Geologie en Mijnbouw 67: 443–457 (1988)

Geochemistry of wall-rock alteration and of mixed volcanic-exhalative facies at the Proterozoic Stollberg Fe–Pb–Zn–Mn(–Ag)-deposit, Bergslagen, Sweden

IUGS UNESCO IGCP 247

Magnus Ripa
Geological Institute, University of Lund, Sölvegatan 13, S-223 62 Lund, Sweden

Received 22 July 1987; accepted in revised form 20 November 1987

Key words: alteration, exhalites, ores, Proterozoic, Sweden, volcanic rocks

Abstract

The Proterozoic Fe-Pb-Zn-Mn(-Ag) ores at Stollberg in Bergslagen ore province, south central Sweden were formed as stratiform, stratabound exhalites in a volcano-sedimentary environment. The surrounding rhyolitic rocks were altered hydrothermally. This alteration predominantly affected the foot-wall rocks. The metamorphic mineral assemblages in the altered rocks were formed during a subsequent episode of regional metamorphism. They comprise gedrite, biotite and muscovite, indicating chlorite and sericite as original hydrothermal alteration products. Structures resembling hydrothermal breccias support an alteration model. More than 2500 samples have been taken from drill-cores and outcrops, and analyzed for major and trace elements. The geochemistries and the densities of the least and the most altered samples have been used to estimate gains and losses during hydrothermal alteration. Fe, Mg, Mn, Ti and K have been added, whereas Si, Ca, and Na have been removed. Plotting elements along the length of a drill-core, cutting the skarn-altered exhalitic horizon, shows that the exhalites comprise potassium-rich meta-volcanic material mixed with chemical precipitates. Relative to unaltered volcanites these rocks are richer in Si, Fe, Mg, Ca, Mn, Pb and Zn, and poorer in Ti, Al, Ba, Na and K. The metamorphic mineral assemblages (ortho- and clino-amphiboles, garnet, diopside, epidote, gahnite, cordierite, staurolite, serpentine/olivine, fluorite, calcite, quartz, micas and feldspar) are developed in rocks with a bulk marly composition.

Introduction

As mining operations in the Stollberg ore field were about to end in the early 1980's after five centuries of mining, the Swedish Board for Technical Development (STU) approved a geochemical project, which aimed to evaluate the relationships between ores and geochemical haloes. Approximately 2500 analyses for major and trace elements were carried out on samples from drill-cores and outcrops. This material was treated statistically by O. Selinus at the Swedish Geological Survey (SGU). By means of discriminant and factor analyses, Selinus defined distinctive haloes of considerable extent around the mineralizations (Selinus, 1983). The present study is a follow-up of that investigation, aiming to define the geochemical patterns and to relate these to the mineralogy. In this paper the original and altered petrography and the alteration geochemistry will be considered. A hypothetical model of ore-formation is discussed.

Regional geology

The Stollberg ore field is located in an early Proterozoic volcano-sedimentary suite of rocks, which is called informally the 'Leptite formation' (e.g. Lundqvist, 1979). The Leptite formation comprises ca. 1.9 Ga old Svecofennian volcanic and sedimentary rocks, intruded by gabbros and syn- to serorogenic ca. 1.9–1.8 Ga old Svecofennian granitoids. The volcanics from a bimodal, basaltic-rhyolitic suite which is dominated by siliceous rocks (Lundqvist, 1979). Locally, dacites and rhyodacites are present. The felsic rocks are dominated by crystal ash-tuffs (ignimbrites to fall tuffs, (e.g. Van der Velden *et al.*, 1982), with minor occurrences of lavas, deposited in both subaqueous and terrestrial environments (Lundström, 1987). Concordant, occasionaly spilitized, meta-basalts occur at different stratigraphic levels (Fig. 2). Later cross-cutting meta-basaltic dykes are also present. The sediments comprise epiclastic argillites and greywackes, mostly resting on top of the volcanics. Carbonate rocks are found at different stratigraphical levels within the volcanic pile. The supracrustals predominantly occur in synclines or synclinoria between synorogenic Svecofennian granitoid plutons. Their strata usually dip very steeply. The metamorphic grade varies from high-amphibolite to greenschist facies (Lundqvist 1979). The general stratigraphy and the lateral variations on a regional scale within the Leptite formation are outlined in Lundström (1987).

The general chemical trend and settings of formation have been much debated recently, opinions ranging from sub-alkaline rocks in a continental rift environment (e.g. Oen *et al.,* 1982) to predominantly calc-alkaline lithologies associated with plate subduction (e.g. Lundqvist, 1979). The volcanic rocks of the Leptite formation have traditionally been subdivided into lower, sodium-rich and upper, potassium-rich units, but alkali-intermediate compositions are found at all stratigraphic levels. The origin of this alkali stratigraphy has been attributed to regional hydrothermal metasomatism (e.g. Lagerblad & Gorbatschev, 1985).

The Leptite formation contains innumerable ore-bodies, mainly magnetite iron ores, but also several complex (Cu–)Pb–Zn sulphide ores. The ores are normally associated with tuffitic (= pyroclastic material reworked or sorted through slow deposition in water), laminated volcanic rocks and exhalative chert and carbonate units. Recent information on the rocks of the Leptite formation can be found in Hjelmqvist (1966), Frietsch (1982), Oen *et al.* (1982) and Lundström (1987). Major works on the ores within the Leptite formation include Tegengren (1924), Geijer & Magnusson (1944) and Magnusson (1970, 1973).

Geology of the Stollberg ore field

The Stollberg ore field is situated ca. 5 km NE of the town of Ludvika, Bergslagen, Sweden (Fig. 1). The ores consist of several separate massive galena- and/or sphalerite-impregnated magnetite bodies, as well as galena and sphalerite bodies lying along a 4 km long, NS-trending line. Minor, non-economic prospects of arsenopyrite, pyrrhotite, pyrite and chalcopyrite are also present (Selinus, 1983). The galena is sometimes argentiferous. The grade in the magnetite ores is 25% Fe, 5% Mn, 2% Pb and 4% Zn (Magnusson, 1973), and in the sulphide ores 5–15% Pb, 3–5% Zn and 20–320 ppm Ag.

Deformation resulted in the redistribution of ores into fold-hinges, often producing rod or lens shaped ore bodies which dip steeply (70–80°) to the east. Ores exposed at or close to earth's surface extend down to at most 600 m. The ores are associated with Mn-rich, skarn-altered volcanic rocks (skarn is used here for calc-silicate rocks formed by the regional metamorphism of volcanic and chemically precipitated material), Mn-rich carbonates and quartz-mica (hydrothermally altered) rocks. Stratigraphically, they occur within the upper potassic level of the volcanic pile, but rather close to the sodic level (Fig. 2).

The local sodium-rich level predominantly comprises fine-grained, quartz- and feldspar-porphyritic crystal ash-tuffs along with minor occurrences of very fine-grained, laminated tuffites. The potassium-rich level comprises minor occurrences of fine-grained, quartz- and feldspar-phyric crystal ash-

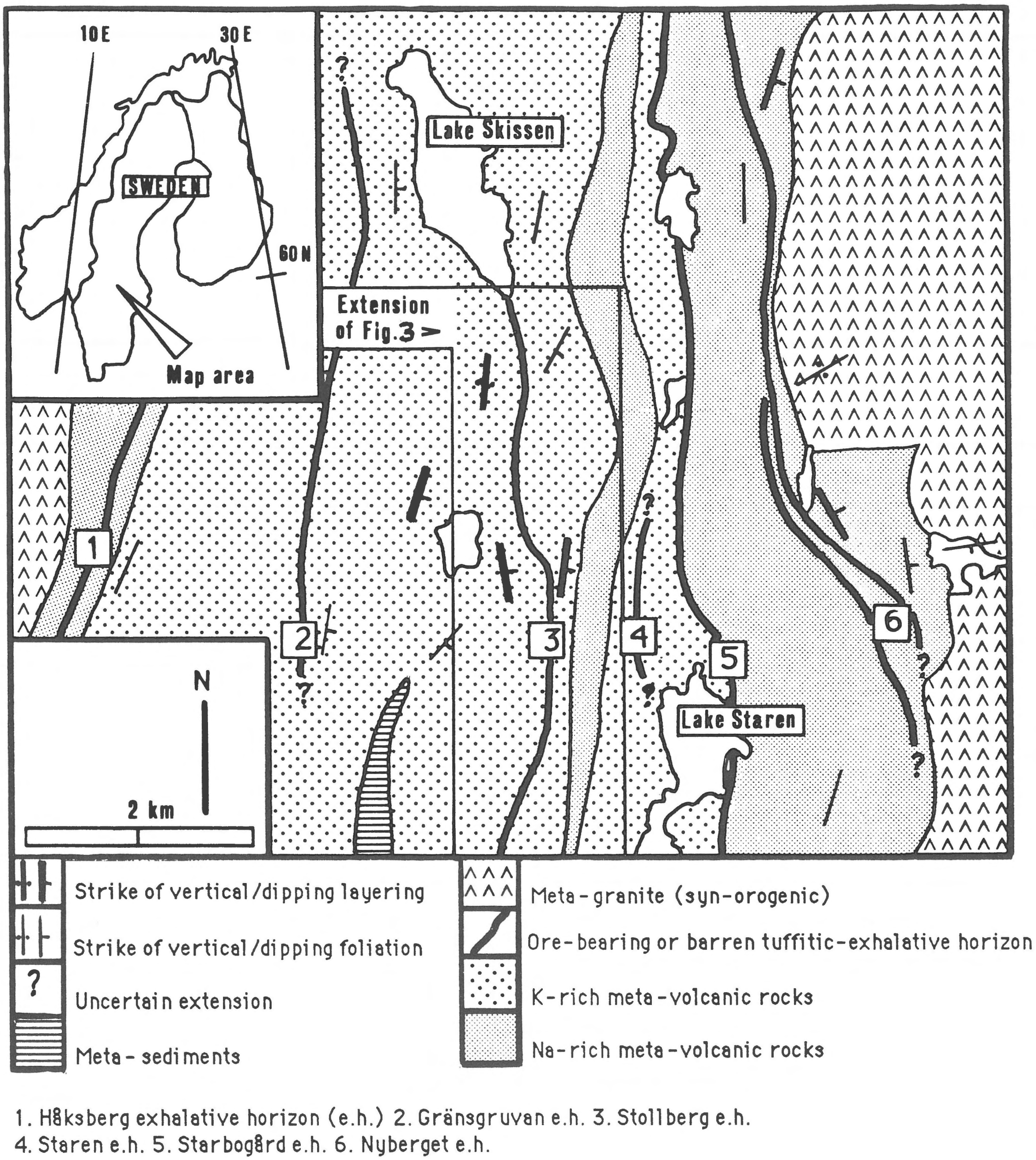


Fig. 1. Simplified geological map of the Stollberg synclinorium including the Stollberg ore field area. The extension of Fig. 3 is indicated. A schematic model of folding is shown in Fig. 5f.

tuffs, and predominantly very fine-grained, laminated tuffites. Compositionally, all felsic lithologies are rhyolites to rhyodacites. From Fig. 1 it can be seen that the ores lie in the eastern limb of a NS-trending syncline. These strata dip 70–80° to the east and are slightly overturned. Traditionally, the area indicated in Fig. 1 has been considered to represent a simple large syncline (e.g. Magnusson, 1970). If, however, all potassic volcanic rocks lie stratigraphically above the sodic volcanic rocks

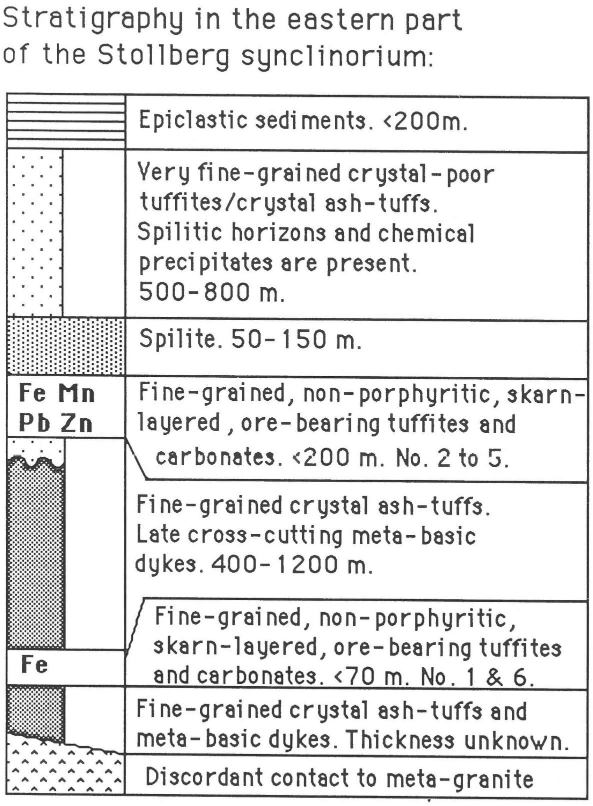


Fig. 2. The stratigraphy in the eastern part of the synclinorium is outlined with approximate thicknesses of lithologies (in m). Fe, Mn, Pb and Zn denote types of ore. Nos. 1 to 6 defined in fig. 1.

(Hjelmqvist, 1966), the geochemical patterns suggest the main structure is a synclinorium (Fig. 5f). The multiple recurrence of similar lithologies, i.e. ore-bearing or barren tuffitic and exhalative strata, also indicates intense folding. In either case, the Stollberg ore field lies at a high stratigraphic position, and the younging direction is unchanged, so that the following discussion remains valid despite any tectonic complications.

A late phase of compressional deformation acting in a NS-direction produced a lineation indicated by the shapes of some of the ore-bodies. A third phase of deformation caused dip-slip faulting in the rocks (Fig. 3).

Fig. 3 shows the local geology as well as the sample locations of this study. Apart from a 100–200 m-wide zone immediately surrounding the ore-bearing horizon, outcrops are scarce. The hanging-wall lithologies are normally better exposed than the foot-wall. Poor exposure means that the geological relationships shown in Fig. 3 can only be regarded as approximate. Studies at different depth levels in the mines indicate similar lithologies and structures down to 600 m (Selinus, 1983), though the ores pinch out at depth. The rocks normally have a S1-foliation indicated by biotite and muscovite growth sub-parallel to the layering (Fig. 1), and an S2-foliation indicated by muscovites growing across the S1-structures. Peak metamorphism was in the amphibolite facies, indicated by the presence of staurolite and cordierite (Winkler, 1979). The secondary metamorphic event retrograded the rocks, as indicated by local chloritization. No discordant, pipe-like alteration zones associated with the ores have yet been recognized.

Petrography

Gedrite-bearing meta-volcanic rocks

This rock type (Fig. 3) is easily identified in the field since it contains 1 to 5 cm large bundles or star-shaped porphyroblasts of black gedrite. High amphibole contents are normally accompanied by increased amounts of sulfide minerals. The matrix is normally reddish-grey and fine-grained. It contains porphyritic quartz grains.

Since outcrops are rare and mostly small, it is hard to map exactly the variation in amphibole content. It appears that highly amphibole-bearing patches occur in lens-shaped zones tending to conform with the local directions of strike. These zones are thin (0.1–0.5 m) and do not extend for more than a few metres. The transition to rocks lower in amphibole is gradational.

In thin section, quartz, as well as albite-twinned plagioclase, forms phenocrysts 0.4 to 1.3 mm in size. The plagioclase phenocrysts sometimes show subgrains. Phenocrysts form 2 to 8 vol % of the rock.

The matrix consists of quartz, plagioclase and occasionally biotite. Epidote and opaques are accessory minerals. The gedrites grow across the other phases, and form up to 64 vol % of the rock. Increasing amounts of amphibole are accompanied

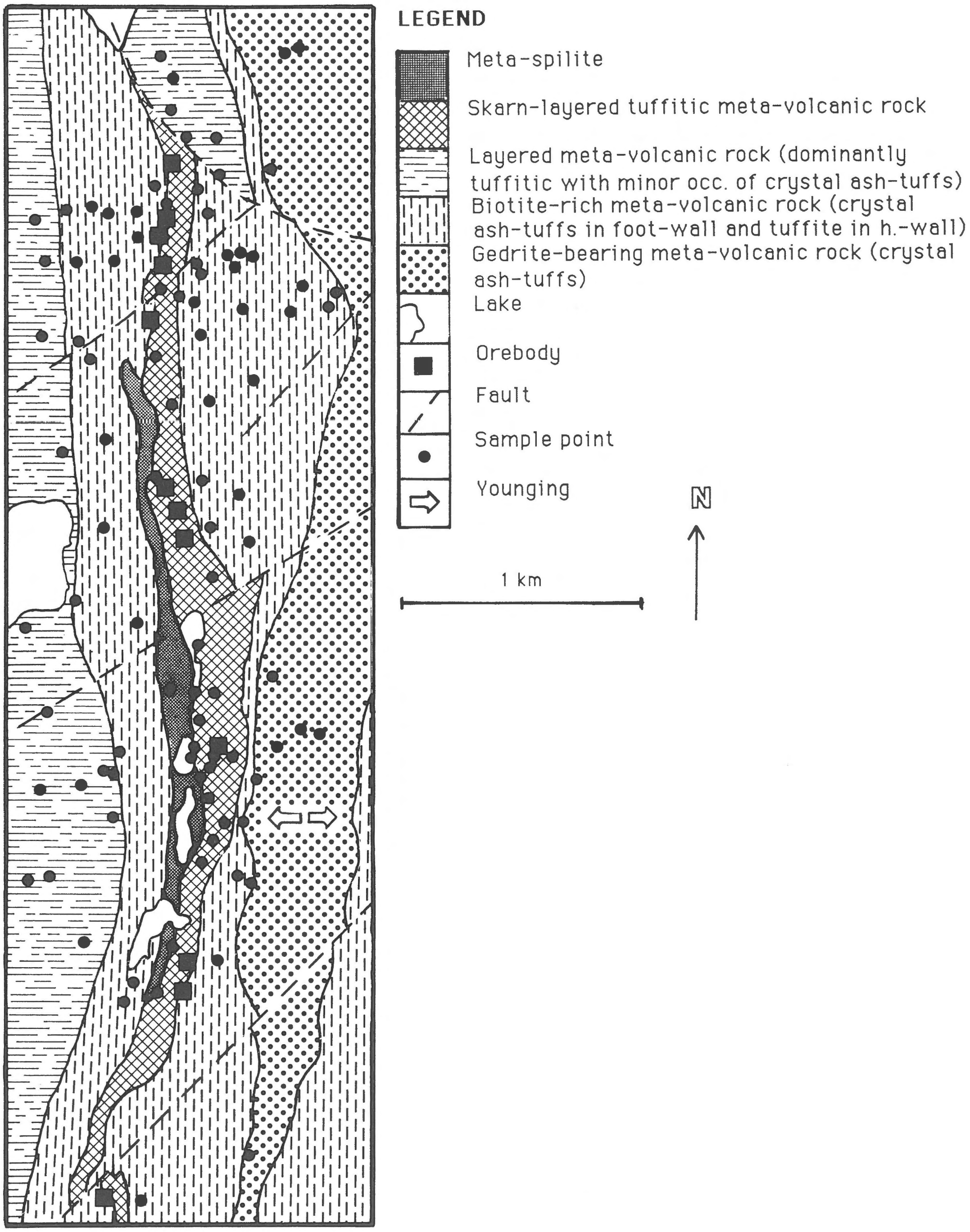


Fig. 3. Geological map of the Stollberg ore field. The orebodies are (from north to south): Lustigkulla, Marnäs, Springa, Carl, Cedercreutz, Alexandra, Mygg, Ryss, Ko-Lång, Dammberget, Stoll, Helena and Brus.

by decreasing amounts of quartz and feldspar. The grainsize of the matrix is unevenly distributed forming seriate textures. The individual grains are less than 0.2 mm across.

Biotite-rich foot-wall meta-volcanic rocks

Macroscopically these rocks are grey, fine-grained, locally feldspar-phyric, and garnet-porphyroblastic meta-volcanics with various amounts of biotite. Normally the micas are uniformly distributed, but in foliated rocks the micas are concentrated in thin laminae. In rock types with a high mica content the micas penetrate the rock in waved bands, with 1 to 2 cm long, ellipsoid patches of less mica-rich rock in between. On outcrop scale, such a mica distribution gives the rock a brecciated appearance. Rocks of this kind tend to occur close to mineralizations and therefore they may indeed be interpreted as hydrothermal alteration breccias. As in the case of the gedrite-bearing rocks, breccia-like textures occur in distinct lenses seemingly conformable with the strike direction.

In thin section, the phenocrysts are seen to consist of K-feldspar, plagioclase and quartz. The K-feldspar sometimes have microcline-twins. The plagioclase exhibit nice albite-twinning varying through wedgy anorthoclase-like twinning to almost chequer-like textures. Some plagioclase phenocrysts contain patches of microcline, which may be due to exsolution, while others show an irregular distribution of K-feldspar, suggesting K-alteration. Some phenocrysts are sericitized. The phenocrysts range from 0.3 to 0.9 mm in size, and form 4 to 11 vol % of the rock.

The matrix consists of quartz, K-feldspar, plagioclase, biotite, chlorite and muscovite. Garnets, epidote and opaques (including chalcopyrite) are accessory minerals. Biotite grows on, and replaces chloritized plagioclase, which can be deduced from the fact that corroded feldspar remnants are completely surrounded by biotite and chlorite. The micas form 25 to 60 vol % of the rock, with 5 to 10 times as much biotite as muscovite. The grain-size distribution is uneven, the individual grains being smaller than 0.2 mm.

Skarn-layered meta-volcanic rocks

The major orebodies are situated within this horizon (Fig. 3). The rocks have a banded appearance due to the presence of alternating 5 to 10 cm thick layers of green and red skarns, mainly composed of garnets and amphiboles, and layers of slightly skarn-altered meta-volcanic rocks. Apart from massive ores, the strata contain various amounts of disseminated ore minerals in both the skarn-rich and the slightly skarn-altered volcanic layers. The skarn locally grades into carbonate rock. From field observations of rock distribution it can be concluded that the ore-bearing horizon represents an episode of intermittent hydrothermal exhalation and deposition of volcanic materials.

Except for the presence of various amounts of skarn minerals, the meta-volcanic layers have mineralogies similar to those of normal meta-rhyolites. They consist of quartz, plagioclase, K-feldspar, biotite and some muscovite. They have seriate textures, and the grain-size is below 0.3 mm. In thin section, the skarn-rich layers show a broad variety of minerals including amphiboles (gedrite, hornblende and actinolite), garnet, diopside, epidote, gahnite, cordierite, staurolite and calcite. Serpentine replaces olivine. Fluorite occurs in some samples.

Meta-spilite

This rock is greenish black, fine- to medium-grained and massive. Locally there are small (1 to 3 mm) cavities partly filled with quartz or feldspar. Although the rock is clearly effusive, it is not certain whether it represents a lava or a tuff.

Only two samples have been studied both by chemical analyses and in thin sections. The rock mainly consists of plagioclase, sericite and hornblende. Quartz, calcite, biotite and chlorite occur in accessory amounts. The plagioclases show partial to almost complete sericitization. One of the samples is a spilite, the other a K-altered meta-basic rock. Mineralogically, the potassium enrichment is reflected by higher amounts of sericite and biotite.

Biotite-rich, hanging-wall meta-volcanic rocks

Macroscopically these rocks are grey, very fine-grained, equigranular and layered meta-volcanics. Minor exhalative strata are found within this horizon.

Fine grain size (below 0.1 mm) makes it hard to identify the individual minerals. The rocks have seriate textures and the mineral components appear to be quartz, feldspars, biotite, muscovite and minor garnet. The amount of biotite is higher than in normal rhyolites. However, contrary to the foot-wall biotite rock, this horizon always has the micas uniformly distributed, i.e. no breccia-like textures are present.

Hanging-wall layered meta-volcanic rock

This rock is similar to the layered volcanic described above, both in grain size and matrix composition, but the content of biotite is somewhat lower. There are phenocrysts of quartz, plagioclase and K-feldspar. Their grain size ranges from 0.3 to 1.6 mm.

Biotite forms aggregates. Muscovite is intergrown with biotite or grows on sericite. Exhalative strata are present also within this horizon.

General remarks

The foot-wall rocks (below the ore-bearing, skarn-layered horizon) are porphyritic and distinctly coarser grained than the hanging-wall rocks. The skarn-layered horizon is about as coarse grained as the foot-wall rocks but non-porphyritic. The hanging-wall rocks are non-porphyritic in the lower (biotite-rich) parts, and somewhat porphyritic higher up in the stratigraphy. The phenocrysts in all lithologies vary from subhedral to anhedral.

Since it is reasonable to assume that all the volcanic rocks have been affected by the same metamorphic events, the present differences in grain sizes reflect primary differences. At the time of chemical precipitation, the volcanic materials that settled had changed in character from crystal tuffs to tuffites. After the ore-forming event very fine-grained tuffites were deposited. These very fine-grained tuffites, in turn, were overlain by very fine-grained crystal tuffs. It thus seems that a time-relation between chemical sedimentation and the nature of the volcanic activity existed. This can be seen in many Bergslagen deposits, indicating a similarity in ore-forming processes.

Table 1. Comparison of geochemistries in corresponding rock types in Bergslagen and Stollberg. Na-r is Na-rich rocks ($Na_2O/K_2O > 5$), K-r is K-rich rocks ($Na_2O/K_2O < 0.2$), AIM is alkali-intermediate rocks. All is Na-r + K-r + AIM and *n* is number of samples. Regional values from B. Lagerblad (pers. comm.)

		Regional Bergslagen				Stollberg			
		All	Na-r	AIM	K-r	All	Na-r	AIM	K-r
SiO_2	wt%	75.40	77.03	74.88	74.63	73.28	74.76	73.81	72.93
TiO_2		0.20	0.17	0.21	0.21	0.17	0.15	0.17	0.17
Al_2O_3		12.44	12.19	12.62	12.29	12.46	10.24	12.32	12.58
Fe_2O_3		2.19	1.43	2.41	2.60	4.28	6.08	3.84	4.51
MnO		0.04	0.01	0.03	0.04	0.14	0.26	0.14	0.13
CaO		0.77	0.69	0.84	0.69	1.15	0.97	1.44	0.98
MgO		0.87	0.75	0.94	0.86	1.64	1.64	1.60	1.67
BaO		0.08	0.02	0.09	0.12	0.08	0.01	0.07	0.09
Na_2O		3.43	5.80	3.29	0.67	1.08	4.73	2.28	0.28
K_2O		3.45	0.55	3.58	6.96	5.06	0.45	3.63	6.02
Zn	ppm	17	10	21	18	464	6920	554	291
Pb		10	7	11	12	365	444	371	360
Rb		84	20	88	159	109	15	95	119
Sr		46	48	52	27	18	21	27	12
Y		39	41	38	37	14	17	14	14
Zr		208	204	204	226	175	163	178	173
Th		15	16	15	15	17	18	17	17
n		584	154	314	116	1331	15	498	818

Geochemistry

Sampling and analytical work

The majority of the Stollberg samples (ca. 2500) were collected by Selinus (1983), mostly from drill cores, due to the lack of outcrops, except in the vicinity of the ore horizons (Fig. 3). The drill holes were driven perpendicular to the strike and dip of the rocks. They extend about 100 metres stratigraphically above and below the ores. About 150 samples were taken from outcrops. The procedures of sampling and analyzing have been described by Selinus (1983). For the present study, more than 100 additional samples were taken from outcrops. Unweathered pieces of about 1 kg each were chosen. All samples were analyzed by XRF, the first ones in Lund by Ingrid Johansson, the later ones by M.E.S.A., Nottingham, U.K.

General geochemistry

Some of the general geochemical characteristics of the meta-volcanic rocks in the Bergslagen part of the Leptite formation have been described by Lagerblad & Gorbatschev (1985). Some aspects of the local geochemistry in the Stollberg area have also been considered before (Selinus, 1983).

Lagerblad & Gorbatschev (1985) concluded that the composition of the alkali-intermediate volcanic rocks most closely resembles the original composition of the felsic meta-volcanic rocks. Compared to these, the Stollberg meta-volcanic rocks generally have higher contents of K, Ca, Mg, Fe, Mn, Rb. Th, Pb and Zn, and lower contents of Si, Ti, Al, Na, Sr, Y, Zr and Ba (Table 1). From the preceding petrographic descriptions it is clear that most of the Stollberg samples were taken from hydrothermally altered rocks within the K-rich, upper part of the Leptite formation. The chemical differences are therefore attributable to the hydrothermal imprint on these rocks.

Geochemistry

The geochemistries of individual lithologies as defined above are presented in Table 2. All samples are from surface outcrops, since the samples from the drill-cores only comprise skarn-layered rocks.

Gedrite-bearing rocks. The chemistry of this unit shows it belongs to the Na-rich level of the meta-volcanic rocks. Compared to most sodic volcanic rocks (Table 1), these rocks have higher contents of Fe, Mg, Mn, Na and Zn, and lower contents of Ca,

Table 2. Geochemistry of different lithologies (defined in text) in Stollberg. Figures in brackets show standard deviation. FBR is foot-wall biotite-rich rocks, SLR is skarn-layered rocks, HBR is hanging-wall biotite-rich rocks, HLR is hanging-wall layered rocks and n is number of samples.

		Gedrite rocks	FBR	SLR	Spilites	HBR	HLR
SiO_2	wt%	73.46 (3.35)	71.22 (3.31)	73.49 (8.46)	49.58 (2.29)	74.56 (2.93)	74.09 (4.54)
TiO_2		0.24 (0.05)	0.24 (0.05)	0.16 (0.09)	1.11 (0.55)	0.17 (0.06)	0.22 (0.11)
Al_2O_3		12.90 (0.60)	13.01 (1.06)	9.44 (3.48)	13.25 (0.12)	12.59 (1.68)	12.69 (1.89)
Fe_2O_3		4.88 (3.03)	5.56 (1.51)	7.63 (4.80)	12.29 (0.41)	2.47 (0.67)	2.64 (1.21)
MgO		1.15 (0.70)	1.60 (0.80)	1.87 (1.09)	9.78 (3.45)	1.62 (0.86)	1.17 (0.53)
CaO		0.21 (0.08)	0.45 (0.77)	2.25 (5.37)	9.73 (0.15)	0.90 (0.98)	1.57 (1.35)
MnO		0.04 (0.03)	0.08 (0.03)	0.31 (0.56)	0.28 (0.03)	0.08 (0.05)	0.09 (0.05)
BaO		0.00 (0.00)	0.12 (0.06)	0.06 (0.06)	0.04 (0.01)	0.10 (0.05)	0.11 (0.04)
Na_2O		6.23 (0.81)	2.08 (1.82)	1.13 (1.53)	2.67 (0.92)	2.29 (1.63)	1.90 (1.36)
K_2O		0.13 (0.09)	5.14 (2.10)	3.02 (2.44)	0.90 (0.25)	4.57 (2.53)	4.80 (2.03)
Pb	ppm	10 (10)	27 (22)	238 (660)	133 (25)	64 (72)	41 (20)
Zn		18 (13)	29 (14)	921 (2942)	167 (15)	41 (21)	48 (26)
Rb		5 (5)	91 (45)	64 (62)	32 (17)	101 (36)	130 (44)
Sr		17 (6)	13 (8)	9 (9)	130 (25)	26 (16)	25 (14)
Y		45 (10)	26 (14)	17 (12)	12 (1)	16 (16)	13 (11)
Zr		193 (13)	195 (26)	152 (67)	80 (10)	200 (66)	178 (63)
n		11	24	25	2	15	15

K, Rb, Sr and Zr. Contents of other elements are the same as in the regional samples.

Biotite-rich foot-wall rocks. These rocks are enriched in K and, compared to regional K-rich rocks (Table 1), they have higher contents of Fe, Mg, Mn, Pb and Zn, while Ca, Sr, Y and Zr are lower.

Skarn-layered rocks. The samples from this horizon are skarn-altered volcanics. Like the biotite-rich rocks, the skarn-layered rocks belong to the K-enriched meta-volcanics. However, total alkali contents are low. The same goes for Ti, Al, Ba, Sr, Y and Zr, whereas Fe, Mg, Ca, Mn, Pb and Zn appear to be enriched. The low content of Al must be due to dilution of volcanic materials by chemical input. Hydrothermal alteration either does not affect the Al_2O_3-content (e.g. alkali alteration, Table 1) or increases it (e.g. chloritization, Table 3; cf. MacGeehan, 1978; Morton & Nebel, 1984). Chemical precipitates, in contrast, are poor in Al and also in Na and K which accounts for the simultaneous drop in alumina and total alkalis.

Biotite-rich hanging-wall rocks. Apart from slightly higher contents of Mg, Mn, Pb, and Zn, and low contents of Ti and Y, these rocks are chemically similar to the regional alkali-intermediate to K-rich meta-volcanic rocks (Table 1). The differences are presumably due to the addition of exhalitic components to this horizon.

Hanging-wall layered rocks. In this horizon too, the presence of exhalitic components results in slightly higher contents of Ca, Mg, Mn, Pb and Zn and slightly lower contents of Y and Zr than those found in the regionally developed meta-volcanics.

Overall alteration processes. The chemistry and mineralogy of each rock stratum around the Stollberg ores suggest that all are hydrothermally altered, in so far as all are more or less alkali differentiated. In the gedrite-bearing rocks, the foot-wall and the lower hanging-wall biotite rocks, a secondary hydrothermal alteration leading to enrichment of ore elements and of Mg is superimposed onto the alkali alteration. Hydrothermal ac-

Table 3. Chemical composition of least and most altered rocks. Analyses are normalized to 100 wt% on water-free basis. X is the change for an element.

Rock type	Gedrite rocks			Biotite rocks			
No.	S84:10	S84:7		R58	R60		
Alteration	L.A. = Xa	M.A. = Xb	X	L.A. = Xa	M.A. = Xb	X	
SiO_2	78.60	64.74	– 19.61	73.62	60.13	– 25.59	wt%
TiO_2	0.25	0.38	0.10	0.20	0.38	0.10	
Al_2O_3	12.63	13.86	0.00	12.66	15.85	0.00	
Fe203*	0.98	13.69	11.50	4.09	10.37	4.19	
MgO	0.23	3.02	2.52	0.83	4.55	2.80	
CaO	0.31	0.15	– 0.17	0.32	0.15	– 0.20	
BaO	0.00	0.00	0.00	0.13	0.09	– 0.06	
MnO	0.01	0.13	0.11	0.08	0.08	– 0.02	
Na_2O	6.81	3.83	– 3.32	3.96	2.35	– 2.08	
K_2O	0.18	0.20	0.00	4.12	6.05	0.71	
Total	100.00	100.00		100.00	100.00		
Density	2.70	3.02		2.64	2.97		g/cm^3

All analyses on water-free basis.
L.A. = least altered sample.
M.A. = most altered sample.
Fe203* = total iron.

Calculations (Gresens, 1967):
X = FvXbDb/Da – Xa
X = change for each element
Fv = volume factor
Xb, XA = concentration of element in altered and unaltered rock
Db, Da = density of altered and unaltered rock

tivity continued all through the deposition period of the volcanics, which can be seen from the presence of chemical precipitates in all strata stratigraphically above the foot-wall biotite rocks.

Chemistry along a profile across the skarn-layered horizon

To examine the chemical effects of the exhalative process in detail, a number of element contents and two element ratios have been plotted along the length of two drill-cores, driven across the skarn horizon at the 270 m subsurface depth level. The results are shown in Fig. 4. All other drill-cores that have been examined, in essence also exhibit the same elemental distribution pattern. Two groups of elements can be distinguished, based on their variation across the exhalites. One group comprising K, Al, Ba and Rb, decreases in content as the proportion of exhalite material increases, whereas the other group comprising F, Mn, Fe, Ca, Mg, Y, Zn, Pb, Sr, P and Cl shows the opposite behaviour. The Na-contents are uniformly low along almost all the drill-cores, except, surprisingly, at their stratigraphically uppermost terminations.

These chemical variations correlate clearly with variations in mineralogy. The skarn layers are characterized by amphiboles, garnet, diopside, epidote, staurolite, cordierite, olivine/serpentine, fluorite, gahnite, and calcite. In addition, disseminated ore minerals similar to those in the major orebodies are present. The elements that enter these phases are those which correlate positively with the amounts of exhalite components and negatively with the amounts of volcanic materials.

Wall-rock alteration

Both the gedrite-bearing rocks and the foot-wall biotite-rich rocks carry zones or lenses with higher modal contents of amphibole and mica, respectively. The breccia-like appearance of the biotite-rich zones and the thin zones of progressively more gedrite-rich rock argue against interpreting the rock simply as a primary mixture of more and less siliceous volcanic materials. Neither mineralogy nor chemistry of the amphibole/mica zones are compatible with metamorphosed, fresh or altered, intermediate to mafic rocks. Consequently, textures, mineralogy and chemistry suggest that these zones represent hydrothermally altered felsic rocks rather than primary or altered mafic rocks.

In Table 3 analyses of the most and least altered samples of each rock type are listed. There are basically two ways of calculating gains and losses through alteration; either immobility for an element is assumed, or the differences in density between the least and most altered samples are considered (Gresens, 1967). In many areas Al has been found to be immobile during alteration (e.g. Baker & De Groot, 1983; Morton & Nebel,1984), but the presence of H^+- and F^--ions in the solution may cause Al to be both soluble and mobile. As long as the exact chemical and physical conditions of the solutions are not known, it is safer to consider changes in densities and to regard Al as immobile at the same time.

The results of these calculations are listed in Table 3. It is evident that the chemical changes are basically the same in both the amphibole rock and in the mica rock. Fe, Mg, and Ti have been added, whereas Si, Ca and Na have been depleted in both rock types. Mn is added to the gedrite group, but depleted from the mica group. The gedrite group neither gains nor loses K and Ba, whereas the mica group gains K and loses Ba.

Mineral reactions

Though the chemical changes in both the gedrite- and biotite-muscovite-bearing rocks were found to be about the same, the present mineralogy differs markedly. In the following discussion it is considered that neither gedrite nor biotite formed as primary alteration products. Rather, they are thought to represent upper-greenschist to amphibolite facies products of an assemblage pre-dating the regional metamorphism. Muscovite may originate from recrystallized sericite. Biotite probably formed by several reactions involving basically chlorite. According to MacGeehan (1978), gedrite may form from chlorite during metamorphism and preliminary studies suggest that gedrite is stable in upper-greenschist facies rocks where K-concentrations are too low for biotite to form (Ripa, in prep.). Consequently, what is needed for the production of biotite, muscovite and gedrite is sericite

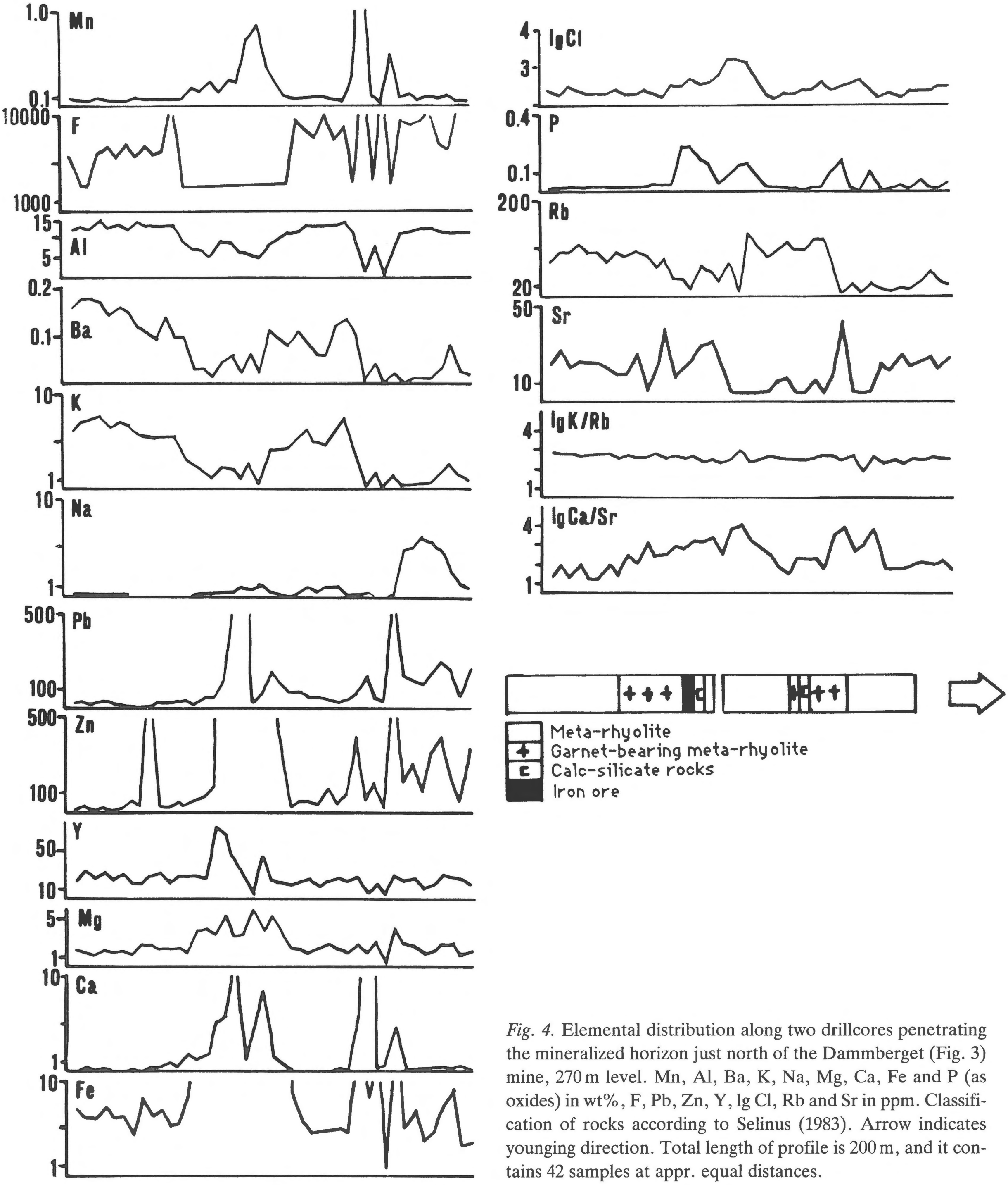


Fig. 4. Elemental distribution along two drillcores penetrating the mineralized horizon just north of the Dammberget (Fig. 3) mine, 270 m level. Mn, Al, Ba, K, Na, Mg, Ca, Fe and P (as oxides) in wt%, F, Pb, Zn, Y, lg Cl, Rb and Sr in ppm. Classification of rocks according to Selinus (1983). Arrow indicates younging direction. Total length of profile is 200 m, and it contains 42 samples at appr. equal distances.

and chlorite. Since the least altered rocks mainly consist of quartz, feldspars and biotite, reactions involving these minerals and producing chlorite and sericite are needed. Morton & Nebel(1984) suggested the following reactions:

$$\text{albite} + K^+ + H^+ = \text{sericite} + \text{quartz} + Na^+ \quad (1)$$

$$\text{sericite} + (Fe, Mg)^{2+} + \text{quartz} + H_2O = \text{chlorite} + K^+ + H^+ + H_4SiO_4 \quad (2)$$

$$\text{albite} + (Fe, Mg)^{2+} + \text{quartz} + H_2O = \text{chlorite} + H^+ + H_4SiO_4 + Na^+ \quad (3)$$

An additional reaction may be:

$$\text{K-feldspar} + H^+ = \text{sericite} + \text{quartz} \quad (4)$$

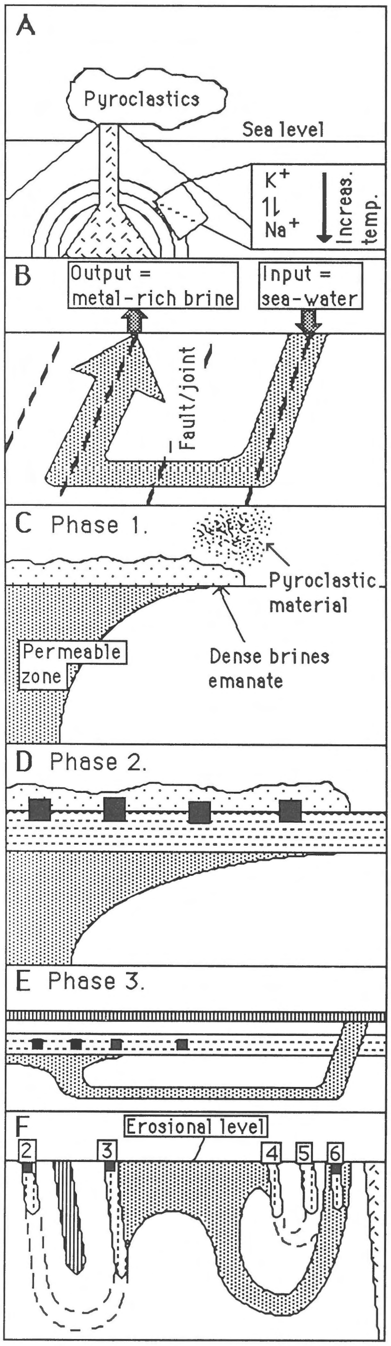
An important feature of these reactions is that (1) and (4) require a low pH solution, while (2) and (3) will lower the solution pH. In the stratigraphically lower gedrite horizon, no sericite and no secondary biotite have been observed. From the analyses (Table 3) it can be deduced that the feldspar present must be sodic. The most suitable reaction then is (3), which reacts sodic feldspar directly to produce chlorite. Muscovite (from sericite) is present in the mica horizon, and the chemical analyses indicate that both sodic and potassic feldspars are present. In this case (1) and (4) followed by (2) seems likely.

Discussion

In the field it is evident that the Stollberg ores are stratiform, strata-bound exhalites formed in a volcano-sedimentary environment. The ores lie interbedded in alternating layers of meta-volcanic and chemical sedimentary rocks. Hence, the ores are still in their original position, with respect to the host rocks, except where remobilization due to deformation has been shown. The ores lack any form of zoning in terms of metal ratios (Amcoff, pers. comm.). The absence of a discordant pipe-like alteration zone and the low Cu-contents in the ores and wall-rocks suggest a distal position far from an exhalative vent. However, the ores and the associated exhalative phases are underlain by conformable, stratabound alteration zones.

Field evidence suggests that the exhalative phases, including the ores, precipitated contemporaneously with the deposition of the volcanic (tuffitic) materials. When the chemical sedimentation culminated, the volcanic activity was low because nearly pure ores and carbonate rocks were formed. A three-step hypothetical model of formation is outlined in Fig. 5 (c to e). The transitions between the steps are thought to have been gradational. During step 1, volcanic material is deposited. At the same time hydrothermal fluids (presumably evolved seawater) percolate upwards towards the seafloor. The circulating and rising fluids react with, and alter, the volcanic material already deposited. Mixing and dilution of these fluids by seawater causes the conditions for solubility to change drastically. Thus, temperature, pH, Eh, ionic strength and possibily also pressure change, causing several minerals to precipitate. During step 2, the hydrothermal activity reaches its peak, while the volcanic activity wanes. This is when the majority of chemical precipitation takes place, forming ores and a thick interval of carbonates. Since biological carbonate production was low or absent in early Proterozoic days, thick Mn-rich carbonate strata more likely formed from exhalation, especially when associated with exhalative ores. In step 3 there is an increase in volcanic activity and a corresponding decrease in hydrothermal activity.

To evaluate the conditions prevailing during the formation of the ores, the stability-fields of some of the primary exhalative phases have been plotted in a pH–Eh-diagram (Fig. 6). Some, but not all, of the minerals in the exhalite horizon listed above may have formed directly at the time of deposition. Some minerals, such as carbonates, oxides, sulfides, fluorite and possibly olivine, are likely to have formed directly by precipitation from the hydrothermal fluid. Even structurally more complex minerals like talc have been reported to form by direct precipitation from smokers at active spreading ridges (Haymon & Kastner, 1981). However, several of the observed minerals are more likely to have formed by reactions during regional metamorphism. Some skarns have been reported to replace carbonates in the Stollberg ore-field supporting this model (Magnusson, 1973). Most of the minerals listed above can be accounted for in terms of standard metamorphic reactions (Winkler,



←

Fig. 5. Hypothetical phases of formation for the Stollberg ores: (A) Pyroclastic material forms the volcanic pile. The thermal gradient (half-circles) causes migration of seawater in the deposited crystal ash-tuffs. In the lower (hotter) parts Na-feldspar stabilizes, while K-feldspar stabilizes in the upper (cooler) parts. (B) A more intense secondary cell of convecting hydrothermal fluids, along zones of high permeability (faults, joints and unconsolidated tuffs (densily dotted area)), causes breakdown of feldspars to form chlorite and sericite. (C) The fluids exit as dense brines (lightly dotted area) contemporaneously with the setting of pyroclastic material → hybride volcanic/chemically precipitated rock (broken lines). Step 1 in text. (D) Peaking hydrothermal activity and no or minor volcanic activity → ores (black squares), carbonates and other chemical phases precipitate. Step 2 in text. (E) Volcanic activity commences anew, while the hydrothermal activity wanes. Step 3 in text. Thus, very fine-grained crystal ash-tuffs and tuffites, containing lenses of chemical sediments, form the hanging-wall volcanic rocks. On top of these epiclastic greywackes and argillitic sediments settle (vertical lines). (F) Isoclinal folding produces a repetition of the same stratigraphic level at sites 2, 3, 4 and 5 (c.f. Fig. 1), whereas site 6 is at a lower level.

1979). If iron and manganese are added to the carbonate and/or marly systems, the results may well be the Stollberg skarns. The pH must have been within the range of magnetite stability, and the redox-conditions may be evaluated from the fact that no sulphates (e.g. barite) are present. This restricts the possible area in Fig. 6 to be somewhat reducing and alkaline.

Since several of the precipitated and hydrothermally added elements are the same, it seems logical to assume that the altered rocks in the foot-wall lithologies (gedrite- and mica-rocks) were altered by the fluids that later exhaled onto the seafloor and precipitated the ores. Therefore it is plausible that the ores directly overlie a stratabound alteration zone, and in part are proximal to a vent.

The low Cu-content of the ore still must be explained. Dispersed, disseminated chalcopyrite is present in the foot-wall biotite-rich volcanics, but only in uneconomic amounts. The most obvious explanation is that the ore-forming solutions had low Cu-contents. The felsic rocks from which the ore metals were leached had initially low Cu-contents, so the fluid could never become Cu-enriched (e.g. Stanton & Ramsay,1980).

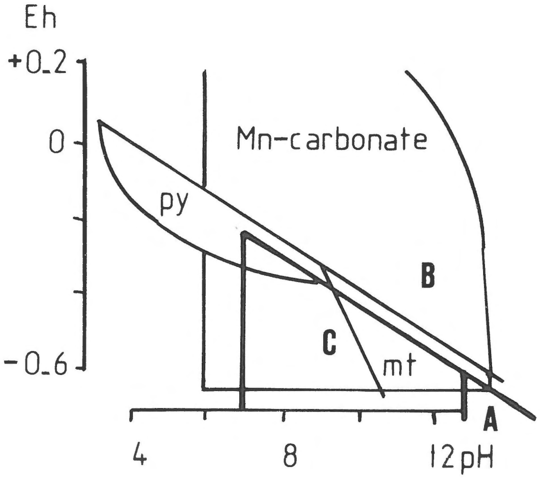


Fig. 6. Stability fields for some of the primarily precipitated phases in Stollberg. Letters A, B and C denotes stability of S^{2-}, SO_4^{2-} and HS^-, respectively. Py = pyrite and mt = magnetite. Compiled from Krauskopf (1979).

The primary geometry of the alteration zone is not completely established. Most alteration zones are cross cutting and tube- or funnel-shaped (e.g. Larson, 1984; Riverin & Hodgson, 1980; Baker & de Groot, 1983; Morton & Nebel, 1984). However, several factors can control the shape of the zones: i.e. faults, rock permeabilities, the shape of the temperature gradient, hydrostatic pressure, presence of impermeable 'cap-rocks' etc. Thus it is conceivable that the fluids percolated laterally through poorly consolidated volcanic materials. They were concentrated particularly to zones of still higher permeability now represented by rocks with the highest gedrite and biotite contents, before exhaling onto the seafloor over vast areas rather than in distinct tube-like spots. In Fig. 5 such a low-angle alteration zone has been outlined. Unfortunately the drillcores are not long enough to confirm or reject this proposed geometry. However, conformable alteration has been recognised elsewhere (e.g. Robinson, 1984). The solutions within the Stollberg 'pipe' reacted in low stratigraphic levels with the Na-rich volcanic rocks (reaction no. 3 above). The volcanic rocks altered into a chlorite-rich rock, while the solutions became more acid. These more acid solutions then encountered K-rich volcanic rocks at higher levels, forming a chlorite-sericite rock (reactions 1, 4 and 2 above). The solutions finally exhaled on the seafloor and precipitated the ores. Later isoclinal folding turned the strata into their present position, with the lower Na-rich levels (gedrite rocks) in an anticlinal position to the east of K-rich rocks (biotite rocks) (Fig. 5).

It is also suggested that the hydrothermal activity continued after the deposition of the ores, since exhalative strata are present in the hanging-wall lithologies. The high amount of biotite, in the lower hanging-wall rocks, may also indicate alteration.

Conclusions

(1) The Stollberg ores were formed as stratiform, stratabound exhalites in a volcano-sedimentary environment.
(2) At the time of their deposition, the exhalites mixed with volcanic materials.
(3) The character of the volcanic material indicates a correlation in time between volcanic evolution and hydrothermal activity, since the ores formed in tuffites and not in crystal tuffs.
(4) This mixture of volcanic and exhalative components produced a bulk composition equivalent to a marly rock. Later regional metamorphism induced the reactions which formed the present skarn-altered volcanic rocks.
(5) The ores overlie a mushroom-like, semi-concordant alteration zone, suggesting a proximal to vent type of ore. The mineral assemblages of this zone are gedrite (via chlorite) in the lower, Na-rich rocks and biotite-muscovite (via chlorite-sericite) in the upper, K-rich rocks.
(6) Due to a low concentration of Cu in the ore-forming solutions, no Cu-rich stockwork ore was formed, though minor amounts of disseminated chalcopyrite are present in the foot-wall biotite-rich rocks.
(7) Hydrothermal activity peaked at the time of ore-formation, but continued afterwards, which can be deduced from the presence of exhalative strata in the hanging-wall rocks.

Acknowledgements

This study was partly financed by STU. The author wishes to thank the following persons for criticism and improvements of the original manuscripts: Roland Gorbatschev, O Selinus, P.B. Larson, R.L. Morton, James Baker & Rob Hellingwerf.

References

Baker, J.H. & De Groot, P.A. 1983 Proterozoic seawater – felsic volcanics interaction W. Bergslagen, Sweden. Evidence for high REE mobility and implications for 1.8 Ga seawater compositions – Contrib. Mineral. Petrol. 82: 119–130.

Frietsch, R. 1982 Alkali metasomatism in the ore-bearing metavolcanics of central Sweden – Sver. Geol. Unders. Ser. C 791: 54 pp.

Geijer, P. & Magnusson, N.H. 1944 De mellansvenska järnmalmernas geologi – Sver. Geol. Unders. Ser. Ca 35: 654 pp.

Gresens, R.L. 1967 Composition-volume relationships of metasomatism – Chem. Geol. 2: 47–65.

Haymon, R.M. & Kastner, M. 1981 Hot spring deposits on the East Pacific Rise at 21 N: preliminary description of mineralogy and genesis – Earth Planet. Sci. Lett. 53: 363–381.

Hjelmqvist, S. 1966 Beskrivning till berggrundskarta över Kopparbergs län – Sver. Geol. Unders. Ser. Ca 40: 217 pp.

Krauskopf, K.B. 1979 Introduction to Geochemistry – McGraw-Hill (New York): 617 pp.

Lagerblad, B. & Gorbatschev, R. 1985 Hydrothermal alteration as a control of regional geochemistry and ore formation in the central Baltic Shield – Geol. Rundsch. 74: 33–49.

Larson, P.B. 1984 Geochemistry of the alteration pipe at the Bruce Cu-Zn volcanogenic massive sulphide deposit, Arizona – Econ. Geol. 79: 1880–1896.

Lundqvist, T. 1979 The Precambrian of Sweden – Sver. Geol. Unders. Ser. C 768

Lundström, I. 1987 Lateral variations in supracrustal geology within the Swedish part of the southern Svecofennian volcanic belt – Precamb. Res. 35: 353–365.

MacGeehan, P.J. 1978 The geochemistry of altered volcanic rocks at Matagami, Quebec: a geothermal model for massive sulphide genesis – Can. J Earth Sci. 15: 551–570.

Magnusson, N.H. 1970 The origin of the iron ores in central Sweden and the story of their alterations. Part I – Sver. Geol. Unders. Ser. C 643: 000 pp.

Magnusson, N.H. 1973 Malm i Sverige, vol. 1: Mellersta och södra Sverige. Almqvist & Wiksell (Stockholm): 320 pp.

Morton, R.L. & Nebel, M.L. 1984 Hydrothermal alteration of felsic volcanic rocks at the Helen Siderite Deposit, Wawa, Ontario – Econ. Geol. 79: 1319–1333.

Oen, I.S., Helmers, H., Verschure, R.H. & Wiklander, U. 1982 Ore deposition in a Proterozoic incipient rift zone environment: a tentative model for the Filipstad-Grythyttan-Hjulsjö region, Bergslagen, Sweden – Geol. Rundsch. 71: 182–194.

Riverin, G. & Hodgson, C.J. 1980 Wall-rock alteration at the Millenbach Cu-Zn mine, Noranda, Quebec – Econ. Geol. 75: 424–444.

Robinson, D.J. 1984 Silicate facies iron-formation and strata-bound alteration. Tuffaceous exhalites derived by mixing – Evidence from Mn garnet-stilpnomelane rocks at Redstone, Timmins, Ontario – Econ. Geol. 79: 1796–1817.

Selinus, O. 1983 Factor and discriminant analysis to lithogeochemical prospecting in an area of central Sweden – J. Geochem. Explor. 19: 619–642.

Stanton, R.L. & Ramsay, W.R.H. 1980 Exhalative ores, volcanic loss and the problem of the island arc calc-alkaline series: a review and an hypothesis – Norges Geol. Unders. 360: 9–57.

Tegengren, F. 1924 Sveriges ädlare malmer och bergverk – Sver. Geol. Unders. Ser. Ca 17: 406 pp.

Van der Velden, W., Baker, J.H., De Maesschalck & Van Meerten, T. 1982 Bimodal early Proterozoic volcanism in the Grythytte field, and associated volcanoplutonic complexes, Bergslagen, Sweden – Geol. Rundsch. 71: 171–181.

Winkler, H.G.F. 1979 Petrogenesis of metamorphic rocks. 5th ed. Springer-Verlag: 348 pp.