Endbericht

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Identifikation und Klassifizierung potentieller Hochtechnologie-Metall Ressourcen in ostalpinen Blei-Zinklagerstätten

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Berichterstatter: Frank Melcher, Peter Onuk

Lehrstuhl für Geologie und Lagerstättenlehre, Montanuniversität Leoben

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Abstract

The chemical composition of sphalerite in base metal mineralizations of the Eastern Alps was investigated using laser ablation-ICP-MS methods. A total of more than 5500 in-situ analysis were carried out on sphalerite grains from 311 polished sections representing 27 individual ore deposits. The deposits comprise carbonate-hosted Pb-Zn deposits of the Bleiberg-type hosted by Triassic carbonate sequences, stratiform sediment-hosted base metal deposits hosted by Paleozoic metasediments and metavolcanic rocks, as well as vein-type mineralization crosscutting Paleozoic sequences. The analytical results prove a broad grouping into two sphalerite types: (1) sphalerite is carbonate-hosted non metamorphic sediments is poor in Fe (<1%), Mn, Co, Ga, In, Sn, Sb, but may be significantly enriched in Ge (up to >500 ppm), As, Tl and Pb; (2) sphalerite in stratiform or vein-type ores hosted by Paleozoic low- to medium grade metamorphic rocks is elevated in Fe, Co, Ni, Cu, Ag, In and Sn. Large variations exist among both groups, and unusual compositions have also been encountered, e.g. vein-type ores showing a Ge-Sb-Co association at Metnitz, Gurktal nappe.

From a regional point of view, sphalerites hosted by Ladinian and Carnian carbonate rocks of the Drauzug-Gurktal nappe system (type locality Bleiberg) and the South Alpine (Raibl, Salafossa, Mezica) resemble each other and differ only in the magnitude of trace element enrichment or depletion; ores from Fladung/Hochobir carrying elevated Ga are an exception. Sphalerite from coeval rocks in the Northern Calcareous Alps (Tyrolean-Noric nappe system), however, are enriched in Ag. In metamorphosed Anisian carbonates at the base of the Brenner Mesozoic, Zn sulphides are poor in trace elements but carry about 3.5% Fe. Stratiform ores in the Graz Paleozoic and the Gurktal nappe generally carry more Fe-rich sphalerites (1-9% Fe) that may become enriched in Co, Ag, Ga, Sb and In. In the pyritic “Kies” deposit Walchen in the Ennstal phyllite zone, Fe-In-Co-Cu-rich sphalerite coexists with In-rich chalcopyrite. The high-grade metamorphic Schneeberg deposit is characterized by the association Fe-Co-Cu-In. Vein deposits may carry elevated concentrations of all trace elements, but may also be poor in rare elements, such as at Achselalm in the Habach series of the Tauern Window.

The trace element distribution both, within a given deposit and within an ore type, generally is heterogeneous. The large dataset, however, is statistically significant for many deposits and reflects the trace element distribution in the Zn ores. Using these data, resources of critical and rare metals may be calculated, provided that reliable data on ore reserves or resources are available. For better comparison, such calculations have been made using resource and reserve data published by Cerny and Schroll (1995) and other available sources. The (original) critical metal potential hosted by sphalerite in the investigated ores from the Austroalpine and South Alpine units comprises (median values) 1,418 t Ge, 21 t Ga, 6.5 t In and 91 t Co, as well as 59 t Ag, 14,500 t Cd and 600 t Tl from 115 Mt base metal ores. The remaining potential of the deposits investigated is calculated to 78 t Ge, 4.5 t Ga, 5.7 t In and 57 t Co, as well as 9 t Ag, 1,650 t Cd and 15 t Tl from 6.6 Mt ore. Using the statistical data distribution, a confidentiality interval may be calculated comprising 50% of the data. With regards to the future supply of critical metals, the focus is clearly on Ge in Zn-rich ores in the Eastern and Southern Alps. Additional investigation of other major sulphide minerals such as chalcopyrite and Fe sulphides will significantly increase these potentials because these minerals also have characteristic trace element concentrations. This way, properly processed sulphide ore concentrates may become economically interesting by using modern metallurgical extraction methods for minor and trace metals.

Zusammenfassung

Die chemische Zusammensetzung von Sphaleriten aus Buntmetallvererzungen im Ostalpenraum wurde mittels Laser Ablation-ICP-MS Methoden untersucht. Insgesamt wurden mehr als 5500 Punktanalysen auf 311 polierten Dickschliffen durchgeführt, die 27 individuelle Erzvorkommen repräsentieren. Diese Vorkommen stammen aus karbonatgebundenen Pb-Zn-Erzen vom Bleiberg-Typ in triassischen Nebengesteinen, aus stratiformen sedimentgebundenen Buntmetallerzen in paläozoischen Sediment- und Vulkanitabfolgen, sowie aus diskordanten Gangvererzungen in paläozoischen Gesteinen. Die Analysenergebnisse belegen zwei klar abzugrenzende Sphalerittypen: (1) in nicht metamorphen Karbonatsedimenten sind die Sphalerite typischerweise arm an Fe (<1%), Mn, Co, Ga, In, Sn und Sb; sie können jedoch zum Teil erhebliche Konzentrationen der Elemente Ge (bis >500 ppm), As, Tl und Pb aufweisen. (2) In stratiformen und Ganglagerstätten in niedrig- bis mittelgradig metamorphen Gesteinen sind die Sphalerite an Fe, Co, Ni, Cu, Ag, In und Sn angereichert. Es gibt jedoch große Variationen in beiden Gruppen, sowie ungewöhnliche Elementassoziationen, wie z.B. Ge-Sb-Co in der Ganglagerstätte Metnitz in der Gurktaldecke.

Regional betrachtet sind die Sphalerite in der ladinischen und karnischen Stufe des Drauzug-Gurktal-Deckensystems (Typlagerstätte Bleiberg) und des Südalpins (Raibl, Salafossa, Mezica) recht ähnlich und unterscheiden sich im Wesentlichen in der Magnitude ihrer Elementanreicherungen; hier reißt nur das Vorkommen Fladung/Hochobir mit erhöhten Ga-Konzentrationen aus. Vorkommen in gleichalten Gesteinen der Nördlichen Kalkalpen (Tirolisch-Norisches Deckensystem) sind demgegenüber an Ag angereichert. Sphalerite in höher metamorphen anisischen Gesteinen des Brennermesozoikums sind auffallend arm an Spurenelementen und führen etwa 3.5% Fe. Die stratiformen Erzlager des Grazer Paläozoikums und der Gurktaldecke führen generell Fe-reichere Sphalerite (1-9% Fe), die meist nur gering an Co, Ag, Ga, Sb und In angereichert sind. In der Kieslagerstätte Walchen (Ennstaler Phyllitzone) treten Fe-In-Co-Cu reiche Sphalerite neben In-reichem Chalkopyrit auf. Die stratiforme, hochmetamorphe Lagerstätte Schneeberg ist ebenfalls durch die Assoziation Fe-Co-Cu-In charakterisiert. Ganglagerstätten können erhöhte Konzentrationen aller Spurenmetalle führen, sind teilweise aber auch auffallend arm an seltenen Elementen, z.B. Achselalm (Habachserie des Tauernfensters).

Die Verteilung der Spurenelemente innerhalb eines Vorkommens sowie eines Lagerstättentyps ist generell heterogen. Der große Datensatz ist jedoch für viele Vorkommen statistisch relevant und spiegelt die Spurenelementverteilung in den Erzen wider. Daraus lassen sich Ressourcenwerte für die kritischen und seltenen Elemente errechnen, wenn verlässliche Daten zu Erzreserven oder Ressourcen zur Verfügung stehen. Die Berechnungen wurden zur besseren Vergleichbarkeit mit den von Cerny and Schroll (1995), sowie mit anderweitig publizierten Ressourcen- und Reservenzahlen durchgeführt. Das (ursprüngliche) Gesamtpotenzial der an Sphalerit gebundenen kritischen Metalle in den untersuchten Vorkommen des Ost- und Südalpins beträgt (Medianwerte) 1,418 t Ge, 21 t Ga, 6.5 t In und 91 t Co, sowie 59 t Ag, 14,500 t Cd und 600 t Tl aus 115 Mt Erz. Das verbliebene Restpotenzial aus den untersuchten Vorkommen wird mit 78 t Ge, 4.5 t Ga, 5.7 t In und 57 t Co, sowie 9 t Ag, 1,650 t Cd und 15 t Tl aus 6.6 Mt Erz berechnet. Aufgrund der statistischen Verteilung der Daten kann ein Vertrauensbereich angegeben werden, in dem 50% der Analysen zu liegen kommen. Im Hinblick auf die zukünftige Versorgung mit kritischen Metallen liegt die Bedeutung von Zn-reichen Erzen in den Ost- und Südalpen klar auf Ge. Weiterführende Untersuchungen der Begleitminerale Chalkopyrit und Fe-Sulfide werden das vorhandene Potential jedoch deutlich vergrößern, da diese Minerale ebenfalls charakteristische Spuren- und Nebenelementverteilungen aufweisen. Entsprechend aufbereitete Sulfiderzkonzentrate könnten dann durch Anwendung moderner metallurgischer Verfahren für die Extraktion von Nebenmetallen in Frage kommen.

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1. Introduction

Austria is known as a country hosting numerous, albeit small ore deposits (Friedrich 1953). Mining of base metals, including copper, zinc and lead, dates back to the Copper and Bronze ages, at least 5000 years BC, and stopped in the early 1990ies due to low metal prices, exhaustion, difficult mining situations and the lack of exploration within the last decades. The rich mining history has been documented in many publications (e.g. Stöllner and Thomas 2015). IRIS, the Interactive Raw Material Information System maintained by the Geologische Bundesanstalt (GBA), summarizes all mineral deposits and occurrences known to date. It is based on an extensive publication on the metallogeny of Austria (Weber et al. 1997), and is presently updated by a team of economic geologists led by L. Weber under the auspices of the BVÖ. IRIS represents a compilation of present knowledge but must also be regarded as a contribution to future mineral supply.

The European Union has investigated the future European raw materials demand based on a number of criteria, including supply risks and importance for domestic production. In the 2014 version, 20 raw materials have been classified as “critical” (EU 2014). Due to low, and partly non-existing mining activities related to most of the critical raw materials, there is an urgent need to explore the geological potential of critical raw materials in European countries. In Austria, some of the critical raw materials have been or are currently being mined or produced, including graphite, magnesite, fluorspar, cobalt, tungsten, antimony and germanium. Others, including indium, gallium, niobium, magnesium, beryllium, platinum-group elements, rare earth elements, phosphates and borates have never been exploited.

A close link exists between ore types, geology and some of the critical raw materials (Skirrow et al. 2013). Therefore, a geological database such as IRIS can be used to identify potential targets.

In Austria, occurrences of base metal ores are widespread. They are known to be potential hosts of some of the critical raw materials. In the present project, we focus on germanium, gallium, indium and cobalt in a variety of base metal occurrences. The first data on the concentrations of these elements in Austrian ores date back to Schroll (1950, 1953, 1954a,b) who was among the first worldwide to address the trace element concentrations in ores based on their distribution in various host minerals. In a number of publications, E. Schroll has pointed out the importance of mineral chemical data to understand and develop metallogenetic concepts (e.g., Schroll 1978). In a project funded by the GBA, Cerny and Schroll (1992, 1995) investigated the trace element concentrations in concentrate samples from active and dormant mines (see Appendix, Table 18.). They were able to present calculations on the available resources of the critical elements Ge, Ga and In (Table 1).

Table 1. Potential of speciality metals in tons (Cerny and Schroll 1992)

	Germanium	Thallium	Gallium	Indium
Bleiberg-Kreuth	36	12	2	
“Kalkalpine Trias”	40-50	7-8	6-8	
Pb-Zn-(Cu) occurrences in Paleozoic rocks				3-4

2. Project goals

The findings of Schroll (1950 and later), Cerny et al. (1982) and Cerny and Schroll (1992, 1995) indicated that some of the more interesting and valuable trace elements are incorporated into zinc sulphides, mainly into sphalerite and wurtzite. Schroll (1954a,b) investigated the concentrations of Mn, Fe, Co, Ni, Ag, Cd, Hg, Ga, In, Tl, Ge, Sn, As, Sb and Bi in Zn sulphide, and of Ag, As, Sb, Bi, Tl, Sn and Te in galena. Pyrite may contain elevated concentrations of Ni, Co and As (Schroll, 1997), but was only rarely analysed because it was not in the focus of mining activities. The data available is mainly based on spectrometric analysis of a comparatively large sample volume from single crystal or ore samples, or on bulk analysis of concentrates by wet chemical methods. In-situ analyses have been carried out using the electron microprobe starting in the 1970ies, and using PIXE in the 1980s (Pimminger et al. 1985a,b). The superior detection limits and good spatial resolution of laser ablation-ICP-Mass Spectrometry (LA-ICP-MS), available as a routine method since the early 2000s, render a re-evaluation of Austrian base metal ores possible. The advantages of the method also include short measurement times and little sample preparation (no dissolution) and thus enable the creation of large data sets. These can then be used to evaluate the variation in element concentration within a single crystal, a sample, an ore type, a deposit or a group of deposits (district). As a result, robust statistical data (median concentration numbers and their distribution based on probability diagrams) will be available for mineral phases. This would translate into data for element grade and expected variation in a processed mineral concentrate, in this case sphalerite. Provided that reserve/resource data are available, tonnages of critical elements that might be produced may be calculated.

3. Brief metallogeny of the Eastern Alps

IRIS “New” is based on an updated geological and structural map of the Eastern Alps developed by the GBA. In a simplified form, the units relevant for this study are, from bottom to top, the Penninic units and the Austroalpine units. The Penninic units include the Subpenninic units as their basement derived from the European margin, covered by the Jurassic-Cretaceous Penninic ocean. The Austroalpine units are subdivided into the Lower and Upper Austroalpine nappe systems composed of Early Paleozoic to Cretaceous sedimentary and magmatic rocks that have experienced a number of orogenic and metamorphic events including the Variscan orogeny (ca. 340-300 Ma), the Permian tectonothermal event (ca. 280-240 Ma) and the Eoalpine orogeny (ca. 100-90 Ma) (Schmid et al. 2004). The Southern Alps (Southalpine units) south of the Periadriatic Lineament show a lithostratigraphic section similar to the Upper Austroalpine units but have not been included into Alpine nappe tectonics and are not affected by Alpine metamorphism. Within the Upper Austroalpine nappes, five major nappe systems are identified, starting with the Silvretta-Seckau nappe system, followed by the Koralpe-Wölz, Ötztal-Bundschuh, Drauzug-Gurktal and Tyroelan-Noric nappe systems. Except the Koralpe-Wölz system, all are composed of a metamorphic basement of Pre-Alpine age, low-grade metamorphic Paleozoic series unaffected by granite intrusion, and low-grade to unmetamorphosed Mesozoic cover rocks. The latter usually start with Permian to Lower Triassic clastic rocks (“Permoskyth”) followed by thick, commonly shallow-water carbonate successions in the Triassic, and a deeper marine Jurassic to Lower Cretaceous sediment sequence. The Paleozoic units consist of sedimentary and volcanic rocks of Ordovician to Lower Carboniferous age, and are locally overlain by Permomesozoic rocks with stratigraphic contacts outlined by a major unconformity. Granite intrusions are frequent only in some of the basement rocks; the most extensive granite province in Alpine Austria is the Central gneiss of Carboniferous age exposed within the Subpenninic units of the Tauern Window. It is important to note, that the Austroalpine and Southalpine units do not only share a similar stratigraphic record, but also a similar metallogeny. This is depicted in Figure 1 in an attempt to present geology, stratigraphy and metallogeny in one image. It is obvious that metals and types of ore deposits (stratiform, vein, metasomatic) are correlated throughout the structural units, outlining common depositional and metallogenic features. This applies especially to base metals (e.g. stratiform Pb-Zn in all Mesozoic carbonate units, stratiform Pb-Zn-(Ag-Cu)-barite in many Paleozoic sedimentary-volcanogenic units).

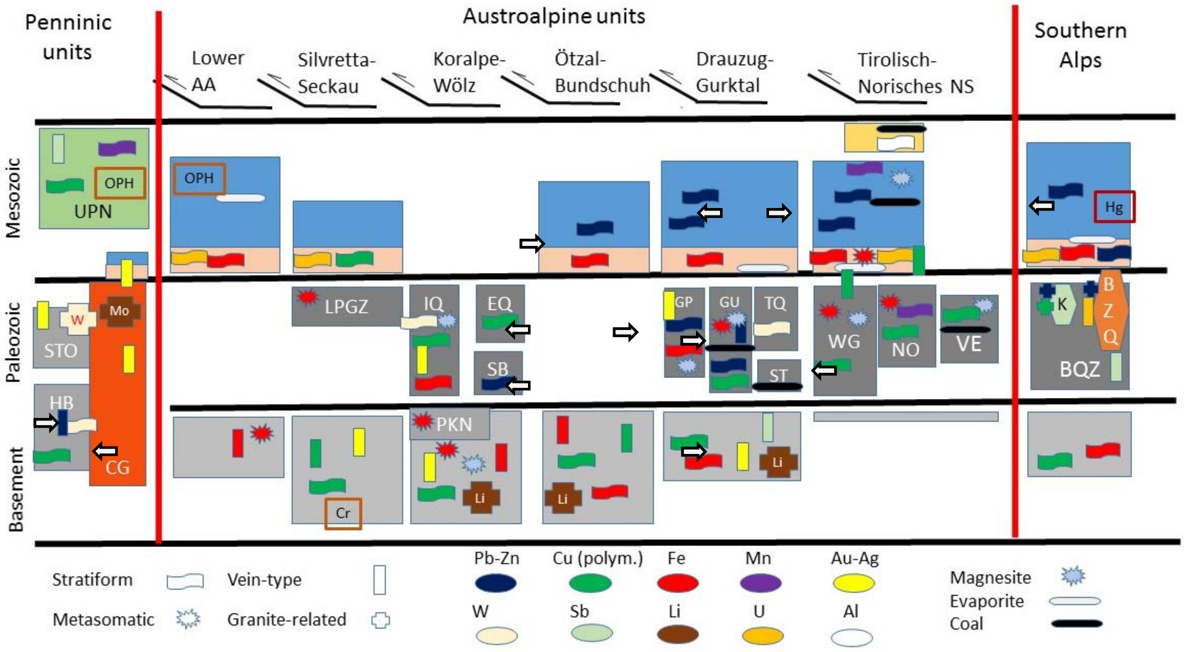


Figure 1. Summary of the metallogenetic evolution in the Eastern and Southern Alps, based on IRIS data. Abbreviations used, from left to right: UPN, Upper Penninic nappes; OPH, ophiolite; STO, Storz nappe; HB, Habach Series; CG, Central gneiss; LPGZ, Landeck quartz phyllite zone; IQ, Innsbruck quartz phyllite zone; EQ, Ennstal phyllite zone; SB, Schneeberg Zug; PKN, Plankogel nappe; GP, Graz Paleozoic; GU, Gurktal Paleozoic; TQ, Thurntal quartz phyllite zone; ST, Steinach nappe; WG, Western Greywacke zone; NO, Noric nappe; VE, Veitsch nappe; K, Klausen diorite; BZQ, Bozen quartz porphyry; BQZ, Brixen quartz phyllite. Arrows point to position of locations sampled in this study (see Table 5).

Base metal occurrences are widespread in the Penninic and Austroalpine basement, Paleozoic and Mesozoic cover series. IRIS New lists 57 "base metal ore districts" with a total of more than 1400 occurrences in Austria. One of the largest ore districts is the "Blei-Zinkerzbezirk Drauzug-Gurktaler-Deckensystem - Drauzugmesozoikum Karn (Bleiberg)" with 213 occurrences. In Table 2, the Austrian base metal districts are listed, indicating their tectonic affiliation, prevalent deposit type, and type locality. Most prominent are members of 10 "Pb-Zn ore districts" (some with barite and/or fahlore; n = 511 occurrences), followed by 23 districts with 377 occurrences classified as "Polymetallic ore district". "Kies ore districts" (7 districts) associated with volcanic rocks rank number three with 177 occurrences.

The Austrian Mineral Resources Plan (Weber 2012) has identified areas in Austria that should be protected for future mining activities based on the data available. In total, nine occurrences of base metal ores have been classified as resources worthy of safeguarding, or as resources of provisory worth of safeguarding. These comprise: **Lafatsch, Radnig, Pirkach, Metnitz-Vellach, Koprein, Mitterberg Nord, Schwarleo, Rabenstein, Großstübing**. The list does not include mining operations that have been closed in the more recent past, such as Bleiberg-Kreuth. Brief descriptions of these locations are found in Table 3 and Table 4. The deposits correspond to the ore districts (Table 2) 13 (Rabenstein, Großstübing), 16 (Radnig, Pirkach, Bleiberg), 18 (Lafatsch), 21 (Vellach-Metnitz), 121 (Mitterberg) and 158 (Schwarzleo). Koprein (Paleozoic of the Karawanken Mountains) is a single occurrence and not part of a metallogenic district.

Table 2. Base metal ore districts in Austria, based on IRIS "New", sorted by type of ore district

District_ID	Ore district	Tectonic and stratigraphic position		Prevalent ore type	Number
196	Antimon-(Arsen)erzbezirk	Kreuzeck-Gailtaler Alpen-Decke - Michelbach-Strieden Komplex	Rabant	vein-type	30
147	Arsen-Silbererzbezirk	Murau-Decke	St. Blasen	vein-type	6
12	Blei-Zink (Fahlerz-)bezirk	Anis Tirolisch-Norisches Deckensystem der Nordtiroler Kalkalpen	Sankt Veit-Tarrenton	Alpine-type	48
15	Blei-Zink (Fahlerz-)bezirk	Tirolisch-Norisches-Deckensystem - Nördliche Kalkalpen Anis	Arikogel	Alpine-type	14
13	Blei-Zink-Barytbezirk	Grazer Paläozoikum - Schönberg Formation (Arzberg)	Arzberg	SEDEX	52
20	Blei-Zinkerzbezirk	Bundschuh-Decke - Stangalm Mesozoikum	Erlacher Bock	Alpine-type	10
17	Blei-Zinkerzbezirk	Tirolisch-Norisches- und Bajuvarisches-Deckensystem - östl. Nördlichen Kalkalpen Karn	Weyer	Alpine-type	17
16	Blei-Zinkerzbezirk	Drauzug-Gurktaler-Deckensystem - Drauzugmesozoikum Karn	Bleiberg	Alpine-type	213
14	Blei-Zinkerzbezirk	Drauzug-Gurktaler-Deckensystem - Drauzugmesozoikum Anis	Kellerberg	Alpine-type	28
18	Blei-Zinkerzbezirk	Tirolisch-Norisches- und Bajuvarisches-Deckensystem - Nordtiroler Kalkalpen Karn	Lafatsch	Alpine-type	107
21	Blei-Zinkerzbezirk (Gänge)	Murau-Decke	Vellach-Metnitz	vein-type	15
19	Blei-Zinkerzbezirk (Lager)	Murau-Decke	Meiselding	SEDEX	7
89	Fahlerzbezirk	Tirolisch-Norisches Deckensystem	Schwaz-Brixlegg	vein-type	42
120	Fahlerzbezirk	Tirolisch-Norisches-Deckensystem - Wildseeloder-Einheit	Brunnalm	stratiform, mobilisates	20
110	Kieserzbezirk	Bajuvarisches-Deckensystem - Raibl-Gruppe Außerfern	Säuling	Alpine-type	18
114	Kieserzbezirk	Kreuzeck-Gailtaler Alpen Decke - Michelbach-Strieden Komplex	Politzberg	VMS? (In-reicher sph)	42
188	Kieserzbezirk	Matrei Nordrahmen Zone Deckensystem	Großfragant	VMS	13
112	Kieserzbezirk	Untere Penninische Decken - Bündnerschiefer-Gruppe Tauernfenster	Hüttschlag	VMS	71
111	Kieserzbezirk	Untere Penninische Decken - Rechnitzer Fenster	Bernstein	VMS	12
79	Kieserzbezirk	Unteres Radstädter Deckensystem - Katschberg-Quarzphyllit-Komplex	Kleines Gurpitscheck	VMS	6
82	Kieserzbezirk	Drauzug-Gurktaler Deckensystem - Thurntaler Komplex	Tessenberg	VMS	15
198	Kupfer- (Fahlerz-)erzbezirk	Schladming-Seckau Deckensystem	Krombach, Giglerbaue	vein-type	19
76	Kupfer-Eisenerzbezirk	Silvretta Decke - Venet-Komplex Landecker Phyllitgneise	Thialkopf	stratiform	17
119	Kupfer-Eisenerzbezirk	Tirolisch-Norisches-Deckensystem - Glemmtal-Einheit	Kelchalm, Kupferplatte	VMS	61
121	Kupfererzbezirk	Tirolisch-Norisches Deckensystem	Mitterberg-Mühlbach-Larzenbach	vein-type, stratiform	26
201	Kupfererzbezirk	Kupfererzbezirk Permomesozoikum - Schladming-Seckau Deckensystem	Hochwurzen	stratiform, VMS?	14
45	Kupfererzbezirk	Permoskyth Bajuvarisches-Deckensystem	Arlberg	vein-type	10
46	Kupfererzbezirk	Permoskyth Silvretta-Decke	Bartholomäberg	vein-type	10
122	Kupfer-Fahlerzbezirk	Tirolisch-Norisches Deckensystem - Glemmtal-Einheit	Röhrerbühel	VMS	31
123	Kupfer-Uranerzbezirk	Venediger-Deckensystem - Tauernfenster	Rauris	stratiform, mobilisates	5
74	Polymetalischer Erzbezirk	Ennstaler-Quarzphyllite	Walchen	stratiform, VMS?	9
78	Polymetallischer Erzbezirk	Untere Penninische Decken - Pfunds Zone	Pfunds	VMS?	8
146	Polymetallischer Erzbezirk	Altpaläozoikum Seengebirge-Decke	Plescherken	stratiform, mobilisates	9
190	Polymetallischer Erzbezirk	Koralpe Wölz Deckensystem - Rappold-Komplex	Oberzeiring	vein-type	20
219	Polymetallischer Erzbezirk	Koralpen-Wölz-Deckensystem - "Glimmerschiefer Decke"	Moosburg	stratiform	18
187	Polymetallischer Erzbezirk	Koralpe-Wölz-Deckensystem - Prijakt-Polinik Komplex	Teuchl	stratiform, mobilisates	19
157	Polymetallischer Erzbezirk	Koralpe-Wölz-Deckensystem - Radenthein-Komplex	Ramingstein	VMS?	6
149	Polymetallischer Erzbezirk	Mittlere Penninische Decken - Fimber-Zone	Rotenstein, Serfaus	stratiform	9
143	Polymetallischer Erzbezirk	Ötztal-Bundschuh Deckensystem - Stubai-Ötztal-Komplex	Tösens	SEDEX, VMS, vein-type	78
137	Polymetallischer Erzbezirk	Ötztal-Bundschuh-Deckensystem - Stubai-Brennermesozoikum	Griesbach	Alpine-type	6
142	Polymetallischer Erzbezirk	Permomesozoikum Seengebirge-Decke	Rosegg	vein-type	7
158	Polymetallischer Erzbezirk	Tirolisch-Norisches Deckensystem - Wildseeloder-Einheit	Leogang	stratiform, vein-type	2
199	Polymetallischer Erzbezirk	Schladming-Seckau Deckensystem	Zinkwand-Vötternspitze	vein-type	5
150	Polymetallischer Erzbezirk	Schladming-Seckau Deckensystem	Duisitz-Eschach-Roßblei	vein-type	30
80	Polymetallischer Erzbezirk	Schober Decke - Durreck-Komplex	Blindis-Tögisch	stratiform	23
81	Polymetallischer Erzbezirk	Silvretta Decke - Silvretta-Komplex	St. Christoph	vein-type	29
151	Polymetallischer Erzbezirk	Stolzalpen-Decke	Schwabegg-Ruden	vein-type	9
191	Polymetallischer Erzbezirk	Stuhleck-Kirchberg-Decke	Steinhaus-Knappenkeusche	vein-type	12
152	Polymetallischer Erzbezirk	Vorau-Decke	Prinzenkogel-Waldbach	vein-type	10
155	Polymetallischer Erzbezirk	westliche Südkarawanken	Alt,- Neufinkenstein	Alpine-type	25
209	Polymetallischer Erzbezirk	Venediger-Deckensystem - Peitingalm-Komplex	Hochfeld	stratiform	6
210	Polymetallischer Erzbezirk	Drauzug-Gurktal-Deckensystem - Gailtalkristallin	Abfaltersbach	vein-type	7
145	Polymetallischer Erzbezirk	Venediger-Deckensystem - Hollersbach Komplex	Mühlbach/Brenntal	vein-type	36
116	Polymetallischer Kieserzbezirk	Tirolisch Norisches Deckensystem - Glemmtal-Einheit	Zell/See – Radstadt – Mandling	VMS	46
206	Polymetallischer Skarnerzbezirk	Drauzug-Gurktal-Deckensystem Lienz-Hochstein	Lienzer Schlossberg	skarn	9
197	Polymetallischer Skarnerzbezirk	Kreuzeck-Gailtaler Alpen-Decke - Michelbach Komplex	Schlaiten	skarn	6
169	Silbererzbezirk	Kreuzeck-Gailtaler Alpen-Decke - Michelbach-Strieden Komplex	Dechant	vein-type	23

Table 3. Resource-relevant data prepared for the Austrian Mineral Resources Plan

Deposit	Extension	Shape	Thickness	Dip	Reserves	Grade	Resources	Metal content
Lafatsch	500-1500m	Layer- to lens-like	<1.5-4m	60-90°	600,000 t	8% Zn, 1.5% Pb	4,000,000 t	
Großstübing-Silberberg	<50-500m	Layer- to lens-like	<1.5-4m	10-60°		5-10% sulphides	300,000-1,000,000 t	
Koprein	<50-200m	Layer- to lens-like, vein-like	1.5-2m			unknown	Unknown (estimate 100,000 t)	
Vellach-Metnitz	50-200m	Vein-like	<1.5m	60-90°	297,000 t	8% PbS, 20% ZnS	500,000 t	
Mitterberg Nord	500-1500m	Vein-like	<1.5-4m	40-60°				300,000 t Cu, x 10,000t Ni
Pirkach		Layer- to lens-like	<1.5m	60-90°		4% Zn, 1% Pb, 2% CaF_2	400,000 t	
Rabenstein, Arzwaldgraben	<50-500m	Layer- to lens-like	<1.5m	60-90°		5% metal content	300,000-1,000,000 t	
Radnig	<50-200m	Layer- to lens-like	<1.5m	60-80°	75.000 t		250,000 t	
Schwarzleo	<50-200m	Massive, impregnation, layer- to lens-like, vein-like	<1.5m	40-60°	2000 t Cu, 500-1000 t Ni, 500-1000 t Co	0.6% Cu, 0.1% Ni, 0.006-0.15% Co		

Table 4. Published grade and tonnage data of base metal deposits in the Alps referred to in the text

	Tonnage (t)	% Zn	% Pb	%Cu	Length (m)	Width (m)	Type of resource and source of data
Bleiberg	43,000,000	5.9	1.1		8000	1000	Total resource, https://mrdata.usgs.gov/sedznpb/show.php?labno=47
Raibl	18,100,000	5.97	1.22		1400	2500	Total resource, https://mrdata.usgs.gov/sedexmvt/show.php?labno=177&place=fIT
Salafossa	10,000,000	4.9	1.0		650		Total resource, mined out (Cerny 1989) USGS Mineral Resources On-Line Spatial data
Mezica	34,000,000	3.4	2.4		1400	2500	https://thediggings.com/mines/usgs10073155; total resource (Cerny 1989)
Lafatsch	1,000,000	6.2	1.6				https://mrdata.usgs.gov/sedznpb/show.php?labno=48
Lafatsch	600,000	8	1.5				Cerny (1989), proven reserves
Walchen	423,470	2.75	2.1	1.53	4000		Unger (1968), proven reserves
Meiselding	50,000 – 100,000	3.7	9				Cerny & Schroll (1995), estimated potential
Fladung	300,000	3.5	2.0		1000		Cerny & Schroll (1995), C2 potential
Jauken Süd	50,000	6.0	0.5		250		Cerny (1989); Cerny & Schroll (1995), maximum estimate of remaining resource
Schneeberg	1,200,000	6.6	1.26				Baumgarten et al. (1998), production 1870-1960
	1,500,000						Baumgarten et al. (1998), remaining proven and estimated reserves

In order to classify base metal occurrences into ore types, a grouping of primary sulphide ores into four groups is proposed:

(1) Carbonate-hosted lead-zinc deposits (IRIS districts 12, 14, 15, 16, 17, 18, 20, 137, 155)

These deposits are widespread in the Triassic carbonate sequences of the Northern Calcareous and Southern Alps, and also in the Mesozoic cover sequences of the Austroalpine basement units. They are usually observed in three distinct stratigraphic intervals: Anisian (e.g. Topla, Slovenia; Brenner Mesozoic), Ladinian (e.g. Lafatsch, Radnig, Bleiberg) and Carnian (e.g. Bleiberg, Pirkach). Ores are stratiform, occasionally strata-bound but usually epigenetic, low-temperature (<200°C) and relatively small (usually < 1 million tons ore) carrying from 3 to 10% Pb and Zn. Common critical trace elements are germanium and gallium, besides cadmium and thallium, all hosted by sphalerite, and fluorite as a gangue mineral in many occurrences.

The deposit Bleiberg-Kreuth was closed in 1993 after more than 700 years of mining. This large deposit (>3 million tons of ore mined yielding Zn/Pb ratios of 5-6) is regarded as a world-class deposit and represents the type locality of "Alpine-type" (APT) or "Bleiberg-type" Pb-Zn deposits. This type differs from the frequently cited Mississippi Valley-type by much lighter sulphur isotope values and a different depositional model (Cerny 1989, Schroll 1978, 1996, 2008, Henjes-Kunst 2014, Henjes-Kunst et al. 2017). Alpine-type Pb-Zn ores share a simple mineralogy consisting of low-Fe sphalerite, galena, pyrite and/or marcasite, locally wulfenite, fluorspar, barite, dolomite and calcite. The ores formed mainly epigenetically about 200 million years ago (Melcher et al. 2010) from at least two distinct sulphur reservoirs in which bacteriogenic and thermochemical sulphate reduction played a role. Most of the Alpine-type deposits are characterised by high Cd (ca. 2000 ppm), Ge (200-400 ppm) and Tl concentrations (ca. 100 ppm) in sphalerite and a lack of Cu, Co, Ni and Ag. Pb/Zn ratios may be extremely variable from 2:1 to 1:20 within a deposit (Cerny 1989), but are commonly close to Pb/Zn = 1:4 or 1:5.

(2) Sediment-hosted, submarine-exhalative lead-zinc(-copper) deposits („SEDEX"-type; IRIS districts 13, 19, 74, 143, 157)

Ores consist of massive sulphides often containing >50% sulphide minerals, commonly sphalerite, pyrite, pyrrhotine, galena and chalcopyrite, and may form large orebodies exceeding 20 to >200 million tons. They are observed worldwide mainly in clastic rocks of the Early to Middle Proterozoic (1700 to

1400 million years) and Lower to Middle Paleozoic (500 to 320 million years). Possible by-products include germanium gallium, indium and cobalt, besides cadmium, tellurium, selenium and barite as gangue minerals. From the type deposit Rammelsberg (Harz Mountains), 7 million tons metals have been produced from 968 until mine closure in 1988. The ore contained 19% Zn, 9% Pb, 1-2% Cu, 160 ppm Ag, 20 ppm In, 3 ppm Ge, 150 ppm Co and 0.5-1 ppm Au (Kraume 1955). Zinc concentrates from the giant Red Dog deposit, Alaska, carry about 100 ppm Ge which is extracted at the TECK zinc smelter in Trail, B.C. (Melcher and Buchholz 2014; Kelley et al. 2004).

In the Eastern Alps, SEDEX deposits are known from the Paleozoic of Graz and the Gurktal nappe (Meiselding), both parts of the Austroalpine Paleozoic low-grade metamorphosed basement units (Figure 1). The deposits of the “lead-zinc ore district Graz Paleozoic” formed in the Lower Devonian in restricted euxinic basins within the Rannach and Hochlantsch facies, accompanied by submarine volcanism (Weber 1990). Exploration activities by the Bleiberger Bergwerks Union (BBU) from 1973 until 1978 led to identification of prospective areas at Haufenreith, Peggau-Taschen and Großstübing-Guggenbach. Further stratiform ores of probable SEDEX affinity occur in Austroalpine basement complexes; these ores are often multiply metamorphosed up to amphibolite facies and underwent mobilization processes producing vein-type ores. They include deposits in polymetallic ore districts such as Ramingstein (district 157) and Schneeberg, South Tyrol, located in the Ötztal-Stubai Complex (district 143).

(3) Volcanic-hosted massive sulphide deposits (copper, zinc; „VMS-type“; examples in IRIS districts 78, 111, 112, 116, 119)

VMS deposits comprise stratiform syngenetic sulphide and sulphate mineralization forming from hot (>300°C) metal-rich fluids on and below the seafloor in association with mafic or bimodal mafic-felsic volcanic activity along oceanic spreading ridges or centers. Black and white smoker systems are actuogeologic equivalents of the exhalative portions of such systems. Although the largest fossil occurrences may reach sizes exceeding 100 million tons (e.g. Kidd Creek, Ontario), deposits are usually small containing 0.1-10 million tons ore grading <10% Cu + Pb + Zn. Typical by-products are Ag and Au; critical metals include In, Ge, Co, besides Te and Bi. However, concentrations of trace elements scatter widely. Indium was an important by-product of the primary zinc ore from Kidd Creek, Ontario.

In the Eastern Alps, a large number of Cu and “Kies” (pyritic) ores are known within the Austroalpine and Penninic units. Examples include the Subpenninic Habach Series, the Penninic Bündnerschiefer Formation, the Austroalpine Ennstal quartz phyllite and the Greywacke Zone. Elevated concentrations of In have been reported for the small Zn-Cu-Pb deposit of Koprein (Karawanken Mountains, Carinthia) which may either represent a VMS type or a vein-type deposit (Cerny and Schroll 1995).

(4) Vein-type deposits of variable origin and age (examples in IRIS districts: 21, 46, 89, 121, 145, 150)

Most occurrences of base metal ores in the Eastern and Southern Alps may be attributed to one of the aforementioned stratiform types. However, numerous vein-type deposits have been mined in the past that formed during the Eoalpine and Palogene orogenic events (Pohl & Belocky 1999). The famous “Mitterberger Hauptgang” is an example of remobilization of originally stratiform mineralization by later processes (Weber et al. 1997). Such processes may also account for some of the fahlore-dominated Cu – barite ores in Paleozoic carbonates, e.g. in the polymetallic Cu-Ni-Co-Hg ore district Leogang. A further example from the Gurktal nappe shows deformed and metamorphosed SEDEX Pb-Zn-(Ag) ores at Meiselding, and vein-type Pb-Zn ores at Vellach-Metnitz that are controlled by NW-SE trending tectonic structures (Weber et al. 1997). In other ore districts, members of the so-called “Five-element-veins” hosting Bi-Co-Ni-Ag-U (±As±Sb) have been identified (e.g. Zinkwand-Vöttern/Schladming), which is a genetically complex and not fully understood ore type from which historical production of critical metals has taken place. The spectrum of critical and rare metals present in vein-type deposits thus may include Co, In, Ge, Ga, Sb, Ni, Ag, Au, U, and Bi.

4. Sampling

The sampling campaign was structured to cover the most important ore districts, including those deposits that are classified as "worthy of safeguarding". A total of 356 samples were collected from 26 occurrences (Table 5). In addition, samples were analysed from collections (Joanneum Graz, Montanuniversität Leoben MUL, Leopold Franzens Universität Innsbruck). Spatially, the focus is on central and eastern Austria, mainly Carinthia, Styria and Salzburg, with a few samples from Tyrol. Additional ore samples from Italy (Raibl, Salafossa, Schneeberg) and Slovenia (Mezica) were analysed for comparative reasons. Zinc-Pb ores in the polymetallic district 143 "Stubai-Ötztal complex (Tösens)" are currently evaluated separately in a parallel MRI project led by Dr. Thomas Angerer from the University of Innsbruck in cooperation with the Chair of Geology and Economic Geology, MU Leoben. Only a few samples from Schneeberg, the largest base metal mineralization known in Austroalpine units west of the Tauern Window, were included in the present study. Samples from the Mitterberg vein-type deposit and from Oberzeiring (collection MUL) were screened but not further taken into account due to the scarcity of sphalerite. Sample locations for Austria are displayed in a simplified geological map (Figure 2); their tectonic and stratigraphic position is illustrated with arrows in Figure 1

Table 5. Locations of sampling

Geological unit	Occurrence	Province	Number of samples	Type and location of samples
Eisenkappel Paleozoic	Koprein	Carinthia	24	dumps
Gurktal nappe	Meiselding	Carinthia	20	underground exposures
	Metnitz	Carinthia	14	underground exposures, former open pit, dumps
Graz Paleozoic	Silberberg	Styria	7	underground
	Guggenbach Poyd	Styria	24	dumps
	Friedrichstollen	Styria	7	underground
	Elisabethstollen	Styria	14	underground
	Rabenstein	Styria	12	dumps
	Arzberg	Styria	16	underground
	Haufenreith	Styria	9	dumps
Wölz mica schist	Walchen	Styria	16	dumps and underground
Habach group	Achselalm, Flecktrogalm	Salzburg	44	underground
	Brenntal	Salzburg	1	dump
	Sprinzgasse	Salzburg	1	collection W. Paar (MUL)
Drauzug Mesozoic	Hochstadel/Rosengarten	Carinthia	-	no mineralized samples found
	Pirkach	Carinthia	27	underground and Friedrich collection (Joanneum, Graz)
	Jauken Nord	Carinthia	9	underground and dumps
	Jauken Süd	Carinthia	25	dumps
	Radnig	Carinthia	27	dumps

	Bleiberg	Carinthia		collection MUL
Karawanken Mesozoic	Fladung	Carinthia	26	dumps
	Eisenkappeler Hütte	Carinthia	8	dumps
Mesozoic of the Northern Calcareous Alps	Lafatsch	Tyrol	22	collection Uni Innsbruck
Brenner Mesozoic	Stubaital	Tyrol	2	surface outcrops (collection F. Melcher, MUL)
Schneeberg Zug	Schneeberg	South Tyrol	8	surface and underground outcrops (collection F. Melcher, MUL)
Kreuzeck group	Drassnitz	Carinthia	1	surface outcrop

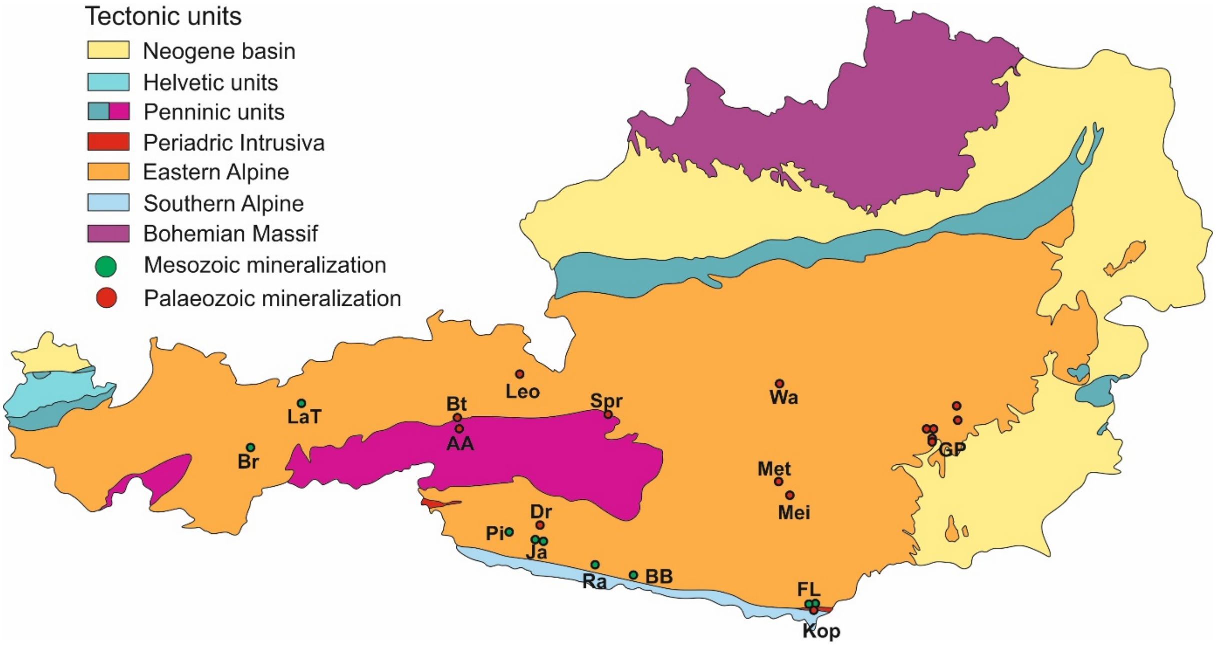


Figure 2. Simplified geological map showing the locations of sampling. Abbreviations: LaT, Lafatsch; AA, Achselalm; Leo, Leogang; Wa, Walchen; Ja, Jauken; Ra, Radnig; BB, Bleiberg; Fl, Fladung; Pi, Pirkach; KOP, Koprein; Mei, Meiselding; Met, Metnitz-Vellach; GP, Graz Paleozoic (various locations); Br, Brenner Mesozoic; Dr, Drassnitz; Bt, Brenntal; Spr, Sprinzgasse.

5. Analytical methods

Samples were cut using a diamond saw and prepared as polished thick sections of ca. 100 µm thickness. These sections were analysed using optical and electron microscopes to identify the overall mineralogical composition, grain size and texture. In the following, the sections were analysed using LA-ICP-MS for a number of 23 minor and trace elements in sphalerite.

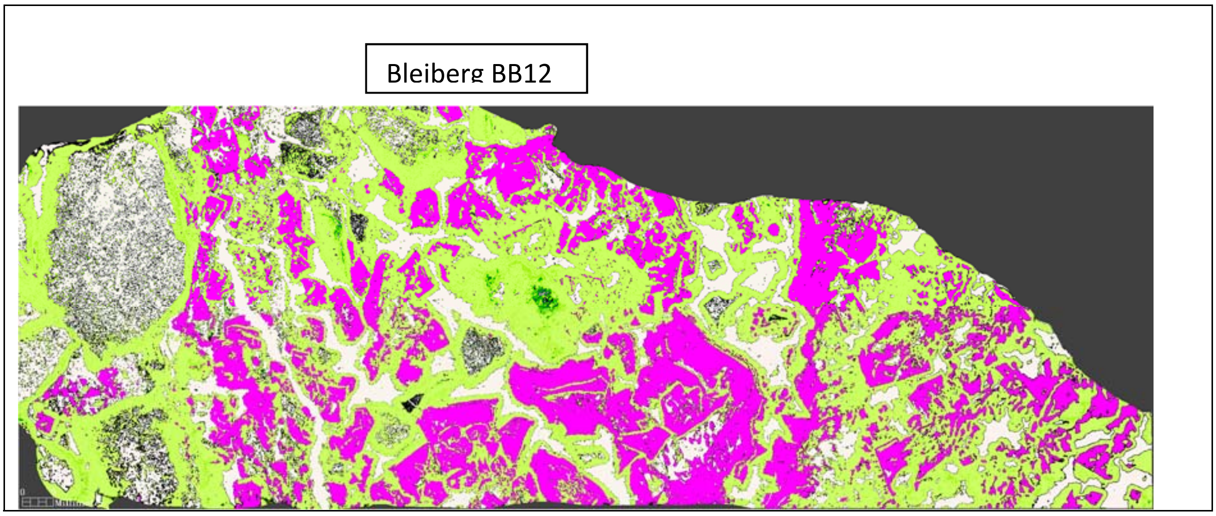
A small number of ore samples have been characterized using a TORNADO µ-XRF at the BGR, Hannover. Results in mineral percent are presented in Table 6. False colour photographs of some samples are displayed in Figure 3.

Major and trace element contents of sphalerite were mainly determined by LA-ICP-MS with a New Wave Research (NWR 213) Nd:YAG 213 nm Nano second laser ablation system updated with a TV2 ablation cell, coupled to an Agilent 8800 triple quadrupole ICP-MS (QQQ-ICP-MS) installed at the Chair of Analytical Chemistry, Montanuniversität Leoben (Austria). For quantification of the element content the matrix matched sintered powder pressed pellet MUL-ZnS 1 reference material (Onuk et al. 2017), and for quality control, the USGS powder pressed polysulphide reference material MASS-1 (Wilson et al. 2002) were used. Sphalerite shows stoichiometric sulphur composition, therefore sulphur was used as internal standard. The LA-QQQ-ICP-MS was optimized to maximum sensitivity on mid-mass isotopes. Production of molecular oxide species to reach $^{232}Th^{16}O/^{232}Th$ and doubly charged species measured on $^{140}Ce^{++}/^{140}Ce^{+}$ was maintained to a level below 0.3% using the standard reference material NIST 612. Laser ablation was performed in pure helium atmosphere (750 ml/min), the laser beam size was 80 µm with a repetition rate of 10 Hz and a laser energy density (fluency) of 2 J/cm^2. The aerosol-He mixture from the ablation cell was gas diluted with 0.9 l/min Ar within a glass bulb signal smoothing device (Günther and Heinrich 1999). Each analysis was performed in a time-resolved mode, which includes sequential peak hopping throughout the mass spectrum using dwell times per isotope depending on the mass fraction between 10 and 50 msec. The analysis time for each sample was 120 seconds, 30 seconds for measuring the background (and laser warm-up with closed aperture), 60 seconds analysis with laser on and 30 seconds wash out time. The following isotopes were monitored: ^{33}S, ^{34}S, ^{51}V, ^{52}Cr, ^{55}Mn, ^{56}Fe, ^{57}Fe, ^{59}Co, ^{60}Ni, ^{63}Cu, ^{66}Zn, ^{71}Ga, ^{74}Ge, ^{75}As, ^{82}Se, ^{95}Mo, ^{107}Ag, ^{111}Cd, ^{115}In, ^{118}Sn, ^{121}Sb, ^{205}Tl, ^{208}Pb and ^{209}Bi. Data reduction was carried out using the Iolite V3.1 software (Paton et al. 2011).

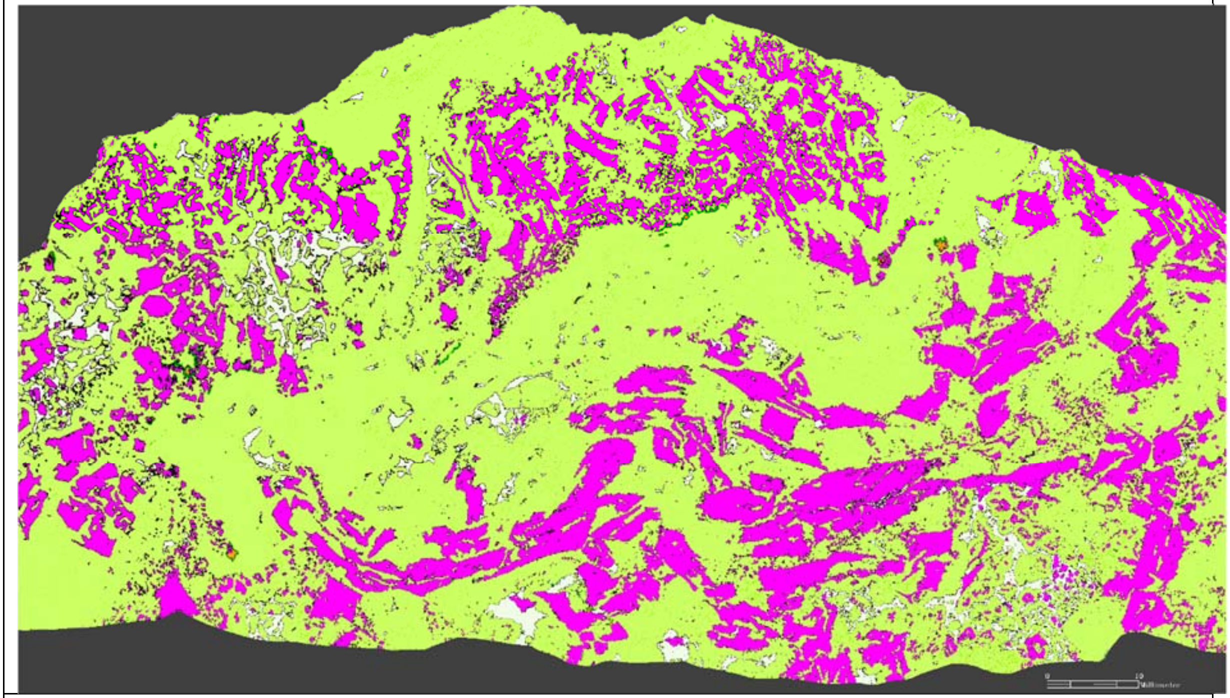
A subset of the ore samples was ground in an agate disc mill for whole rock analysis. Pressed powder pellets were produced using 1 g Hoechst Wax micro powder and 4 g powdered sample. The pressed powder pellets were analysed by wavelength-dispersive X-ray fluorescence analysis (WD-XRF, Panalytical Axios Max) using the program Omnian. The same powders were digested in a microwave oven using 0.5 g of powdered sample, 2 ml HCL, 5 ml HNO_3 and 2 ml H_2O_2. The solutions were analysed by ICP-MS for trace elements.

Table 6. Quantitative mineralogy of ore samples calculated from µ-XRF imaging on large polished sample slabs

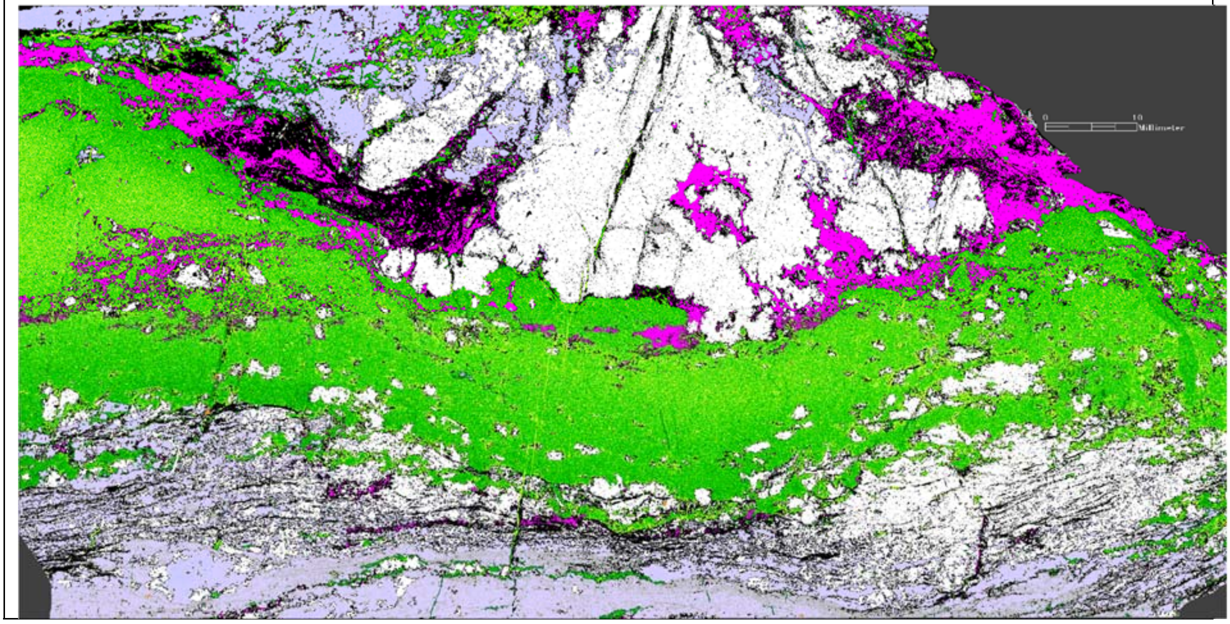
	Bleiberg	Bleiberg	Bleiberg	Bleiberg	Radnig	Walchen	Mitterberg	Friedrichstollen
Sample	**BB12**	**BB13**	**BB14**	**BB17**	**RA18**	**WA3**	**MB1**	**FS1**
Mineral	**wt%**	**wt%**	**wt%**	**wt%**	**wt%**	**wt%**	**wt%**	**wt%**
Sphalerite	40,89	69,22	46,82	57,37	16,48	1,11	0,00	40,53
Galena	40,75	1,23	0,24	36,85	0,00	0,89	0,00	12,33
Chalkopyrite	0,00	0,00	0,00	0,00	0,00	5,47	44,58	0,00
Pyrite	0,00	0,16	0,05	0,04	0,00	27,62	4,66	0,04
Pyrrothine	0,01	0,08	0,05	0,00	0,00	14,30	2,31	0,07
Quartz	0,71	0,00	0,02	0,00	0,00	13,28	3,18	18,89
Siderite	0,04	0,50	0,59	0,00	0,07	0,32	4,31	9,42
Ankerite	0,00	0,04	0,06	0,00	0,00	0,13	0,01	2,06
Calcite	8,78	14,30	16,24	0,57	59,49	0,00	0,00	0,03
Fluorite	3,76	2,02	27,82	1,48	20,81	0,01	0,00	0,06
Barite	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
Gersdorffite	0,00	0,00	0,00	0,00	0,00	0,00	29,76	0,00
Host rock	5,07	12,45	8,11	3,69	3,15	36,87	11,19	16,57



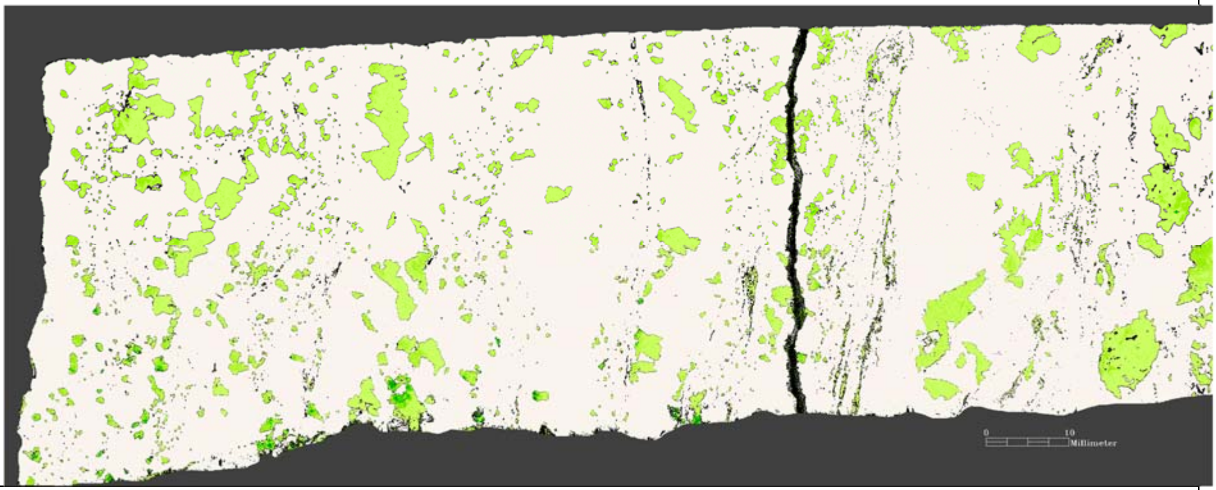
Bleiberg BB17



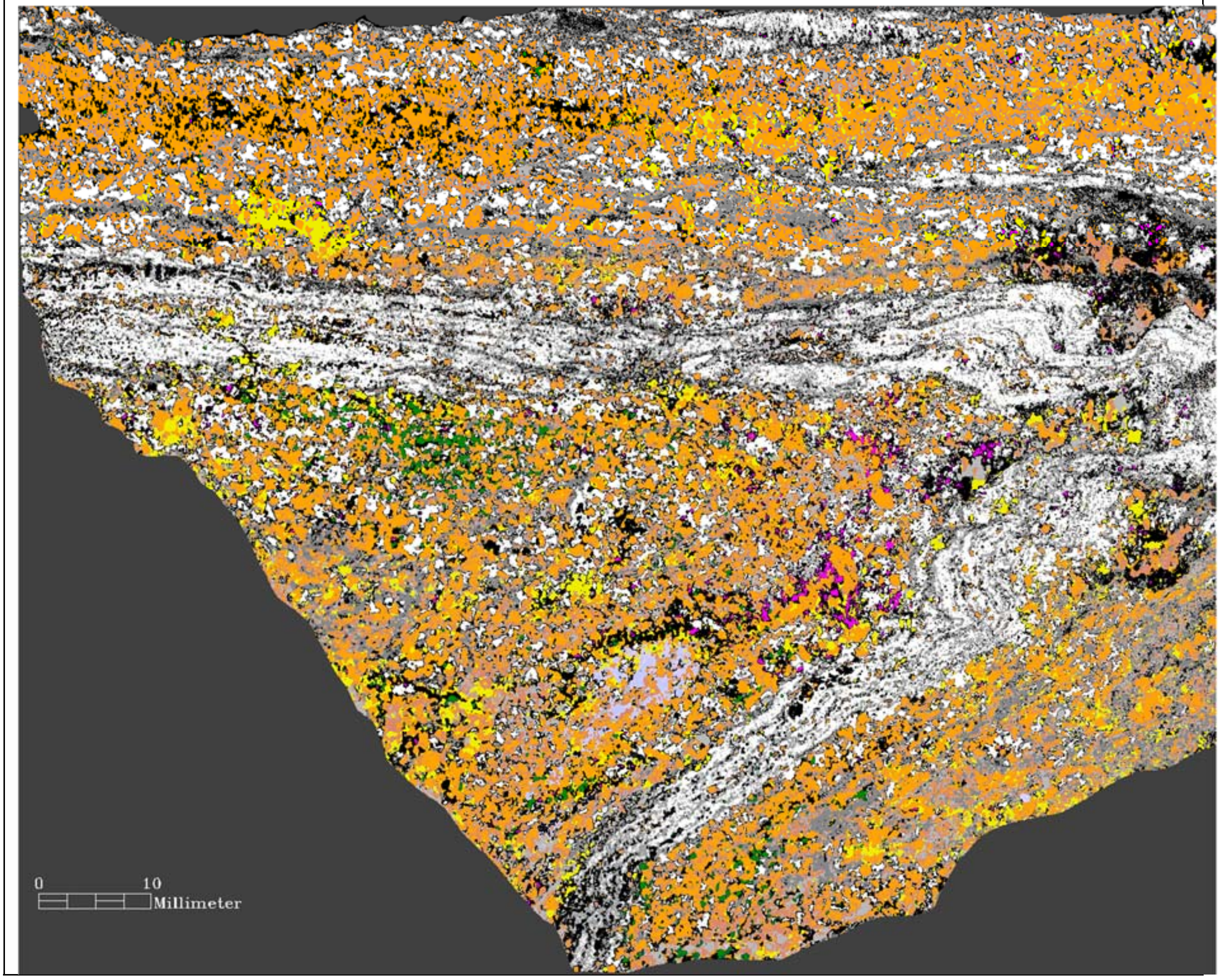
Friedrichstollen FS1



Radnig RA18



Walchen WA3



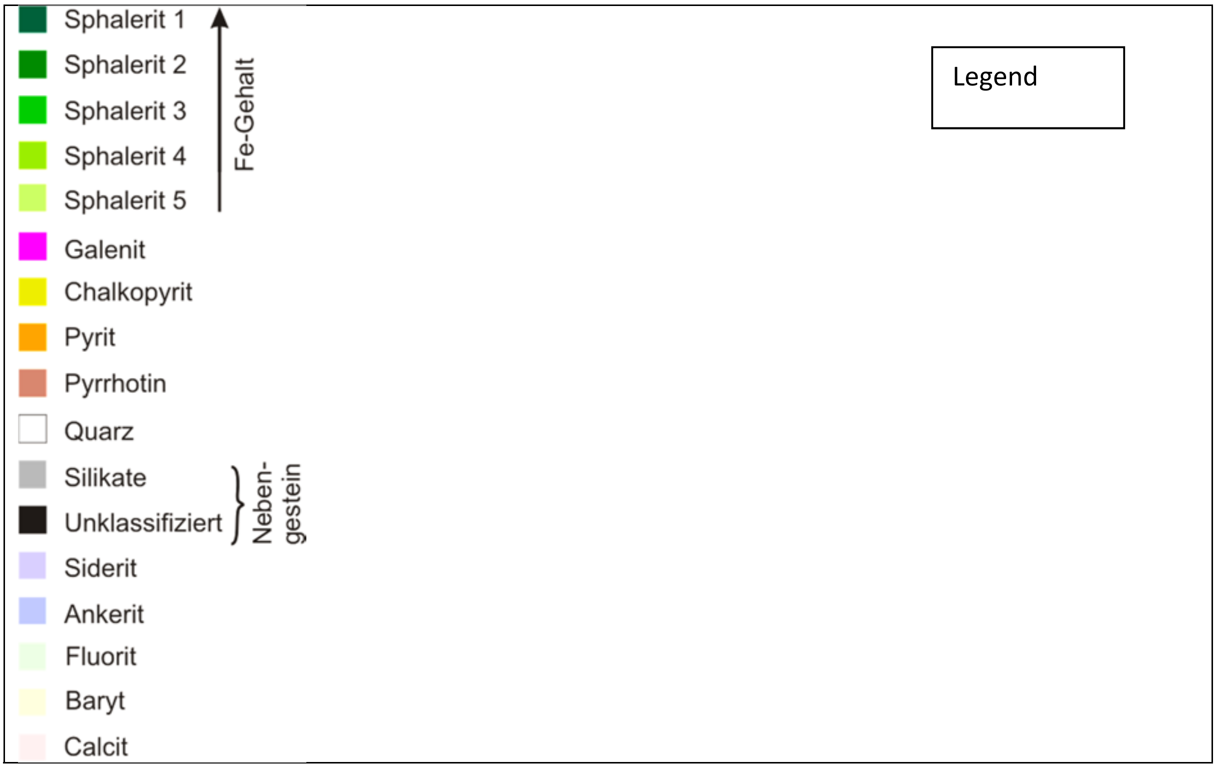


Figure 3. False colour quantitative mineral maps (TORNADO) of mineralized samples

6. Results

In total, more than 5500 laser ablation point analyses were carried out on sphalerite grains from 311 polished thin sections (Table 7). We also included samples from former mining districts in the Eastern Alps that were not part of the detailed study; these include Schneeberg, Raibl, Salafossa (Italy), and Mezica (Slovenia). However, sampling was not representative and the numbers generated are unlikely to represent the deposit median and overall variation of trace elements.

Table 7. Overview on number of analyses carried out

Location	Unit	Nappe system	Ore type	Sections	LA-ICP-MS	XRF whole rock
Achselalm	Subpenninic	Venediger	vein-type	24	404	2
Arzberg	Austroalpine	Drauzug-Gurktal	sediment-hosted stratiform	12	167	2
Bleiberg	Austroalpine	Drauzug-Gurktal	carbonate-hosted Pb-Zn	49	795	3
Brenntal (Mühlbachtal)	Subpenninic	Venediger	stratiform/vein-type	1	12	0
Draßnitz	Austroalpine	Drauzug-Gurktal	vein-type	5	104	0
Elisabethstollen	Austroalpine	Drauzug-Gurktal	sediment-hosted stratiform	8	150	2
Fladung	Austroalpine	Drauzug-Gurktal	carbonate-hosted Pb-Zn	19	304	0
Flecktrogalm	Subpenninic	Venediger	vein-type	19	386	2
Friedrichstollen	Austroalpine	Drauzug-Gurktal	sediment-hosted stratiform	6	110	5
Guggenbach	Austroalpine	Drauzug-Gurktal	sediment-hosted stratiform	15	328	3
Haufenreith	Austroalpine	Drauzug-Gurktal	sediment-hosted stratiform	6	80	0
Jauken Süd	Austroalpine	Drauzug-Gurktal	carbonate-hosted Pb-Zn	6	128	0
Koprein	Austroalpine	Drauzug-Gurktal	vein-type, volcanic-hosted	21	399	6
Lafatsch	Austroalpine	Tirolisch-Norisch	carbonate-hosted Pb-Zn	22	339	9
Leogang	Austroalpine	Tirolisch-Norisch	carbonate-hosted Pb-Zn	5	78	0
Meiselding	Austroalpine	Drauzug-Gurktal	sediment-hosted stratiform	18	302	3
Mezica (Slovenien)	Austroalpine		carbonate-hosted Pb-Zn	2	47	0
Rabenstein/Deutschfeistritz	Austroalpine	Drauzug-Gurktal	carbonate-hosted Pb-Zn	8	139	7
Radnig	Austroalpine	Drauzug-Gurktal	carbonate-hosted Pb-Zn	19	353	0
Raibl (Italien)	Southalpine		carbonate-hosted Pb-Zn	8	224	0
Salafossa (Italien)	Southalpine		carbonate-hosted Pb-Zn	1	20	0
Schneeberg (Italien)	Austroalpine	Koralpe-Wölz	sediment-hosted stratiform	4	70	0
Seibach-Griesbach	Austroalpine	Ötztal-Bundschuh	carbonate-hosted Pb-Zn	3	59	0
Silberberg	Austroalpine	Drauzug-Gurktal	sediment-hosted stratiform	3	54	1
Sprinzgasse (Rotgülden)	Subpenninic	Venediger	stratiform	3	60	0
Vellach-Metnitz	Austroalpine	Drauzug-Gurktal	vein-type	14	365	0
Walchen	Austroalpine	Koralpe-Wölz	sediment-hosted stratiform	10	102	0
			Total	311	5579	45

XRF data of ore samples

A total of 45 ore samples from 12 locations were analysed by XRF methods (Appendix, Table 19). In addition, trace elements were analysed in 58 sample solutions digested in a microwave oven.

The compositions of the samples vary due to different host lithologies. In general, samples from carbonate-hosted Pb-Zn ores (Bleiberg, Lafatsch) have low concentrations of Si, Al, K, Ti and Fe, but high Ca, Zn and Pb. In the sample suite investigated, calculated ZnS concentrations range from 26 – 87%, those of PbS from <0.1 – 19%, and CaO from 5 – 60%; As and Cd are detected as significant trace elements. Twenty samples from 9 locations in the Graz Paleozoic display a wide variation, but are generally higher in Al, Si, K and Ti than carbonate-hosted ores. CaO ranges from 0 -40%, and MgO from 0 – 8%, respectively. The ores may be highly enriched in Fe_2O_3 (up to 57%) and MnO (up to 2.4%), and carry 0.3 – 57% ZnS, 0.1 – 44% PbS, up to 0.6% Cu and up to 60% $BaSO_4$. Several samples have elevated Ag and Cd concentrations. Three ore samples from Meiselding have compositions comparable to those of the Graz Paleozoic, with 12 – 28% Fe_2O_3, 0.5 – 2.9% MnO, 6 – 33% CaO, 3.4 – 8.1% MgO, 2 – 7% Al_2O_3, 19 – 46% SiO_2, and 0.1 – 1% TiO_2. ZnS ranges from 0.25 – 10.6%, PbS from 0.9 – 6.7%, and Cu from 0.7-1.2%. Five vein-type samples from the Koprein deposit are high in CaO (16 – 38%), moderate in SiO_2 (5 – 24%), Al_2O_3 (0.8 – 7.6%), Fe_2O_3 (3.5-5.4%) and low in MgO (up to 1.4%) and K_2O (up to 1.2%); the ore is characterized by high ZnS (15 – 56%), variable PbS (0 – 43%), low Cu (<0.3%) and carries some $BaSO_4$. Among the trace elements, median values of 0.036% Co and 0.172% CdS are noteworthy. Mineralized samples from Achselalm-Flecktrogalm have low ZnS (0.04- 4.2%) and PbS (0.01 – 7.5%) contents; they are variably enriched or depleted in Ca, Mg, Al, Si, K and Fe. Copper concentrations are <0.015%.

LA-ICP-MS analyses

A summary of median, P25 and P75 values from all locations is provided in Table 8. The data are presented as probability diagrams of element concentrations for individual deposits (Figure 4). Further, they are grouped into four major deposit classes, namely (1) carbonate-hosted deposits in Mesozoic sequences (Figure 5); (2) sediment-hosted deposits in the Graz Paleozoic (Figure 6); (3) sediment-hosted deposits in Paleozoic units outside the Graz Paleozoic (Figure 7); and (4) vein-type deposits in various Paleozoic units (Figure 8).

The figures illustrate the distribution of data points around the median (probability P = 50); straight lines indicate (log-) normal distribution, kinked lines and curved lines indicate the presence of subpopulations (e.g., several ore types). Steep slopes point to a low degree of variability (i.e., for normal distributions, low standard deviation), whereas flat slopes indicate a high variability. For sphalerite hosted by Mesozoic carbonate rocks, many of the element distributions shown in Figure 6 are parallel, indicating similar variability and distribution, albeit at differing concentration levels (e.g., Cd in Jauken and Fladung; Ga in Radnig and Fladung). The distribution of data points for the Bleiberg deposit, for which a large data set is available, is normally distributed for most trace elements except for Fe (e.g. showing a second population at higher Fe levels, representing schalenblende samples). Sphalerite from Fladung is most enriched in Cd, Ga and Ge. Lafatsch contains the highest Ag concentrations (Md >50 ppm) in sphalerite, whereas in all other carbonate-hosted deposits, more than 50% of the Ag concentrations are <1 ppm. There is a clear succession of Ag concentrations above P50, with Lafatsch > Bleiberg > Fladung > Radnig > Jauken. The highest median Ge value is from Fladung (close to 1000 ppm), the lowest from Lafatsch (ca. 50 ppm); Bleiberg, Jauken and Radnig have very similar median values (ca. 200-400 ppm) and Ge distributions. For Tl, Bleiberg and Fladung have similar high median values > 70 ppm, whereas the remaining deposits have similar, and lower median Tl concentrations of around 20-30 ppm.

Table 8. Median, P25 and P75 values for trace elements from all locations sampled in the present study

		Number	V	Cr	Mn	Fe	Co	Ni	Cu	Ga	Ge	As	Se	Mo	Ag	Cd	In	Sn	Sb	Tl	Pb	Bi
Achselalm	P75	426	0,01	0,52	271	28665	70	8,42	84	44,78	0,06	0,32	9,68	0,01	1,46	2893	3,22	0,53	1,62	0,00	8,75	0,02
Achselalm	Median	426	0,01	0,37	231	12170	57	3,31	38	21,55	0,02	0,12	7,00	0,00	0,56	2201	1,88	0,28	0,51	0,00	3,14	0,01
Achselalm	P25	426	0,00	0,27	171	6858	43	1,59	21	6,28	-0,01	0,05	5,50	0,00	0,35	1947	1,05	0,18	0,13	0,00	1,05	0,01
Arzberg	P75	181	0,03	0,79	145	19100	234	0,79	1741	10,95	0,19	0,29	9,00	0,00	180	1851	8,42	0,66	13,89	0,12	330	0,23
Arzberg	Median	181	0,01	0,45	103	14020	27	0,17	936	2,12	0,11	0,14	7,10	0,00	78	1292	4,03	0,37	5,87	0,03	70	0,09
Arzberg	P25	181	0,00	0,17	35	10490	11	0,05	125	0,59	0,03	0,06	5,80	0,00	11	975	2,56	0,21	2,41	0,01	15	0,01
Bleiberg	P75	795	0,03	0,46	52	11003	0,12	0,20	10	4,09	778	4124	7,03	0,02	1,29	1502	0,00	0,09	3,01	736	8393	0,00
Bleiberg	Median	795	0,01	0,35	25	1739	0,05	0,09	2	0,65	460	2188	5,50	0,01	0,29	853	0,00	0,07	0,74	322	4880	0,00
Bleiberg	P25	795	0,00	0,27	11	448,5	0,03	0,03	-1	0,07	214	877	4,00	0,00	0,25	549	0,00	0,05	0,25	130	2020	0,00
Brenntal	Median	12	0,08	1,28	16	13175	0,32	0,15	87	1,23	0,67	0,35	118,05	4,05	3,30	2947	34,08	0,27	1,04	0,01	9,06	1,16
Drassnitz	P75	104	0,01	1,41	6881	119600	41	0,24	8395	38,44	0,28	0,33	17,33	0,34	92	3868	129	245	5,10	0,08	67	0,04
Drassnitz	Median	104	0,00	1,21	5112	114500	37	0,13	4715	19,27	0,16	0,12	14,55	0,22	48	3630	55	135	2,15	0,04	21	0,01
Drassnitz	P25	104	-0,01	1,01	3482	107250	31	0,06	2692	10,91	0,11	0,03	12,90	0,06	28	3509	43	53	0,98	0,01	6	0,00
Elisabethstollen	P75	150	0,03	0,41	69	62175	177	1,88	63	22,80	0,39	0,08	3,20	0,01	24	2330	0,35	0,11	12,90	0,01	61	0,02
Elisabethstollen	Median	150	0,01	0,27	50	57750	168	1,14	35	10,30	0,21	0,01	2,40	0,00	14	2168	0,20	-0,27	7,81	0,00	26	0,01
Elisabethstollen	P25	150	-0,01	0,13	35	53450	147	0,31	25	4,00	0,11	-0,05	1,70	0,00	10	2024	0,04	-0,71	4,20	0,00	15	0,00
Fladung	P75	282	0,03	0,90	20	8318	0,16	0,50	158	27,79	1127	445	12,31	0,02	1,58	7323	0,08	0,11	2,86	219	770	0,01
Fladung	Median	282	0,01	0,63	17	5196	0,10	0,07	93	10,33	846	310	11,34	0,00	0,47	5515	0,05	0,06	0,52	137	594	0,00
Fladung	P25	282	0,00	0,51	13	865	0,06	0,03	63	3,15	356	86	9,28	0,00	0,37	4099	0,03	0,04	0,17	25	396	0,00
Flecktrogalm	P75	386	0,01	0,43	268	19605	73	13,87	79	85,68	0,04	0,33	7,40	0,00	1,17	2927	2,62	0,59	1,98	0,00	8,23	0,02
Flecktrogalm	Median	386	0,00	0,34	178	10865	62	7,77	36	32,41	0,01	0,13	5,40	0,00	0,54	2263	1,49	0,33	0,63	0,00	3,77	0,01
Flecktrogalm	P25	386	0,00	0,20	145	4656	51	5,04	14	8,01	-0,02	0,08	2,10	-0,01	0,29	1898	0,42	0,19	0,20	0,00	1,43	0,00
Friedrichstollen	P75	110	0,02	0,33	68	56650	338	3,22	159	33,71	0,38	0,25	3,80	0,00	40	3047	6,53	0,37	11,10	0,00	44	0,02
Friedrichstollen	Median	110	0,01	0,22	49	48000	280	2,24	63	19,87	0,14	0,12	2,45	0,00	25	2673	2,23	0,01	7,56	0,00	23	0,01
Friedrichstollen	P25	110	0,00	0,12	41	41650	162	1,50	33	9,41	0,03	0,03	1,70	0,00	15	2511	0,27	-0,73	5,26	0,00	14	0,01
Guggenbach	P75	364	0,02	0,99	104	54800	157	3,02	1005	20,84	0,24	1,30	5,50		30	1558	2,96	1,35	8,69	0,04	60	0,13
Guggenbach	Median	364	0,01	0,68	74	49800	134	1,75	919	7,41	0,09	0,50	4,50		19	1132	0,19	0,85	4,31	0,01	23	0,08
Guggenbach	P25	364	0,00	0,47	65	44143	103	0,95	602	2,78	0,03	0,26	3,20		10	981	0,13	0,62	1,62	0,01	9	0,03
Haufenreith	P75	80	0,05	0,26	137	33935	156	4,18	434	3,34	0,03	0,89	2,83	0,00	6,23	1114	29	0,85	2,12	0,01	20,16	0,00
Haufenreith	Median	80	0,01	0,21	110	16090	147	2,88	424	1,55	0,00	0,60	1,67	0,00	2,99	893	21	0,70	1,25	0,00	9,66	0,00
Haufenreith	P25	80	0,00	0,15	93	14720	133	1,47	414	0,55	-0,04	0,40	1,12	0,00	1,06	849	16	0,50	0,66	0,00	6,42	0,00
Jauken Süd	P75	93	0,20	0,85	52	5880	0,23	0,29	568	2,83	556	65	10,98	0,07	0,51	1496	0,09	0,62	0,26	45	467	0,19
Jauken Süd	Median	93	0,02	0,65	39	4508	0,17	0,17	555	1,55	389	38	6,45	0,01	0,34	1249	0,07	0,48	0,13	23	246	0,12
Jauken Süd	P25	93	0,00	0,52	29	3351	0,12	0,09	49	0,58	230	23	5,50	0,00	0,27	929	0,01	0,13	0,08	14	158	0,00
Koprein	P75	399	0,02	0,36	75	43300	734	1,12	608	5,73	0,49	0,37	2,90	0,00	50	3135	34	107	19,17	0,10	127	0,05
Koprein	Median	399	0,00	0,10	55	34720	644	0,66	306	4,06	0,29	0,16	2,10	0,00	28	2890	17	36	9,04	0,03	66	0,03
Koprein	P25	399	-0,02	-0,31	37	28100	553	0,35	136	2,58	0,03	0,06	1,40	-0,01	15	2620	11	13	4,85	0,01	32	0,02
Lafatsch	P75	439	0,04	1,35	2,25	962	0,05	0,08	702	5,17	72	939	11,60	0,01	106	3443	0,06	1,14	3,50	87	1199	0,02
Lafatsch	Median	439	0,01	0,65	0,87	520	0,04	0,04	133	1,22	42	273	10,66	0,00	43	1911	0,02	0,08	1,03	16	330	0,01
Lafatsch	P25	439	0,00	0,53	0,20	192	0,02	0,01	69	0,28	25	75	7,00	0,00	18	1093	0,01	0,04	0,32	3	95	0,00
Leogang	P75	78	0,02	0,96	235	91063	148	2,26	2325	1,62	0,16	0,25	26,50	0,01	27	2560	270	1,95	5,35	0,11	86	6,89
Leogang	Median	78	0,01	0,81	143	79985	128	0,23	865	1,05	0,11	0,15	23,05	0,00	11	2042	247	0,89	2,65	0,03	17	0,57
Leogang	P25	78	0,00	0,71	57	23040	79	0,08	226	0,73	0,04	0,07	11,78	0,00	4	1734	4	0,58	1,21	0,01	5	0,02
Meiselding	P75	302	0,03	0,68	669	91975	301	1,49	920	0,87	0,33	1,78	8,50		29	4532	23	1,46	13,13	0,16	198	0,03
Meiselding	Median	302	0,01	0,49	454	88300	213	0,46	748	0,67	0,13	1,09	7,00		13	3960	16	1,22	5,50	0,02	12	0,01
Meiselding	P25	302	-0,01	0,26	331	83025	139	0,19	586	0,49	0,04	0,34	5,33		7	3603	10	0,94	2,00	0,00	3	0,01
Metnitz	P75	364	0,02	0,85	86	64900	470	0,67	1733	74,63	374	4,70	6,80	0,00	27	2199	0,22	4,43	27,30	0,08	36	0,02
Metnitz	Median	364	0,00	0,70	73	58950	405	0,46	1220	37,60	149	3,60	4,85	0,00	14	1931	0,11	2,38	13,06	0,03	10	0,01
Metnitz	P25	364	-0,03	0,56	63	52600	347	0,31	928	10,37	26	2,40	3,40	0,00	7	1673	0,08	1,62	4,94	0,01	3	0,01
Mezica	P75	47	0,04	0,68	5,68	305	0,05	0,16	1294	6,92	55	427	13,10	0,07	64	4034	0,02	0,09	4,05	35	1221	0,01
Mezica	Median	47	0,02	0,58	3,48	107	0,04	0,11	363	5,00	21	74	12,20	0,01	26	3641	0,02	0,03	2,08	8	669	0,00
Mezica	P25	47	0,01	0,52	1,09	65	0,03	0,07	132	0,63	5	15	11,75	0,00	15	2850	0,01	0,02	1,05	6	188	0,00
Rabenstein	P75	190	0,22	0,94	20	13010	45	5,15	1011	10,37	0,13	0,64	6,80	0,01	39	1801	7,96	0,73	13,25	0,02	39	0,16
Rabenstein	Median	190	0,02	0,64	7	6300	28	2,63	940	5,59	0,06	0,38	5,90	0,00	20	1534	1,01	0,57	6,66	0,01	15	0,12
Rabenstein	P25	190	0,00	0,36	5	4290	9	1,02	886	2,08	0,01	0,25	5,00	0,00	11	1209	0,36	0,37	3,36	0,00	7	0,10
Radnig	P75	318	0,01	0,66	35	7573	0,10	0,08	50	4,98	523	129	10,88	0,01	0,72	1794	0,01	0,11	0,29	38	436	0,00
Radnig	Median	318	0,01	0,54	24	4229	0,08	0,04	41	1,86	325	56	9,14	0,00	0,44	1383	0,01	0,06	0,19	16	243	0,00
Radnig	P25	318	0,00	0,37	7	1277	0,05	0,00	1	0,80	121	6	5,60	0,00	0,33	955	0,00	0,04	0,12	2	57	0,00
Raibl	P75	224	0,03	0,46	52	11003	0,12	0,20	10	4,09	778	4124	7,03	0,02	1,29	1502	0,00	0,09	3,01	736	8393	0,00
Raibl	Median	224	0,01	0,35	25	1739	0,05	0,09	2	0,65	460	2188	5,50	0,01	0,29	853	0,00	0,07	0,74	322	4880	0,00
Raibl	P25	224	0,00	0,27	11	448,5	0,03	0,03	-1	0,07	214	877	4,00	0,00	0,25	549	0,00	0,05	0,25	130	2020	0,00
Salafossa	P75	20	0,12	0,73	4,88	153	0,10	0,39	898	10,85	9,37	19	13,03	0,41	12,79	4140	0,02	0,05	0,66	7,47	362	0,01
Salafossa	Median	20	0,05	0,61	2,88	62	0,07	0,18	479	5,43	6,24	12	12,35	0,14	7,52	3445	0,01	0,04	0,43	6,07	116	0,00
Salafossa	P25	20	0,01	0,56	0,97	45	0,06	0,08	117	2,57	5,17	7	11,68	0,06	4,96	2293	0,01	0,02	0,31	4,09	46	0,00
Schneeberg	P75	70	0,01	0,48	253	120700	204	0,35	464	8,13	0,09	0,17	23,40	0,01	6,55	3922	31	0,72	1,70	0,01	7,05	0,13
Schneeberg	Median	70	0,00	0,42	200	94550	57	0,16	150	5,82	0,05	0,06	19,00	0,00	4,45	3240	14	0,51	0,70	0,00	3,70	0,01
Schneeberg	P25	70	-0,01	0,36	113	83700	45	0,07	69	4,78	-0,01	-0,04	16,95	0,00	2,73	2995	13	0,34	0,41	0,00	1,89	0,01
Seibach-Griesbach	P75	59	0,21	0,56	1282	37400	0,03	0,21	68	9,44	0,17	4,50	13,30	1,08	0,45	2321	0,17	0,79	2,66	1,60	166	0,01
Seibach-Griesbach	Median	59	0,04	0,48	1087	35300	0,01	0,11	64	2,45	0,08	1,76	12,20	0,26	0,33	2054	0,07	0,34	1,35	0,78	47	0,00
Seibach-Griesbach	P25	59	0,02	0,41	420	29920	-0,01	0,05	61	2,26	0,02	1,06	10,95	0,05	0,31	1320	0,04	0,23	0,85	0,50	20	0,00
Silberberg	P75	54	0,46	1,36	29	32828	127	0,37	1180	11,39	0,24	0,15	3,37	1,55	23	3308	6,69	0,18	7,82	0,01	49	0,17
Silberberg	Median	54	0,09	0,50	12	30295	86	0,22	490	6,10	0,12	0,04	2,29	0,45	20	2650	3,23	-0,08	5,17	0,00	29	0,09
Silberberg	P25	54	0,03	0,07	-1	7890	8	0,13	237	1,38	0,03	-0,03	1,84	0,00	17	2535	2,40	-1,83	3,05	0,00	20	0,05
Sprinzgasse	P75	60	0,01	1,34	1278	74025	88	3,12	149	86,85	0,35	0,60	56,40	0,05	4,00	3880	27,72	1,62	2,52	0,01	4,08	0,00
Sprinzgasse	Median	60	0,00	1,25	1244	72620	16	2,08	112	72,05	0,27	0,42	48,00	0,04	3,03	3766	0,78	0,73	0,94	0,00	1,58	0,00
Sprinzgasse	P25	60	0,00	1,20	1132	71530	12	0,70	105	64,75	0,24	0,37	44,90	0,04	2,64	3695	0,41	0,63	0,39	0,00	1,03	0,00
Walchen	P75	109	0,01	0,43	131	88700	97	0,18	690	4,30	0,10	0,25	29,30	0,00	20	2092	173	3,73	8,40	0,06	270	3,10
Walchen	Median	109	0,01	0,37	73	84300	55	0,06	288	1,53	0,07	0,09	23,10	0,00	12	1592	98	1,13	3,07	0,01	12	0,81
Walchen	P25	109	0,00	0,31	42	77900	12	0,02	178	0,91	0,04	0,04	17,30	0,00	9	1364	64	0,54	1,11	0,00	3	0,14

Sphalerites in sediment-hosted deposits of the Graz Paleozoic, although collected from individual deposits within the same stratigraphic ore horizon, exhibit large variations in trace elements, and many kinked distributions point to the presence of several ore types or sphalerite generations (Figure 4, Figure 8). The measurements show elevated Fe (mostly >1%), Co, Ag and Cu, and low concentrations of Ga, In and Ge. The Graz Paleozoic thus serves as an example of heterogeneity within and between individual deposits in a geographic and geological province. Samples from Friedrich, Elisabeth, Haufenreith and Guggenbach are highest in Co, and Haufenreith sphalerite carries in excess of 20 ppm In. Copper and Ag concentrations are most elevated at Arzberg, probably partly due to intergrowth with Ag-bearing fahlore and also chalcopyrite.

For sediment-hosted deposits outside of the Graz Paleozoic, only Walchen and Meiselding are displayed (Figure 5, Figure 9). Both have similar Fe, Ag and Cu distributions. However Walchen is considerably enriched in Ga and In, whereas Meiselding is elevated in Cd, Mn and Co.

Four examples of vein-type deposits are illustrated in Figure 5, Figure 6 and Figure 10. Achselalm and Flecktrogalm in the Subpenninic nappes of the central Tauern Window display similar trace element distributions characterized by low Fe, Co, Ag, Sn compared to Koprein and Metnitz, both located in Austroalpine Paleozoic units. Koprein shows elevated Co, Ag, Sn and Cd, whereas Metnitz is elevated in Fe, Ga and Ge (not shown).

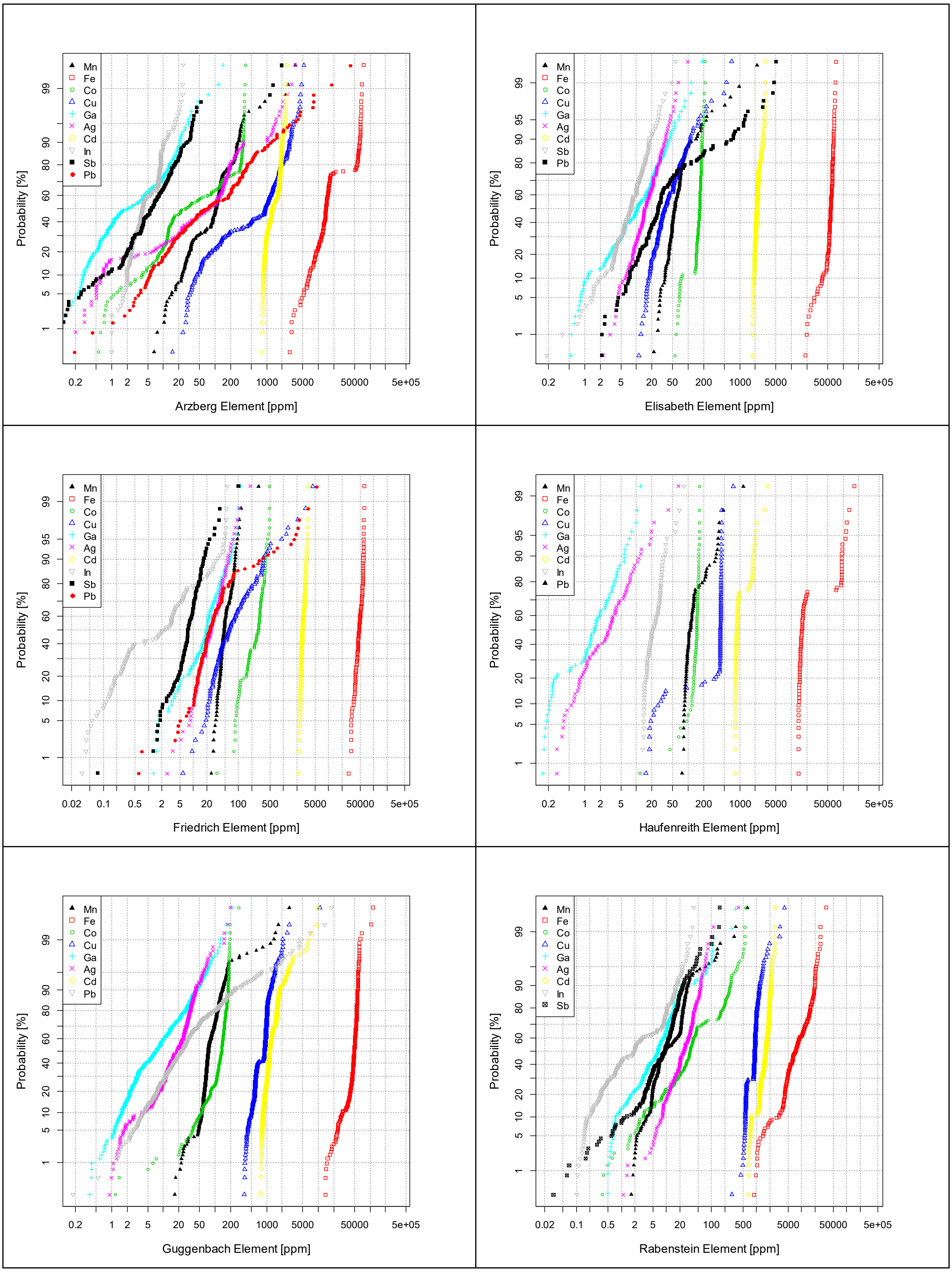


Figure 4. Probability diagrams for trace elements in sphalerite from different deposits in the Graz Paleozoic

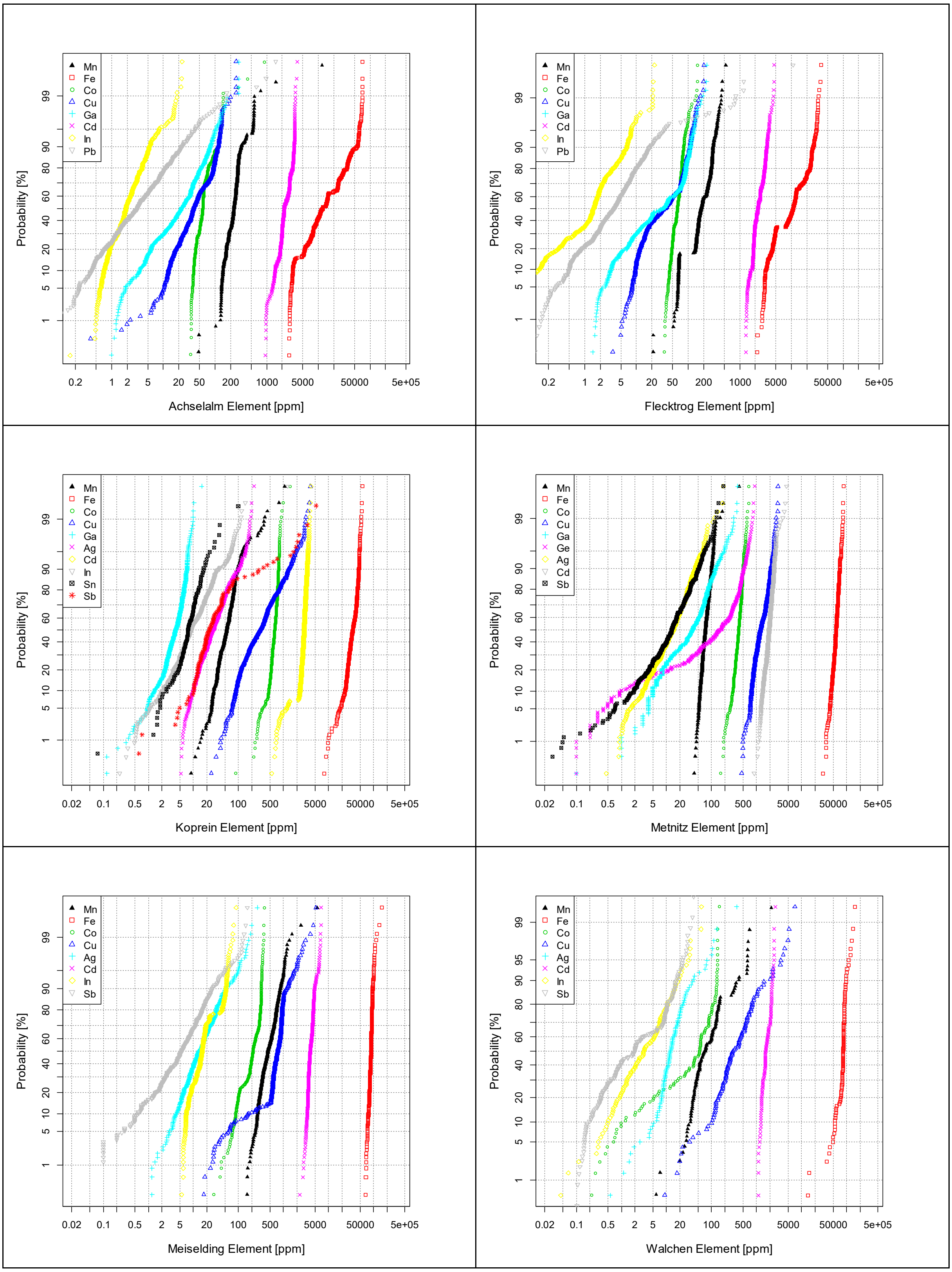


Figure 5. Probability diagrams for trace elements in sphalerite from different vein-type (Achselalm, Flecktrogalm, Koprein, Metnitz) and sediment-hosted deposits (Meiselding, Walchen).

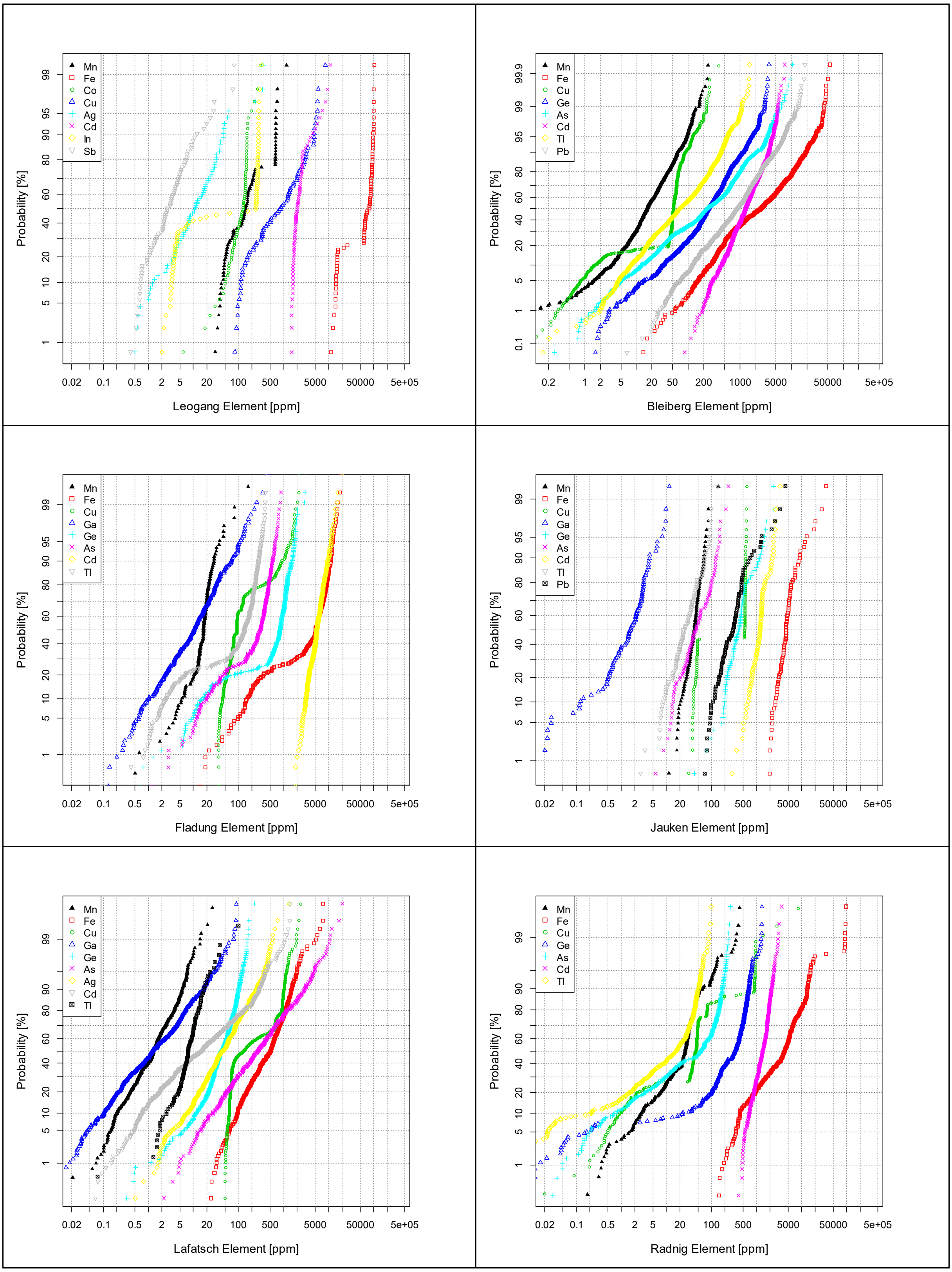
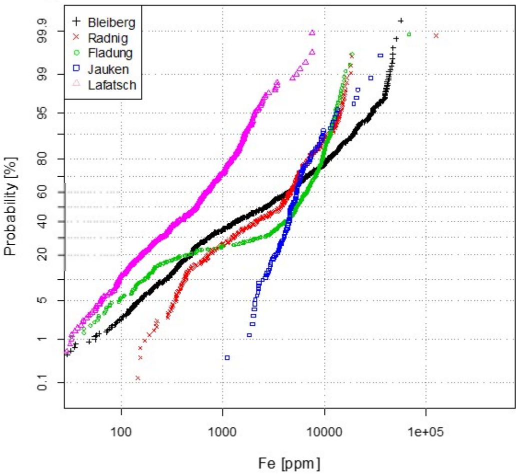


Figure 6. Probability diagrams for trace elements in sphalerite from different carbonate-hosted deposits

Carbonate-hosted deposits in Mesozoic sequences

a



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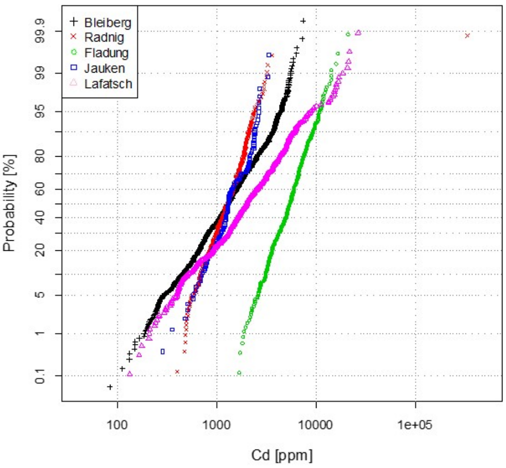

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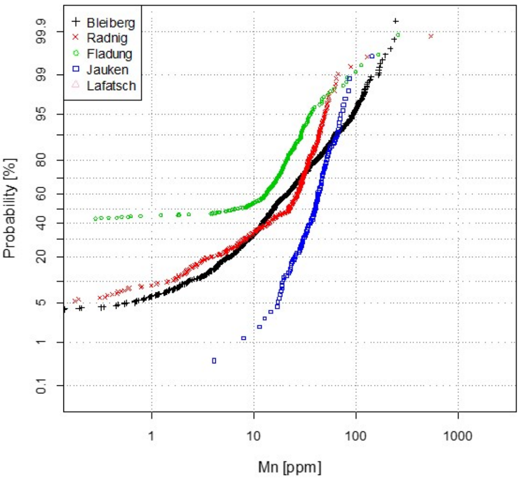
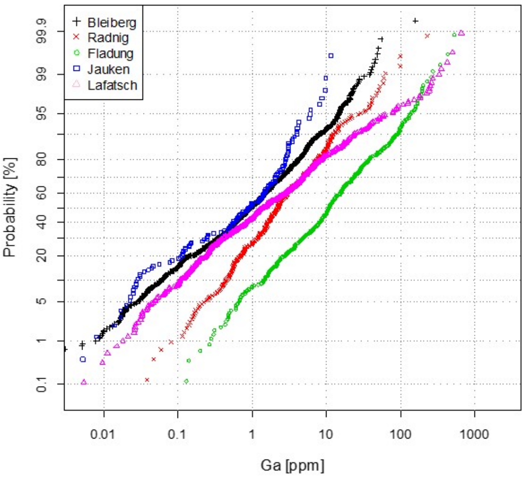
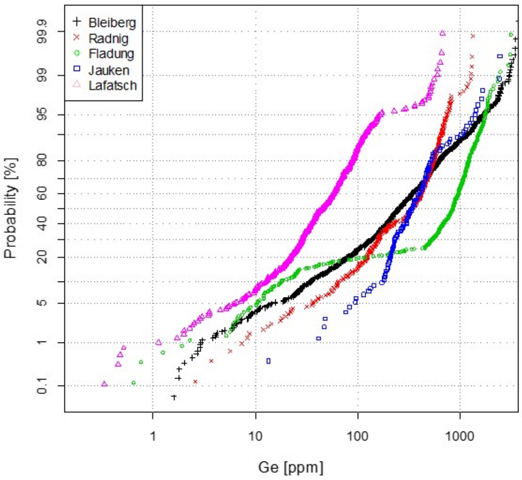


d



e



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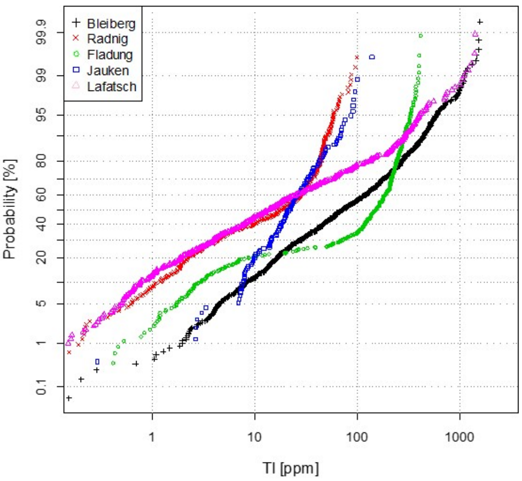


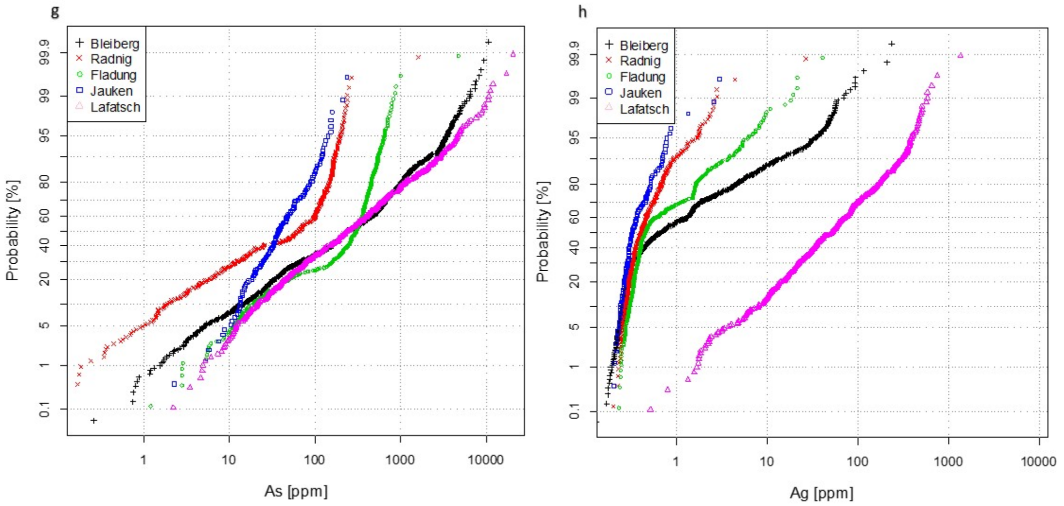
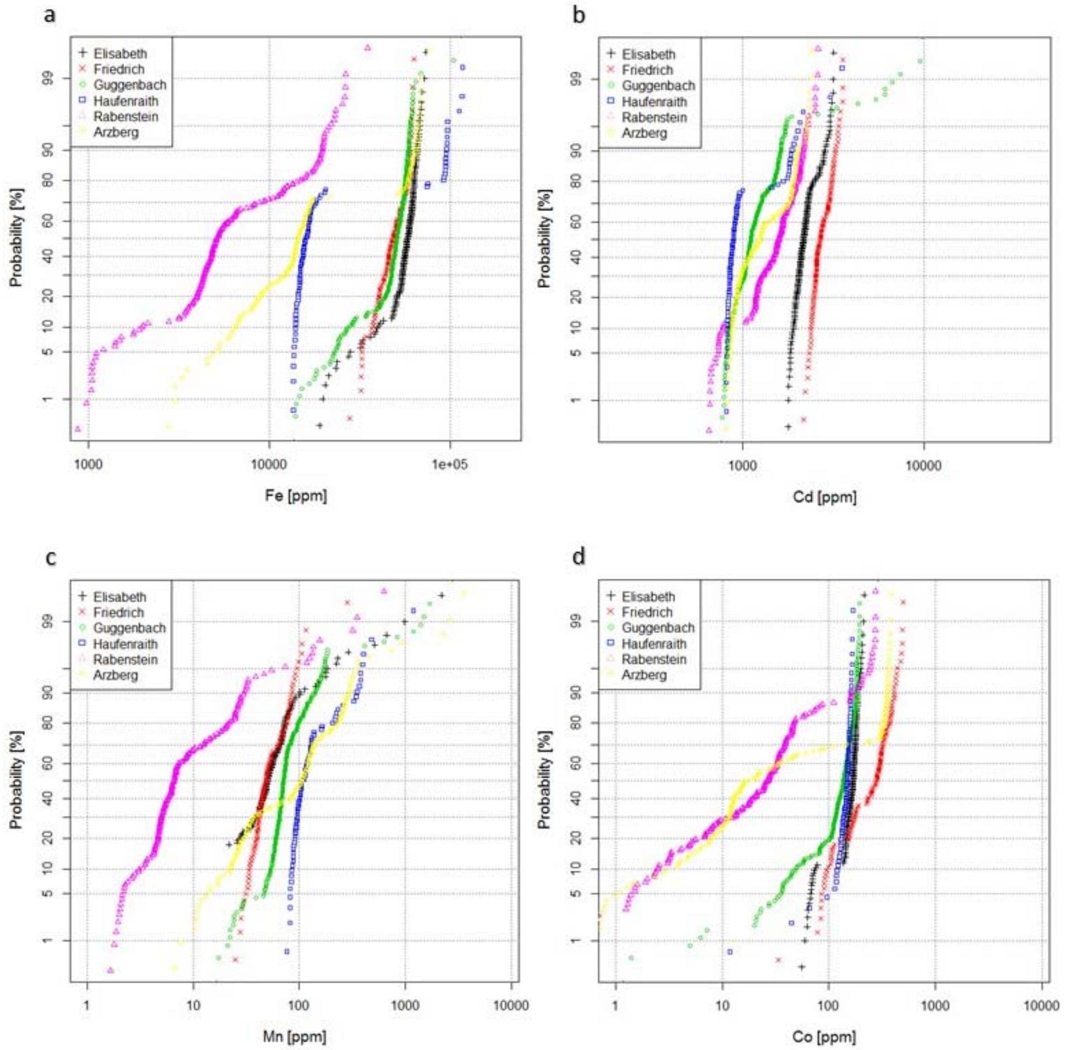


Figure 7: Probability plots of the most important trace elements (a) Fe, (b) Cd, (c) Mn, (d) Ga, (e) Ge, (f) Tl, (g) As and (h) Ag from Bleiberg, Radnig, Fladung, Jauken and Lafatsch.

Sediment-hosted deposits in the Graz Paleozoic



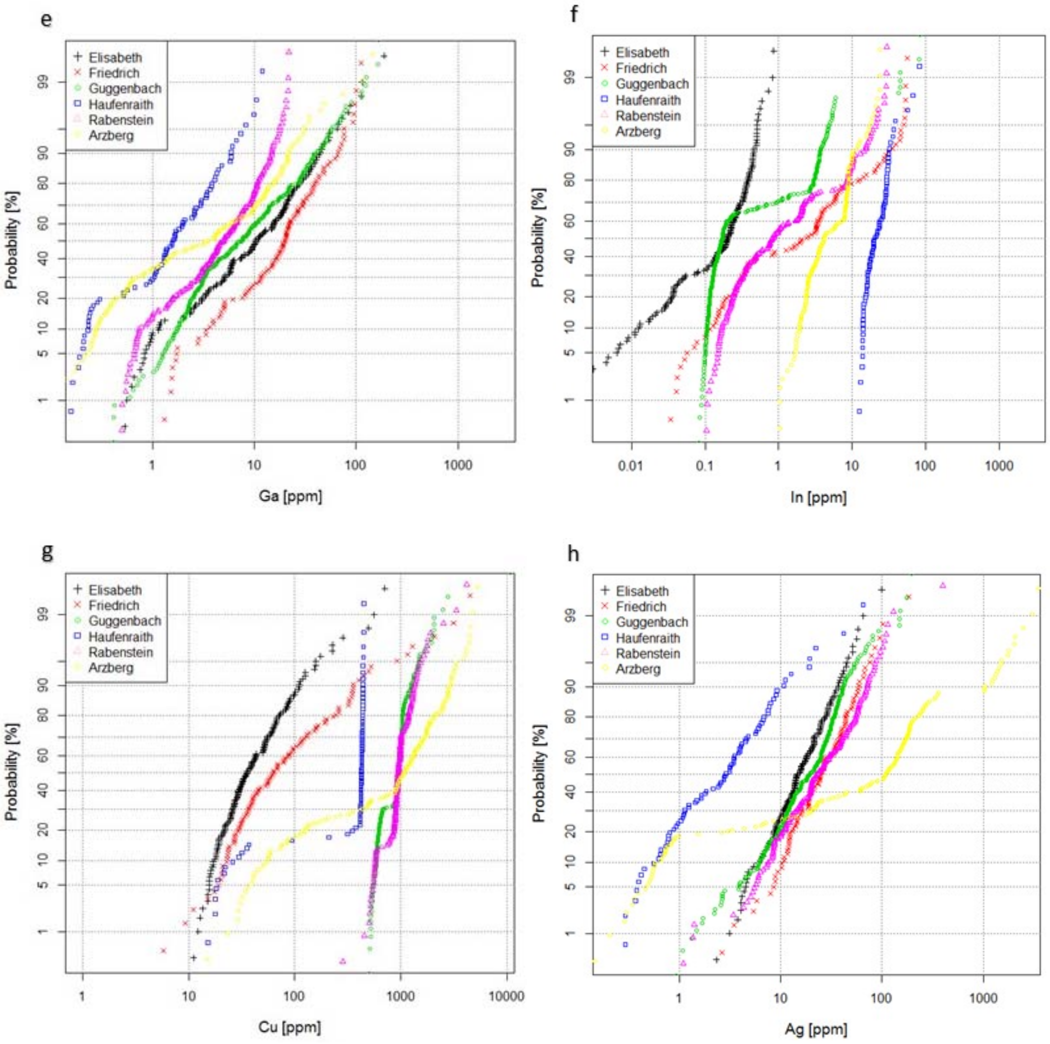
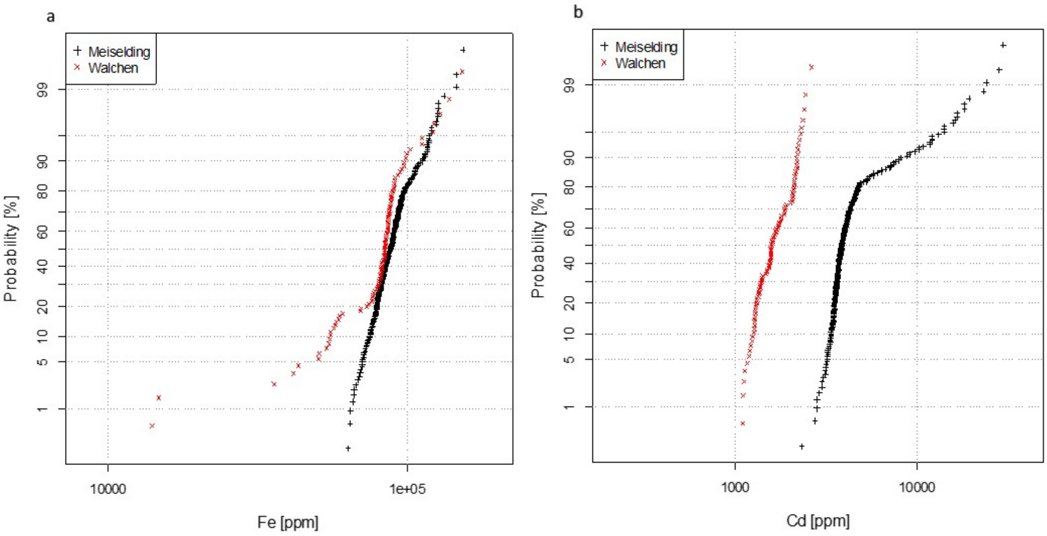


Figure 8: Probability plots of the trace elements (a) Fe, (b) Cd, (c) Mn, (d) Co, (e) Ga, (f) In, (g) Cu and (h) Ag from SEDEX deposits hosted in the Graz Paleozoic.

SEDEX deposits hosted in Paleozoic units outside the Graz Paleozoic



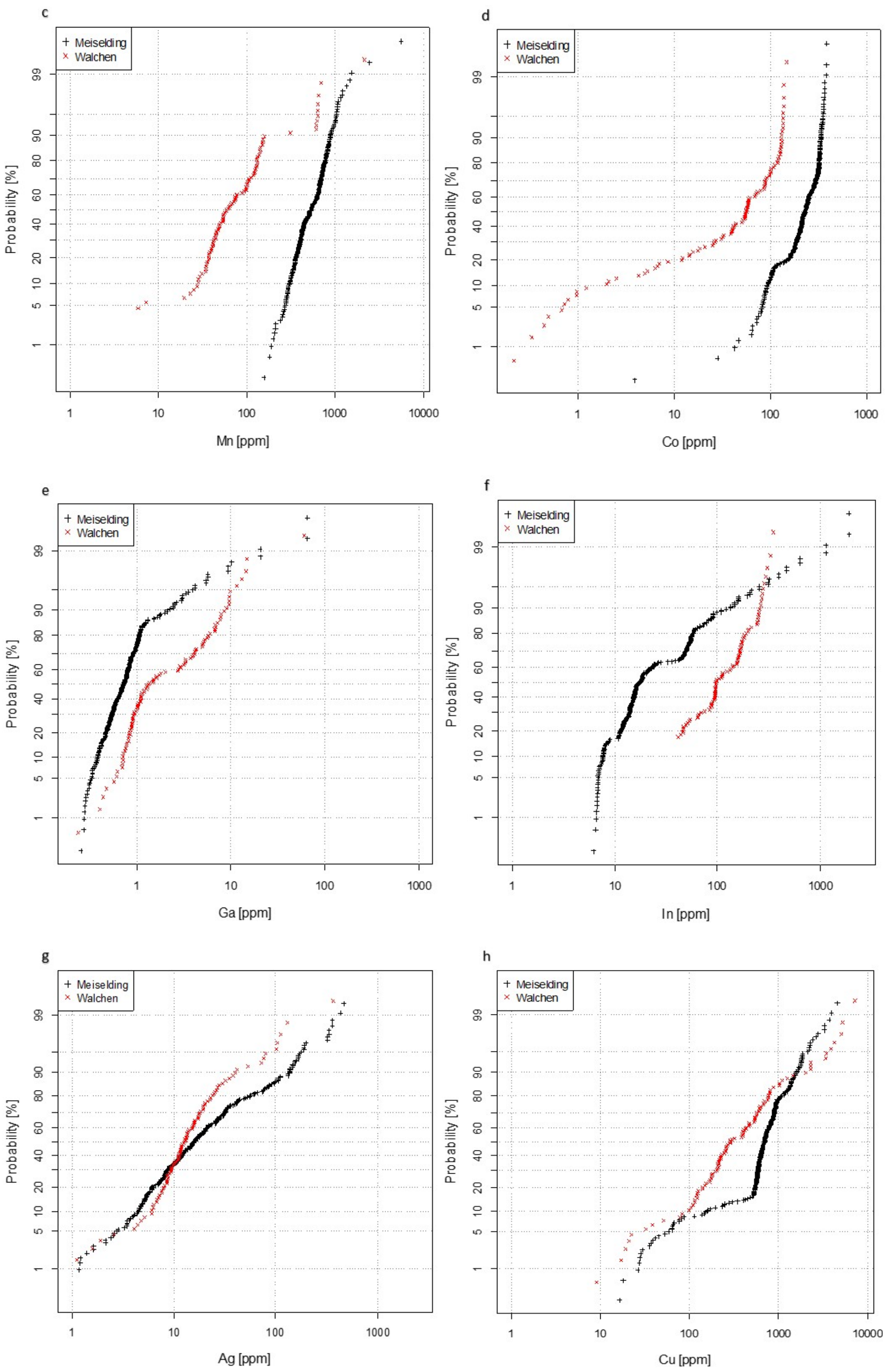
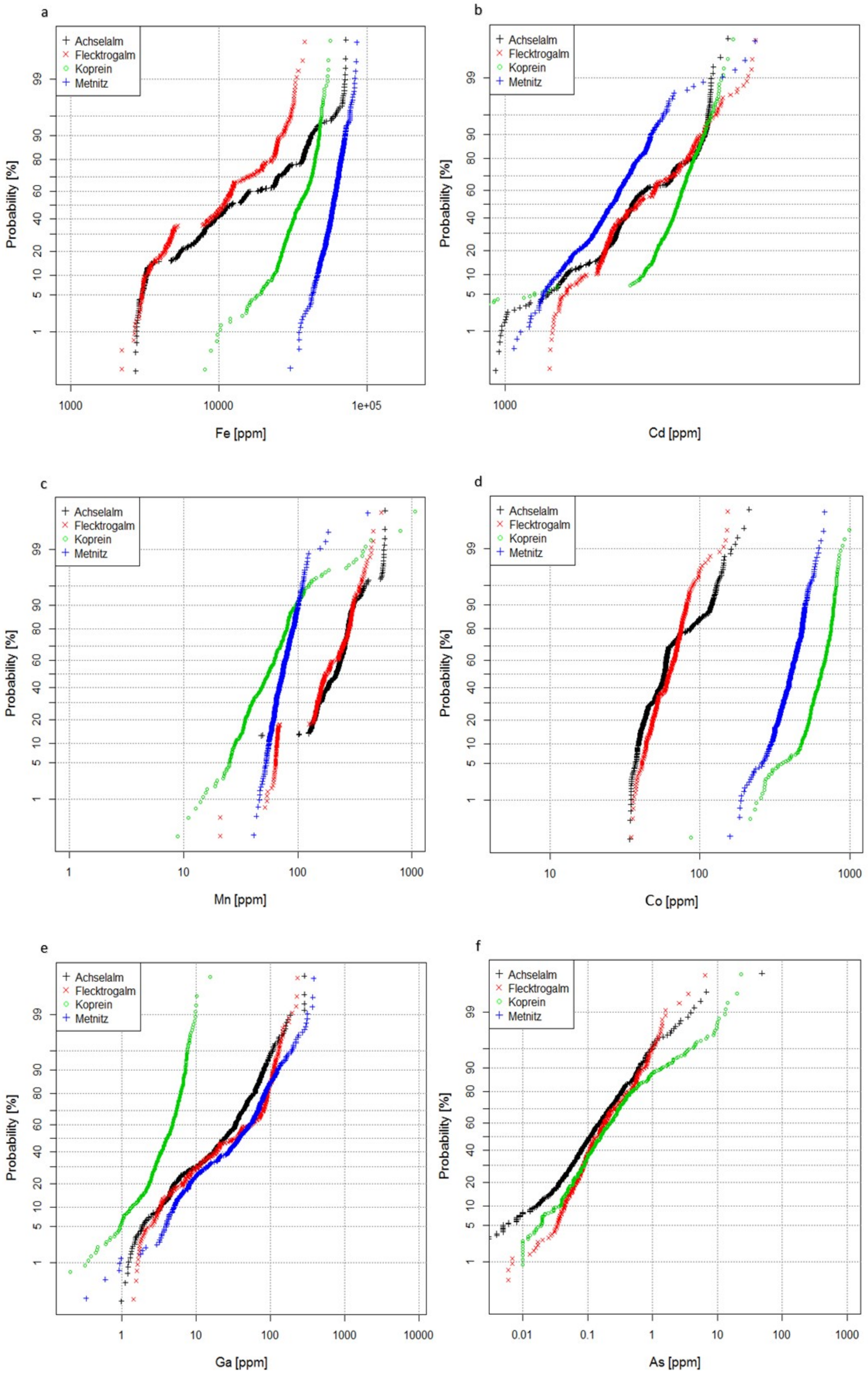


Figure 9: Probability plot of the trace elements (a) Fe, (b) Cd, (c) Mn, (d) Co, € Ga, (f) In, (g) Ag and (h) Cu of SEDEX deposits hosted in Paleozoic units outside the Graz Paleozoic.

Vein type deposits hosted in Paleozoic units



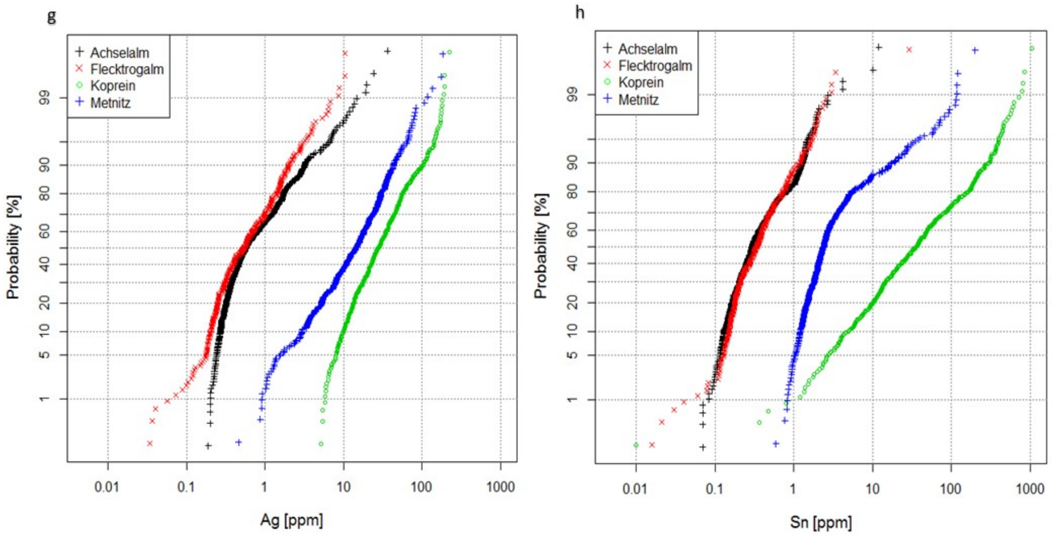


Figure 10: Probability plot of the trace elements (a) Fe, (b) Cd, (c) Mn, (d) Co, (e) Ga, (f) As, (g) Ag and (h) Sn of different vein-type deposits.

7. Discussion

Data evaluation follows four major steps: (1) within-deposit variability; (2) variability within a deposit or ore type; (3) estimation of robust median concentration levels of critical elements in sphalerite; (4) calculation of critical element tonnages in sphalerite concentrates from the deposits.

Trace element variability

Within-deposit variability is best displayed in probability diagrams of trace elements in a single deposit (Figure 4 to Figure 6). In general, variability is low with regards to Fe and Cd, and higher for elements with lower concentrations. Larger variations are observed for Pb, Cu, in some cases Co, In, Ge and Ag. In the following table, characteristic observations are reported describing trace element variability in sphalerite (Table 9).

Table 9. Magnitude of trace element variability and steps/kinks in probability curves

Location	Variability			Steps/kinks
	<1 order of magnitude	1-2	>2	
Achselalm	Cd, Mn, Co	Fe, Cu, Ga, In	Pb	Fe, Mn, Cu
Flecktrogalm	Fe, Cd, Mn, Co	Cu	Ga, Pb, In	Fe, Mn, Cu
Koprein	Fe, Cd, Co, Ag	Cu, Mn, In, Ga	Sb	Sb, In, Mn, Co, Cd
Metnitz	Fe, Cd, Cu, Co, Mn	Ga, Ag	Ge, Sb	(Ge)
Arzberg	Cd	Fe, Mn, In	Cu, Pb, Sb, Ag, Ga	
Elisabeth	Fe, Cd, Co	Mn, Cu, Ag, Sb	Ga, Pb	Fe, Co, Sb, Ag, Cu
Friedrich	Fe, Cd, Co, Mn, Ag, Pb	Sb	Cu	
Guggenbach	Fe, Cu	Co, Mn, Ag, Ga	Pb	Fe, Cu, Mn
Haufenreith	Cd, Co, Mn, In, Pb	Fe, Cu, Ga, Ag		Fe, Cd, Cu, Mn, Ga
Rabenstein	Cd, Cu	Fe, Ag, Mn, Ga, Sb	Co, In	Fe, Cu, Co, Cd, In
Leogang	Fe, Cd, Co	Cu, Mn, Sb, Ag	In	In, Fe, Mn
Meiselding	Fe, Cd, Mn	In, Co	Sb, Ag, Cu	Cu, In, Co
Walchen	Fe, Cd	Mn, Cu, Sb, In, Ag	Co	Mn, Sb
Bleiberg		Pb, Cd	Mn, Tl, As, Ge, Fe	Ge
Fladung	Fe, Cd, Mn, Cu	Ga, Ge, Cd??	Tl	Fe, Mn, As?
Jauken	Fe, Cd	Cu, Ge, Pb, Tl, As	Ga	Cu
Lafatsch		Cd, Fe, Cu, Mn, Ga, Ge	As, Ag	Cu
Radnig	Cd	Fe	Ge, Mn, Cu, Tl	

Steps or kinks in probability curves point to the presence of different populations. In most cases, only one step is observed in a given element probability curve, and such steps commonly affect more than one element in a given deposit. This may be due to two different sphalerite generations, one commonly Fe-rich, the other less Fe-rich. However, it may also point to biased or inadequate sampling. Deposits for which larger data sets are available (e.g., Bleiberg with n = 795), tend to not show such steps, and have an overall higher element variability. This implies that these particular deposits received representative sampling. But it is also obvious that sphalerite data for deposits within a genetic group or ore district share common features, e.g. those in the Graz Paleozoic all have low variability in Fe, Mn, Cd and Co. Extreme variations exceeding two orders of magnitude(e.g., 0,1 to >10 ppm) are observed for almost every trace element except of Cd.

Variability in ore types

In order to compare trace element patterns in sphalerite between different deposit types, a normalization procedure was developed using the median concentration of trace elements determined in a landmark paper on sphalerite geochemistry reporting 287 LA-ICP-MS analyses (Cook et al. 2009). The median may be regarded as a first estimate of an average sphalerite composition based on worldwide data from various deposit types, including epithermal, skarn, stratabound and VMS deposits. The full statistics of this compilation is provided in Table 10; in the following, the Cook et al. (2009) median is termed “SpC09”.

Table 10. Statistics derived from the Cook et al. (2009) dataset

Statistics	Mn	Fe	Co	Ni	Cu	Ga	Ge	As	Se	Mo	Ag	Cd	In	Sn	Sb	Te	Au	Tl	Pb	Bi
max	99443	163123	2828	36,96	41504	1137	345,5	121789	3687	149	31901	132317	67341	33917	117467	665	17,9	176	59607	4149
P90	29940	97172	589	9,924	4358	179	14,66	402	73,6	3,72	361,6	10170	287	258	171	10,705	1,028	15	3578	45
P75	4193	69128	284	3,37	1602	64	2,16	139	21,1	1,6	40,25	7119	67	15	26	1,3625	0,23	1,09	247	7
Md	**2152**	**16959**	**26**	**0,85**	**443**	**4,6**	**1,19**	**15**	**7,9**	**0,45**	**7,3**	**4968**	**17**	**1,425**	**1,23**	**0,465**	**0,06**	**0,14**	**14**	**0,45**
P25	509	4001	6	0,33	68	1,0375	0,905	1,2575	2,8	0,14	2,675	3362	0,9	0,1625	0,1	0,27	0,02	0,047	1,42	0,07
P10	20	928	0,428	0,16	14	0,389	0,79	0,525	1,75	0,07	1,6	2058	0,12	0,07	0,04	0,18	0,01	0,024	0,345	0,03
min	0,43	62	0,01	0,04	1,9	0,06	0,47	0,34	0,82	0	1,3	423	0,03	0,05	0	0,02	0,01	0,007	0,05	0,01
number	287	287	239	185	286	280	287	82	265	159	287	287	277	266	235	106	105	153	270	247
all values in ppm																				

Median concentrations of individual deposits are compared to SpC09 in Table 11. Enrichment (+) and depletion (-) factors are graphically illustrated for reasons of better readability. A grouping of sphalerite compositions into two major groups becomes obvious. Group 1 comprises sphalerite hosted by Mesozoic carbonate rocks; these sphalerites are, with few exceptions, highly enriched in Ge, As, Tl and Pb, but also highly depleted in Mn, In, Co, Ni, Sn and Ag. Fe, Ga and Cd are slightly depleted compared to SpC09; the median values for Cu and Sb scatter. Group 2 comprises sphalerite hosted by Paleozoic sedimentary and volcanic rocks, either as stratiform orebodies or as vein-type orebodies. Group 2 sphalerite is generally enriched in Fe, Co, Cu, Ag, Sb, but values scatter between individual deposits; median values of In and Sn may be highly elevated, but scatter widely. Ge concentrations are elevated only in one deposit (Metnitz), and associated with Co and Sb. Otherwise, group 2 sphalerite is low in Ge, As, and Tl. Concentrations of Pb, Cd and Se are comparable to SpC09.

Table 11. Summary of trace element median from different Eastern Alpine Pb/Zn deposits in comparison to the median values published by Cook et al. 2009.

Location	Mn	Fe	Co	Ni	Cu	Ga	Ge	As	Se	Ag	Cd	In	Sn	Sb	Tl	Pb
median Cook et al. 2009	2152	16959	26	0.85	443	4.59	1.19	14.95	7.9	7.3	4968	16.8	1.425	1.23	0.14	13.95
Bleiberg	---	-	--	--	-	-	+++	++	~	--	-	---	--	-	++	++
Lafatsch	---	--	--	--	-	-	++	++	~	+	-	---	--	~	++	++
Radnig	---	-	--	--	--	-	+++	+	~	--	-	---	--	-	++	++
Jauken Süd	---	-	--	-	~	-	+++	+	~	--	-	---	-	-	++	++
Fladung	---	-	--	--	-	+	+++	++	~	--	~	---	--	-	++	++
Meiselding	--	+	+	~	~	-	-	--	~	~	~	~	~	+	-	~
Silberberg	---	~	+	-	~	~	--	---	-	+	~	-	--	+	-	++
Friedrichstollen	--	+	++	+	-	+	-	---	-	+	~	-	---	+	bdl	~
Elisabethstollen	--	+	+	+	--	+	-	---	-	+	-	--	---	+	bdl	~
Arzberg	--	~	~	-	+	-	--	--	~	++	-	-	-	+	-	+
Haufenreith	--	~	+	+	~	-	---	--	-	~	-	~	-	~	--	~
Rabenstein	---	-	~	+	+	~	--	--	~	+	-	--	-	+	--	~
Guggenbach	--	+	+	+	+	~	--	---	~	+	-	--	~	+	-	~
Leogang	--	+	+	-	~	-	--	---	+	~	-	++	~	+	-	~
Walchen	--	+	+	--	~	-	--	--	+	~	-	+	~	+	--	~
Draßnitz	+	+	~	-	++	+	-	--	~	+	~	+	+	~	-	~
Koprein	--	~	++	~	~	~	-	-	-	+	~	~	+	+	-	+
Metnitz	--	+	++	-	+	+	+++	-	~	~	-	---	~	++	-	~
Flecktrogalm	--	~	+	+	--	+	--	---	~	--	-	--	-	~	bdl	-
Achselalm	--	~	+	+	--	+	--	---	~	--	-	--	-	-	bdl	-

Legend	compare to median after Cook et al. 2009
+++	> 100 times
++	> 10 times
+	> 2 times
~	equal
-	< 2 times
--	< 10 times
---	< 100 times

The following diagrams (Figure 11, Figure 12, Figure 13, Figure 14) illustrate normalized median concentrations of trace elements in several deposits evaluated in this study. Deposits are grouped into genetically related types. Median values calculated for these deposit types are plotted against the SpC09 reference value in Figure 11. It is obvious that carbonate-hosted deposits of the Bleiberg type show most differences to SpC09: they are particularly low (depleted by >100 times) in Co, Ag, In, Sn and Sb, and highly enriched (>1000x) in Ge, As and Tl. Among individual deposits, Fladung is most enriched in Ge and Tl, and Lafatsch in Ag (Figure 12). The stratiform deposits sampled in Paleozoic units are slightly enriched in Co, Cu and Sb compared to SpC09 (Figure 11), and slightly depleted in Mn, Ga, Ge and Se. Within this group of deposits, the Graz Paleozoic is represented by median and P25/P75 values of 7 individual deposits (Figure 13). Leogang and Walchen are enriched in In both compared to SpC09, Meiselding and Walchen; all members of the Paleozoic group have higher Fe and Co concentrations than SpC09, and are low in As and Tl (Figure 13). Vein-type sphalerite from various deposits scatter widely; Achselalm and Flecktrogalm are higher in Ni, Ga, Sb, and low in Ge, As and Tl (Figure 14). Sphalerite from the vein-type deposit Metnitz is highly enriched in Co, Ge and Sb – an unusual element combination for sphalerite – whereas the few analyses available for the Drassnitz vein-type deposit indicate high Ag, Sn and Sb. The Koprein deposit in the Karawanken Mountains is elevated in Co, Sn and Sb.

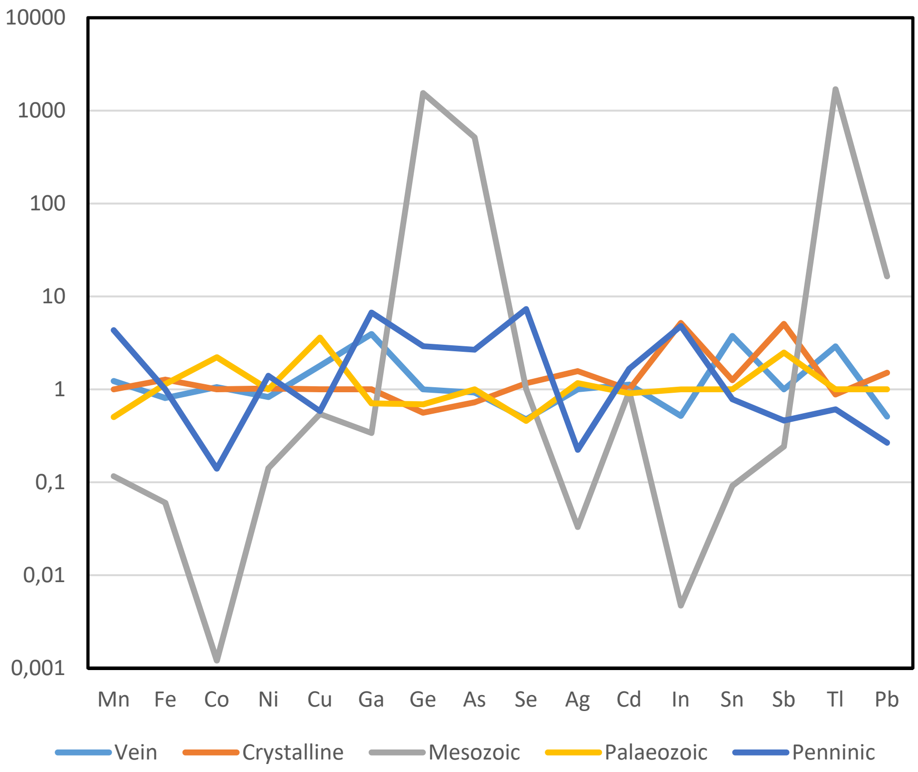


Figure 11: Spider plot of trace element median from deposits hosted in the Austroalpine Mesozoic and Paleozoic units, Penninic units and vein type deposits, normalized against the median values after Cook et al. 2009.

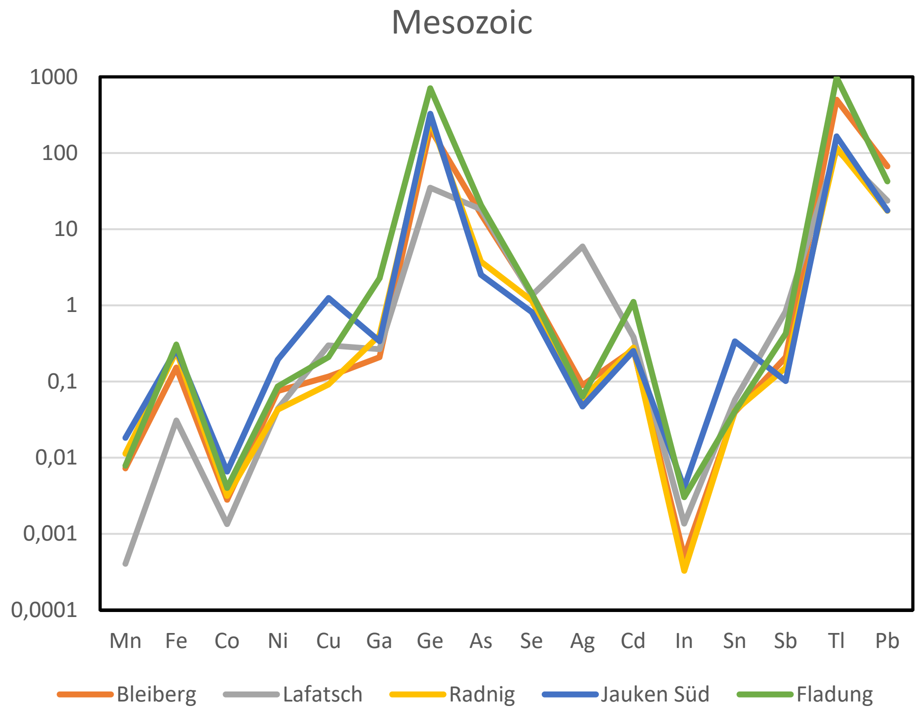


Figure 12: Spider plot of trace element median from sphalerite hosted in Mesozoic units, normalized against the trace element median values after Cook et al. 2009.

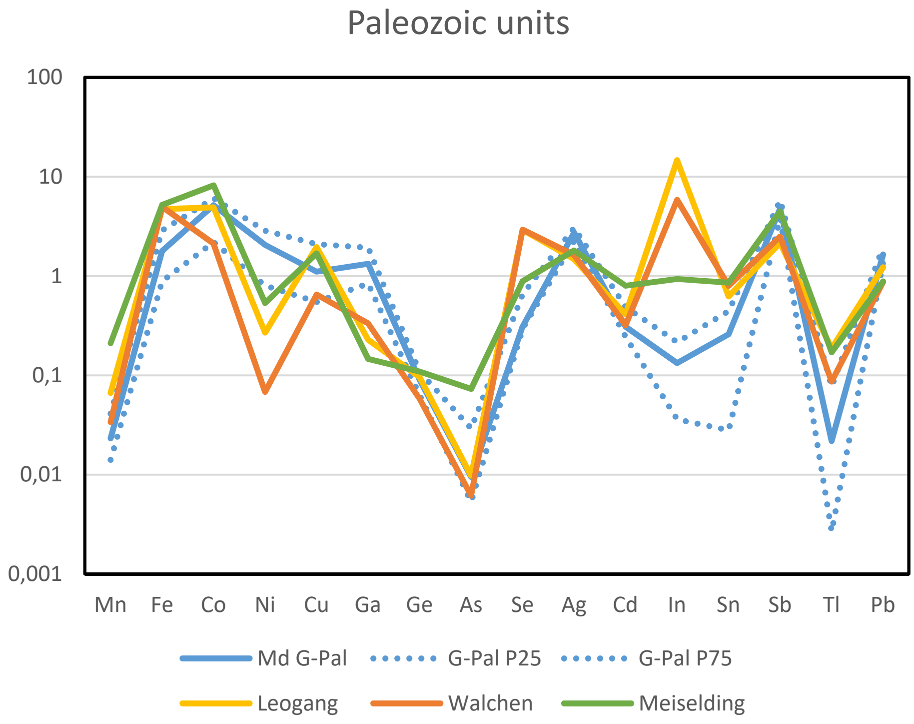


Figure 13: Spider plot of trace element median from sphalerite hosted in Paleocoic units, normalized against the trace element median values after Cook et al. 2009. Md G-Pal includes different deposits of the Graz Paleozoic (n= 6).

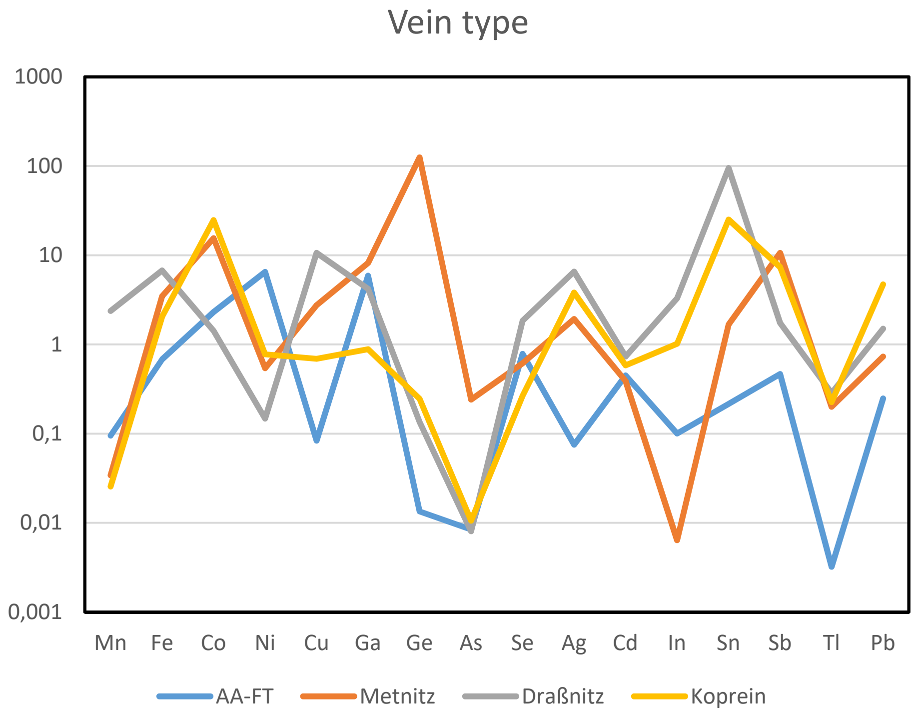


Figure 14: Spider plot of trace element median of vein type deposits hosted in different Austroalpine units, normalized against the trace element median values after Cook et al. 2009.

Estimation of robust median concentration levels of critical elements in sphalerite

Critical element concentrations as median and 25% percent deviation from the median are illustrated in Table 12for every deposit. These values provide a measure of trace elements in sphalerite concentrates prepared from sulphide ores. To estimate the total quantity of the elements contained, two further estimates are needed: sphalerite content in the ore (estimated using the whole-rock/ore Zn concentration), and tonnage of ore available (see Table 3, Table 4, Table 17). Assuming a recovery of 90% sphalerite from such concentrates, a total recoverable element content may be calculated. We refrained from introducing elemental recovery from concentrates, as metallurgical methods have not been evaluated and might differ between various ore types studied.

Unfortunately, neither accurate resource nor reserve data are available for any of the deposits and occurrences studied. The same applies for the average Zn grade; however, the use of published data – especially on the large deposits - will guide into the right direction. The situation is even worse for an estimation of remaining accessible reserves; for the large, non-operating deposits, these numbers are simply not known or published. Therefore, the grade and tonnage data used in this report are a mere "best guess" based on published data, own measurements and observations, and oral communications with experts.

Table 12. Median concentrations and variability of critical elements, expressed as percent deviation relative to the median (in ppm). P25 and P75 bracket 50% of the measurements.

Location	Co			Ge			Ga			In			Sph %	Tonnage
	Md	P75	P25	Md	P75	P25	Md	P75	P25	Md	P75	P25		estimate
Achselalm	57	22%	25%	0.02	179%	130%	22	108%	71%	1.9	71%	44%	0.05	10^5
Flecktrogalm	62	17%	19%	0.01	208%	256%	32	164%	75%	1.5	75%	72%	2.1	10^5
Drassnitz	37	11%	16%	0.16	77%	30%	19	100%	43%	55	133%	22%	15	10^4
Koprein	644	14%	14%	0.29	69%	89%	4.1	41%	37%	17.1	101%	38%	14	10^5
Metnitz	405	16%	14%	149	151%	82%	38	98%	72%	0.1	107%	25%	20	5 x 10^5
Sprinzgasse	16	441%	25%	0.27	31%	9%	72	21%	10%	0.78	3438%	48%	10	10^4
Arzberg	27	766%	58%	0.11	80%	74%	2.1	417%	72%	4.0	109%	36%	12	2.5 x 10^5
Elisabeth	168	6%	12%	0.21	83%	49%	10.3	121%	61%	0.2	73%	80%	11	2.5 x 10^5
Friedrich	280	21%	42%	0.14	168%	80%	20	70%	53%	2.2	193%	88%	30	2.5 x 10^5
Guggenbach	134	16%	23%	0.1	167%	73%	7.4	181%	63%	0.19	1480%	32%	2.5	2.5 x 10^5
Haufenreith	147	6%	10%	0.002	1638%	1988%	1.5	116%	64%	21	39%	23%	10	2.5 x 10^5
Rabenstein	28	58%	68%	0.06	124%	86%	5.6	86%	63%	1.0	688%	64%	5.5	2.5 x 10^5
Silberberg	86	47%	91%	0.12	103%	76%	6.1	87%	77%	3.2	107%	26%	3	2.5 x 10^5
Leogang	128	16%	38%	0.11	39%	64%	1.05	55%	31%	247	10%	98%	1	2 x 10^3
Meiselding	213	41%	35%	0.13	155%	69%	0.67	30%	27%	15.6	47%	35%	6.3	10^5
Schneeberg	57	254%	21%	0.05	64%	113%	5.8	40%	18%	14.3	119%	9%	9.8	3 x 10^6
Walchen	55	77%	79%	0.07	48%	49%	1.5	1781%	40%	98	76%	34%	4	4.2 x 10^5
Bleiberg	0.07	155%	41%	229	131%	59%	1.05	203%	69%	0.01	75%	47%	8.8	4.3 x 10^7
Fladung	0.1	56%	41%	845	33%	58%	10.3	169%	70%	0.05	53%	35%	5.2	3 x 10^5
Jauken	0.17	35%	30%	389	43%	41%	1.5	82%	63%	0.07	32%	86%	8.9	5 x 10^4
Lafatsch	0.04	46%	34%	42	72%	39%	1.2	323%	77%	0.02	180%	46%	9.2	4 x 10^6
Mezica	0.04	14%	30%	21	166%	76%	5	38%	87%	0.017	15%	18%	3.6	34 x 10^7
Radnig	0.08	26%	41%	325	61%	63%	1.9	168%	57%	0.006	143%	86%	7.5	2.5 x 10^5
Raibl	0.05	125%	42%	460	69%	53%	0.65	532%	89%				9	18 x 10^7
Salafossa	0.07	44%	14%	6.2	50%	17%	5.4	100%	53%	0.01	57%	44%	7.3	10 x 10^7
Seibach	0.01	108%	146%	0.08	133%	78%	2.4	286%	8%	0.07	153%	37%	4	10^4

Sph %: sphalerite content calculated from literature data (Zn grades) and whole-rock XRF data
Tonnage: estimated total resource, respectively total accessible resource

Estimation of the resource potential

The resource data available for the deposits covered in this report add to a total potential of **116 Mt ore** containing **7.5 Mt sphalerite** (ca. 5 Mt Zn metal); this includes the "big five" – Triassic carbonate-hosted Pb-Zn deposits of Bleiberg, Mezica, Raibl, Salafossa and Lafatsch – as well as smaller Mesozoic carbonate-hosted, Paleozoic sediment-hosted and three vein-type deposits (Table 13). These deposits had an original resource of about **90 tons Co** in sphalerite, **1,400 tons Ge**, **20 tons Ga**, **6.4 tons In**, **57 tons Ag**, **14,500 tons Cd** and **600 tons Tl**. These numbers were calculated from median concentrations of trace elements in sphalerite analysed in this study (Table 12). Their variation is described as the 25% deviation from the median of the element concentration and does not include the large uncertainties imposed by the grade and tonnage estimates. According to these calculations, the rare metal potential contained in sphalerite concentrates in the Eastern Alps ranges from 70 – 202 tons Co, 650 – 3,100 tons Ge, 6.5 – 53 tons Ga, 5.1 – 13.7 tons In, 30 – 145 tons Ag, 10,000 – 22,000 tons Cd and 260 – 1,700tons Tl.

Table 13. Tonnages of critical and rare elements contained in sphalerite of various deposits in the Eastern and Southern Alps. Tonnages indicated represent total resources (where available), respectively estimated remaining resources. Tonnages of critical and rare metals are calculated using median element concentrations from Table 12 and published or estimated grade data (Table 3, Table 4, Table 17).

	Type	Tonnage thousand tons	Tons ZnS concentrate	Co tons	Ge tons	Ga tons	In kg	Ag tons	Cd tons	Tl tons
Bleiberg	1	43,000	3,405,600	0.26	780	3.6	36	2.5	4696	176
Mezica	1	34,000	1,101,600	0.04	23	5.5	19	29.1	4011	9
Raibl	1	18,100	1,466,100	0.08	674	1.0	0.7	0.04	1251	472
Salafossa	1	10,000	657,000	0.05	4	3.6	8.8	0.49	2263	4
Lafatsch	1	4,000	331,200	0.01	14	0.4	7.6	14.4	633	5
“Big Five”	1	109,100	6,961,500	0.43	1494	14.1	72.1	51.3	12854	666
Fladung	1	300	14,040	0.00	11.87	0.15	0.7	0.01	77	0.19
Jauken Süd	1	50	4,005	0.00	1.56	0.006	0.3	0.00	5	0.09
Radnig	1	250	16,875	0.00	5.49	0.030	0.1	0.01	23	0.28
Seibach	1	10	360	0.00	0.001	0.001	0.0	0.00	0.7	0.000
Arzberg	2	250	27,000	0.73	0.003	0.057	1089	2.10	35	0.001
Elisabethstollen	2	250	24,750	4.15	0.005	0.255	5	0.36	54	0.000
Friedrichstollen	2	250	67,500	18.89	0.009	1.341	150	1.66	180	0.000
Guggenbach	2	250	5,625	0.76	0.000	0.041	1	0.10	6	0.000
Haufenreith	2	250	22,500	3.31	0.000	0.035	471	0.07	20	0.000
Rabenstein	2	250	12,375	0.35	0.001	0.069	12	0.25	19	0.000
Silberberg	2	250	6,750	0.58	0.001	0.041	22	0.13	18	0.000
Graz Paleozoic	2	1,750	166,500	28.77	0.020	1.840	771	4.68	332	0.001
Meiselding	2	100	5,670	1.21	0.001	0.004	89	0.07	22	0.000
Walchen	2	423	15,245	0.84	0.001	0.023	1494	0.80	24	0.000
Schneeberg	2	3,000	265,518	15.25	0.014	1.545	3809	1.18	860	0.001
All Paleozoic	2	5,273	452,933	46.06	0.036	3.413	6162	6.11	1239	0.002
Achselalm/ Flecktrogalm	3	200	1,935	0.12	0.000	0.062	3	0.00	4	0.000
Koprein	3	100	12,600	8.11	0.004	0.051	215	0.35	36	0.000
Metnitz	3	500	90,000	36.41	13.42	3.384	10	1.27	174	0.003
All vein-type	3	800	104,535	44.64	13.42	3.497	228	1.62	215	0.003
Total resource (Md)		115,783	7,554,248	91.15	1,418	20.8	6455	58.9	14463	598
Total resource (P75)				149	3095	46.5	13188	143	21021	1706
Total resource (P25)				70.1	661	6.8	5166	30.6	9834	259

Regarding the share of trace element tenor in different ore types, carbonate-hosted Pb-Zn deposits of the Alpine-type account for 93% of the sphalerite concentrates, 99% of the Ge, 67% of the Ga, 90% of the Ag, 94% of the Cd and 100% of the Tl originally contained. Three stratiform Paleozoic deposits (including the large Schneeberg deposit) account for 5.7% of the concentrates, but 50% of the Co, 16% of the Ga, 95% of the In and 7% of the Ag contained. Vein-type deposits host only 1.4% of the sphalerite, but 49% of the Co, 17% of the Ga and 4% of the In contained in sphalerite in the Eastern Alps.

Stratiform deposits in the Graz Paleozoic that were investigated in greater detail, comprise an estimated ore tonnage of 1.75 Mt and a Zn resource of 166,500 tons. Trace elements in sphalerite are rather low; this study demonstrates that between 20 – 40 tons Co, 6 – 46 kg Ge, 0.8 – 3.5 tons Ga, 0.5 – 1.5 tons In, 1.8 – 9 tons Ag, 300 – 400 tons Cd might be extracted.

Comparison with the data of Cerny and Schroll (1992, 1995)

Table 14 summarizes tonnages of critical and speciality metals present in sphalerite concentrates. The upper table was calculated using analytical data from ore concentrates published by Cerny and Schroll (1992, 1995) that indicated overall Ge resources of 103 tons, 22 tons Ga, 13 tons Tl, 1145 tons Cd and 6.7 tons In; Co (46 tons) and Ag (24 tons) have been added to the original table. The lower three tables were calculated from the same tonnage data, but using our LA-ICP-MS measurements for median, P25 and P75. The data lines "Pirkach", "Panzendorf" and "Ausservillgraten" have been deleted, because no material was available for study. Instead, lines for Meiselding, Walchen and Schneeberg have been added, because reasonable resource estimates are available. The potential of trace metals present in sphalerite concentrates, based on a vast set of in-situ measurements, is now estimated to the following tonnages for about 15 locations sampled (deviation from the median expressed as P25 and P75, respectively).

Ge: 78 tons (32 – 160 tons)
Ga: 4.4 tons (1.6 – 9.4 tons)
Tl: 15 tons (5 – 46 tons)
Cd: 1640 tons (1180 – 2165 tons)
In: 5.7 tons (3.3 – 9.3 tons)
Co: 57 tons (30 – 95 tons)
Ag: 8.8 tons (5.9 – 18.1 tons)

The estimates provided by Cerny and Schroll are within the 50 % data population around the median for Ge (16% higher than the new median), Tl (26% lower than the median), Cd (10% higher), and Co (3% lower). The data are outside this range for Ga, In and Ag (Figure 15).

Median concentrations of critical elements display reasonable correlation with the concentrate data set of Cerny and Schroll (1992, 1995) only for Co ($R^2 = 0.99$) (Figure 16). For Ge, the correlation is positive with an outlier for the Jauken deposit, for which the concentrate analysis resulted in a high value of 1500 ppm. Gallium and In concentrations determined by LA-ICP-MS are much lower than in concentrates, although a correlation of data points clearly exists (Figure 16). This indicates either a calibration problem for the trace elements in concentrates, or the presence of discrete Ga and In minerals in addition to sphalerite that contributed to elevated concentrations; the latter point is unlikely from a mineralogical point of view because additional phases have not been detected using microscopic work. The results of this study therefore imply that the tonnages calculated from trace element data by Cerny and Schroll (1992, 1995) must be updated, because they overestimate some elements present in sphalerite. On the other hand, elevated concentrations in some deposits that have not been investigated by Cerny and Schroll (1992, 1995) add to the resources currently available in Austria.

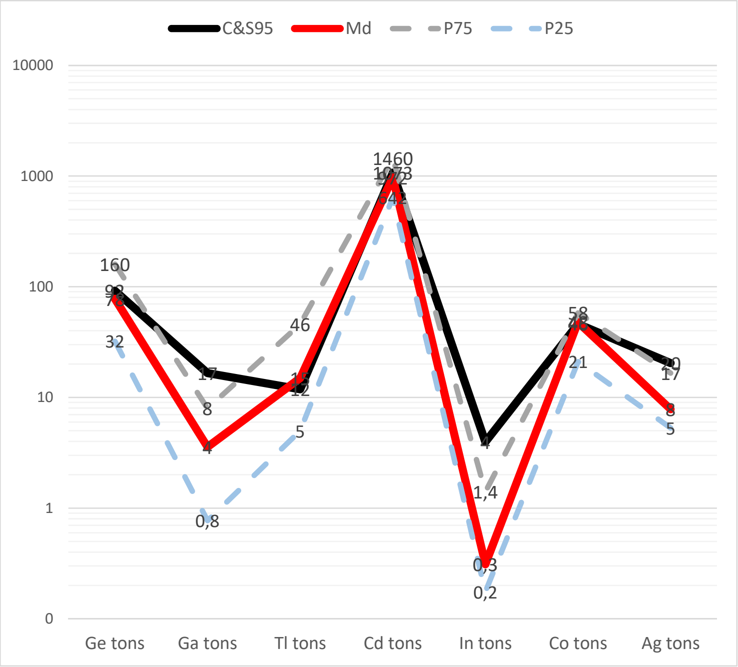


Figure 15. Resource tonnages for critical and speciality metals calculated from data published by Cerny and Schroll (1995; C&S95) – black line, and analyses performed in the present study, expressed as median, P25 and P75.

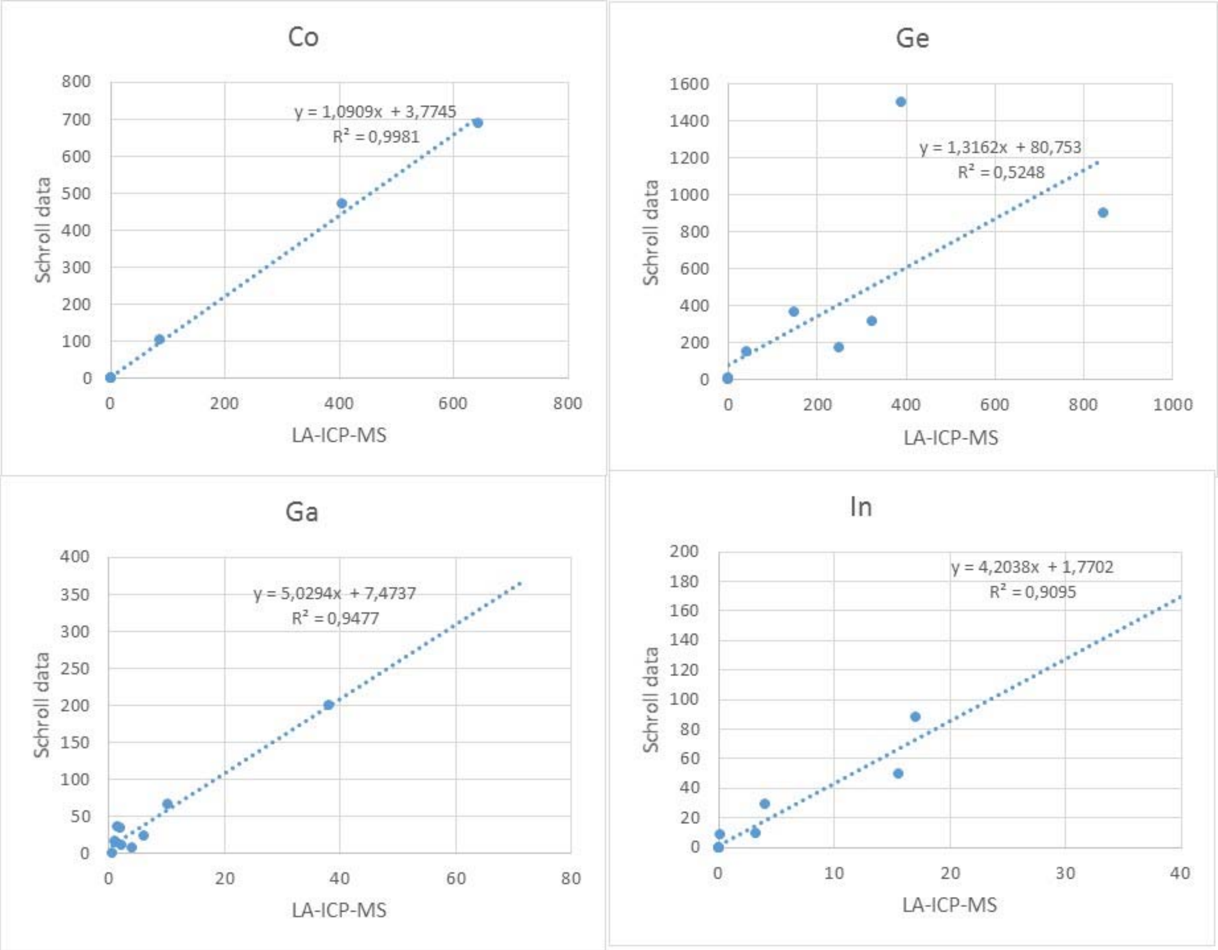


Figure 16. Comparison of median values for sphalerite analysed by LA-ICP-MS and concentrate analyses from Cerny and Schroll (1992, 1995).

Table 14. Resource potential of critical and speciality metals in some ore deposits in the Eastern Alps. Upper table calculated from data published by Cerny and Schroll (1992, 1995). The following three tables represent tonnages calculated for the same resource tonnage, using median, P27 and P25 values obtained from LA-ICP-MS data.

Cerny & Schroll 1992

Former Mine	Resource class	Million tons	Concentrate 57% ZnS	Ge tons	Ga tons	Tl tons	Cd tons	In tons	Co tons	Ag tons
Bleiberg/Kreuth	A,B,C_1	2,00	210000	35,70	2,00	2,60	378	0,02	0,11	1,67
Graz Paleozoic	C_2	1,50	158000	1,58	3,16	0,79	319	2,32	16,59	4,11
Radnig	C_2	0,08	6580	2,11	0,23	0,05	11	0,00	0,01	0,07
Jauken	C_2	0,05	5300	7,95	0,19	0,37	7	0,00	0,00	0,00
Pirkach	C_2	0,40	28000	11,20	5,40	1,09	105	0,00	0,03	0,03
Hochobir	C_2	0,30	18400	16,56	1,21	3,50	70	0,00	0,02	0,16
Lafatsch	C_2	0,60	84200	12,63	1,26	3,79	194	0,01	0,08	10,10
Metnitz	C_2	0,30	42100	15,58	8,42	0,72	61	0,38	19,79	2,78
Koprein	C_2	0,10	14000	0,04	0,10	0,04	34	1,23	9,66	1,54
Panzendorf	C_2	0,40	33000	0,12	0,02	0,40	7	1,42		2,94
Ausservillgraten	C_2	0,13	10800	0,03	0,01	0,05	3	1,32		0,75
total		5,23	552580	103,30	21,88	12,91	1145	6,70	46,28	24,14

Median values

Former Mine	Resource class	Million tons	Concentrate 57% ZnS	Ge tons	Ga tons	Tl tons	Cd tons	In tons	Co tons	Ag tons
Bleiberg/Kreuth	A,B,C_1	2,00	210000	48,09	0,22	10,88	290	0,00	0,02	0,16
Graz Paleozoic	C_2	1,50	158000	0,05	1,38	0,02	282	0,06	21,77	3,00
Radnig	C_2	0,08	6580	2,14	0,01	0,11	9	0,00	0,00	0,00
Jauken	C_2	0,05	5300	2,06	0,01	0,12	7	0,00	0,00	0,00
Hochobir	C_2	0,30	18400	15,55	0,19	2,52	101	0,00	0,00	0,01
Lafatsch	C_2	0,60	84200	3,54	0,10	1,31	161	0,00	0,00	3,65
Metnitz	C_2	0,30	42100	6,27	1,60	0,00	81	0,00	17,03	0,59
Koprein	C_2	0,10	14000	0,00	0,06	0,00	40	0,24	9,02	0,39
Meiselding	C_2	0,10	5670	0,00	0,00	0,00	22	0,09	1,21	0,07
Walchen	A,B,C_1	0,05	15000	0,00	0,02	0,00	24	1,47	0,83	0,18
Schneeberg	A,B,C_1	1,50	165000	0,01	0,90	0,00	622	3,84	7,47	0,70
total		6,58	724250	77,71	4,49	14,96	1640	5,71	57,34	8,76

P75

Former Mine	Resource class	Million tons	Concentrate 57% ZnS	Ge tons	Ga tons	Tl tons	Cd tons	In tons	Co tons	Ag tons
Bleiberg/Kreuth	A,B,C_1	2,00	210000	111,20	0,67	33,96	533	0,00	0,04	0,74
Graz Paleozoic	C_2	1,50	158000	0,08	3,08	0,02	347	0,90	27,95	5,02
Radnig	C_2	0,08	6580	3,44	0,03	0,25	12	0,00	0,00	0,00
Jauken	C_2	0,05	5300	2,95	0,01	0,24	8	0,00	0,00	0,00
Hochobir	C_2	0,30	18400	20,73	0,51	4,03	135	0,00	0,00	0,03
Lafatsch	C_2	0,60	84200	6,04	0,43	7,29	290	0,01	0,00	8,94
Metnitz	C_2	0,30	42100	15,73	3,14	0,00	93	0,01	19,78	1,15
Koprein	C_2	0,10	14000	0,01	0,08	0,00	44	0,48	10,27	0,70
Meiselding	C_2	0,10	5670	0,00	0,00	0,00	26	0,13	1,71	0,16
Walchen	A,B,C_1	0,05	15000	0,00	0,06	0,00	31	2,59	1,46	0,30
Schneeberg	A,B,C_1	1,50	165000	0,01	1,34	0,00	647	5,19	33,59	1,08
total		6,58	724250	160,20	9,38	45,79	2165	9,31	94,80	18,12

P25

Former Mine	Resource class	Million tons	Concentrate 57% ZnS	Ge tons	Ga tons	Tl tons	Cd tons	In tons	Co tons	Ag tons
Bleiberg/Kreuth	A,B,C_1	2,00	210000	19,72	0,07	3,53	161	0,00	0,01	0,07
Graz Paleozoic	C_2	1,50	158000	0,03	0,52	0,02	185	0,02	13,35	1,69
Radnig	C_2	0,08	6580	0,80	0,01	0,02	6	0,00	0,00	0,00
Jauken	C_2	0,05	5300	1,22	0,00	0,07	5	0,00	0,00	0,00
Hochobir	C_2	0,30	18400	6,55	0,06	0,47	75	0,00	0,00	0,01
Lafatsch	C_2	0,60	84200	2,13	0,02	0,22	92	0,00	0,00	1,48
Metnitz	C_2	0,30	42100	1,76	0,05	0,65	80	0,00	0,00	1,83
Koprein	C_2	0,10	14000	0,00	0,04	0,00	37	0,15	7,74	0,21
Meiselding	C_2	0,10	5670	0,00	0,00	0,00	20	0,06	0,79	0,04
Walchen	A,B,C_1	0,05	15000	0,00	0,01	0,00	20	0,96	0,18	0,13
Schneeberg	A,B,C_1	1,50	165000	0,00	0,79	0,00	494	2,16	7,44	0,45
total		6,58	724250	32,20	1,57	4,98	1177	3,35	29,52	5,91

8. Conclusion

The data presented in this report illustrate the following:

(1) Base metal deposits in the Eastern Alps may be grouped into at least three types based on their geological position. Group 1 comprises Pb-Zn deposits hosted by Triassic platform carbonates; type locality is Bleiberg, and the mineralogy comprises only galena and Fe sulphide in addition to Fe-poor sphalerite. The second type comprises stratiform deposits hosted by Paleozoic clastic and volcanoclastic sequences that have been metamorphosed under low- or medium-grade conditions. This group is generally enriched in Cu and Ag, hosted by chalcopyrite, fahlore and other phases; sphalerite is Fe-rich. Type locality of this type is Arzberg in the Graz Paleozoic. Slightly differing deposits of this group may be hosted by metacarbonates (Leogang) and are polymetallic and polymineralic. However, sphalerite compositions are similar to typical stratiform deposits such as Walchen. A third geological type includes vein-type deposits in various geological units. These deposits may have characteristics of both, stratiform type-II and carbonate-hosted type-I deposits. A good example is Metnitz, where sphalerite is elevated in Co, Ge and Sb. Some vein-type deposits carry high In, Sn and Sb (e.g. Drassnitz, Koprein).

(2) Base metal deposits in the Eastern Alps may be grouped into two major types based on their trace element composition in sphalerite. The first type is characterized by highly elevated concentrations of Ge, As, Tl and Pb, at low Co, Ga, In and Ag; recovery of Ge may be economic, but As and Tl, along with Cd are deleterious elements to be considered when a process for metallurgical recovery is planned; type locality is Bleiberg (Table 8). The second type is much more variable, but tends to be more enriched in Co, Cu, Fe, Ag and Sb compared to SpC09; Ga, In and Sn may be elevated as well. This type is generally low in Ge, As, Tl and Pb (Table 11). Compared to SpC09, all deposits have low Mn concentrations in sphalerite; this is due to the lack of skarn and epithermal deposits that are most enriched in Mn in the data of Cook et al. (2009).

(3) Calculation of resource numbers using the data presented in this report is only possible for localities from which resource or reserve information is available. This is, unfortunately, not the case for most occurrences. The data calculated (Table 13, Table 14) need to be regarded as approximate at most.

A total of 57 ore districts of base metal ores are listed in IRIS (Table 2); this number also includes several districts in which base metals are regarded as a minor commodity, e.g. Ag, As, Ag, Sb, Hg, U districts. In many districts, fahlore minerals are present, forming the major Cu and Ag mineral; fahlore is known to contain trace elements (Weber et al. 1997), but was not in the scope of this study. However, the data available for some occurrences in these districts indicate a certain potential for valuable elements contained in sphalerite. Thus, if for some reason activities may be resumed in the future, base metal by-products will add to the value of these resources. From the data obtained in the present study and data available in the literature, Table 15. summarizes the concentration levels of critical metals that may be expected to occur in sphalerite concentrates recovered from ore deposits in geological units and ore districts listed in Table 2. VMS and skarn deposits have not been evaluated in the present study; their Zn concentrations are generally low, and critical metals more likely are associated with Fe-Cu sulphides. In stratiform deposits hosted by Paleozoic rocks, chalcopyrite, pyrite, pyrrhotite and Ag-bearing fahlore are potential further host of critical elements. This will be evaluated in a separate project phase.

Carbonate-hosted Pb-Zn deposits have the highest potential for Ge; however, the occasional presence of Ge in vein-type deposits and the association with fahlore and reniérite in the Leogang deposit warrant further examination of these deposit types. For Ga, the potential is small and lower than predicted in the previous study conducted by Cerny and Schroll (1992, 1995). Indium is enriched only in a few deposits, mainly hosted by Paleozoic sedimentary and volcaniclastic rocks. The unknown size and small remaining reserves of these deposits also require additional investigations. In addition to sphalerite, significant concentrations of In may reside in chalcopyrite; the role of chalcopyrite in the Alpine metallogenetic provinces has yet to be evaluated. Mineral processing tests using ores from the Walchen deposit are currently under way, conducted in an "r^4" resource technology project financed by the German government. Cobalt, becoming an increasingly important critical element, is present as a trace element only in sphalerite of some vein-type and stratiform deposits; most of the Co in these deposits is hosted by pyrite, pyrrhotine, Fe-Co-Ni sulpharsenides and other minerals; thus, Co extraction from sphalerite will constitute only a minor by-product. In addition to the critical elements, elevated concentrations of Ag, Cd and Tl hosted by sphalerite in some deposit types may add to the economic value of sulphide deposits in the Eastern Alps.

Table 15. Summary of base metal ore types and their sphalerite content and composition (in ppm), based on the present study and literature data

Ore type	IRIS Districts numbers	Occurrences (number)	Sph %	Co in sph	Ge in sph	Ga in sph	In in sph
Pb-Zn, Bleiberg-type in Mesozoic rocks	12, 14, 15, 16, 17, 18, 20, 137	403	10-40	<0.5	1-1000	1-10	<0.1
Pb-Zn, stratiform in Paleozoic rocks (Arzberg, Meiselding)	13, 19, 143	137	5-40	20-300	<0.5	2-20	0.2-20
"Stratiform" (Walchen)	74, 76, 80, 120, 123, 146, 149, 158, 187, 201, 219	151	1-5	50	<0.1	1-6	10-100
VMS (Großfragant)	78, 79, 82, 111, 112, 114, 116, 119, 122, 157, 188	311	<5				
Skarn	197, 206	15	?				
Vein-type (Koprein, Achselalm)	21, 45, 46, 81, 89, 121, 142, 145, 147, 150, 151, 152, 169, 190, 191, 196, 198, 199, 210	346	1-10	10-650	<0.1-150	4-70	<1-60

Economic outlook on critical metal production associated with Zn ore

The demand for critical and rare metals has tremendously increased over the last years due to the development of new technologies. This trend will continue. Domestic production of these metals in Europe, and especially in the European Union is on a very low level, and import dependence from unstable countries (Co from the DR Congo) or large economic competitors (Ge, Ga and In from China) are highly unfavourable for the European industries. Table 16 compares current reserves, production numbers for the past 15 year (Weber and Zsak 2006, Reichl et al. 2017), actual prices, and potentials from sphalerite concentrates in the Eastern Alps.

The data show that while global Zn production has increased by 62% within 15 years, European production (including Turkey and European Russia) has increased only by 2% and EU production by 5%. The share of the European Zn production compared to global production is 7.3% for 2015, down from 11.6% for 2000. Members of the European Union – chiefly Ireland and Sweden - account for 74% of the European Zn production.

Considering the critical metals, the situation is worse: although the global Co production has increased by 472% over the past 15 years, European production is only 1.8% of the global production (Finland

and Russia), down from 2.9% in 2000. Global Ge production has doubled within 15 years, and 17.5% of the total 95 tons are produced in Europe (Finland) from imported secondary raw materials. The situation is similar for Ga, where the European production is about 12% of the global production of 146 tons (2015). However, global production has increased by 800%, whereas European production has increased by just 240% in the same time frame. This production is currently from Ukraine and Russia, not from members of the EU. The global In production has tripled to 655 tons in 2015, but decreased in Europe by 22% in 15 years. This (metallurgical) production is from Belgium and France and accounts for 9.3% of global production, down from 35% in 2000. The raw materials are imported from secondary sources.

The global Cd production has increased by just 36% within 15 years, and has decreased by 23% in Europe in the same interval. This is due to the toxicity of the product, and of the low price levels making Cd production less attractive. The data presented for Ag show a 50% increase in global production, with Europe currently accounting for 8.3% of the global production and the EU holding 83% (mainly Poland) of the European share.

Table 16. Production and reserve data of critical and rare elements compared to Zn production. Production data for Co, Ge, Ga, Ag, Cd and Zn from Weber and Zsak (2006) and Reichl et al. (2017); for In from USGS[1]

		Co tons	Ge tons	Ga tons	In tons	Ag tons	Cd tons	Zn tons
Reserves	USGS[1]	7,000,000	unknown	unknown	unknown	570,000	unknown	220,000,000
Production	World 2015	140,713	80	146	655	27,689	22,835	13,296,477
	World 2000	24,586	41	16	220	18,508	16,761	8,220,559
	Europe 2015	2,517	14	17	61	2,294	2,039	969,446
	Europe 2000	700	0	5	78	1,960	2,665	953,218
	EU 2015	2,109	13	0	61	1,906	1,729	717,946
	EU 2000	0	0	0	78	579	1,943	684,323
	Austria 2015 and 2000	-	-	-	-	-	-	-
Resource[2]	This work	91	1,418	21	6.5	59	14,463	5,000,000
Metal price[3]		52,335 US$/t (LME)	729 US$/kg (Dioxide)	130 US$/kg	2111 US$/kg	17.3 US$/troz	1.8 US$/kg	2,850 US$/t

[1] USGS Mineral Commodity Summaries, Commodity Statistics (2017); https://minerals.usgs.gov/minerals/pubs/commodity/

[2] Total resource from Table 13

[3] DERA, Dec 2016 – Nov 2017; https://www.bgr.bund.de/DERA/DE/Home/dra_node.html

Production of Zn and by-products Cd and Ge from deposits in the eastern and southern Alps has terminated in the 1990ies and was never resumed, although demand and metal prices have significantly increased. This study indicates a potential for Zn and related metals in the Alpine metallogenic province. The original resource of the province was at least 2% of the currently known global Zn reserves. The production of 172 tons Ge from Zn ores treated at the Arnoldstein smelter already proves the importance for this critical metal. The overall metal endowment could have been 15-20 times current global production. However, the remaining reserves estimated from data presented in this study would suffice for one year of production. The significance of Co, Ga and In hosted by sphalerite is much lower, but due to high prices these metals could constitute important by-products once the production of base metal ores has been resumed.

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10. Appendix

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Data tables

Table 17. Resource potential of speciality metals in some ore deposits and occurrences (Cerny and Schroll 1992).

Former Mine	Resource class	Million tons	Concentrate 57% ZnS	Ge tons	Ga tons	Tl tons	Cd tons	In tons
Bleiberg/Kreuth	A,B,C_1	2	210,000	35.7	2	2.6	378	-
Graz Paleozoic	C_2	1.5	158,000	-	3.8	-	332	-
Radnig	C_2	0.075	6,580	2.1	0.2	-	10.7	-
Jauken	C_2	0.05	5,300	7.8	0.2	0.3	7.0	-
Pirkach	C_2	0.4	28,000	11.2	5.4	1.0	105	-
Hochobir	C_2	0.3	18,400	16.6	1.2	3.5	70	-
Lafatsch	C_2	0.6	84,200	12.6	1.2	3.8	193	-
Metnitz	C_2	0.3	42,100	15.6	8.4	-	60	-
Koprein	C_2	0.1	14,000	-	-	-	33	1.2
Panzendorf	C_2	0.4	33,000[1]	-	-	-	-	1.4
Ausservillgraten	C_2	0.13	10,800[1]	-	-	-	-	1.3

[1]: ZnS 6%

Table 18. Composition of sulphide concentrates analysed by Cerny and Schroll (1992, 1995).

Probe	Locality	Remark	District ID (IRIS)	Sample type	Zn	Ge	Ga	Cd	In	Tl	Se	Te	Fe	Sb	Mn	Sn	Cu	V	Ag	As	Bi	Au	Hg	Co	Mo	Ni	Pb	Ca	Mg	S
			or single location		%	ppm	ppm	ppm	ppm	ppm	ppm	ppm	%	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	%	%	%	%
	Bleiberg	Md of 62 concentrates	16	Zn concentrates	60,925	173,5	16,5	1744,5	0,1	74	0,2	1	0,5	1,85	24	0,12		2,6	7,95	161	0,03			0,5	1,55	4	0,1885	1,385	0,195	33,3
T/10	Windisches Alpl	Cardita 3 horizon	16	Zn concentrate	61,2	250	7,8	1583	0,1	150	1	1	0,7	3	38	0,45		1	3,3	496	0,03			0,5	4,2	2	1,54	0,12	0,07	30,8
T/13	Radnig	Wettersteinkalk	16	Zn concentrate	61,9	320	35	1634	0,1	8	0,81	1	0,2	3,8	47	0,41		4,1	11	47	0,03			0,8	2,4	1,7	0,05	1,29	0,26	31,5
T/14	Jauken	Wettersteinkalk	16	Zn concentrate	61,9	1500	36	1318	0,1	70	0,2	1	0,4	0,5	130	0,44		3,3	0,6	20	0,03			0,6	2,3	1	0,13	0,87	0,43	33,4
T/16	Kolm/Dellach	Anis	14	Zn concentrate	60,2	14	4,5	908	0,35	42	0,69	1	0,4	88	79	0,56		1,1	0,48	33	0,2			0,7	0,43	1	0,68	0,84	0,45	32,9
T/24	Pirkach	Cardita 3 horizon	16	Zn concentrate	53,3	400	193	3762	0,1	39	0,45	1	2,6	27	12	2,1		8,7	1	230	0,03			1	2,2	1,7	0,07	5,77	0,05	32,2
T/24a	Pirkach	Cardita 3 horizon	16	kies concentrate	2,2	30	25	233	0,1	44		1	34,4	100		1,3			1,2	2000	0,1						0,6			36,8
S/24	Pirkach		16	Zn+Fe mixed conc	50	325	164	3485	0,1	28	0,42	1	6,7	16	26	1,4		5,9	0,6	349	0,03			1,3	3,2	1,2	0,06	5,74	0,04	32,3
T/17	Hochobir /Fladung	Wettersteinkalk	16	Zn concentrate	61,1	900	66	3828	0,1	190	0,2	1	0,3	6	24	0,36		2,1	8,5	89	0,03			1	0,75	9,1	0,32	1,11	0,11	33,4
T/1	Mesica	Graben	Slovenia	Zn concentrate	60,4	1100	30	1311	0,03	208	0,5	1	1,07	1	27	0,05		1,3	1,6	800	0,03			0,5	2	7,7	0,38	1,34	0,72	30,2
T/26	Mesica	Graben	Slovenia	Zn concentrate	60,6	76	40	3482	0,03	4	0,8	1	0,01	1	23	0,11		1,3	14	17	0,03			0,5	2,6	1	0,22	1,54	0,68	29,7
T/28	Mesica	Graben	Slovenia	Zn concentrate	61,7	250	78	2829	0,03	8	0,6	1	0,01	1	18	0,05		0,4	2,2	20	0,03			0,5	0,65	1	0,05	0,783	0,42	30,4
T/	Lafatsch	mean of 28 analyses	18	Zn concentrates		150	15	2300	0,1	45		1	0,05	4	4			1,8	120	300	0,4			1			0,1			
T/21	Nassereith	Wettersteinkalk	18	Zn concentrate	60,4	44	3,6	2379	0,1	57	0,2	1	0,5	78	9	0,18		1,8	188	293	0,03			0,5	0,3	1,3	0,5	1,5	0,09	33,2
T/22	St. Veith im Tegestal (Heiterwand)	Anis	12	Zn concentrate	59,7	135	59	2475	0,1	13	1,3	1	0,5	98	22	40		2	48	301	0,03			1,1	1,8	3,1	0,73	1,29	0,23	33,2
P/1	Meiselding		19	Pb-Cu concentrate	3,7	3	0,25	200	50	25	67	2	24,2	500		47	42000		740	60	100						32,4	2,1	0,01	17
P/2	Metnitz-Vellach		21	Zn concentrate	56,5	370	200	1442	9	17	0,29	1	6,76	115	385	12		2	66	1	0,12			470	4,1	22	0,23	0,95	0,02	34,8
P/3	Koprein		Loc 1337	Zn concentrate	58,9	3	7,1	2418	88	3	1,5	1	3,9	62	170	80		1,1	110	8	1			690	2,5	7,1	0,53	0,32	0,03	34,8
P/4	Oberzeiring		190	Zn concentrate	49,9	3,2	5,7	0,47	6,3	3,9	2	2	2,1	700		40	700		448	5	0,5						0,3	0,1	0,01	21
	Silberbergstollen	2. Hangendlager	13	Zn concentrate	61,3	10	24	2200	10	5			3,6	100					40	9				105			0,78			
	Übelbach	Ludwigstollen	13	Zn concentrate	61,1	10	25	2050	5	5			4,25	17						4							0,14			30,4
	Arzberg-Haufenreith		13	Zn concentrate	60,1	10	11	1800	29	5	5	5	4,52	17					12	16							0,3			31,6
P/6	Tösens		143	Zn concentrate	57,5	15	45	2800	47	2,7	2	2	5,1	1000		100	800		102	60	0,5						2,3	0,3	0,01	20,5
P/8	Kirchbachgraben	mixed sample	loc 1219	Zn+Fe mixed conc	29,2	2,5	0,28	1344	1,7	1,3	8	11	26,7	100		1	3000		1,7	500	29						4	1,7	0,01	32
S/7	Kirchbachgraben		loc 1219	kies concentrate	0,04	0,2	0,05	3,3	2	1	12	7	43,1	240		1	7000		53	400	18	0,31					0,02	0,2	0,01	44,6
S/9	Naintsch	sample from 30 cm lager	loc 1786	kies concentrate	0,04	0,1	0,1	2,1	0,1	0,5	2	2	47	100		1	100		0,9	400	0,1	0,03					0,01	0,01	0,01	45,1
S/17	Panzendorf		82	kies concentrate	6	3,5	0,5	216	43	12	23	2	41,7	800		400	78000		89	2200	118	0,72					1,5	0,2	1,2	34
S/18	Ausservillgraten	pyrrhotine ore	82	kies concentrate	6,3	3,2	0,9	300	122	4,3	82	2	42,6	100		700	103000		69	1000	158	0,72					1,3	0,04	1	30
S/19	Tessenberg		82	kies concentrate	0,7	0,1	0,1	21	12	0,8	37	2	52	50		60	22000		5,6	700	148	0,62					0,03	0,03	0,7	40,9
S/21	Erzberg Eisenerz	open pit	52	kies concentrate	0,05	0,5	0,1	4,2	0,4	0,5	57	2	47,5	2300		28	91000		5	600	4,8	0,03					0,01	0,3	0,7	39,1
S/25	Jenig/Danz (Gailtal)		48	kies concentrate	0,25	1,6	24	30	1,3	4,5	74	6	44,5	65000		1	1400		4,35	100	5	0,06					0,01	0,3	0,01	28,5
S/28	Pusterwald		101	kies concentrate	0,2	0,1	3,2	13	0,3	2,7	64	2	48,3	40		1	1000		3,1	1100	0,68	0,03					0,01	0,3	0,8	37,9
M/2	Politzberg		114	kies concentrate	2,3	3,3	0,9	108	25	10	32	6	44,7	150		68	13000		56	700	90	0,25					1,9	0,1	1,1	36
M/8 I	Nöckelberg		158	mixed ore sample	0,21	1300	8,7	17	22	0,4	2	2	33,4	2000		300	202000		24	24000	53	0,09					0,26	0,2	2,6	29
M/8 II	Nöckelberg		158	mixed ore sample	0,18	900	16	14	24	0,5	2	2	36	1800		300	270000		268	18000	41	0,03					0,25	0,1	2,6	27
M/9	Nöckelberg		158	kies concentrate	0,07	1135	14	4	17	0,5	2	6	34,2	1900		130	304000		28	16400	38	0,03					0,018	0,07	1,3	29
F/1	Falkenstein		89	Fahlore sample	5,3	1,7	0,1	300	3,6	4,7	2	5	1,7	2E+05		1	343000		2579	65000	1045	0,03					0,01	1,4	2,8	18
F/2a	Abfaltersbach		210	Fahlore sample	0,3	2	0,1	61	6,2	11	55	2	9,1	3E+05		90	46000		936	700	500	0,28					31,2	0,1	0,5	15,3
F/2b	Abfaltersbach		210	Fahlore sample	0,2	1,7	0,1	14	5,8	4,4	35	2	31,4	2E+05		5	30000		577	2000	220	0,4					18,9	0,4	5,6	10
F/5	Nöckelberg		158	Fahlore sample	0,17	700	5	20	29	0,8	2	2	28,4	3000		600	229000		32,6	75000	50	0,03					0,06	0,5	6,1	27
F/6	Leogang/Hütten	Danielstollen	158	Fahlore sample	0,03	1	3	1	3	0,3	2	2	11,5	100		10	25000		238	1100	80	0,03					0,01	6,2	31	
F/7	Leogang/Hütten	Maria Heimsuchung	158	Fahlore sample	0,01	0,5	3	1	3	0,3	2	2	24,5	100		3,5	4800		63,8	3800	18	0,03					0,01	4	19,3	

Table 19. Results of WD-X-ray fluorescence analysis on mineralized samples (normalized to 100% total)

Sample	AA5	AA7	AB6	AB7	BBR6	BBR7	BBR8	ESD10	ESD12	FSD1	FSD2	FSD3	FSD4	FSD5
Location	Achselalm		Arzberg		Bleiberg, Ramservererzung			Elisabethstollen		Friedrichstollen				
SiO_2	41,92	64,56	28,80	18,74	0,77	3,22	7,80	28,33	15,25	20,69	42,61	13,82	50,04	60,37
TiO_2	0,90	0,13	1,31	0,36			0,08	0,03		0,48	0,36	0,07	0,66	0,11
Al_2O_3	14,17	5,60	8,07	1,98	0,04	0,38	1,93	3,22	1,67	0,80	3,41	0,75	4,19	2,60
Cr_2O_3	0,01	0,01					0,01			0,01	0,01	0,02	0,00	
Fe_2O_3	19,04	4,13	11,32	14,03	0,10	0,31	0,63	57,49	56,02	9,83	4,63	2,57	4,00	7,29
MnO	0,17	0,14	0,38	0,81	0,02	0,03	0,01	2,34	2,38	0,36	0,17	0,03	0,18	0,37
MgO	10,88	1,45	2,71	2,21	0,10	0,15	0,93	2,23	3,76	0,11	0,75	0,05	1,35	1,13
CaO	4,25	20,12	12,39	18,30	30,80	55,06	58,58	0,70	3,39	4,82	3,17	0,32	4,33	4,04
Na_2O	0,10	0,75												
K_2O	8,18	0,48	2,23	0,74		0,12	0,62	0,02	0,29	0,58	0,63	0,17	0,86	0,34
P_2O_5	0,01	0,10	0,12	0,05	0,02	0,03	0,03	0,02	0,04	0,09	0,19	0,03	0,20	0,05
SO_3	0,11	2,29	4,49	8,14	0,01	0,01	0,01	0,04	0,04	0,01	0,88	0,07	0,16	3,46
Cl			0,015		0,069	0,055	0,047	0,014	0,018	0,006				0,026
Co	0,022								0,044	0,037	0,025	0,011	0,008	
Ni					0,015			0,012		0,011	0,007	0,013		0,004
Cu	0,002	0,017		0,080				0,014	0,027	0,624	0,010	0,018		
ZnS	0,044	0,085	14,334	12,730	47,994	40,161	26,283	5,292	16,099	57,371	37,407	37,618	17,431	18,779
Ga	0,002	0,002												
Ge						0,009								
As														
Rb	0,095	0,003												
Sr	0,007	0,035	0,115	0,162			0,005	0,002	0,010	0,008	0,005		0,008	0,009
Mo												0,003		
Ag			0,007							0,009	0,004	0,017	0,014	0,231
CdS			1,216	0,040	0,287	0,111	0,101	0,015	0,047	0,246	0,158	0,110	0,068	0,053
In											0,006		0,004	0,002
Sn				0,003	0,015							0,007		
Sb				0,006		0,021						0,072		
Cs	0,037													
$BaSO_4$	0,057	0,075	9,711	17,805					0,054	0,090	0,076		0,091	0,115
Hg				0,007						0,016	0,015	0,038	0,015	0,015
Tl				0,003										
PbS		0,015	2,786	3,800	19,763	0,317	2,940	0,232	0,855	3,802	5,496	44,195	16,387	1,013

Sample	FT16	FT17	GB-P11	GB-P12	GB-P13	KOP2	KOP3	KOP4	KOP8	KOP14	LaT4	LaT9	LaT11	LaT16
Location	Flecktrogalm		Guggenbach Poyd			Koprein					Lafatsch			
SiO_2	77,39	0,54	61,65	50,33	30,78	5,16	12,10	15,32	24,16	13,39	0,56	2,74	0,09	0,10
TiO_2	0,15		0,16	0,11	0,06	0	0,07	0,07	0,25	0,22	0	0,04		
Al_2O_3	4,00	0,02	3,20	2,40	1,77	0,84	1,91	1,92	7,60	6,16	0,20	1,29	0,02	0,02
Cr_2O_3									0,01					
Fe_2O_3	1,18	0,03	26,44	35,20	28,82	4,28	3,94	3,50	5,37	3,65	0,09	0,34	0,07	0,11
MnO	0,13		1,53	1,90	1,61	0,50	0,28	0,50	0,29	0,19				
MgO	0,68	0,01	1,83	2,33	3,53	0,25	0,46	0,49	1,38	1,00	2,35	0,43	0,28	0,12
CaO	9,25	91,51	3,06	3,38	22,63	37,44	23,62	38,39	18,25	16,47	49,32	55,52	56,85	10,82
Na_2O			0,96											
K_2O	1,06	0,01	0,37	0,24	0,06	0,11	0,20	0,23	1,01	1,15	0,06	0,42		
P_2O_5	0,10	0,00	0,12	0,09	0,23	0,01	0,01	0,02	0,04	0,02		0,00	0,00	0,04
SO_3	0,03	0,01	0,02	0,05	0,09	0,01	0,02	0,01	0,01	0,02	0,00	0,01	0,00	
Cl	0,062			0,016	0,027		0,020	0,019	0,014		0,020	0,024	0,025	0,027
Co						0,044	0,039	0,030	0,036	0,015				
Ni			0,011				0,009							
Cu	0,011	0,016			0,014	0,032	0,150	0,268	0,038				0,006	0,011
ZnS	4,182	0,293	0,304	3,675	3,144	50,066	55,585	38,841	39,868	14,831	47,195	37,966	41,567	87,183
Ga												0,018		
Ge												0,013		
As														0,029
Rb	0,006													
Sr	0,015	0,007	0,007	0,009	0,013	0,013	0,008	0,017	0,014		0,008	0,011	0,011	
Mo	0,010			0,003										
Ag			0,004		0,005	0,003		0,003		0,037	0,009	0,022	0,006	0,010
CdS	0,015			0,016	0,009	0,173	0,194	0,133	0,172	0,060	0,143	0,918	0,107	0,251
In							0,006				0,007			
Sn			0,017			0,008			0,005	0,033		0,183		
Sb	0,018													
Cs														
$BaSO_4$	0,055		0,139	0,121				0,235						
Hg		0,003					0,012			0,027				
Tl								0,004						
PbS	1,682	7,563	0,186	0,129	7,203	1,054	1,364		1,475	42,751	0,026	0,065	0,959	1,281

Sample	LaT17	LaT19	LaT22	MEI3	MEI4	MEI13	RaD7	RaD9	RaD10	RaD12	RaD13	RaD14	RaD15	SB319
Location				Meiselding			Rabenstein/Deutschfeistritz							Silberberg
SiO_2	1,33	2,60	0,12	44,71	19,01	46,25	12,31	64,64	24,09	28,39	63,06	36,76	14,25	42,47
TiO_2				1,02	0,13	1,09	0,17	0,84	2,31	1,13	0,38	2,09		0,26
Al_2O_3	0,50	0,29	0,03	6,99	2,33	7,05	1,07	5,10	7,81	9,31	2,89	15,18	0,93	7,73
Cr_2O_3								0,02	0,02	0,01	0,01	0,03		
Fe_2O_3	0,22	0,41	0,36	12,21	28,52	13,42	33,18	11,87	19,89	13,45	7,03	27,41	0,45	34,17
MnO	0,01			0,48	2,87	0,39	1,78	0,58	1,17	0,60	0,37	1,20		1,59
MgO	0,31			3,40	8,08	3,68	8,30	1,90	6,14	4,89	1,64	3,47	0,11	2,14
CaO	58,49	46,94	5,46	9,77	33,42	6,02	39,10	5,70	25,30	17,23	5,66	7,46	0,18	7,31
Na_2O									2,07				0,90	
K_2O	0,15	0,32		0,92	0,42	0,82	0,05	0,49	0,13	1,27	0,24	3,15	0,14	1,34
P_2O_5		0,00		0,25	0,06	0,26	0,10	0,17	0,42	0,33	0,09	0,30	0,02	0,13
SO_3	0,01	0,00	0,02	4,69	2,62	2,79	0,01	0,07	0,07	0,02	0,78	0,00	20,98	1,58
Cl	0,024	0,019	0,085	0,023	0,023	0,032	0,019		0,018	0,012				
Co				0,014		0,025	0,039	0,014		0,017		0,023		
Ni	0,004				0,016	0,010	0,010	0,007	0,010	0,006		0,011		
Cu	0,012	0,011	0,018	0,846	1,187	0,746	0,008		0,007	0,023		0,007		
ZnS	38,543	41,542	74,260	7,993	0,266	10,650	3,064	5,584	2,056	16,097	10,155	1,398	1,038	0,471
Ga												0,010		
Ge														
As		0,105	0,172											0,026
Rb												0,006		0,005
Sr	0,009	0,013		0,020	0,051	0,014	0,156	0,017	0,120	0,072	0,023	0,017	0,264	0,013
Mo														
Ag				0,018	0,006	0,020		0,001	0,003		0,005			0,004
CdS	0,116	0,102	0,199	0,036	0,007	0,062	0,012	0,018	0,013	1,553	0,033			
In				0,003			0,004						0,016	
Sn				0,015			0,006							
Sb				0,015										
Cs														
$BaSO_4$	0,097						0,065	0,225	5,910	0,740	1,182	0,978	60,465	0,508
Hg									0,007					
Tl														
PbS	0,183	7,649	19,283	6,591	0,971	6,660	0,542	2,737	2,426	4,863	6,460	0,505	0,236	0,257