

Syn-tectonic sulphide remobilization and trace element redistribution at the Falun pyritic Zn-Pb-Cu-(Au-Ag) sulphide deposit, Bergslagen, Sweden



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ABSTRACT

Mineralization types at the Palaeoproterozoic Falun base metal sulphide deposit are predominantly pyritic Zn-Pb-Cu-rich massive sulphide mineralization, disseminated to semi-massive Cu-Au mineralization, auriferous quartz veins, and mineralized shear zones of talc-chlorite-dominated schist. The massive and disseminated to semi-massive sulphide mineralization types were subject to polyphase ductile deformation (D_1 and D_2) and metamorphism under low-P, lower-amphibolite facies conditions, which led to the development of ore textures and paragenetic relationships indicating both mechanical and chemical remobilization of sulphides. In the massive sulphide mineralization, rare inclusion-rich pyrite occurs as relic cores inside inclusion-poor metamorphosed pyrite. Imaging and spot analysis using multielement laser ablation inductively-coupled plasma mass spectrometry (LA-ICP-MS) reveal that inclusion-poor pyrite was depleted in trace elements, which were originally present as non-stoichiometric lattice substitutions or in mineral inclusions. The inclusion-rich pyrite was shielded from depletion and, at least partly, retained its initially higher trace element concentrations, including Au.

Gold is also associated with chalcopyrite in the disseminated to semi-massive Cu-Au mineralization and in the system of auriferous quartz veins hosted therein, the latter being also affected by the D_2 ductile strain. It is inferred that emplacement of the vein system took place after the peak of metamorphism, which occurred between D_1 and D_2 , but prior to and possibly even shortly after completion of the D_2 deformational event. Similarities in trace element signatures in chalcopyrite are compatible with the interpretation that the quartz veins formed by local chemical remobilization of components from the Cu-Au mineralization. Transport of liberated Au from pyrite during grain growth in the massive sulphide mineralization may have upgraded the Au endowment in the quartz veins, leading to the additional formation of native gold in the veins. A strong correspondence between elements liberated from pyrite (e.g. Pb, Bi, Se and Au) and those forming discrete and characteristic mineral phases in the quartz veins (Pb-Bi sulphosalts, native gold) supports this hypothesis.

Trace element signatures for the main sulphide minerals pyrite, chalcopyrite, sphalerite and galena are similar to previously published data from other metamorphosed massive sulphide deposits. The association of the Falun mineralization with elevated Bi is reflected by its occurrence in sulphide minerals (e.g. galena) and in abundant mineral inclusions of Pb-Bi sulphosalts (e.g. weibullite), especially in the disseminated to semi-massive Cu-Au mineralization. Elevated Sn concentrations in the lattice and/or as cassiterite inclusions in chalcopyrite, sphalerite and galena are compatible with a hot, acidic and reducing fluid during formation of the syn-volcanic, base metal sulphide mineralization and associated host-rock alteration.

1. Introduction

Ductile deformation and metamorphism can significantly change the configuration of ore minerals and metals in base metal sulphide deposits. Processes of remobilization may upgrade existing mineralization or even

lead to the formation of new mineralization types and deposits (e.g. Cox, 1987; Marshall and Gilligan, 1987, 1989, 1993; Marshall et al., 2000). The trace element distribution in sulphides can help elucidate such processes, and also aid in understanding conditions of ore formation, differentiating mineralization types, assessing the chemical effects of metamorphism and

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defining vectors towards mineralization (e.g. Hawley and Nichol, 1961; Bralia et al., 1979; Walshe and Solomon, 1981; Roberts, 1982; Huston et al., 1995; Cook et al., 2009; George et al., 2015).

The major ore province inside the Bergslagen lithotectonic unit in the Svecokarelian orogen (2.0–1.8 Ga), south-central Sweden (Fig. 1), hosts several thousand Fe oxide and base metal sulphide deposits (Stephens et al., 2009). The Falun pyritic Zn-Pb-Cu-(Au-Ag) sulphide deposit in the north-western part of this province has been one of the most important base metal producers in Sweden. The Falun mine was in continuous operation for several hundred years until 1992 with a total production of approximately 28–35 Mt of ore at grades of up to 5% Zn, 2% Pb, 0.6–4% Cu, 13–35 g/t Ag and 0.5–4 g/t Au (Tegengren, 1924; Grip, 1978; Allen et al., 1996). Significant exploration potential exists in the area, as testament by exploration activities during the past decade.

Major mineralization types at Falun include predominantly pyritic Zn-Pb-Cu-rich massive sulphide mineralization and disseminated to semi-massive Cu-Au mineralization in quartz-anthophyllite-rich altered rock. Subordinate mineralization types comprise auriferous quartz veins on the eastern side of the Falun deposit, and disseminated pyrite and chalcopyrite in shear zones composed of talc-chlorite-(quartz-biotite) schist. Partly Zn-Pb-(Ag) mineralized diopside-hedenbergite or tremolite skarn form a separate and subordinate type of mineralization (Fig. 2; cf. Kampmann et al., 2017). The deposit and its hydrothermal alteration envelope were affected by polyphase deformation and metamorphism under low-P, lower-amphibolite facies conditions at 1.9–1.8 Ga (Wolter and Seifert, 1984; Kampmann et al., 2016b).

This study aims firstly to characterize the different mineralization types at Falun with regards to ore textures in the main sulphide minerals pyrite, chalcopyrite, sphalerite and galena. Whole-rock multi-element data on some ore samples are included here to elucidate their composition and to identify possible indicator elements for e.g. Au. Secondly, trace element analysis using the LA-ICP-MS (laser ablation inductively-coupled plasma mass spectrometry) technique has been used to characterize the texturally different types of sulphide mineralization chemically. The integrated data set has been evaluated against the known framework of structural evolution of the Falun deposit. This allows for a more detailed discussion on the evolution of the deposit from initial syn-volcanic deposition of massive sulphides, to metamorphism, deformation and potential remobilization.

A previous study (Åberg and Fallick, 1993) attempted to reconstruct the properties of the fluid that formed the auriferous quartz veins. However, that study did not address whether these veins formed from an independent mineralizing event, or from remobilization from pre-existing auriferous mineralization. The trace element data acquired in the present study will be used to address the relationship of the auriferous syn-tectonic quartz veins to the pre-existing syn-volcanic mineralization types.

2. Geological setting

The Bergslagen lithotectonic unit (BLU) is dominated by 1.90–1.87 Ga, variably metamorphosed calc-alkaline granitoids with subordinate diorite, gabbro and ultramafic rocks (GDG intrusive rock suite in Stephens et al., 2009; Fig. 1A). Metamorphosed supracrustal rocks form the oldest component and commonly occur as inliers inside the GDG plutons, as in the inlier where the Falun base metal sulphide deposit is situated (Fig. 1B). The supracrustal rocks of the BLU consist of a succession of metamorphosed felsic volcanic and sub-volcanic rocks (1.91–1.89 Ga), which is stratigraphically underlain and overlain by siliciclastic metasedimentary rocks. Marble and skarn (non-genetic term for stratabound or stratiform rocks dominated by calc-silicate minerals such as garnet, clinopyroxene, and/or clinoamphibole; Törnebohm, 1875; Meinert, 1992) are locally interbedded with the metavolcanic rocks. Large portions of the sub-volcanic rocks overlap with the GDG intrusive rocks in terms of age and chemical composition.

Subsequent magmatic activity at 1.87–1.84 Ga and 1.81–1.78 Ga emplaced alkali-calcic granite, granodiorite, quartz monzonite and quartz monzodiorite, and subordinate gabbro and ultramafic rocks (GSDG intrusive rock suites in Stephens et al., 2009; Fig. 1A). Bodies of granite with high concentrations of U and/or Th, locally associated with pegmatite and showing a similar age of formation as the compositionally more heterogeneous GSDG rocks, also occur (GP intrusive rock suite in Stephens et al., 2009; Fig. 1A). All these younger intrusive rock suites are present in the vicinity of the Falun inlier (Fig. 1B).

The majority of base metal sulphide deposits have been categorized as ‘Falun’- (Magnusson, 1950, 1953) or ‘SVALS’ (stratabound volcanic-associated limestone-skarn-hosted)-type deposits (Allen et al., 1996). They are commonly spatially associated with marble and skarn in the felsic volcanic sequence, formed from limestone deposited in a shallow marine environment (Allen et al., 1996), as well as Fe oxide deposits. Other characteristic features are the stratabound nature of the ores and their spatial association with hydrothermally altered zones comprising phyllosilicate-rich and/or quartz-rich rocks with porphyroblasts of, for example, cordierite, garnet and amphibole. These rocks represent metamorphosed equivalents to hydrothermally altered volcanic rocks (herein referred to as ‘altered silicate-rich rocks’), in contrast to the marbles and skarns after a limestone precursor (e.g. Trägårdh, 1991; Allen et al., 1996; Stephens et al., 2009; Jansson and Allen, 2015; Kampmann et al., 2017). Falun- or SVALS-type deposits have been distinguished from another type of base metal sulphide deposits in Bergslagen, the so-called ‘Ämmeberg’- (Magnusson, 1950, 1953; Sundblad, 1994) or ‘SAS’ (stratiform ash-siltstone hosted)-type (Allen et al., 1996), represented by e.g. the Zinkgruvan deposit (Fig. 1).

The altered silicate-rich rocks at the Falun deposit have been subdivided according to their mineral associations (Fig. 2; Kampmann et al., 2016b, 2017) into biotite-quartz-cordierite-(anthophyllite) schist (BQC schist) and quartz-anthophyllite-(biotite-cordierite/almandine) metamorphic rock (QA rock), as well as the subordinate types biotite-almandine-(anthophyllite) and biotite-cordierite-(anthophyllite) schists (BA and BC schist, respectively). Talc-chlorite-(quartz-biotite) schist (TC schist) occurs along shear zones, which bound the central massive sulphide mineralization (Fig. 2). These mineral associations are products of metamorphic reactions from pre-metamorphic chlorite, sericite and quartz (Kampmann et al., 2017). Sub-volcanic intrusions and dykes commonly occur inside or close to the hydrothermally altered zones at Falun and other SVALS deposits (e.g. Jansson and Allen, 2011; Kampmann et al., 2016a).

The timing of hydrothermal alteration and mineralization at SVALS deposits has been constrained to a narrow time span (< 10 Myr) at c. 1.89 Ga during the syn-volcanic stage (Jansson and Allen, 2011; Kampmann et al., 2016a). Suggested ore-genetic processes for these deposits have involved volcanic-exhalative or sub-seafloor, volcanogenic massive sulphide (VMS) models, the latter at least partly comprising carbonate replacement (cf., for example, Koark, 1962; Boström, et al., 1979; Oen, 1987 with Allen et al., 1996; Jansson et al., 2013; Kampmann et al., 2017). Many SVALS deposits, such as the Ryllshyttan and Falun deposits, show both VMS- and skarn-like features, resulting from rapid burial of an originally sub-seafloor hydrothermal system to a deeper, contact-metasomatic regime (Jansson and Allen, 2015; Kampmann et al., 2017). In contrast, SAS deposits are inferred to have formed by exhalation of hydrothermal fluids on the seafloor (Allen et al., 1996).

Polyphase deformation and metamorphism under low-pressure and variable-temperature conditions affected the supracrustal rocks and mineralizations, as well as the GDG and, in part, the GSDG and GP intrusive rock suites inside the BLU during the Svecokarelian orogeny (Stephens et al., 2009; Beunk and Kuipers, 2012). The Falun inlier is situated in the northern part of a structural domain where regional D₂ folding with axial surface traces trending NE–SW to E–W is prominent (Fig. 1). The F₂ structures inside this inlier show large-scale S-asymmetry (Fig. 1B) and D₂ ductile shear zones are commonly parallel to the

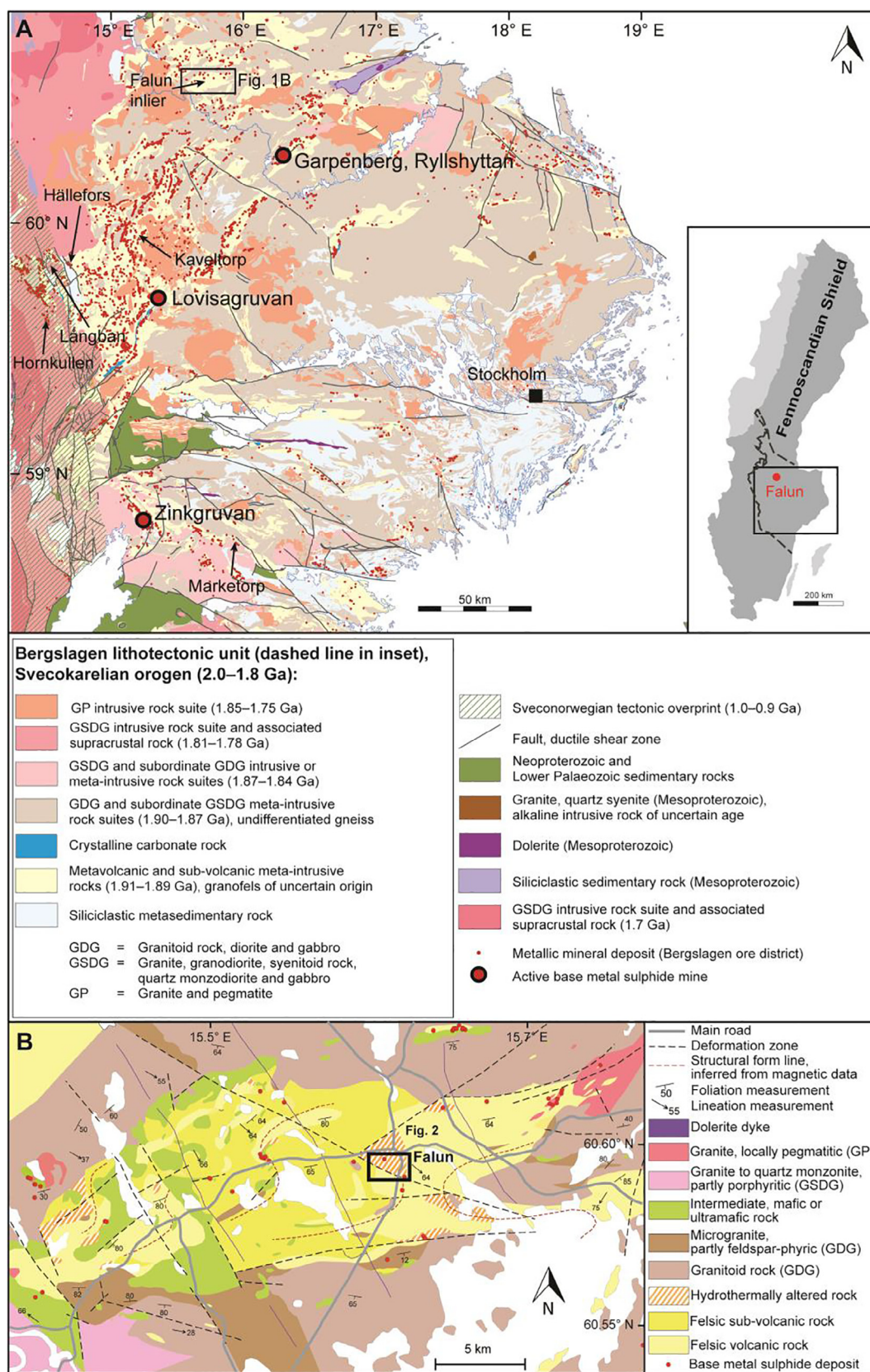


Fig. 1. (A) Geological map of the south-central part of Sweden situated predominantly inside the Bergslagen lithotectonic unit (modified from Stephens et al., 2009). The location of the study area at Falun and of other metallic mineral deposits, showing their common spatial association with metamorphosed, 1.91–1.89 Ga volcanic and sub-volcanic rocks, is included. The names of base metal sulphide deposits currently being mined are also shown. The inset map illustrates the location of the geological map and the boundaries of the Bergslagen lithotectonic unit (dashed line) inside the Fennoscandian Shield, Sweden. (B) Geological map of the Falun inlier, based on recent mapping results by the Geological Survey of Sweden, publicly available from their bedrock map database. Non-metamorphic terminology is used in the legend.

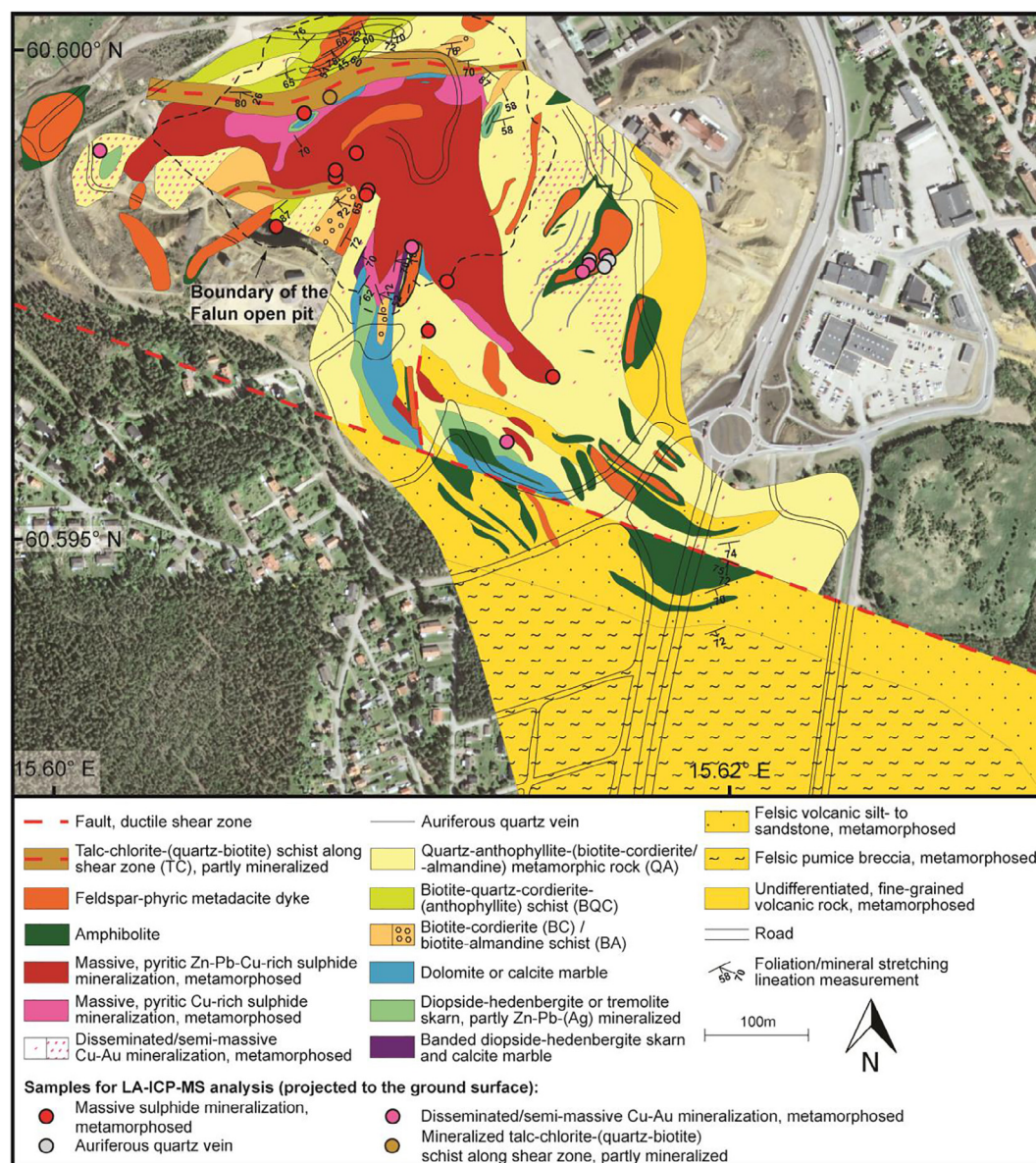


Fig. 2. Geological map of the Falun base metal sulphide deposit, including locations of the studied sulphide samples projected to the ground surface. The map is based on earlier work (Koark, 1962) that integrated mapping results from the ground surface (+150 m above sea level) and at depth (+100 m above sea level). The map has been modified using new field observational data in and around the open pit, a study of legacy mine maps and the logging of drill core situated < 50 m below the ground surface. The locations of auriferous quartz veins on the eastern side of the deposit are from Åberg and Fallick (1993).

axial surface traces to these folds. The D_2 folding deformed an earlier ductile fabric (D_1) at Falun and throughout the BLU (Stephens et al., 2009). A megascopic, reclined F_2 fold (Weijermars, 1987), interpreted as one or several steeply plunging F_2 sheath folds (Kampmann et al., 2016b), controls the geometry of the mineralized bodies, which occur as rod-shaped structures pinching out at approximately 450 m below sea level. The peak of metamorphism occurred between D_1 and D_2 , with peak conditions at Falun constrained at 2.5 ± 1 kbar and 550 ± 50 °C (Wolter and Seifert, 1984).

The D_1 and D_2 tectonothermal phases in the BLU occurred at around 1.86 Ga and 1.84–1.81 Ga, respectively (Andersson et al., 2006; Stephens and Andersson, 2015; Johansson and Stephens, 2016). U–Pb (monazite) geochronology at Falun documents the influence of the later event (Kampmann et al., 2016a). The BLU rocks formed along a convergent, active continental margin, involving processes related to subduction (e.g. Andersson et al., 2004; Hermansson et al., 2008; Stephens et al., 2009). Allen et al. (1996) proposed a continental back-arc basin setting. Transpressive deformation during the D_1 and D_2 phases is

thought to reflect successive advancing arc modes, each preceded and followed by a retreating arc mode with extension or transtension (Hermansson et al., 2008; Stephens et al., 2009; Beunk and Kuipers, 2012).

3. Methodology

3.1. Sampling

Twenty samples were collected for textural and chemical sulphide characterization with the aim to study sulphides from different mineralization types and different parts of mineralized bodies (Fig. 2). Ten samples are from legacy drill core material stored at the national drill core archive at the Geological Survey of Sweden (SGU) in Malå, Sweden. Seven samples were taken from drill core provided by the exploration company Drake Resources Ltd., whereas three samples are from the ground surface exposure in the Falun open pit. Ten samples represent massive sulphide mineralization, six are from disseminated to

semi-massive Cu-Au mineralization, three from auriferous quartz veins in the Cu-Au mineralization east of the central massive sulphides, and one sample is from the locally mineralized shear zone bounding the deposit to the north (Fig. 2).

3.2. Whole-rock multielement analysis

A selection from the 20 samples above were cleaned and surficial weathering removed with a rock saw. The samples were crushed and milled to pulps using low-chrome steel grinding mills at ALS Minerals in Örebro, Sweden. Pulps were analyzed for Mg, S, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Mo, Ag, Cd, Pb and Bi using a four-acid ($\text{HNO}_3\text{-HClO}_4\text{-HF-HCl}$) digestion and the inductively-coupled plasma atomic emission spectroscopy (ICP-AES) technique at ALS Minerals, Vancouver, Canada. Pb in one massive sulphide sample exceeded the upper detection limit of the method ($> 20 \text{ wt}\%$) and was quantified by titration. Au was measured by fire assay and gravimetric analysis. The multielement data passed both the internal laboratory QA/QC test and our test based on randomly interspersing two standards and one blank (all provided by Boliden Mineral AB) with the study samples.

3.3. Textural analysis of base metal sulphide minerals

Polished, round epoxy mounts (sections) with 25.5 mm diameter were prepared to allow characterization of ore textures and sulphide mineralogy, using an ore microscope (Nikon ECLIPSE E600 POL). Observations on a smaller scale and semi-quantitative mineral chemistry analyses were made using a field emission scanning electron microscope (FE-SEM, Merlin Zeiss Gemini) at Luleå University of Technology, equipped with an energy-dispersive X-ray spectroscopy (EDS) unit. Mounts selected for SEM were carbon-coated with a thickness of $\sim 15 \text{ nm}$. For EDS analysis, the acceleration voltage was set to 20 keV with an emission current of 1.1 nA.

3.4. Multielement LA-ICP-MS spot analysis of sulphides

Sulphide minerals in the polished sections of all 20 samples were analyzed at the CODES laser ablation analytical facility, University of Tasmania (Hobart, Australia), using a RESolution 193 nm ArF excimer Laser Ablation System. This unit has a large format S155 sample chamber, and is combined with an Agilent 7700 Quadrupole ICP-MS. The aerosol obtained from ablation in a He atmosphere was mixed with Ar immediately after leaving the sample chamber for entrainment and transport into the ICP-MS.

A beam size of $51 \mu\text{m}$ was used for 170 spot analyses (105 on pyrite, 39 on chalcopyrite, 26 on sphalerite), whereas a spot size of $29 \mu\text{m}$ was used for 17 spot analyses (3 on sphalerite, 14 on galena). The laser pulse rate was 10 Hz at a fluence of 2.7 J/cm^2 . Calculation of mass fractions and correction for instrument drift were carried out using the in-house standards STDGL2b2 (Danyushevsky et al., 2011) and GSD-1G (USGS, USA). The in-house pyrite standard ‘J-Py’ was used for calibration of S in pyrite. Dwell times for measured elements were: 0.01 s for ^{51}V , ^{90}Zr , ^{93}Nb , ^{53}Cr , ^{157}Gd , ^{178}Hf , ^{181}Ta , ^{232}Th and ^{238}U ; 0.02 s for ^{57}Fe , ^{59}Co , ^{60}Ni , ^{65}Cu , ^{66}Zn , ^{75}As , ^{77}Se , ^{95}Mo , ^{107}Ag , ^{109}Ag , ^{111}Cd , ^{118}Sn , ^{121}Sb , ^{125}Te , ^{182}W , ^{195}Pt , ^{197}Au , ^{202}Hg , ^{205}Tl , ^{206}Pb , ^{207}Pb , ^{208}Pb and ^{209}Bi ; and 0.005 s for ^{23}Na , ^{24}Mg , ^{27}Al , ^{29}Si , ^{34}S , ^{39}K , ^{43}Ca , ^{49}Ti and ^{55}Mn . The total sweep time was measured at 0.682 s. The gas background was recorded for 30 s prior to the activation of the laser and recording of the signal for 60 s. ^{57}Fe was used as an internal standard for pyrite, pyrrhotite and chalcopyrite; ^{208}Pb for galena and ^{66}Zn for sphalerite.

3.5. Multielement LA-ICP-MS imaging of sulphides

LA-ICP-MS images of pyrite and chalcopyrite were acquired as a series of parallel line rasters. Spacing between the lines was chosen to

be identical with the spot size to obtain total coverage of the image area. The laser rasters traversed at a rate of 16, 23 or $34 \mu\text{m/s}$, dependent on the spot size, and at a pulse rate of 10 Hz and a laser fluence of 2.7 J/cm^2 . The duration for the acquisition of each image was 1–2 h. Contamination from previously ablated lines was cleaned by a single pre-ablation pass prior to each analysis (Large et al., 2009). The standard glasses STDGL2b2 and GSD-1G, as well as gas blanks for standards and samples were analyzed before and after each image to calculate element concentrations in pyrite and chalcopyrite, and to correct for instrumental drift, if necessary. The following isotopes were measured: ^{23}Na , ^{24}Mg , ^{27}Al , ^{29}Si , ^{34}S , ^{39}K , ^{43}Ca , ^{49}Ti , ^{51}V , ^{53}Cr , ^{55}Mn , ^{57}Fe , ^{59}Co , ^{60}Ni , ^{65}Cu , ^{66}Zn , ^{75}As , ^{77}Se , ^{90}Zr , ^{93}Nb , ^{95}Mo , ^{107}Ag , ^{109}Ag , ^{111}Cd , ^{118}Sn , ^{121}Sb , ^{125}Te , ^{157}Gd , ^{182}W , ^{178}Hf , ^{181}Ta , ^{182}W , ^{195}Pt , ^{197}Au , ^{202}Hg , ^{205}Tl , ^{206}Pb , ^{207}Pb , ^{208}Pb , ^{209}Bi , ^{232}Th and ^{238}U . Dwell times for all masses was 0.005 s, except for Mo, Ag, Cd, Sn, Sb, W, Hg, Tl, Pb and Bi at 0.08 s and Se, Te, Pt and Au at 0.01 s. The total sweep time amounted to $\sim 0.346 \text{ s}$.

4. Character of mineralization types

The mineralogy and character of mineralization types at Falun, based on investigation of the polished sections, are summarized in Table 1 and illustrated in Fig. 3, whereas whole-rock multielement data of different mineralization types are presented in Table 2. Due to the small number of samples, the mass fractions for some of the measured elements, e.g. Au, may not be representative for the mineralization type as a whole. Local Zn-Pb-(Ag) mineralization in diopside-hedenbergite- or tremolite-rich skarn, mainly situated several 100 m to the south-east of the deposit (Fig. 2), represents a separate mineralization type (Kampmann et al., 2017) and is not addressed further.

4.1. Massive sulphide mineralization

The central mineralized body at Falun consists of predominantly pyritic Zn-Pb-Cu-rich massive to semi-massive sulphides, with some more Cu-rich zones along its margins (Fig. 2; Geijer, 1917; Kampmann et al., 2016b). The pyritic character of this mineralization type is reflected in high Fe concentrations (up to 39.7 wt%; Table 2). One sample with a low Fe concentration (2.98 wt%; Table 2) is from a veinlet of massive galena and sphalerite in the massive sulphide mineralization. In the upper levels of the mine and at the ground surface, this body is elongate and extends in a north-westerly direction. At depth towards the base of the body, its shape more closely resembles a downward-thinning rod (Kampmann et al., 2016b).

Typical grain sizes of the pyritic groundmass range between 0.5 and 3 mm (Fig. 3A), even though domains with finer grain size occur. Semi-massive varieties, which occur throughout the entire massive sulphide body, contain mostly quartz and subordinate silicates (e.g. biotite, sericite, anthophyllite) as gangue (Törnebohm, 1893; Geijer, 1917; Kampmann et al., 2017). The presence of silicate gangue in most of the massive sulphide body is reflected by variable Mg concentrations up to 5.19 wt% (Table 2). Fragments of dolomite or calcite marble, varying in size from mm to m scale, are present along the margins of the massive sulphide mineralization (Fig. 3B; Geijer, 1917; Kampmann et al., 2017). Larger carbonate fragments are frequently cut by veins of opicalcite (serpentinized humite-group minerals in a calcite groundmass). Main ore minerals in the massive sulphide mineralization are sphalerite, chalcopyrite and galena. These occur as minor phases in strongly pyritic varieties, but can also form massive veinlets of variable thickness with little or no pyrite, especially in the case of sphalerite and galena (Fig. 3C). Pyrrhotite is subordinate in the massive sulphide mineralization. The local occurrence of minerals of the tetrahedrite-tennantite series, as well as magnetite have also been reported (Sjögren, 1880; Weijermars, 1987).

Table 1
Mineralogical and textural character of the samples used in this study.

Mineralization type	Sample	Latitude (°N)	Longitude (°E)	Depth (m above sealevel)	Mineralogy	Character and ore textures
Massive sulphide mineralization	TKN15-6A	60.599368	15.611082	51	Py, sil, sph, cpy	Cataclastic py; interstitial sph; cpy disease
	56/1-ore1	60.597104	15.613431	– 305	Py, sph, sil	Weakly elongate and fractured py; sph inclusions in and interstitial between py
	79/17-ore4	60.597649	15.613971	– 177	Sph, py, gn, cpy	Massive sph pod; tectonoclastic py; elongate py in py-rich domains; interstitial gn between sph; cpy disease
	82/20-ore4	60.59842	15.612324	– 143	Gn, sph, py, sil	Massive gn and sph domains; tectonoclastic py and sph in gn
	82/22-ore2	60.598519	15.612363	– 165	Py, cpy, po, sph, sil	Fractured py; interstitial cpy, sph and po; cpy disease
	82/9-ore1	60.596067	15.616369	48	Py, po, sph, cpy, sil	Cataclastic py; interstitial cpy and sil; vein sph; band po
	83/8-ore2	60.598809	15.611747	– 151	Py, sil, cpy, sph	Elongate py; sph inclusions in py; interstitial cpy
	83/8-ore3	60.598746	15.611728	– 150	Py, dol, cpy, sph, sil	Fractured py; carbonate replacement by sph; interstitial cpy and po; cpy disease
	88/12-ore2	60.598969	15.612079	– 75	Gn, py, sph, po, sil, cc	Vein gn; tectonoclastic py and sph
	TKN15/19A	60.598177	15.610439	116	Sph, gn, sil	Semi-massive aggregates of sph and gn; tectonoclastic sph in gn; sph weakly fractured
Disseminated/semi-massive Cu-Au mineralization	10/18-5	60.598975	15.60682	129	Sil, py, sph, gn	Subhedral py porphyroblasts; Sph and gn inclusions in py;
	10/27-3A	60.597697	15.617186	119	Sil, cpy, py	Disseminated cpy and py in sil groundmass; impingement of py and sil
	10/27-3B	60.597697	15.617186	119	Sil, cpy, py, po, mcs	Veinlet and disseminated cpy; py and po spatially associated with cpy; mcs after cpy
	10/30-1	60.597715	15.617223	105	Sil, cpy, py, mcs, sph	Veinlet and disseminated cpy; mcs after py and cpy; sph inclusions in cpy; cpy disease
	62/9-ore2	60.595479	15.615299	71	Sil, cpy, sph, po	Veinlet and disseminated cpy; ragged cpy grain boundaries; cpy disease; rounded po inclusions in cpy (tectonoclastic?)
	79/14-ore2	60.597832	15.613263	– 173	Sil, po, cpy, py, sph	Vein po; py and cpy inclusions in po; interstitial sph between po; cpy disease
Auriferous quartz vein	10/27-2A	60.597706	15.617222	122	Sil, cpy, py, po, mcs	Quartz-dominated; py and po inclusions in vein/semi-massive cpy; rare mcs after cpy
	10/27-2B	60.597706	15.617222	121	Sil, cpy, po, py	Quartz-dominated; py and po inclusions in vein/semi-massive cpy
	10/30-2	60.597645	15.616783	85	Sil, cpy, po, py	Quartz-dominated; py and po inclusions in vein/semi-massive cpy
	TKN15/1B	60.599591	15.611579	55	Sil, py, cpy	Tectonoclastic py; shear bands in sil

cc = calcite; cpy = chalcopyrite; dol = dolomite; gn = galena; mcs = marcasite; po = pyrrhotite; py = pyrite; sil = silicates; sph = sphalerite;

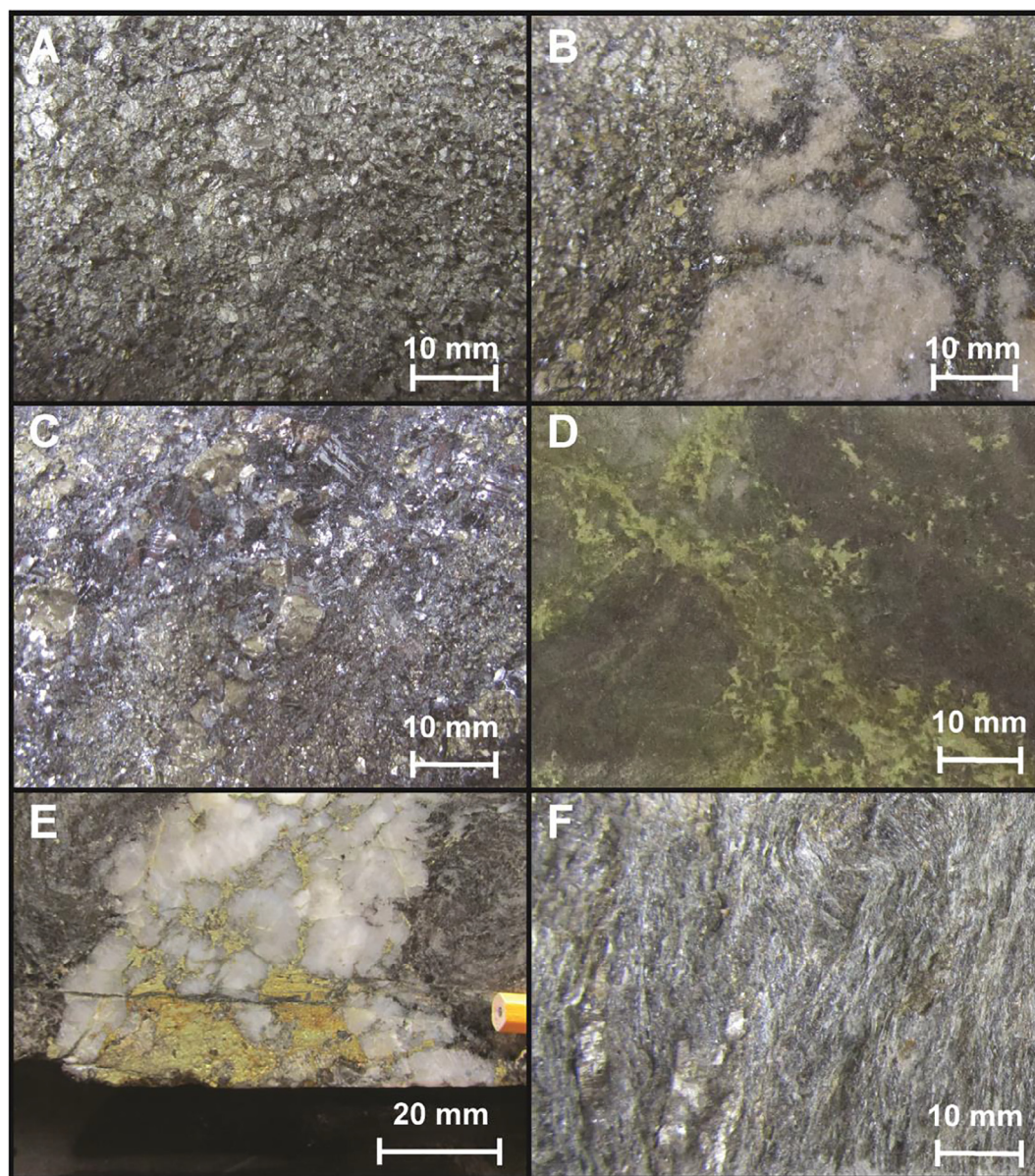


Fig. 3. Character of mineralization types at the Falun deposit, as observed in drill core (see also Fig. 2). (A) Pyritic massive sulphides from the central part of the main massive sulphide body. (B) Pyritic massive sulphides with fragments of dolomite marble from the peripheral parts of the main massive sulphide body. (C) Galena-, sphalerite- and pyrite-rich domain in the main massive sulphide body. (D) Disseminated to semi-massive Cu-Au mineralization in the stratigraphic footwall rocks to the main massive sulphide body. (E) Auriferous quartz vein inside mineralized stratigraphic footwall rocks to the east of the main massive sulphide body. (F) Pyrite-chalcopyrite-mineralized talc-chlorite-(quartz-biotite) schist from a shear zone bounding the main massive sulphide body to the north.

4.2. Disseminated to semi-massive Cu-Au mineralization

On nearly all sides of the central massive sulphide mineralization, sulphides (mainly pyrite and chalcopyrite) occur, at least in trace amounts, in all types of intensely altered silicate-rich rocks. Economic mineralization of this type, commonly occurring as veinlets (Fig. 3D), has mainly been encountered in the QA rock. Quartz in silicate-rich altered rocks has a dark appearance in hand specimen. Two major zones, to the east and west (Fig. 2), were mined with grades of up to 6 wt% Cu and 2–3 g/t Au (Geijer, 1917; Grip, 1978). In the western zone, semi-massive varieties of Cu-Au mineralization are present (cf. Törnebohm, 1893). The whole-rock multielement data confirm the dominance of Cu (between 0.706 and 4.81 wt%; Table 2) and Au (between 0.4 and 10.15 g/ton; Table 2), and the subordinate Zn (up to 0.257 wt%; Table 2) and Pb (up to 0.013 wt%; Table 2) concentration in this mineralization type. The disseminated to semi-massive Cu-Au

mineralization has been suggested to represent a feeder zone in the stratigraphic footwall of the massive sulphide mineralization (Koark, 1962; Kampmann et al., 2017).

4.3. Auriferous quartz veins

In the hydrothermally altered zone east of the massive sulphide mineralization, up to 10 cm thick veins of massive quartz (Figs. 2 and 3E) can readily be distinguished from the surrounding altered rocks by the white colour of the medium- to coarse-grained quartz and the rarity of other minerals typical of the altered silicate-rich rocks (e.g. cordierite, anthophyllite, biotite, almandine garnet). They were emplaced into altered silicate-rich rocks, including those with disseminated to semi-massive Cu-Au mineralization. Semi-massive Cu mineralization (coarse-grained chalcopyrite) is locally present in the quartz veins (Fig. 3E).

Table 2

Whole-rock multielement data of samples from the mineralization types referred to as pyritic Zn-Pb-Cu-rich massive sulphide, disseminated to semi-massive Cu-Au and auriferous quartz veins at Falun.

Mineralization type	Massive sulphide mineralization					Disseminated/semi-massive Cu-Au mineralization			Auriferous quartz vein
Sample	TKN15/1C	TKN15/3A	88/12-ore 2	TKN15/19A	TKN15/6A	10/30-1	TKN13/52A	10/27/-1	10/30/-2
Mg (wt%)	4.61	1.58	5.19	0.07	3.68	1.03	3.56	0.96	2.81
S (wt%)	26.5	43.8	28.4	17.8	36.4	4.5	1.05	3.01	0.27
Cr (wt%)	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	0.002	< 0.002	< 0.002	0.002
Mn (wt%)	0.15	0.05	0.23	0.06	0.04	0.04	0.03	0.03	0.07
Fe (wt%)	18.75	39.7	25.2	2.98	37.1	8.89	6.05	7.13	8.87
Co (wt%)	0.0044	0.0023	0.0022	< 0.0005	0.0021	0.0024	0.0012	0.0024	0.0028
Ni (wt%)	0.001	0.001	0.001	0.001	0.002	< 0.001	< 0.001	< 0.001	< 0.001
Cu (wt%)	0.037	0.046	0.179	0.041	0.077	4.81	0.706	2.35	0.145
Zn (wt%)	15.5	2.2	3.69	21.8	0.435	0.257	0.069	0.075	0.084
As (wt%)	0.017	0.034	0.023	0.004	0.015	< 0.001	0.002	0.001	0.001
Mo (wt%)	0.001	0.001	0.002	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
Ag (ppm)	75	10	37	838	12	21	4	9	1
Cd (wt%)	0.045	0.009	0.014	0.121	0.001	0.001	< 0.001	< 0.001	< 0.001
Au (ppm)	0.13	0.07	0.26	< 0.05	0.07	10.15	0.4	2.98	0.33
Pb (wt%)	3.55	1.06	2.91	48.71	0.388	0.009	0.013	0.01	0.009
Bi (wt%)	0.001	< 0.001	0.002	0.003	0.002	0.013	< 0.001	0.004	0.001

Table 3

Reported Pb-Bi sulphosalts in the Falun deposit. Nomenclature follows Moëlo et al. (2008).

Pb-Bi sulfosalts	Chemical formula	Reference
Bismuthinite	Bi_2S_3	Karup-Møller (1970)
Bournonite	CuPbSbS_3	Koark et al. (1986)
Cosalite	$\text{Pb}_2\text{Bi}_2\text{S}_5$	Koark et al. (1986)
Galenobismutite	PbBi_2S_4	Mumme (1980a)
Geocronite	$\text{Pb}_{14}(\text{Sb,As})_6\text{S}_{23}$	Koark et al. (1986)
Ikunolite	Bi_4SeS_2	Koark et al. (1986)
Laitakarite	$\text{Bi}_4(\text{Se,S})_3$	Karup-Møller (1970)
Nordströmite	$\text{CuPb}_3\text{Bi}_7(\text{S,Se})_{14}$	Mumme (1980a,b)
Pekoite	$\text{CuPbBi}_{11}(\text{S,Se})_{18}$	Mumme and Watts (1976)
Weibullite	$\text{Ag}_{0.33}\text{Pb}_{5.33}\text{Bi}_{8.33}(\text{S,Se})_{18}$	Karup-Møller (1970), Mumme (1980a)
Wittite	$\text{Pb}_8\text{Bi}_{10}(\text{S,Se})_{23}$	Mumme (1980a)

The occurrence of native gold, specifically restricted to the veins, has been reported (Nordenström, 1882; Törnebohm, 1893; Geijer, 1917; Åberg and Fallick, 1993), although discrete grains or aggregates of native gold on the macro- to microscopic scale could not be identified in the samples used in this study. Pb-Bi sulphosalts and cassiterite are common, mainly on μm -scale (i.e. under the SEM), occurring as inclusions in quartz and chalcopyrite, as well as in interstitial positions. The variably seleniferous Pb-Bi sulphosalts in the quartz veins at Falun have been the subject of previous mineralogical studies (e.g. Karup-Møller, 1970; Mumme and Watts, 1976; Mumme, 1980a,b) and a summary of the mineral phases occurring in this group is provided in Table 3.

The analyzed quartz vein has a similar whole-rock multielement composition as the disseminated to semi-massive Cu-Au mineralization (Table 2), except for lower S (0.27 wt%; Table 2) and Ag (1 ppm; Table 2) in the vein. The relatively low Au concentration in the sample (0.33 ppm; Table 2) likely reflects a nuggety Au distribution. More samples of the veins are needed to be able to quantitatively characterize their Au concentrations. Legacy mine data or previous publications do not allow metal grades for the quartz veins to be differentiated from other mineralization types.

The parallel system of auriferous quartz veins varies in strike from NE-SW to N-S (Fig. 2) and dips $\sim 70^\circ$ to the SE or E (Åberg, 1990; Åberg and Fallick, 1993). The veins pinch and swell (Åberg and Fallick, 1993) and anastomose (Fig. 3E) but parallel the tectonic foliation in most cases. The contacts to the surrounding altered silicate-rich rocks vary in orientation, are sharp without alteration haloes and commonly bulbous (Fig. 3E), consistent with the interpretation that they were

folded and mullioned during ductile deformation. There are some indications of internal deformation in the veins, such as fracturing and undulose extinction of quartz crystals, although fluid inclusions of up to 22 μm have been preserved (Åberg and Fallick, 1993). Locally, fractures filled with chlorite cross-cut both the quartz veins and the surrounding disseminated to semi-massive Cu-Au mineralization (Fig. 3E).

4.4. Mineralized shear zones

The central massive sulphides are bounded to the north and south by shear zones with mineral associations including talc, chlorite, as well as minor quartz and biotite (Fig. 3F). Pseudomorphs of talc after anthophyllite and chlorite after cordierite have been observed (Weijermars, 1987; Kampmann et al., 2017). The major (10–20 m thick) shear zone of this type, located directly to the north of the massive sulphides, strikes approximately E–W (Fig. 2). Pyrite and subordinate chalcopyrite and sphalerite are common as disseminations along the shear zones, and economic, semi-massive domains have been reported, but were largely mined out already at the beginning of the 20th century (Geijer, 1917; Grip, 1978).

5. Textures in sulphide minerals

The textures, including microstructures, in the dominant sulphide minerals in the four main mineralization types outlined above are addressed here, the order of abundance generally being pyrite, sphalerite, chalcopyrite and galena (Geijer, 1917; Grip, 1978).

5.1. Massive sulphide mineralization

The groundmass of the massive sulphide mineralization is dominated by subhedral to euhedral and inclusion-poor pyrite with a typical grain size around 0.5 mm and a mainly granoblastic appearance (Fig. 4A, B). The pyrite grains are commonly in contact with each other and show fine impingement cracks, developed approximately perpendicular to the contact (Fig. 4A, B; cf. Passchier and Trouw, 2005). Despite impingement and possible grain rotation, pyrite grains tend to form interfacial angles of approximately 120° (i.e. dihedral angles) in many cases (Fig. 4A). This is characteristic of growth or recrystallization due to grain boundary area reduction, which tends to minimize grain surface areas and interfacial tension (e.g. Craig and Vokes, 1993; Craig and Vaughan, 1994; Passchier and Trouw, 2005). Local inclusions of quartz, amphibole and pyrrhotite occur in pyrite.

In semi-massive sulphide domains with significant quartz gangue,

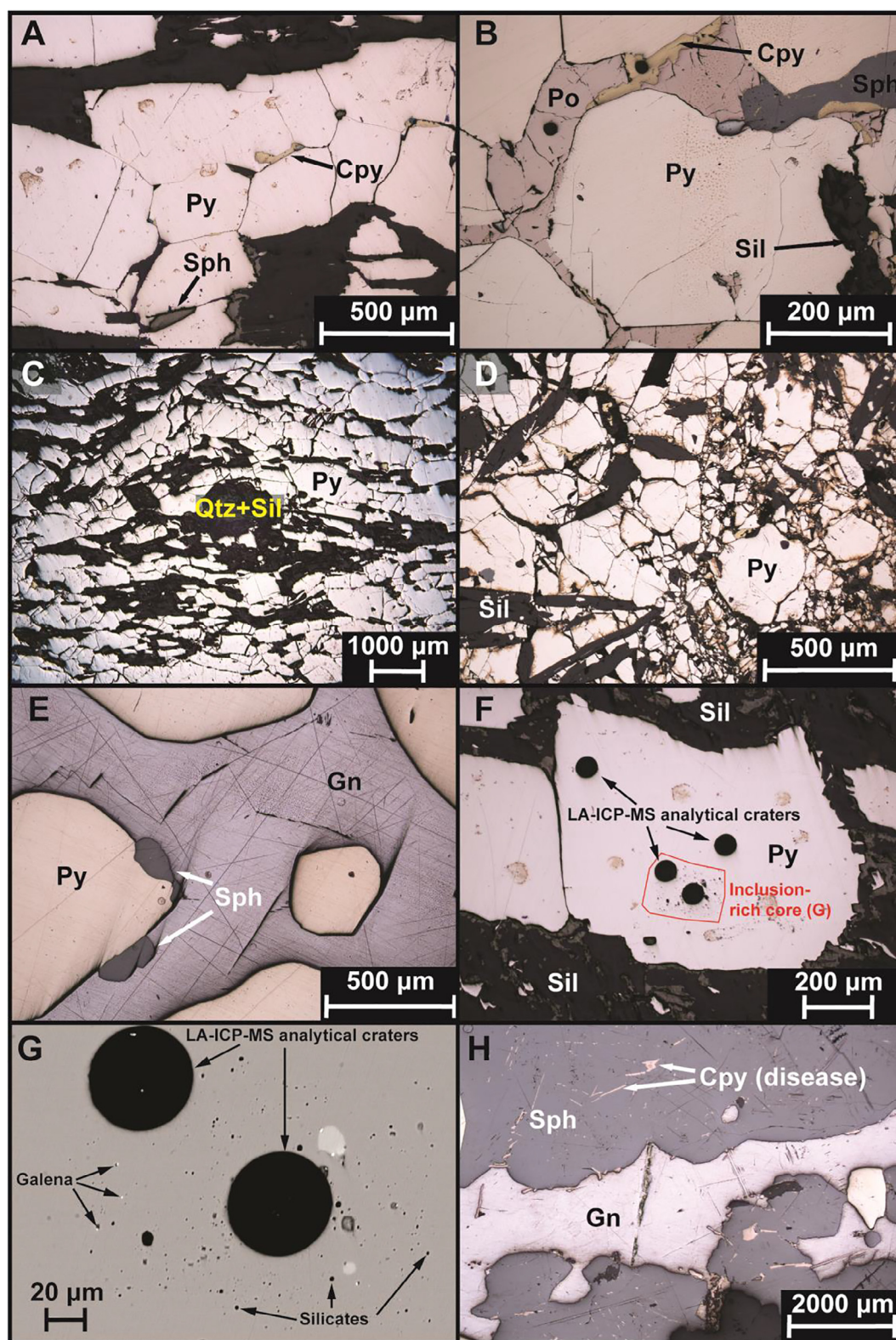


Fig. 4. Photomicrographs in reflected, plane-polarised light of ore textures in the massive sulphide mineralization at the Falun deposit. (A) Subhedral, inclusion-poor pyrite grains with interstitial sphalerite and chalcopyrite (massive sulphide mineralization). Minor inclusions of quartz occur. The pyrite grains show impingement cracks along contact surfaces with other pyrite grains. (B) Subhedral inclusion-poor pyrite, enveloped by pyrrhotite and subordinate sphalerite and chalcopyrite (massive sulphide mineralization). Pyrrhotite occurs also as minor inclusions in the pyrite. Pyrite overgrows anthophyllite and chlorite (dark silicate phases in picture). The pyrite grains show impingement cracks. (C) Elongate pyrite grains, together with silicates, including quartz (massive sulphide mineralization). (D) Cataclastic pyrite domain (massive sulphide mineralization) in close vicinity to a shear zone. (E) Tectonoclastic (“durchbewegt”), rounded pyrite and sphalerite in massive galena veinlet (massive sulphide mineralization). (F) Subhedral pyrite (massive sulphide mineralization) with an inclusion-rich core and an inclusion-poor rim. (G) BSE image of the inclusion-rich core shown in F. (H) Irregular galena veinlet in massive sphalerite aggregate (massive sulphide mineralization). Sphalerite contains fine-grained inclusions of chalcopyrite (“chalcopyrite disease”; Barton and Bethke, 1987). *Abbreviations:* Cpy = chalcopyrite; Gn = Galena; Po = pyrrhotite; Py = pyrite; Qtz = quartz; Sil = silicates; Sph = sphalerite.

pyrite grains are elongate with a sub-parallel orientation of their long axes (Fig. 4C). This fabric locally bends around quartz grains (Fig. 4C). Growth of pyrite under non-isotropic stresses is inferred. Intensely cataclastically deformed pyrite has been observed locally in pyrite-dominated domains, proximal to shear zones containing TC schist (Fig. 4D). Gangue in such domains comprises less competent silicates such as orthoamphibole, chlorite and local talc. Significant fracturing and grain size reduction due to pyrite-pyrite impingement, as well as the development of cataclastic deformation bands of strongly brecciated pyrite characterize such domains. Fractures in pyrite grains are commonly filled by less competent silicates such as chlorite (Fig. 4D).

Pyrite porphyroblasts inside massive veinlets of less competent sulphides (mainly galena, but also sphalerite and rarely chalcopyrite) exhibit rounded grain boundaries and typically lack fractures and grain elongation due to recrystallization under anisotropic stress (Fig. 4E). Sphalerite grains in galena show similar characteristics (Fig. 4E). This microstructure is interpreted as resulting from ductile shearing during which grains of a relatively competent sulphide (e.g. pyrite) were rotated within a massive aggregate of a less competent sulphide such as galena. The pyrite porphyroblasts would have been shielded from internal brittle deformation, since strain was partitioned to the matrix. This microstructural feature is commonly observed in metamorphosed and deformed massive sulphides, and is herein referred to as “tectonoclastic” (after Cook et al., 1993). In the literature, it has also been referred to as “durchbewegung” structure (e.g. Vokes, 1969; Marshall and Gilligan, 1989) and, in the context of Swedish sulphide deposits, as “ball ore” (cf. Geijer, 1971).

In the core of subhedral, less deformed pyrite grains, an inclusion-rich pyrite variety occurs locally (Fig. 4F). Widespread micro-inclusions of galena, sphalerite and silicates (e.g. biotite) were identified in this pyrite variety by EDS analysis during BSE imaging (Fig. 4G). Due to the similar shape of the core and the rim (Fig. 4F), pyrite is interpreted to have grown during metamorphism, probably from pre-existing smaller grains (cf. Craig et al., 1998). This mechanism is common in massive sulphides as a response to tectonothermal influence by grain boundary area reduction (Craig et al., 1998; Passchier and Trouw, 2005). Expulsion of mineral inclusions commonly occurs during metamorphic growth or recrystallization processes in pyrite (e.g. Huston et al., 1995). During this process, cores with unswept grain boundaries and preserved inclusions, as observed at the Falun deposit, can be retained in the centre of former mineral aggregates, which have undergone the inferred growth process (Passchier and Trouw, 2005). Further characterization of the two pyrite types has been carried out using LA-ICP-MS data and is addressed below.

Sphalerite, chalcopyrite and pyrrhotite are situated in interstitial positions between coarser pyrite grains. Sphalerite and chalcopyrite are usually fracture-free (Fig. 4A, B). Chalcopyrite is free of inclusions, and also occurs as commonly crystallographically oriented rows of fine-grained blebs and rods in larger sphalerite aggregates (Fig. 4H). This texture, referred to as “chalcopyrite disease”, has been described from numerous metamorphosed massive sulphide deposits previously (Hutchinson and Scott, 1981; Barton and Bethke, 1987). Galena is present in the massive sulphides either as a massive matrix around tectonoclastic pyrite in up to 5 cm wide veinlets (Fig. 4E), or as veinlets inside domains of massive sphalerite (Fig. 4H). Margins of other sulphide minerals are commonly rounded in contact with galena (Fig. 4E, H). There are no indications of fracturing in galena.

5.2. Disseminated to semi-massive Cu-Au mineralization

Pyrite porphyroblasts in disseminated to semi-massive Cu-Au mineralization are subhedral and 0.2–5 mm in diameter (Fig. 5A). They are weakly fractured and richer in mineral inclusions than pyrite in the massive sulphides, mainly comprising silicates (e.g. biotite and quartz; Fig. 5A), Pb-Bi sulphosalts and other sulphides (mainly chalcopyrite

and sphalerite). Local domains hosting pyrrhotite rather than pyrite occur.

Chalcopyrite is the main sulphide mineral in this mineralization type. It forms anastomosing and branching veinlets, as well as disseminated grains and fragments in the silicate groundmass (Fig. 5B). In semi-massive varieties, the veinlets can form a complex network enveloping isolated lenses of quartz and other silicates, resembling a stockwork. Irregular, rounded grain boundaries and bleb-shaped grains of chalcopyrite are most common. Grains and aggregates of sphalerite (Fig. 5B) and pyrite occur both inside and along the margins of the chalcopyrite veinlets. BSE imaging reveals the presence of micro-inclusions of cassiterite in both pyrite and chalcopyrite (Fig. 5C).

5.3. Auriferous quartz veins

In general, quartz and sulphides have coarser grain sizes in the auriferous quartz veins, compared to the surrounding disseminated to semi-massive Cu-Au mineralization (Fig. 5D). Veinlets of chalcopyrite form networks along the interstitial spaces between quartz grains and aggregates (Fig. 3E). The main orientation of the veinlets is parallel to the walls of the quartz vein, and they do not extend into the surrounding altered silicate-rich rock (Fig. 3E). Inclusions of medium- to coarse-grained pyrite and quartz, as well as rare fine-grained sphalerite occur in the veinlets (Fig. 5D). Pyrite and pyrrhotite are moderately fractured and inclusion-bearing, similar to the disseminated to semi-massive Cu-Au mineralization (Fig. 5D). Micro-inclusions of Pb-Bi sulphosalts (Table 3) were observed in the sulphides and quartz-rich groundmass, but only in BSE images (Fig. 5E).

5.4. Mineralized shear zones

Pyrite grains from this mineralization type are 50–200 µm in size, are slightly elongate along the main foliation and exhibit variably rounded grain boundaries (Fig. 5F). Tectonoclastic rotation and rounding of pyrite grains in a less competent groundmass of mainly talc and chlorite due to shearing is inferred. Chalcopyrite and sphalerite occur as disseminated fragments, usually with grain sizes < 20 µm.

6. Trace element chemistry in sulphide minerals

The LA-ICP-MS depth profiles (Fig. 6) of sulphides from Falun suggest the presence of micro- to macro-inclusions in approximately 15% of the spot analyses. In general, such spot analyses have been excluded from further data processing. However, 12 spots, representing inclusion-rich pyrite, have been retained in the dataset, to be able to characterize this textural type in pyrite. In general, the figures and sections below include only measurements above the median lower detection limit for the respective mineral and element (cf. Tables 4–7). The entire data of the LA-ICP-MS spot analyses are attached as [supplementary material](#) (Table A1).

6.1. Pyrite

A generally low and even distribution of trace elements in inclusion-poor pyrite (massive sulphide mineralization) is indicated by the LA-ICP-MS data (Table 4) and depth profiles (Fig. 6A), as well as the multielement imaging (Fig. 7A). Significantly large signals (> 10² counts) are only recorded for Co, Ni, As, Se, Pb and Bi, and to a lesser degree Cu and Sb. More strongly elevated, homogeneous distributions for Co, As and Se in the inclusion-poor pyrite are corroborated by the LA-ICP-MS depth profiles (Fig. 6A). This is compatible with the incorporation of these elements in the pyrite crystal lattice (Huston et al., 1995). A subtler zoning (less than two orders of magnitude count difference) is visible for As, as well as for Co and Ni (Fig. 7A). These three elements are relatively enriched in the centre of the grain.

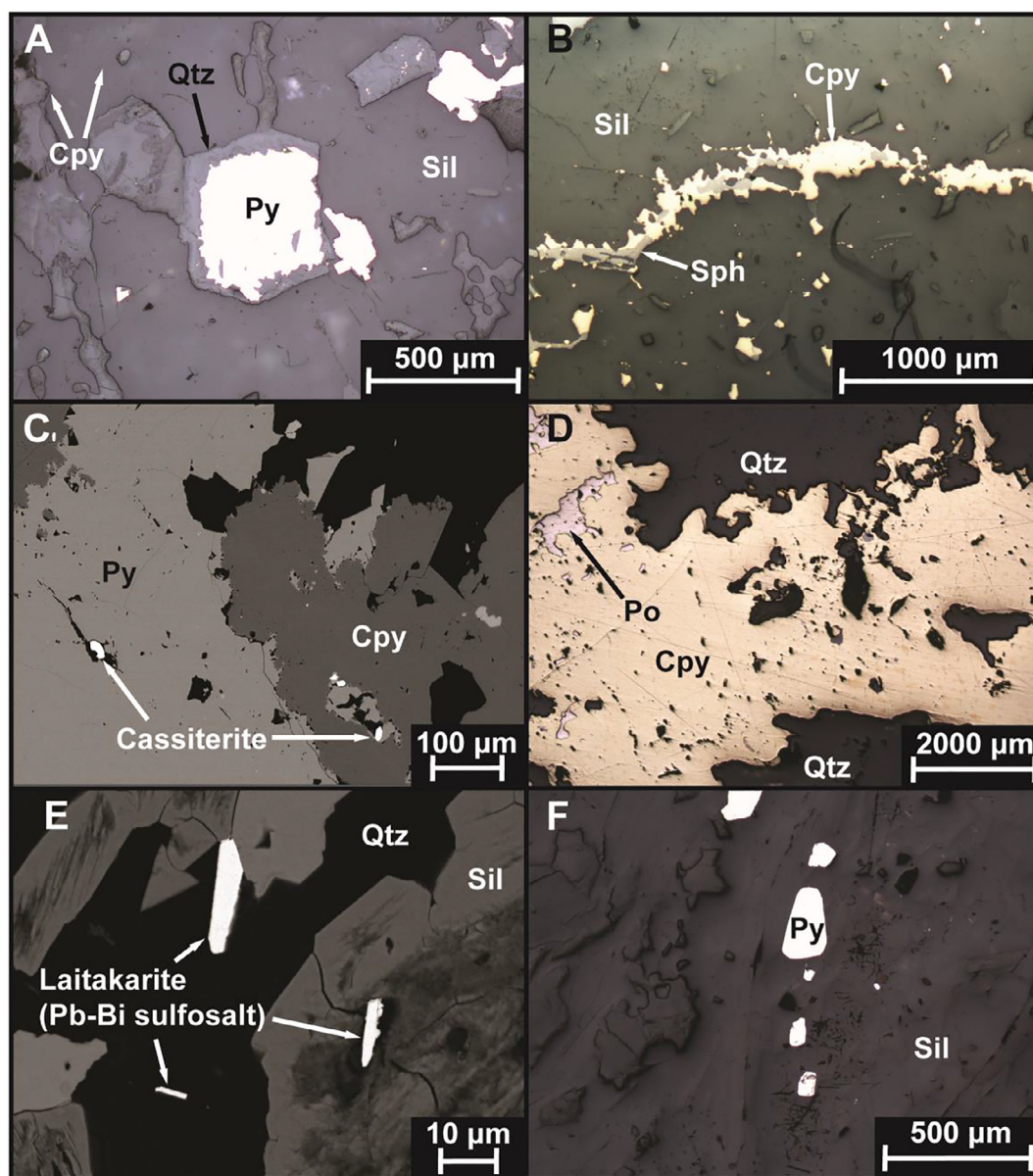


Fig. 5. Photomicrographs in reflected, plane-polarised light of ore textures in other mineralization types at the Falun deposit. (A) Subhedral pyrite porphyroblast with minor quartz inclusions and impinged on quartz in silicate groundmass (disseminated to semi-massive Cu-Au mineralization). (B) Veinlet of chalcopyrite and subordinate sphalerite in silicate groundmass (disseminated to semi-massive Cu-Au mineralization). (C) BSE image of cassiterite micro-inclusions in pyrite and chalcopyrite (disseminated to semi-massive Cu-Au mineralization). (D) Coarse-grained chalcopyrite with irregular pyrrhotite and quartz inclusions (auriferous quartz vein). (E) BSE image of micro-inclusions of Pb-Bi sulphosalts in quartz and silicates (auriferous quartz vein). (F) Disseminated, rounded (tectonoclastic) pyrite (TC schist along shear zone). *Abbreviations:* Cpy = chalcopyrite; Po = pyrrhotite; Py = pyrite; Qtz = quartz; Sil = silicates; Sph = sphalerite.

The increased concentration of Pb along the pyrite grain boundary (Fig. 7A) is probably due to Pb contamination from sputtering of the surrounding galena groundmass, and not from Pb in the pyrite itself. Strongly elevated concentrations of Se, Ag, Sn, Sb, Tl, Pb and Bi are present both in the surrounding galena and in local spots inside pyrite, indicating the presence of isolated mineral inclusions of galena, possibly together with Pb-Bi sulphosalts and/or tetrahedrite and minor cassiterite. Subordinate micro-inclusions of galena are also indicated by the LA-ICP-MS depth profiles of inclusion-poor pyrite (Fig. 6A).

Trace elements in inclusion-rich pyrite (massive sulphide mineralization) show higher concentrations and a more uneven distribution, suggested by LA-ICP-MS depth profiles (Fig. 6B) and multielement imaging (Fig. 7B). Both As and, at lower levels, Co and Se show fairly even distributions in the analyzed volume, with depth profiles parallel to those of Fe and S, similar to inclusion-poor pyrite (Fig. 6B).

Numerous elements, including Mn, Cu, Zn, Ag, Sn, Sb, Au, Pb and Bi, show uneven distributions due to their presence as micro-inclusions in various minerals (Figs. 6B and 7B). These may include galena, sphalerite and silicates (cf. Fig. 4G), as well as sphalerite, tetrahedrite, cassiterite and native gold. A zone of enriched Mn, Co, Cu, Zn, Se, Sn and W is conspicuous along the margin of the inclusion-rich pyrite core (Fig. 7B). Some of these elements are also enriched along the external grain boundaries of the inclusion-poor pyrite rim.

Inclusion-poor and inclusion-rich varieties in pyrite (massive sulphide mineralization) are distinct in that the latter shows higher concentrations of Cu, Zn, Ag, Sn, Sb, Tl, Au, Pb and Bi, and to a lesser degree As (Fig. 8; Table 4). None of these elements can be stoichiometrically incorporated into the pyrite crystal lattice, and are instead present mainly in mineral inclusions or as non-stoichiometric lattice substitutions (i.e. As, Tl and Au; cf. Huston et al., 1995). The Co and Ni

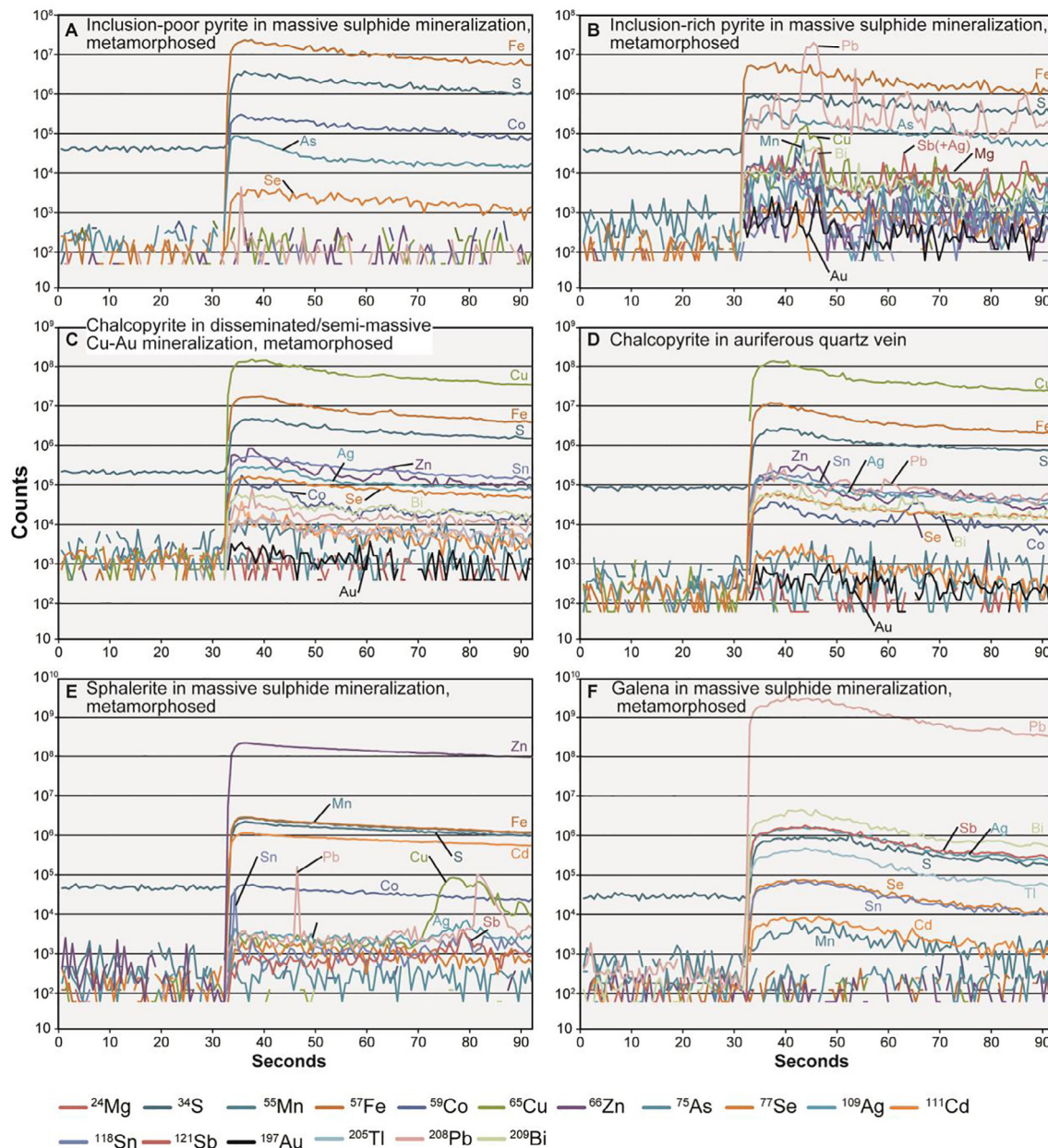


Fig. 6. Representative LA-ICP-MS depth profiles for the major sulphide minerals at the Falun deposit. (A) Inclusion-poor pyrite, sample 79/14-ore4 (massive sulphide mineralization). (B) Inclusion-rich pyrite core (subhedral grain), sample 82/22-ore2 (massive sulphide mineralization). (C) Chalcopyrite (veinlet), sample 10/30-1 (disseminated to semi-massive Cu-Au mineralization). (D) Chalcopyrite (semi-massive), sample 10/27-2A (auriferous quartz vein). (E) Sphalerite (massive veinlet), sample TKN15/19A (massive sulphide mineralization). (F) Galena (massive veinlet), sample 88/12-ore2 (massive sulphide mineralization).

concentrations in the two pyrite varieties in the massive sulphides are similar (Fig. 8; Table 4). Similar concentrations are also observed for Se, which is mainly present as a stoichiometric lattice substitution (Fig. 6A, B).

Trace element concentrations in pyrite from the disseminated to semi-massive Cu-Au mineralization are similar to those in inclusion-poor pyrite (massive sulphide mineralization) for Cu, Zn, Ag, Sn, Sb, Pb and Bi; Au and Tl could not be detected (Fig. 8; Table 4). Concentrations of Co, Ni and Se (stoichiometric lattice substitutions) in the Cu-Au mineralization are consistently relatively low, although partly overlapping with those in pyrite from the massive sulphides (Fig. 8).

Pyrite from auriferous quartz veins shows variable concentrations in Co, Ni, Cu, Zn, Ag, Tl and Pb, compared with the close to log-normal distributions for pyrite from the other mineralization types (Fig. 8). Concentrations of As, Se and Pb are more constant (Fig. 8; Table 4). A

moderate correlation between high concentrations of Bi and Se and, to a lesser degree, Cu and Pb, is consistent with the common occurrence of micro-inclusions of Pb-Bi sulphosalts in the auriferous quartz veins. Thus, high Se concentrations do not only reflect Se in the pyrite lattice. Only few LA-ICP-MS data are available for pyrite from mineralized TC schist along shear zones bordering the massive sulphide mineralization (Fig. 8; Table 4). Concentrations for all measured trace elements are in the general range of those in inclusion-poor pyrite from the massive sulphide mineralization.

A linear correlation exists between As and Au in pyrite from Falun, for which concentrations of these elements are above the median detection limit, i.e. mostly in inclusion-rich pyrite (Fig. 9A). This is consistent with Au incorporation into the pyrite lattice via a coupled substitution with As (Cook and Chrysosoulis, 1990; Huston et al., 1995; Reich et al., 2005). The additional structural site is in this case most

Table 4
Summary statistics for trace element concentrations in pyrite.

Mineralization type/ textural type	Inclusion-poor pyrite in massive sulphide mineralization				Inclusion-rich pyrite in massive sulphide mineralization				Pyrite in disseminated/ semi-massive Cu-Au mineralization			
	38				12							
	Element (ppm)	Median DL (ppm)	Low	Median	High	MDL (%)	Low	Median		High	MDL (%)	
Number of analyses												
Mg	0.07	< 0.07	< 0.07	< 0.07	18.75	26	< 0.07	31.70	294	92		
Al	0.18	< 0.18	< 0.18	< 0.18	29.19	13	< 0.18	27.66	283	83		
Si	41.00	< 41.00	< 41.00	< 41.00	< 41	0	< 41.00	< 41.00	2616	33		
Ti	0.87	< 0.87	2.19	< 0.87	3.64	95	< 0.87	3.35	43.43	58		
V	0.02	< 0.02	< 0.02	< 0.02	0.24	5	< 0.02	< 0.02	0.12	33		
Cr	0.22	< 0.22	0.28	< 0.22	11.73	58	< 0.22	< 0.22	1.81	33		
Mn	0.20	< 0.20	0.37	< 0.20	0.83	97	1.53	5.06	59.98	100		
Fe	2.20	465,500	465,500	465,500	465,500	100	465,500	465,500	465,500	100		
Co	0.02	3.29	61.86	295	295	100	1.01	162	380	100		
Ni	0.02	0.08	2.29	22.54	22.54	100	< 0.02	0.61	1.61	92		
Cu	0.09	0.15	0.34	0.85	0.85	100	5.67	128	715	100		
Zn	0.17	0.26	0.45	17.75	17.75	100	2.44	44.19	199	100		
As	0.44	107	548	1601	1601	100	926	1727	3392	100		
Se	2.14	6.28	33.26	430	430	100	11.25	128	695	100		
Mo	0.01	< 0.01	< 0.01	< 0.01	0.60	16	< 0.01	< 0.01	0.06	50		
Ag	0.01	< 0.01	< 0.01	< 0.01	0.25	21	0.58	5.33	46.29	100		
Cd	0.02	< 0.02	0.01	0.32	0.32	8	< 0.02	0.46	1.81	92		
Sn	0.02	< 0.02	0.03	0.07	0.07	68	0.25	2.08	1187	100		
Sb	0.01	< 0.01	< 0.01	0.23	0.23	29	0.62	31.86	164	100		
Te	0.10	< 0.10	< 0.10	< 0.1	< 0.1	0	< 0.10	< 0.10	0.28	17		
W	0.01	< 0.01	< 0.01	0.04	0.04	8	< 0.01	1.43	23.58	58		
Au	0.01	< 0.01	< 0.01	0.01	0.01	8	0.05	0.68	3.05	100		
Tl	0.01	< 0.01	< 0.01	0.02	0.02	5	0.03	1.09	23.26	100		
Pb	0.01	< 0.01	0.07	240	240	95	41.10	840	6077	100		
Bi	0.01	< 0.05	< 0.05	0.09	0.09	13	0.23	6.11	22.87	100		
Th	0.00	< 0.003	< 0.003	< 0.003	< 0.003	0	< 0.003	< 0.003	< 0.003	0		
U	0.00	< 0.002	< 0.002	0.63	0.63	13	< 0.002	< 0.002	2.03	42		
Mineralization type/ textural type	Pyrite in disseminated/ semi-massive Cu-Au mineralization				Pyrite in auriferous quartz vein				Pyrite in mineralized TC schist along shear zone			
Number of analyses	14				7				6			
Element (ppm)	Median	High	MDL (%)		Low	Median	High	MDL (%)	Low	Median	High	
Mg	< 0.07	98.51	36		0.13	0.27	87.16	100	< 0.07	< 0.07	< 0.07	
Al	< 0.18	5.14	21		< 0.18	0.75	107	57	< 0.18	< 0.18	0.26	
Si	20.50	179	7		< 41.00	318	4064	86	< 41.00	< 41.00	< 41	
Ti	2.63	3.68	93		< 0.87	1.58	3.76	86	1.70	2.20	2.61	
V	< 0.02	< 0.02	0		< 0.02	< 0.02	< 0.02	0	< 0.02	< 0.02	0	
Cr	< 0.22	0.40	36		< 0.22	0.26	0.30	57	< 0.22	0.24	0.33	
Mn	0.39	0.47	100		0.25	0.40	4.02	100	0.29	0.35	0.41	
Fe	465,500	465,500	100		465,500	465,500	465,500	100	465,500	465,500	100	
Co	5.68	18.60	100		4.91	62.45	524	100	9.79	11.34	15.30	
Ni	0.26	0.52	100		< 0.02	< 0.02	8.25	57	0.51	0.81	0.98	
Cu	< 0.09	6.61	29		0.39	1.05	548	100	0.71	0.81	1.22	
Zn	0.51	1.11	100		0.38	1.05	7.93	100	0.40	0.59	1.12	
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Table 4 (continued)

Mineralization type/ textural type Number of analyses	Pyrite in disseminated/ semi-massive Cu-Au mineralization 14				Pyrite in auriferous quartz vein 7				Pyrite in mineralized TC schist along shear zone 6			
	Median	High	MDL (%)	Low	Median	High	MDL (%)	Low	Median	High	MDL (%)	MDL (%)
As	44.15	51.49	100	< 0.44	5.32	8.27	71	77.37	118	268	100	100
Se	14.57	17.69	100	487	994	1804	100	358	405	424	100	100
Mo	< 0.01	0.08	14	< 0.01	< 0.01	0.06	29	< 0.01	< 0.01	0.01	17	17
Ag	< 0.01	< 0.01	0	0.05	0.14	74.39	100	< 0.01	< 0.01	0.38	17	17
Cd	< 0.02	< 0.02	0	< 0.02	< 0.02	0.86	43	< 0.02	< 0.02	< 0.01	0	0
Sn	0.03	0.05	71	0.04	0.43	35.91	100	< 0.02	< 0.02	0.07	33	33
Sb	< 0.01	0.07	29	< 0.01	0.35	0.55	100	< 0.01	< 0.01	0.92	33	33
Te	< 0.10	< 0.10	0	< 0.10	< 0.10	< 0.10	0	< 0.10	< 0.10	< 0.10	0	0
W	< 0.10	< 0.01	0	< 0.01	< 0.01	2.25	43	< 0.01	< 0.01	< 0.01	0	0
Au	< 0.01	< 0.01	0	< 0.01	< 0.01	0.14	57	< 0.01	< 0.01	0.02	17	17
Tl	< 0.01	< 0.01	0	0.01	0.05	5.46	100	< 0.01	< 0.01	0.03	17	17
Pb	0.03	2.62	93	1.05	2.93	108	100	0.02	0.03	20.27	100	100
Bi	< 0.05	< 0.05	21	0.88	3.10	27.57	100	< 0.05	< 0.05	0.01	33	33
Th	< 0.003	< 0.003	0	< 0.003	< 0.003	< 0.003	0	< 0.003	< 0.003	0.01	17	17
U	< 0.002	0.08	21	< 0.002	< 0.002	0.003	14	< 0.002	0.002	0.42	50	50

Median DL = Median lower detection limit, MDL (%) = Percentage of analyses above the median lower detection limit.

commonly occupied by Fe^{3+} , and more rarely by Au^{3+} (Cook and Chrysosoulis, 1990). The trend line (Fig. 9A) indicates a strong molar surplus of As over Au. At the measured concentrations of As and Au in pyrite, all Au should be present as lattice substitution (cf. Reich et al., 2005).

6.2. Chalcopyrite

LA-ICP-MS data (Table 5), depth profiles and multielement imaging of chalcopyrite in disseminated to semi-massive Cu-Au mineralization and auriferous quartz veins indicate elevated and homogeneously distributed concentrations of Co, Zn, Se and Ag (Figs. 6C, D and 10), consistent with stoichiometric lattice substitution of these elements (Huston et al., 1995). Tin has been shown to be preferentially hosted in chalcopyrite in the presence of other co-crystallizing sulphides (George et al., 2017), which may explain elevated concentrations of this element (Fig. 6C, D and 10). LA-ICP-MS depth profiles for Zn are somewhat more erratic (Fig. 6C, D), which may be due to the additional presence of sphalerite micro-inclusions (cf. Fig. 5B). High count rates and fairly homogeneous distribution of Cd, Pb and Bi are conspicuous (Fig. 6C, D and 10), elevated Cd being commonly associated with sphalerite inclusions.

Multielement imaging indicates some spatial correlation between Pb and Bi (Fig. 10), neither of which can be substituted into the chalcopyrite lattice (Huston et al., 1995). Hence, these elements likely occur in evenly distributed Pb-Bi sulphosalt nano-inclusions. Gold is present and quite evenly distributed in chalcopyrite from both disseminated to semi-massive Cu-Au mineralization and auriferous quartz veins (Figs. 6C, D and 10). In the multielement image of the latter, Au is concentrated in parallel bands (Fig. 10B), which are inferred to represent redistribution along internal growth zones during metamorphic recrystallization. Since only one such image was acquired for chalcopyrite in quartz veins, it cannot be concluded how common this phenomenon is. Manganese and Tl are common along grain boundaries, fractures and in mineral inclusions (Fig. 10).

Histograms of LA-ICP-MS spot analyses reveal a similarity in trace element concentration between chalcopyrite from disseminated to semi-massive Cu-Au mineralization and auriferous quartz veins (Fig. 11). This includes Co, Zn, Sb, Au and, to a lesser degree, Se, Cd, and Bi, whereas Ag, Sn and Pb are less abundant in the veins. The composition of chalcopyrite from the massive sulphide mineralization is distinct from the other mineralization types (i.e. for Co, Se, Sn, Sb, Au and Bi; Fig. 11; Table 5). This includes lower concentrations of Co, Se and Bi, and higher concentrations of Sn and Sb in chalcopyrite from the massive sulphides.

6.3. Sphalerite

Sphalerite with sufficient grain size for LA-ICP-MS spot analysis has only been encountered in the massive sulphide and disseminated to semi-massive Cu-Au mineralizations (Fig. 12). LA-ICP-MS data (Table 6) and depth profiles in the former (Fig. 6E) indicate elevated ($> 10^4$ counts) concentrations of Mn, Cd, Co and Fe. The flat and smooth depth profiles for these elements indicate an even distribution, suggesting lattice substitution; up to several thousand ppm of Mn and Cd, and several hundred ppm of Co may be incorporated in the crystal lattice of sphalerite (Fleischer, 1955; Becker and Lutz, 1978; Huston et al., 1995; Cook et al., 2009). The Fe concentration in natural sphalerite can range from trace levels to > 15 wt% (e.g. Scott and Barnes, 1971; Lepetit et al., 2003; Cook et al., 2009).

Apart from the elements discussed above, Se, Cu, Ag, Sn, Sb, Pb and Bi are abundant in many samples (several tens to hundreds of ppm; Fig. 12; Table 6). Higher Cu concentrations in sphalerite (up to 52,957 ppm; Table 6) can be attributed to chalcopyrite inclusions (chalcopyrite disease; Fig. 4H). All these elements show flat, but more erratic LA-ICP-MS depth profiles, especially for Cu, Sn, Pb, and Zn

Table 5
Summary statistics for trace element concentrations in chalcopyrite.

Mineralization type Number of analyses		Massive sulphide mineralization 5				Disseminated/semi-massive Cu-Au mineralization 13				Auriferous quartz vein 19			
Element (ppm)	Median DL (ppm)	Low	Median	High	MDL (%)	Low	Median	High	MDL (%)	Low	Median	High	MDL (%)
Mg	0.11	< 0.11	0.59	38.15	60	< 0.11	1.47	285	92	< 0.11	< 0.11	3.41	42
Al	0.29	< 0.29	< 0.29	26.58	40	< 0.29	2.57	231	77	< 0.29	< 0.29	3.43	32
Si	63.69	< 63.69	< 63.69	414	20	< 63.69	< 63.69	295	31	< 63.69	< 63.69	82	16
Ti	1.36	< 1.36	1.86	2.68	80	< 1.36	1.66	6.65	69	< 1.36	2.09	4.22	84
V	0.02	< 0.02	< 0.02	0.03	20	< 0.02	< 0.02	0.02	8	< 0.02	< 0.02	0.02	11
Cr	0.38	< 0.38	< 0.38	< 0.38	0	< 0.38	< 0.38	0.98	23	< 0.38	< 0.38	0.58	5
Mn	0.30	0.54	4.11	8.99	100	< 0.30	0.79	7.22	85	< 0.30	0.81	106	95
Fe	3.57	304,300	304,300	304,300	100	304,300	304,300	304,300	100	304,300	304,300	304,300	100
Co	0.02	< 0.02	0.02	0.78	60	< 0.02	4.02	43.58	85	5.03	10.10	79.08	100
Ni	0.04	< 0.04	0.12	0.89	80	< 0.04	0.13	1.27	92	< 0.04	0.07	0.36	68
Cu	0.68	350,393	355,046	358,902	100	335,766	352,266	358,997	100	312,547	353,210	361,622	100
Zn	0.24	587	1076	1860	100	432	670	1823	100	504	826	8313	100
As	0.64	< 0.64	< 0.64	5.64	20	< 0.64	< 0.64	0.81	8	< 0.64	< 0.64	< 0.64	0
Se	4.27	100	105	346	100	43	1256	2121	100	1241	1359	1841	100
Mo	0.20	< 0.20	< 0.20	< 0.20	0	< 0.20	< 0.20	0.39	23	< 0.20	< 0.20	< 0.20	5
Ag	0.02	110	115	372	100	63	152	380	100	96	106	142	100
Cd	0.04	5.15	7.53	8.86	100	1.97	8.37	11.54	100	7.61	14.90	60.93	100
Sn	0.03	354	1124	1171	100	83	149	1558	100	30	152	321	100
Sb	0.02	4.18	7.89	12.90	100	< 0.02	0.26	8.71	92	< 0.02	0.20	0.86	89
Te	0.13	< 0.13	< 0.13	< 0.13	0	< 0.13	< 0.13	0.35	23	< 0.13	< 0.13	< 0.13	0
W	0.01	< 0.01	< 0.01	< 0.01	0	< 0.01	< 0.01	2.53	15	< 0.01	< 0.01	0.02	11
Au	0.01	< 0.01	< 0.01	0.01	40	< 0.01	0.10	0.61	85	< 0.01	0.09	0.41	84
Tl	0.01	0.03	0.16	0.22	100	< 0.01	0.15	0.75	92	< 0.01	0.02	0.82	79
Pb	0.01	2.27	6.70	127	100	2.18	57.64	700	100	0.82	2.24	28.80	100
Bi	0.01	0.02	0.02	0.11	100	< 0.01	15.01	668	92	0.90	3.01	19.45	100
Th	0.003	< 0.003	< 0.003	< 0.003	0	< 0.003	< 0.003	0.72	8	< 0.003	< 0.003	< 0.003	0
U	0.002	< 0.002	< 0.002	0.01	20	< 0.002	< 0.002	1.18	31	< 0.002	< 0.002	0.11	5

Median DL = Median lower detection limit, MDL (%) = Percentage of analyses above the median lower detection limit.

Table 6
Summary statistics for trace element concentrations in sphalerite.

Mineralization type Number of analyses		Massive sulphide mineralization 14				Disseminated/semi-massive Cu-Au mineralization 5			
Element (ppm)	Median DL (ppm)	Low	Median	MDL	Low	Median	High	MDL	MDL
Mg	0.06	< 0.06	0.06	2679	50	< 0.06	0.52	138	80
Al	0.14	< 0.14	< 0.14	11.14	36	0.50	1.87	95.41	100
Si	30.32	< 30.32	51.13	2885	93	47.62	78.25	4283	100
Ti	0.44	0.93	1.69	32.97	100	< 0.44	1.38	2.43	80
V	0.01	< 0.01	< 0.01	0.04	36	< 0.01	< 0.01	0.02	0
Cr	0.16	< 0.16	< 0.16	42.47	36	< 0.16	< 0.16	0.38	0
Mn	0.15	464	2631	4421	100	159	746	870	100
Fe	1.17	58,029	71,043	78,081	100	66,283	72,288	94,041	100
Co	0.01	< 0.01	0.34	33.46	93	11.62	11.84	323	100
Ni	0.01	< 0.01	0.03	0.86	57	< 0.01	0.02	2.76	60
Cu	0.09	33.64	125	15,214	100	10,477	20,523	52,957	100
Zn	0.71	558,393	568,536	587,295	100	535,389	566,743	575,398	100
As	0.22	< 0.22	0.24	0.77	50	< 0.22	0.46	1.94	60
Se	1.13	18.85	49.39	181	100	160.66	167	1207	100
Mo	0.004	< 0.004	< 0.004	1.07	14	< 0.004	< 0.004	0.11	40
Ag	0.01	2.67	5.90	189	100	13.66	20.26	34.77	100
Cd	0.04	1663	2225	3550	100	2435	2542	2992	100
Sn	0.01	0.12	1.31	110	100	2.21	8.31	57.98	100
Sb	0.01	0.11	3.57	40.58	100	0.02	0.08	0.85	100
Te	0.05	< 0.05	< 0.05	< 0.05	0	< 0.05	< 0.05	0.15	60
W	0.004	< 0.004	< 0.004	0.05	7	< 0.004	< 0.004	0.01	0
Au	0.003	0.02	0.10	0.20	100	0.05	0.07	0.21	100
Tl	0.003	< 0.003	0.02	0.79	79	< 0.003	0.004	0.57	80
Pb	0.01	0.67	7.77	1189	100	2.95	10.68	156	100
Bi	0.002	< 0.002	0.03	0.37	86	3.96	11.90	124	100
Th	0.002	< 0.002	< 0.002	0.004	7	< 0.002	< 0.002	0.04	20
U	0.002	< 0.002	< 0.002	0.08	29	< 0.002	< 0.002	0.24	20

Median DL = Median lower detection limit, MDL (%) = Percentage of analyses above the median lower detection limit.

Table 7
Summary statistics for trace element concentrations in galena.

Mineralization type Number of analyses		Massive sulphide mineralization 14			
Element (ppm)	Median DL (ppm)	Low	Median	High	MDL (%)
Mg	0.07	< 0.07	< 0.07	0.09	7
Al	0.22	< 0.22	< 0.22	0.31	7
Si	45.39	< 45.39	< 45.39	49.49	7
Ti	0.70	< 0.70	< 0.70	7.73	29
V	0.02	< 0.02	< 0.02	0.01	0
Cr	0.28	< 0.28	< 0.28	2.80	7
Mn	0.22	< 0.22	< 0.22	1.61	50
Fe	2.66	< 2.66	< 2.66	1.33	0
Co	0.02	< 0.02	< 0.02	0.02	7
Ni	0.03	< 0.03	< 0.03	0.06	29
Cu	0.15	< 0.15	< 0.15	0.35	14
Zn	0.43	< 0.43	< 0.43	3.48	14
As	0.38	< 0.38	< 0.38	0.58	7
Se	1.08	20.89	491	2243	100
Mo	0.01	< 0.01	< 0.01	0.05	29
Ag	0.02	1126	1419	2235	100
Cd	0.04	7.83	16.31	31.44	100
Sn	0.02	5.77	36.42	56.58	100
Sb	0.06	697	1280	1687	100
Te	0.07	< 0.07	0.31	1.24	86
W	0.02	< 0.02	< 0.02	< 0.02	0
Au	0.02	< 0.02	< 0.02	0.03	7
Tl	0.01	8.03	73.09	156	100
Pb	0.50	866,000	866,000	866,000	100
Bi	0.02	74.63	1098	2601	100
Th	0.00	< 0.002	< 0.002	0.004	7
U	0.00	< 0.004	< 0.004	0.02	7

Median DL = Median lower detection limit,

MDL (%) = Percentage of analyses above the median lower detection limit.

(Fig. 6E) indicating that they are probably present in both the sphalerite lattice and in mineral inclusions. Copper, Sn and Pb are probably present as chalcopyrite, cassiterite and galena micro-inclusions, respectively (Fig. 4H).

The trace element concentration in sphalerite from the massive sulphide mineralization and the disseminated to semi-massive Cu-Au mineralization overlap, with the latter tending towards relatively higher concentrations in Co, Cu, Se, Sn and Bi (Fig. 12). The highest Fe concentrations are also recorded in sphalerite from the Cu-Au mineralization (9.4 wt%; Table 6; Fig. 12).

6.4. Galena

Galena with sufficient grain size for LA-ICP-MS spot analysis has only been encountered in the massive sulphide mineralization (Fig. 4E, H). Significant concentrations of trace elements in galena (> 100 ppm in median values) have been recorded for Se, Ag, Sb and Bi (Table 7). Other trace elements present in galena (10–100 ppm) are Cd, Sn and Tl. LA-ICP-MS depth profiles suggest that all these elements are present as lattice substitutions (Fig. 6F), consistent with the lack of mineral inclusions in galena (Fig. 4E, H).

Silver and/or Tl, together with Sb and/or Bi substitute for Pb in the galena lattice via coupled substitution (Amcoff, 1984; George et al., 2015). A strong linear correlation can be observed for Sb + Bi vs. Ag in galena from the massive sulphide mineralization at Falun (Fig. 9B). The slope of the regression line (0.88) is close to the 1:1 molar correlation suggested by Amcoff (1984), indicating a slight surplus of Sb and/or Bi over Ag in galena. George et al. (2015) obtained similar results for galena in Sb and/or Bi-rich ores, and inferred that Bi and Sb can be incorporated into galena by leaving a non-ideal vacancy in the monovalent cation site. At the Falun deposit, this may correspond to the rare

case where insufficient Se is available to form Pb-Bi sulphosalts from excess Bi. Concentrations of Sb and Bi are variable (Tables 7 and A1), with samples containing low Sb having higher Bi and vice versa.

Cadmium is stoichiometrically substituted for Pb, and Sn can be incorporated in its more stable valence state (Sn^{4+}) for 2Pb^{2+} by the creation of vacancies or, in its less stable +2 valence state, using simple bivalent cation substitution (Stwertka, 1998; George et al., 2015).

7. Discussion

7.1. Tectonothermal sulphide modification including remobilization

The structural, mineralogical, lithogeochemical and geochronological data suggest that the principal types of mineralization at the Falun deposit (i.e. the massive sulphide and disseminated to semi-massive Cu-Au mineralizations) constitute metamorphosed, syn-volcanic base metal sulphide mineralization (Kampmann et al., 2017). The paragenetic and textural relationships in the principal mineralization types addressed here are consistent with the modification of the main ore minerals by ductile deformation and metamorphism under lower-amphibolite facies conditions (cf. Marshall and Gilligan, 1993; Marshall et al., 2000). These relationships include: (1) grain size increase of pyrite due to growth and grain boundary area reduction as a response to tectonothermal modification (Figs. 4 and 5); (2) predominantly brittle deformation of pyrite as the most competent sulphide mineral (Fig. 4A–D); (3) paragenetically late positions of sulphides in interstitial spaces and fractures within and between more competent pyrite grains, indicating remobilization (Fig. 4A, B); (4) veinlets of remobilized sulphides in massive aggregates and domains of more competent sulphides (Fig. 4H); and (5) tectonoclastic rotation and rounding of more competent sulphide porphyroblasts within massive veinlets of plastically deformed, less competent sulphides (Fig. 4E) and silicates (Fig. 5F) due to shearing.

In natural systems, solid-state, mechanical remobilization is commonly accompanied by fluid-assisted, chemical remobilization. Transposition of material during the latter generally facilitates ductile deformation, and vice versa (Marshall et al., 2000; Andersson et al., 2016). The presence of, for example, tectonoclastic structures (Fig. 4E), which are related to mechanical remobilization, as well as sulphide veinlets (Fig. 4E, H), indicative of fluid-assisted remobilization of metals and sulphur, suggests that both processes occurred at Falun. Symetamorphic remobilization of base metal sulphides has been demonstrated at several other mineral deposits in Bergslagen, for example Saxberget (Selkman, 1984), Långban (Jonsson, 2004), in the Hällefors area (Wagner et al., 2005), Ryllshyttan (Jansson and Allen, 2015) and Hornkullen (Andersson et al., 2016).

Pyrite is the most abundant sulphide mineral in the Falun deposit. Growth of pyrite in connection with the deformation and metamorphism at the deposit probably commenced and was most efficient during the prograde metamorphic phase (cf. Craig and Vokes, 1993; Craig et al., 1998; Passchier and Trouw, 2005). Inclusions of quartz and biotite in pyrite, especially in the disseminated to semi-massive Cu-Au mineralization, suggests that pyrite grew before penetrative ductile deformation had ceased (cf. Kampmann et al., 2016b). Substantial pyrite growth probably occurred when major static grain growth of cordierite, garnet and andalusite took place during the inferred extensional or transtensional tectonic phase between D_1 and D_2 (Kampmann et al., 2016b).

The competency of pyrite under tectonothermal influence is higher than other common sulphides (e.g. Marshall and Gilligan, 1987; Barrie et al., 2007, 2010a,b). However, recent studies suggest that ductile deformation can operate in pyrite grains at temperatures as low as 320 °C (Freitag et al., 2004; Barrie et al., 2010a,b). It is inferred that the brittle deformation common in pyrite at the Falun deposit occurred during the retrograde cooling stage when ductile deformation became

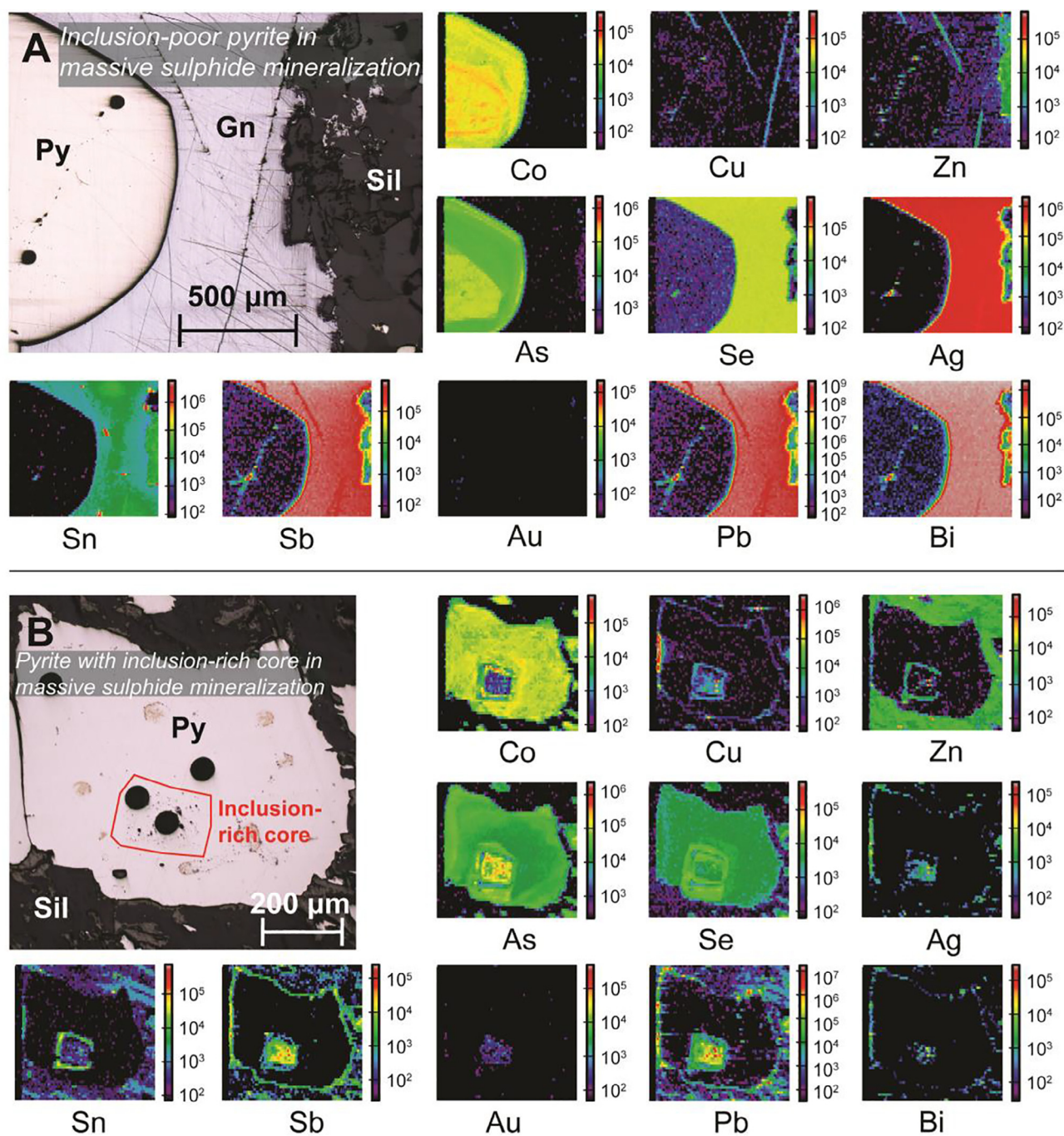


Fig. 7. Multielement LA-ICP-MS trace element images of pyrite in massive sulphide mineralization. (A) Inclusion-poor, tectonoclastic pyrite inside massive galena veinlet. (B) Subhedral pyrite with an inclusion-rich core and an inclusion-poor rim (Fig. 4F, G). Scales in counts per second. Abbreviations: Py = pyrite, Gn = galena, Sil = silicates.

restricted to shear zones (Kampmann et al., 2016b). The tectonoclastic modification of pyrite in shear zones shows that pyrite growth had largely ceased during this stage.

Infilling of fractures in pyrite by other sulphide minerals at Falun is rare (cf. Fig. 4), which suggests that effective remobilization of these minerals ceased before the onset of brittle deformation of pyrite. Indeed, the lower limit of the temperature window in which effective remobilization occurs (350 °C; Marshall and Gilligan, 1993) is near the temperature for the brittle-ductile transition for pyrite (~320 °C; Barrie et al., 2010a). The lack of fractures in chalcopyrite, sphalerite and galena is consistent with their mobility and sensitivity to recrystallization

until the late stages of the tectonothermal evolution (Clark and Kelly, 1973; Marshall and Gilligan, 1987). Thus, static recrystallization probably continued after ductile deformation had ceased. Additional studies on the internal deformation in the sulphide minerals, e.g. using etched samples, would be required to corroborate this interpretation.

Application of trace elements in sulphides for geothermometric constraints on metamorphism has been attempted elsewhere (George et al., 2016), but is beyond the scope of this study. Revisiting our trace element data regarding this aspect is recommended in future work, so as to better constrain the metamorphic P/T conditions that are currently based solely on the silicate assemblages at Falun.

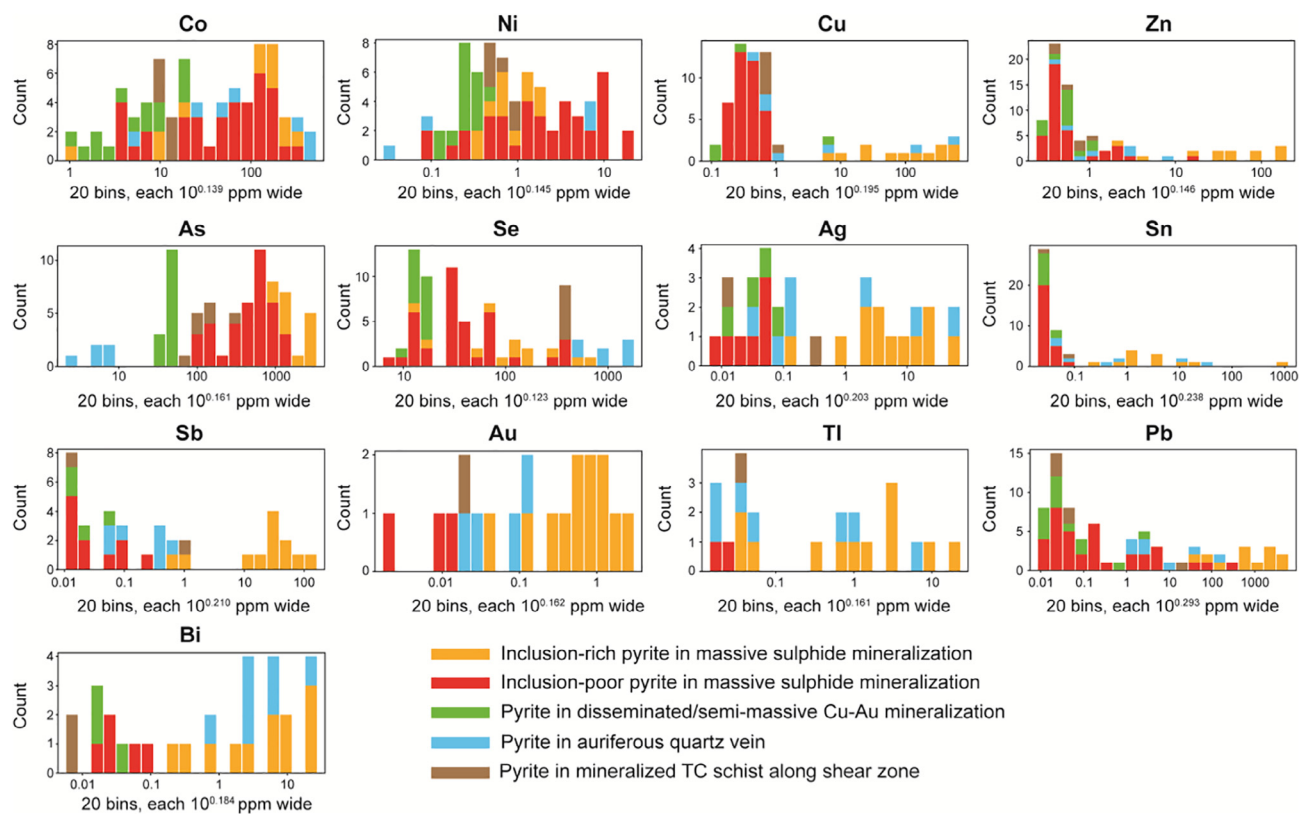


Fig. 8. Stacked histograms showing the distribution of trace elements in pyrite, based on multielement LA-ICP-MS spot analysis. Logarithmic scale in ppm.

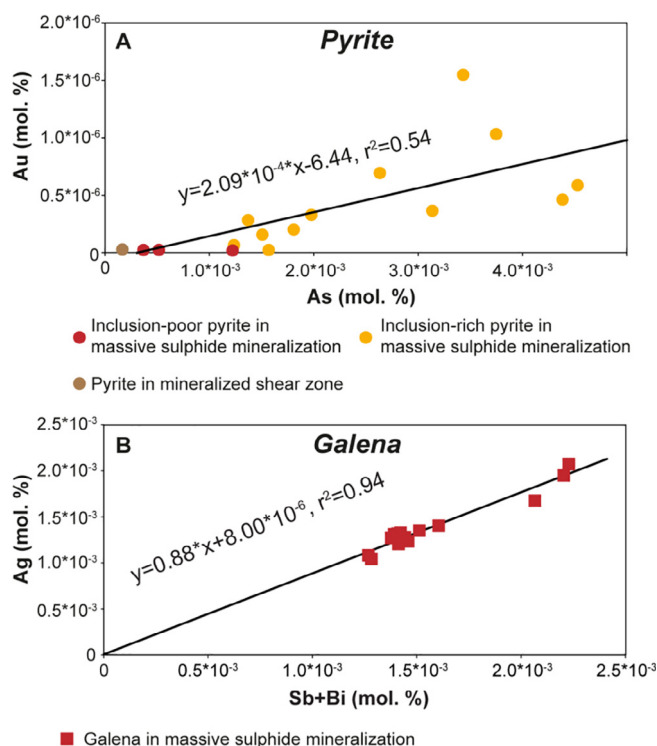


Fig. 9. Binary diagrams showing the correlation between selected elements (in mol. % for analyses above the median detection limit) in pyrite and galena, including linear regression trend lines. (A) As vs. Au in pyrite. (B) Sb + Bi vs. Ag in galena.

7.2. Trace element (including Au) liberation from pyrite during metamorphism

Metamorphic growth and/or recrystallization of pyrite has been shown to result in expulsion of the majority of mineral inclusions and trace elements (e.g. Huston et al., 1995). However, initial concentrations of elements that are present as stoichiometric substitutions in the pyrite crystal lattice are retained (e.g. Co and Ni; Huston et al., 1995). Hence, the observed similarities in Co and Ni concentrations in inclusion-rich and inclusion-poor pyrite in the massive sulphide mineralization support the interpretation that inclusion-poor pyrite is a product of metamorphic growth of initially smaller grains of inclusion-rich pyrite. The minor depletion of As in inclusion-poor relative to inclusion-rich pyrite is consistent with this interpretation, due to the sensitivity of this element to removal by metamorphic growth or recrystallization as a non-stoichiometric lattice substitution (Cook and Chrysosoulis, 1990; Huston et al., 1995). With progressive depletion of As, pyrite loses its potential to host Au and Tl in the lattice (Fig. 9A; Cook and Chrysosoulis, 1990; Reich et al., 2005), leading to a simultaneous depletion of these elements.

We suggest that the inclusion-poor pyrite represents pyrite overgrowth from pre-existing smaller grains, which have largely lost their initial inclusions and trace element budget during the tectonothermal modification. The inclusion-rich pyrite is interpreted to represent relic cores of pre-metamorphic pyrite, which were preserved within a growing pyrite aggregate, and, thereby, at least partly retained their inclusions and initial trace element budget during metamorphism and ductile deformation. LA-ICP-MS imaging of the two types of pyrite suggests that the liberated trace elements included Cu, Zn, As, Se, Ag, Sn, Sb, Au, Pb and Bi (Fig. 7A). A similar process may have affected

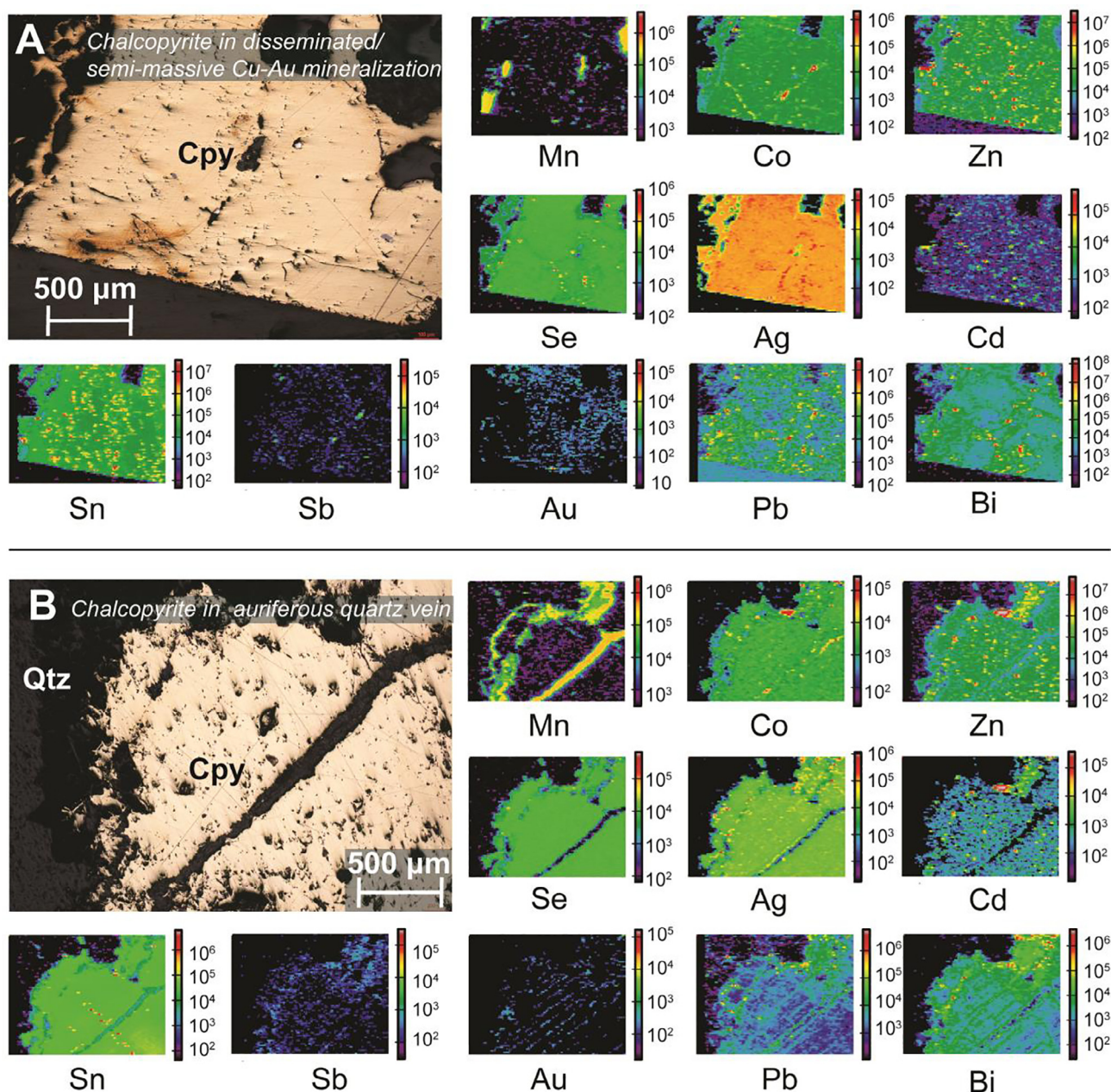


Fig. 10. Multielement LA-ICP-MS trace element images of chalcopyrite. (A) Veinlet chalcopyrite in disseminated to semi-massive Cu-Au mineralization, sample 10/30-1. (B) Semi-massive chalcopyrite in auriferous quartz vein, sample 10/27-2A. Scales in counts per second. *Abbreviations:* Cpy = chalcopyrite, Qtz = quartz; Sil = silicates.

sphalerite in the massive sulphide mineralization, even though relic pre-metamorphic sphalerite could not be identified in this study. It has been demonstrated that concentrations of Pb and Bi, and, to some degree, Cu and Ag decrease in sphalerite with increasing metamorphic grade, thereby liberating these elements to form discrete minerals elsewhere (Lockington et al., 2014).

7.3. Origin of auriferous quartz veins

Åberg and Fallick (1993) showed that the auriferous quartz veins formed after the massive sulphide mineralization and noted that they, along with barren quartz veins, are oriented parallel to the main foliation direction, i.e. they are structurally controlled. Structural observations presented in this study support a syn-tectonic emplacement. The metal content in the veins may have been derived from the surrounding principal mineralization types (remobilization) or from

material derived in an unrelated source (mineralization overprint).

A considerable inheritance of trace elements in chalcopyrite from the disseminated to semi-massive Cu-Au mineralization to the auriferous quartz veins is corroborated by the similar, although not identical trace element signatures (Figs. 6C, D and 10). This is consistent with the vein chalcopyrite representing either a relic mineral from the surrounding Cu-Au mineralization, which was altered to some extent by the auriferous quartz vein fluid, or a remobilized portion from the Cu-Au mineralization into the veins. The overall fracture-filling configuration and coarser grain size of the vein chalcopyrite (Figs. 3E and 5D) favour the interpretation as a hydrothermal mineral formed during generation of the auriferous quartz veins, possibly post-dating the main stage of quartz growth. The preferential remobilization of Au-bearing (Fig. 11) chalcopyrite into the auriferous quartz veins (Figs. 3E and 5D) resulted in a pronounced Au endowment in the veins.

In addition to the similar trace element signature in chalcopyrite, all

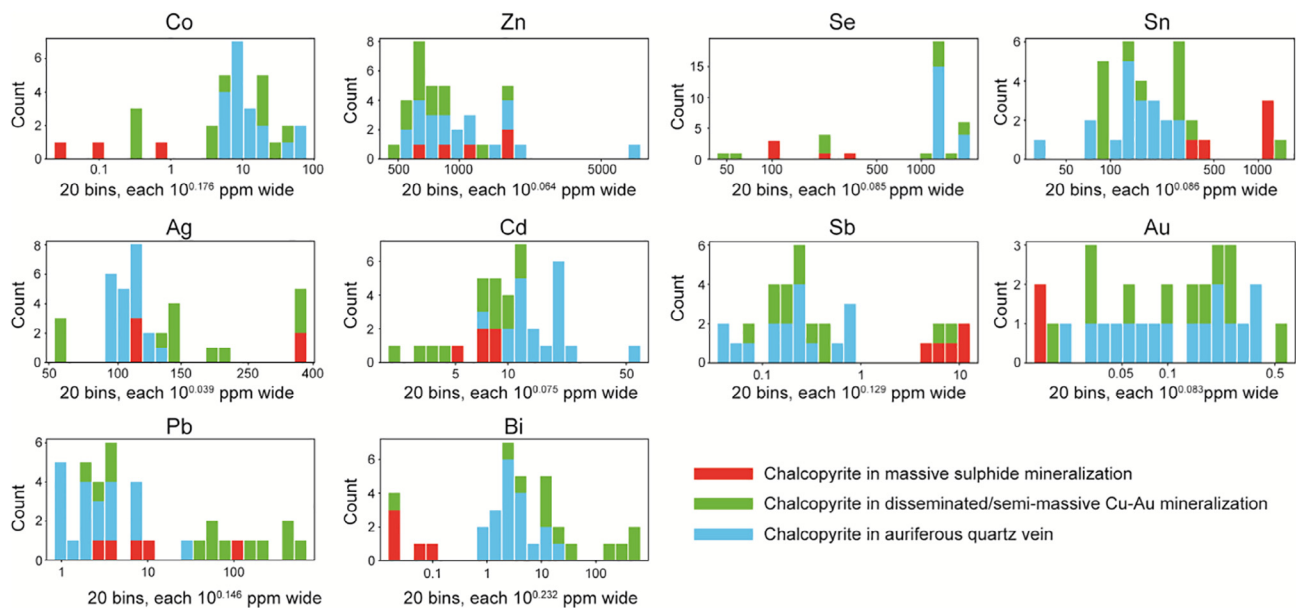


Fig. 11. Stacked histograms showing the distribution of trace elements in chalcopyrite, based on multielement LA-ICP-MS spot analysis. Logarithmic scale in ppm.

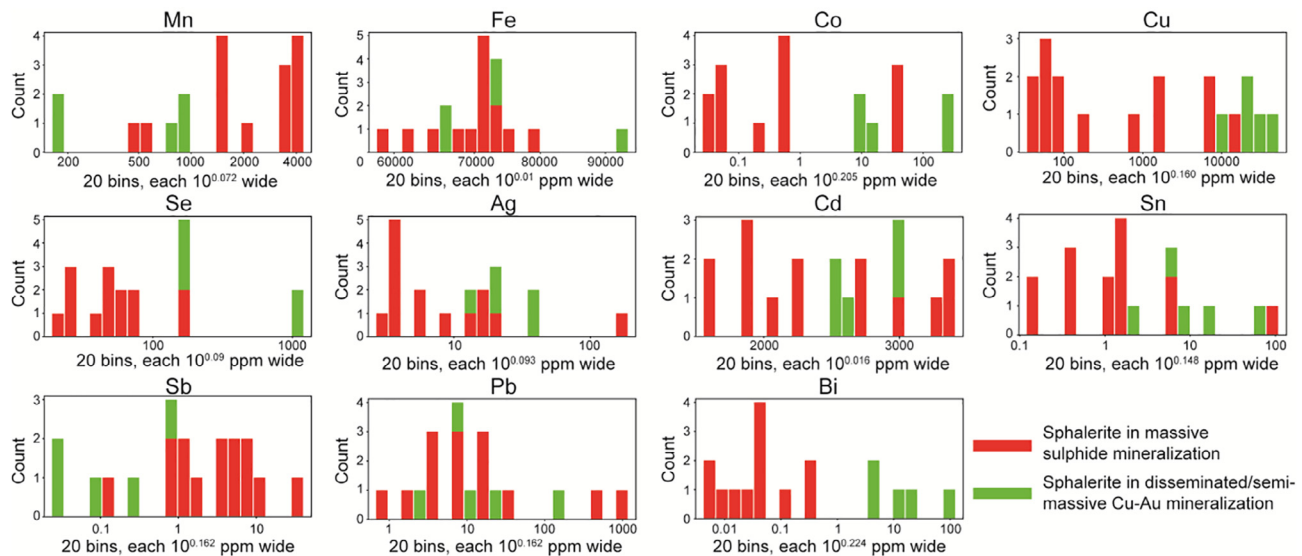


Fig. 12. Stacked histograms showing the distribution of trace elements in sphalerite, based on multielement LA-ICP-MS spot analysis. Logarithmic scale in ppm.

elements encountered in the vein minerals were present in the hydrothermally altered zone prior to quartz vein formation. Furthermore, there is a striking correspondence between elements that have been liberated from pyrite (e.g. Pb, Bi, Se, Au) and possibly sphalerite (cf. Lockington et al., 2014) in the massive sulphide mineralization and those enriched in discrete minerals in the veins, comprising e.g. abundant Pb-Bi sulphosalts and native gold. Hence, Au expelled from pyrite in the massive sulphide mineralization, which was most likely liberated during the earlier prograde metamorphism, could also have contributed to the Au endowment in the quartz veins and led to the presence of native gold. The common presence of sulphosalts in quartz veins formed from remobilization has been documented earlier (e.g. Wagner et al., 2007).

These considerations suggest a vein formation model by remobilization of components from the principal mineralization types with the aid of a fluid, and provide no support to a model in which the veins represent a mineralization from an independent source, i.e. the mineralization overprint model. Indeed, the close spatial association between two unrelated and temporally distinct mineralization events is

unlikely, and probably would have been detected in contrasting trace element signatures.

By using O and H isotope systematics, as well as microthermometry of fluid inclusions, Åberg and Fallick (1993) placed some constraints on the composition and properties of the fluid that formed the auriferous quartz vein system. They proposed a variably saline fluid (0.3–17.4 equiv. wt% NaCl) and a wide range of fluid temperatures (116–350 °C). Fluid mixing or several pulses of fluids with variable properties over time were inferred (Åberg and Fallick, 1993). A dominant meteoric source for the fluid and modification by water–rock interaction or fluid mixing are suggested by variable, but constantly negative $\delta^{18}\text{O}$ values (–8 to –2 ‰) and constant δD values around –65 ‰. It has to be kept in mind that δD values from crush-leach analysis commonly do not preserve primary signatures of the vein fluid, as they can include abundant H from later meteoric water inclusions (e.g. Goldfarb and Groves, 2015). Oxygen isotopes are less likely to be modified by later fluid ingress and are also the most sensitive indicators for meteoric water signatures. For these reasons, the O isotope data in Åberg and Fallick (1993) are judged to be more reliable, whereas the reported H

isotope data may not reflect the primary vein fluid signature.

The folded and mullioned appearance of the auriferous quartz veins and the occurrence of some internal ductile deformation suggest that they were affected by the D₂ ductile deformation. Even though the microthermometric data in Åberg and Fallick (1993) were not corrected for pressure (which means that inferred fluid temperatures are minimum estimates), these temperatures are considerably lower than the peak lower-amphibolite facies metamorphic conditions (Wolter and Seifert, 1984).

It is inferred that the emplacement of the auriferous quartz vein system occurred between peak metamorphism in the D₁ to D₂ interlude and the completion of D₂, i.e. during the overall retrograde stage that took place spatially beneath, but progressively closer to the brittle-ductile transition zone. The apparent absence of deformation in a portion of the veins (Åberg and Fallick, 1993), which have not been encountered in this study, suggests that vein emplacement possibly even continued shortly after completion of the D₂ deformation phase. Fluid-induced alteration of monazite in the altered silicate-rich rocks occurred at 1831 ± 8 Ma during the D₂ tectonothermal phase (Kampmann et al., 2016a). If this monazite alteration was related to the hydrothermal event that formed the auriferous quartz veins, then the c. 1.83 Ga age may provide an estimate for the timing of emplacement of the vein system. However, bearing in mind the discussion above, it is possible that the veins formed over a protracted time interval, even prior to and shortly after D₂.

Provided that the classification of a portion of the fluid inclusions by Åberg and Fallick (1993) as primary is correct, one possibility for the origin of the auriferous quartz veins is that several pulses of fluids from a solely meteoric source were involved in the formation of the quartz vein system (cf. Åberg and Fallick, 1993). Heterogeneity of, for example, $\delta^{18}\text{O}$ and reduction of the fluid would, in this case, be attributed to progressive water–rock interaction. The possibility of meteoric fluid penetration into the ductile regime of an active orogenic system (New Zealand Alpine System), including their contribution to mineralization, has been demonstrated (Menzies et al., 2014). Progressive reduction of these meteoric fluids and an increase of $\delta^{18}\text{O}$ with increasing temperature and depth have also been documented (Jenkin et al., 1994; Pitcairn et al., 2006). An increasing role of meteoric fluid influx with progressively shallower depth of the system during the retrograde (post-peak) stage of metamorphism is conceivable.

A second possibility involves fluid mixing of different pulses of, for example, meteoric and metamorphic water to explain the variability of the fluid system regarding $\delta^{18}\text{O}$ values, temperature and salinity. Upgrading mechanisms for Au from base metal massive sulphide mineralization in quartz veins have been suggested for numerous metamorphosed VMS deposits (Marshall and Gilligan, 1987; Larocque et al., 1993, 1995; Marshall et al., 2000; Wagner et al., 2007). These studies infer the involvement of metamorphic instead of meteoric fluids. At Falun, metamorphic fluids are likely to have been generated by dehydration reactions in the hydrothermally altered zone from chlorite and sericite to form anhydrous silicates (e.g. cordierite, garnet and andalusite) during the interlude between D₁ and D₂ (Kampmann et al., 2016b, 2017). Such fluids could have been responsible for the liberation of S and metals including Au from the massive sulphides (cf. Tomkins, 2010). The metamorphic fluid may have been mobilized later, in connection with the tectonic disturbance of the system during D₂. Additional data, such as the O and H isotope signatures of late-metamorphic hydrous silicates (e.g. anthophyllite; Kampmann et al., 2016b), are needed to resolve the question of fluid types.

The spatial restriction of the veins to the area of Cu–Au mineralization (Fig. 2) suggests that the transport mechanism was inefficient over larger distances. Instead, there was a decrease in metal solubility shortly after their liberation from the surrounding rocks. Effervescence is a possible mechanism rapidly decreasing the solubilities of dissolved metal and gangue constituents within the hydrothermal fluid (e.g. Sibson et al., 1988; Robb, 2005). This process is common in the

mesothermal regime following crack–seal mechanisms and associated rapid pressure reduction (Robb, 2005). The presence of single-phase CO₂ fluid inclusions in the auriferous quartz veins is compatible with effervescence (Åberg and Fallick, 1993). This would have occurred during seismic events and associated vein emplacement. Precipitation of Au together with the other metals in solution (e.g. Cu, Pb, Bi and Se) would have resulted. Alternatively, even subtle changes in pH and/or redox conditions of a reduced (pyrite-stable) fluid would have given rise to changes in the solubility of Au (e.g. Craw and Chamberlain, 1996; Wood and Samson, 1998; Robb, 2005).

7.4. Implications for syn-volcanic sulphide mineralization

A chemical (pH) trap mechanism for the formation of the massive sulphide mineralization at Falun due to interaction between limestone and a hot, acidic, reducing and metal-bearing fluid has been discussed recently (Kampmann et al., 2017). The proposed model involves massive sulphide mineralization in the sub-seafloor environment by replacement of limestone, and by infill of overlying porous pumice breccia and space created during syn-volcanic faulting. The predicted pH-controlled dominant precipitation of Zn and Pb over Cu in the massive sulphide mineralization (Kampmann et al., 2017) is supported by generally low concentrations of Cu (up to 0.179 wt%) and elevated concentrations of Zn (between 0.435 and 21.8 wt%) and Pb (between 0.388 and 48.71 wt%; Table 2).

In contrast to the dominant neutralization mechanism for the massive sulphide formation, cooling has been suggested as the main trigger for the stratigraphically lower disseminated to semi-massive Cu–Au mineralization (Kampmann et al., 2017). Gold is associated with chalcopyrite in this part of the deposit (Fig. 10; Table 5), which is in agreement with their inferred coeval precipitation (Kampmann et al., 2017).

Assuming no change in the concentrations of Co and Ni throughout metamorphism, this study shows that pre-metamorphic pyrite in the Cu–Au mineralization had different, but overlapping compositions compared with pyrite in the massive sulphide mineralization; both Co and Ni show slightly higher concentrations in the massive sulphide mineralization (Fig. 8). This is in contrast to observations from other metamorphosed massive sulphide deposits, where higher concentrations of Co in the stockwork with respect to massive sulphides have been observed (Huston et al., 1995). Decreasing Co concentrations in the hydrothermal fluid with progressive cooling or dilution of Co concentrations by mixing with seawater (0.05 ppb Co; Brewer, 1975) have been inferred (Huston et al., 1995). Our data suggest instead relatively constant fluid temperatures between the Cu–Au mineralization and the massive sulphide mineralization, supporting the inferred dominance of the chemical trap mechanism over cooling and mixing with seawater for massive sulphide formation at Falun, as outlined above (Kampmann et al., 2017).

The shear zone containing TC schist to the north of the massive sulphide mineralization (Fig. 2) has been discussed as a possible structural conduit for metal-bearing fluids during the syn-volcanic stage (Kampmann et al., 2017). Trace element concentrations in pyrite overlap with those in the massive sulphide mineralization and also the disseminated to semi-massive Cu–Au mineralization (Fig. 8), with which the shear zone is in direct contact (Kampmann et al., 2017). Thus, the disseminated pyrite and chalcopyrite in this zone could represent syn-volcanic mineralization formed in a feeder to the ore system, a remobilized portion of sulphides from the principal mineralization types or a combination of both.

The common occurrence of Sn in chalcopyrite and galena (lattice substitution and as cassiterite inclusions), as well as in sphalerite (as cassiterite inclusions) is consistent with a hot (300–400 °C), acidic and reducing fluid responsible for hydrothermal ore formation (Kampmann et al., 2017). This type of fluid is required for the efficient transport of Sn in solution (e.g. Jackson and Helgeson, 1985; Heinrich, 1990; Kitto,

1998). High Fe concentrations in sphalerite (~6 to 9 wt%; Table 6; Fig. 12) corroborate this (Scott and Barnes, 1971; Scott, 1973; Huston et al., 1995).

7.5. Comparison with other metamorphosed massive sulphide deposits

Trace element levels, especially for “immobile” stoichiometrically substituted elements such as Co and Ni, are in the range of concentrations in pyrite from metamorphosed massive sulphide deposits elsewhere (Bralia et al., 1979; Huston et al., 1995). Only limited trace element data on chalcopyrite are available from recent literature. Trace elements in Falun chalcopyrite are generally similar in distribution to those of VMS deposits elsewhere (Huston et al., 1995). A similar pattern of elevated Se concentrations in chalcopyrite from the disseminated to semi-massive Cu-Au mineralization compared to the chalcopyrite from stratigraphically higher massive sulphides at Falun occur in corresponding mineralization types in VMS deposits in Eastern Australia (Huston et al., 1995).

The trace element concentrations in Falun sphalerite are similar to those reported from VMS deposits (Cook et al., 2009; George et al., 2015). Chemical data on sphalerite from the Bergslagen ore province have been published on base metal sulphide deposits at Hällefors (Wagner et al., 2005), Kaveltorp and Markertorp (Cook et al., 2009), as well as at Zinkgruvan (Axelsson and Rodushkin, 2001; Cook et al., 2009). Compared with all the other Bergslagen deposits, Sn is about one order of magnitude higher in Falun sphalerite. In the case of SVALS-type deposits (Falun, Hällefors, Kaveltorp), most trace elements show similar ranges, suggesting similarities in ore formation (e.g. Allen et al., 1996; Jansson et al., 2013; Kampmann et al., 2017). By contrast, sphalerite from the Zinkgruvan and Markertorp deposits, the former belonging to the SAS-type (Allen et al., 1996), have one order of magnitude higher Co concentrations than sphalerite from Falun, Hällefors and Kaveltorp. As far as Zinkgruvan is concerned, this may reflect ore-forming fluids with properties markedly different from those that formed the Falun deposit. It has been suggested that the deposit formed by reduction of oxidized, near-neutral and highly saline brines (Jansson et al., 2017), oxidized fluids generally being inefficient in the transport of Sn in solution (e.g. Cooke et al., 2000).

Trace element ranges in Falun galena resemble those from VMS deposits elsewhere, even though the concentrations of Sb, Ag, Sn, Cd and Se also overlap with galena in other deposit types (e.g. epithermal, skarn and SEDEX deposits; George et al., 2015). Bi concentrations in Falun galena (1098 ppm median value; Table 7) are similar to those from skarn deposits (George et al., 2015), but are three orders of magnitude higher than in VMS deposits. Bismuth concentrations in Falun galena are high, similar to Zinkgruvan galena (George et al., 2015). In addition, Se concentrations are approximately ten times higher and Ag concentrations about twice as high in the galena from Falun, compared to Zinkgruvan galena.

Cassiterite is rare in Bergslagen deposits, but has been reported as a primary (pre-remobilization) phase from the Lindbom's prospect base metal sulphide deposit in western Bergslagen (Jonsson et al., 2013), which is compatible with the interpretation at the Falun deposit (cf. Kampmann et al., 2017).

8. Conclusions

During the 2.0–1.8 Ga Svecokarelian orogeny, polyphase ductile deformation (D₁ and D₂) and low-P, lower-amphibolite facies metamorphism induced mechanical and chemical remobilization of pre-metamorphic, syn-volcanic sulphides and metals at the Falun, pyritic Zn-Pb-Cu-(Au-Ag) sulphide deposit. Metamorphic growth of pyrite occurred mainly during the prograde stage of metamorphism that peaked in the interlude between D₁ and D₂, expelling inclusions and non-stoichiometrically substituted trace elements such as Au, although rare inclusion-rich and Au-bearing pyrite cores were preserved. Gold is also

associated with chalcopyrite in the disseminated to semi-massive Cu-Au mineralization stratigraphically beneath the massive sulphide mineralization.

Local remobilization of trace elements, including Au, from the Cu-Au mineralization formed a system of auriferous quartz veins after the peak of metamorphism, but prior to and possibly even shortly after the completion of the D₂ ductile strain event. The veins are enriched in Pb-Bi sulphosalts (e.g. weibullite), chalcopyrite and native gold. Fluid-assisted transport of liberated Au from pyrite in the massive sulphide mineralization during syn-metamorphic grain growth may also have contributed to the Au endowment in the quartz vein system. The suite of trace elements that have been largely liberated from pyrite (e.g. Pb, Bi, Se and Au) corresponds strongly to those elements forming the discrete and characteristic mineral phases in the quartz veins (Pb-Bi sulphosalts, native gold), thereby corroborating the remobilization model.

Trace element signatures for the main sulphide minerals pyrite, chalcopyrite, sphalerite and galena are similar to previously published data from other metamorphosed massive sulphide deposits. However, the ore system at Falun is associated with high Bi concentrations, which is reflected in the common occurrence of structurally bound Bi (e.g. in galena) and in the abundant inclusions of Pb-Bi sulphosalts, especially in the disseminated to semi-massive Cu-Au mineralization and the auriferous quartz veins. Elevated Sn concentrations in the lattice and/or as cassiterite inclusions in chalcopyrite, sphalerite and galena can be explained by Sn mobility in a hot, acidic and reducing fluid, which was responsible for the syn-volcanic, base metal sulphide mineralization and associated host-rock alteration.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.oregeorev.2018.04.010>.

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