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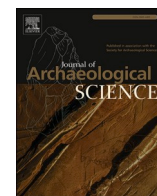


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Towards better reconstruction of smelting temperatures: Methodological review and the case of historical K-rich Cu-slugs from the Old Copper Basin, Poland

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ABSTRACT

Temperature is a crucial factor influencing the effectiveness of metal smelting process. When studied in historical slags it provides information on the evolution of smelting technologies over time and how humankind approached metal recovery. Methodological approaches to temperature reconstruction using pyrometallurgical slags vary and this study serves as a critical review of the methods used so far with the complex historical smelting site used as an example of the application of the methods. The example includes silica-undersaturated, potassium-rich Cu slags from four sites in the Old Copper Basin (Stare Zagłębie Miedziowe), Poland, and is of particular interest because (a) K-rich slag compositions are not widely found and this provides additional challenge to temperature reconstruction approach and (b) the site provides material of different ages (18th and 19th century) and, therefore, gives insight into potentially different pyrometallurgical processes. Several methods are compared and include phase diagrams, geothermometry (Cpx-WR), thermodynamic modelling with MELTS software and temperature XRD analyses with the main implication that most of the methods have their merits, but modelling by MELTS software returns the most reliable estimates of liquidus temperature. In fact, MELTS is the only method that returns differences of 200 °C in reconstructed temperatures between the studied sites, which signifies a change in smelting technique probably related to the change in input material. More importantly, MELTS may also be used to estimate crystallization interval (temperature difference between solidus and liquidus) that together with liquidus temperature gives insight into metal extraction efficiency for a given site and provides information on society advancement in metallurgy. The software can also be used cost-effectively for a large number of samples and its combination with experimental approach (temperature XRD analyses) provides the most promising tool to reconstruct differences in smelting technologies of ancient and historical metallurgical sites.

1. Introduction

Copper has been one of the most important metals in human history. Mined and smelted for nearly 7 millennia, it influenced the development of social structure, industry and technology (Radetzki, 2009). Copper smelting was one of the first human technological breakthroughs. Pyrometallurgical process changed over the years, especially concerning the use and types of furnaces applied for metal smelting. In historical and modern smelting with more advanced types of furnaces, numerous smelting parameters evolved as people learned how to separate ore and metal most efficiently.

Temperature is a crucial factor controlling the efficiency of metal

separation from ore, which is the core of metal smelting process. Currently, the process is strictly controlled and temperatures in the furnace are well-maintained using advanced equipment, but it has been that way only for the last 50–100 years. Before that, some smelters provided documentation with details including temperature (Agricola 1556), however, these were typically eye-based estimations, which were far from exact. Fortunately, written documents are not the only records of smelting conditions. Slag is another type of residue, which provides significant information regarding the smelting process. Slags are a by-product of pyrometallurgical metal production and an additional source of information on smelting techniques. We can only read from slags recently because of the enormous development of analytical

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techniques, which allow for detailed phase identification and precise chemical analyses. However, slags as a research material have been analysed by archaeologists for decades allowing archaeometallurgy to emerge (e.g. Tylecote, 1974; Gordon and Killick, 1993). From the archaeometric point of view, slags are irreplaceable for recreating conditions of historical smelting processes (Manasse and Mellini, 2002; Ettler et al., 2009a; Warchulski et al., 2015) and constitute a valuable addition to written documents with the advantage of often being preserved in better shape and larger quantities.

Reconstructions of exact temperatures are important to recognize different approaches to metal smelting between human populations (Humphris et al., 2009) as well as the cultural background of the metallurgical tradition and its social presentation (Pryce et al., 2007). Different questions arise for ancient and historical smelting as the changing smelting temperature can be either associated with differences in the ore or flux composition as well as with the evolution and different construction of the furnace. Any reconstructions also have to consider on-site variations reflecting inhomogeneous conditions in the furnace, especially for ancient smelting (Humphris et al., 2009). When accurate, temperature reconstructions of smelting process may answer many questions. However, estimated temperatures are often known to be imperfect and indistinguishable among different technologies (Pryce, 2008). Therefore, in order to perfect our interpretations of the transmission of ideas and technology among ancient and modern societies we need to use high-resolution temperature estimations.

Various methods have been applied for reconstructing temperatures achieved in furnaces during historical metal smelting (Table 1). Experimental studies focused on the fuel/ore ratio and construction of the crucible or furnace (Tylecote et al., 1977; Rothenberg, 1999). Experimental temperature reconstructions, i.e. with the application of thermocouples (Pryce et al., 2007; Catapotis et al., 2008) distinguished temperatures required to smelt metal accordingly to the chosen type of technology. The research also observed that temperatures achieved in the furnace often exceed liquidus (e.g. Merkel, 1990; Juleff, 1996; Catapotis et al., 2008; Pryce et al., 2010), suggesting that liquidus temperature should be interpreted as a minimal smelting temperature. Later studies aspired to reconstruct temperatures using smelting remains with the application of phase diagrams showing the mineral stability in low P (pressure) and high T (temperature) conditions. For example, VDE atlas (1981) assembles numerous simple and complex phase diagrams suitable for interpreting phase composition and formation temperatures of metallurgical slags (Manasse et al., 2001; Manasse and Mellini, 2002; Manasse and Mellini, 2002b). Tetrahedral diagram $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-FeO}$ has been established as most useful for slags, mainly because the mentioned oxides constitute dominant components of most slag types (Piatak and Seal, 2010; Hauptmann, 2014; Piatak et al., 2015). Advances in thermodynamics and an increasing number of experimental results produced more complex diagrams taking into account e.g., high concentration of metals in an oxidized form such as ZnO or PbO (Ettler et al., 2009a; Pelton et al., 2015), numerous components in the system (Jak et al., 1995), and partial pressures of oxygen (Kongoli and Yazawa, 2001; Burger et al., 2010) or the oxygen fugacity, a term used more often among Earth-scientists working in archaeometallurgy (Vitková et al., 2010; Benvenuti et al., 2016). Another approach used both chemical and mineral constituents in a single phase diagram ($\text{SiO}_2\text{-CaAl}_2\text{Si}_2\text{O}_8\text{-FeO}$) (Mascaro et al., 1995; Sáez et al., 2003; Costagliola et al., 2008). Thermodynamic modelling can be done by software such as FACT (Jak et al., 1995; Ettler et al., 2009a; Pelton et al., 2015) or MELTS (Álvarez-Valero et al., 2009) that return the most precise temperature estimations. Some argue, however, that because of the presence of glass, phase equilibrium still cannot be properly calculated without the legitimate database (Álvarez-Valero et al., 2009). Recently, a new approach using rock geothermometers aimed to achieve more exact estimations (Warchulski, 2016). Unfortunately, there are numerous restrictions for applying this method such as equilibrium cooling, the large size of phase grains and quality research equipment

for analysing only the centre of a chosen grain, not always applicable to fine-grained crystalline mixtures constituting slags.

Only some of the published articles engaged in a discussion regarding problems associated with detailed temperature reconstructions (Bassiakos and Catapotis, 2006; Ettler et al., 2009a; Pryce et al., 2010; Kierczak and Pietranik, 2011; Warchulski et al., 2015). These studies showed that several features need to be considered for proper temperature estimation. Slag chemistry and phase composition, amount of the metallic phases (and their separation from ore), as well as slag's texture, are worth considering (Table 1). These features are a result of equilibrium (or a lack of equilibrium) conditions during cooling. Quenched slags tend to be amorphous (Álvarez-Valero et al., 2009) whereas slowly, air-cooled slags might crystallize in equilibrium developing holocrystalline texture (Kierczak et al., 2009), both of which have been used for various approaches to temperature reconstruction (e.g. Ettler et al., 2001; Thondhlana et al., 2016). It has been proven that in bloomery iron smelting, conditions might vary significantly even within a single smelting episode (Humphris et al., 2009). This is, however, not the case in regard to historical copper smelting, where with more organized mining and standardized smelting, a statistically reliable number of samples of big enough size provides a coherent set of data, as presented further in our research.

In this study, we aim to summarize the most applicable temperature-estimation methods proposed in the literature and suggest the best solution, which we apply to chemically unusual (K-rich) Cu-slugs from historical smelting sites – Leszczyna and Kondratów located in the Old Copper Basin (OCB), southwestern Poland. We stress the fact that each slag is different and often a “personalised” approach is needed to successfully “read” the recorded temperatures. Also, well-established phase composition and phase chemistry are required for achieving a reliable estimation. We show that with more advanced methods, disequilibrium samples – more common in slags – provide useful and trustworthy temperatures. We also aim to define which temperatures can, in fact, be reconstructed and consider differences in ancient and historical smelting processes.

2. Temperature reconstructions – hopes and problems

2.1. Experimental studies

Experimental studies developed a basis of archaeometallurgical science allowing for verification of furnaces construction, achieved temperatures and oxygen conditions in the furnaces (Merkel, 1990; Timberlake, 2007; Burger et al., 2010; Hanning et al., 2010). Experiments can be conducted in the field, reconstructing the actual smelting procedure with directly measured temperatures (e.g. analysing the temperature in different parts of the furnace, Catapotis et al., 2008). The interpretations are based on the comparison between the ancient and the created wastes (Friede et al., 1984). The problem related to such experimental studies is the fact that smelting involves numerous varying parameters (furnace design and construction materials (Catapotis et al., 2008)) and such complex conditions can be difficult to recreate. Also, application of thermocouple arrays is generally restricted to the temperature of approx. 1250–1300 °C. Thus, overstepping of the liquidus temperature can be confirmed, but with no other details on the exact smelting temperature (if high temperatures are maintained for a longer period of time, thermocouples must be removed).

Another way to reconstruct temperatures are laboratory experiments, which are a promising, but rather uncommon technique (Bourgarit, 2019). Slags can either be remelted in a crucible (Burger et al., 2010; Hanning et al., 2010) or observed in the form of pyrometric cones (e.g. Hsieh, 2019). The latter is often applied to pottery analyses, but rarely to archaeometallurgy. A promising technique is X-Ray Diffraction (XRD) combined with thermal analysis that returns information on changes in phase composition with contemporaneous changes in material temperature up to liquidus. The final method is proposed in this

Table 1
Summary of previous temperature-focused studies.

Type of slag	Smelting activity	Site	Method used for temperature estimation	Achieved temperatures	Comments	Phase composition	Reference
Cu slags	3rd century BC	Cabezo Juré, Huelva, Spain	phase diagram SiO ₂ -anorthite-FeO; minerals stability diagram: $\log(fO_2)$ -T	1) >1100°C (furnance) 2) 900–1000°C (crucible refining)	- temperature estimations are based on mineral association in the slag - temperatures returned by the phase diagram are too high	1) Qz, Mgh, Mt, Px (Di-Hd), Pl, Cpr, Delaf, Fa, Qz, sulphides 2) Qz, Alb, Kfs, Mt, Mgh, sulphides	Sáez et al. (2003)
Cu slags	1) 1st century BC – 5th AD 2) 19th century AD	São Domingos, Portugal	MELTS software; TWQ software phase diagrams FeO-Al ₂ O ₃ -SiO ₂ FeO-CaO-SiO ₂ phase diagrams FeO-CaO-SiO ₂ Fe-Cu-S	MELTS 1200–1400°C phase diagrams 1000–1400°C 1150–1300°C	- phase equilibria cannot be calculated with conventional thermometry – absence of proper thermodynamic database with glass as a phase - unfused material present in the slag leads to temperature overestimation in phase diagram - magnetite is a common first phase to crystallize in historical slags but is not included in phase diagrams - liquidus temperature depends on the redox conditions	Gl, Ol (Fa-Kir), Fe-oxides, Qz, sulphides,	Álvarez-Valero et al. (2009)
Cu slags	Bronze Age	Chrysokamino, Greece				Gl, Px (Hd), Ol, Qz, Wus, Mt, Cu prills, sulphides	Bassiakos and Catapotis (2006)
Cu slags	14th – 16th century AD	Rudawy Janowickie Poland	phase diagram SiO ₂ -FeO-Al ₂ O ₃	1200°C, locally 1300°C (crystalballite presence)	- disequilibrium conditions during cooling result in unbelievable estimations with phase diagrams - temperatures in phase diagrams are often too high for historical smelting - additional chemical components or an unmelted furnace charge change melt equilibrium, thus make reconstructions on the basis of phase diagrams unbelievable - samples plot near tridymite field but no SiO₂ crystals are present	Gl, Ol (Fa), 2) Gl, Ol (Fa), Spl (Hc), Px, Crs, Fs, Qz, sulphides, metallic phases	Kierczak and Pietranik (2011)
Cu slags	19th – 20th century AD	Lower Area One, Buttle, Montana, USA	phase diagram CaO-SiO ₂ -FeO	1100–1300°C		Gl, Ol (Fa, Kir), Px (Hd), Mt, Hm	Kaplan (2016)
1) Cu slags, 2) Fe slags	7th century BC - 1st century AD	Populonia-Baratti, Italy	phase diagram CaO-FeO-SiO ₂	~1150°C		1) Gl, Ol (Fa), Px, Mt, 2) Gl, Ol (Fa, Kir), Wus, Qz, Sch,	Benvenuti et al. (2000) Franzini and Perchiazzi, 1992
1) Pb, Cu, Ag slags 2) Cu slags	10th-14th century AD	1) Rocca San Silvestro, 2) Campiglia, Italy	phase diagram SiO ₂ -anorthite-FeO; diagram: $\log(fO_2)$ -T	1100–1150°C	equilibrium is required for correct temperature estimations	1) Gl, Ol (Fa), Px (Hd, Jh) 2) Pb slags – Kir-glaucocroite; sulphide	Mascaro et al. (1995)
Cu slags (Pb, Ag)	8th – 1st century BC, 11th century AD	Capattoli, Italy	phase diagram CaO-SiO ₂ -FeO Fa-Kfs phase diagram	1100–1150°C olivine phase diagram 800–1000°C	- inaccurate location of the curves on the olivine phase diagram - olivine diagram not applicable for Ca-poor samples	Gl, Ol (Fa, Kir), Px (Hd), Qz,	Manasse et al. (2001)
Cu, Pb/Ag slags	13th-14th century AD	Massa Martima, Arialla, Rocchette Pannocchieschi, Italy	VDF calibration (not specified)	1150–1300°C	- the estimated solidification temperature represents a minimal furnace temperature - high-temperature phases (mellite, olivine) support high-temperatures estimations	Gl, Px, Mll, Spl, Ol (Kir, Fa)	Manasse and Mellini (2002)
Cu slags	3rd millennium BC	Cabrières Hérault, France	slags microstructures, Sb concentration	1000–1200°C	>1080°C – needed to liquefy Cu with 1–5% Sb - iron in the melt composition dramatically lowers liquidus temperature	Gl, Qz, Crs, Spl (Mt), Cpx (Ag, Sl), Wlm, sulphides	Bourgarit et al. (2003)
Cu-Fe slags	18th-20th century AD	Servette - Saint-Marcel, Val D'aosta, Western Italian Alps	phase diagram FeO-SiO ₂ -Al ₂ O ₃ Fe-Fa solid solution diagram Cu/Fe ratio	1100–1380°C	Fe-enriched olivine core indicates a high crystallization temperature	Gl, Ol, Spl, Wus, sulphides, Fe-Cu alloy	Tumlati et al. (2005)

(continued on next page)

Table 1 (continued)

Type of slag	Smelting activity	Site	Method used for temperature estimation	Achieved temperatures	Comments	Phase composition	Reference
1) Fe slags 2) Cu slags	1st millennium AD	Shankare Hill, South Africa	phase diagram $\text{FeO-SiO}_2(\text{TiO}_2 + \text{Al}_2\text{O}_3)\text{-CaO}$ ($+\text{MgO} + \text{P}_2\text{O}_5$)	1100–1300°C >1250°C – exsolved Fe in the copper prills	- complex chemical composition affects the melting point - Fe exsolutions in Cu prills appear in > 1250°C 15%–30% vol. of Fe exsolutions in Cu prills >1400°C - Quartz presence in the slag – liquidus T not achieved or insufficient melting time or over addition of SiO_2 flux - variations in sulphides chemistry – associated with various temperatures - For vitreous samples – glass as a representative chemical composition	1) Ol, Spl, Wus, Fe 2) Ol (Fa), Spl (Md), Cu, Gl	Thondhlana et al. (2016)
Cu-Co slags		Nkana, Mufulira, Chambishi Zambia	phase diagram $\text{SiO}_2\text{-FeO-CaO}$	1150–1400°C		Cpx (Di-Hd), Ol (Fa, Frs, Kir, Mct), Cu and Zn oxides, Lct, An, Spl (Mt), Gl, Qz, sulphides and metallic phases	Vitková et al. (2010)
1) Fe slags, 2) base metal slags	1) Etrusco-Roman times, 2) Middle Ages	Pecora River Vakkey, Italy	phase diagram $\text{SiO}_2\text{-anorthite-FeO}_{\text{tot}}$	1100–1200°C		1) Gl, Fa, Wu, Mt, Hc, Gth, Qz, Pl, 2) Fa, Hd, Ptd, Mt, Mll, Qz	Costagliola et al. (2008)
Polymetallic slags	13th–15th century (slags 16th–18th)	Kutná Hora, Czech Republic	phase diagram (CaO–MgO)–($\text{SiO}_2\text{-Al}_2\text{O}_3$)–(FeO-MnO)	1150–1300°C 1) 1200–1300°C 2) 1150–1200°C	the estimated solidification temperature represents a minimal furnace temperature	Cpx (Hd), Ol (Fa), Sp, Fbs, Qz	Manasse and Mellini (2002)
1) Pb 2) Pb–Zn	13th century AD	Hartz Mountains, Germany	phase diagrams 1) CaO–FeO– SiO_2 2) CaO–ZnO– SiO_2	1) 1250–1400°C 2) 1150°C	high CaO/SiO_2 ratio – result of a high melting temperature	Ol (Fa, Mct), Wlm, Sp, Mll, Hyl, Px (Hd), Pl (An), sulphides	Chaudhuri and Newesely (1993)
Pb, Ag slags	14th century AD	Bohutín, Příbram district, Czech Republic	phase diagram CaO– SiO_2 –FeO	1150–1450°C, mean 1300°C	chemical composition of surface glass corresponds to the composition of the initial slag melt	Ol (Fa, Kir), Cpx–Hd, Mll, Spl, Gl, sulphides	Ertler et al. (2001)
Pb, Ag slags	14th century AD	Bohutín, Příbram district, Czech Republic	phase diagrams 1) $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-FeO}$ 2) $\text{SiO}_2\text{-PbO-FeO}$ FactSage software	1) 1300–1700°C, 2) 800–1200°C 700–1200°C (modelling)	- phase diagrams return overestimated temperatures - unmelted quartz and residual feldspars in slag – liquidus T not achieved or insufficient melting time	Fa, Px (Fs-Di), Fsp, Qz, Crs, Gl, Spl, Hm, Gln, Pb	Ertler et al. (2009a)
Zn–Pb slag	19th–21st century AD	1) Piekary Śląskie, 2) Katowice, 3) Ruda Śląska, Poland	geothermometers: Ol–WR, Px–WR, Fsp–WR phase diagrams CaO– SiO_2 –MgO CaO– SiO_2 – Al_2O_3 FeO– SiO_2 – Al_2O_3 CaO– SiO_2 –FeO MgO– SiO_2 – Al_2O_3 phase diagrams $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-CaO}$ $\text{SiO}_2\text{-CaO-FeO}$ $\text{SiO}_2\text{-CaO-FeO}$ olivine composition experimental study phase diagrams CaO– SiO_2 –FeO $\text{Al}_2\text{O}_3\text{-SiO}_2\text{-CaO}$ $\text{Al}_2\text{O}_3\text{-SiO}_2\text{-CaO}$ Fe-based thermometer Fe–As phase diagram	geothermometers 1) 987–1314°C 2) 1141–1353°C 3) 1063–1261°C phase diagrams: 1) 1100–1800 2) 1300–1500 3) 1300–1600 1200–1500°C 1500–1700°C – inclusions and residual glass experiments: liquidus ~950–1100°C solidus ~875–950°C phase diagrams 1200°C 1400°C 1720°C Thermometer: 1100°C	phase diagrams return unbelievable estimations for historical smelting equilibrium conditions during crystallization are required when reconstructing liquidus T on the basis of geothermometers	1) Gl, Spl, Px, Pl, 2) Mll, Ol (Kir–Mct), Lct, Nph, sulphides, 3) Ol (Kir–Mct), Fsp, Sp, Hm, sulphides	Warchulski (2016)
Zn–Pb slags	18th–19th century AD	Orzeł Biały, Bytom-Piekary Śląskie, Poland			olivine composition (Mg concentration in the core and rim) used to estimate temperature range during crystallization	Gl, Spl, Hm, Zn, Ol (Mct–Kir), Px, Mll, Fsp, Nph, Kls, Lct, Tnt, Mw, Gln, sulphides	Warchulski et al. (2015)
Pb–As slags	1st–2nd century AD, 19th century AD, analysed slags 888–1010 BP	Wiesloch, Heidelberg, Germany			- Fe thermometer can only be applied with large grains for EMPA analyses - ternary diagrams are too simple for complex chemical composition - small amount of alkali lowers the liquidus temperature	Gl, Ol (Fa, Kir), Wus, Spl, Lsc, Lct, Hd, sulphides	Ströbele et al. (2010)

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Table 1 (continued)

Type of slag	Smelting activity	Site	Method used for temperature estimation	Achieved temperatures	Comments	Phase composition	Reference
Fe slags	18th–19th century AD	Hopewell Furnace National Historic Site, Pennsylvania, USA	phase diagrams MgO–SiO ₂ –Al ₂ O ₃ , CaO–SiO ₂ –Al ₂ O ₃ , åkermanite-gehlenite phase diagram	1300–1500 °C 1300–1400 °C Mellite diagram: ~1400 °C	- cristoballite presence – may be stable <1470 °C but still points to high furnace temperatures - temperatures based on the phase diagram are overestimated due to the presence of unmelted quartz	Gl, Px, Qz, Crs, Ol, Mill, Grt, Sp, Pl, Kfs, other, sulphides	Piatak and Seal II (2012)
Fe slags	3rd–4th century AD	Aksu, Ethiopia	phase diagram FeO–SiO ₂ –Al ₂ O ₃	1150 °C		Gl, Fa, Spl (Mt, Hc)	Severin et al. (2011)
Fe slags	Iron Age 1st century AD	Johannesburg Africa	phase diagram SiO ₂ –anorthite–FeO	1150–1180 °C 1440–1490 °C	- SiO₂–anorthite–FeO – limited, inaccurate estimations - phase diagram not adequate for Ca- and Al-rich as well as Fe-poor samples and more than 3 main components	Wus, Fa	Friede et al. (1984)
Fe slags	19th century AD	Uganda	phase diagram FeO + MgO–SiO ₂ –Al ₂ O ₃	1100–1250 °C		Gl, Ol (Fa)	Humphris et al. (2009) Rehren et al. (2007)

Abbreviations after Whitney and Evans, 2010: Anorthite = An, Augite = Ag, Cristoballite = Crs, Clinopyroxene = Cpx, Cuprite = Cpr, Delafosite = Delaf, Diopside = Di, Fayalite = Fa, Feldspar = Fsp, Ferrobustamite = Fbs, Ferrosilite = Fs, Forsterite = Frs, Galena = Gln, Garnet = Grt, Glass = Gl, Goethite = Gth, Hedenbergite = Hd, Hematite = Hm, Hercynite = Hc, Hyalophane = Hyl, Iscorite = Isc, Johannsenite = Jh, Kalsilite = Kls, K-feldspar = Kfs, Kirschsteinite = Kir, Leucite = Lct, Maghemite = Mgh, Magnetite = Mt, Mellite = Mll, Merwinite = Mw, Monticellite = Mct, Nepheline = Nph, Olivine = Ol, Petedunnite = Prt, Plagioclase = Pl, Pyroxene = Px, Quartz = Qz, Salite = Sl, Scheelite = Sch, Sphalerite = Sp, Spinel = Spl, Titanite = Tnt, Willemite = Wlm, Wustite = Wus, Zincite = Znc.

study and undoubtedly yields exact estimations, however, as with all experimental techniques, it is costly and cannot be applied for a large number of samples. For slag studies, it is a drawback, because slags may be highly heterogeneous in different scales (sample heterogeneity, on-site heterogeneity and between sites heterogeneity). Additional technique is required to take into account this variety.

2.2. Chemical phase diagrams (oxides)

Chemical phase diagrams are based on experiments and thermodynamic calculations and show stabilities of phases at range of compositions and temperatures. Therefore, knowing slag composition, one should be able to estimate the temperature when it is fully molten. However, uncertainties in the reconstruction of the physicochemical conditions of metal smelting this way are often mentioned (Sáez et al., 2003; Bassiakos and Catapotis, 2006; Pryce, 2008; Chiarantini et al., 2009). The chemical phase diagrams are developed for three to four major elements. Even if these oxides comprise 50–90 wt% of the bulk composition, a few other components might also constitute more than 10 wt% each, affecting liquidus temperature and temperatures of phase crystallization (e.g., Friede et al., 1984; Kongoli and Yazawa, 2001; Vitková et al., 2010; Kierczak and Pietranik, 2011; Killick et al., 2016). Despite that, tetrahedral system SiO₂–Al₂O₃–CaO–FeO (Osborn and Muan, 1960) is widely used (e.g. Rehren et al., 2007; Warchulski et al., 2015; Artemyev et al., 2018) quite often without emphasizing if the total composition reflects that of the diagram i.e. how applicable the diagram is for selected samples. Usually the range of temperatures reconstructed from the diagrams is wide (Ettler et al., 2009a; Warchulski, 2016) and presumably, temperatures are overestimated because addition of other elements is not taken into account (Maldonado and Rehren, 2009; Ströbele et al., 2010; Kong et al., 2013). Especially high relative proportion of silica in comparison to CaO, Al₂O₃ or FeO at the low total SiO₂ content (40–50 wt%), results in samples plotting close to the silica end-member, in the field of high-temperature silica polymorphs. These polymorphs (tridymite, cristoballite) are rarely present in slags, indicating that the reconstructed temperatures are not valid. This may be due to too many components in the system or because equilibrium was not attained (Kierczak and Pietranik, 2011 and references there). Also, most common chemical phase diagrams consider temperatures significantly higher than 1300 °C (SiO₂–CaO–Al₂O₃: 1300–2570 °C; SiO₂–CaO–FeO: 1093–2570 °C; SiO₂–Al₂O₃–FeO: 1148–2020 °C) (Table 2) which constitute unlikely conditions for historical metal smelting. Naturally, slags usually do not plot in the highest temperature fields, instead commonly plotting in a range of 1150–1300 °C. This, however, suggests either that slags from different periods and locations were smelted in very similar temperatures or that results achieved with this diagrams are too generalized.

2.3. Chemical phase diagrams (metallic elements)

Chemical phase diagrams based on minor elements have also been applied to reconstructing smelting temperatures (Tumiati et al., 2005). Copper-iron (Cu–Fe) eutectoid alloy compositions seem suitable for recognizing liquidus temperature of Cu-slugs, which can contain Cu–Fe alloys (Potysz et al., 2015). Such alloys are however rather uncommon (Manasse and Mellini, 2002b; Vitková et al., 2010; Kądziołka et al., 2019) or chemically complex (Piatak et al., 2003) and signify the failure of the smelting process. Therefore, this method may be applied in rare cases to study why Cu–Fe metal alloy was produced instead of the required Cu metal.

2.4. Mineral phase diagrams

Mineral phase diagrams are based on a higher number of components than the chemical phase diagrams (Table 2). Particularly SiO₂–anorthite–FeO system (Friede et al., 1984; Mascaro et al., 1995;

Table 2

Set of methods applicable for temperature reconstructions with accessible range of temperatures and notes to what kind of samples the method may be applied.

Method	Detailed	T (min-max)	Applicable for
Chemical phase diagram	1) CaO–SiO ₂ –Al ₂ O ₃ 2) CaO–SiO ₂ –FeO 3) SiO ₂ –Al ₂ O ₃ –FeO	1) 1300–2570°C 2) 1093–2570°C 3) 1148–2020°C	samples with a high concentration of SiO ₂ –Al ₂ O ₃ –CaO–FeO or at least three of these components (that should constitute at least 80–90% of the total composition). Temperature estimations are reliable only for samples crystallizing in equilibrium conditions (Kierczak and Pietranik, 2011) and low amount of alkali additives
Chemical phase diagram	Cu–Fe	700–1500°C	slags with Cu–Fe alloys displaying signs of surpassing solvus (exsolution of Cu and Fe among a single phase)
Mineral phase diagram	SiO ₂ –CaAl ₂ Si ₂ O ₈ –FeO	1070–1713°C	slags dominated by phases present on the diagram, where the sum of chemical elements constitutes at least 70–80 wt%
Mineral phase diagram	KAlSi ₂ O ₆ –MgCaSi ₂ O ₆ +CaSiO ₃ –CaAl ₂ Si ₂ O ₆	1249–1413°C	SiO ₂ unsaturated slags with phase composition dominated by pyroxenes, plagioclase and leucite
Olivine composition	1) Mg ₂ SiO ₄ –Fe ₂ SiO ₄ 2) Fe ₂ SiO ₄ –CaFeSiO ₄	1) 1200–1890°C 2) 700–1200°C	relatively slowly-cooled slags containing euhedral, big and preferably zoned olivines. Bowen and Schairer (1935) diagram is better suited for the Mg-rich system, Bowen et al. (1933) for the Ca-rich system
Geothermometers	Px-bulk rock Olivine-bulk rock Feldspar-bulk rock	no limits	slags containing clinopyroxenes, olivines or feldspars, preferably crystallizing in equilibrium conditions; for believable results, a couple of models should be applied
MELTS	1) bulk-rock	no limits	all samples, useful especially for amorphous slags
FactSage and ThermoCalc	2) EMPA glass	no limits	all materials, useful especially for samples of uncommon chemical composition
XRD	1) room temperature 2) high temperature		all materials, a complementary method for recognition of tridymite or cristoballite presence and for analyses of samples texture in near-liquidus temperature

Costagliola et al., 2008; Addis et al., 2016) is applied for reconstructing smelting temperature. The temperatures are generally lower than those reconstructed from chemical phase diagrams, however usually phases in the diagrams do not correspond to those present in the slag. For example, the SiO₂–anorthite–FeO system mixes chemical and mineral components and its application leads to incorrect estimations as the amount of crystallized SiO₂ or FeO is incomparably lower than anorthite. Phase composition of metallurgical slags varies strongly depending on numerous factors e.g., ore chemical and mineral composition and the regional setting which influences the type of flux added as well as redox conditions in the furnace. Another problem is that slag phases might often have chemical compositions deviating from their natural counterparts and crystallize in slightly different temperatures as a consequence. The implication is that not all mineral phase diagrams can be used for slags and a chosen diagram should be based on major phases present in the sample. This approach cannot be used for vitreous materials. However, well-chosen mineral diagrams should yield better temperature estimates than chemical diagrams and this is illustrated by the diagram chosen for K-rich slags analysed in this study.

2.5. Olivine composition

Olivine is a common constituent of slags (e.g., Lottermoser, 2002; Piatak et al., 2004; Mateus et al., 2011; Rozendaal and Horn, 2013; Potysz et al., 2016). Olivine crystallizing in near equilibrium conditions might be used for temperature estimation based on forsterite to fayalite ratio (Bowen and Schairer, 1935; Tumiaty et al., 2005; Bourgarit et al., 2008; Warchulski, 2016). However, the system fayalite–forsterite is chemically too simple for most of the slags, in a similar way the chemical diagrams are, and the reconstructed temperatures in the range of 1200–1900 °C are too high and highly uncommon for historical smelting. For simple Ca-rich slags, Bowen's (et al., 1933) fayalite–kirschsteinite system is better suited for reconstructing smelting temperatures (Manasse et al., 2001) with a range of temperatures between 800 and 1200 °C (Table 2). However, to use this approach effectively, a combination of two systems (fayalite–forsterite and fayalite–kirschsteinite) should be used only for samples dominated by olivines. This approach would allow to focus on most interesting temperature range of 1100–1400 °C covered by the two systems.

2.6. Geothermometers

So far, geothermometry has been used only twice for slags (Warchulski, 2016; Toffolo et al., 2018), but it shows a great promise in temperature estimations. Geothermometers were previously extensively applied to reconstruct crystallization temperatures of igneous rocks (Putirka et al., 2003; 2007, references therein) and currently it is possible to choose from a wide set of thermometers, fitting the sample's chemical and mineral/phase composition. Especially glass, olivine–liquid (whole rock or glass) (Putirka et al., 2007; Putirka, 2008), pyroxene–liquid and feldspar–liquid (Putirka, 2005) thermometers should provide useful information when applied to slags as all of these components are common in phase assemblages and glass, a good approximation of liquid composition, is usually present and easy to analyse. Models are well-developed and give the possibility to calculate temperatures for anhydrous compositions and temperature range lower than 1650 °C (Beattie, 1993), the conditions typical for slag formation. Warchulski (2016) applied olivine-, feldspar-, and pyroxene-based geothermometers for the reconstruction of temperature conditions of 19th-century Zn-slugs and achieved coherent results for all of the geothermometers with no clear trends of higher temperature assigned to one of the methods. In Toffolo et al. study (2018) olivine–spinel geothermometry based on the Fe–Mg partitioning (Sack and Ghiorso, 1991) was applied and resulted in varying estimations in the range of 860–1400 °C. Authors mentioned, however, that these results are ambiguous to interpret as both olivine and spinel, i.e. high-temperature phases, could have formed during the initial heating without significant transformation during smelting (commented also in Friede et al., 1984). We believe that although geothermometers do not return liquidus temperatures, they provide valuable information on heating and cooling conditions.

2.7. Thermodynamic reconstructions

MELTS Software (Sack and Ghiorso, 1991; Asimow and Ghiorso, 1998) offers highly advanced thermodynamic calculations for specific chemical composition and pressure–temperature (P–T) conditions. Besides MELTS, FactSage, Thermo-Calc and other, slightly less advanced softwares such as PELE and Petrolog3 were developed. To some extent,

these softwares return similar results. MELTS, FactSage and Thermo-Calc are irreplaceable for samples of specific chemical composition as only these acknowledge minor elements in calculations and already proved useful for slags of specific chemical composition (Ettler et al., 2009a). MELTS was chosen for this study as the modelling may be executed in the surface pressure (0.1 MPa) and for this reason, is well suited for slags crystallization. MELTS has been previously used only once for slag analysis (Álvarez-Valero et al., 2009). Although water addition in the starting melt composition presented in the study is unlikely, authors achieved temperatures approximately 1230–1290 °C which seem believable as smelting temperatures for both, historical and modern slags. With software's simple layout and rules, it is a powerful tool for characterizing the smelting and crystallization processes. Information obtained from MELTS modelling includes (a) the liquidus temperature, (b) amount of phases crystallized in selected temperature intervals, (c) predicted chemical changes in melt and phases, as well as (d) the temperature difference between the liquidus and solidus, further called crystallization interval. The information obtained from MELTS should be verified based on the comparison between observed and predicted phase and chemical compositions, since numerous studies have shown that modelled and observed chemical compositions of phases often differ due to the limitations of MELTS algorithm (Eskandari et al., 2018, references there). Therefore, it is obligatory to accept models consistent with observed phase assemblage and verify them through detailed mineralogical and chemical study.

3. The case study of K-rich slags from the OCB

3.1. Materials and methods

3.1.1. Geological and historical setting

The research area is located in southwestern Poland about 80 km west of Wrocław in Lower Silesia (Fig. 1). This is the western part of the Sudety Mountains, Kaczawskie Foothills region, south-eastern margin of the North Sudetic Basin. In the 20th century, the area was named the 'Stare Zagłębie Miedziowe' - Old Copper Basin (OCB) in reference to Cu-mineralization and its historical mining. Earliest findings of Au–Ag mining in the OCB are dated back to the 13th century AD (Stolarczyk et al., 2015). First official attempts of Cu-mining took place around the 15th century in Złotoryja area. Soon exploitation started in the Leszczyna Basin. The exploitation of Cu-ore shales and marls of Zechstein Kupferschiefer formation had been conducted on a small scale for several centuries since the beginning of the 16th century (Potysz et al., 2018). As the ore was not rich and not thick enough, the process was problematic. Several quarries opened but failed after a few decades with *Character* (17th century), *Leszczyńska* (17th century) and *Stilles Glück* (19th century) being the most successful. In a similar way, metal smelting was established a couple of times but was most successful with *Stilles Glück* smelter, working in Leszczyna with a mine of the same name.

Based on the archaeological record sites of slags occurrence have different ages (Stolarczyk, 2009; Stolarczyk, 2010). Two smelters mentioned in historical records were confirmed by archaeological

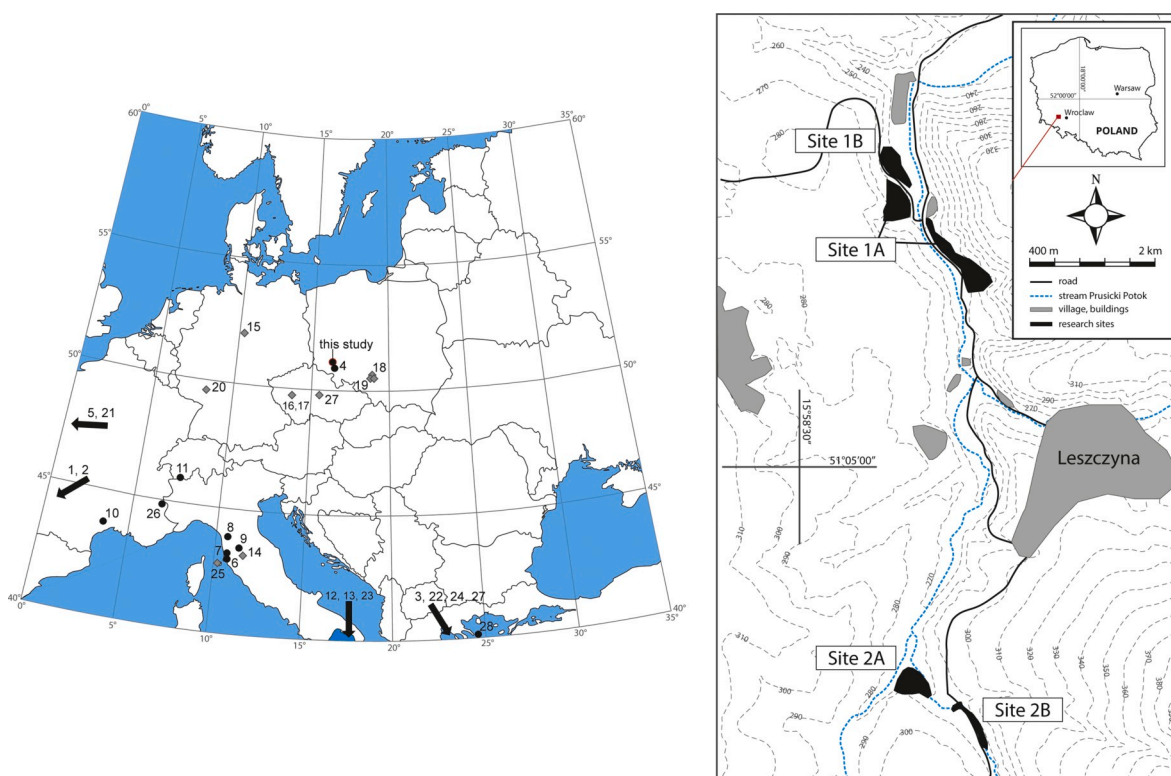


Fig. 1. A: Map of central Europe with sites for which temperature reconstructions were carried out. Circle: Cu slags, diamond: other slags. B: Simplified map of the study area with sites location (1) Sáez et al., 2003, (2) Álvarez-Valero et al., 2009, (3) Bassiakos and Catapotis, 2006, (4) Kierczak and Pietranik, 2011, (5) Kaplan, 2016, (6) Benvenuti et al., 2000; Franzini and Perchiazzi, 1992, (7) Mascaro et al., 1995, (8) Manasse et al., 2001, (9) Manasse and Mellini, 2002b, (10) Bourgarit et al., 2003, (11) Tumiati et al., 2005, (12) Thondhlana et al., 2016, (13) Vitková et al., 2010, (14) Costagliola et al., 2008, (15) Chaudhuri and Newesely, 1993, (16) Ettler et al., 2001, (17) Ettler et al., 2009b, (18) Warchulski, 2016, (19) Warchulski et al., 2015, (20) Ströbele et al., 2010, (21) Piatak and Seal, 2012, (22) Severin et al., 2011, (23) Friede et al., 1984, (24) Humphris et al., 2009, Rehren et al., 2007, (25) Benvenuti et al., 2016, (26) Bourgarit et al., 2008, (27) Pryce et al., 2007, (28) Pelton et al., 2015.

research (Stolarczyk et al., 2015; Stolarczyk, 2012). These include the *Stilles Glück* (Silent Luck) smelter operating between 1865 and 1882 (Festenberg-Packisch, 1881) – Site 1A – and an unnamed older smelter located in the southern part of the area – Site 2A – operating for an unknown period in the 18th century (Fechner, 1903). Sites 1B and 2B are located in the close proximity to 1A and 2A, respectively, but its age is uncertain due to varying macroscopic appearance (Site 1B) and signs of post depositional displacement (Site 2B). Various ages among Sites 1A and 2A, as well as the uncertainties regarding 1B and 2B, allowed to assume that the smelting temperatures should differ. This assumption was based on the mentions of larger shaft furnaces in *Stilles Glück* smelter constructed a couple of years of the smelters activity (1A) (Stolarczyk et al., 2015). For this reasons, the OCB slags constituted valuable research material to verify various approaches to temperature reconstruction.

3.1.2. Sampling

The material chosen for this study consist of 33 slag fragments from two localities – Leszczyna (Site 1) and Kondratów (Site 2) (Fig. 1). Both sites were divided into A and B sections with A sections located nearby historical smelter with the assumption that the slags are concurrent, whereas B sections located in a close neighbourhood but the slags cannot be clearly linked to the smelter production.

Site 1 (51°5'25.569"N 15°58'46.167" E) in Leszczyna is a group of historical mines, shafts and waste heaps. Stolarczyk et al. (2015) suggested that most of the slag production at this site was limited to the 19th century (1865–1882) with *Stilles Glück* mine and smelter activity (Site 1A). We expect the marginal heaps located west from the stream (Prusicki Potok) not to be associated with a dominating activity in the *Stilles Glück* smelter due to a separated location and varying macroscopic appearance (Site 1B). Therefore samples taken at the Site 1A are related to dominating 19th-century metal production and samples collected at the Site 1B are of an unknown age. Slags in both sites form individual blocks up to a 50 cm in diameter, which are black and highly porous, usually of irregular or ovoid shape (Fig. 2).

Within Site 2 (Fig. 1) only the approximate location of the smelter operating in 18th century was recognised (51°4'34.108"N 15°58'35.354" E) with a small number of wastes spread in the area (Site 2A). A large amount of slags occurs about 150 m east of the smelter in the form of 50 m long section along the stream Prusicki Potok, which was distinguished as Site 2B. This observation is consistent with the archaeological record (Stolarczyk, 2009). Slags from Site 2 are massive and distinctly smaller than those found at Site 1, they also tend to vary in

colour including black, brown, green, blue and red.

Altogether, 13 slag samples were collected at Site 1A, 5 samples at Site 1B, 11 samples at Site 2A and 4 samples at Site 2B.

3.1.3. Analytical methods

Detailed description of the analytical procedures is given in Supplementary Materials 1 (SM1), here we present only a summary of the methods used in the study. Petrographic observations were conducted using polarizing and electron (Scanning Electron Microscope – SEM) microscopes. Crushed slag samples were analysed for major and minor elements (with ICP-OES and ICP-MS) and electron microprobe (EMPA) was used for acquisition of phases chemistry. Experimental thermal XRD analyses were conducted to check on the validity of temperature estimations achieved with three pyroxene-whole rock geothermometers (Putirka et al., 1996, Putirka et al., 2003) and the MELTS-rhyolite v.1.0.2. software package (Gualda et al., 2012; Ghiorso and Gualda, 2015). The laboratory XRD-based experiments were conducted for two samples, whereas thermodynamic calculation for fourteen yielding better characterization of the heterogeneity of the sites.

3.2. Results

3.2.1. Bulk-rock geochemistry

The studied slags plot in two fields in the FeO–SiO₂–CaO ternary diagram (Fig. 3). Interestingly, most of the slags show Fe-poor composition typical for slags originating from iron production (Piatak et al., 2015) (Fig. 3). Detailed chemical compositions of all analysed samples are presented in the Supplementary Materials 3 (SM3). The chemical composition is dominated by SiO₂ (42.5–49.8 wt%), CaO (12.6–27.4 wt%) and Al₂O₃ (9.6–18.9 wt%). Within minor constituents Fe₂O₃ (4.7–11.6 wt%), K₂O (3.4–6.7 wt%), MgO (1.7–3.6 wt%) and Cu (0.15–4.4 wt%) are present. In particular, relatively low amounts of SiO₂ and high K₂O are specific for the analysed slags resulting from a CaO and K₂O-rich chemical composition of ore-bearing rocks (marls and shales). The amount of metallic elements commonly appearing in the slags is low, not exceeding 1300 mg/kg Zn, 250 mg/kg Co, 185 mg/kg Pb and 80 mg/kg As. The S contents are also low (on average 0.3 wt%).

Slags from three of the studied Sites (1A, 1B, 2B) are chemically alike with apparent variations in SiO₂, Al₂O₃ and K₂O concentration (Fig. 4A, D). However, some differences are observed between Site 1B and the others. For example, an average SiO₂ content is lower – 43 wt% in comparison to 47–48 wt% in Sites 1A, 2A, 2B (Fig. 4D). Also, Site 1B samples are enriched in CaO (26 wt% on average compared to 17–20 wt

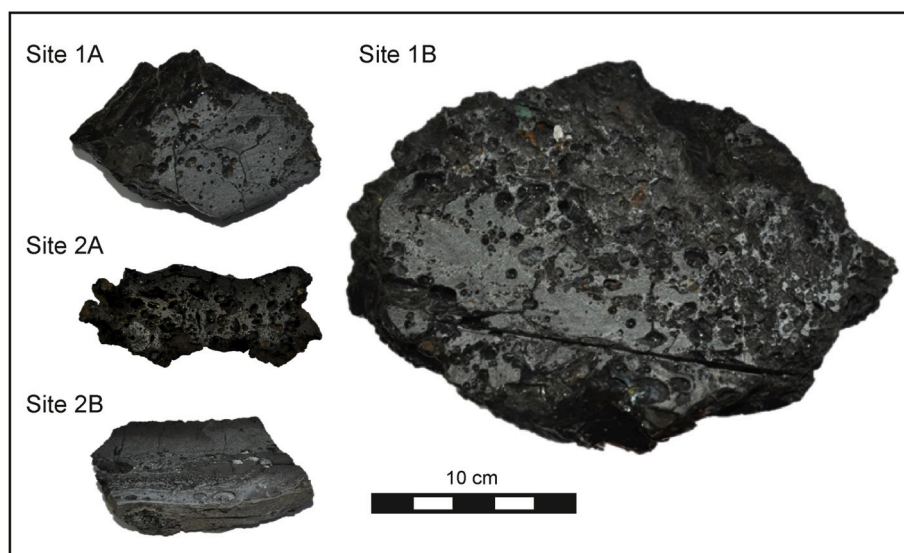


Fig. 2. Macroscopic overview of the samples from four sites, to one scale.

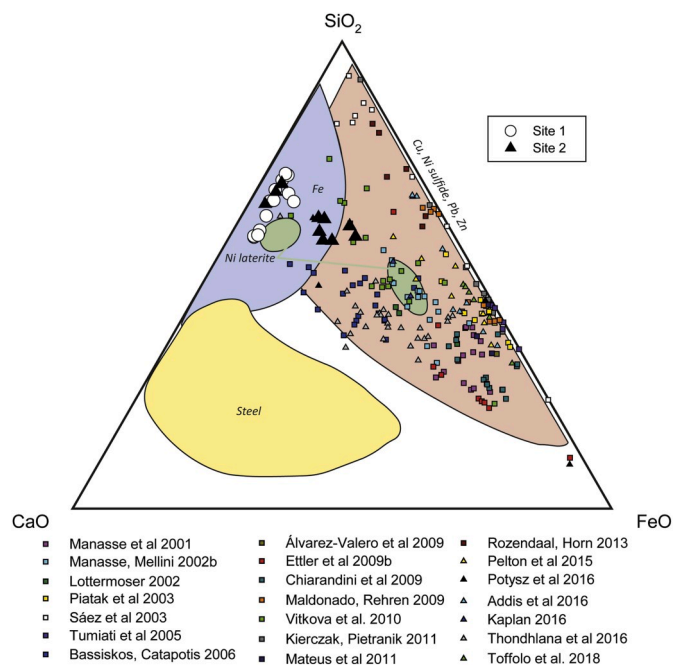


Fig. 3. Analysed slags chemistry compared to all published Cu-slag compositions excluding chemical compositions analysed via SEM-EDS (diagram modified after Piatak et al., 2015).

% in other sites) and present the most homogenous group. Although Site 1A and 2B wastes are similar to those from Site 1B, variations in chemical composition are much larger compared to Site 1B suggesting less standardized smelting process and lower technological level (lower control of the smelting parameters or addition of more varying flux) at Sites 1A and 2B. Because of a strong resemblance for numerous components as well as coherent trends in chemical diagrams (Fig. 4), it seems that chemically the samples from Sites 1A, 2B can be classified as a single type of slag. In contrary, the chemical composition of wastes from Site 2A is different from the remaining samples. The material is depleted in Al₂O₃, K₂O, TiO₂ (Fig. 4A and B) and highly enriched in Fe₂O₃ (Fig. 4C). Also, these slags contain higher concentrations of metallic elements such as Cu and Co (Fig. 4E).

3.2.2. Mineralogy

All samples present strong heterogeneity both in porosity, colour and amount of crystalline phases. Amorphous and crystalline slags are distinguished as two general types of textures but these are not unambiguously associated with porosity level. Glassy slags are distinguished as those with less than 20 vol% of crystalline phases in a modal composition and these samples dominate in Site 1B as well as Site 2B and constitute around 50% of samples in Sites 1A and 2A.

We distinguished four assemblages with the phase composition of different complexity (Table 3). The first assemblage is present at all sites and consists of silicate glass and metallic phases, usually present as separated Cu-prills (Fig. 5A). The second assemblage is specific for slags originating from Site 1B and comprises silicate glass, melilite, leucite and metal-enriched phases (Fig. 5B). The third assemblage appears only on Site 2A and consists of pyroxenes (Fig. 5C). Fourth phase assemblage is present at all the sites and it comprises silicate glass, leucite, chemically variable pyroxene (pigeonite, augite, diopside-hedenbergite,

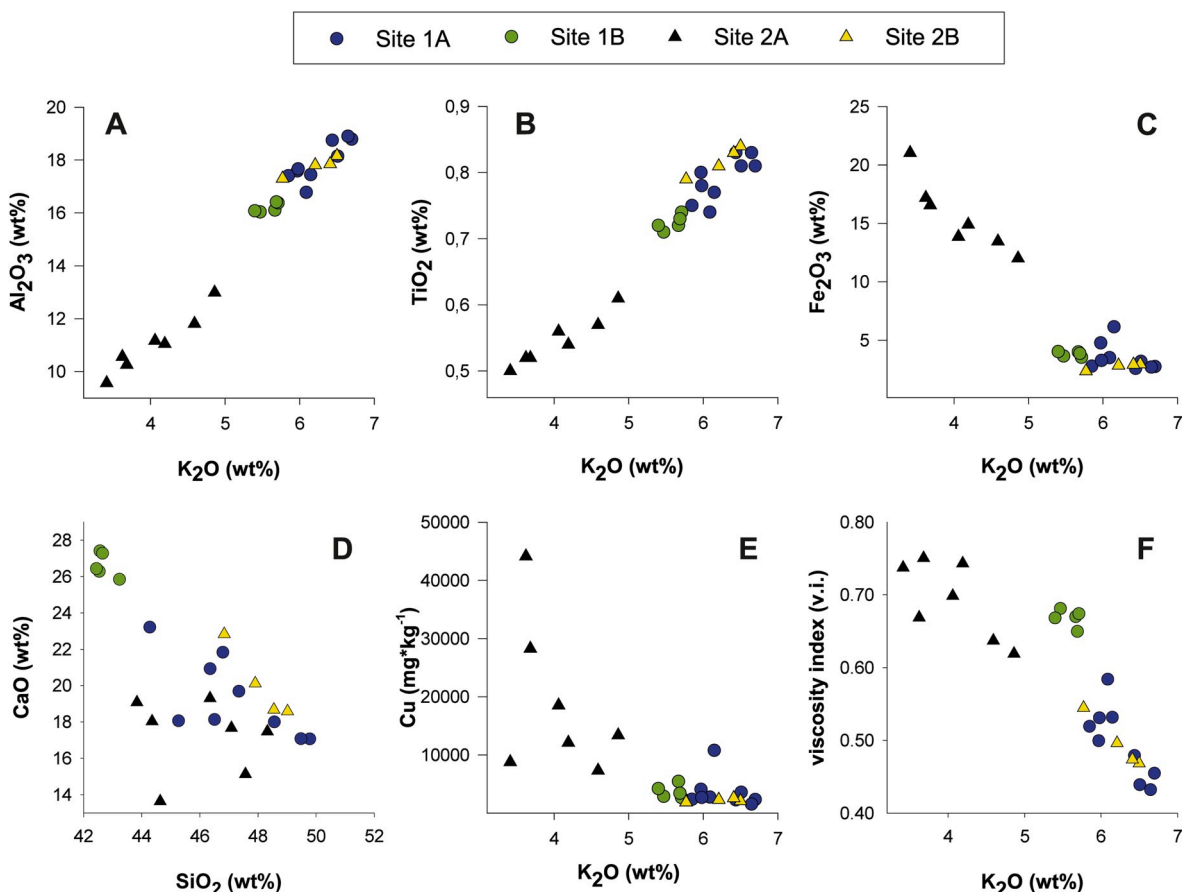


Fig. 4. Chemical composition of slags from four studied sites.

Table 3

Phase assemblages in the Old Copper Basin slags determined by EMPA analyses. lct = leucite, mll = melilite, px = pyroxene, wo = wollastonite, an = anorthite, qz = quartz (mineral abbreviations after: [Whitney and Evans, 2010](#)).

	phases	Site
Assemblage I	glass ± lct	1A, 1B, 2A, 2B
Assemblage II	glass + mll ± lct	1B
Assemblage III	glass + px	2A
Assemblage IV	glass + lct + px + wo ± an ± mll ± qz	1A, 1B, 2A, 2B

esseneite, [Fig. 6](#)), wollastonite, anorthite, melilite, orthoclase and quartz ([Fig. 5D](#)). Among metallic phases, various copper and iron sulphides (chalcopyrite, pyrrhotite, bornite and chalcocite), as well as metallic Cu and Fe, are observed.

Neither magnetite nor wüstite occurs in the analysed samples. This is fairly uncommon compared to the phase composition of other historical Cu-slugs ([Table 1](#)). At the same time, lack of these phases can be explained by low Fe and high Ca content of the studied slags. Magnetite and wüstite crystallize when the Fe/SiO₂ wt% ratio exceeds c.a. 1.5 ([Kongoli and Yazawa, 2001](#)), whereas in the OCB slags this ratio is about 0.1.

Detailed phase compositional data and description are shown in the Supplementary Materials 2 (phase description) and Supplementary Materials 3 (chemical data).

3.2.3. Normative mineralogy

Chemical analyses of glass obtained with EMPA as well as bulk-rock composition were recalculated to the normative mineralogy, i.e. the CIPW norm (calculations are based on the whole rock/slag chemical composition and return typical phases that may crystallize from an anhydrous melt at low pressure). In fact, this approach is perfect for slags because they are anhydrous melts formed at low pressures.

Diopside, plagioclase, leucite and wollastonite are dominating

phases (in various amounts), constituting 5–57%, 16–51%, 0–35%, 0–34% of the calculated assemblages, respectively. Strong variability in results is observed for calculations from different sites – samples from Site 1A and 2B contain comparable amounts of each of the mentioned phases. With small deviations, there is generally about 30% of diopside and wollastonite (together), 31% of plagioclase and about 20% (±6%) of leucite. Orthoclase and larnite appear in some samples, but not for all calculations. Some results (two samples) from Site 1B resemble those of the Sites 1A and 2B (although always contain 10–20% of larnite) but other two present strong depletion in diopside and wollastonite (10% in total) and high enrichment in larnite – commonly reaching 28%. In these samples, there is also some olivine (5%) present. Slags from Site 2A also differ from the remaining set. Samples are dominated by diopside and wollastonite (55–74%) with some addition of plagioclase (approx. 20%) and varying amounts of leucite (7–27% with one exception of 0%). In the place of leucite, orthoclase appears alternatively as potassium-bearing phase (usually around 10%). A trace amount of nepheline and ilmenite (up to 2%) is also commonly present.

Naturally, the presented normative mineralogy is based on a generalized model and not all of the calculated phases are always present in modal mineralogy. In our case larnite is absent in the samples. This is due to the fact that CIPW assumes full crystallization whereas in smelting remains this process is often stopped rather quickly resulting in quenching amorphous slag. Nonetheless CIPW calculations are a good approximation that can be used in selecting the most appropriate mineral phase diagram for the studied system.

3.3. Phase diagram-based temperature reconstructions

Four geochemical systems comprising three chemistry- and one mineralogy-based phase diagrams were considered for establishing liquidus temperatures for the slag samples. For the chemistry-based system, two ternary diagrams ([Fig. 7](#)) including four main slags

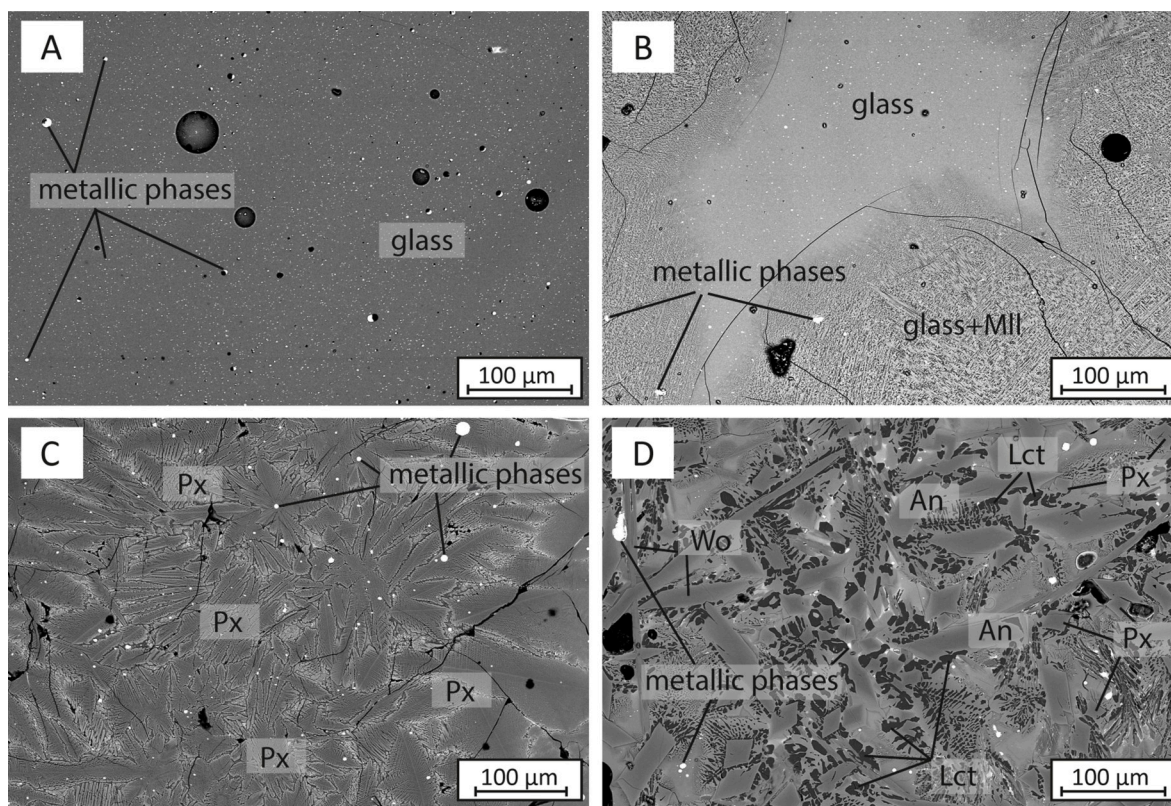


Fig. 5. BSE images of phase assemblages present in slags from the Old Copper Basin, A: assemblage I (glass), B: assemblage II (glass + melilite), C: assemblage III (pyroxene), D: assemblage IV: leucite, pyroxenes, anorthite, wollastonite, melilite, quartz. Abbreviations on the photographs after: [Whitney and Evans, 2010](#)

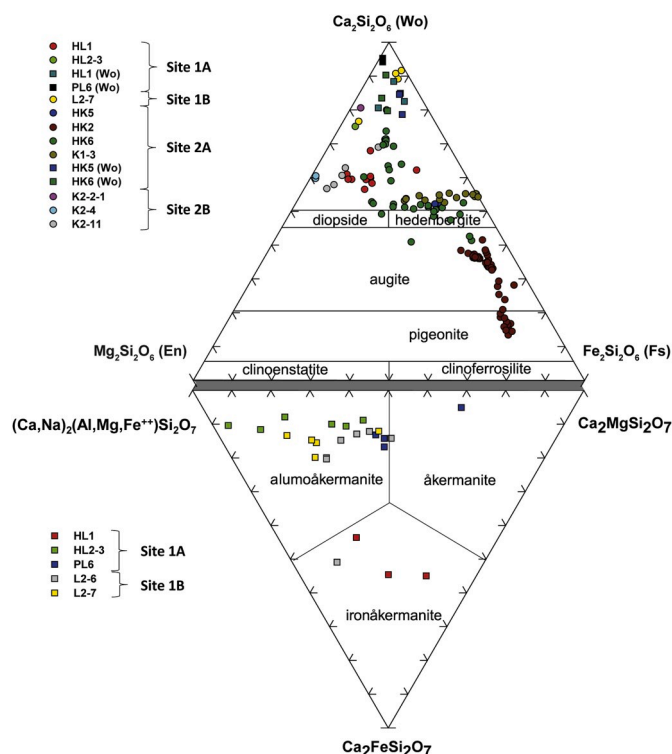


Fig. 6. Classification of pyroxenes (based on Morimoto, 1988) (top) and melilites (bottom) based on electron microprobe analyses.

components were selected. The CaO–SiO₂–Al₂O₃ system covers 68–87 wt% (82 on average) of the chemical composition whereas CaO–SiO₂–FeO includes 69–83 wt% (73 on average), making the first one more reliable. In the case of CaO–SiO₂–Al₂O₃ system, the results plot in a narrow compositional range (Fig. 7A). Samples from Sites 1A, 1B and 2B are located in the anorthite stability field with the corresponding temperature between 1300 and 1400 °C. Results for slags from Site 2A plot close to anorthite, pseudo-wollastonite and tridymite eutectic point suggesting temperature lower than 1300 °C. Temperatures reconstructed from Ca–Si–Fe diagram are higher (over 1400 °C) with most samples plotting in tridymite and cristoballite fields. Systems including K₂O (VDE, 1981) yield a wide variety of temperatures and phases, generally not corresponding to the phases present in the slag.

Considering chemistry and mineralogy of OCB slags mineralogical phase diagram created originally for silica-undersaturated, potassium-rich rocks was used (Gupta, 2015). The diagram comprises leucite, anorthite and diopside as end-member phases and is based on SiO₂–Al₂O₃–MgO–CaO–K₂O components, which constitute 74–96 wt% of chemical composition with over 90% on average) (Fig. 7C and D). A slight modification of the diagram was necessary and diopside component included both diopside and wollastonite. This was because slags younger than the 18th century are often enriched in CaO (Ettler et al., 2009) and Px–Wo solid solution can be present in slag melts.

Two groups are observed in the diagram: higher temperature pyroxene group and lower temperature eutectic group. Most of the analysed slags (Site 1A, 2B) plot close to the eutectic point and indicate crystallization temperature close to 1249 ± 5 °C (EP group). Similar to chemical diagrams, slags from Site 2A form a separate group plotting in the pyroxene stability field with higher crystallization temperature ranging between 1275 and 1303 °C. Interestingly, glass composition changes nearly parallel along An–Px cotectic following the initial crystallization of leucite i.e. melt becomes leucite-poor and results plot further from the eutectic point (Fig. 7C). This observation is consistent for both, pyroxene and eutectic-point groups and proves early crystallization of leucite, but shows that glass composition is out of

equilibrium.

3.4. MELTS simulations

The major phases and temperatures of their crystallization, as well as liquidus temperatures, were modelled using MELTS software (Ghiorsio and Sack, 1995; Gualda et al., 2012). Modelling conditions are described in Supplementary Materials 1 and detailed numeric results are presented in the Supplementary Materials 3. We selected four samples from the pyroxene-rich group (Site 2A), five samples from the eutectic-point group (three from Site 1A, two from Site 2B) and also four samples from Site 1B as two varying sets of normative mineralogy were distinguished for this site. For each sample, 5 sets of modelling were conducted using bulk-rock chemistry, the average result of all EMPA glass analyses and randomly selected 3 glass analyses as starting compositions.

Modelled liquidus temperatures are consistent within the sites and divide analysed set of slags in two groups: (1) smelted in approx. 1200–1250 °C (Sites 1A, 2A, 2B) and (2) smelted in about 1400 °C (Site 1B, Table 4, Fig. 11B, bulk-MELTS). The distinction is crucial as it was not clearly shown by any other method. Temperatures modelled from the glass composition are usually 30–65 °C lower. The MELTS results confirm those derived from the Lct–Px–Pl diagram (Fig. 7C and D) where pyroxene group (Site 2A) samples show higher liquidus temperatures: approx. 1220–1240 °C compared to those of the eutectic point group 1200 °C (Sites 1A and 2B). Also, results confirm chemical observations suggesting that slag from Site 1A and 2B are probably material that originated in the same place and during related technological process. Estimated temperatures are similar and slightly lower than the ones for Site 2A. The interval of 1200–1250 °C is an estimation adequate for historical slags and possibly most exact from the chosen methods as it considers all major elements and surface pressure.

Modelled crystallization paths are similar for all simulations from Sites 1A, 2A, 2B despite various starting bulk-rock compositions (Supplementary Materials 3 – MELTS modelling section). Modelling results also agree with petrological observations and experimental research, and always yield a consistent set of phases: leucite, clinopyroxenes and feldspar (Fig. 8). Models, as well as EMPA glass analyses observed in the Lct–Px–Pl diagram, indicate that melt chemical evolution is controlled by the early formation of leucite, which crystallizes as the first phase around 1200 °C (Fig. 8). This is followed by clinopyroxene and feldspar crystallization, with a small temperature difference between the two phases. Contrasting behaviour was noted for models based on glass analyses. Liquidus temperatures are lower and leucite is usually the last phase to crystallize after Cpx or Pl, depending on the sample. The distinction is probably caused by varying chemistry of starting compositions and chemical differentiation of glass that follows initial crystallization of leucite depleting glass in K₂O.

Various crystallization intervals were recognised for Sites 1A–2B and 2A where temperature interval between liquidus and 50% of liquid remaining is low for Site 1A and 2B (50–120 °C) and relatively high for Site 2A (110–140 °C), i.e. eutectic composition of the input material was not efficiently achieved for Site 2A. Modelling results are distinctly different for slags from Site 1B, where, besides considerably higher liquidus temperatures, only melilite (~1400 °C) and leucite (~1180 °C) crystallize in a temperature interval of 250–320 °C (50% of crystallization) suggesting that similarly to Site 2A eutectic composition is not met.

Depending on the crystallinity of the sample, melts chemical composition changes with amorphous slags having the most homogeneous composition and well in agreement with modelled composition (Fig. 10A). Crystalline samples, tend to scatter on the diagram consistent with chemical differentiation and more varied composition than the modelled one (Fig. 10B and C). For this reason, besides amorphous slags, modelled chemical changes in liquid should not constitute a base for considerations of the solidification temperature. The model may be,

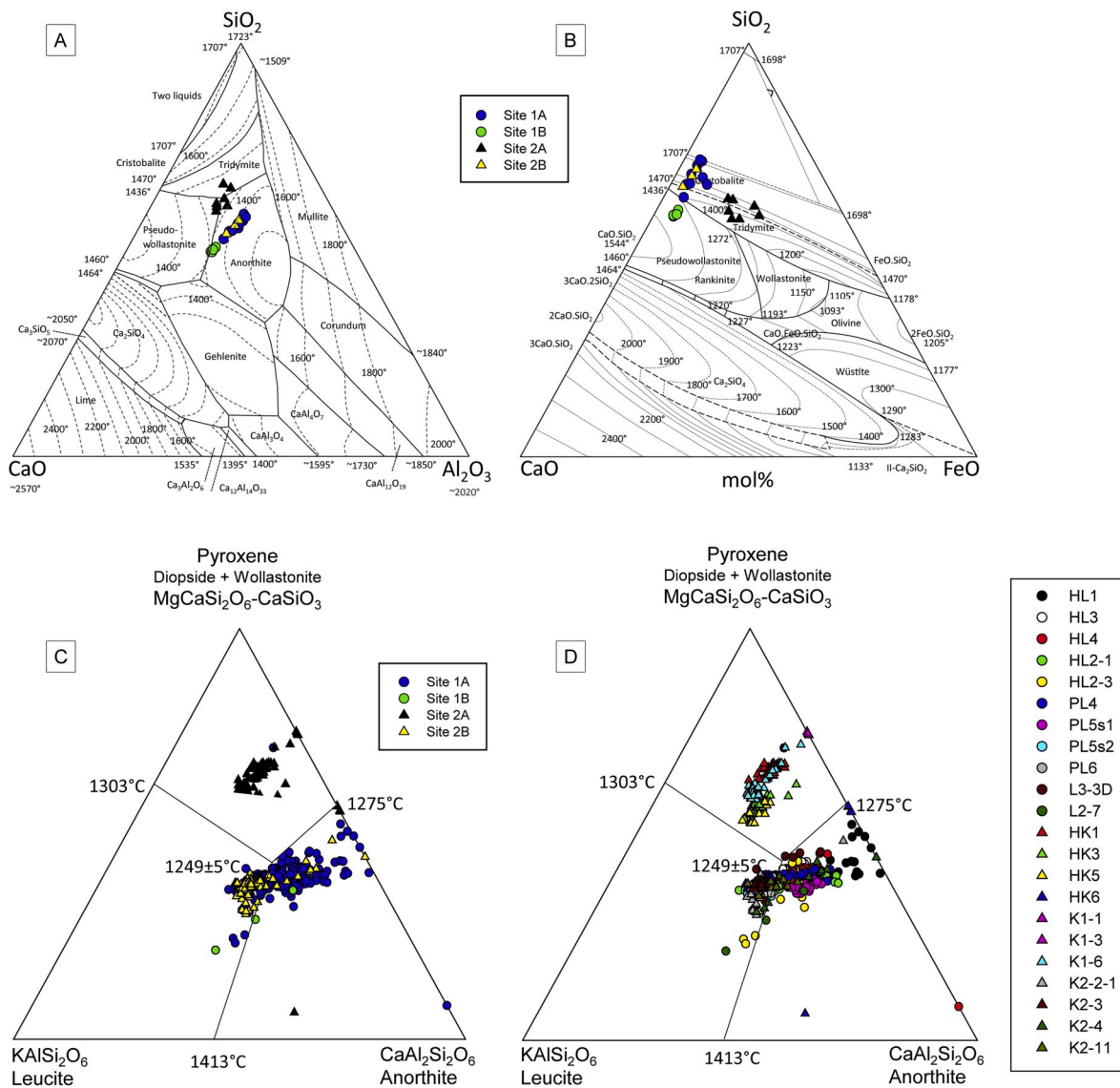


Fig. 7. A, B: Chemical composition of slags in the CaO–SiO₂–Al₂O₃ and CaO–SiO₂–FeO phase diagrams (after [Muan and Osborn, 1965](#); [Piatak et al., 2015](#)), Bottom: Glass chemistry in a Leucite–Pyroxene–Plagioclase system based on CIPW calculations presented for sites (C) and individual slag samples (D) (after [Gupta, 2015](#)). Samples from site 1B appear close to the eutectic line but only half of the samples (and a limited number of analyses among them) reached the required level of crystallizing at least 70% of diopside, plagioclase, leucite and wollastonite together. For this reason, most of the results do not appear on the diagram and temperatures estimated with this method are not certain for samples from this site.

Table 4

Results of MELTS simulations (liquidus temperature for bulk and average glass composition).

Cpx group							
sample	HK1		HK3		HK5		K1-3
liquidus (T (°C)) bulk-rock	1216.99		1229.77		1264.45		1244.73
liquidus (T (°C)) glass	1166.41		1166.21		1199.41		1209.61
EP group							
sample	HL1	HL4	PL5	HL2-1	HL2-3	K2-11	K2-2-1
liquidus (T (°C)) B	1211.52	1212.70	1193.55	1201.76	1239.06	1213.87	1208.59
liquidus (T (°C)) G	1185.35	1182.23	1196.29	1168.95	1210.94	1184.18	1191.21
Site 1B							
sample	L2-3		L2-5		L2-6		L2-7
liquidus (T (°C)) B	1445.70		1369.29		1444.56		1366.02
liquidus (T (°C)) G	1516.60		1433.01		1353.91		1347.85

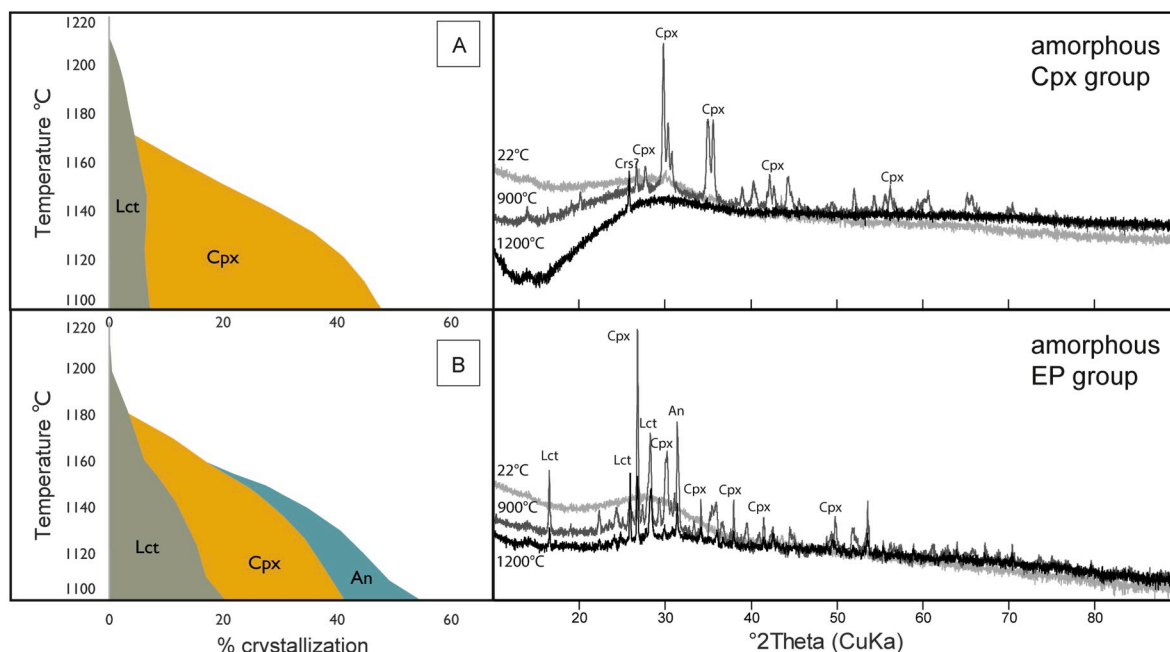


Fig. 8. Comparison of crystallization path modelled with MELTS software and thermal XRD in 22, 900 and 1200 °C presented for amorphous slags from Cpx (A) and EP (B) groups.

however, applied to the reconstruction of crystallization time interval.

3.5. Temperature XRD analyses

To check on accuracy of MELTS models we performed laboratory experiments for two samples using thermal XRD analyses (Fig. 8). In room temperature (22 °C, Fig. 8) both samples are amorphous. After heating to 900 °C samples show crystalline texture with a presence of clinopyroxene (Fig. 8A) and leucite, clinopyroxene and anorthite (Fig. 8B). With the exception of cristoballite, analyses in 1200 °C yielded no phases in the first sample (Fig. 8A) whereas the second sample again crystallized leucite, clinopyroxene and anorthite (Fig. 8B). When compared to modelled composition the presence of all crystalline phases is expected at 900 °C (Fig. 8), whereas in 1200 °C both samples should crystallize only a small amount of leucite. Nevertheless, presented trends are still consistent with the modelled behaviour, where crystallization in the first sample begins later, is slower and generally limited to clinopyroxene (Fig. 8A) whereas the second is faster and generates more phases (Fig. 8B).

3.6. Pyroxene-melt thermometry

Eleven samples – two from Sites 1A, 1B, 2B and four from Site 2A – analogous to the set selected for MELTS modelling, were selected for thermal calculations. Pyroxene-liquid models under air-pressure (0.1 MPa) were calculated and resulted in a set of temperatures of pyroxenes crystallization (SM3 - Px-WR geothermometers section). Olivine appears as an accessory phase in the OCB slags and it was not possible to include olivine-based geothermometers.

For most samples, different thermometers resulted in difference lower than 50 °C, i.e. results are similar for all selected models (Fig. 9). Slags from Site 2A present the lowest temperatures of clinopyroxenes crystallization: 945–1148 °C, depending on the model selected. Results for Site 1A are on average 100 °C higher than 2A. Samples from Sites 1B and 2B present similar temperatures, on average another 100 °C higher than slags from Site 1A (~1220 °C) (Fig. 11, px-WR).

Data strongly agree with MELTS modelling with the resulting

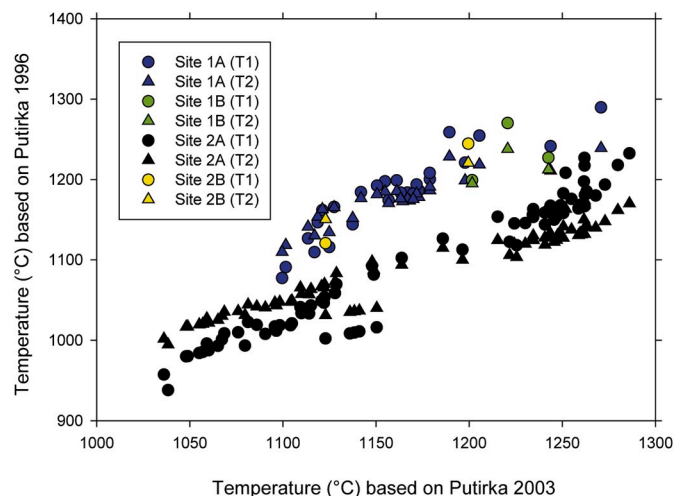


Fig. 9. Comparison of results from three Px-WR geothermometers.

temperatures (based on Putirka et al., 1996, 2003) slightly lower than those calculated by MELTS at the onset of clinopyroxenes crystallization. Based on the interval between liquidus temperature and the end of recorded pyroxene crystallization, two groups were distinguished. Eutectic group (Site 1A and 2B) presented a narrow range of temperatures and quick clinopyroxenes crystallization while pyroxene group (Site 2A) demonstrated prolonged crystallization of pyroxenes (Fig. 9). This observation is not consistent with the applied Lct-Px-Pl mineral diagram (Fig. 7C), according to which pyroxenes are the first phase to crystallize. This path is, however, present in MELTS modelling where crystallization begins with leucite. Long crystallization of pyroxene is also visible in the case of samples from Site 1B (Fig. 11) which is surprising as all of the samples collected at the site are amorphous with only a few crystallized pyroxenes, usually present in limited areas surrounded

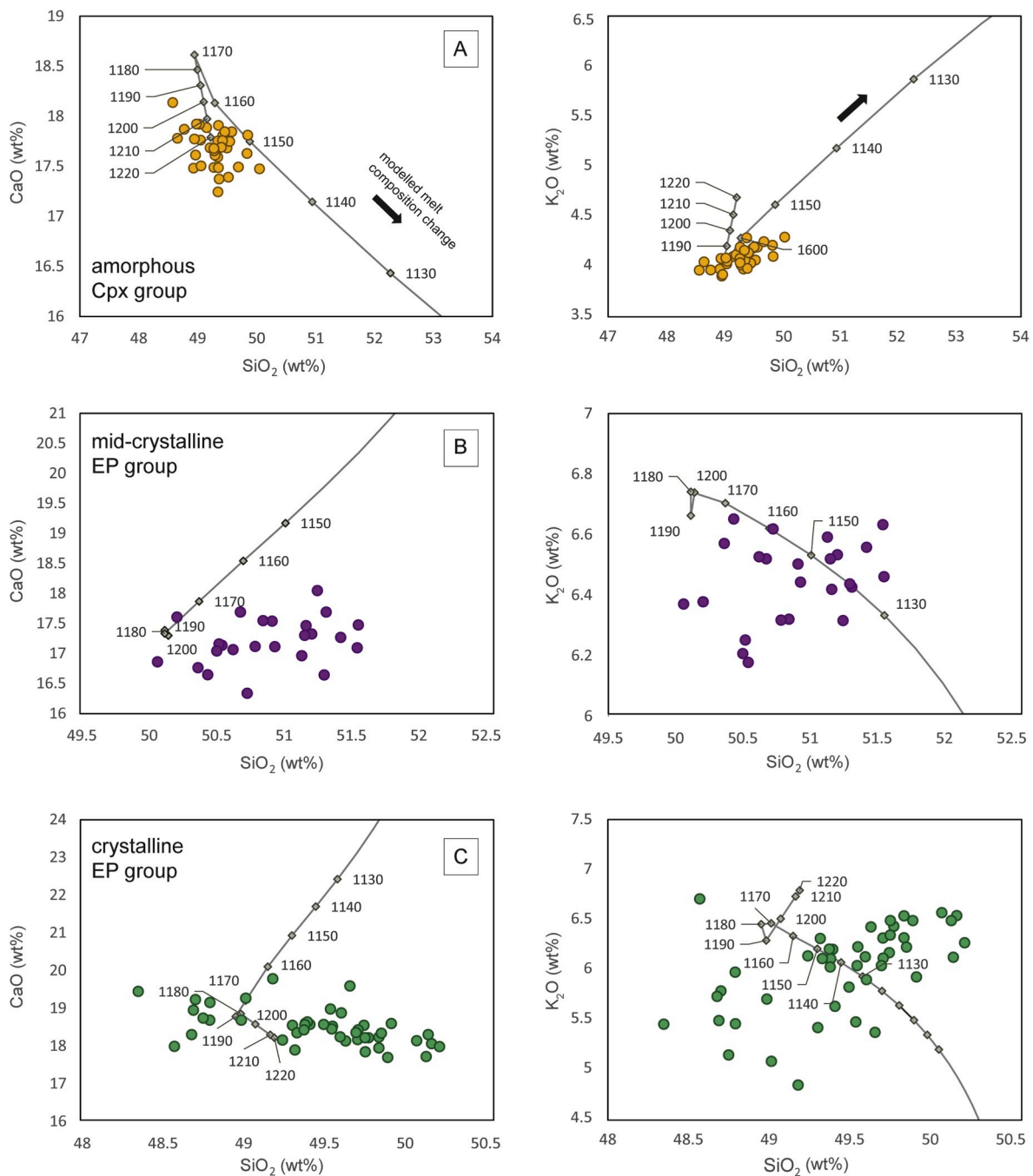


Fig. 10. Modelled and observed chemical composition of liquid (glass) in slag samples from site 1A and 2A. Top: quenched amorphous slag, middle: amorphous slag with a few crystalline phases, bottom: crystalline sample.

by melilite. Possibly these areas created specific local-equilibrium conditions that resulted in late crystallization of pyroxene as the formation of melilite tends to start in high temperatures and take a certain amount of time for the AlO₄ tetrahedra diffusion (Fredericci et al., 2000).

Results for all thermometers seem comparable (Fig. 9, Supplementary materials 3 – Px-WR geothermometers section) but only Equation (1) (Putirka et al., 1996 T1) provides statistically reliable data that passes the normality test for three out of four samples. For this reason, we based our geothermometer-related conclusions on this model.

4. Discussion

4.1. What temperatures are we reconstructing?

Our summary shows that it is extremely important to specify which temperature is being estimated during reconstructions (Fig. 12) because not all of the methods reconstruct liquidus temperature of slag melt, i.e. temperature where all slag mass is liquid. Liquidus temperature is most probably lower than the highest temperature achieved in the furnace, however, it provides the best estimate of smelting temperature that can be obtained. It shall thus be named a minimal furnace temperature and analysed with the awareness that it was most probably surpassed for

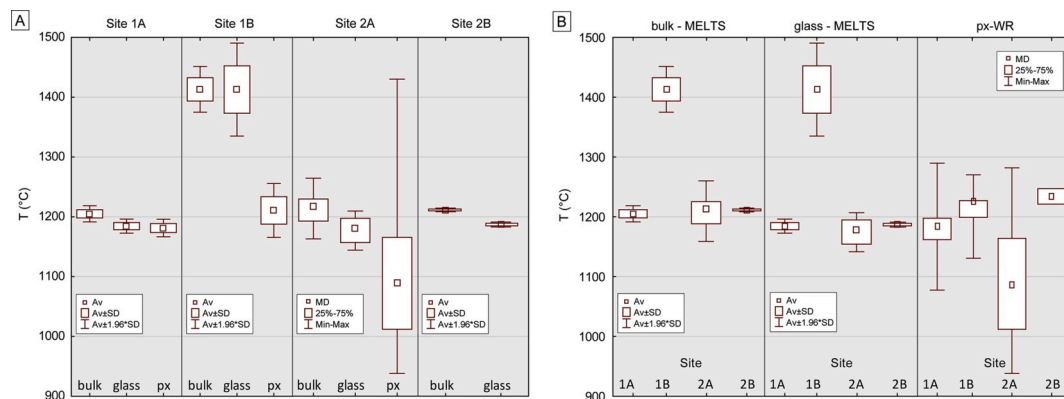


Fig. 11. A: Box and whiskers plots comparing differences between Sites in temperature estimations for each method: MELTS liquidus temperature using bulk rock composition (bulk), MELTS liquidus temperature using average glass composition (glass) and temperature calculated by Cpx-whole rock (WR) thermometer of Putrika (1996 T1). The assumptions of parametric tests was checked for data distribution using Shapiro-Wilk normality test and for homogeneities of variances using Brown-Forsythe's test. Based on the results parametric test one-way ANOVA analyses of variance was used for bulk and glass for between-site comparison with Tukey honest significant difference *post hoc* test. Data distribution for Cpx was not normal in Site 2A and non-parametrical Kruskal-Wallis test by ranks was used for comparing the Cpx -WR temperatures between sites followed by post-hoc comparisons of mean ranks of all pairs. The null hypothesis was rejected if $P < 0.05$. Significant differences were noted for Site 1B (bulk and glass) and Site 2A (Cpx). B: Box and whiskers plots comparing calculated temperatures for each site using three approaches: MELTS liquidus temperature using bulk rock composition (bulk), MELTS liquidus temperature using average glass composition (glass) and temperature calculated by Cpx-WR thermometer of Putrika (1996, T1). The assumptions of parametric tests was checked for data distribution using Shapiro-Wilk normality test and for homogeneities of variances using Brown-Forsythe's test. Based on the results parametric test one-way ANOVA analyses of variance was used for Site 1A, 1B and 2B for within-site comparison with Tukey honest significant difference *post hoc* test. Data distribution for Cpx was not normal in Site 2A and non-parametrical Kruskal-Wallis test by ranks was used for comparing the temperatures followed by post-hoc comparisons of mean ranks of all pairs. The null hypothesis was rejected if $P < 0.05$. Significant differences were noted for Site 1B and Site 2 A between Px and both bulk and glass and for Site 2 A between bulk and glass. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

most effective metal separation (Fig. 12). Still, this minimal furnace temperature is currently the most objective and comparable method to be applied to archaeometallurgy. Among methods discussed in the article, only MELTS modelling based on the bulk chemistry returns liquidus temperature (Fig. 11B, bulk-MELTS). Other methods, such as geothermometry may provide temperatures close to liquidus or lower depending on the crystallization interval and cooling rate and the presence of equilibrium conditions (Fig. 11B). On the other hand,

chemical and mineral phase diagrams provide higher temperatures, which usually implies that the chosen diagram is too simple to model complex slag system and the results are only a rough estimation. Another approach to the liquidus reconstruction is associated with experimental studies but the strength of thermodynamic modelling is that it can be used for numerous samples, yielding good statistical results. The modelling is also relatively cost-effective. Therefore, for the best results, an experimental and modelling approach should be combined with a representative composition used for the experiment as a reference point and a variety of heterogeneous slag samples for modelling to constrain possible variations of smelting temperatures within site and between studied sites.

The validity of liquidus as a smelting temperature may be challenged because, as we have mentioned, slag melt is often overheated to achieve best metal separation. If this is the case, high-temperature silica polymorphs could be used as a confirmation of melt reaching high temperatures, e.g. 1470 °C, the temperature of cristoballite formation (in silica-pure system) (Piatak and Seal, 2010; Piatak and Seal, 2012). However, cristoballite might also appear in the metastable form in >900 °C (Mollah et al., 1999). Thermal XRD in near-liquidus temperatures can indicate if cristoballite appeared in lower temperatures. Within the analysed set of slags, thermal XRD proved cristoballite presence in one of the Site 2A samples (Figs. 8A and 1200 °C). No other method, however, implied melt overheat (sample HK1, Table 5, Fig. 10A) and we conclude that considering specific chemical composition of the analysed slags, cristoballite formation is expected in significantly lower temperatures, thus its presence does not indicate overheating of the melt (Toffolo et al., 2018).

However, liquidus temperature is not the only one useful for historical reconstructions. Temperature interval of steady-state crystallization named ‘crystallization interval’ (Cr.I. in Fig. 12) can also be modelled using smelting wastes. Technically to calculate Cr.I. using MELTS we use the difference between the liquidus temperature and the temperature where about 50% of liquid crystallized. Obtaining real solidus temperatures is impossible, because the melt evolves to unusual composition, which are not covered by experimental databases and thermodynamic calculations. Cr.I. based on 50% melt remaining is a

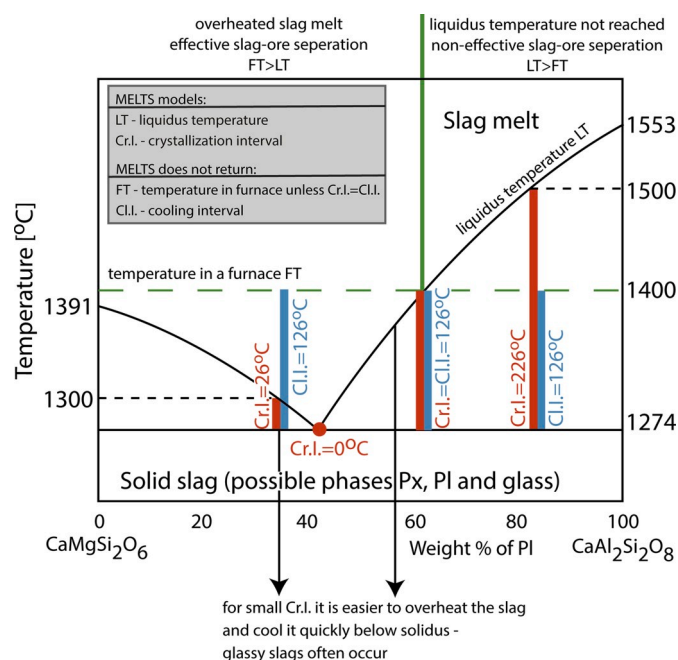


Fig. 12. The relation between the actual furnace temperature, liquidus temperature and crystallization interval depending on the quality of the furnace input (ore-flux composition) presented in a simple two-component eutectic diagram (Dp-An after [Bowen, 1915](#)).

Table 5

Summary of the temperatures reconstructed with phase diagrams, MELTS simulations and geothermometers.

Method	Site 1A (°C)	Site 1B (°C)	Site 2A (°C)	Site 2B (°C)
Chemical diagram CaO–SiO ₂ –Al ₂ O ₃	1300–1400	1300–1400	<1300	1300–1400
Chemical diagram CaO–SiO ₂ –FeO	1436–1707	~1440	1436–1500	1436–1707
Mineral diagram	~1249	~1249 (a few samples)	1275–1303	~1249
Leucite–Pyroxene–Plagioclase				
MELTS modelling, bulk chemistry	1184–1239	1366–1445	1208–1214	1209–1214
MELTS modelling, glass analyses	1163–1211	1348–1516	1144–1210	1184–1191
Geothermometry (Px-WR)	1077–1290	1199–1270	938–1233	1120–1251

valid approach because (a) the results are comparable for slags of similar chemistry and (b) it is the value at which a rapid decrease in melt proportion is observed, suggesting that the system approaches solidus. The crystallization interval provides information on obtaining effective smelting mixture of ore and flux and for this reason we suggest it should be introduced to archaeometallurgical studies. In general, the longer the interval of sample crystallization is, the less effective was the ore-flux mixture to lower the smelting temperature (Fig. 12). This conclusion is also confirmed when geothermometers yield significantly lower temperatures than the modelled liquidus temperature.

It was stated that the core composition of a phase used as geothermometer might record smelting temperature (Warchulski, 2016) and this may be the case for high-temperature phases, such as olivines and spinels (Toffolo et al., 2018). On the other hand, in our study pyroxene geothermometry tends to yield temperatures noticeably lower than the liquidus, especially for slags from sites characterized by larger crystallization interval. Therefore, geothermometers often do not provide information on liquidus temperatures, however, they carry other significant information regarding time and temperature interval of phases crystallization (cooling of the slag) (Figs. 9 and 11B). Slow cooling results in higher variations in the chemical composition of the phases (Kierczak and Pietranik, 2011). This observation can also be applied to changing chemistry of the liquid (Fig. 10) which compared to the Cr.I. and modelled composition, supplement geothermometers results (Fig. 9) and together provide set of temperatures suggesting an actual period of samples crystallization from the steady-temperature stage through cooling to solidification (Toffolo et al., 2018).

4.2. Better archaeometallurgical temperature reconstructions: what is to be gained?

Ancient and historical smelting generally face different issues in the matter of reconstruction of the smelting process. Bourgarit (2019) pointed that so far ancient smelting (before medieval times) has received much more attention compared to historical processes. This distinction between smelting technology in proto- and historical periods has been well understood for over 20 years when ‘crucible’ and ‘furnace’ smelting were defined (Rothenberg, 1999). Crucible smelting (together with bloomery iron smelting) was more varied between localities and periods, but also easier to reconstruct experimentally, therefore, it has dominated archaeological interest (Tylecote, 1974; Catapotis et al., 2008; Pryce, 2008; Burger et al., 2010). In this study we focused on the historical copper blast furnace smelting, characterized by higher standardization (Morin, 2013). Organized production resulted in better selection of ore, fuel and fluxes. The process was better replicated and the smelting conditions more consistent among smelting episodes. Consequently, slag material tends to be more homogenous and temperature reconstructions should be more reliable than in the case of ancient wastes.

Nonetheless, we believe it is crucial to search for methods to perceive the most exact temperature ranges for different types of smelting. For historical smelting, temperatures demonstrate how the smelters operated and whether smelting episodes were standardized or not. With long

operating smelters, ore and/or flux supply changes can be noted. Changes in temperatures can also prove that furnaces were expanded to larger sizes, thus metal smelted more effectively, which could be further correlated with general increase in metallurgical knowledge or economic growth. The temperature studies allow for a great technological recognition but the archaeological context needs to be included as some changes may appear due to the cultural alterations, not simply better technology (Gordon and Killick, 1993). Still, especially in historical times, smelters operated on a high technological level and within blast and shaft furnaces, cultural impact was rather restricted.

On the other hand, ancient smelting was less standardized and one might ask a question about a reason for more accurate temperature reckoning. First, good reconstruction of liquidus temperature allows us to compare smelting episodes and assess if the same ores and fluxes were used. Second, liquidus temperature plus crystallization interval show if effective ore-flux mixing was obtained and that can be analysed for a single site as it evolved in time with different archaeological contexts or between different groups or societies. Third, separated ancient populations could have transferred technological knowledge on the effective smelting among each other and the exact reconstruction is crucially important for the recognition of the spread of ideas and connections among societies. Exact liquidus temperature as well as changing crystallization intervals can be important factors in the recognition of such transmissions.

We also need to separate ferrous and non-ferrous smelting. This is because bloomery iron smelting was highly specific (Ströbele et al., 2010), and its waste is a mixture of slag and matte thus its crystallization is far from equilibrium which is required for detailed temperature reconstructions. These wastes tend to vary significantly between smelting episodes due to a) varying technological level and furnace constructions (Gordon and Killick, 1993), b) high dependence on the ore chemistry, c) low control over smelting parameters and d) lack of repeatability resulting from the need of building new construction for each smelting episode (Humphris et al., 2009). We want to point, that for bloomery iron smelting, thermodynamical approach might still be unavailable. This is due to the software limitations, requiring close-to-equilibrium composition for proper calculations. Still, application of geothermometers for bloomery iron smelting wastes should result in an excellent record of crystallization period and also amount of metal smelted within one episode through comparison of slags textures from different smelting episodes. This approach, naturally, requires exact chemical data of phase composition.

4.3. Temperature reconstructions in the OCB

The applicability of the approach proposed in this study can be evaluated on the historical slags from four sites in the OCB. The chosen methods allowed to distinguish variations in liquidus temperatures and crystallization intervals modelled by MELTS as well as compare them to the temperatures returned by pyroxene geothermometers (Fig. 11A and B, Table 5). Temperatures for Sites 1A, 2A, 2B are alike and present no statistically important differences. Nevertheless, slags from Sites 1A and 2B have slightly lower liquidus temperatures (1210 °C) compared to

older slags from Site 2A (1225 °C). This difference was already noted using phase diagram for K-rich Si-undersaturated rocks, where Site 2A plotted in the pyroxene stability field and not close to the eutectic point as Sites 1A and 2B. However, slags from Site 2A are also specific, because they are characterized by large crystallization interval of up to 130 degrees Celsius, which is also confirmed by the statistical difference between liquidus temperature (estimated with MELTS) and pyroxene crystallization temperature (estimated with geothermometers) of 150 ± 50 degrees Celsius (Fig. 10A, Site 2A) consistent with our conclusion that geothermometers may record any temperature along the crystallization path. Higher liquidus temperature and larger liquidus-to-solidus crystallization interval implies lower control over the eutectic melt composition. It is possible that temperatures required for a proper smelting were not reached in this case and this resulted in lower metal extraction (average Cu concentration in samples from Site 2A is 1.89 wt %). Slags from Sites 1A and 2B have similar chemical composition and crystallization interval (50–120 °C at Site 1A and 90–100 °C at Site 2B) but differ in the Cu content in the slag (avg. 3573 mg/kg at Site 1A and avg. 2207 mg/kg at Site 2B). Slags 2B are also commonly amorphous what suggests a good control over the cooling process. The implication is that Site 2B may present subtle technological predominance compared to the Site 1A.

On the other hand, Site 1B differs from all other sites as modelled liquidus temperatures are nearly 200 °C higher than the remaining set (Table 5,). This reflects differences in chemistry, especially in total SiO₂ and CaO concentration (Fig. 4). Since the higher temperature is accompanied by large crystallization interval of up to 320 °C, we interpret that a new material was added to the furnace and control on eutectic composition was lost. Shales and marls present in the area vary in thickness and at late stages of *Stilles Glück* (Site 1A) smelter activity, the ore could have become restricted to marls, increasing CaO and decreasing SiO₂ concentrations in the furnace input and eventually in slags. Such change would also result in higher liquidus temperature. It seems, however, that this effect was well-controlled by the smelter. Due to the chemistry changes, higher temperature was applied and metal recovery was achieved on the satisfactory level (on average 3690 mg/kg Cu left in the slag).

Different liquidus temperatures and different crystallization intervals also provide information on cooling rates. In theory, cooling rate can be estimated from slag texture with glassy slags being quickly undercooled below solidus temperatures, slags with skeletal crystals showing moderate cooling rates and fully crystalline slags representing slow cooling (Donaldson, 1976; Ettler et al., 2009). The cooling rate of slag would mainly depend on the environment where this slag cools, i.e. inside furnace cooling versus outside furnace cooling (tapped slag) versus specific cooling technique, e.g. water cooling. However, the efficiency of cooling may also depend on the crystallization interval as undercooling is easier to achieve for slags with small crystallization interval. Therefore, in our study, quickly obtaining temperatures below the crystallization interval should be challenging for Site 1B. However, slags from this site are dominated by amorphous samples which is a proof of well conducted cooling system. We interpret this fact as a record of furnace and cooling system development that took place in 1868 AD when three bigger circular furnaces and modified water-cooling system were introduced in the *Stilles Glück* smelter. If correct, this would prove that slags from the Site 1B originate from the same smelter as 1A and 2B wastes but differ in age, being the youngest of analysed materials. Therefore, the samples recorded technological advances such as obtaining higher furnace temperatures and better control on cooling.

5. Conclusions

Our study reviewed methods of temperature reconstructions based on slag material created during metal smelting process. With the example of Cu-slugs from the OCB in Poland produced in the 18–19th century we were able to estimate minimal smelting (liquidus), steady-

state crystallization and near-solidus temperatures, presenting almost a full thermal history of slags from four selected sites. Each of the estimated temperatures or temperature-related parameters has its potential for reconstructing and comparing different approaches to metal smelting and their differences in time and space. In detail, liquidus temperatures are the best estimation of temperatures in the furnace and record technological development. However, liquidus temperatures should be always interpreted in relation to the crystallization interval (temperature difference between liquidus and solidus), which is a valuable record of how well ore + flux mixture was designed. This is of the highest importance to the society, since for badly designed input material, efficiency of metal extraction decreases (as shown in this study for slags from the oldest Site 2A). Lastly, cooling rate can be estimated and in the past this has been based on the sample texture (amorphous versus crystalline slags). We show that the interpretation of cooling procedure should not only be based on textural observations but also linked to liquidus temperature and crystallization interval (it is easier to undercool slag melt with low Cr.I. than with the large one and if this is the case as in Site 1B special cooling techniques should be introduced) as well as geothermometry, recording actual temperatures of slag's crystallization (cooling).

This is the first attempt to adapt all methods applicable for temperature reconstruction and (1) achieve most detailed estimations, (2) verify which methods present reliable and coherent results. We discovered that the age of analysed materials was ambiguously associated with temperature. In fact, the oldest slags (18th century) yielded temperature approx. 1225 °C, intermediate slags approx. 1210 °C and the youngest much higher temperature of approx. 1400 °C.

Our research provides the following insights regarding temperature reconstructions:

- commonly used methods such as chemical and mineral phase diagrams usually fail to provide reliable liquidus temperature estimations as slags represent chemically complex systems crystallizing in disequilibrium conditions,
- application of thermodynamic modelling allows achieving statistically reliable and detailed liquidus temperatures as all major elements, atmospheric pressure and oxygen fugacity are included in calculations. Considering specific conditions of slags crystallization it is crucial to confirm that models are supported by petrographic observations,
- attention should be paid to bulk and glass chemical composition as both may record various temperatures. Bulk composition is by all means the closest to the initial melt composition and constitutes a base for reconstruction of liquidus temperature. Glass composition, however, provides melts composition on varying stages of sample's crystallization,
- various geothermometers investigate the following stages of crystallization and record cooling conditions of slag samples,
- to obtain full picture of the smelting process, the temperature reconstruction should include calculating crystallization interval and comparing it to the slag structure and the extraction efficiency.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jas.2020.105142>.

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