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Pyrometallurgical relics of Pb–Cu–Fe deposits in south-eastern Germany: An exploration tool and a record of mining history

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ABSTRACT

Pyrometallurgical relics from smelting of iron as well as base metal ores are mineralogically and chemically investigated and dated using the radiocarbon method and optically stimulated luminescence. This study addresses the question whether these pyrometallurgical remains may be used as an exploration tool enabling geologists to discriminate between false and true gossans. Moreover, these investigations make a historical contribution and demonstrate how mining and smelting activities spread across NE Bavaria, Germany.

Iron minerals in slags may be used to interpret the physicochemical conditions during which these artifacts formed, while Ca–Mg–Fe silicates provide additional information serving as a rough indicator for stratabound ore deposits. Multicolored glassy smelting residues and secondary minerals staining slags may be taken as an indication of the existence of pyrite-bearing Cu ore deposits. Slags originating from false gossans are enriched in P and Mn, with base metal contents not exceeding crustal background values. True gossans evolving from SEDEX Fe deposits are rich in Fe and Mn. Vein-type siderite deposits create slags rich in Pb, Cu, Zn and Sn. Around 400 BC, Celtic miners headed N following the Regensburg Embayment where soft iron ores were easily accessible. From 700 to 1000 AD they entered the densely forested NE Bavarian Basement for firewood to run the kiln. Between 900 AD and 1630 AD siderite veins and SEDEX Fe deposits were exploited in NE Bavaria. It was not until the 17th century that stratabound sulphidic ores were discovered in this region.

1. Introduction

There are few professions, such as hunter and farmer which date back as far as miner and exploration geologist. Mining operations focusing on metals such as Cu, Au and Ag are among the most long-lasting operations, starting off with the chalcolithic age (copper age) between 5500 and 3000 BC. Numerous studies have focused on the artifacts and archaeometallurgical relics they left behind to reveal the techniques applied for the recovery of pure metals Cu, Au, Ag, Pb, Sb, Sn and Fe from the various types of ore and shed some light on the life of people exploring and exploiting these natural raw materials (Bachmann, 1982; Crew, 1991; Dill 1995, Adams and Genz, 1995; Mascaro et al., 1995; Amar, 1997; Alimov et al., 1998; Manasse et al., 2001; Manasse and Mellini, 2002; Adams, 2003; Bode et al., 2005, 2007; Gassmann et al., 2005; Hauptmann and Gambaschidze, 2006). While the study of archaeometallurgical remains enables mineralogists, chemists and researchers in the field of age dating to generally contribute to the cultural heritage and industrial history of a region, slags also provide valuable information on ancient mines which were mined out or left abandoned by the ancient miners for different reasons. Our ancestors may have faced difficulties during drifting and tunneling in terms of rock mechanics, water management or encountered at depth elements, they then had no use for, e.g., Zn, W, REE, U. Archaeometallurgy may also give an answer to the question of "true gossans" concealing a deposit at depth or a "false gossan" that is nothing but a ferricrete or superficial concentration of Fe, Mn, Al and Si with no commercial accumulation of base metals to be expected underneath (Dill, 1985a, Tardy and Nahon, 1985; Phillips, 2000; Anand, 2001; Dill et al., 2007). The subject under investigation in the present study is the mining and metallurgical history of an area in SE Germany, extending along the boundary between the uplifted basement block of the Bohemian Massif and its Mesozoic foreland (Fig. 1). Dumped relics at seven archaeometallurgical sites located not far away from karst and bog Fe ores, siderite vein-type deposits, Lahn–Dill-type Fe deposits and pyritiferous Cu deposits were investigated mineralogically, chemically and chronologically using charcoal for radiocarbon dating (Dill et al. 1995, 2003) and quartz and feldspar in the host rocks of the archaeometallurgical debris for optically stimulated luminescence (OSL) dating techniques (Dill et al., 2008). The archaeometallurgical data obtained throughout this study are correlated with data gathered during the previous study of ore deposits in the same region. The aim is to enquire whether smelting artifacts may be traced back to the sources of the ore to compare them with different slags from archaeometallurgical sites elsewhere where a precise correlation between slags and types of ore deposits has already successfully been performed (Dill, 1985b — see further literature cited there). It is an ancient truism in exploration geology

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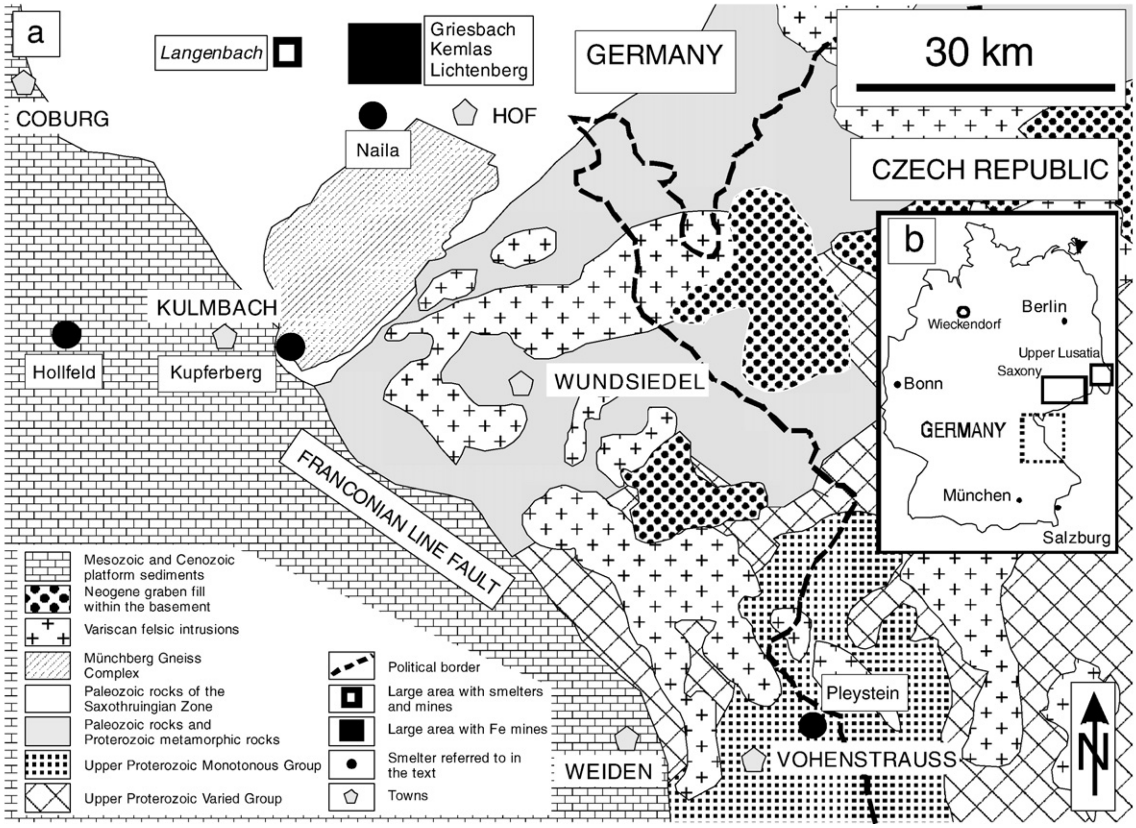

Fig. 1. Geological setting and index map of the areas under investigation in NE Bavaria, SE Germany. a) Geological setting and topographic position of sites of archaeometallurgical importance referred to in the text. The full square denotes the position of the Langenbach stratabound Lahn–Dill-type hematite deposit. Geology modified from Dill (1989). b) The inset gives the various localities of slags discussed in this study (bold faced line). The position of the working area in NE Bavaria is denoted by the framed area (stippled line).

that "if you look for a mine look near a mine". This study extends this to include the imperative "if you look for a mine look for smelting artifacts." Some communal smelting sites may be taken as a "metallurgical record office" to get a quick overview of the mineral associations in an area of interest for exploration.

2. Methodology

Minerals are identified by examination of thin and polished sections, SEM-EDX and X-ray diffraction analysis, all of which are basic techniques in mineralogical studies and, hence, need not to be described in detail here. Major and trace elements were analyzed by X-ray fluorescence spectrometry (XRF). The XRF was run in the conventional mode using beads with borate as flux material. The precision of the method may be assessed from the lower reporting limits at 0.01 wt.% SiO_2. Monitor samples and more than 50 certified reference materials (CRM) are used for the correction procedures. Radiocarbon dating was carried out in the conventional way described by Geyh and Schleicher (1990). Luminescence dating, which was applied only at one site has been described in Dill et al. (2008). Detailed information of the theory can be found in Aitken (1998) and Wintle (1997).

3. Geological and geographic settings

3.1. Geological outline

The oldest rocks exposed in the SE part of the study area are of Upper Proterozoic age (Franke, 1989) (Fig. 1). These pre-Variscan basement rocks form part of the Moldanubian zone at the north-Gondwana margin and were subdivided into the Monotonous and Varied Groups (Von Raumer et al., 2002, 2003). The Monotonous Group consists of paragneisses derived from greywackes and arenites, whereas the Varied Group is made up of amphibolites, metabiolites, marbles and calcsilicates which may be interpreted as a volcano-sedimentary series (Dill, 1989).

Low to medium grade metamorphic Paleozoic and Upper Proterozoic rocks of the Saxothuringian zone occupy much of the central part of the study area in the NE Bavarian Basement. Towards the NW, unmetamorphosed sedimentary and volcanic rocks of Middle Cambrian through Early Carboniferous age developed. The Münchberg Gneiss Complex is interpreted as a tectonic klippen. Late stages of Variscan convergence during mid-Carboniferous times resulted in the deformation and folding of these afore-mentioned rocks and the emplacement of synorogenic granites (Seltmann and Faragher, 1994). Continental and marine sequences made up of clastic rocks alternating with calcareous and evaporitic beds were deposited during the Triassic, which was followed by a marine transgression during the Jurassic leaving behind a vast carbonate platform. After an emersion during the early Cretaceous the sediments were drowned again and invaded from the southern Tethys Ocean along the "Strait of Regensburg" by the Upper Cretaceous sea (Fig. 2). During the Cenozoic the basement was again strongly uplifted along the Franconian Line Fault. Along with this uplift small grabens subsided within the basement, proper, taking up the debris from denudation of the crystalline basement rocks around (Fig. 1).

3.2. Geographic outline

A low-relief landscape in the basement evolved during the Neogene under subtropical climates (Louis, 1984; Borger et al., 1993). By the end

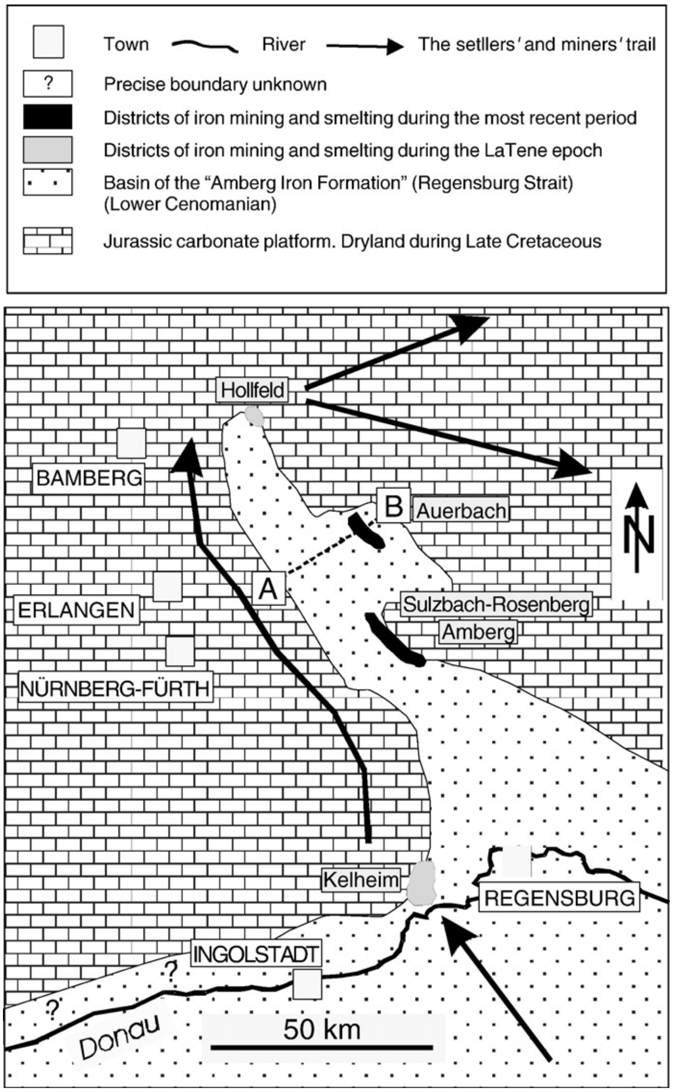

Fig. 2. The Regensburg Embayment ("Regensburg Stasse") during the Upper Cretaceous and the mining and smelting sites in NE Bavaria based on the exploitation of Fe ore from the LaTene era through the mid 1980s. Geology modified after Gudden (1984). The arrowheads mark the trail of miners and settlers during the early period of Fe exploitation in NE Bavaria based on this study. The dashed line from A to B denotes the transect of the idealized cross-section illustrated in Fig. 8.

of the glacial period, channels of the present-day fluvial drainage systems incised into the rocks and shaped the northeastern part of the NE Bavarian basement which is characterized by a rather rugged terrain at an altitude of between 500 and 1000 m a.s.l. with rivers draining it mainly towards the SW. The mountainous area is still today densely covered with forests predominantly of coniferous trees. The landscape is much more variegated in the foreland than in the mountainous regions towards the NE where rolling hills at moderate heights and deciduous trees are typical of the forests.

4. Results

4.1. Mineralization and geology of ore deposits in the smelting area

4.1.1. Pleystein area

The geology of this area is characterized by Upper Proterozoic paragneisses composed of variable amounts of biotite, sillimanite, cordierite, quartz, garnet, and feldspar as part of the Monotonous Group (Forster, 1965) (Fig. 1). The metamorphic country rocks were subsequently intruded by late Paleozoic granites. In the wake of these granitic intrusions aplites and pegmatites that were significantly different in their mineral compositions evolved. Some of them are strongly enriched in Nb oxides and Li–Mn phosphates (Strunz et al., 1976) (Fig. 3a, Table 1). When these pegmatites suffered erosion, they contributed to the mineral assemblage of alluvial–fluvial placer deposits by delivering "nigrine", cassiterite, Mn garnet and monazite to these terrigenous sediments. "Nigrine" is not a mineral but an intergrowth of ilmenite and rutile. Zircon, apatite and almandine-enriched garnet of the mineral assemblage of these Quaternary placer deposits around Pleystein originated from denudation of the metamorphic country rocks exposed in the catchment area of these creeks which contain the heavy mineral pay streaks (Dill et al., 2008). At Pleystein, Fe "limonite" has been concentrated in the course of supergene alteration of the basement rocks near the channels hosting the placer deposits. In parts "pebble iron ores" deriving from reworking of these ferricretes were washed onto the placer deposits and incorporated into the alluvial and fluvial deposits (Fig. 3b).

4.1.2. Kupferberg area

The Kupferberg deposit is located close to the "Fränkische Linie" lineamentary fault zone (Franconian Line Fault) which terminates the Variscan basement by an uplift of approximately 1000 m towards the Mesozoic calcareous and siliciclastic sedimentary rocks spreading across in the southwestern foreland (Fig. 1). The main phase of fault displacement was during the Cenozoic. South of the Münchberg Gneiss Complex, Ordovician, diabases (metabasalts), keratophyres (Na

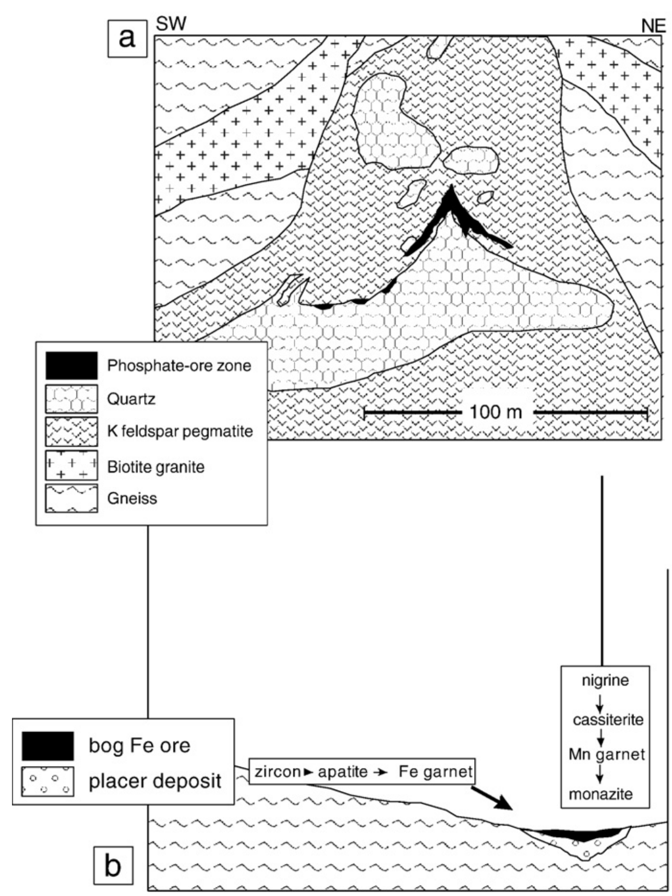

Fig. 3. Mineral deposits in the Pleystein area. a) The late Variscan Li–Fe–Mn phosphate-bearing pegmatite Hagendorf South, reference type of pegmatites in the Hagendorf–Pleystein Pegmatite Province (redrawn from Strunz et al. 1976). b) Tin and titanium alluvial–fluvial Quaternary placer deposits with accessory minerals and their provenance areas (Dill et al. 2008). The arrows denote where the minerals in the boxes came from (vertical: pegmatite, horizontal: metamorphic country rocks). On top of these placer deposits and blanketing the overbank deposits of the channels, bog iron ores formed during the Quaternary.

Table 1
Comparison between ore deposits and pyrometallurgical remains in NE Bavaria

Site	Hollfeld			Pleystein	Griessbach			Naila			Blankeneck	Lichtenberg			Kupferberg		
Age of slag	395 BC to 210 AD			685–805 AD to 18th century	900 to 1155 AD			1245±55 AD			1290±130 AD	1170 to 1630 AD			1594±150 AD		
Country rocks	Jurassic limestones covered by a Cretaceous through Cenozoic regolith			Upper Proterozoic paragneisses	Upper Devonian shaly diabasic (metabasalt) tuffs			Lower Carboniferous to Upper Devonian slates and greywackes, locally intercalations of diabasic (metabasalt) volcanic rocks			Upper Devonian to Lower Carboniferous diabasic volcanic and volcaniclastic rocks	Upper Devonian to Lower Carboniferous diabasic volcanic and volcaniclastic rocks, greywackes, quartzites			Ordovician slates, arenaceous clayshales, diabases (metabasalts), keratophyres (Na trachyte)		
Mineral assemblage of source ore (smelter feed)	Goethite			Goethite, "nigrine"	Siderite, barite, galena, sphalerite, goethite			Hematite, quartz			Siderite, goethite, chalcopyrite	Siderite, galena, sphalerite, goethite, cassiterite, fluorite, calcite, barite			Pyrite, minor pyrrhotite, chalcopyrite, sphalerite		
Types of deposits close to the smelting site	Lacustrine to fluvio-lacustrine ironstones of limonitic and sideritic iron ore			Li–Fe–Mn phosphate-bearing pegmatites Alluvial–fluvial Ti–Sn placers	Wabana-type ironstone ("Thuringitities") SEDEX ("Lahn–Dill") Fe ore Fe Skarn deposits Supergene Fe (Mn) ore			Vein-type Fe–Cu ore with minor Ni–Co arsenides			Wabana-type ironstone ("Thuringitities") SEDEX ("Lahn–Dill") Fe ore Fe Skarn deposits Supergene Fe–(Mn) ore				Talc deposits Polymetallic (Co–Cu–Ni–Bi) vein-type deposits		
Ore type (smelter feed)	Karst Fe ore			Bog Fe ore	Gossan Pb–Zn–Fe vein ore			SEDEX stratabound Fe ore (Lahn–Dill-type)			Gossan Fe–Cu vein ore	Gossan Pb–Zn vein ore			Stratabound Cu ore (Besshi Type)		
Mineralogy of slag	Wuestite, fayalite, quartz, magnetite, iron, hercynite (?)			Fayalite, quartz, ilmenite, hilgenstockite (Ca-phosphate)	Quartz, fayalite, amorphous substances, feldspar, goethite, rutile, wuestite			Fayalite, hematite, goethite			Fayalite, magnetite, iron, goethite, ferrihydrite, magnesioferrite	Amorphous substances (fayalite, magnetite, iron)			Feldspar (anorthite), fayalite, forsterite, amorphous substances quartz, graphite, brochantite, traces of tenorite, magnetite, hedenbergite		
	Max	Mean	Min		Max	Mean	Min	Max	Mean	Min		Max	Mean	Min	Max	Mean	Min
SiO_2	23.87	18.93	9.42	24.57	42.10	29.70	18.50	31.47	31.09	30.71	20.54	57.36	29.05	14.89	52.29	42.96	33.32
TiO_2	0.13	0.11	0.09	0.27	1.74	1.04	0.33	0.66	0.63	0.61	0.54	1.36	0.58	0.19	1.66	0.89	0.28
Al_2O_3	3.24	2.42	1.70	6.10	13.62	8.95	4.39	5.33	5.05	4.76	3.69	9.29	5.66	3.85	12.70	8.26	4.47
Fe_2O_3	93.54	81.33	75.31	64.51	72.94	41.80	19.12	61.77	60.39	59.00	70.66	93.63	62.90	1.43	34.03	29.69	26.40
MnO	0.75	0.51	0.28	0.51	2.22	1.77	0.97	2.54	2.40	2.26	0.90	2.08	1.27	0.87	0.53	0.38	0.22
MgO	1.53	0.85	0.45	0.82	3.78	2.26	1.44	0.87	0.84	0.80	1.14	1.22	0.63	0.33	4.87	2.89	1.22
CaO	1.95	1.07	0.37	4.55	29.79	8.50	1.11	1.34	1.29	1.23	1.25	23.25	8.75	1.50	13.73	9.74	5.41
Na_2O	0.01	0.01	0.01	0.21	0.38	0.31	0.18	0.14	0.10	0.05	0.05	0.14	0.07	0.04	0.39	0.34	0.28
K_2O	0.29	0.18	0.05	1.53	2.21	1.65	0.95	1.65	1.59	1.53	1.33	1.89	1.48	1.27	1.25	1.01	0.72
P_2O_5	1.06	0.87	0.68	2.91	0.55	0.41	0.15	0.43	0.41	0.38	0.58	0.43	0.29	0.02	0.31	0.18	0.10
SO_3	0.01	0.01	0.01	0.05	3.71	0.94	0.01	0.07	0.07	0.07	0.07	0.12	0.05	0.01	1.67	1.20	1.01
As	58	21	2	18	66	25	7	11	9	7	20	95	73	30	88	44	7
Ba	128	92	18	618	1750	792	468	529	509	489	387	864	568	420	8833	4500	171
Co	65	45	19	8	345	100	13	7	7	7	19	3	3	3	276	153	55
Cr	376	241	73	172	169	122	87	180	141	101	152	36	20	12	241	100	29
Cu	670	113	10	59	143	47	10	10	10	10	1164	143	106	32	25593	12426	1612
Ni	53	24	3	3	426	142	22	49	28	7	35	40	28	3	174	64	3
Pb	4	4	4	4	7968	1996	4	51	41	30	10	323	223	23	11	7	4
Sb	5	5	5	5	80	24	5					58	49	32	5	5	5
Sn	6	5	4	2	2	2	2	5	4	3	10	140	99	16	2	2	2
V	153	121	100	131	184	124	53	121	120	119	118	72	55	21	268	157	63
W	12	8	5	40	21	10	3	10	10	10	10	156	106	5	3	3	3
Zn	24	17	9	16	26323	6602	13	44	37	30	7	317	219	24	5272	2098	47
Zr	71	55	44	96	237	168	97	82	77	71	67	124	63	33	144	106	66
Mn/Fe	0.008	0.006	0.003	0.008	0.116	0.058	0.013	0.041	0.040	0.038	0.013	1.454	0.491	0.009	0.020	0.013	0.006
Pb/Fe	0.047	0.019	0.000	0.062	416.73	104.27	0.055	0.864	0.675	0.486	0.486	16.084	7.661	3.450	0.345	0.213	0.151

The age of the smelting period is based on charcoal using the radiocarbon technique and optically-stimulated luminescence (OSL) for quartz and feldspar of sediments hosting the smelting artifacts.
The lithology and age of the country rocks in the environs of the smelting site and the potential ore deposits where the slag-producing ore might have come from.
Mineral assemblage of source ore (smelter feed).
Different types of deposits close to the smelting site under consideration.
Ore type used as kiln feed.
Mineralogical composition of slags.
Chemical composition of slags (max: maximum, mean: average, min: minimum) of slags under investigation from NE Bavaria. SiO_2 through SO_3 are given in wt.% and As through V are given in ppm.

trachyte) are interbedded with neritic clastic sediments including slates and arenaceous clayshales (Franke, 1989). In these early Paleozoic volcano-sedimentary series a stratabound-stratiform pyrite-chalcopyrite ore typical of Besshi-type deposits evolved near Kupferberg (Fig. 4). The chemical composition of the ore includes Fe, Zn, and Cu, but only minor quantities of Pb. Au is present in amounts of

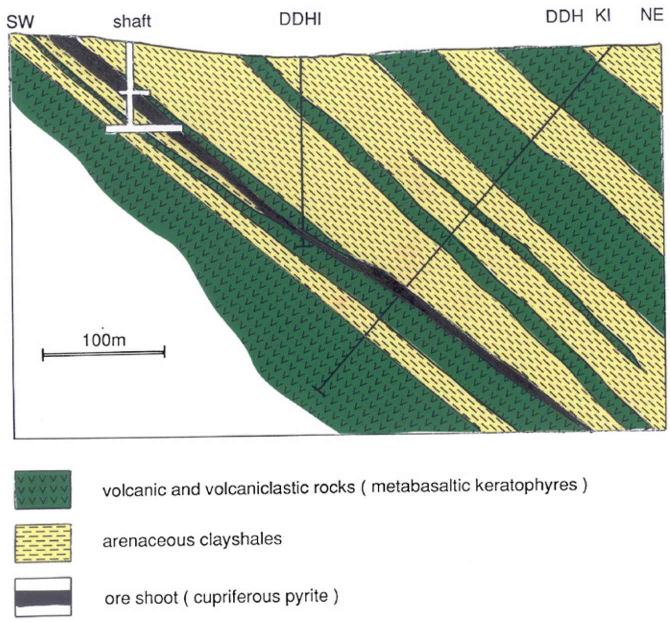

Fig. 4. Mineral deposits in the Kupferberg area. Stratabound-stratiform pyrite-chalcopyrite deposits of Besshi-Type/VMS-Type (volcanic massive sulfide). For location see Fig. 1.

as much as 2 ppm (Urban and Vache, 1972). Massive sulfide deposits at the *locus typicus* in Japan, are hosted by series of clastic rocks associated with marine volcanic rocks, mainly (meta)basalts (Fox, 1984). At the type locality it is a Cu–Zn mineralization with pyrite, pyrrhotite, chalcopyrite and sphalerite with little or no galena. Some may be enriched in Co and Au (Blanchflower et al., 1997). Cobalt-bearing vein-type deposits containing galena, bornite, Co arsenides, native bismuth, siderite, native copper and chalcocite were described by Ibach (1940). Their position relative to the stratabound ore can no longer be confirmed for lack of exposure and mining files. Along the south-western margin of the Münchberg Gneiss Complex east of Kupferberg, talc was mined (Klinkhammer and Rost 1975, Schmidt and Weinelt, 1978; Dill, 1981). This talc-forming event is bound to serpentinites mainly at their contacts towards the enclosing country rocks.

4.1.3. Griessbach–Kemlas–Lichtenberg area

The region of Griessbach, Lichtenberg and Blankeneck–Kemlas is underlain by siliciclastic sedimentary rocks and diabases of Carboniferous and Devonian age which underwent deformation during the Variscan orogeny (Fig. 5, Table 1). Relevant vein-type deposits mined for fluorite, Cu, Pb, Zn and Fe are shown together with the sampling sites of slags (Horstig von, 1972). The vein mineralization is dominated by fluorite, siderite, calcite and chalcopyrite. Galena, sphalerite, cassiterite, barite and Bi–Co–Ni arsenides are minor constituents. A precise dating cannot be carried out due to the absence of minerals suitable for radiometric age dating. A close spatial relationship between these veins and the Neogene peneplain stresses a Cenozoic age of formation of the vein mineralization. Mining files report on some other deposits in the region which were mined before the Second World War. Samples of these deposits whose precise location in the field is difficult to be given were investigated by Dill (1985b). The chemical composition of these ores are listed in Table 2. Marine ironstones are of the so-called Wabana-type. According to Zitzmann (1977), the Wabana ores are hematitic Fe ores with siderite and chamosite (51 wt.% Fe, 12 wt.% SiO_2, 1 wt.% P). As representatives of this type of Fe ore the “Thuringites” named after the Fe chlorite thuringite from Thuringia, Germany, were subject of some trial mining in this area (Dill 1985b). The SEDEX iron ore of Lahn–Dill-type is dealt with in the following section. Skarn iron ore with garnet and Fe-bearing pyroxene formed through contact metasomatic alteration of early Paleozoic limestones and contains some W and Sn minerals besides magnetite and hematite (mushketovite) (Dill, 1985b). It is a typical calcic Fe skarn genetically related to the Late Variscan granites as they were described among others by Einaudi and Burt (1982),

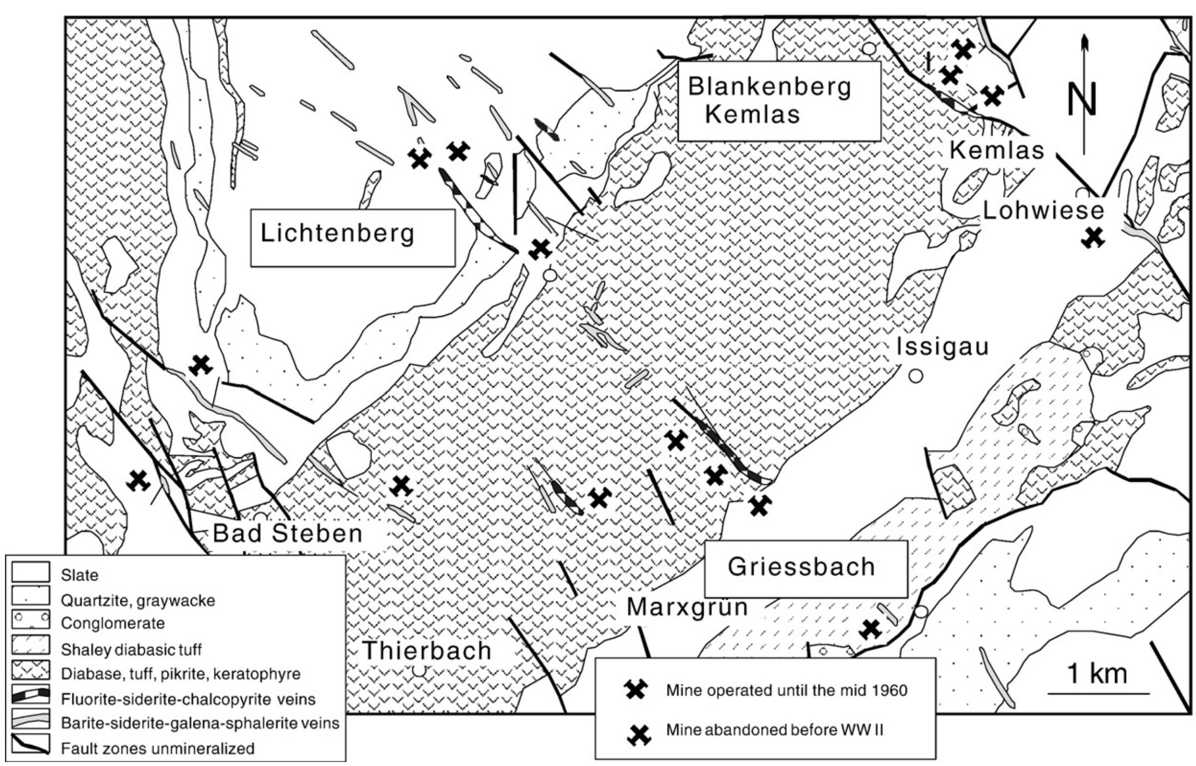

Fig. 5. Mineral deposits in the Lichtenberg–Griessbach–Blankeneck/Kemlas area.Slag dumps are given by locality names in boxes. Unframed locations refer to major towns and villages. For location see Fig. 1.

Table 2
Comparison of slags from Blankeneck with ores from various ore deposits in the smelting area

Element	Slag	Marine ironstone	SEDEX iron ore	Skarn iron ore	Vein-type iron ore	Supergene iron ore
	wt.%	wt.%	wt.%	wt.%	wt.%	wt.%
SiO_2	20.54	17.03	31.55	13.77	19.89	16.06
TiO_2	0.54	0.59	0.08	.15	0.06	0.22
Al_2O_3	3.69	12.66	0.64	2.68	1.65	4.99
Fe_2O_3	70.66	50.30	59.98	79.13	63.56	58.39
MnO	0.90	0.16	0.29	0.05	0.18	0.67
MgO	1.14	2.48	0.16	0.10	0.08	0.32
CaO	1.25	1.68	0.24	0.09	1.49	0.14
P_2O_5	0.58	2.63	0.08	0.06	0.36	4.14
	ppm	ppm	ppm	ppm	ppm	ppm
Ba	387	0	70	177	27	198
Ce	63	10	0	0	27	21
Co	19	26	0	0	0	55
Cr	152	92	0	1	6	43
Cu	1164	60	5	1119	365	5
Ni	35	134	142	16	19	456
Pb	10	64	5	9	5	10
Sn	10	20	20	8136	20	20
V	118	409	71	124	37	62
Zn	7	204	32	516	30	803
Zr	67	85	5	79	17	59

Chemical composition of major and trace elements.

Meinert (1992), Ray and Webster (1990) and Aksyuk (2000). The chemical composition of vein iron ore on display in Table 2 is representative of the siderite veins mined in this area. Elevated Cu contents in the chemical composition of the vein ore derived from chalcopyrite which was the only base metal sulfide of economic interest during the past mining operations. Supergene iron ore refers to the Hunsrück-type Fe–(Mn) deposits (Bottke, 1969; Dill, 1985a). Oxide hydroxides of Al, Fe-bearing silcretes, goethite, poorly-hydrated Mn oxides and manganomelane are the main components of these supergene Hunsrück-type Fe–(Mn) deposits that may be subdivided into five principal types: (1) ferricretes *sensu stricto*, (2) pebble Fe ores, (3) ferruginous conglomerates and breccias with Fe–Mn cement, (4) Fe–Mn replacement ores, and (5) limonitic gossans (Dill 1985a). The Fe–Mn enrichments, irrespective of their host rocks, were taken as

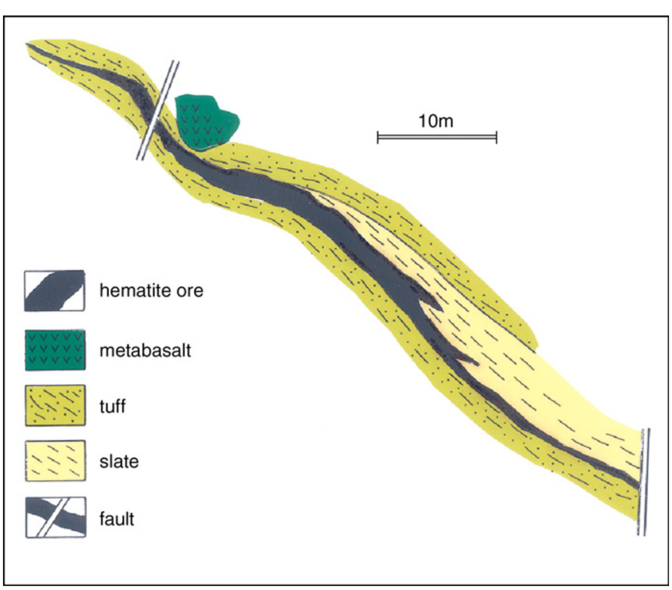

Fig. 6. Cross-section through the stratabound–stratiform hematite deposit of Lahn–Dill-type/SEDEX-Type (sedimentary exhalative) in the Langenbach mining district, Germany. For location see Fig. 1.

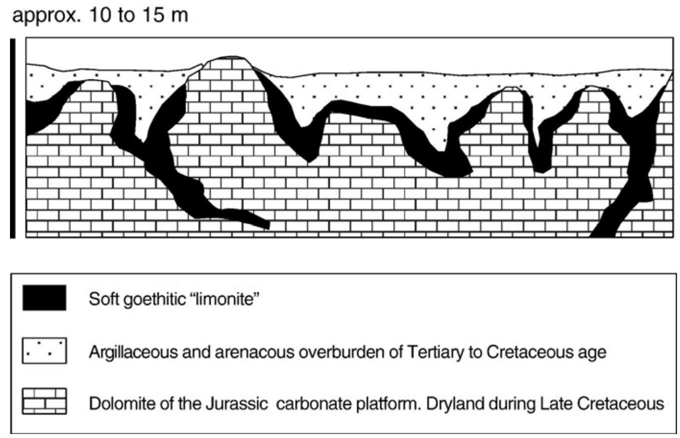

Fig. 7. Limonitic iron ore deposits in karst cavities evolving on Upper Jurassic platform limestones during the Cretaceous (after Meyer 1972).

remnants of hydromorphic soils of non-lateritic origin (Plio-Pleistocene).

4.1.4. Naila area

The geological situation around Naila is not very much different from the afore-described study area (Fig. 1). Devonian and Lower Carboniferous greywackes, slates and diabases are the principal country rocks in this part of the Saxothuringian zone. Swarms of chalcopyrite–siderite veins with little Ni–Co arsenides but barren as to fluorite — see Lichtenberg–Kemlas–Griessbach-cluster around Naila (Dill, 1985b). Another type of Fe ore deposit which was mined until 1920 near Langenbach is bound to Upper Devonian metabasalts and pyroclastic rocks (Fig. 1, 6). The volcanic- to sediment-hosted Fe deposits of the Lahn–Dill-type have formed the basis of iron smelting for decades in central Europe (Bottke 1963, 1965). Facial differentiation of the Fe ore changing from calcareous hematite, magnetite, siderite to siliceous Fe ore or even pyrite (melnikovite) ore is considerable and depends mainly on the Eh and pH conditions within the basin. Siliceous Fe ore is supposed to represent the proximal vent facies grading at 38 to 45 wt.% Fe. Calcareous hematite ore has a lower Fe content in the range 25–35 wt.% Fe. The Mn content ranges from 0.1 to 0.2 wt.% Mn. Phosphate averages 0.16 wt.% P and the S content lies between 0.15 and 0.6 wt.% S.

4.1.5. Hollfeld area

The "Regensburg Kreidebucht" (Regensburg Strait) is an embayment that subsided during the upper Cretaceous into Upper Jurassic platform carbonates (Gudden, 1972, 1984) (Fig. 2). The embayment of the Regensburg Strait is filled with terrigenous fluvial to near-shore marine deposits and the surrounding Jurassic platform sediments are made up of marine limestones undergoing etchplanation during the Lower Cretaceous. This time was crucial for the formation of bean and pocket iron ores (Fig. 7, Table 3). Bean Fe ores or karst cavity fillings of

Table 3
Chemical composition of karst iron ore from the latest mining period around Hollfeld in the 19th century (Klockmann, 1908) (nd: not determined)

Site	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5
Hollfeld mining district	22.29	nd	4.47	59.00	1.38	nd	0.06	nd	nd	0.68
Hollfeld mining district	29.78	nd	4.94	52.57	0.59	nd	0.07	nd	nd	0.67
Hollfeld mining district	19.40	nd	5.50	61.65	0.70	nd	0.08	nd	nd	0.85
Hollfeld mining district	20.62	nd	5.12	61.53	0.41	nd	0.10	nd	nd	0.94
Hollfeld mining district	19.10	nd	7.12	58.82	2.35	nd	0.22	nd	nd	0.71

limonite developed under tropical to subtropical humid climatic conditions during the Neogene and early Pleistocene. Goethite pisolites filled karst pockets and cavities in the platform limestones from the Swiss Jura to the Franconian Jura, Germany. Ascending meteoric fluids precipitated elements near the surface and developed case-hardened ferrous encrustations. While these near-surface ferricretes were susceptible to erosion, another type of Cretaceous ironstones has "self-sealing capacities" which preserved the newly-formed siderite and goethite ironstones from erosion by landslides from the uplifted flanks (Fig. 8). These lacustrine ironstones were completely blanketed by erratic limestone blocks in course of mass wasting triggered by normal faulting (Fig. 8). Meteoric fluids abundant in organic chelate complexes were able to carry Fe into these ponds on the karstic landscape. Goethite, collomorphous siderite, apatite and Fe–Mn-REE phosphate precipitated with bivalent Fe carbonate at depth and trivalent Fe oxide hydrate on top.

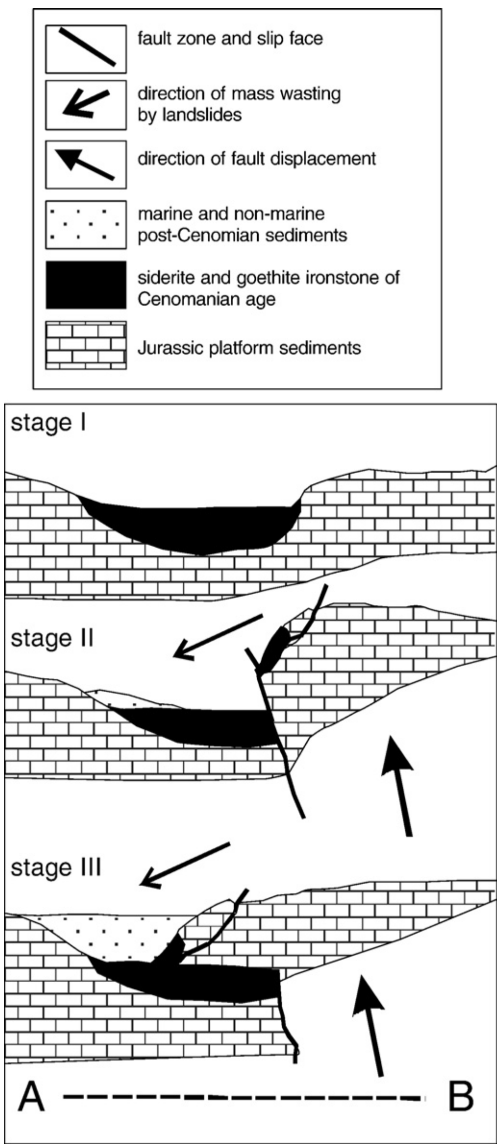

Fig. 8. A three-stage model to depict the Fe concentration in karstic depressions within the Upper Cretaceous Amberg Ore Unit, Germany, and the protection of the ore body from erosion by landslides (after Gudden 1984). For orientation of cross-section see Fig. 2 transsect A–B. Stage I: Infilling the karstic depression with siderite and goethite originating from organo-mineralic solutions transported into the depocenter from the exposed Jurassic platform sediments. Stage II: Normal faulting along the eastern boudary of the depression triggered mass wasting whose landslides began covering the Fe ore. Initial phase of deposition of post-Cenomanian sediments. Stage III: Sealing of the Fe ore body by landslides and post-Cenomanian marine and non-marine sediments.

Pyrometallurgical remains from smelting of various ore types have been used during discussion (bog Fe ore from Lower Saxony and Lussatia, Germany, ore from volcanic massive sulfide (VMS), Cyprus, sandstone-hosted Cu ore from Israel and base metal vein ore for Saxony, Germany). Their mineralogical and chemical data are listed in Table 4 but not reported in the same way as the samples from the study area in NE Bavaria because these data were mainly taken from the literature and often lack the completeness of equivalent data collected at sites in NE Bavaria.

4.2. Mineralogical and chemical composition of pyrometallurgical relics in the smelting area

4.2.1. Pleystein area

The prevailing mineral in the archaeometallurgical remains at Pleystein is fayalite with little quartz. The minerals are intergrown in a spinifex-like texture. Ilmenite is a rare constituent in the slags under study and only known from the Pleystein sampling site where this mineral was found in amygdules of fayalitic slags (Fig. 9). Pyrometallurgical remains from Pleystein are abundant in phosphate (Table 1, Fig. 10). Phosphate is always correlated with calcium reaching a correlation coefficient of $r=0.99$. This close link between Ca and P may be explained by the hilgenstockite phase ($Ca_4P_2O_9$) a chemical compound exclusive to Fe slags (Trojer, 1963). Charcoal was not found in any of these porous slags so that the common way of direct radiocarbon dating did not work in this area. The age of these slags was chronologically constrained taking a sedimentological–physical approach. These man-made accumulation of iron are interbedded with the topstrata of placer deposits which can be dated using calibrated ^{14}C data of wood fragments combined with data from optically stimulated luminescence (OSL) of feldspar and quartz. This approach is not as good as any direct dating method and only an age interval covering the time span from 685 to 805 AD to the 18th century can be delivered. The upper limit is deduced form old mining records. Some tests of diatoms washed into the porous fayalite-bearing slags at Pleystein and forming an "internal sediment" point to a dump site near or within sediments of a fluvial drainage system of Quaternary age.

4.2.2. Kupferberg area

The smelting artifacts from Kupferberg have the most variegated mineral assemblage of all sites under study, including feldspar, fayalite, amorphous/vitreous substances, magnetite, hedenbergite and the Cu minerals tenorite and brochantite (Table 1). Forsterite the Mg-enriched end member of the olivine s.s.s. was only found in one sample from Kupferberg (Table 1) as it is with graphite spotted in some polished sections. Magnetite is present in many of these slags and occurs in two different modifications. There are irregularly-shaped magnetite aggregates (<0.5 at.% Ti) and some well-crystallized aggregates shaped as octahedra. The latter modification of magnetite has to be denominated as titaniferous magnetite based upon the Ti contents of as much as 16 at.% Ti. The Kuperberg slags stand out from the group of slags investigated in NE Bavaria by their abundance in silica and earth alkaline elements and the anomalously high Cu contents (Fig. 10, Table 1). This is also mineralogically proved by the presence of tenorite and brochantite. Brochantite ($Cu_4(SO_4)(OH)_6$) is coating slags dumped near the mining sites. Even with the naked eye greenish and bluish earthy substances may be spotted on slags. Direct dating of these slag by means of the radiocarbon method on charcoal yielded an age of 1594±150 AD.

4.2.3. Griessbach–Kemlas–Lichtenberg area

All samples from this smelting area contain fayalite (Table 1). Fayalite occurs in slender crystal aggregates lined up in a chain-like way or showing a globular collomorphous texture. When broken apart, these globular fayalite aggregates reveal their interior cored by

Table 4
Mineralogical and chemical composition of slags taken for reference (max: maximum, mean: average, min: minimum)

Site	Wieckendorf (Lower Saxony, Germany)			Upper Lusatia (Germany)			Kalavassos–Asgata (Cyprus)			Shiqmim (Israel)			Saxony 1 (various sites) (Germany)			Saxony 2 (various sites) (Germany)		
Age of slag				800–300 BC to 1200 AC						4500 to 3500 BC								
Mineralogy of slag	Fayalite, quartz, cristobalite, amorphous substances			Fayalite, wuestite			Wuestite, magnetite, tenorite, goethite, fayalite, brochantite, wroewolfeite, posnjakite, devilline, gypsum, spertiniite			Magnetite, delafossite, quartz, glass, cuprite			Wuestite, fayalite, glass, leucite, calsilite, metallic iron			Glass, dentritic fluorite hyalophane, alite pyrrhotite, chalcopyrite, bornite, galena, chalkopyrrhotite, Ni–Sb–As, Cu–Sn–Sb compounds, FeBaCuKS to $(FeBaCuK)_{11}S_9$		
Ore type	Bog Fe ore			Bog Fe ore			Volcanic massive sulfide (VMS)			Sandstone-hosted Cu ore			Pb–Cu–Sn vein ore			Pb–Zn vein ore		
Reference	Unpublished data of the author			Heimann et al. (1998)			Unpublished data of the author			Golden et al. (2001)			Eckstein et al. (1994)					
	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min
SiO_2	39.22	30.67	22.11	32.50	24.26	15.10	22.19	17.42	13.50	17.90	12.44	7.72	57.00	35.34	19.00	52.80	40.91	21.70
TiO_2	0.22	0.18	0.13				0.18	0.11	0.07				0.96	0.46	0.25	0.60	0.35	0.07
Al_2O_3	4.93	3.78	2.62	3.80	2.27	0.57	3.89	2.76	2.29				20.20	6.57	2.80	7.10	4.68	3.10
Fe_2O_3	66.39	43.74	21.08	77.65	66.68	54.20	78.80	74.58	70.10	44.30	33.10	16.50	77.44	52.69	11.55	41.33	16.65	1.44
MnO	3.17	2.33	1.48	10.40	2.30	0.16	0.06	0.04	0.03	0.04	0.02	0.01	0.70	0.32	0.10	2.40	0.67	0.20
MgO	3.31	2.09	0.87				1.50	0.98	0.62	0.38	0.32	0.25	4.00	1.41	0.73	1.65	0.76	0.42
CaO	22.11	13.17	4.23	1.88	1.14	0.54	3.84	2.45	1.79				11.80	3.96	1.50	27.90	15.37	2.40
Na_2O	0.36	0.22	0.08				0.07	0.02	0.01				1.10	0.61	0.28	0.55	0.26	0.10
K_2O	2.28	1.78	1.27	0.97	0.54	0.19	0.54	0.33	0.23				5.30	3.00	1.54	4.10	1.68	1.00
P_2O_5	4.42	4.09	3.75	3.73	2.02	0.47	0.25	0.19	0.15									
SO_3	0.14	0.11	0.07				1.97	1.03	0.58	6.40	5.49	4.33						
As	8	7	5				87	53	14				200	91	10	720	180	30
Ba	2397	1548	699	5067	1306	150	81	56	30				9853	2289	896	389630	134982	1791
Co	8	8	7				704	580	440				220	119	70	950	165	20
Cr	131	125	118				60	36	24									
Cu	49	30	10				40302	21,541	9827	391,200	331,467	272,000	630	254	40	16000	1935	65
Ni	7	7	7				7	4	3	550	283	150	150	70	20	250	79	20
Pb	10	10	10				43	18	4	770	440	220	464	144	93	52913	17828	1207
Sb	nd	nd	nd				5	5	5	110	90	70	160	102	30	2650	431	10
Sn	3	3	3				bld	bld	bld				1060	261	100	820	206	100
V	222	168	114				110	74	52									
W	13	12	10				bld	bld	bld									
Zn	7	7	7				6471	5402	4642	40	23	10	80	80	80	65879	6986	80
Zr	189	167	144				14	9	3									
Mn/Fe	0.15	0.09	0.02				0.00	0.00	0.00									

The ore type refers to the kiln feed for each slag. The age of the smelting period is given based on charcoal dating using the radiocarbon dating technique of smelting artifacts. SiO_2 through SO_3 are given in wt.% and As through Zr are given in ppm. If not otherwise stated the results have been derived from studies of the author (nd: not determined, bld: below detection limit, blank: not reported in the reference literature).

wuestite as at Griessbach. At Griesbach, Ti is accommodated in the lattice of rutile. Goethite, hematite and ferrihydrite are found coating the slags, or infilling amygdules of the slags. Magnesioferrite is a rare constituent of the mineral assemblage of slags and was only detected in samples from Blankeneck. Magnesioferrite a spinel-type oxide shows a rugged surface and slag-type porous outward appearance. Native iron was detected bordering remnants of charcoal in the Blankeneck slag. Towards the margin of the slag, goethite crusts cover native iron and shelter it from further oxidation. There are some pyrometallurgical remains from Griessbach and Lichtenberg that stand out from the overall slags under consideration by their vitreous outward appearance, their conchoidal fractures and conspicous blue and greenish tints. Neither by optical methods nor by X-ray diffraction methods any well-crystallized chemical compound could be identified. Consequently, the material was categorized as (X-ray) amorphous substance. With the aid of the SEM-EDX in some of these vitreous slags, however, domains made up of fayalite and magnetite were delineated, including some droplets of native iron. Among the smelting sites in NE Bavaria, these sites are remarkable for their increased Pb contents (Griessbach and Lichtenberg) and elevated Cu contents (Blankeneck) (Fig. 10, Table 1). All samples taken at these smelting sites were dated using the radiocarbon method. Samples span the period of time from 900 AD to 1630 AD (Table 1).

4.2.4. Naila area

The slags taken from dumps near Naila are not out of the ordinary neither in light of their mineralogical assemblage (fayalite, hematite, goethite) nor regarding their chemical composition, with the exception of Mn (Fig. 10). Charcoal scattered in the pyrometallurgical remains yielded an age of formation of 1245±55 AD.

4.2.5. Hollfeld area

Iron slags were dumped in the environs of Hollfeld not far away from near-surface ironstone deposits at the northern edge of the "Regensburg Kreidebucht" (Regensburg Strait) (Hollfelder, 1989) (Fig. 1, 2). Not surprisingly, the Hollfeld slags warrant mentioning for their most elevated Fe contents ever found in the area under study and divers intergrowth of Fe oxides and silicates (Fig. 9, 10). Only Fe-bearing minerals with some quartz and cristobalite were identified in the slags under investigation. Wuestite droplets are disseminated within fayalite which shows up in slender crystal aggregates lined up in a chain-like way or it occurs in collomorphous aggregates. Rhomb-shaped euhedral crystals of fayalite as open space filling of Fe slags evolve from chain-type fayalite. Spinifex textures are common to these Fe oxide-silicate intergrowth. Only moderate Ca-(max. 1.2 wt.% Ca) and Mn contents (max. 1.2 wt.% Mn) have been analyzed from the slags, ruling out any significant amounts of shannonite (Ca_2SiO_4) and tephroite (Mn_2SiO_4),

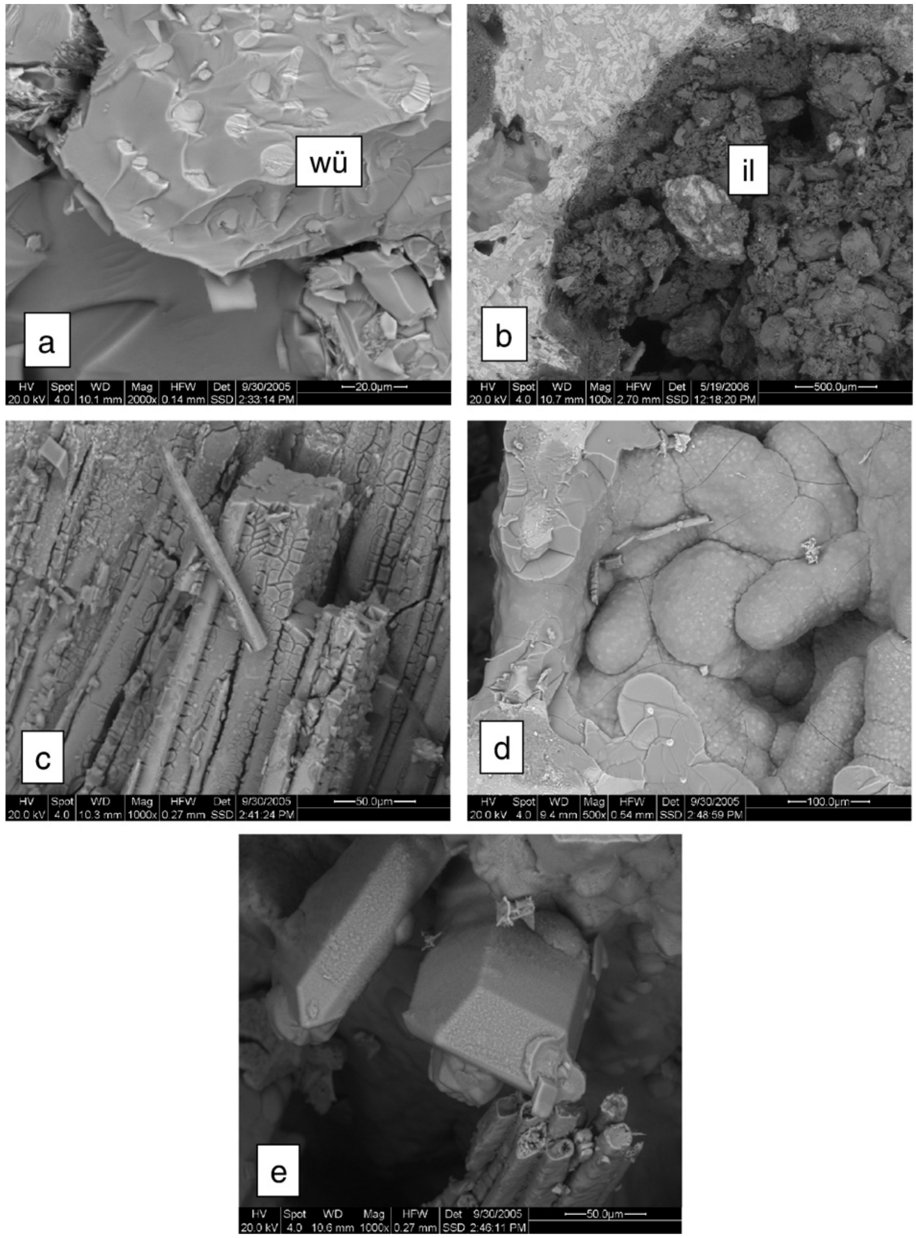

Fig. 9. Iron oxides and -silicates in slags investigated by SEM-EDX. a) wuestite droplets (wü) disseminated within fayalite (dark). Site: Hollfeld. b) ilmenite (il) in amygdules of a fayalitic slag. Site: Pleystein. c) fayalite in slender crystal aggregates lined up in a chain-like way. Site: Hollfeld. d) collomorphous fayalite aggregates cored by wuestite(white). Site: Hollfed. e) rhomb-shaped euhedral crystals as open space filling of Fe slags evolving from chain-type fayalite. Site: Hollfeld.

respectively, mixed up with fayalite (Fe_2SiO_4) in the olivine solid solution series (s.s.s.). To prove hercynite by XRD failed due to its minor grain size. Dating of charcoal particles from these specimens gave an age of formation of 395 BC to 210 AD, the oldest age of man-made “ferricretes” ever found in this region.

5. Discussion

5.1. The mineral assemblage of pyrometallurgical remains an evidence for archaeometallurgical processes and a guide to ore

Can silicates, oxides and native elements in slags be used as ore guide to the deposits where the kiln feed has derived from? The paragenetic relations between and the chemical composition of the prevailing Fe–Ca–Mn oxides and -silicates are controlled by the physico-chemical conditions during which they evolved. Platy to columnar habits of fayalite described by Donaldson (1976) and spinifex textures by Pyke et al. (1973) as well as the collomorphous outward appearance of fayalite are a function of viscosity and the cooling rate of the melt, which was rather viscous in the samples under study from Hollfeld and Pleystein. Considering the data published by Hartmann et al. (1984), the temperature reached during the smelting process in Hollfeld and Pleystein is supposed to have occurred at approx. 1200 °C. Native iron and wuestite in the slags furnish evidence of SiO_2 limitation and reducing conditions occurring at least in parts of the blast furnace near or around coalified matter. Magnetite, in places very abundant, was not transferred from the Fe ore into the melt as a would-be armored relic but generated by Fe reacting with oxygen — see Myers and Eugster (1983). Low oxygen fugacity and high temperatures caused fayalite to form; more elevated oxygen fugacity along with decreasing temperatures led to wuestite and magnetite, ending up with hematite, which did not develop in any of these slags. The smelting techniques at Naila, Griessbach, Lichtenberg and Blankeneck are similar to those reported for Hollfeld and Pleystein; neither compositional nor textural differences exist between these slags as far as the principle Fe components are concerned. Pure Fe oxides and

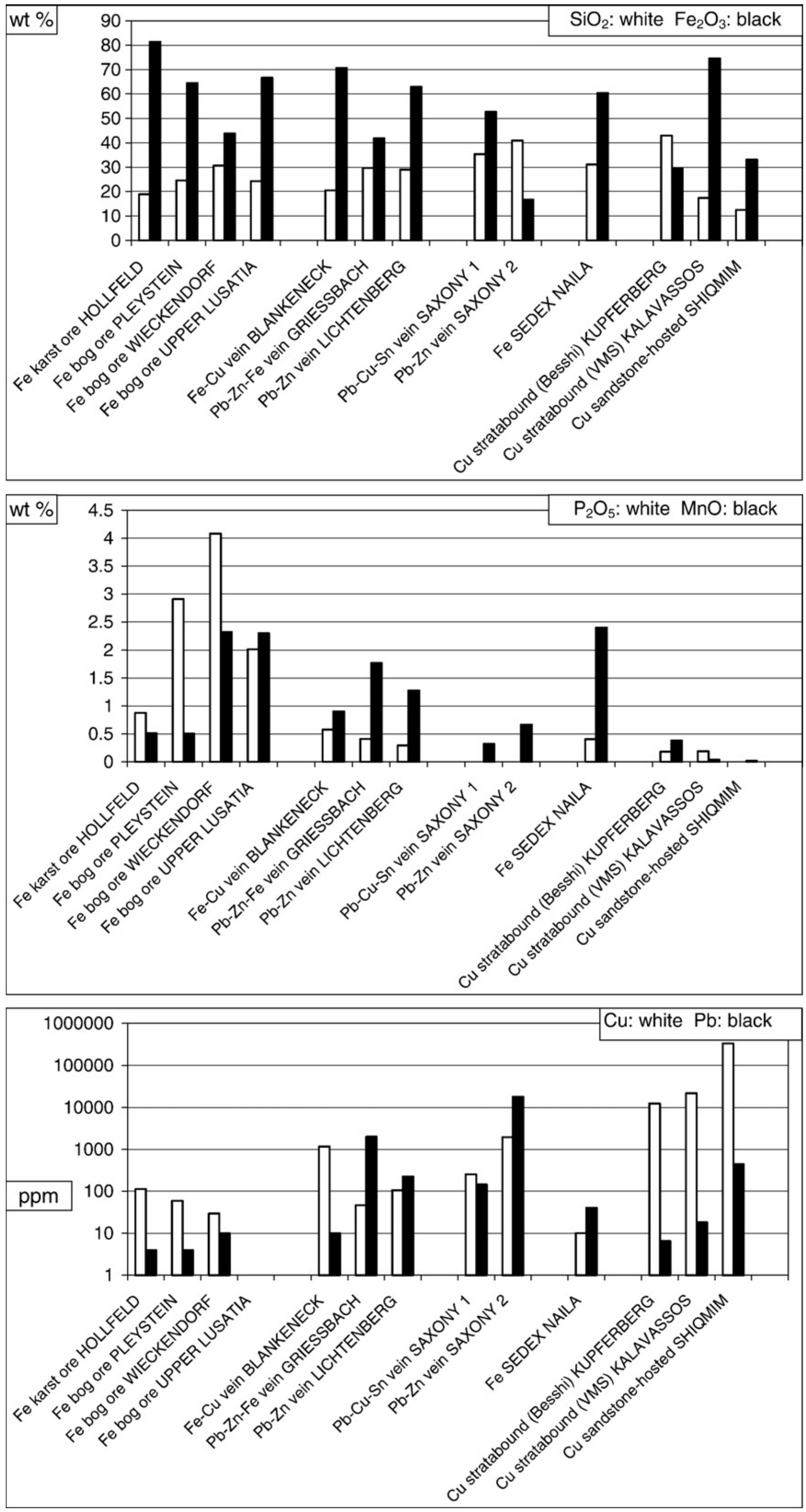

Fig. 10. Columnar diagrams to show the major commodities of the slags under study compared with some reference data from literature and analyses carried out by the author in different dump sites of slags. See also for numerical data Tables 1, 2 and 4.

silicates are only suitable to interpret the archaeometallurgical processes.

The presence of minerals like hedenbergite, forsterite and anorthite in slags from Kupferberg demonstrate alteration of Ca–Mg-bearing gangue under rather high firing-temperatures in the furnace similar to what is known from reducing calcic skarn deposits in nature (Einaudi et al. 1981, Einaudi and Burt 1982). These Ca–Mg–Fe silicates furnish circumstantial evidence that ore minerals were intimately intergrown with Ca–Mg–Fe-enriched silicates in these self-running ores from the stratabound Cu ore of Kupferberg.

Rutile and ilmenite do not form an integral part of the smelting process in the slags under study from Pleystein and Griessbach. Experimental results and phase diagrams published by Van Dyk and Pistorius (1999) and Zietsman and Pistorius (2004) demonstrate that temperatures of more than 1600 °C would have been necessary for the reduction of Fe–Ti oxides. Ilmenite has been incorporated into the slags from "nigrine" placers in the small rivulets and gorges draining the area around Pleystein (Dill et al. 2007). In case of Griessbach rutile has derived from gangue.

Multicolored glassy material or amorphous substances have only been found in slags of elevated base metal contents (Table 1). Ettler et al. (2001) who studied slags from the Pb–Zn vein-type deposit Príbram, Czech Republic, recorded abnormally high base metal contents to be especially incorporated in the vitreous slags. Base metals as incompatible elements used to be concentrated in the late-stage glassy metallurgical remains.

The most diagnostic minerals in the pyrometallurgical remains useful as an ore guide are secondary minerals like brochantite and tenorite, which occur only in slags abundant in Cu and Fe sulfides from stratabound Cu ore such as Kupferberg. This is also corroborated by finds made by Golden et al. (2001) in sandstone-hosted Cu deposits in Israel, and unpublished data from VMS deposits in Cyprus (Table 4).

The process how they come into existence is shown below starting of from the smelting processes of pyritiferous Cu ores. Pyrite is roasted under silica-limited conditions to wuestite and sulfur dioxide and in the presence of quartz to fayalite:

$$2FeS_2 + 5O_2 + SiO_2 \rightarrow Fe_2SiO_4 + 4SO_2$$

$$2FeS_2 + 5O_2 \rightarrow 2FeO + 4SO_2$$

Roasting of chalcopyrite in a two-step process resulted in the formation of wuestite and native copper forming covellite as an intermediate product:

$$2CuFeS_2 + 3O_2 \rightarrow 2FeO + 2CuS + 2SO_2$$

$$CuS + O_2 \rightarrow Cu + SO_2$$

Some slags still contain pyrite attesting to an incomplete smelting process.

The abnormally high Cu content in the slags is due to the presence of tenorite that evolved from cuprite:

$$2Cu_2O + O_2 \rightarrow 4CuO$$

Malachite which is widely known from gossans where it was mined during the initial phases of exploitation of Cu deposits can also be held accountable for the formation of tenorite simply by the release of water and carbon dioxide:

$$Cu_2(CO_3)(OH)_2 \rightarrow 2CuO + CO_2 + H_2O$$

In the blast furnace native copper is produced under limited access of oxygen:

$$CuO + CO \rightarrow Cu + CO_2$$

The physico-chemical conditions under which tenorite and the Cu sulfate brochantite, including wroewolfeite, posnjakite and devilline are stable in these slags are modeled in Fig. 11. Tenorite only can exist under alkaline conditions and Eh values above 0. When the meteoric fluids turn more acidic Cu sulfates form instead.

At log $_{Cu}$ <−6 and log $_{SO4}$=−4 the stability field of $CuOH^+$ increases, whereas at log $_{Cu}$=−5 and log $_{SO4}$=−4 its stability field disappears. On getting a solution of $CuSO_4$ more alkaline, causes posnjakite to precipitate which ages to the more stable brochantite (=$CuSO_4 \cdot 3Cu(OH)_2$)) (Marani et al., 1995). This reaction is demonstrated by the simple equation:

$$CuSO_4 + 2OH^- \rightarrow Cu(OH)_2 + SO_4^-$$

Delafossite and cuprospinel which were recorded by Golden et al. (2001) from slags aged 4500 to 3500 BC at Shiqmin, Israel, are stable only at slightly reducing to oxidizing conditions (Yund and Kullerud, 1964; Ono et al., 1972). Delafossite is thus not expected in slags of this more recent period from 900 to 1630 AD in Germany.

5.2. The chemical composition of pyrometallurgical remains a tool to discriminate true and false gossans

Sulphide deposits formed at depth convert into gossans near-surface under climates stimulating pervasive chemical weathering. Such supergene alteration zones developed well under tropical and subtropical climates. Earthy or boxwork-like gossans suffering iron mobility may end up looking similar to ordinary ferricretes. The word ferricrete is used as a pure descriptive term for indurate, iron-rich material without any direct connotation to climate or particular types of regolith such as laterite (Bourman, 1996; Eggleton and Taylor, 1999). In fact, the massive ferricretes could have derived from regional ferruginization of a saprolite material, by fluctuating ground water tables, broken apart and washed together in cavities and pockets (Tardy, 1993). Slags have an edge over natural ferricretes scattered across the landscape as these artificial products underwent already a

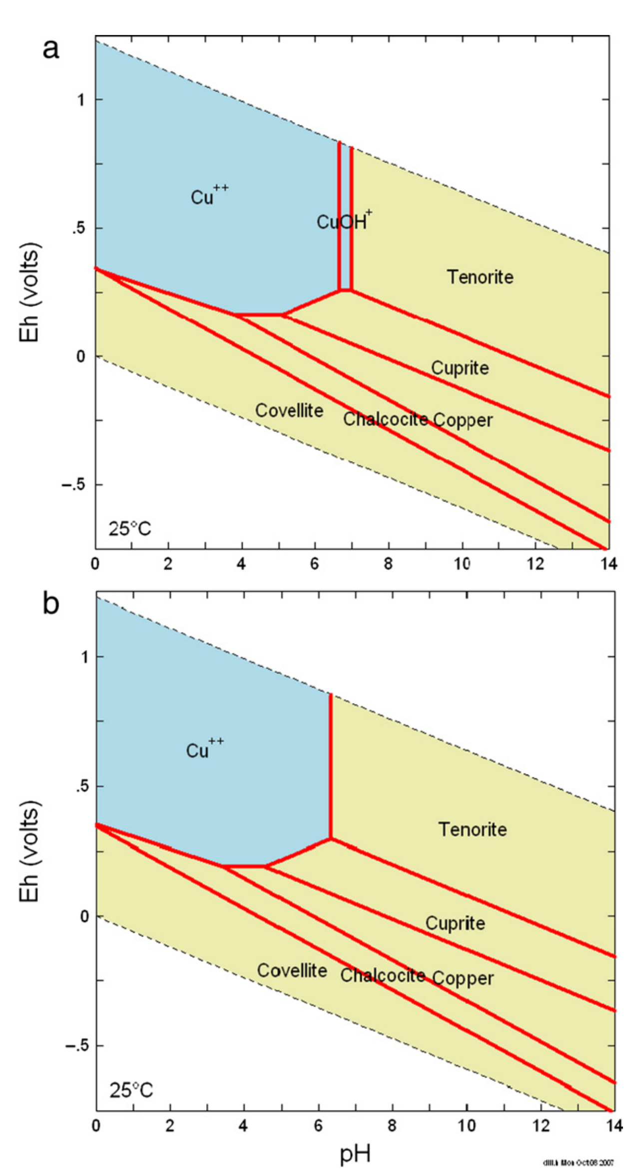

Fig. 11. Eh–pH diagrams in the system Cu–S showing the spread of the stability field of $Cu(OH)^+$, Cu^{++} (e.g. brochantite) and tenorite. Cu^{2+} (a: log $_{Cu}$=−6, b: log $_{SO4}$=−4). SO_4^{2-} (a: log $_{Cu}$=−5, b: log $_{SO4}$=−4).

preselection by man and the contents of certain elements were upgraded in the course of smelting.

Hollfeld, Pleystein and the reference sites near Wieckendorf and in Upper Lussatia have all derived from ferruginization and are representatives of false gossans, with no primary ore deposit underneath. They are located near karst and bog iron ores very low in base metals but rather high in P and/or Mn contents (Fig. 10. Table 1). Phoscretes and ferricretes developed under a subtropical palaeoclimate during the Neogene in what is called today Central Europe and still being formed in Central Africa (Goudie and Pye, 1983; Wilson, 1983; Dill 1985a, Dill et al., 1991; Anand et al., 1997; Phillips et al., 1997). Phosphate-bearing pegmatites in Pleystein may be ruled out as a source for P in the slags at Pleystein as these P-bearing rocks were not exposed during Neogene times (Fig. 3a). This is also valid for the limonitic-sideritic ironstone deposit illustrated in the cartoon of Fig 8 which is a prime example for self-preservation of ore against erosion.

Connecting the slags from Naila with a special type of ore without a proper knowledge of the local geology is difficult. Iron slags only stand out from the group of Fe slags by abnormally high Mn contents while being poor in most other elements (Table 1, Fig. 10). These Fe slags were correlated with mining activities focused on Lahn–Dill-type SEDEX Fe deposits. Vein mineralizations containing Ni-, Co-, Cu and Fe minerals found in the same area may be ruled out as there are no anomalously high concentrations to be found in the slags. Low P and high Mn contents are markers for this kind of deposit. Manganese contents in Lahn–Dill-type Fe deposits may increase to such an extent so as to form a separate entity of a Mn SEDEX ore, as near Battenberg in Hessen, Germany (Schaeffer 1998). Anomalously high Mn contents are known as proximity indicators of the feeder channels of stratabound base metal and iron deposits (Stumpfl, 1979).

Anomalously high Cu contents in the slags from Blankeneck leave no doubt that ore from chalcopyrite-bearing siderite veins was taken to feed the kiln. Various ore types nearby were sampled and their chemical composition was compared with that of the slags under study. The chemical data listed in Table 2 show the best fit with the vein-type iron ore (Dill, 1985b). Which of the different vein mineralizations has contributed most to the kiln-feed? This question may be answered in favor of the fluorite–siderite–chalcopyrite veins, because no barite or elevated Ba contents were found in the slag. In Griessbach the source cannot be pinpointed with the same precision as in Blankeneck. The site is likely to have been a communal smelter where ore from different mines operating vein mineralization in the immediate surroundings were processed. At Lichtenberg ore enriched in Pb and Zn was used to feed the kiln. In addition, these slags have the highest Sn contents found in slags from this region. Near Kemlas, Pb–Zn veins occur in an area otherwise known for its cassiterite mineralization (Dill, 1985b). The Late Variscan disseminated cassiterite mineralization albeit not the target of mining has left its imprint on the Pb–Zn vein mineralization traced through the entire smelting process. Slags produced by smelting of ore from vein-type deposits in NE Bavaria resemble in their chemical composition slags from Saxony in the foreland of the Erzgebirge Mts. that contain anomalously high amounts of base metals too (Eckstein et al., 1994).

The slags at Kupferberg originated from smelting processes of stratabound Besshi-type sulphidic ore using self-fluxing charges and creating reducing conditions with sulphur removal being rather incomplete (Table 1). They have the highest Zn and Cu contents reported from the area under consideration and are quite similar to the VMS deposits from Cyprus. Polymetallic vein mineralization may be ruled out as kiln feed at Kupferberg as it is the topmost part of the talc deposits. Slags taken for reference from Cyprus have higher Cu contents than slags from Kupferberg in Germany. This is mineralogically substantiated by the presence of a variegated spectrum of hydrated Cu sulfates in the slags from Asgata and Kalavassos mines, Cyprus.

The metallurgical procedure applied to recover Cu from the ore was less efficient in Cyprus than in Kupferberg, with only partial liberation of the copper from the ores. This is held to be an indication of a more ancient technique applied to recover Cu from the Cypriot ores than in Kupferberg.

5.3. The age of pyrometallurgical remains a record of the history of mining

The area of origin of the old miners and settlers is located in Austria. Around 400 BC, Celtic tribesmen from Western Europe settled in the eastern Alps. The earliest period of Celtic domination in Europe was named after the village near Salzburg in Austria, Hallstatt era which lasted from the 7th to early 5th centuries BC (Fig. 1). They crossed the river Donau (Danube) and headed north guided by the iron deposits lined up along the boundary between the Cretaceous sediments of the Regensburg Embayment and the underlying Jurassic platform sediments (Fig. 2).

The Regensburg Embayment was not only a pathway for the marine ingression during the Late Cretaceous leaving behind economic iron concentrations but also an inlet for the Celtic miners and smelters (Fig. 2). Smelting artifacts near Hollfeld may be assigned a late LaTene age (200 AD to 0) (Table 1). Further to the south and older than the Celtic smelter at Hollfeld, smelters were also discovered near Kehlheim to mark the onset of mining activities in that area (Schwarz et al., 1967; Zahn, 1981) (Fig. 2).

Based on these age data of slags one can conclude that Celtic miners gradually migrated northward following iron ore accumulated near-surface along the ancient coastal zone of the Cenomanian basin fill of the Regensburg Embayment. More profitable siderite–goethite ironstones in the basal parts of the Cretaceous basin fill as shown in Fig. 8 were only opened up during modern days in the Auerbach –Sulzbach–Rosenberg–Amberg area (Gudden 1984). They were not accessible to the ancient miners at that time for technical reasons. The ancient miners and smelters were forced to exploit shallow karst Fe ores in pockets and cavities along the western edge of the embayment (Fig. 2, 7).

From 700 to 1000 AD they dared to enter the densely forested eastern parts of the NE Bavarian Basement, where the last mines and exploration shafts were shut down during the second half of the last century. They were probably attracted by the abundance of copious firewood to run their kilns and so decided to enter the more rugged and densely forested terrains of the NE Bavarian Basement to look for Fe ore as close as possible to the energy resources, as at Pleystein. In the Pleystein area some old tombs have been excavated but with no direct link to the mining and smelting activity in the region.

Between 900 AD and 1630 AD the shallow parts and gossans of the base metal-bearing siderite veins in NE Bavaria were exploited by ancient miners. During this Medieval mining period, smelting was no longer carried out only at the site of exploitation but short-distance transports in the range from 5 to 10 km from an operating mine to a central smelting site are no longer out of the ordinary. In a mining district, as exemplified by the Lichtenberg–Kemlas–Issigau–Griessbach mining district, there are mine-based smelters, e.g. Blankeneck, and sites were different types of ore were collectively smelted through time, e.g. Griessbach and Lichtenberg mainly for better supply of firewood, proximity to transport routes and water (Fig. 2). These three sites act as a local “metallurgical record office” saving the data from various types of mineralization from Sn-bearing Pb–Zn deposits to base metal-bearing siderite vein-type deposits.

The SEDEX Fe deposits and base metal-bearing veins were operated during the same period of time. This is indicated by the overlapping ages of Blankeneck and Naila (Table 1). Until that time, Fe was the prime target and Cu, if mined at all, was won only as byproduct.

Sulphidic ore closely interbedded with siliciclastic and metabasic volcanic rocks were discovered in that region for the first time only in the 17th century as a concentration of Cu that could be mined and smelted economically. Although the technique to recover Cu from the Kupferberg ore was not yet very much efficient around 1600 AD, the technique was much more effective than those techniques applied between 3500 and 4500 BC in Israel and around 2800 BC in Cyprus (Tables 1, 4).

6. Conclusion

The main Fe minerals in slags may only be used to interpret the physicochemical conditions during which these artifacts formed. Yet, they have no meaning as an ore guide. Inherited Ti compounds which are incorporated into the melt but not "digested" can give a rough idea of the country rocks where the ore came from but do not qualify as mineralogical ore guide. Ca–Mg–Fe silicates are indicative of stratabound ore where the ore minerals are more intimately intergrown with Ca–Mg–Fe gangue minerals rather than in massive vein-type mineralizations. Multicolored glassy pyrometallurgical fragments are a "quick-and-dirty" marker in the field for base metals to be involved in the smelting process. Staining of slags with green and blue secondary minerals may be taken as a clear indication of pyrite-bearing Cu ores to have been part of the kiln feed and massive sulfide deposits in the close vicinity.

Slags originating from false gossans or surface ferruginization without connection to an ore body underneath are shown to be enriched in phosphate and locally in manganese too. Their base metal contents do not exceed crustal background values. True gossans evolving from SEDEX Fe deposits are abundant in Fe and Mn which can be used as proximity indicators. As to the base metal contents, slags based on ore from SEDEX (Lahn–Dill-type) Fe deposits resemble those from false gossans.

Ore from vein-type siderite deposits may create slags abundant in Pb, Cu, Zn and Sn, even when the primary mineralization was moderate but display the overall rather monotonous mineralogy of slags derived from iron ores. Base metal contents are too low for supergene alteration minerals to form and the sulfur contents of chalcopyrite, galena and sphalerite are insufficient to create a near-ambient environment of formation favorable for base metal sulfates under the recent climatic conditions.

By contrast, all slags from pyritiferous Cu deposits may easily be recognized even with the naked eye in the field and diagnosed at site as Cu slags. They qualify as an ore guide to massive sulfide deposits.

Around 400 BC, Celtic tribesmen headed N following the Regensburg Embayment where soft iron ores were easily accessible. From 700 to 1000 AD they dared to enter the densely forested eastern parts of the NE Bavarian Basement probably attracted by the abundance of copious firewood to run the kiln. Between 900 AD and 1630 AD base metal-bearing siderite veins and SEDEX Fe deposits were exploited by ancient miners in NE Bavaria. Stratabound sulphidic ore was recognized in that region for the first time only in the 17th century.

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