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Cu-Zn slags from Røros (Norway): a case study of rapid cooling and crystal nucleation

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Abstract

The mining town of Røros located in central Norway was established in 1644 and it is known of historical mining industry related to copper. Røros was designated as an UNESCO World Heritage Site in 1980 on the base of mining culture represented by, e.g., unique wooden architecture. Slag pieces are composed of three parts differing in glass to crystallites ratio. Røros slags are composed of olivine- and pyroxene- group minerals accompanied by sulphides, with glass in the interstices. Temperature gradient and volatiles content were determined as the main factor influencing crystallization process in this material.

Key words: Røros, slags, olivine, clinopyroxene, crystallization

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Introduction

Location

The Røros mining town is located in Sør-Trøndelag District, central Norway (Olsvik et al. 2001; Fig.1), at a valley bottom marked by Glåma, Håelva and Hitterelva rivers in southern central-part of the Scandic Mountains (Jones 1999). Nowadays the area is famous of its environmental richness preserved in Forollhogna and Femundsmarka National Parks and plenty of nature reserves.

History

Røros was established in 1644 and it is known of historical mining industry related to copper production in the years from 1646 to 1977 (Jones 1999; Prøsch-Danielsen and Sørensen 2010). In 1646 at the Røros site the first technological step included open-air roasting process, associated with releasing of high amounts of SO_2. This, accelerated by the Bossemer smelting process introduced in 1888, caused massive pollution at this location, e.g., causing acid rains and regular crop failures. It was necessary to stop the production during grass-growing season each year. Building the hydroelectric plant in 1896 revolutionized mining especially in case of transport and water pumping. After the World War II the smelting work at Røros was closed in 1953, while entire copper works proclaims itself bankrupt in 1977. In 333-years of work total ore production reached ca. 6.5 Mt with average Zn and Cu content in ore being 4.2–5.0% and 2.7%, respectively (Bjerkgård et al. 1999). The only commercial product extracted for entire production period was copper. Røros was designated as UNESCO World Heritage Site in 1980 by its unique wooden architecture

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and cultural treasures related to its mining environment (http://whc.unesco.org/en/list/55).

Geological setting

Five major tectonostratigraphic components are distinguished in the Caledonian mountain belt in Scandinavia – single autochton and four overlying allochthonous complexes (Fig. 1; lower, middle, upper and uppermost; Roberts and Gee 1985). The Røros mining district was contained within the Upper Allochthon, consisting of continental rocks considered as the outermost margin of Baltica and ophiolitic rocks thought to represent mainly lithosphere of the Iapetus Ocean (Hacker and Gans 2005). During Scandian orogenesis Røros district has been under lower greenschist to lower amphibolite facies conditions (Grenne et al. 1999). It hosts sulfide ore deposits related to Late Ordovician calcareous phyllites and metagreywackes. Røros orefield consists of stratabound, massive pyrite- and/or pyrrhotite-rich polymetallic sulphide deposits (Barrie et al. 2010).

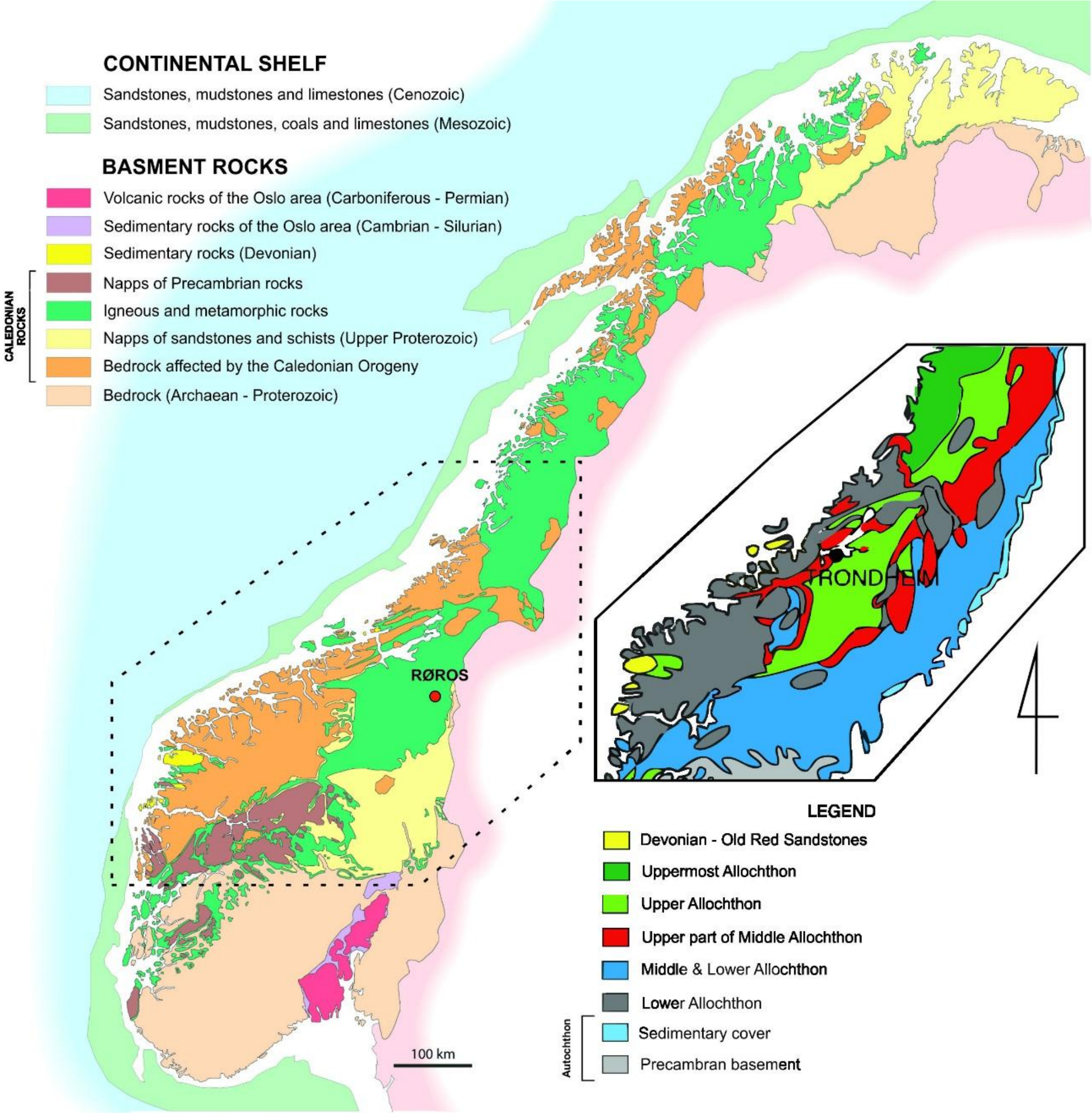

Fig.1. Simplified geological map of Norway with the Røros Village location (modified from: www.ngu.no; Gee et al. 2010).

Methods

The aim of this paper is to present characteristics of slags crystallizing rapidly at undercooling conditions and indicate main factors influencing phase dependencies. To accomplish this goal following methodology was applied: 10 samples of slags were collected between 2009 and 2011. Only two of them show obvious signs of rapid cooling. On the base of macro- and microscopic observation one sample was chosen for further investigations. Polished thin section were examined for texture properties and phase composition using polarizing Olympus BX-51 microscope, scanning electron microscope (SEM; FET Philips XL30) with an energy-dispersive spectrometer (EDS) at the Faculty of Earth Sciences, University of Silesia, Sosnowiec, Poland. Electron probe micro-analyzer (EPMA) and backscattered electron (BSE) imaging of phases were carried out on a CAMECA SX 100 apparatus in the Inter-Institution Laboratory of Microanalysis of Minerals and Synthetic Substances, Institute of Geochemistry, Mineralogy and Petrology, Faculty of Geology, University of Warsaw, by standard conditions (15 keV accelerating voltage, 10.0 beam current and beam diameter up to 5 µm, with standards: Ag – Ag_2Te; Al – $KalSi_3O_8$; As – GaAs; Ca – $MgCaSi_2O_6$; Cu – $CuFeS_2$; Fe – $CuFeS_2$; K – $KAlSi_3O_8$; Mn – $MnSiO_3$; Na – $NaAlSi_3O_8$; P – $Ca_5[PO_4]_3[OH,F,Cl]$; Pb – PbS, $PbCrO_4$; S – $CuFes_2$, $BaSO_4$; Se – Bi_2Se_3; Si – $MgCaSi_2O_6$; Ti – $CaTiO_5$; Zn – ZnS).

Results

On the base of microscopic observations it is possible to distinguish three zones (Fig.2) of slags: inner (20 – 30 mm), consisting of mainly glass with dispersed rare crystallites; outer (10 – 20 mm), characterized by the presence of dense net of needle-shaped crystallites with glass in the interstices; rim 2-5 mm thick, composed of crystallite aggregates arranged perpendicularly to the slag surface (Fig. 2).

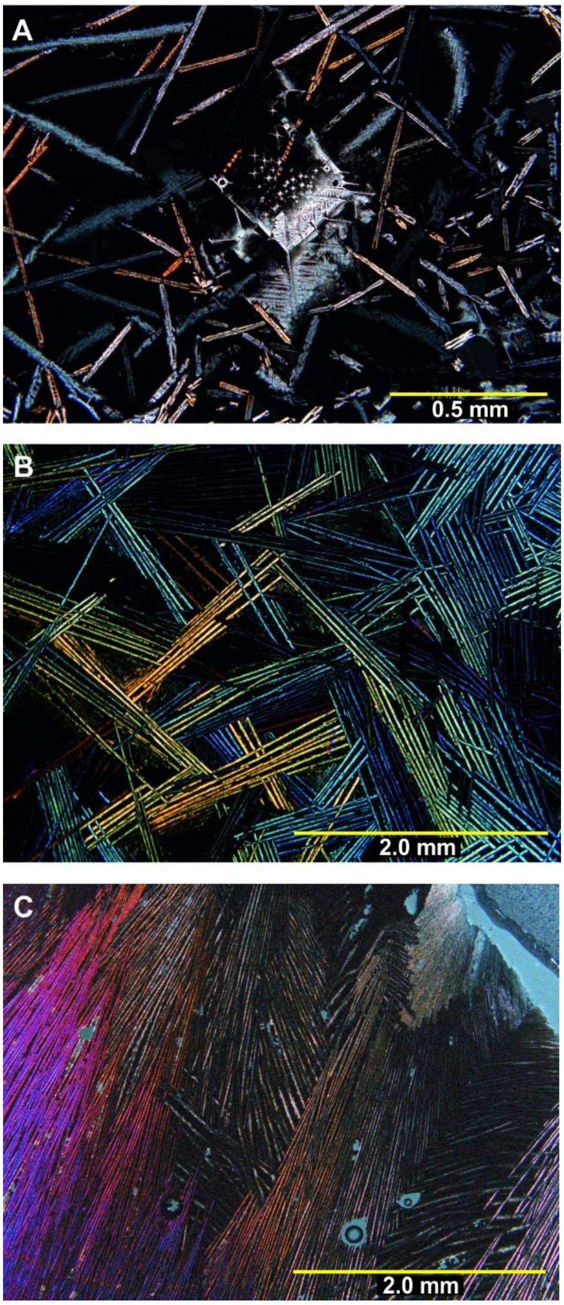

Fig.2. Microphotographs of thin section from three different parts of the Røros slags. **A)** Picture of the inner part of the slag with rare olivine crystallites. **B)** The outer part of slag with dense olivine net. **C)** Rim with olivine aggregates arranged perpendicularly to the slag surface.

The presence of sulphides was noted in every zone of the slag and no correlation between the crystal/glass ratio and their presence was noted. The main crystalline component is Fe-rich olivine-group mineral (Fa_{66-86}; Tab.1 ol), in some cases overgrown by a clinopyroxene of the composition near to diopside ($Wo_{50,23}En_{48,81}Fs_{0,96}$; Tab.1 cpx). The glass (Tab.1 gls), filling space between the crystals has picrobasaltic to basaltic andesite composition (Fig. 3). Sulphides in slags are represented by galena remnants (Tab.2 ga), Zn-sulphide (Tab.2 ZnS) and pyrrhotite (Tab.2 po). In some cases presence of an undefined Cu sulphide was noted (Fig. 4), but grain size did not allow to obtain high-quality EPMA results. No correlation between the qualitative phase composition and the data-point location within the particular zones was noted

Tab.1. Representative chemical compositions of olivine (ol), clinopyroxene (cpx) and glass (gls) from the investigated slags from Røros. EPMA data; nd – not detected.

	ol		**cpx**	**gls**	
wt. %	1	2	1	1	2
CaO	0.25	0.10	25.34	2.36	3.39
K_2O	0.21	0.00	0.00	2.15	2.66
FeO	59.62	54.00	0.62	32.32	19.25
MnO	0.36	0.32	0.00	0.30	0.16
TiO_2	0.05	0.07	0.02	0.84	1.09
Na_2O	0.18	0.08	0.16	1.26	1.83
SiO_2	31.78	31.61	54.97	43.63	53.78
Al_2O_3	1.21	0.13	0.44	14.36	16.59
MgO	4.44	10.94	17.70	0.49	0.20
ZnO	2.04	2.02	nd	2.53	1.88
P_2O_5	nd	nd	nd	0.15	0.09
SO_3	nd	nd	nd	1.24	0.69
Total	**100.13**	**99.25**	**99.27**	**101.63**	**101.60**

Tab.2. Representative chemical compositions of galena (ga), Zn-sulphide (ZnS) and pyrrhotite (po) from selected slags from Røros.

	ga		ZnS		po	
wt.%	1	2	1	2	1	2
As	0.00	0.00	0.00	0.00	0.00	0.02
Se	0.03	0.00	0.02	0.03	0.05	0.02
S	1.27	13.59	34.16	34.37	38.45	39.92
Pb	87.26	85.41	0.00	0.00	0.00	0.00
Ag	0.00	0.00	0.08	0.00	0.03	0.00
Fe	0.00	0.07	13.63	22.42	60.45	59.60
Mn	0.00	0.01	1.07	1.12	0.19	0.07
Cu	0.00	0.00	0.00	1.56	0.09	0.06
Zn	0.02	0.16	50.27	41.09	0.09	0.03
Total	**100.59**	**99.24**	**99.22**	**100.60**	**99.34**	**99.71**

Discussion

Phases described in this paper are characteristic for pyrometallurgical Cu, Zn or Pb slags (Warchulski and Szopa 2013; Puziewicz et al. 2007; Piatak and Seal II 2010; Ettler et al. 2009), although they differ in morphology. It raises the question of importance of ore chemistry on slag composition - Røros orefield is related with calcareous phyllites and metagreywackes containing massive pyrite- and/or pyrrhotite-rich polymetallic sulphide deposits (Barrie et al. 2010), while in Poland we deal with Mississippi Valley-Type Lead-Zinc ores from composed mainly of sphalerite, pyrite, markasite, galena and oxysulphides in dolomite rocks (Heijlen, Muchez et al. 2003) and northern Namibia sulphidic metallogenic province consists of limestones and dolomites in which ore minerals like chalcocite, enargite, galena, sphalerite are present (Frimmel et al. 1996.). Although technological process also varies depending on site location, main characteristics is similar. Process involves enriching of ore (usually flotation), crushing, sieving, smelting in atmospheric pressure and high temperature (at least 1000°C; Puziewicz et al. 2007) and rapid cooling on slag dump. In conclusion it seems that technological process is the main factor determining slag composition.

Our observations are in agreement with experimental studies of Lofgren (1980) underlining that in the same degree of undercooling olivine nucleates more readily than pyroxene, which in some cases is forms the rims around olivine. Microscopic examination suggest that the nucleation was inhomogeneous and steered by both temperature gradient between the outer and inner parts and volatiles contents. Volatiles decrease the rate of nucleation/crystallization (Vernon 2004), so the smallest crystal ratio in the internal part of the slag portions could be an effect of higher volatile content, which is expressed in higher vesicle content.

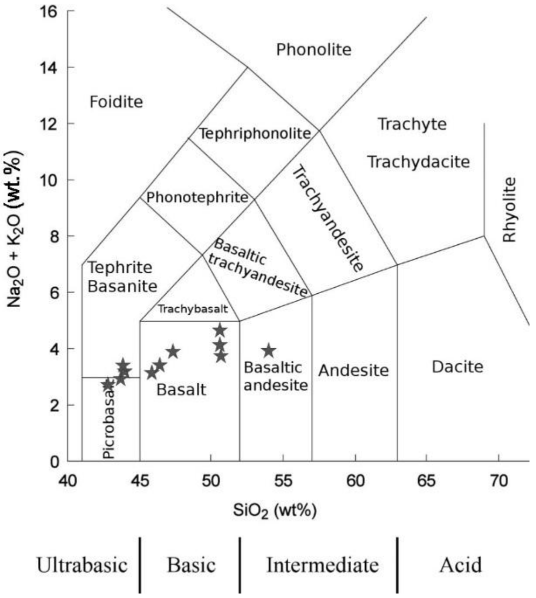

Fig.3. TAS diagram (from Le Maitre et al. 1989) showing the chemical compositions of glass from the Røros slags.

Conclusions

Slag management at Røros Copper Works resulted in undercooling of melt which resulted in crystallization of the olivine aggregates. Crystallization rate in studied slags depends mainly on temperature gradient and volatiles content. The most important factor determining composition of slag is technological process at site, while ore chemistry seems to have minor influence. Presented results suggest that cooling slags could be an analogue of fast-cooling basaltic lavas, similar textures and similar sequence of crystallization observed.

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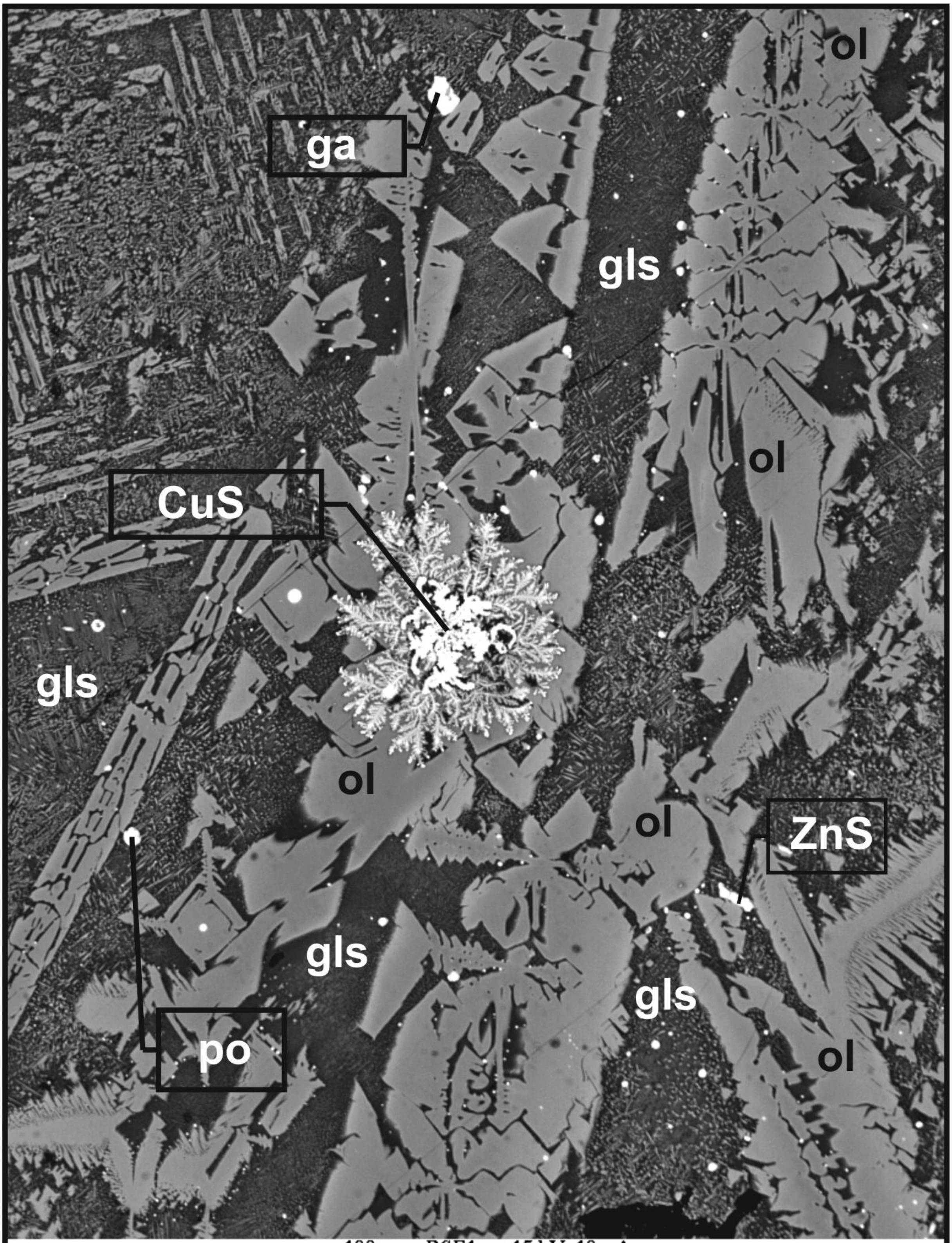

Fig.4. Main phases in slags (outer section) from Røros: ol-olivine, gls-glass, ga-galena, po- pyrrhotite, ZnS- Zn-sulphide, CuS – Cu sulphide. BSE image.

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