig. 2:** Schematic structure of the HTMET database showing stored contents and connections between primary, secondary and tertiary indicators.

(2) Aggregated mineral chemistry results (LA-ICP-MS, EMPA data based on 17,000 data sets and 457 samples) with special consideration of minor and HT trace elements of the related ore samples ( $\mu$ -EDXRF data, 457 samples).

(3) Bulk geochemistry results of selected industrial and sample concentrates (ICP-MS/OES data, 101 ore concentrates).

Detailed descriptions and the corresponding literature for each of the methods used are included in the database (methodological manual). Literature data on outdated geochemical results and sporadic hints on remaining amounts of mineral/metal resources are not included in the database due to large differences in the quality of the data (however, all

available references for both are provided for further studies of the users).

Secondary indicators were included for eight clusters of deposits. They focus on an evaluation of infrastructure and environmental aspects within the defined clusters of important mine sites, such as:

(1) Accessibility of the cluster area (railway, main roads or river ports).

(2) Summary of the legal situations at individual mine sites (e.g. historic monuments, sensitive uses of sites, priority areas for resource extraction).

(3) Regional constraints (e.g. availability of energy, water, skilled personnel, processing industry).

The screenshot shows the HTMET - Deposit Grund web interface. The window title is "HTMET - Deposit Grund". Below the title bar, there are tabs for "Location" and "Settings". The main content area has a navigation bar with tabs: "General", "Samples", "Ore types", "Diagrams", "Concentrates", "Location", "Ore processing", and "Methodological manual". The "General" tab is active. On the left, there is a map of Germany with a red dot indicating the location of the deposit. On the right, there is a photograph of a mineral specimen with a 20 cm scale bar. Below the map and photo, there is a table of general data:

<b>Deposit:</b>	Grund
<b>Location:</b>	Bad Grund
<b>Country:</b>	Germany
<b>Federal State:</b>	Lower Saxony
<b>District:</b>	Harz
<b>Cluster:</b>	Erzbergwerk Grund
<b>Coordinates (WGS84) in degrees:</b>	51.8058 / 10.225
<b>Map sheet (KOR200):</b>	CC 4726 Goslar

Below this table, there are several sections of descriptive text:

- Deposit type:** Hydrothermal veins
- Deposit description:** Hydrothermal quartz-siderite veins with lead and zinc ores
- Target commodities of historical mining:** 1564 - 1992: mining of lead and silver ore; last operating period primary zinc ore and secondary copper ore
- Major ore types present:** Sphalerite dominated, Sphalerite-Galena, Sphalerite-Chalcopyrite, Sphalerite-Galena-Chalcopyrite, Chalcopyrite dominated, Galena dominated
- By-products of mining:** Calcite, Barite
- Non-metallic raw materials:** -
- Interfering minerals:** -

**References:**

- [27] Sperling, H.; Stoppel, D., Die Blei-Zink-Erzgänge des Oberharzes - Beschreibung der Oberharzer Erzgänge (einschließlich der Neuaufschlüsse im Erzbergwerk Grund seit Erscheinen der Lieferung 2), Geologisches Jahrbuch, Reihe D, Heft 34, Monographien der deutschen Blei-Zink-Erzlagerstätten Lieferung 3, Hannover, 352 S., 1979
- [35] Ließmann, W., Historischer Bergbau im Harz, Springer Verlag Berlin, Heidelberg, 470 S., 2010
- [43] Friedensburg, F., Die NE-Metall-Lagerstätten in der Bundesrepublik Deutschland und die Möglichkeiten für ihre Ausnutzung, Bundesanstalt für Bodenforschung, Hannover (Archivstück), 1971
- [57] Bartholomé, P.; Batacchi, A.; Catalano, M., Raw Materials - Research and development. Dossiers No. II Lead and zinc, Commission of the European Communities. Directo, 1979

At the bottom left, there is a section for the "Methodological manual":

1.1.1 Selection of ore occurrences/deposits and samples (region/duster and amount)

**Fig. 3:** Screenshots of the front end connected to the HTMET database for primary indicators of the “Grund” ore deposit (Harz district) showing (a) general data and (b) mean, median and 25/75 percentiles of mineral chemistry investigations (LA-ICP-MS/EMPA data) aggregated for sphalerite/chalcopyrite and ore types.



(4) Summary of environmental risks/nature conservation for the cluster area (e.g. nature reserves/biotopes, effects on urban settlements, karst areas, active mine water treatment, water protection areas).

For the acquisition of tertiary indicators, mineral processing tests were conducted at the TU Clausthal on a laboratory scale using large volume bulk samples. The focus of these tests was a method development for the separation of HT metals from typical base metal ores. The results of these investigations are out of the scope of this manuscript and will be discussed in further publications.

#### 4.1.2 Front end of the database

In order to conveniently visualise the database contents, a graphical user interface has been developed as a front end to the database. It is written in C++ using the Qt framework. As well as the database itself, the structure of the front end is data driven, i.e. the design (e.g. the size of tables, the contents of lists, etc.) depends on the database contents and is dynamically generated at program start. By now the interface is realised as a Windows application, the database access is via hostname and port of the database server. For the future, a purely web-based application is to be implemented

to generate access for the German State Geological Surveys (SGD), domestic industry as well as for interested private individuals, to important data compiled in the database.

Screenshots illustrating the functionality of the front end connected to the HTMET database are shown in Figs. 3 and 4 using the “Grund” ore deposit (Harz district) as an example. Fig. 3a presents the summary page of the compiled general data for the location with links to the available literature and the respective pages of the methodological manual. Fig. 3b illustrates representative  $\mu$ -EDXRF mineral distribution maps for each ore type of the deposit. The results of the mineral chemistry investigations using LA-ICP-MS and/or EMPA are summarised for each ore type and are separately presented for either sphalerite or chalcopyrite; the embedded table lists the compiled data for all relevant ore types of the deposit. Semi-quantitative ternary (In-Ga-Ge) and quantitative XY diagrams (Ga-Ge; In-Ga) are used to classify the results of the mineral chemistry in a broader context by visualising cluster-, district- or country-based datasets (Fig. 4a). The results of bulk geochemistry analysis of concentrates (industrial concentrates and sample concentrates produced in the lab) for the “Grund” mine and pictures of the material used are shown in Fig. 4b. The database provides an export routine for data sheets for individual deposits, presenting compiled general deposit data, mineral proportions, mineral

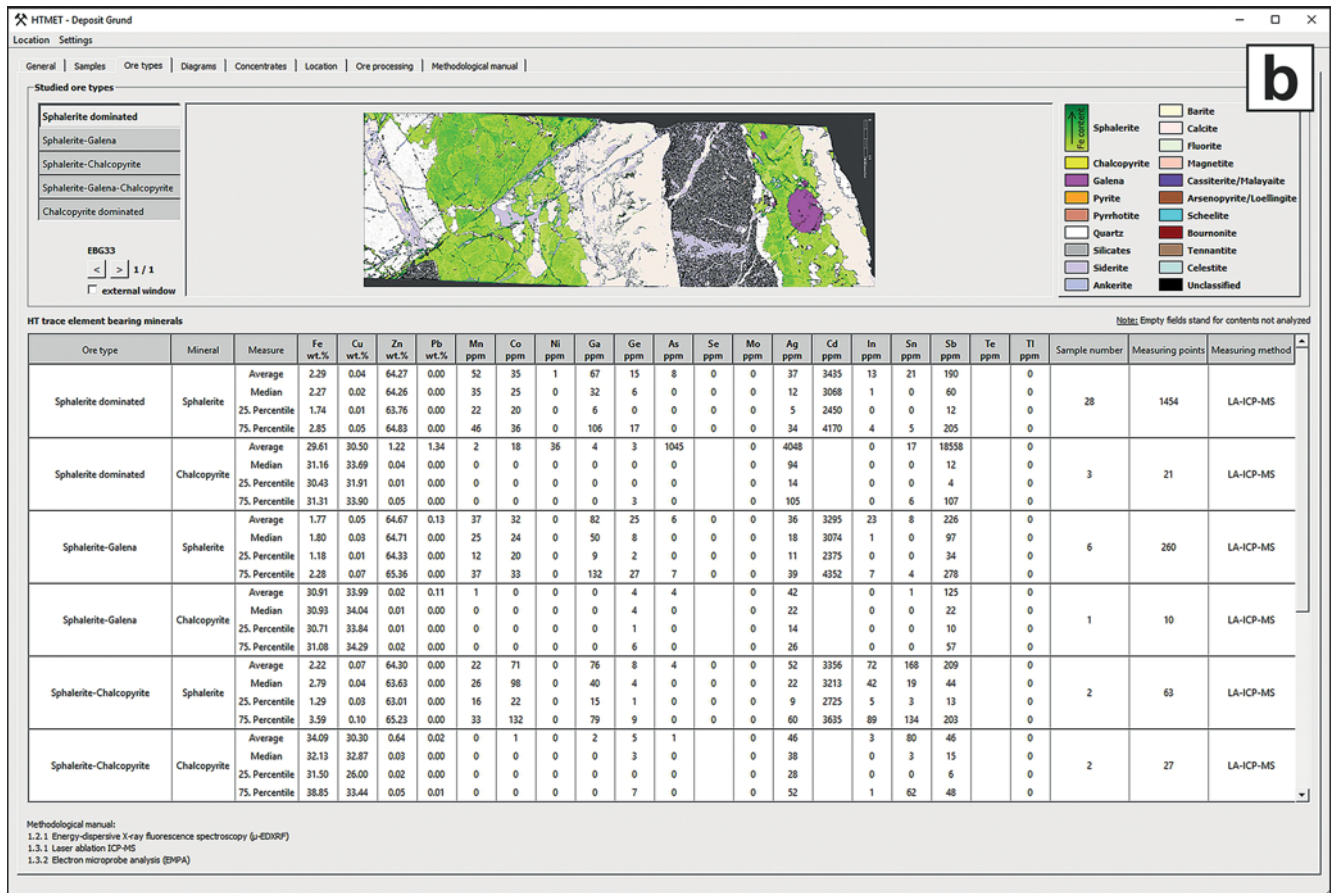
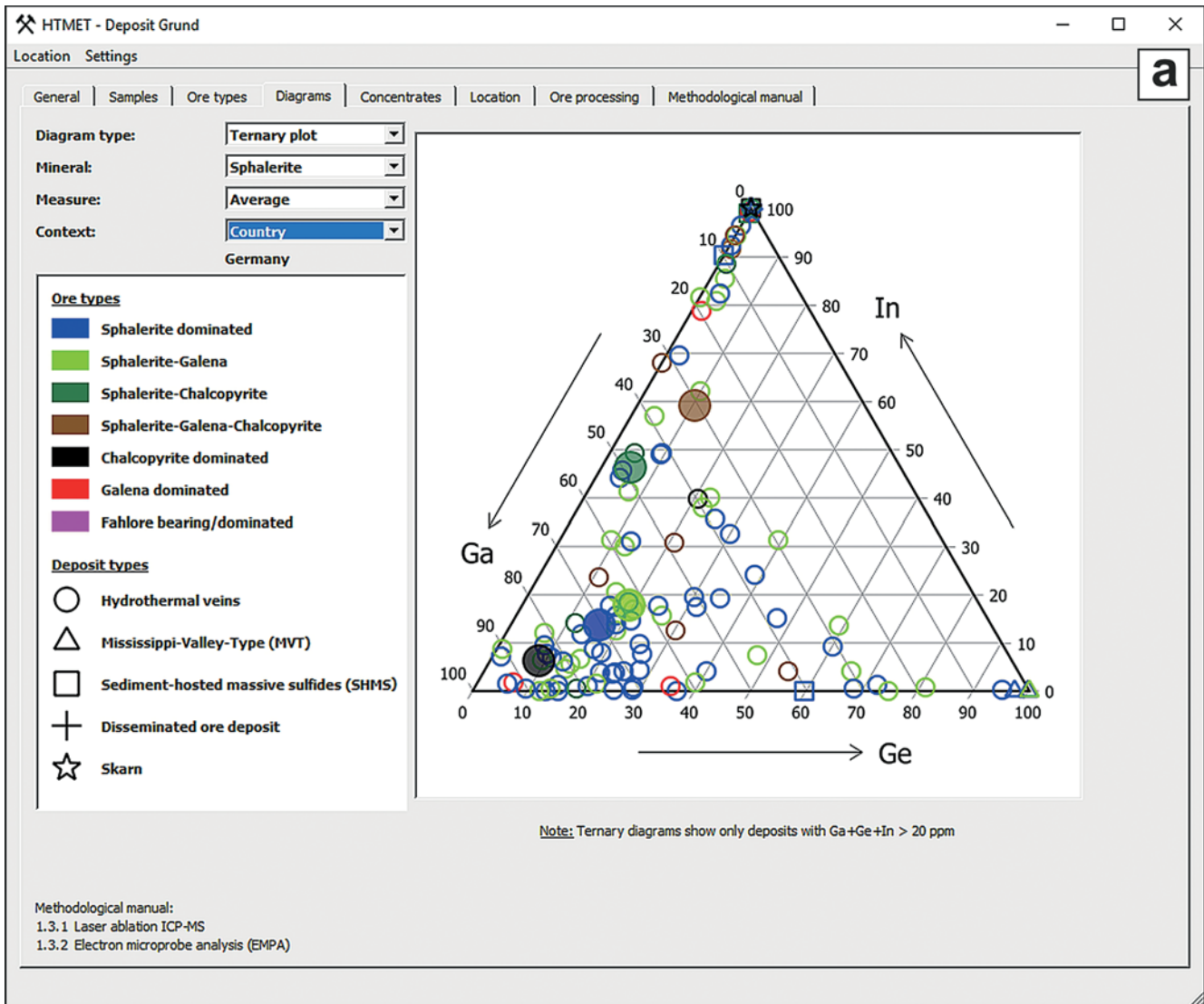


Fig. 3: cont.



**Fig. 4:** Screenshots of the front end connected to the HTMET database for primary indicators of the “Grund” ore deposit (Harz district) showing (a) semi-quantitative visualisation of the mineral chemistry results (ternary diagram) in a broader context (nationwide/country) and (b) bulk ore geochemistry data for industrial and sample ore concentrates.

distribution maps, mineral chemistry, and bulk geochemistry results, as well as the semi-quantitative ternary and quantitative XY diagrams.

#### 4.1.3 Multicriterial evaluation tool

An interactive tool was created based on the results collected for the primary indicators to evaluate the potentials of HT trace element-enriched ore types in Germany (Fig. 5). Fig. 5a shows an example for the application of the visualisation sub-tool for mineral chemistry data: From a menu for data processing the following selections are used (i) host mineral is “sphalerite”, (ii) results for the HT trace elements “Germanium/Gallium/Indium” are plotted, (iii) calculated “median values” of the mineral chemistry results are given, and (iv) the selected reference level is “cluster of deposits”. The data

in the list of clusters were sorted in descending order using the concentrations of the element “Ge”. For each cluster a colour coded segmented circle is shown that indicates the respective HT trace element concentrations from high (green) to low (red). The threshold values for the colour coding are adjustable depending on the current market situation or on the users’ interests. Furthermore, filters can be applied to limit the number of shown clusters/deposits to those with the highest concentrations of a given HT element. By clicking into the table the user will be automatically directed to the multicriterial evaluation tool (Fig. 5b).

The multicriterial evaluation tool exists in a first version to estimate the raw material potentials of clusters of deposits by combining the results of the bulk geochemistry, the mineral chemistry data as well as all information on associated non-metallic raw materials and harmful minerals. The

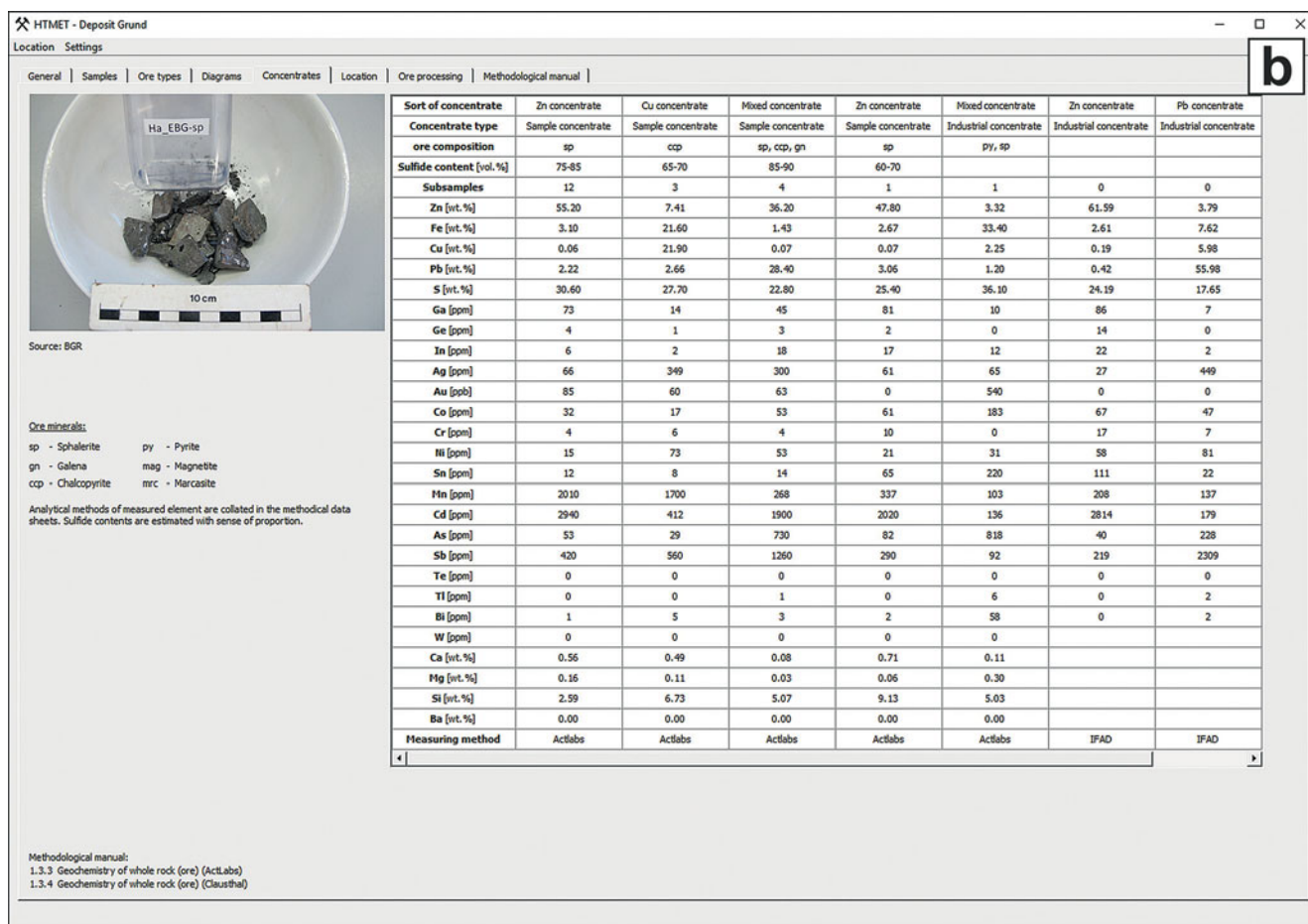


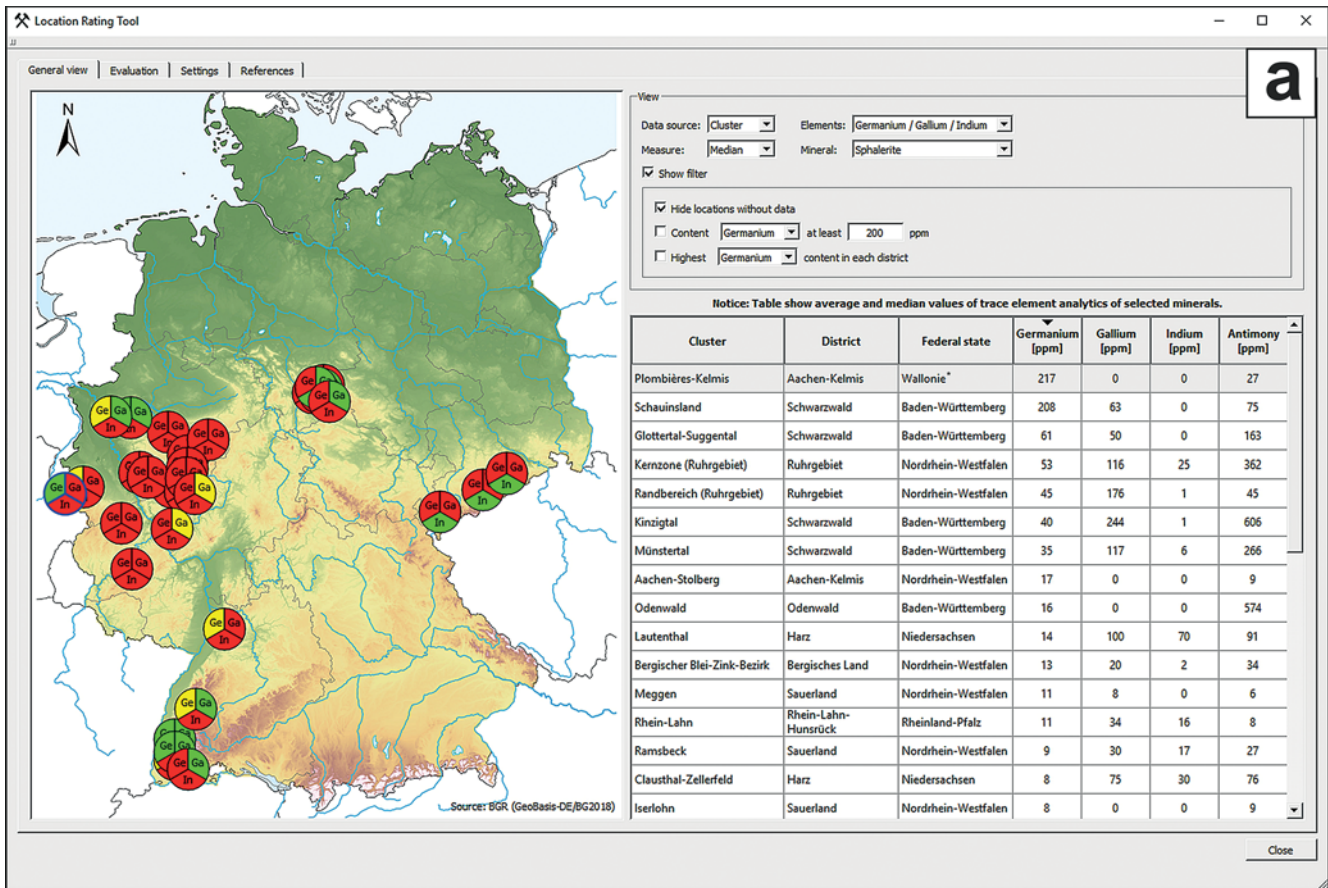
Fig. 4: cont.

user is prompted to do his selection between different deposit types, types of concentrates, and minerals that will subsequently be used for the estimation of a raw material potential for the given cluster. All bulk geochemistry results used for data processing inside the evaluation tool are normalised to the mean sulphur concentration of all concentrates in the database (by now: 23.61 wt.%). This enables a comparison of chemistry data for concentrates having different sulphide contents. The threshold values used for classification of the concentrations of the HT trace elements (Ge, Ga, In) into the categories high, moderate and low (colour coded: green, yellow and red), and also their weighting factors, can be adjusted in the settings for the calculation, depending on the special demands of the individual user. The same holds true for bonus points given for associated raw materials (e.g. fluorite and barite of good quality or hard coal).

A more detailed investigation of the ore-related potentials (primary indicators) for a pre-selected cluster is carried out using the weighting factors (see above) for the selected trace elements from bulk geochemistry, mineral chemistry and the presence of probably economically important amounts of associated raw minerals. Intermediate results for

the HT element concentrations are presented in the tool using the above-mentioned colour coding (representing 2, 1 and 0 point, respectively, for calculation of a final score). The scored points characterise the HT potential of the cluster and are shown compared to a maximum possible score for the user settings (Fig. 5b).

In case that exploration and mining activities are planned for target regions, not only the known metal concentrations in ore types and possible amounts of resources form important parameters for pre-selection of possible study sites, infrastructural and environmental aspects also have a huge effect on the economic viability of mining operations. The overall degree of development of the infrastructure, length and nature of possible transport routes for mining-related materials to a mine site or from a mine to the nearest processing plant as well as the availability of water, energy and skilled workers, are very important mine site-related factors. If environmentally sensitive areas, competing use of mining sites (e.g. tourism, recreation areas) or numerous legal requirements are present, even districts with an estimated high potential for the primary indicators, or substantial parts of them, have to be excluded from exploration projects. These infrastructural and environmental issues (secondary indica-



**Fig. 5:** First version of the evaluation tools connected to the HTMET database. (a) Visualisation of mineral chemistry results (median) for sphalerite, data is grouped for clusters of deposits (segmented circles represent high (green) to low (red) HT trace element concentrations); \*all data from Belgium (BE) are added for scientific comparison only. (b) Multicriterial evaluation tool combining the results of bulk geochemistry, mineral chemistry and the presence of associated raw materials and harmful minerals in the cluster “Grund ore mine” and furthermore illustrating the evaluation of secondary indicators.

tors) are also included in the database. They are summarised and evaluated by means of a traffic light system in the multicriterial evaluation tool (Fig. 5b).

## 4.2 Genetic deposit types

The present study focuses on the critical raw material potential of important German mining districts and clusters. A starting hypothesis for the advanced scientific data interpretation is a clear dependency of the HT element “specialisation” of given ores on a genetic deposit type (Schwarz-Schampera & Herzig 2002; Cook et al. 2009; Frenzel et al. 2016) and also on geological features of the respective sampled locations. Fig. 6 illustrates four exemplary false colour mineral distribution maps of samples, which are all assigned to the “sphalerite-dominated” ore type, but derive from different genetic deposit types: (a) Ore samples from the SHMS deposit “Rammelsberg” (Harz) are commonly characterised by banded iron-rich sphalerite, associated pyrite and chalcopyrite (Fig. 6a). This type of deposit forms by uprising hydrothermal fluids in a water reservoir at a temperature be-

tween 180–450 °C (Nielsen 1985). The precipitated ores are deposited on the seafloor simultaneous to the sedimentary host rocks and form characteristic stratiform massive sulphide layers. (b) The ore sample from the skarn deposit “Berggießhübel” (Erzgebirge) contains iron-rich sphalerite as well, but the latter is associated with magnetite and garnet (Fig. 6b). Skarn deposits form due to high-temperature (210–650 °C; Kwak 2007) metasomatic replacement processes (often in carbonate rocks) usually spatially related to magmatic intrusions and are mineralogically complex. (c) Sphalerite in samples from hydrothermal vein deposits can show a variety of textures and iron concentrations, is commonly associated with various other sulphides and gangue minerals and often comprises numerous brecciated host rock fragments (Fig. 6c). The varying iron concentration in sphalerite is indicated in the mineral distribution maps highlighting growth zoning structures in the mineral. Hydrothermal vein deposits form by ore precipitation from uprising mostly low- to moderate-temperature, highly-saline and metal-bearing hydrothermal fluids and show a variety of different mineral paragenesis depending on fluid characteristics and metal sources. (d) Samples from Mississippi-Valley-Type deposits

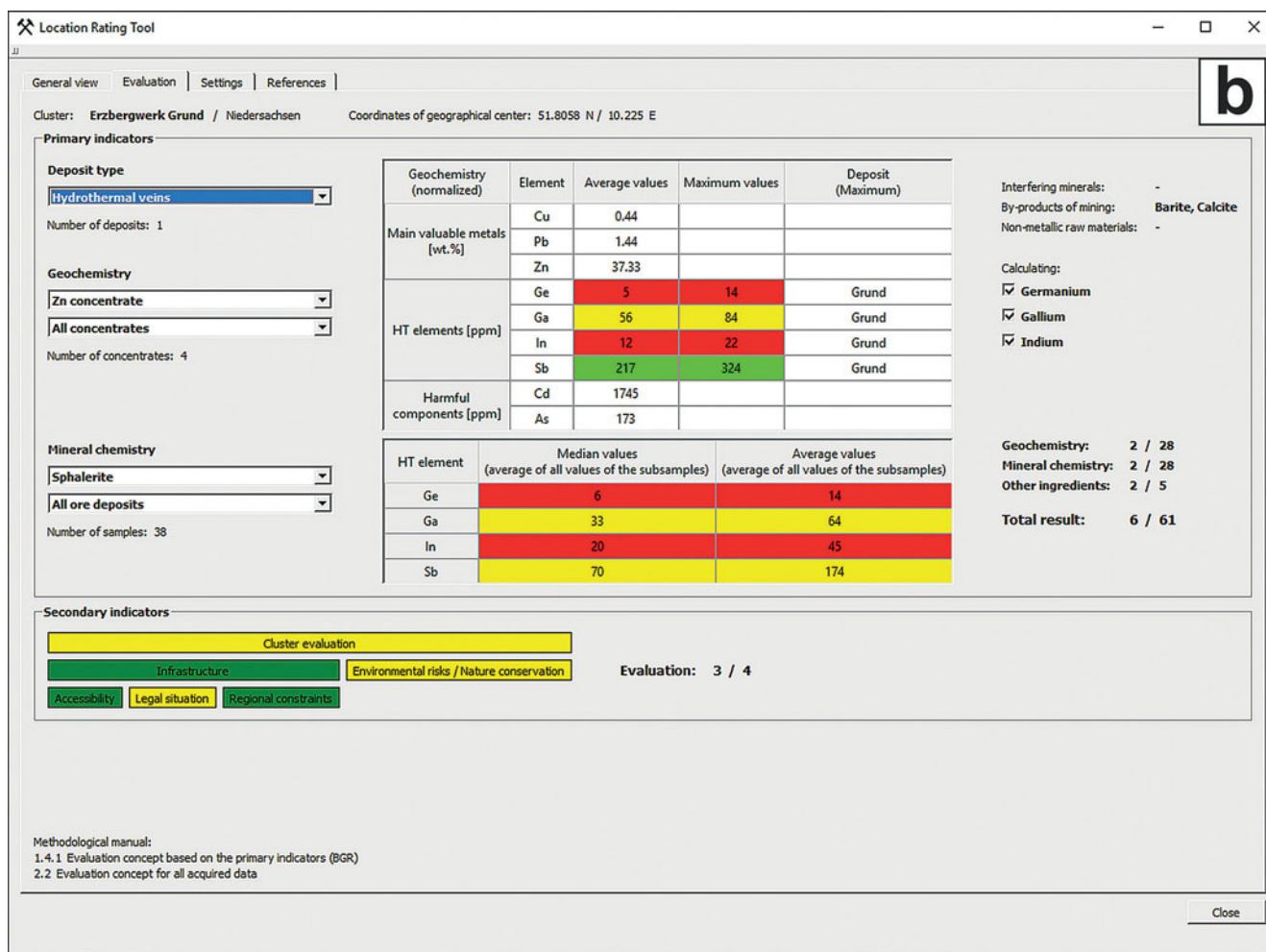


Fig. 5: cont.

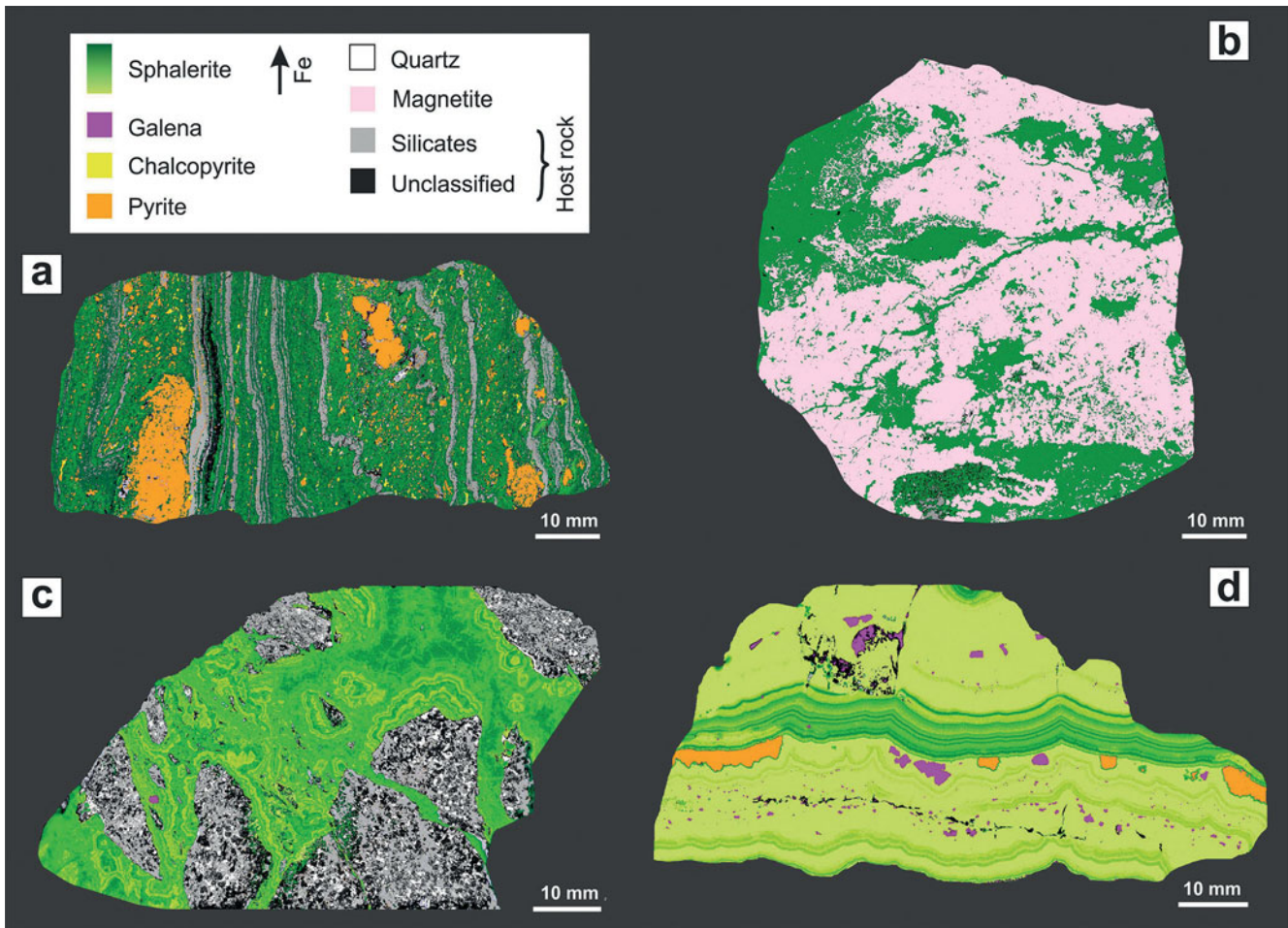
are characterised by typical colloform sphalerite/wurtzite (“Schalenblende”) with varying iron concentrations, often associated with massive iron sulphides and galena (Fig. 6d). These deposits form by low temperature and highly-saline fluids reacting with carbonate rocks such as limestone, marl or dolomite or hosted in cavities. (e) Mineral distribution maps of samples from disseminated base-metal ore deposits are not shown due to the commonly very fine-grained sample material. Disseminated ore deposits, such as the sandstone-hosted lead-zinc deposits of “Maubach” and “Mechernich” (both Eifel), are considered to have formed epigenetically from circulating hydrothermal fluids in pre-existing sandstone.

### 4.3 Trace element distribution in Germany's base metal ore deposits

The obtained comprehensive mineral chemistry data (number of LA-ICP-MS/EMPA spots: sphalerite 16,471; chalcopyrite 1,465) provides a unique basis to study the principles in the HT trace element concentration and specialisation of

sulphides from a large segment of the Variscan Orogen, the important German base metal mining districts. The results of the mineral chemistry analysis for the HT elements Ga, Ge and In in sphalerite are presented as box plot diagrams in Fig. 7. They are grouped according to the genetic deposit types as defined by previous studies and to the ore districts. The box plot diagrams provide an overview of the distribution of trace elements in the sphalerite ores of the German base metal mining districts. For further exploration activities, the results have to be considered in greater detail on a cluster and single deposit scale, due to the observed variability within the districts.

Despite the well-known high natural variability in the distribution of trace elements in natural samples, it can be deduced from the data that sphalerite from all hydrothermal vein deposits is characterised by moderate and more homogeneous Ga concentrations (median 6–81 ppm; Fig. 7a) compared to MVT, SHMS, skarn and DISSEM deposits (all median values <8 ppm; Fig. 7b). The presence of strongly elevated Ge concentrations in sphalerite of hydrothermal vein deposits in Germany was found to be restricted to several deposits in the Schwarzwald and the Ruhrgebiet districts



**Fig. 6:** False colour mineral distribution maps ( $\mu$ -EDXRF) showing “sphalerite-dominated” ore samples from different genetic deposit types: (a) SHMS deposit “Rammelsberg” (Harz); (b) skarn deposit “Berggießhübel” (Erzgebirge); (c) hydrothermal vein deposit “Schauinsland” (Schwarzwald); (d) MVT deposit “Altenberg” (Aachen-Kelmis).

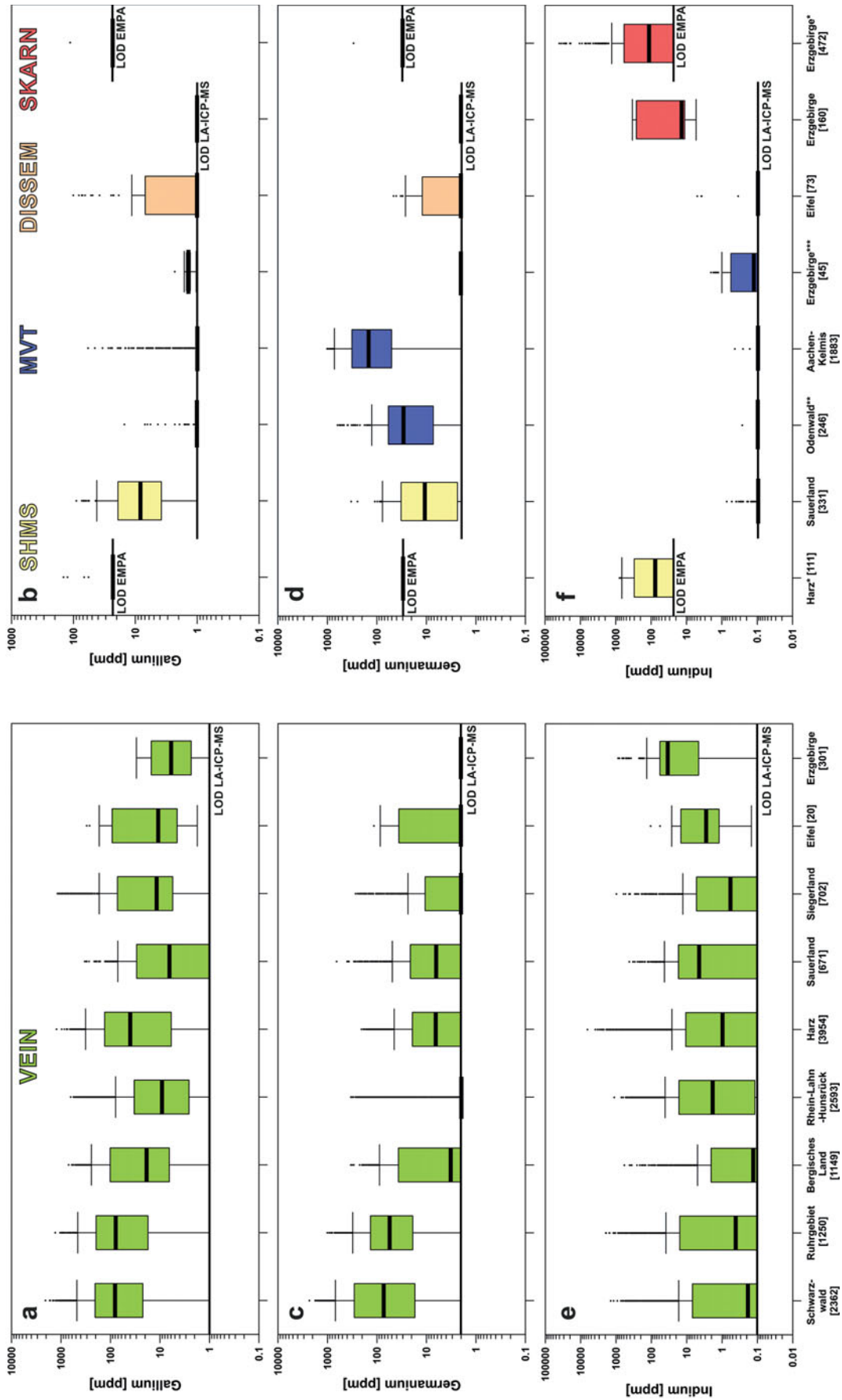
(median 55–73 ppm; Fig. 7c). Besides that, Ge is characteristically enriched in colloform sphalerite/wurtzite (“Schalenblende”) from MVT deposits in the Aachen-Kelmis and Odenwald districts (median 29–147 ppm; Fig. 7d). However, crystalline sphalerite from the MVT deposit Wiesloch (Odenwald; not shown in Fig. 7) and sphalerite from two deposits from the Erzgebirge also attributed to the MVT-type (e.g. Hermsdorf; Schwerdtfeger 2000) is rather poor in all HT trace elements. Sphalerite of the investigated SHMS and skarn deposits is typically depleted in Ge except for the SHMS deposit “Meggen” in the Sauerland district (median 11 ppm; Fig. 7d). In contrast to Ga and Ge, the HT trace element In could not be detected in significant concentrations in sphalerite of hydrothermal vein deposits in Germany (median <4 ppm; Fig. 7e), except for elevated In concentrations in some vein types of deposits in the Erzgebirge district (median 33 ppm; Fig. 7e). However, single laser spots and EMPA analysis reveal a very local enrichment of up to 6,500 ppm In in single sphalerite grains of several hydrothermal vein deposits. The highest enrichment of In was found in the Ram-

melsberg cluster (SHMS; median 75 ppm; Fig. 7f) and skarn deposits of the Erzgebirge (median 14–119 ppm; Fig. 7f).

As mentioned above, investigations on the mineral chemistry of chalcopyrite and geochemical analysis of bulk rock samples were conducted and form a significant part of the database HTMET. The main results are briefly summarised in the following paragraph.

Compared to sphalerite, chalcopyrite appears less frequently in many of the investigated deposits. In most samples, only a few chalcopyrite grains were suitable for analysis (scarcity, grain sizes). Chalcopyrite of the Schwarzwald, Rhein-Lahn-Hunsrück and the Erzgebirge districts contain up to hundreds of ppm of In. Germanium was found in noteworthy concentrations (median up to 142 ppm) in the Schwarzwald and the Ruhrgebiet districts. In contrast to that, Ga is not significantly enriched in chalcopyrite of the German base metal ore districts.

Geochemical bulk ore analyses were conducted on 101 industrial and lab sample concentrates of 59 deposits to cross-check the mineral chemistry data. Despite variations in the proportions of sulphide phases in the investigated sample



**Fig. 7:** Box plot diagrams illustrating LA-ICP-MS and EMPA mineral chemistry results for HT trace elements in sphalerite, grouped for the important German base metal ore districts and genetic deposit types. \*Measured by EMPA; \*\* results for crystalline sphalerite of MVT deposit “Wiesloch” (99 laser spots) are not included; \*\*\*EMPA analysis (48 spots not shown) confirm the LA-ICP-MS result; number of laser spots (n) shown in brackets behind the districts name.

material, the results allow information on the trace element concentrations in larger volumes of ore material. In general, the results confirm the mineral chemistry data for sphalerite and chalcopyrite, e.g. the moderate Ga concentrations in hydrothermal vein deposits, the elevated Ge concentrations in MVT deposits from the Aachen-Kelmis district, the enrichment of Ge in sulphides from hydrothermal veins of the Schwarzwald and Ruhrgebiet districts and the enrichment in In in sulphides from skarn (Erzgebirge) and SHMS (Rammelsberg) deposits. Contrary to the mineral chemistry data, the geochemical data indicates occasionally elevated Ge concentrations in sulphides of hydrothermal vein deposits from the Bergisches Land and the Harz districts (up to 42 ppm) as well as elevated In concentrations in concentrates from a few hydrothermal vein deposits (up to 361 ppm).

#### 4.4 Evaluation of HT trace element potentials

Starting from an evaluation of the mineral chemistry data and all results from the study of mineral concentrates, differences in the trace element specialisations, concentration, and potentials of the various investigated German base metal mining districts became apparent (Table 3, Figs. 5a, 7). In the paragraphs below, these differences will be discussed for each of the HT trace elements separately.

##### Gallium

When comparing base metal deposits, the HT trace element Ga is most commonly incorporated in sphalerite from hydrothermal vein mineralisations. In this study elevated contents with respect to the average crustal abundance (19 ppm; Butcher & Brown 2013) were especially found in sphalerite of the Schwarzwald, Ruhrgebiet and Harz districts (mean 87–160 ppm; median 41–81 ppm; Fig. 7a). According to Cook et al. (2009), Frenzel et al. (2016) and others, Ga is preferentially enriched in deposits formed at lower temperatures. This fits well to the fact that the temperatures of metal-bearing fluids that formed the hydrothermal vein deposits in the above districts are described to be rather low (<200 °C; e.g. Möller 1987; Baatartsogt et al. 2007; Henning et al. 2019) compared to the estimated formation temperatures of skarn (210–650 °C; Kwak 2007) and SHMS deposits (180–450 °C; Nielsen 1985).

However, not only the temperature seems to play a significant role in the enrichment of metals, but also the host rocks that act as potential metal sources. A probable source for the elevated Ga concentrations in hydrothermal vein deposits is the interaction of highly saline fluids with the widespread clastic rocks that typically host the hydrothermal vein deposits. Often packages of sedimentary rocks are characterised by elevated proportions of aluminosilicate minerals such as feldspar and mica that contain Ga in trace concentrations (e.g. Schirmer et al. 2017), due to similar properties of Ga<sup>3+</sup> and Al<sup>3+</sup> in charge and ionic radius. As a consequence of the intense interaction of the hydrothermal fluids with the adjacent host rock, Ga is released from these minerals into the hydrothermal fluids (Timofeev & Williams-Jones 2014;

Sahlström et al. 2017). Such a process is also indicated by the presence of secondary clay minerals such as kaolinite or illite, which are commonly found close to the hydrothermal vein mineralisation (Buschendorf et al. 1951; Werner et al. 2002).

An obvious lack of the above mentioned Ga source also explains the Ga poor sphalerite from MVT and DISSEM deposits in Germany. These deposits were formed by similar high-salinity and low temperature hydrothermal fluids (basinal brines; MVT: 75–200 °C, Paradis et al. 2007; DISSEM: 100–160 °C, Laznicka 2010) as the hydrothermal veins, but the mineralisation is localised in feldspar and mica poorer environments (carbonate rocks, MVT); sandstones and conglomerates, DISSEM). Typically, Ga contents in MVT deposits are rather low (e.g. mean 2.2 ppm; Goffin et al. 2015), however, MVT deposits containing 50 ppm Ga on average are also described in the literature (Moskalyk 2003).

Assuming a successful establishment of an adequate resource basis and sufficiently high metal prices on the world market, there might be a potential for the extraction of Ga as a by-product following mining of the major metals (Zn, Pb, Cu) and gangue minerals (e.g. fluorite, barite) in the Schwarzwald, Ruhrgebiet and Harz districts in the future. However, Ga is extracted solely as a by-product of aluminium production of bauxite (average contents 50 ppm) at present (Butcher & Brown 2013).

##### Germanium

The average abundance of Ge in the continental crust is 1.6 ppm (Taylor & McLennan 1985). Considering all studied base metal mineralisations in Germany, Ge is especially enriched in collomorphic sphalerite of MVT deposits in the Aachen-Kelmis and Odenwald districts (mean 62–210 ppm; median 29–147 ppm; Fig. 7d). This result is in accordance with investigations conducted by Pfaff et al. (2011; median 37 ppm Ge) and Goffin et al. (2015; mean 302 ppm Ge) for the “Wiesloch” mine in the Odenwald district and for several Belgian MVT deposits. However, sphalerite from several hydrothermal vein deposits of the Ruhrgebiet and the Schwarzwald districts also contain significantly elevated Ge contents (median 55–73 ppm; Fig. 7c). Germanium enrichment in hydrothermal ore from the latter district (“Schauinsland” mine) was also reported by Werner et al. (2002).

Similar to Ga, Ge is also expected to be preferentially bound to deposits that have formed at lower temperatures (Cook et al. 2009; Frenzel et al. 2016). This statement fits well to the elevated Ge values observed in the low-temperature MVT, low-temperature hydrothermal vein deposits and, also, to the low Ge values in the investigated high-temperature skarn and SHMS deposits (Table 3; Figs. 5a, 7). However, low-temperature hydrothermal vein deposits do not necessarily contain sphalerite with elevated Ge concentrations. Vein sphalerite with low Ge concentration is also commonly present (e.g. in the Bergisches Land and Rhein-Lahn-Hunsrück districts). On the other hand, sphalerite from VHMS and SEDEX deposits (up to 100 ppm Ge; Kelley et al. 2004; Höll et al. 2007), as well as “Tsumeb-type” polymetallic deposits containing Ge (up to 427 ppm), are also described in the literature (Emslie & Beukes 1981).



**Table 3:** HT raw material potential of historic German base metal mining districts and deposit types as estimated by the evaluation of the primary, ore chemistry-related indicators.

Historical mining district	Germanium	Gallium	Indium	Genetic deposit type
Harz	no	<b>increased</b>	no	VEIN
	no	no	<b>increased</b>	SHMS
Ruhrgebiet	<b>increased</b>	<b>increased</b>	no	VEIN
Sauerland	no	low	no	VEIN
	low	low	no	SHMS
Bergisches Land	no	low	no	VEIN
Siegerland	no	low	no	VEIN
Aachen (DE)-Kelmis (BE)	<b>increased</b>	no	no	MVT
Eifel	no	no	no	DISSEM
	no	low	no	VEIN
Rhein-Lahn-Hunsrück	no	low	no	VEIN
Odenwald	<b>increased</b>	no	no	MVT
Schwarzwald	<b>increased</b>	<b>increased</b>	no	VEIN
Erzgebirge	no	no	<b>increased</b>	SKARN
	no	no	no	MVT
	no	low	<b>increased</b>	VEIN

This means that the degree of Ge enrichment in base metal deposits is not only a function of the temperature of formation of the mineralisation. One important aspect is the biophile affinity of Ge, resulting in its close association with organic matter (e.g. lignite, hard coal, bitumen, carbonaceous sediments; Bernstein 1985; Höll et al. 2007). The mobilisation of Ge from organic matter-rich sedimentary rocks by hydrothermal fluids is assumed to be an important process especially in MVT and “Tsumeb-type” deposit formation (Melcher et al. 2006; Saini-Eidukat et al. 2016). These authors suggested that the occurrence of larger amounts of organic matter plays an important role in the transport and enrichment of Ge in sphalerite of base metal deposits.

As Ge is, in contrast to Ga, not enriched in sulphides of all hydrothermal vein districts, a ubiquitously available source like its release as a result of silicate weathering (similar properties of  $\text{Ge}^{4+}$  and  $\text{Si}^{4+}$ ), does not seem likely for these local Ge enrichments. Here, the associated occurrence of organic matter (e.g. hard coal [Ruhrgebiet]) might have played an important role on the strong Ge enrichment in the adjacent base metal mineralisation. The incorporation and transport mechanisms, possible HT metal sources and the required physico-chemical fluid properties that led to the enrichment of HT trace elements in hydrothermal vein deposits of the Schwarzwald and Ruhrgebiet districts are a focus of detailed scientific studies (Henning et al. 2018, 2019).

The moderate to elevated Ge concentrations in sphalerite from the Schwarzwald, Ruhrgebiet, Aachen-Kelmis and Odenwald districts provide an increased potential for the extraction of Ge as a by-product related to base metal and

gangue mineral mining, as the prices for Ge are much higher compared to In and Ga. Furthermore, Ge is already processed from zinc ore concentrates besides its extraction from coal ashes (Melcher & Buchholz 2013).

### Indium

The continental crust contains about 0.05 ppm of In on average (Taylor & McLennan 1985). According to this study sphalerite from vein and skarn deposits in the Erzgebirge district (median 33–109 ppm; Figs. 7d, f) and from the SHMS deposit “Rammelsberg” in the Harz district (median 75 ppm; Fig. 7f) shows a strong enrichment in In; this fits well to literature data (Mehner 1993; Schwarz-Schampera & Herzig 2002; Seifert & Sandmann 2006). In contrast to Ge and Ga, In is expected to be enriched in deposits that formed at higher temperatures (Schwarz-Schampera & Herzig 2002). This statement supports the In enrichment in the skarn deposits and the SHMS deposit “Rammelsberg” and, on the other hand, the lack of In in MVT and DISSEM deposits as observed in this study.

Except for the hydrothermal veins in the Erzgebirge district (median 33 ppm; Fig. 7e), the base metal veins of all other vein districts in Germany are characterised by overall low (all median values <4 ppm; Fig. 7e), but, on a local scale, occasionally highly variable In concentrations. Although most of these veins are expected to have formed at lower temperatures (<250 °C), several zones with up to 6,500 ppm of In in sphalerite grains were found by LA-ICP-MS; here, In enrichment in narrow growth zoning related bands is confirmed by EMPA element maps (Henning et al. 2019). These elevated In contents are also confirmed by bulk

ore analyses from ores of hydrothermal vein deposits that contain up to 360 ppm of In.

Indium is commonly enriched in the late stage, high-temperature step of massive sulphide, vein type and replacement ore body formations that are related to volcanic and intrusive magmatic environments and generally associated with elevated contents of Cu or Cu-rich minerals (Schwarz-Schampera & Herzig 2002). This idea is suitable for the explanation of elevated In concentrations in sphalerite of the complex SHMS (“Rammelsberg”) and skarn (Erzgebirge) mineralisations. However, it does not explain the partly elevated In concentrations in sphalerite of the low to moderate temperature hydrothermal vein deposits that formed from migrating basinal brines and meteoric fluids. In these deposits, fluid/rock interaction and transport mechanisms, as well as the recrystallisation and replacement processes of In-hosting sphalerite may have played a significant role in the enrichment of In and especially the contribution of higher temperature fluid pulses needs further scientific investigation.

Indium is extracted as a by-product from sulphidic base metal ores using residues from Zn and Cu extraction. Taking into account the economically relevant In contents of worldwide zinc ores and concentrates deriving from VHMS and SHMS deposits (20–200 ppm; Schwarz-Schampera 2013), it is obvious that there is a potential for the extraction of the HT trace element In as a by-product from some German base metal ores. The “Rammelsberg” mine produced In in the past and the area around the mine just recently formed the focus of a new exploration campaign (Mehner 1993; Eichhorn 2011). Furthermore, there are also ongoing exploration activities in the Erzgebirge district, which hosts some interesting targets for In extraction (Saxore 2015).

In general, extraction of HT trace elements can only be economic as a by-product of the mining of major metals (e.g. Pb, Zn, Cu, Sn) and associated raw materials (e.g. calcite, fluorite, barite). Furthermore, the knowledge on the proportions of the base metals in the ore and the remaining ore resources in the old mining districts is indispensable for a final evaluation of possible exploration activities. In some districts, important mines were closed due to strongly increased costs for mine dewatering, rapid falls in base and precious metal prices or unsolvable problems with the beneficiation of important ore types (e.g. vein deposits of the Harz and Schwarzwald districts, skarn deposits of the Erzgebirge district); consequently, significant quantities of raw materials are occasionally still present in such deposits. The mineralogical and geochemical data in the HTMET database, as well as the first approach on evaluating the collected data for the primary indicators, form a fundamental basis for future studies and exploration work. The database can be expanded for further ore types, commodities and additional ore districts. The secondary indicators present important infrastructural data for possible exploration activities, but also exclusion criteria for mining activities in ecologically sensitive areas.

## 5. Conclusions

The systematic mineralogical and geochemical investigations represent a fundamental basis for planning of exploration activities in the old German base metal mining districts. The resulting HTMET raw material database provides a systematic overview of HT trace element potentials in these ore districts. Base metal ores of some mining districts indicate a potential for further exploration activities under special consideration of the HT metals. Although trace element mining alone will probably never be economic (except for some precious metals), these metals can be processed as by-products to major metals and associated raw materials such as fluorite, barite or calcite, to improve the profitability of a mining project.

The present study proves sphalerite as the main carrier of the HT trace elements Ge, Ga and In in the investigated sulphide mineralisations. The assumed dependency of HT trace element specialisation and concentration on the genetic ore deposit type is mostly confirmed by our data, but HT trace element inventory also forms a function of the district- and location-related variable geological environments such as source-rock and fluid composition or organic content of rock:

(1) Gallium is primarily enriched in sphalerite from hydrothermal base metal vein deposits due to intense fluid/rock interaction of the mineralisation-related basinal brines with adjacent feldspar- and mica-bearing source-rocks.

(2) Germanium is especially enriched in sphalerite of mineralised bodies that are somehow spatially related to significant volumes of organic matter or carbonaceous sediments, such as hard coal in the Ruhrgebiet or bituminous substance in MVT environments. Germanium-rich sulphides occur partly independent of the genetic deposit type.

(3) Indium is commonly enriched in deposits that formed at higher temperatures (e.g. SHMS, skarn type deposits), however, the partly elevated In concentrations in distinct zones of sphalerite from low to moderate temperature hydrothermal vein deposits remain unexplained. Higher-temperature fluid pulses, recrystallisation processes of sulphides and transport mechanisms need to be investigated.

The new database and first approach on an attached multi-criterial evaluation are useful tools to illustrate a systematic overview of the HT trace element potentials of important German base metal districts as a basis for future exploration work. Further data can be easily added and an expansion of the HTMET database is possible for further regions (EU/worldwide), deposit types (e.g. copper shale) and elements (e.g. rare earth elements). To be fully useful as an exploration tool, data on proportions and amounts of major metals and on the quality of associated raw materials have to be added to the database and the evaluation tool has to be further developed. Whether the domestic metal ores can actually be economically produced in the future depends primarily on developments in world market prices. A restart of metal mining in Germany requires mining licensing procedures and substantial investments in new mining equipment and processing plants.

The mineralogical and geochemical data on trace element concentrations in sulphide minerals from different genetic deposit types obtained during this research project is under further use for various studies on distribution, transport and incorporation mechanisms of these critical HT trace elements (Franke et al. 2018; Henning et al. 2018, 2019).

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