Laser microprobe sulphur isotope analysis of arsenopyrite: experimental calibration and application to the Boliden Au–Cu–As massive sulphide deposit

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Abstract

Metamorphic remobilization of arsenopyrite-rich ores is a globally important process which can lead to significant concentrations of gold. In order to understand this and related processes, relations of sulphur isotopes can give a number of important clues. To resolve such relations in detail, we have successfully calibrated and applied a laser combustion system for in situ analysis of sulphur isotopic compositions of arsenopyrite. Experimental calibration of the laser fractionation factor ($+0.4‰$) was obtained by using compositionally and isotopically homogeneous natural samples from ore deposits at Boliden (Sweden) and Freiberg (Germany); subsequent to detailed microscopic study, the S isotope ratios of these samples were measured by conventional and laser combustion techniques.

The present application to different types of arsenopyrite in the Palaeoproterozoic metamorphosed VHMS ores of the Boliden Au–Cu–As deposit, Skellefte district, northern Sweden, shows that the sulphur isotope composition of arsenopyrite is essentially unmodified during medium-grade metamorphic recrystallization and remobilization. Here, massive arsenopyrite ore is crosscut by later veins that carry a complex quartz–sulphosalt–sulphide assemblage. The latter ore type is markedly Au-rich compared to the host ore, and thus of significant economic interest. We find that both ore types exhibit very similar sulphur isotope compositions, ca. $+2‰$ to $+3‰$ (V-CDT), which is similar to most massive sulphide deposits in the Skellefte district. Thus, the crosscutting Au-rich vein ore has inherited the sulphur isotope composition from sulphur liberated by metamorphic reactions affecting the massive ore, and most likely also inherited the Au through this mechanism. The latter finding clearly has important implications both for the general discussion on, and the prospecting for, similar high-grade Au ores in this world-class mining region.
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1. Introduction

Arsenopyrite is one of the more refractory among the common sulphides (Marshall and Gilligan, 1987; Craig and Vokes, 1993; Marshall et al., 2000) and is

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widespread in several important classes of ore deposits, notably volcanic-hosted massive sulphide, shear zone-hosted gold and Sn−W vein-type deposits. The refractory nature and the commonly observed complex textural and compositional zonation patterns (Cabri et al., 1989; Fleet et al., 1993; Fleet and Mumin, 1997) make it possible to utilize arsenopyrite for deciphering and reconstructing a variety of genetic and post-genetic processes in these ore types. In addition to an essentially process-oriented approach, the extensively documented intimate association between arsenopyrite and major concentrations of visible and invisible gold (Cabri et al., 1989, 2000; Cook and Chryssoulis, 1990; Arehart et al., 1993; Genkin et al., 1998; Yang et al., 1998) provides a strong economic impetus to investigate the mineralogical and geochemical properties of arsenopyrite in a wide variety of ore-forming environments.

The remobilization of arsenopyrite-rich ores during metamorphism is a widely recognized process and may assist significant redistribution and local enrichment of gold. Remobilization of gold can take place during peak metamorphic recrystallization of the arsenopyrite, via heterogeneous nucleation and growth of larger gold particles in fractures and voids within the arsenopyrite host (e.g., Mumin et al., 1994). Alternatively, the gold content of arsenopyrite can also be efficiently remobilized via prograde metamorphic decomposition of arsenopyrite to a löllingite–pyrrhotite assemblage, which leads to the diffusion-controlled growth of gold particles along the reaction interface (Barnicoat et al., 1991; Tomkins and Mavrogenes, 2001). Interaction with a metamorphic fluid, which is commonly present as an intergranular phase (e.g., Cox et al., 2001; Carlson, 2002; Dohmen and Chakraborty, 2003), strongly enhances the progress of remobilization and facilitates compositional modifications. In addition to the remobilization of gold, other compositional characteristics, including the As/S ratio (Kretschmar and Scott, 1976; Sharp et al., 1985) and the trace element inventory (e.g., Cabri et al., 2000), as well as the sulphur isotope composition, can also be effectively modified during the different pathways of metamorphic recrystallization and reaction processes affecting arsenopyrite. The effects on sulphur isotope systematics during arsenopyrite remobilization are, however, very poorly constrained.

Characterization of the sulphur isotope systematics of recrystallization/remobilization of arsenopyrite requires the application of an in situ technique such as the laser or ion microprobe. This is necessary to be able to resolve variations beyond the capability of conventional techniques and to simultaneously achieve sufficient textural control. To address the problem, we have experimentally calibrated an in situ laser combustion system for analyzing sulphur isotopes in arsenopyrite. We have then applied the technique to different textural types of arsenopyrite in metamorphosed massive sulphide ores of the world-class Boliden Au−Cu−As deposit, northern Sweden. The results of our study show that the sulphur isotope composition of arsenopyrite is essentially unmodified during greenschist to amphibolite grade metamorphic recrystallization and remobilization. Crosscutting Au-rich sulphosalt–quartz–sulphide vein ores have inherited the sulphur isotope composition from sulphur liberated by metamorphic reactions affecting the massive ores. By implication, it is most likely that Au was also inherited through this mechanism.

2. The Boliden deposit

The Boliden Au−Cu−As massive sulphide deposit is located in the Palaeoproterozoic Skellefte district, in Västerbotten County, northern Sweden (Fig. 1). The Skellefte district forms an approximately E−W-trending belt of predominantly metasupracrustal rocks, which include a large number of mainly submarine metavolcanic-hosted massive sulphide ore deposits (Rickard, 1986; Weihed et al., 1992; Hannington et al., 2003). The host rocks to the ore were formed in a volcanic arc setting at ca. 1.89 to 1.85 Ga (Billström and Weihed, 1996) and comprise a complex succession of submarine volcanic and subvolcanic rocks, with intercalations of clastic sedimentary units (Allen et al., 1996; Bergström, 2001). The Skellefte district was affected by regional Svecokarelian metamorphism of greenschist to amphibolite grade at ca. 1.83 to 1.81 Ga (Billström and Weihed, 1996); peak metamorphic conditions in the Boliden area attained ca. 430 °C and 5 to 7 kbar (Berglund and Ekström, 1980). Most of the massive sulphide deposits occur close to the boundary between the upper metavolcanic rocks (rhyolites to dacites) of the Skellefte Group and the overlying
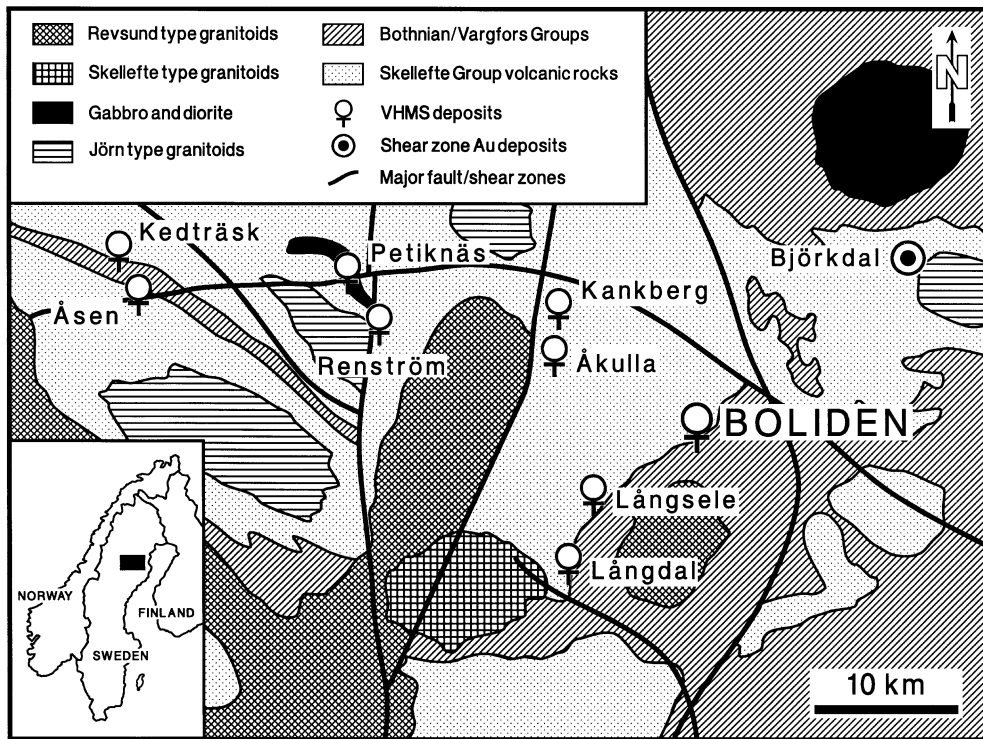
Fig. 1. Geological sketch map of the central part of the Skellefte district, Sweden, showing the location of the Boliden deposit. Redrawn and modified after Bergman Weihed et al. (1996).

metasedimentary rocks (greywackes and mudstones) of the Vargfors Group (Bergman Weihed et al., 1996).

Earlier studies considered the massive sulphide deposits in the Skellefte district as metamorphosed equivalents of Kuroko-type ores (Rickard and Zweifel, 1975; Vivallo, 1987). In contrast, recent structural and geochemical investigations indicate that some may actually represent high-sulphidation-type epithermal sub-seafloor infiltrations and replacements (Allen et al., 1996; Bergman Weihed et al., 1996). The Boliden deposit itself is hosted by a metavolcanic unit, which represents a subaqueous to partially subaerial rhyolitic cryptodome-tuff volcano. The wall rocks to the massive sulphide ore display a distinctly zoned alteration pattern, with an inner envelope dominated by white mica ± andalusite and an outer chlorite zone (Ödman, 1941; Bergman Weihed et al., 1996; Hallberg, 2001). The massive sulphide ores occur as elongate lenses stretched along an approximately E–W-oriented structure, which has been related to a local shear zone (Bergman Weihed et al., 1996). Ore formation was

initiated with the deposition of massive sulphide ores (pyrite and arsenopyrite ores) and the coeval alteration of the wall rocks. Subsequent deformation caused the stretching and detachment of the massive orebodies and the formation of crosscutting sulphosalt–quartz– sulphide veins and quartz-tourmaline veins; the latter occur mainly below the footwall contact of the massive orebodies (Ödman, 1941; Bergman Weihed et al., 1996). Both vein ore types carry significant gold enrichments, with local grades up to about 300 to 600 g/t; a single major quartz-tourmaline vein had an average Au grade of 50 g/t, compared to 15.5 g/t for all ore types (Grip and Wirstam, 1970). Deformation continued after the formation of these vein ores, which is indicated by the widespread deformation textures in the sulphosalts and sulphides.

Bergman Weihed et al. (1996) suggest that the initial vein-forming event occurred prior to the ca. 1.85–1.82 Ga peak Svecokarelian metamorphism, whereas the abundant recrystallization of sulphides took place during peak metamorphic conditions.

Recent mineralogical re-investigation of the arsenopyrite-hosted vein ores, assessed together with mineral geothermobarometry (Berglund and Ekström, 1980), fluid inclusion data (Åberg, 1995; Broman, 1987, 1992) and inferences from phase equilibria, indicates that the sulphosalt-rich vein assemblages were formed during the peak metamorphic stage (Wagner and Jonsson, 2001). However, a significant question remains as to whether the gold enrichment within the sulphosalt–quartz–sulphide veins was related to metamorphic remobilization from the massive arsenopyrite and pyrite ores, or alternatively if metamorphogenic fluids focused within local shear zones could have introduced major amounts of gold into the vein structures. The presence of several shear zone-hosted gold deposits in the Skellefte district, notably at Björkdal located 20 km NE from the Boliden mine, may indicate that metamorphic or early magmatic fluids carried significant amounts of gold in this region (Broman et al., 1994; Billström et al., 1997).

3. Textural relationships of the Boliden ores

The massive sulphide orebodies of the Boliden deposit are essentially composed of pyrite ore, with abundant lenses of massive arsenopyrite and minor pyrrhotite. All types of massive sulphides are crosscut
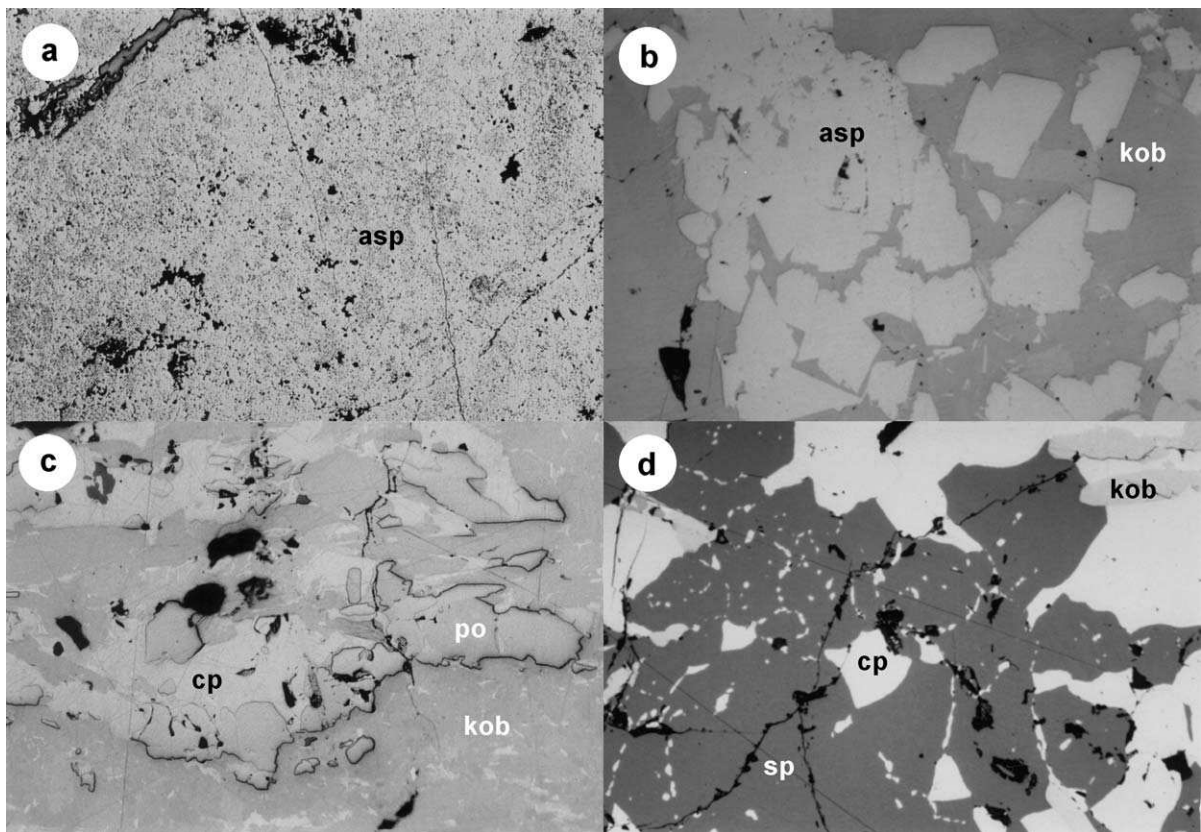

Fig. 2. Representative textures of arsenopyrite and vein-type ore of the Boliden deposit. (a) Fine-grained massive arsenopyrite (asp) containing numerous silicate and sulphide inclusions. The massive arsenopyrite is crosscut by microfractures and veinlets filled by remobilized sulphides and sulphosalts. Sample EJ-B2. Width of field: 2.0 mm. (b) Strongly recrystallized arsenopyrite (asp) crystals in a matrix of kobellite (kob). In contrast to the massive arsenopyrite, recrystallized arsenopyrite shows idiomorphic terminations and is essentially free from silicate and sulphide inclusions. Sample EJ-B3b. Width of field: 670 μm. (c) Elongated pyrrhotite (po) and chalcopyrite (cp) grains in a matrix of kobellite (kob). The sulphide minerals have been strongly deformed. Sample EJ-B8. Width of field: 500 μm. (d) Typical vein ore assemblage of sphalerite (sp) and chalcopyrite (cp). Sample EJ-B7. Width of field: 1.18 mm.

by vein ores, which form a fine network of mm-sized veinlets in brecciated arsenopyrite and distinctly larger veins within the pyrite (Grip and Wirstam, 1970; Bergman Weihed et al., 1996). These veinlets carry a relatively complex quartz–gold–sulphide–sulphosalt assemblage, with Hg-rich electrum, chalcopyrite, pyrrhotite, sphalerite, kobellite $(Cu,Fe)_2(Pb,Bi,Sb)_{26}(S,Se)_{35}$, tetrahedrite, bournonite $CuPbSbS_3$, and laitakarite $Bi_4(Se,S)_3$ being the dominant ore minerals (Ödman, 1941; Wagner and Jonsson, 2001). The sulphide–sulphosalt assemblage in quartz-tourmaline veins is very similar to the one within brecciated and veined arsenopyrite ore (Bergman Weihed et al., 1996). The current study has focused on the brecciated arsenopyrite ore and the vein assemblage within the arsenopyrite, which carries some of the most prominent gold grades of the Boliden deposit (Ödman, 1941; Grip and Wirstam, 1970).

The massive arsenopyrite ore, forming lenticular and irregular bodies, is generally fine-grained, spongy-textured and contains numerous silicate and sulphide inclusions, notably chalcopyrite and pyrrhotite (Fig. 2a). This arsenopyrite shows extensive brecciation and veining, with veinlet dimensions generally in the range between 20 μm and 10 mm. In contrast to the massive arsenopyrite, the arsenopyrite present within or close to the veinlets is characterized by an idioblastic texture and the absence of silicate and sulphide inclusions (Fig. 2b). Most of the idioblastic arsenopyrite protrudes into the sulphide–sulphosalt matrix of the vein ores. This arsenopyrite shows a distinct growth zonation, which is caused by variations in the Co content (Bergman Weihed et al., 1996).

The textural features indicate an intense fluid-assisted recrystallization of arsenopyrite during the vein-forming event. The quartz–sulphide–sulphosalt vein assemblages exhibit many textural features indicative of extensive deformation, notably ductile shearing and Durchbewegung (e.g., Marshall and Gilligan, 1989), depending on the contrast in competence between the respective ore and gangue minerals. Most of the wider veinlets are filled by kobellite, which shows a typical foliated texture and commonly hosts elongated inclusions of pyrrhotite and chalcopyrite (Fig. 2c). Fine veinlets in fractured arsenopyrite show infilling by irregularly shaped anhedral grains of chalcopyrite, sphalerite and minor amounts of sulpho-

salts (Fig. 2d). Portions of the kobellite, in particular along narrow zones close to the grain boundaries between kobellite and the arsenopyrite, display abundant decomposition textures (e.g., symplectitic intergrowths of laitakarite with tetrahedrite or bournonite), which post-date the deformation of the vein-type ores (Wagner and Jonsson, 2001).

4. Experimental methods

Sulphur isotope analysis has been performed in the stable isotope laboratory at SUERC. The experimental calibration of the laser fractionation factor of arsenopyrite was carried out using two coarse-grained natural samples (ASP-1 and ASP-2) from ore deposits at Boliden (Sweden) and Freiberg (Germany). The samples have been checked for textural and compositional homogeneity by reflected light microscopy and electron probe microanalysis. The chemical compositions of the two samples are very similar; $Fe_{1.00}As_{0.97}S_{1.02}$ (ASP-1) and $Fe_{1.00}As_{0.94}S_{1.05}$ (ASP-2). Isotopic homogeneity has been established by performing a series of conventional sulphur isotope analyses of each potential reference sample. Material was extracted from several 3 mm diameter holes in the polished slabs using a microdrill, and subsequently converted to SO_2 by combustion with cuprous oxide under vacuum at 1070 °C (Robinson and Kusakabe, 1975). The SO_2 gas produced was cryogenically purified and analyzed on a VG SIRA II gas mass spectrometer. Calculation of $\delta^{34}S$ values from raw machine $\delta^{66}SO_2$ data was carried out by calibration with international standards NBS-123 (+17.1‰) and IAEA-S-3 (−31‰), as well as SUERC's internal lab standard CP-1 (−4.6‰). Reproducibility of the analytical results was controlled through replicate measurements of these standards. The sulphur isotope compositions are reported in standard notation, relative to Vienna Cañon Diablo Troilite (V-CDT).

Subsequently, a number of in situ laser combustion analyses were carried out on each polished block of the respective sample. The polished blocks were inserted into a sample chamber, which was evacuated and subsequently filled with an excess of oxygen gas. Previously selected sample areas were combusted using a SPECTRON LASERS 902Q CW Nd:YAG laser (1-W power), operating in TEM_{00} mode. Details

of the system design, laser characteristics and experimental conditions are described in Fallick et al. (1992) and Kelley et al. (1992). In order to minimize the effects of small-scale sample heterogeneity, each laser extraction was carried out by excavating a single long trench of approximately 3–11 mm in length during the analysis; the width of these trenches is typically ~ 50 μm (Fallick et al., 1992). Applying this technique, the extracted sample volume approaches the order of magnitude of the minimum volume combustible during conventional analysis. The combustion reaction of arsenopyrite is less intense than most other sulphide minerals for a given laser power, not least compared to pyrite, chalcopyrite and sphalerite. The SO_2 gas produced by each laser combustion was purified in a miniaturized glass extraction line, using a CO_2/acetone slush trap to remove water and a standard n-pentane trap to separate SO_2 and trace CO_2 (Kelley and Fallick, 1990). Determination of the sulphur isotope composition of the purified SO_2 gas (δ^{34}S) was carried out online on a VG SIRA II gas mass spectrometer.

The analytical results are summarized in Table 1; the full set of analytical data is contained in Table A1 in Appendix A. The laser correction factors obtained for both arsenopyrite samples are relatively small and essentially identical (+ 0.4‰). Since the chemical compositions of both arsenopyrite reference samples are very similar, we could not evaluate the effect of compositional variation, in particular the As/S ratio, on the laser fractionation factor. The results of our work demonstrate that it is possible to analyze arsenopyrite using the in situ laser combustion technique with a good level of analytical precision, comparable to conventional methods. This has important implications for future detailed small-scale work on arsenopyrite-rich ore assemblages, such as zoned arsenopyrite crystals in mesothermal Au deposits and arsenopyrite ores in massive sulphide deposits.

The small-scale sulphur isotope study of the arsenopyrite-rich ores from the Boliden deposit was performed with the laser extraction technique we have used for the calibration of the arsenopyrite fractionation factor. Instead of excavating a single long trench, sample areas of approximately 400 by 400 μm have been combusted by moving the laser in a rastering technique, thereby producing several, small parallel trenches. The laser fractionation factors for sphalerite (+ 0.4‰), chalcopyrite (+ 0.7‰) and pyrrhotite (+ 0.4‰) are well constrained by previous work (Kelley and Fallick, 1990; Fallick et al., 1992), whereas the correction factor for kobellite (+ 1.0‰) has been interpolated from the linear relationship between the laser fractionation and the molar fraction of PbS established for Pb–Sb sulphosalts (Wagner et al., 2002). It should be noted that kobellite is never a pure Pb–Sb sulphosalt, but contains considerable concentrations of Bi, Cu and Fe (e.g., Makovicky and Mumme, 1986; Moëlo et al., 1995). Therefore, we consider this factor as preliminary and the kobellite data (two analyses) are given in brackets throughout, indicating that they should be treated with some caution.

5. Sulphur isotope data of the Boliden ores

Table 2 lists both gas and mineral δ^{34}S values for arsenopyrite and different vein minerals from the Boliden deposit. The sulphur isotope composition of the massive arsenopyrite ore is characterized by very homogeneous δ^{34}S values in the range + 2.1‰ to + 3.2‰ (Fig. 3; Table 2); the mean of all the data is

Table 1
Summary of arsenopyrite sulphur isotope calibration data

Sample	δ^{34}S, conv. (‰)	δ^{34}S, laser (‰)	Correction (‰)	S.E. (‰)	Comment
ASP-1 (Boliden)	+ 2.35 ± 0.11 ($n=7$)	+ 2.00 ± 0.23 ($n=12$)	+ 0.35 ± 0.26	0.08	Reaction less intense than pyrite. Deposits of brown–black As-oxide close to laser pit.
ASP-2 (Freiberg)	+ 0.38 ± 0.21 ($n=3$)	− 0.01 ± 0.31 ($n=10$)	+ 0.39 ± 0.37	0.16	

The total 1σ external precision of the laser correction factor (correction factor = $\delta^{34}S_{CONV} - \delta^{34}S_{LASER}$) has been calculated according to the equation for error propagation given in Kreyszig (1970).

Table 2
Sulphur isotope data of arsenopyrite and vein sulphides from the Boliden massive sulphide deposit. $\delta^{34}S_{mineral} = \delta^{34}S_{gas} +$ correction factor

Sample	Mineral	$\delta^{34}S_{V\text{-}CDT}$ (‰(gas)	$\delta^{34}S_{V\text{-}CDT}$ (‰(mineral)
Massive arsenopyrite ore			
EJ-B2-1	Arsenopyrite	+2.7	+3.1
EJ-B2-2	Arsenopyrite	+2.6	+3.0
EJ-B3a-4	Arsenopyrite	+2.8	+3.2
EJ-B4-4	Arsenopyrite	+2.6	+3.0
EJ-B6a-1	Arsenopyrite	+1.7	+2.1
EJ-B8-1	Arsenopyrite	+1.9	+2.3
EJ-B8-4	Arsenopyrite	+2.6	+3.0
Recrystallized arsenopyrite			
EJ-B3a-1	Arsenopyrite	+2.6	+3.0
EJ-B3a-2	Arsenopyrite	+2.4	+2.8
EJ-B6a-2	Arsenopyrite	+1.8	+2.2
EJ-B6a-4	Arsenopyrite	+2.0	+2.4
EJ-B8-2	Arsenopyrite	+3.0	+3.4
Vein sulphides			
EJ-B3a-3	Kobellite	+0.6	(+1.6)
EJ-B4-1	Pyrrhotite	+1.9	+2.3
EJ-B4-3	Chalcopyrite	+1.2	+1.9
EJ-B4-5	Chalcopyrite	+2.3	+3.0
EJ-B6a-3	Chalcopyrite	+1.7	+2.4
EJ-B7a-1	Chalcopyrite	+1.7	+2.4
EJ-B7a-2	Sphalerite	+1.6	+2.0
EJ-B7a-3	Chalcopyrite	+1.8	+2.5
EJ-B8-3	Kobellite	+1.1	(+2.1)

$+2.8 \pm 0.4$‰$(n = 7)$. The variation within individual samples is on the same order of magnitude as between different samples (Fig. 4). Compared to the massive arsenopyrite, strongly recrystallized idioblastic arsenopyrite displays nearly identical $\delta^{34}S$ values in the range between $+2.2$‰ and $+3.4$‰ with a mean of $+2.8 \pm 0.5$‰$(n = 5)$. Fig. 4 demonstrates that the isotopic composition of recrystallized arsenopyrite generally reflects the composition of the massive arsenopyrite ore. The different vein sulphides analyzed (chalcopyrite, sphalerite and pyrrhotite), have $\delta^{34}S$ values in the range between $+1.9$‰ and $+3.0$‰ with a mean of $+2.4 \pm 0.4$‰$(n = 7)$, which closely resemble both textural types of arsenopyrite (Fig. 3). Due to their finely intergrown nature, it was not possible to analyze more sphalerite and pyrrhotite grains in the current study. The two analyzed kobellite samples have $\delta^{34}S$ values of $+1.6$‰ and $+2.1$‰ slightly lower than the other vein minerals. The

results of our texturally resolved in situ sulphur isotope analyses compare reasonably well with the data obtained by Gavelin et al. (1960), which show a compositional range in $\delta^{34}S$ between $+2.8$‰ and $+4.7$‰ for different sulphide minerals in the Boliden deposit. It should be noted that Rickard et al. (1979), based on re-analysis and re-evaluation of the standards used in the study by Gavelin et al. (1960), have derived an equation to correct their original $\delta^{34}S$ values. Consequently, we have recalculated the Boliden data by Gavelin et al. (1960) according to this correction procedure.

6. Discussion

The results of our new in situ sulphur isotope analyses of arsenopyrite ore and vein sulphides from the Boliden deposit provide some constraints on the
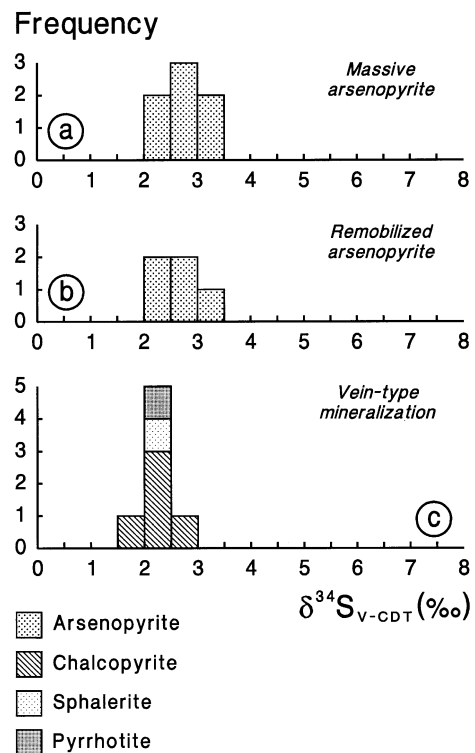

Fig. 3. Histogram displaying the sulphur isotope composition of (a) massive arsenopyrite ore, (b) remobilized arsenopyrite, and (c) vein-type ore.
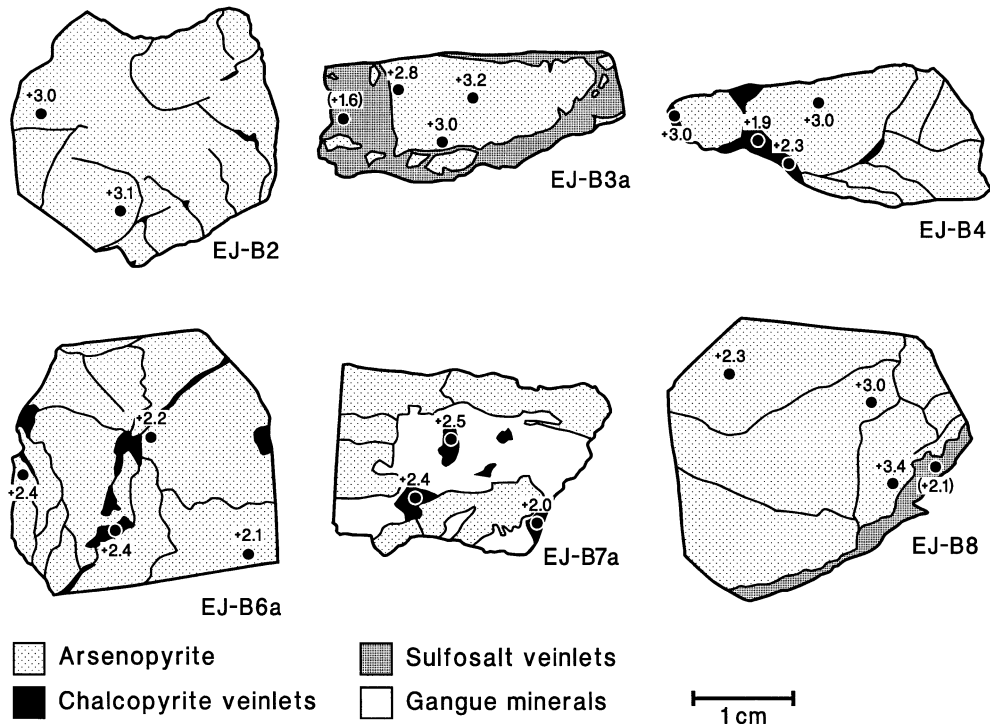
Fig. 4. Sketches showing mm-scale textural relationships and sulphur isotope data for the studied polished sections from Boliden. The marginal zones of massive arsenopyrite ore (contact to vein sulphides and sulphosalts) are strongly recrystallized.

mechanisms involved in the remobilization of massive sulphide ores. In addition, these data complement the existing sulphur isotope data set of the Skellefte district, which allows a comprehensive discussion of the sulphur isotope systematics in this important metallogenic province.

6.1. Remobilization of massive sulphide ores at Boliden

The small-scale study of massive arsenopyrite ore and recrystallized idioblastic arsenopyrite shows that the sulphur isotope compositions of both texturally distinguishable populations are essentially identical (Fig. 3; Table 2). It thus appears from our data that the sulphur isotope composition has not been significantly modified during recrystallization of arsenopyrite. The interaction between arsenopyrite and the metamorphogenic fluid responsible for mineralization during the vein-forming event and the remobilization of massive sulphide ores has not fractionated

the sulphur isotopes at the mm or sub-mm scale. This could possibly be explained by the presence of relatively low concentrations of sulphur in the metamorphic fluids and the rather high temperatures of the veining and recrystallization/remobilization event (350 to 450 °C; Wagner and Jonsson, 2001), where isotopic fractionation factors between common sulphide minerals are very small (Ohmoto and Goldhaber, 1997). Studies in other VHMS ore districts show that the effect of sulphur isotopic homogenization during metamorphism is relatively limited at metamorphic grades up to amphibolite facies (e.g., Skauli et al., 1992; Cook and Hoefs, 1997; Velasco et al., 1998). However, the sulphur isotope variation in the massive arsenopyrite ore prior to deformation and metamorphism is not properly known. Small-scale variation and primary zonation patterns could have been obliterated by fluid-assisted solid-state and grain-boundary diffusion processes during prolonged annealing of the ores. A texturally resolved study by Crowe (1994) has shown that at greenschist

to amphibolite grade conditions, resetting of the primary isotope variation within massive sulphide orebodies, where different sulphide phases are in close grain contact, does readily occur. Within silicified stockwork zones and dispersed wall rock mineralizations, where isolated sulphide grains are locked in silicates, primary isotope variations between different minerals tend to be preserved (Crowe, 1994).

The δ^{34}S values of the vein sulphides ($+1.9\%$ to $+3.0\%$) are identical to both textural types of arsenopyrite, which implies that the sulphur incorporated into the newly formed vein assemblages has been inherited, very locally, from remobilized massive ores. This idea is strongly supported by the consistent isotopic compositions of both massive/recrystallized arsenopyrite and vein sulphides evident even at a very small scale (Fig. 4). It is noted that the recrystallized arsenopyrite is almost free of sulphide inclusions (chalcopyrite, pyrrhotite), which are very abundant in arsenopyrite from the massive ore. Recrystallization of portions of the massive arsenopyrite ore was evidently accompanied by remobilization of these sulphide inclusions, which may thus have been the main source of sulphur for the sulphide assemblages formed within microfractures and veinlets. A major contribution of the metamorphic fluids to the sulphur isotope budget of the vein-type mineralization is not very likely, given the large amounts of sulphur liberated during recrystallization of the massive ores and the comparatively low concentrations of sulphur in the ore-forming fluids of lode gold systems (e.g., Vielreicher et al., 2002; Ridley et al., 2000; Mikucki and Ridley, 1993).

The relative importance of sulphur inherited from arsenopyrite via prograde metamorphism of the massive ores is difficult to assess. Based on available experimental data (Kretschmar and Scott, 1976; Sharp et al., 1985), prograde metamorphism of massive arsenopyrite orebodies should result in a systematic increase in the As/S ratio of the recrystallized arsenopyrite and, therefore, lead to progressive liberation of significant amounts of sulphur. This sulphur would be readily available for the formation of vein sulphides and the isotopic composition of these sulphides should be very similar to the precursor arsenopyrite, given the relatively high formation temperatures. Ideally, the average composition of

strongly recrystallized arsenopyrite should be characterized by elevated As/S ratios (or at.% As), compared to the massive arsenopyrite. The available electron-microprobe data on both textural populations of arsenopyrite do not display such a compositional pattern. Massive spongy-textured arsenopyrite has an average concentration of 31.7 ± 1.0 at.% As ($n = 25$), whereas strongly recrystallized idioblastic arsenopyrite grains at the centre of a kobellite vein have a concentration of 30.2 ± 0.3 at.% As ($n = 15$). The compositional effect of prograde metamorphism on arsenopyrite, i.e., increased As/S ratios, could have been obliterated by re-equilibration during the retrograde metamorphic stage. The observed partial decomposition of sulphosalts originally formed during peak metamorphism, which post-dates the latest deformation of the vein ores (Wagner and Jonsson, 2001), indicates that there was interaction of the vein assemblages with a retrograde metamorphic fluid. Based on mass balance considerations and the assumption of low concentrations of sulphur in the metamorphic fluids, the composition of arsenopyrite within the veins could have been effectively re-equilibrated, whereas the sulphur isotope composition would have been preserved.

There are only very limited data on the sulphur isotope systematics of remobilized ores of the massive sulphide deposits in the Skellefte district, which would allow for a thorough comparison with our Boliden data set. The results of conventional sulphur isotope analyses from Boliden (Gavelin et al., 1960; Rickard et al., 1979) show that the δ^{34}S values of different vein sulphides ($+3.2\%$ to $+4.1\%$) are very similar to the massive ores ($+2.8\%$ to $+4.7\%$). The δ^{34}S values of strongly deformed and remobilized galena and sphalerite ($+0.6\%$ to $+3.1\%$) in sulphide mylonites of the Renström deposit (Duckworth and Rickard, 1993) are indistinguishable from the range of δ^{34}S values displayed by most of the metamorphosed massive sulphide ores in the entire metallogenic province (-2.3% to $+4.7\%$; most of the data are between $+0.1\%$ and $+4.5\%$). Formation of vein-type mineralization via remobilization of massive sulphide ores may locally result in a very significant shift of the sulphur isotope composition. This is the case in some remobilized vein assemblages of the Sulitjelma deposit, Norway, where it was attributed to interaction with highly fractionated late-stage fluids,

which might have evolved in a nearly closed system (Cook and Hoefs, 1997). However, this type of effect has not been observed in the vein-type assemblages of the Boliden deposit and we infer a simple remobilization process leading to inheritance of the sulphur isotope composition from precursor massive ores. The results of our sulphur isotope studies are consistent with conclusions drawn from combined microtextural and Pb isotope studies of remobilization phenomena in multistage hydrothermal vein systems (Marcoux and Moëlo, 1991; Wagner and Schneider, 2002). These studies show that fluid percolation in a mostly open fracture network, like the brecciated arsenopyrite ore of the Boliden deposit, commonly results in strong inheritance effects and homogeneous isotopic composition of the newly formed vein assemblages, which closely resemble the precursor phases.

The sulphur isotope data of recrystallized and remobilized mineral assemblages of the Boliden deposit also place some constraints on the process of gold enrichment in the vein ores. Experimental data provide strong evidence that gold is predominantly transported as bisulphide complexes in a variety of ore-forming solutions, including metamorphogenic fluids (e.g., Seward, 1973; Shenberger and Barnes, 1989; Benning and Seward, 1996). The close chemical association of gold with sulphur in the mineralizing fluids would imply a contribution of sulphur from the metamorphogenic fluids, if these had been the dominant source of ore-forming components (including gold) in the vein-type ore. Alternatively, the sulphur isotope signature of vein sulphides associated with the gold could have been completely inherited via remobilization from the massive arsenopyrite orebodies, even if most of the gold itself was introduced through metamorphogenic mesothermal Au-rich fluids. The presence of such gold-rich hydrothermal systems during the Svecofennian orogeny is well documented by several gold-quartz-(telluride) deposits outside the areas hosting major VHMS deposits (Bergman, 1992; Broman et al., 1994; Weihed et al., 2003). Based on the sulphur isotope data alone, the question of remobilization versus metamorphic introduction of gold cannot be conclusively answered. The observed isotope systematics has to be discussed within the framework of other data, such as gold composition, location and grain size, as well as studies

of gold geochemistry and remobilization of other VHMS deposits.

A number of studies of important VHMS provinces worldwide have addressed the question of distribution and post-depositional remobilization of gold (e.g., Huston and Large, 1989; Huston et al., 1992; Larocque et al., 1993; Tourigny et al., 1993; Leistel et al., 1998; Zaw et al., 1999). Although there are major differences between deposits of the Zn–Au and Cu–Au association, systematic changes of the gold composition, grain size and siting as a consequence of metamorphic remobilization have been detected, which apply to both and in very different types of deposits. The most important feature noted is a redistribution of both fine-grained visible gold and invisible gold present within massive sulphides into microfractures and vein-type structures. Remobilized gold shows an increase in grain size, lower fineness and a larger range in fineness, compared to the primary gold (Huston et al., 1992). This effect is particularly pronounced in deposits of the Cu–Au type, where the primary gold displays a high fineness and a very narrow compositional range (Huston and Large, 1989; Huston et al., 1992).

The available textural and compositional data of gold from the Boliden deposit are consistent with an interpretation as remobilized gold of VHMS origin. Electrum is always present in low-strain sites, has average grain sizes up to 200 μm and is silver-rich, with an average composition of $Au_{0.56}Ag_{0.39}Hg_{0.05}$ (Bergman Weihed et al., 1996). This composition compares well with electrum found in two different vein types of the footwall alteration zone of the Långdal VHMS deposit (located 12 km SSW of Boliden), which have compositions of $Au_{0.24}Ag_{0.56}Hg_{0.20}$ and $Au_{0.47}Ag_{0.53}$, respectively (Weihed et al., 2002). These gold-rich veins have been interpreted as related to post-deformational remobilization processes based on the available structural and mineralogical evidence (Weihed et al., 2002). The close textural association of gold with these elements (Ag, Pb, Sb, Bi, Se, Te), which are preferentially mobilized from massive sulphide ores during prograde metamorphism (Marshall and Gilligan, 1987; Marshall et al., 2000), indicates a similar source for the gold as well. The element and mineral assemblages present in the Boliden vein ores closely resemble those of miner-

alization styles formed via metamorphic remobilization in other overprinted VHMS deposits, e.g., in the Norwegian Caledonides (Cook, 1996; Cook et al., 1998). Considering all available mineralogical, chemical and isotopic data, we conclude that remobilization of gold from the massive arsenopyrite orebodies appears to be the most likely explanation for the gold enrichment in the vein-type mineralization of the Boliden deposit. Our model of local inheritance of gold could possibly also be applied to other, similar deposits within the Skellefte District, e.g., Holmtjärn (Svensson and Willdén, 1986). Further detailed studies of gold grades and small-scale gold distribution using micro-analytical techniques are required to fully understand the mechanisms of gold enrichment in the VHMS deposits in the Skellefte district.

6.2. Sulphur isotope systematics of massive sulphide deposits in the Skellefte district

Sulphur isotope data are available for a number of VHMS deposits in the Skellefte district, including Boliden, Bjurfors, Bjurliden, Ö Högkulla, Kristineberg, Rävliden, Rävlidmyran, Udden, Renström, Åsen and Långdal (Gavelin et al., 1960; Rickard et al., 1979; Duckworth and Rickard, 1993; Frietsch et al., 1995). A compilation of these data together with our new data set from Boliden shows that the $\delta^{34}S_{SULPHIDE}$ values of almost all deposits in the orefield exhibit a limited range between -2.3% and $+4.7\%$ (Fig. 5). The only minor exception is displayed by the massive pyrite ores of the Åsen deposit, which have very variable $\delta^{34}S$ values in the range between -14.8% and -0.5%. The massive pyrite ores of the Åsen deposit are associated with major amounts of barite, which is not a common constituent of the other VHMS deposits in the Skellefte district, and the sulphide has been interpreted as bacteriogenic in origin (Gavelin et al., 1960; Rickard et al., 1979). The quartz vein-hosted gold deposit at Björkdal (Broman et al., 1994; Billström et al., 1997) exhibit sulphur isotope compositions between -1.4% and $+1.4\%$ (Billström et al., in review).

The compositional range displayed by the massive sulphide deposits in the Skellefte district (excluding the Åsen deposit) is very similar to many VHMS metallogenic provinces worldwide and most of the
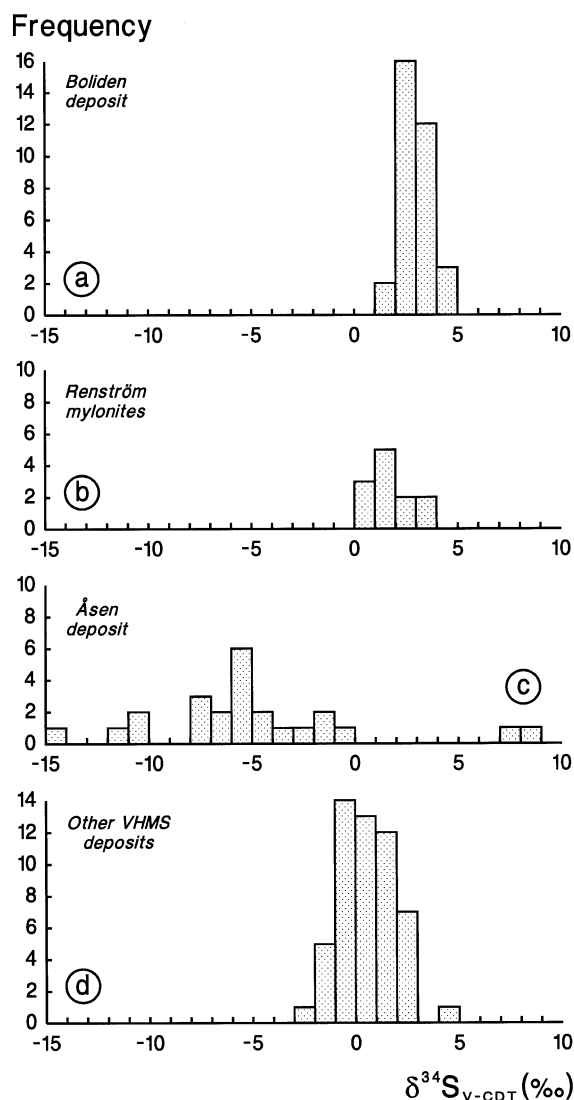

Fig. 5. Synthesis of sulphur isotope data for different massive sulphide deposits in the Skellefte district. (a) Massive sulphides and vein ores of the Boliden deposit. Data from Gavelin et al. (1960) and this study. (b) Sulphide mylonites (sphalerite and galena) of the Renström deposit. Data from Duckworth and Rickard (1993). (c) Massive pyrite ore of the Åsen deposit. Data from Gavelin et al. (1960) and Rickard et al. (1979). (d) Different massive sulphide deposits in the Skellefte district (Bjurfors, Bjurliden, Ö Högkulla, Kristineberg, Rävliden, Rävlidmyran, Udden, Långdal). Data from Rickard et al. (1979) and Frietsch et al. (1995).

active submarine hydrothermal fields in mid-ocean ridge and back-arc settings. The majority of these massive sulphide deposits show a range of their $\delta^{34}S$

values between 0‰ and +10‰ (e.g., Ohmoto, 1996; Herzig et al., 1998; Huston, 1999). The narrow range of δ^{34}S values in many, but not all, VHMS deposits is generally explained by partial inorganic reduction of seawater sulphur in the high-temperature sub-seafloor environment via interaction with volcanic rocks and oxidation of Fe^{2+} in mafic minerals (e.g., Shanks et al., 1981; Ohmoto et al., 1983; Solomon et al., 1988; Huston, 1999). Contributions of reduced sulphur via leaching of rock sulphur and direct incorporation of magmatic sulphur can also account for part of the sulphur budget, in particular in ore districts with a very narrow range of δ^{34}S values. It is commonly observed that the range of sulphur isotope compositions is even smaller for different types of Precambrian VHMS deposits, compared to Phanerozoic deposits (Eastoe et al., 1990; Huston, 1999). A predominance of magmatic-derived sulphur in submarine-hydrothermal systems has been favoured for Precambrian VHMS deposits, based on the isotopic variation and the assumption of low concentrations of sulphate in early Precambrian seawater (e.g., Huston, 1999). Based on the framework of sulphur isotope data from VHMS provinces worldwide, the data set from Boliden is suggestive of leaching of sulphur from Svecofennian volcanic rocks or a direct magmatic contribution to the hydrothermal system. The sulphur isotope characteristics of the Boliden deposit are consistent with both alternative genetic models discussed in the literature, i.e., formation via seafloor VHMS processes (Rickard and Zweifel, 1975; Vivallo, 1987) or by high-sulphidation-type epithermal sub-seafloor infiltrations and replacements (Allen et al., 1996; Bergman Weihed et al., 1996). Our data set does not allow discrimination between both depositional environments.

7. Conclusions

1. This study demonstrates that it is possible to analyze arsenopyrite by means of an in situ laser combustion technique with a resulting level of analytical precision comparable to that of conventional methods. These results have significant implications for future high-resolution studies of arsenopyrite-rich ore assemblages, such as zoned arsenopyrite crystals in mesothermal Au deposits or multi-stage arsenopyrite in massive sulphide deposits.

2. Application of this technique, with our experimentally determined correction factors, to a study of two separate generations of arsenopyrite and associated minerals in the Boliden Au–Cu–As deposit has also led to new insights on the processes of recrystallization/remobilization of arsenopyrite ores and the genesis of vein-type ores in the Boliden deposit.

3. The sulphur isotope data from Boliden are consistent with a process of formation common to other VHMS-type deposits in the Skellefte district, as well as similar Proterozoic deposits globally, being altogether dominated by volcanogenic (magmatic) sulphur. The isotope characteristics would also agree well with a postulated alternative model of sub-seafloor epithermal ore formation.

4. Moreover, we infer that the Au-rich quartz–sulphosalt–sulphide vein ores have inherited their sulphur isotope composition from the massive arsenopyrite host orebodies during vein formation at regional metamorphic (Svecokarelian) conditions. It is likely that the external contribution of sulphur from the metamorphogenic fluids responsible for vein formation was negligible, and that Au was also inherited from the massive arsenopyrite ore.

Appendix A

Table A1
Conventional and laser sulphur isotope analyses used to constrain the fractionation correction factor of arsenopyrite

Sample no.	Line no.	$\delta^{34}S_{V\text{-}CDT}$ (conv.) (‰)	$\delta^{34}S_{V\text{-}CDT}$ (laser) (‰)
ASP 1-A	SA8005	+ 2.4	
ASP 1-A	SA8025	+ 2.4	
ASP 1-B	SA8006	+ 2.2	
ASP 1-B	SA8026	+ 2.5	
ASP 1-C	SA8007	+ 2.2	
ASP 1-C	SA8027	+ 2.4	
ASP 1-D	SA8028	+ 2.4	
ASP 1-2	LS4693		+ 1.9
ASP 1-3	LS4694		+ 1.7
ASP 1-4	LS4695		+ 1.8
ASP 1-5	LS4696		+ 1.9
ASP 1-6	LS4697		+ 2.4
ASP 1-7	LS4698		+ 1.8
ASP 1-8	LS4699		+ 1.8
ASP 1-9	LS4700		+ 1.9
ASP 1-11	LS4702		+ 2.3
ASP 1-12	LS4703		+ 2.2
ASP 1-13	LS4766		+ 2.2
ASP 1-14	LS4767		+ 2.1
ASP 2-B	SA8030	+ 0.1	
ASP 2-C	SA8031	+ 0.5	
ASP 2-D	SA8032	+ 0.5	
ASP 2-5	LS4708		− 0.1
ASP 2-6	LS4709		+ 0.3
ASP 2-7	LS4710		+ 0.1
ASP 2-8	LS4711		− 0.7
ASP 2-9	LS4712		+ 0.0
ASP 2-10	LS4713		+ 0.3
ASP 2-11	LS4714		+ 0.1
ASP 2-12	LS4715		− 0.1
ASP 2-13	LS4768		− 0.3
ASP 2-14	LS4769		+ 0.2

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