

D. Holtstam · J. Mansfeld

Origin of a carbonate-hosted Fe-Mn-(Ba-As-Pb-Sb-W) deposit of Långban-type in central Sweden

Received: 16 May 2000 / Accepted: 19 April 2001 / Published online: 27 June 2001
© Springer-Verlag 2001

Abstract The Sjögruvan deposit is one of the Långban-type Fe-Mn oxide deposits hosted by marble interbeds within Svecofennian metavolcanic rocks in the Bergslagen region, central Sweden. Mineralogical and geochemical studies have been carried out to clarify the premetamorphic origin of this type of deposit, which is set apart from most other Mn mineralizations by a significant enrichment in Ba, As, Sb, Pb, W and Be contained by various oxyminerals. The principal ore types at Sjögruvan are (1) hematite + quartz ± magnetite, (2) hausmannite + calcite + tephroite and (3) braunite + celsian + phlogopite. The Mn ores are compositionally akin to modern Mn deposits formed by submarine hydrothermal processes (with a high Mn/Fe ratio and low contents of Co, Ni, Th, U and REE) and likely owe their existence to similar mechanisms of formation. Pb isotope data indicate that the metal source and timing of deposition is similar to the major stratabound base-metal and iron deposits in Bergslagen. All the key elements have been leached from the local felsic volcanic units and were deposited on the sea floor; the excellent Mn-Fe separation occurred in an Eh-pH gradient that essentially corresponded to the mixing zone of hydrothermal solutions and seawater. The braunite ore is chemically distinct from the hausmannite ore, with a high concentration of refractory elements (Al, Ti, Zr) and a positive Ce anomaly, which indicate a detrital/hydrogenetic contribution to its protolith. Carbon isotope ($\delta^{13}\text{C}$) values around 0‰ (relative PDB) suggest that carbonates in the deposit formed directly from seawater.

Editorial handling: B. Lehmann

D. Holtstam (✉)
Swedish Museum of Natural History, Research Division,
Department of Mineralogy, Box 50 007,
104 05 Stockholm, Sweden
E-mail: dan.holtstam@nrm.se
Fax: +46-8-51954031

J. Mansfeld
Geological Survey of Norway, 7491 Trondheim, Norway

Introduction

Carbonate-hosted Fe-Mn oxide mineralizations, sometimes referred to as Långban-type deposits (Moore 1970; Holtstam and Langhof 1999), occur in the western part of the Bergslagen mining region in central Sweden. The now-abandoned mines at Långban and the minor satellites Jakobsberg, Pajsberg-Harstigen and Sjögruvan witness their economic importance in the past. The ores consist of Fe and Mn ore bodies that are chemically rather well separated but occur in close spatial association. Ore, skarn and vein assemblages enriched in Ba, Sb, As and Pb exhibit a bewildering diversity in terms of mineral species (Nysten et al. 1999). Early genetic interpretations for the type included a wide range of models, inferring magmatic and metasomatic as well as sedimentary processes (summarized by Magnusson 1930). The origin remained an open question until Brotzen (1955) detected textural features of unmistakably sedimentary origin in Långban jasper. There is now a general consensus that the premetamorphic ore progenitors were synsedimentary deposits formed in a submarine environment (Boström et al. 1979; Damman 1989; Bollmark 1999).

To further clarify the ore-forming processes, using new analytical data and benefiting from research on Mn metallogenesis during the last decades, a new look has been taken at the Sjögruvan deposit, situated on the shore of Lake Halvtron, near Grythyttan, Örebro county (lat. 59°40.2'N, long. 14°36.8'E).

Geological setting

The southern segment of the Svecofennian Domain (Fig. 1) on the Fennoscandian shield, in essence corresponding to Bergslagen, mainly comprises metasedimentary and felsic metavolcanic rocks that are Paleoproterozoic (Orosirian) in age (1.9–1.8 Ga) and contain a diverse range of stratabound ores, including

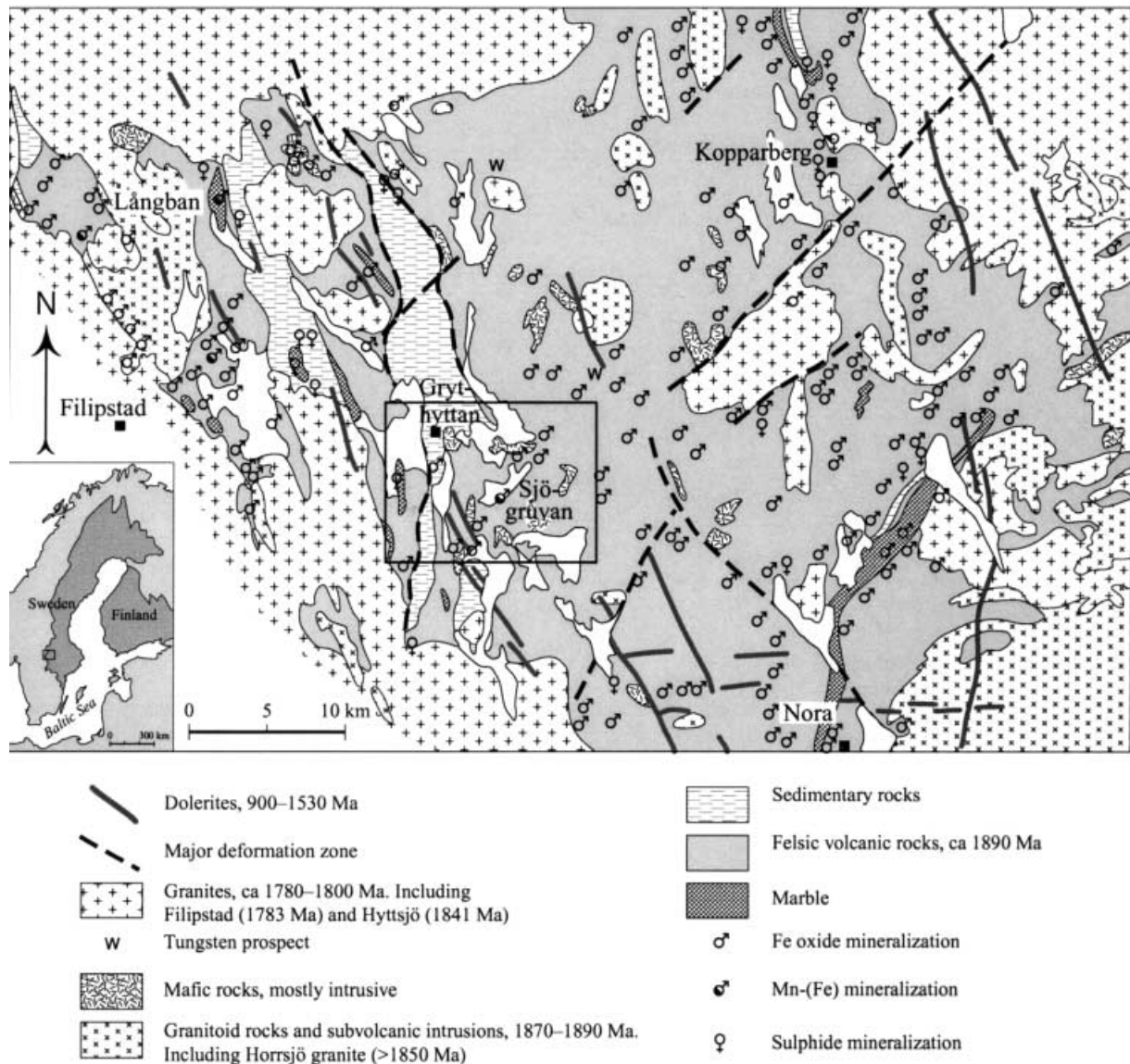


Fig. 1 Geological map of the Filipstad-Grythyttan-Kopparberg areas (in the western part of the Bergslagen region). The *dark area* on the overview map indicates the Svecofennian Domain. The *box* on the main map shows the position of the map given in Fig. 2

innumerable polymetallic sulphide and Fe oxide deposits. The inferred paleoenvironment for their formation was basically a mixed terrestrial and marine, probably back-arc, volcanic area in a continental-margin tectonic setting (Allen et al. 1996).

In the surroundings of Grythyttan the bedrock is dominated by volcanoclastic rocks (arenites to siltstones) of essentially alkali-rhyolitic composition (Fig. 2). The volcanic deposition was in part subaerial, producing juvenile, poorly sorted sediments and remnants of lava flows. Shallow intrusions are occasionally indicated. The common presence of bedded and laminated volcanogenic rocks and carbonate interbeds are, however, evidence of a dominantly subaqueous environment (Lundström 1995). U-Pb dating of zircon crystals ex-

tracted from a meta-ignimbrite (Ekebergshöjden, 12 km N of Sjögruvan), corresponding to the lower stratigraphic level of the *Sängen* volcanic sandstone formation (whose basement is unknown), yielded a precise age of 1891 ± 4 Ma (Lundström et al. 1998). The Sjögruvan deposit belongs to the slightly younger *Älgen* volcanic siltstone formation, which is concordantly overlain by the *Torrvarpen* formation, mainly characterized by bedded argillitic rocks (graphitic slates). The above rocks have been intruded by felsic plutons (ranging from granite to granodiorite in composition) and mafic dikes. Svecofennian orogenic deformation and greenschist-facies metamorphism peaked in the area at ca 1.85 Ga, and the rocks later suffered from Sveconorwegian (1.0 Ga) deformation. Metasomatic, mostly synvolcanic hydrothermal alterations are more the rule than an exception as far as the volcano-sedimentary units are concerned; these processes have redistributed chiefly alkali metals and magnesium, and might in cer-

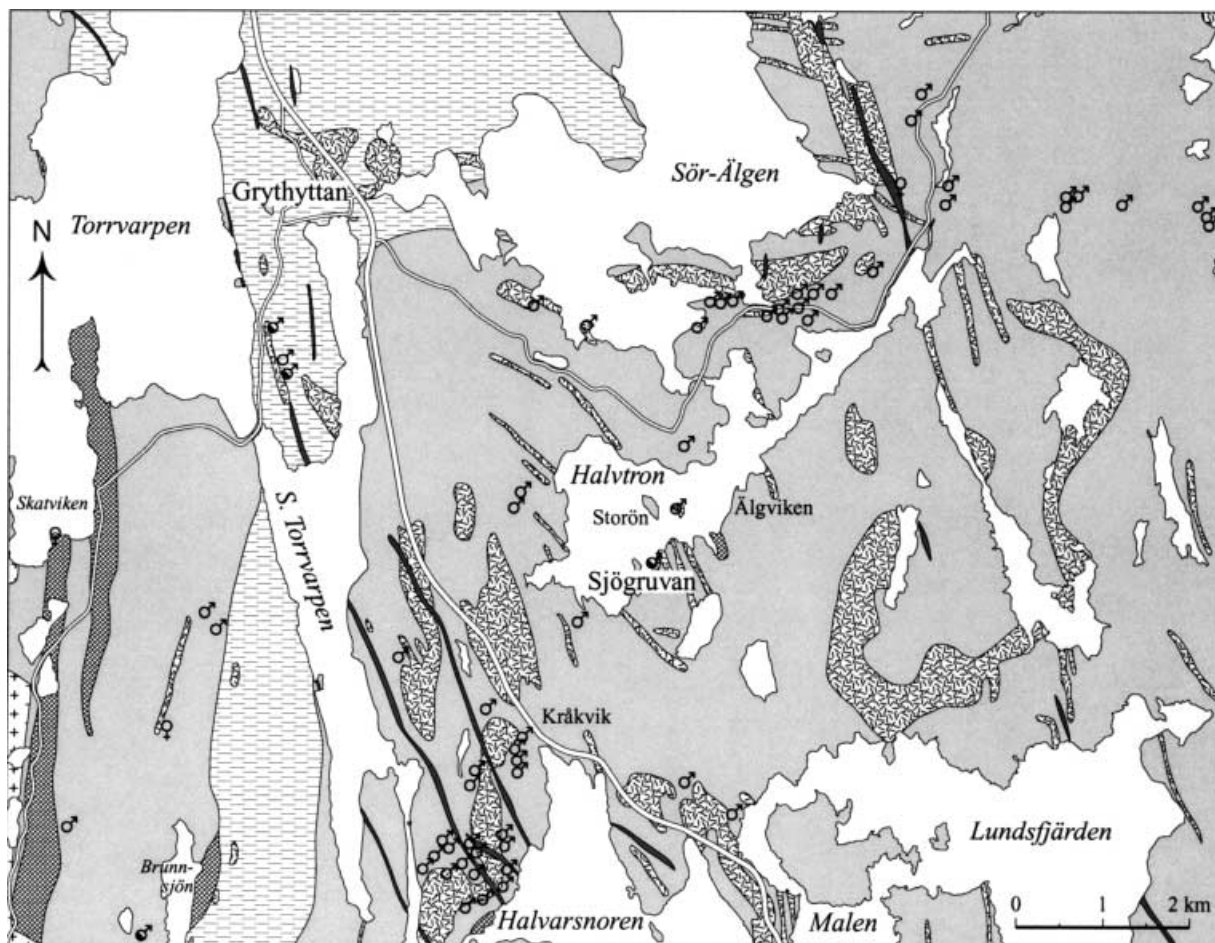


Fig. 2 Bedrock map of the Grythyttan area. Modified from Lundström (1995). For legend, see Fig. 1

tain cases be linked to ore formation (De Groot and Baker 1992).

The large number of small, long-abandoned mines in the area reflects the abundance of Fe oxide ores, which mostly occur in the lower stratigraphic units, whereas sulphide deposits are scarce. Mn mineralizations are sporadic as well. Two minor occurrences of Mn skarn close to the eastern shore of Lake Torrvarpen, 1.5 and 2 km S of Grythyttan, respectively, were examined by Oen et al. (1986). They consist of laminated rocks dominated by manganoan silicates and Ca-Mn carbonates. Carbonate microspheroids were detected at the northernmost locality and interpreted as microbial fossils. An exhalative-sedimentary origin was advocated for this type.

Sjögruvan

Sjögruvan is the sole Långban-type deposit known in the Grythyttan area. Mining activities started as early as in the 17th century, when some Fe ore was won sporadically. Mn extraction occurred over the period 1885–

1889, after which only limited prospecting work has been carried out at the mine. The total production of Fe and Mn ore is estimated at 200 and 300 metric tons, respectively (Sundius 1923).

Information about spatial relations is scarce. The lens-like ore horizon, with a total maximum thickness of 8–9 m, strikes NE-SW and has a dip of 30°S. The host rock is a marble interbed, some 100 m wide and dominated by dolomite. The Mn ores at Sjögruvan consist of hausmannite and braunite layers associated with carbonates and silicate skarns. Hematite and quartz with minor magnetite constitute the Fe ore, which forms a separate layer (~4 m) conformable with the Mn ores (Igelström 1887). Unfortunately, there is no description preserved of the stratigraphic relations of the ore types, but by analogy with the Långban ores (Magnusson 1930; Bollmark 1999) the sequence hematite→hausmannite→braunite is anticipated.

Analytical techniques

Samples collected at Sjögruvan (only dump and museum material was available as the mine itself is long since flooded) or taken directly from the surrounding bedrock within a distance of 500 m were investigated by means of several methods. Mineral compositions and textural relations were determined by optical and scanning-electron microscopy and X-ray powder diffraction techniques.

Rock and ore samples, free from recognizable secondary alterations and veins, were selected for petrographic examination and bulk chemical analyses. Prior to crushing, the sawed fragments were cleaned in deionized water and ethanol using an ultrasonic bath. Major and trace elements, including rare earths (REE), were determined by ICP-AES and ICP-MS, respectively, following LiBO₂ fusion and HNO₃ dissolution. The detection limit for trace elements is generally 2 ppm or better (0.1–0.01 ppm for REE) and the analytical uncertainty is 15% for concentrations close to this level. For samples rich in Ba, REE were determined after ion-exchange separations (Govindaraju and Mebelle 1987). Shale-normalized REE patterns were obtained using the abundances given for the Post-Archaean average Australian Sedimentary rock (PAAS; McLennan 1989).

Fe²⁺/Fe³⁺ was estimated with Mössbauer spectroscopy on selected rock samples, using bulk powders pressed into discs with an Fe concentration of 1–2 mg/cm². Spectrum analysis was carried out assuming thin absorbers and Lorentzian line-shapes using one or two absorption doublets each for Fe²⁺ and Fe³⁺, respectively, plus a sextuplet for hematite-bearing samples. For samples not analysed in this way the total Fe content is reported as Fe₂O₃. Mn is given as MnO, except for the braunite and hausmannite ores where Mn₂O₃ is expected to dominate.

Oxygen and carbon isotopic ratios in carbonates were determined using a SIRA II mass spectrometer at Servicio General de Analisis de Isotopos Estables, Universidad de Salamanca, Spain. Extraction techniques followed essentially those described in McCrea (1950). The δ¹⁸O and δ¹³C data are reported relative to standard mean ocean water (SMOW) and Peedee belemnite (PDB), respectively. Precision was ±0.1 per mil (‰) for δ¹⁸O and ±0.05‰ for δ¹³C.

Minerals to be analysed for their Pb isotopic composition were dissolved in 6 M HCl, except in the case of feldspar (hyalophane) where HF was utilized. Pb was extracted using a simplified ion-exchange procedure adapted after Krogh (1973), and then loaded onto Re filaments using a combined silica gel-phosphoric acid mixture described by Gerstenberger and Haase (1997). Isotopic measurements were performed on a Finnigan MAT261 mass-spectrometer equipped with multiple Faraday cups. Mass fractionation was determined by analyses of the NBS981 common Pb standard to 0.08%/amu. Correction for mass fractionation and error calculation followed Ludwig (1980).

Results

Petrography and litho-geochemistry

Country rocks

The volcanoclastic rocks dominantly have a fine-grained and massive appearance (foliation is weak), with colours ranging from greyish pink to greenish grey. They consist of quartz and feldspar phenocrysts (10–40%), usually angular and irregular in shape, set in a very fine grained, partly recrystallized matrix (silt fraction) with similar mineralogy. The main and accessory minerals are reported in Table 1. The proportions between K-feldspar and albite are highly variable between samples. Lithic fragments are rare or totally absent. The phyllosilicate content is low and dominated by mica (phlogopite–annite in composition); one exception, however, is sample B where elongated grains of a chlorite mineral occur parallel to the foliation. The size of the phenocrysts in these rocks are normally in the range of 0.1–0.3 mm, but two of the samples (R04, R17) contain abundant subrounded, largely unbroken quartz crystals with sizes of up to 1.5 mm.

Chemical analyses of the metavolcanic rocks are given in Table 2. According to the standard TAS classification (Le Maitre 1989) they are rhyolites or dacites. These rocks have, however, undoubtedly been altered to various extents and the data do not represent original compositions. Some samples are extreme in terms of their alkali contents, a common feature in the area (Lundström 1995), and hence fall outside the normal igneous spectrum (Hughes 1972). The MgO concentration is occasionally high, which is a typical sign of the

Table 1 Mineral compositions of analysed rock samples. *vol* metavolcanic rock; *dma* dolomite marble; *mar* marble; **x** major component; **x** minor; (x) trace

Sample	A02 vol	G02 vol	F vol	B vol	R04 vol	R02 vol	R17 vol	R12 vol	H dma	I dma	R05 mar	R01 mar
quartz	x	x	x	x	x	x	x	x	x	x	x	x
K-feldspar	x	x			x	x	x	x			x	
albite	x	x	x	x	x		x					
mica	x	x			x	x	x	x	x	x	x	
amphibole									x			
chlorite			x	x					x	x		
talc									x			
allanite-(Ce)				(x)	(x)		(x)					
titanite							x					
zircon	(x)				(x)		(x)	(x)				
calcite			(x)			(x)		(x)	x	x	x	x
dolomite									x	x		
apatite							(x)					
monazite					(x)		(x)					
xenotime							(x)					
hematite						(x)		(x)			(x)	
scheelite											(x)	
pyrite									x			

Table 2 Whole rock analyses. *vol* metavolcanic rock; *dma* dolomite marble; *mar* marble

Sample Type	A02 vol	G02 vol	F vol	B vol	R04 vol	R02 vol	R17 vol	R12 vol	H dma	I dma	R05 mar	R01 mar
SiO ₂	78.13	77.97	76.91	73.46	71.41	70.90	67.56	66.21	5.18	5.17	5.42	2.58
TiO ₂	0.10	0.07	0.20	0.11	0.24	0.21	0.29	0.27	0.01	0.04	0.01	0.01
Al ₂ O ₃	12.80	11.82	11.32	11.39	14.90	15.21	16.82	17.80	0.62	1.44	0.70	0.14
FeO		1.03		3.72		0.50	1.32			5.42	0.63	
Fe ₂ O ₃	0.46	1.02	1.14	0.51	3.39	2.26	1.80	3.22	7.95	0.00	2.65	0.50
MnO	0.03	0.01	0.01	0.00	0.06	0.07	0.06	0.06	0.98	0.80	2.94	0.47
MgO	0.08	1.16	0.67	3.62	1.90	1.07	2.01	1.23	15.44	17.66	0.61	0.63
CaO	0.12	0.16	1.91	0.21	0.14	0.68	0.14	0.91	29.13	27.91	49.61	53.80
Na ₂ O	6.31	3.03	6.00	3.93	0.39	0.07	0.54	0.07	0.01	0.00	0.03	0.00
K ₂ O	1.47	2.82	0.10	0.52	5.35	5.99	6.06	6.92	0.21	0.13	0.41	0.00
P ₂ O ₅	0.02	0.02	0.07	0.08	0.05	0.04	0.07	0.07	0.01	0.02	bd	bd
LOI	0.16	1.07	1.70	1.79	2.22	2.89	2.45	3.37	40.25	40.30	36.80	40.46
Total	99.68	100.30	100.03	99.34	100.05	99.95	99.27	100.13	99.79	98.89	99.84	98.58
As	13	0.8	0.4	0.1	1.2	2.3	1.5	2.5	1.0	0.3	4.8	1.9
Ba	200	1,333	27	111	2,394	1,786	3,012	1,993	10	7.7	274	21
Be	bd ^a	1.3	bd	1.0	6.7	5.5	7.6	5.8	0.5	0.4	0.4	bd
Bi	bd	bd	bd	bd	0.0	bd	0.1	bd	0.0	0.0	0.1	bd
Cd	0.2	0.3	0.1	0.3	0.1	0.4	0.0	0.2	0.1	0.1	0.2	0.2
Co	0.1	0.5	0.8	3.5	1.1	0.6	0.8	0.4	2.1	2.1	0.4	0.5
Cr	3.8	2.9	3.7	2.5	4.0	1.3	1.3	0.7	2.1	3.7	2.5	1.1
Cs	bd	0.2	bd	0.2	2.1	0.5	1.5	0.5	0.3	0.3	0.2	bd
Cu	3.0	4.5	4.4	3.1	3.7	3.3	5.2	1.8	3.3	3.0	3.8	2.6
Ga	15	17	16	20	21	29	24	33	1.9	4.0	1.6	0.4
Ge	1.0	1.1	0.9	1.6	2.3	2.1	1.9	2.0	0.2	0.3	0.3	0.0
Hf	5.3	4.3	5.4	5.2	6.4	8.0	7.6	8.4	0.3	0.5	0.2	0.1
In	0.0	0.1	0.0	0.0	0.4	0.3	0.4	0.3	0.1	0.1	0.1	0.1
Mo	0.1	0.2	0.2	0.1	1.7	0.2	1.9	0.2	0.2	0.3	0.7	0.1
Nb	14	15	12	11	14	17	15	19	0.5	1.5	0.7	0.1
Ni	1.6	2.3	2.0	2.1	1.3	1.3	1.5	0.9	bd	bd	bd	bd
Pb	35	6.3	3.1	3.8	4.8	4.7	7.0	6.9	4.8	1.4	6.6	4.5
Rb	14	56	1.5	14	140	170	151	192	7.8	5.7	7.7	1.0
Sb	0.7	0.6	0.8	0.1	3.2	7.2	4.2	6.9	0.2	0.1	33	0.3
Sn	2.1	3.6	1.7	1.8	19	12	19	12	0.5	1.0	0.5	0.2
Sr	14	9.6	19	9.0	5.0	5.2	6.0	6.2	28	29	75	168
Ta	1.3	1.5	1.0	1.1	1.2	1.5	1.5	1.7	0.1	0.1	0.1	0.0
Th	17	17	13	16	13	20	16	21	0.6	1.3	0.7	0.2
U	4.3	3.8	3.3	4.7	1.9	6.0	2.5	6.4	0.2	0.3	0.6	bd
V	1.2	6.0	4.4	4.1	6.6	43	8.4	55	2.5	3.6	1.9	0.2
W	1.4	3.9	1.6	1.0	9.2	8.3	9.8	9.6	0.2	0.8	79	0.4
Y	27	27	40	38	17	24	38	28	13	16	3.7	2.1
Zn	2.8	8.9	7.1	10	24	7.5	25	10	49	77	2.8	0.1
Zr	168	119	196	166	230	284	274	320	10	18	9.8	2.7
La	1.1	15.7	56.9	92.5	47.2	30.4	62.9	36.7	6.3	23.2	6.6	2.6
Ce	3.2	29.9	111.2	188.4	94.6	70.3	128.7	77.0	12.2	47.2	10.2	4.0
Pr	0.5	4.2	12.5	21.8	11.3	7.2	14.0	8.6	1.5	5.7	1.2	0.4
Nd	2.7	17.8	45.5	80.4	41.8	28.6	55.0	33.8	6.1	22.5	4.1	1.5
Sm	1.75	4.46	8.11	12.83	7.18	5.54	10.78	6.38	2.20	4.66	0.75	0.54
Eu	0.24	0.65	1.17	1.88	1.52	1.18	2.12	1.35	0.87	1.06	0.26	0.31
Gd	2.56	4.05	6.11	9.39	4.48	4.04	6.83	4.20	2.54	3.81	0.66	0.44
Tb	0.62	0.84	0.97	1.44	0.63	0.58	1.13	0.62	0.41	0.54	0.10	0.07
Dy	4.53	4.86	5.92	7.48	3.58	3.37	6.94	4.18	2.10	2.83	0.53	0.23
Ho	1.25	1.20	1.46	1.70	0.64	0.85	1.49	0.98	0.39	0.50	0.11	0.08
Er	3.32	2.96	3.66	4.26	2.08	2.75	4.35	2.76	0.94	1.35	0.28	0.19
Tm	0.52	0.48	0.59	0.60	0.35	0.50	0.64	0.58	0.12	0.18	0.04	0.02
Yb	4.33	3.58	4.27	4.75	2.44	3.79	4.18	4.19	0.75	1.16	0.28	0.12
Lu	0.73	0.57	0.59	0.73	0.43	0.62	0.71	0.66	0.10	0.17	0.06	0.02

^aBelow detection

synvolcanic hydrothermal overprint commonly encountered in Bergslagen (De Groot and Baker 1992).

Rocks that have been sampled close to mine sections, and therefore occur in proximity to the ore-bearing marbles (denoted by R in the table heads), form a chemically distinct group. A clear indication of a more

altered condition is their relative enrichment of immobile elements. The highest concentrations of most other metals is recorded for this group, in particular Ba, Be, Cs, In, Mn, Rb, Sb, Sn, V and W. In terms of FeO/Fe₂O₃ ratios, these rocks seem to be more oxidized, and their LOI values are the largest. The Eu depletion is less

pronounced for the rocks adjacent to ore-bearing carbonate.

Host rocks

The main mass of carbonate rock is a coarsely crystalline (~0.5 mm), frequently lined dolomite marble. It has a spotted appearance with impurities of chlorite, amphibole and quartz (Table 1). Pyrite crystals are occasionally present. Another type of marble, which is calcite-dominated and massive, occurs adjacent to the ore layers at Sjögruvan and ranges from a pink, nearly monomineralic marble (represented here by R01) to a greyish, impure variant with significant contents of quartz, K-feldspar and mica plus traces of hematite and scheelite (R05). The composition of the rocks (Table 2) is largely governed by the accessory minerals rather than the carbonate phase itself. Total REE contents are in the range 11–80 ppm, and the Eu anomalies vary from weakly to strongly positive. There seems to be a distinct difference in the degree of oxidation; dolomite marble has $\text{FeO} > \text{Fe}_2\text{O}_3$ whereas calcite marble is completely oxidized (consistent with the presence of sulphide and ferric oxide, respectively).

Ore mineralogy

Results from a detailed mineralogical study of the Sjögruvan deposit, including chemical data for various mineral phases encountered, will be presented elsewhere.

A general summary of the mineralogy of the different ore types is given here. The mineral composition of samples subjected to bulk chemical analysis is summarized in Table 3. Unusual mineral species and their chemical formulae are listed in Table 4.

The Fe ore ranges from quartz-dominated cherty material coloured red by microscopic hematite (jasper) to massive, quartz-bearing hematite ore with occasional magnetite porphyroblasts. Common associated phases are calcite and scheelite. Scheelite grains (0.2 mm) are typically irregular in outline and evenly distributed in compact hematite ore. In contact zones to the carbonate host, typical reaction skarn assemblages have developed, with coarse grained actinolite.

Hausmannite ore occurs as both layered and massive types. Euhedral to subhedral hausmannite grains (2 mm) are dispersed in a calcite-dominated carbonate matrix. Rounded tephroite grains are always present. Manganberzeliite, svabite (i.e. members of the ternary series svabite–turneureite–johnbaumite), roméite, dolomite and barite are frequently encountered minor constituents. The arsenates are often interstitial to hausmannite and, in the case of manganberzeliite, sometimes form larger cm-sized pods. Roméite occurs as minute (0.05 mm) subhedral grains in calcite and as occasional inclusions in hausmannite. In the layered kind of ore, hausmannite-rich layers are intercalated

Table 3 Mineral assemblages in ore and skarn samples analysed during this study

g33078	Hematite ore	hem, qtz, mgt, chl, phl, cal, sch ^a
R03	Jasper	qtz, hem, mgt, cal, phl, act
99113	Fe skarn	dol, act, cal, qtz, mgt, hem
94:142	Jacobsite ore	hau, jac, cal, tep, brt, mbz, ktp
87:206	Hausmannite ore	hau, tep, cal, mbz, svb, brt, rom
65:116	Hausmannite ore	hau, cal, tep
94:141	Braunite ore	cn, brn, cal, phl, tep, sps, rds, brt, lbt, byt
94:094	Braunite ore	brn, cn, phl, cal, bal, btc
93:201	Mn skarn	hln, cn, cal, phl, brn, rdn, btc, bdh, hed
g33076	Mn skarn	cal, phl, hln, rom, hed, brt, btc, zrn
94:102	Mn skarn	rdn, hln, cal, hed

^aact, actinolite; bal, banalsite; bdh, bindheimite; brn, braunite; brt, barite; btc, barytocalcite; byt, barylite; cal, calcite; chl, chlorite; cn, celsian; dol, dolomite; hau, hausmannite; hed, hedyphane; hem, hematite; hln, hyalophane; jac, jacobsite; ktp, katoptrite; lbt, längbanite; mbz, manganberzeliite; mgt, magnetite; qtz, quartz; phl, phlogopite; rdn, rhodonite; rds, rhodochrosite; rom, roméite; sch, scheelite; sps, spessartine; tep, tephroite; svb, svabite; zrn, zircon

with pure carbonate. The lamination (2–10 mm) is usually not well developed, being disrupted by deformation and brecciation. Jacobsite-bearing samples represent a subordinate ore type at the deposit, which might be considered as transitional between Mn and Fe ore. Principal minerals are jacobsite, hematite, calcite, rhodonite, spessartine and katoptrite. Iwakiite is more rare, but belongs to a similar mineral association. Sometimes small-scale variations occur, and a hausmannite-dominated layer can be found contiguous to iwakiite/jacobsite in the same petrographic section.

The braunite ore is massive and dense in appearance. It typically consists of small, anhedral to subhedral braunite grains (0.1 mm) adjoined in larger aggregates, intimately associated with celsian, manganian phlogo-

Table 4 End-member composition of some mineral species mentioned in the text and in Table 3

Banalsite	$\text{BaNa}_2\text{Al}_4\text{Si}_4\text{O}_{16}$
Barylite	$\text{BaBe}_2\text{Si}_2\text{O}_7$
Barytocalcite	$\text{BaCa}(\text{CO}_3)_2$
Bindheimite	$\text{Pb}_2\text{Sb}_2\text{O}_6(\text{O},\text{OH})$
Celsian	$\text{Ba}_2\text{Al}_2\text{Si}_2\text{O}_8$
Ferriwinchite	$\text{CaNaMg}_4\text{FeSi}_8\text{O}_{22}(\text{OH})_2$
Friedelite	$\text{Mn}_8\text{Si}_6\text{O}_{15}\text{Cl}_{10}$
Hedyphane	$\text{Pb}_3\text{Ca}_2(\text{AsO}_4)_3\text{Cl}$
Hyalophane	$\text{BaK}_2\text{Al}_4\text{Si}_4\text{O}_{16}$
Iwakiite	$\text{Mn}^{2+}\text{Mn}^{3+}\text{FeO}_4$
Johnbaumite	$\text{Ca}_5(\text{AsO}_4)_3(\text{OH})$
Katoptrite	$\text{Mn}_{13}\text{Al}_4\text{Sb}_2\text{Si}_2\text{O}_{28}$
Långbanite	$\text{Mn}_4^{2+}\text{Mn}_9^{3+}\text{SbSi}_2\text{O}_{24}$
Manganberzeliite	$\text{Ca}_2\text{NaMn}_2(\text{AsO}_4)_3$
Melanostibite	$\text{Mn}_2\text{SbFeO}_6$
Pyrophanite	MnTiO_3
Pyrobelonite	$\text{PbMn}(\text{VO}_4)(\text{OH})$
Roméite	$\text{Ca}_2\text{Sb}_2\text{O}_6(\text{O},\text{OH})$
Svabite	$\text{Ca}_5(\text{AsO}_4)_3\text{F}$
Tilasite	$\text{CaMg}(\text{AsO}_4)\text{F}$
Turneureite	$\text{Ca}_5(\text{AsO}_4)_3\text{Cl}$
Welinite	$\text{Mn}_6\text{WSi}_2(\text{O},\text{OH})_{14}$

pite and calcite. Somewhat larger (~0.3 mm) euhedral hausmannite grains occasionally occur. Frequent but subordinate constituents are rhodonite, barite, rhodochrosite and l ngbanite. Characteristically, the l ngbanite grains (0.05 mm) are similar to braunite in shape and size, and usually in direct contact with this mineral.

Coarse-grained, quartz-free skarn assemblages accompany the Mn ores: feldspar (microcline-hyalophane + albite), rhodonite and clinoamphibole (essentially ferriwinchite) are the major silicates. Tephroite is occasionally important but is normally not associated with the aforementioned minerals. Carbonates, ranging from manganoan calcite to calcian rhodochrosite in composition, are ubiquitous. The ores and skarns

at Sj gruvan are cross-cut by numerous, usually less than 10 mm wide, late-stage veins that contain a range of silicates, carbonates and arsenates. Sulphides are very rare in the deposit as a whole.

Bulk chemical composition of ores and related materials

The hematite-quartz ore is poor in Mn, and most trace elements are close to the background level of the host and country rocks; clear exceptions are, however, W and Mo hosted by scheelite (Table 5). The Fe content of the Mn ores is variable, corresponding to a range of 0.2 to 8 wt% Fe₂O₃. The highest Mn/Fe ratio (= 215) is found

Table 5 Composition of ores and related materials from the Sj gruvan deposit

Sample	g33078 hem o ^a	R03 jasper	99113 Fe sk	94:142 jac o	87:206 hau o	65:116 hau o	94:141 brn o	94:094 brn o	93:201 Mn sk	g33076 Mn sk	94:102 Mn sk
(wt%)											
SiO ₂	32.64	86.87	11.30	6.18	11.00	2.84	21.96	15.66	25.45	16.41	37.82
TiO ₂	0.01	0.00	0.01	0.02	0.01	0.01	0.08	0.08	0.11	0.07	0.00
Al ₂ O ₃	0.89	0.10	0.44	0.60	0.88	0.43	9.92	5.09	13.55	6.33	0.96
Fe ₂ O ₃	64.64	3.47	4.50	7.70	0.37	0.22	2.34	2.30	1.18	0.79	0.30
MnO	0.05	0.30	3.96	43.49					14.80	17.19	44.78
Mn ₂ O ₃					64.38	47.40	38.10	62.00			
MgO	1.11	0.25	15.08	0.72	1.24	2.88	2.79	2.83	5.46	6.20	1.54
CaO	0.32	4.53	28.84	22.60	11.60	25.69	7.83	3.98	12.07	21.87	8.92
Na ₂ O	0.01	0.01	0.05	0.00	0.04	0.01	0.09	0.11	0.16	0.11	0.04
K ₂ O	0.42	0.00	0.10	0.00	0.05	bd	1.65	1.37	4.06	4.07	0.62
BaO	0.00	0.02	0.03	0.49	0.18	0.01	8.00	4.04	11.23	1.49	0.79
P ₂ O ₅	0.04	0.01	0.07	0.18	0.00	0.15	0.27	0.30	0.24	0.12	0.16
LOI	0.13	3.69	33.95	16.30	9.90	21.56	6.77	3.34	11.08	23.11	5.63
Total	100.26	99.25	98.33	98.28	99.65	101.20	99.80	101.10	99.39	97.76	101.56
(ppm)											
As	16	1.5	2.2	984	1760	1298	268	37	24	765	3551
Ba	36	223	272	4,390	1,640	92	71,580	36,210	100,500	13,330	7,043
Be	1.5	0.7	1.8	7.0	bd	4.8	47	15	18	6.9	4.2
Bi	bd	0.0	bd			0.2	1.2	0.2	0.5	0.4	0.1
Cd	bd	0.3	0.3			bd	0.8	0.4	0.7	1.0	6.1
Co	0.8	0.3	0.8			1.4	0.4	0.8	0.9	0.9	0.5
Cr	7.0	2.5	2.1			5.1	1.3	4.2	bd	1.5	bd
Cs	0.6	bd	0.1			bd	2.1	1.7	4.4	3.6	0.1
Cu	9.9	6.9	2.1	bd	19	1.9	24	24	58	30	4.9
Ga	4.9	1.1	2.2			9.5	16	19	12	11	13
Ge	2.3	4.4	1.1			16	7.1	7.9	11	8.5	8.9
Hf	bd	0.0	0.1	0.3	0.2	0.1	5.1	3.3	1.6	3.5	0.1
In	0.1	0.0	0.2			0.1	0.0	0.1	0.0	0.0	0.0
Mo	43	5.0	0.4	5.8	4.3	2.4	0.2	0.5	0.1	0.0	3.9
Nb	1.5	0.5	0.2	0.4	0.3	0.1	11.3	5.8	5.0	7.9	0.0
Ni	5.4	bd	bd			bd	bd	3.1	bd	bd	1.6
Pb	15	26	8.7	200	93	54	728	487	936	3,503	8,237
Rb	25	1.3	6.8			bd	79	78	173	188	8.2
Sb	47	7.3	2.3	1,310	1,180	838	2,256	1,275	3,351	1,171	12
Sn	3.3	1.9	0.4	1.5	1.8	bd	2.1	1.6	1.6	1.4	0.2
Sr	2.4	9.4	50	104	119	116	184	49	245	240	133
Ta	0.1	0.0	0.0			bd	1.5	0.8	1.2	0.8	0.0
Th	0.9	0.3	0.1	0.6	0.3	0.1	13	8.2	3.7	6.5	0.1
U	2.0	0.1	0.0	2.3	1.3	1.2	4.2	1.8	0.4	2.7	bd
V	24	1.4	bd			22	1.4	1.0	bd	1.0	7.8
W	1,560	78	22	92	77	57	55	24	13	8.1	6.6
Y	11	8.3	11	11	12	10	12	9.1	3.8	7.1	9.6
Zn	15	8.1	88	374	224	560	245	229	509	522	1450
Zr	8.1	1.6	3.6	7.9	5.9	9.0	145	110	43	108	5.0

^ao, ore; sk, skarn; bd, below detection

in hausmannite ore. Generally, the Mn ores are enriched in As, Ba, Be, Cu, Pb, Sb, Sr and Zn. The braunite ore and associated skarn assemblages are particularly rich in Ba, mainly hosted by feldspar and barite, and to some extent by micas and carbonates (including barytocalcite). Sb is relatively uniformly distributed, in the form of one or more of the oxyminerals l ngbanite, katoptrite, rom ite and melanostibite. Different arsenate minerals are the main repository for As. Pb occurs in a single arsenate (hedyphane) and in feldspars and carbonates. The increased Be concentration of braunite ore is correlated with the presence of small amounts of barylite. Traces of welinite and scheelite contribute to the W content in the Mn-rich lithologies (mainly hausmannite-jacobsite ore).

Apart from these clear L ngban-type element signatures, some samples are characterized by increased concentrations of Ti, Zr, Hf, Nb and Ta (as manifested in the occasional presence of pyrophanite and zircon). These immobile elements are sympathetic with Al, and two distinct compositional groups can be discerned among the Mn-rich lithologies (Fig. 3): one with $\text{Al}_2\text{O}_3 < 1 \text{ wt}\%$ (corresponding to a hausmannite-jacobsite-tephroite association, HJT) and one with $\text{Al}_2\text{O}_3 > 5 \text{ wt}\%$ (braunite-feldspar-mica, BFM). Th and U are positively correlated, and BFM is associated with the highest concentrations.

Total REE contents in these ores are fairly low (Table 6), in accord with the absence of discrete REE minerals. The normalized patterns are somewhat irregular and complex (Fig. 4), and represent the sum of several factors, including the nature and origin of REE fluxes, adsorption phenomena during precipitation, chemical crystallography of metamorphic minerals, late-stage fluid-rock interaction and analytical uncertainties. A clear positive Ce anomaly is, however, found for the BFM association (except 94:102), whereas the HJT association is negative. The Eu anomalies range from nearly neutral to distinctly positive (relative PAAS). For certain samples there is clearly a significant mineralogical control; the negative Ce anomaly and positive Eu anomaly obtained for the rhodonite-dominated sample 94:102 could to a large extent be governed by the difficulty of rhodonite to host Ce^{4+} and Eu^{3+} , respectively.

Isotope geochemistry

Stable isotopes in carbonates

The results from ^{19}C and ^{18}O isotope analyses carried out are summarized in Table 7. Excluding typical fissure material, the data define a narrow field (Fig. 5). The $\delta^{18}\text{O}$ values range between 8 and 11‰ for the host rocks and main ore and skarn assemblages at Sj gruvan. The corresponding $\delta^{13}\text{C}$ values lie within the range -2.5 and $+1$ ‰. The data points form a tight cluster located close to the larger field represented by 2 Ga old marbles and limestones (Baker and Fallick 1989). Average $\delta^{13}\text{C}$ for host marble and carbonate associated with Mn ore

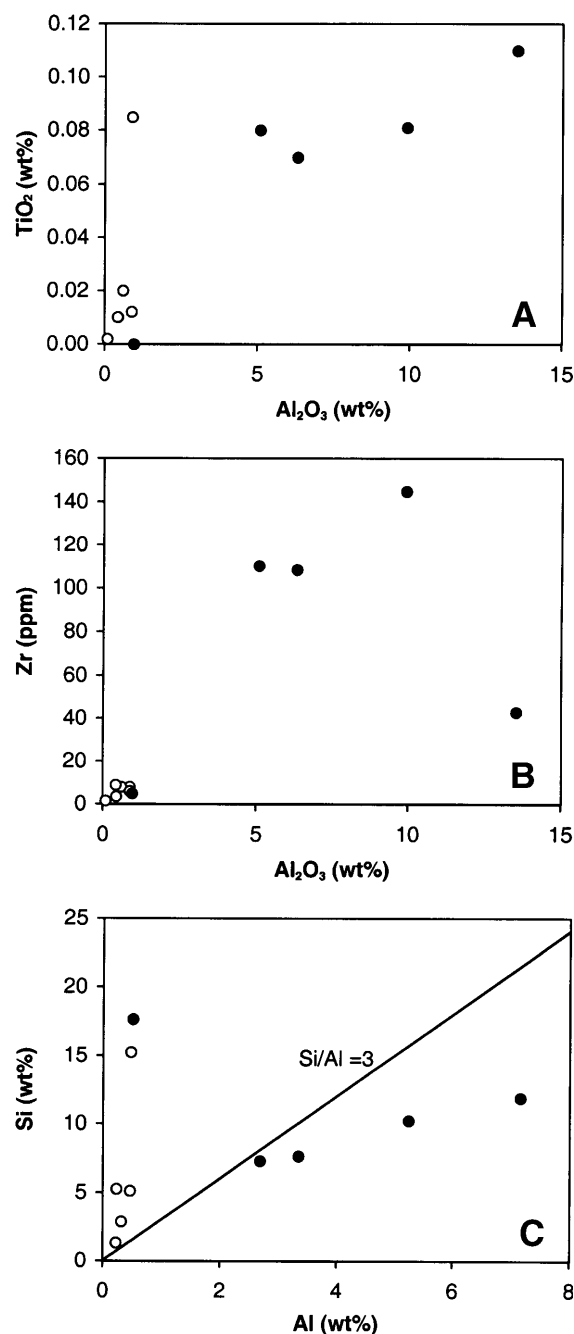


Fig. 3A–C Correlation plots for selected elements in the Sj gruvan ores and skarns. Filled symbols correspond to samples belonging to the BFM association, open symbols are the remaining samples in Table 5

(calcites only) is -0.15 ± 0.39 ‰ ($n = 10$), which is a typical marine signature (Hoefs 1997). The Fe skarn carbonates are shifted towards lighter C compositions ($\delta^{13}\text{C} -2$ ‰), which indicates modification during metamorphism and skarn formation. This could be ascribed to the influence of metamorphic fluids or to pure decarbonation reactions.

The O isotope data cannot be interpreted unambiguously. Based on $\delta^{18}\text{O}$ values, De Groot and Sheppard

Table 6 REE composition of ores and related materials from Sjögruvan. The anomalies are given as Ce_N/Ce^* and Eu_N/Eu^* , where $Ce^* = (La_N + Pr_N)/2$ and $Eu^* = (Sm_N + Gd_N)/2$

Sample	g33078 hem o ^a	R03 jasper	99:113 Fe sk	94:142 jac o	87:206 hau o	65:116 hau o	94:141 brn o	94:094 brn o	93:201 Mn sk	g3,3076 Mn sk	94:102 Mn sk
(ppm)											
La	4.96	7.31	2.80	2.53	9.30	3.70	12.52	5.59	8.16	12.19	3.82
Ce	11.40	14.25	6.29	3.71	12.40	3.15	42.16	26.45	17.74	30.78	3.17
Pr	1.37	1.54	0.94	0.41	1.75	0.69	3.48	1.74	1.37	2.48	0.92
Nd	5.97	6.09	4.55	1.73	7.32	2.41	14.11	7.76	5.51	8.20	3.81
Sm	2.05	1.46	1.70	0.56	1.38	0.48	3.20	1.92	0.81	1.57	1.21
Eu	1.26	0.42	0.71	0.16	0.24	0.21	0.87	0.80	0.25	0.63	0.60
Gd	2.60	1.45	2.07	0.55	1.15	0.91	3.01	1.98	0.60	1.50	1.39
Tb	0.40	0.22	0.29	0.10	0.18	0.14	0.38	0.29	0.12	0.24	0.20
Dy	2.13	1.22	1.80	0.68	1.12	0.88	2.97	1.75	0.64	1.72	1.45
Ho	0.32	0.28	0.36	0.14	0.25	0.23	0.53	0.28	0.14	0.42	0.27
Er	0.69	0.75	0.63	0.33	0.62	0.54	1.25	0.69	0.41	0.81	0.54
Tm	0.08	0.09	0.10	0.05	0.07	0.08	0.22	0.11	0.07	0.16	0.11
Yb	0.45	0.56	0.53	0.30	0.61	0.73	1.46	0.68	0.36	1.08	0.57
Lu	0.06	0.09	0.05	0.05	0.10	0.09	0.23	0.13	0.07	0.13	0.07
Total	33.74	35.74	22.83	11.30	36.49	14.24	86.38	50.15	36.25	61.92	18.14
Ce/Ce*	1.01	0.98	0.88	0.83	0.71	0.45	1.47	1.94	1.21	1.29	0.39
Eu/Eu*	2.52	1.36	1.76	1.35	0.90	1.40	1.32	1.92	1.69	1.93	2.16

^ao, ore; sk, skarn; bd, below detection

(1988) were able to distinguish a field for stratabound Bergslagen carbonates associated with Fe oxide ores, and the present data for the Sjögruvan samples more or less coincide with this. Another field at $12\% < \delta^{18}O < 20\%$ is also given in the diagram (Fig. 5) and corresponds to stratabound carbonate rocks lacking

significant oxide mineralization; differences in temperature of deposition and in the origin of the CO₂-bearing fluids were suggested as possible grounds for this division (De Groot and Sheppard 1988). The $\delta^{18}O$ values for Sjögruvan host rock and ore samples are generally too low to represent a marine sedimentary composition. Postdepositional recrystallization and fluid-mediated isotope exchange during metamorphism has probably

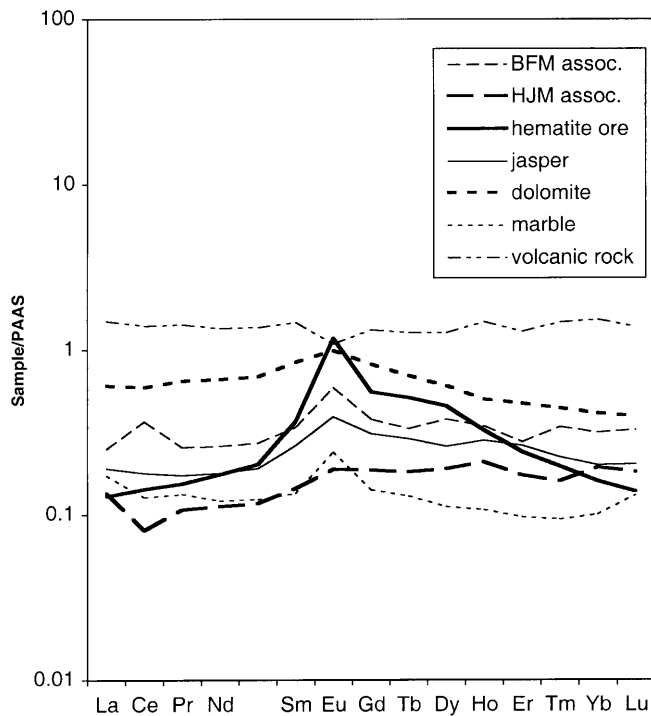


Fig. 4 Shale-normalized REE patterns of selected ores and host rocks at Sjögruvan

Table 7 O and C isotope compositions of carbonates

Sample	Mineral	$\delta^{18}O$ (SMOW)	$\delta^{13}C$ (PDB)
Host marbles			
H	dol	10.70	-1.32
I	dol	9.99	-0.60
R01	cal	9.39	-0.35
R05	cal	9.24	-0.52
Fe skarn			
99113	cal	8.98	-2.22
99113	dol	9.11	-0.68
99122	cal	8.78	-2.36
g15421	cal	8.54	-1.95
BFM association			
86:186 (braunite ore)	cal	8.43	0.37
94:094 (braunite ore)	cal	8.38	0.32
g11130 (skarn)	cal	9.74	0.10
g33076 (skarn)	cal	8.72	0.24
HJT association			
87:198 (hausmannite ore)	cal	8.57	-0.35
87:198 (hausmannite ore)	dol	9.65	0.72
87:206 (hausmannite ore)	cal	8.76	-0.42
94:142 (jacobsite ore)	cal	9.54	-0.78
Veins			
92:078	rds	12.50	-0.83
99116	cal	15.75	-1.02
99127	cal	20.41	-1.41

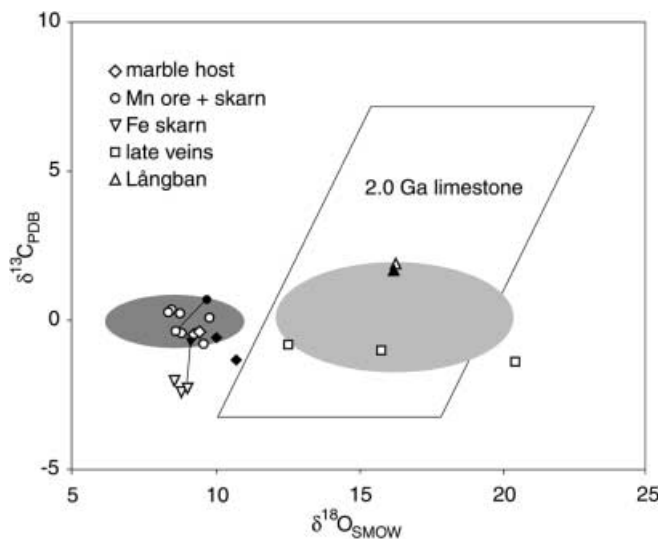


Fig. 5 Carbon vs. oxygen isotope diagram showing the composition of Sjögruvan carbonates. The *dark grey oval* and the larger, *light grey oval* correspond to carbonates cogenetic with Fe oxide deposits and stratabound carbonates without oxide mineralization, respectively, according to De Groot and Sheppard (1988). *Filled symbols* are dolomite, and the tie-lines connect coexisting samples. Långban data were taken from Billström et al (1985) and De Groot and Sheppard (1988)

occurred. The significant difference between Sjögruvan and Långban marbles (Fig. 5) might then be related to the large difference in size of the deposits and their marble envelopes: Carbonate rocks are relatively impermeable and larger volumes naturally help in preserving the original isotope signature (e.g. Valley et al. 1990).

The few ($n=3$) of the present samples representing vein assemblages form a trend towards isotopically heavy oxygen. This might be a temperature effect as Jonsson and Boyce (1999) recently observed a substantial spread (10–23‰) in carbonate $\delta^{18}\text{O}$ signatures from the Långban deposit, where the highest values correspond to late-stage parageneses, for which low temperatures of formation ($< 100\text{ }^\circ\text{C}$) are inferred.

Pb isotopes

Results from the analyses of four Pb-containing minerals are presented in Table 8. The isotopic compositions

Table 8 Pb isotopic composition for selected minerals from the Sjögruvan deposit. Mineral abbreviations are as in Table 3. Measured isotopic ratios corrected for a mass discrimination of $0.08 \pm 0.03\%$ /amu. Errors expressed at the 2σ -level are calculated

Sample	Mineral	$^{206}\text{Pb}/^{204}\text{Pb}$	$^{207}\text{Pb}/^{204}\text{Pb}$	$^{208}\text{Pb}/^{204}\text{Pb}$	μ
332544	hln	15.734 ± 0.012	15.338 ± 0.016	35.216 ± 0.045	9.89
g11130	hln	15.720 ± 0.011	15.323 ± 0.015	35.165 ± 0.044	9.81
g33076	cc	15.706 ± 0.012	15.327 ± 0.016	35.180 ± 0.048	9.85
332589	hed	15.707 ± 0.012	15.338 ± 0.018	35.205 ± 0.054	9.92
89:031	hed	15.729 ± 0.013	15.349 ± 0.019	35.239 ± 0.058	9.97
g33054	native Pb	15.740 ± 0.014	15.371 ± 0.018	35.309 ± 0.050	10.11

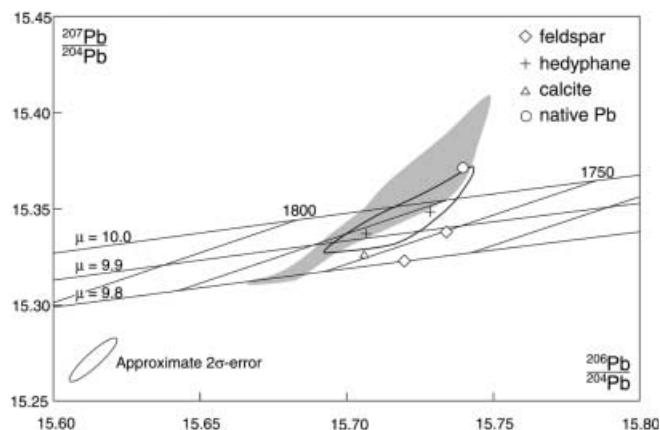


Fig. 6 Isotope plot of Pb minerals from Sjögruvan. Reference lines with μ -values and ages are from the model of Stacey and Kramers (1975). The *grey area* is data from Långban-type deposits in the Filipstad district (Åberg and Charalampides 1986). The second field, indicated by a *thick solid line*, corresponds to galena samples from “interior Bergslagen” according to Sundblad (1994)

are similar to those obtained in general for galena from Fe-oxide and base metal sulphide deposits in Bergslagen (Sundblad 1994), and more specifically resemble those found by Åberg and Charalampides for a range of paragenetically different Pb minerals in the Långban-type deposits of the Filipstad district. In detail, all samples except the two feldspars (hyalophane) form a linear trend in the standard $^{207}\text{Pb}/^{204}\text{Pb}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$ diagram (Fig. 6). In the model of Stacey and Kramers (1975) this line corresponds to a mixing line at ca 1780 Ma between two sources with μ -values of 9.85 and 10.1, respectively. Although the Stacey-Kramers model invariably yields too low model ages in the Fennoscandian Shield (Johansson and Rickard 1985), the diagram suggests that the minerals (exclusive of the feldspars) were formed during the same event. As a comparison, the mixing line is very similar to an ore lead mixing line for stratabound deposits in the Bergslagen interior according to Sundblad (1994). This indicates that the minerals crystallized very close in time to the formation of major stratabound base-metal and iron deposits in Bergslagen. The mineral with the lowest μ value on the mixing line is calcite, which is in accordance with a marine origin as deduced from the C isotope data. The two analysed feldspar samples have model ages that are

from the analytical errors and the uncertainty in the mass discrimination correction using the method of Ludwig (1980). The μ -values are calculated according to Stacey and Kramers (1975)

around 30–40 Ma younger than the rest of the minerals. This could point to formation of this mineral at a later stage, or more likely, that the feldspar contains small amounts of radiogenic lead formed by in situ decay of U and Th. If the latter is the case, minerals like hedyphane and lead-bearing calcite are better at preserving an initial Pb signature than feldspar. Although the Långban samples analysed by Åberg and Charalampides (1986) are slightly less radiogenic and exhibit a larger spread in μ -values, their general conclusion of mineral formation during a short time period with mixing of two sources with different lead isotopic composition is probably also valid for Sjögruvan.

Mode of origin

A prerequisite for a discussion on ore genesis based on geochemical signatures is that the chemical composition of the protoliths has been preserved during metamorphism and deformation of the deposit. An upper temperature limit at ca 470 °C for the Sjögruvan deposit is suggested by the assemblage dolomite + quartz + calcite + talc (Evans and Guggenheim 1988) in adjacent dolomite marble. Examples found in the literature show that Fe-Mn deposits metamorphosed to at least amphibolite-facies conditions have retained their original chemical character (Flohr 1992). However, some of the key elements at Sjögruvan, e.g. As and Sb, are particularly mobile under oxidizing conditions (Wink 1996) and to some extent might have been redistributed during metamorphism and the development of late-stage veins.

Another fundamental issue is the acceptance of the idea that the high concentrations of the elements Ba, As, Pb, Sb and W at Sjögruvan are a result of essentially syngenetic deposition. It has occasionally been vindicated that some elements, in particular those with a lithophile character, were not coeval with Fe and Mn at the Långban-type deposits in general, but introduced metasomatically in connection with granitic magmatism (Magnusson 1930; Moore 1970). Holtstam (2001) has recently concluded that the frequent W mineralization associated with Fe ores at these deposits is syngenetic. The facts behind the arguments, of relevance for the whole set of elements under consideration at Sjögruvan, might be summarized as follows: (1) The petrographic relations, where Sb-silicates and arsenates are intimately associated with the major ore minerals in a metamorphic assemblage and with no signs of replacement. The close association of e.g. braunite with längbanite at other deposits is well established (Magnusson 1930; Nysten and Ericsson 1994). (2) The frequently high contents of Ba, As, Pb and Sb in the Mn-rich lithologies, and the near-background concentrations in the Mn-poor parts, indicate a common origin for these metals and Mn. A late infiltration would have affected all kinds of rock. (3) Field evidence of granite-related magmatic influence in the Sjögruvan area is lacking, and the Filipstad-type granite that is exposed > 10 km away from the mine

postdates the main metamorphic event (Lundström 1995). (4) Highly evolved, reduced magmatic fluids sometimes have affected pre-existing Mn minerals to form e.g. metasomatic Mn-Be-W skarns (Ragu 1994), but there are no examples of deposition of Sb-Pb-As oxyminerals from such systems. (5) Evidence for late-stage hydrothermal activity at Sjögruvan is clearly provided by the many veinlets cutting the earlier foliation and stratification of the ores, but the effect on the wall rock was not pervasive. The fluid source is unknown; from the mineral composition of the veins there is, however, no evidence of introduction of new chemical components (possibly with the exception of Cl and F hosted by late friedelite and tilasite + fluorite, respectively).

Processes

The genetic diversity of Mn deposits in general is considerable (Roy 1988, 1992). The major processes behind primary Mn deposition (i.e. excluding supergene-residual formations) can be classified as (A) hydrothermal, (B) hydrogenetic or (C) diagenetic. The general characteristics of these types can be summarized as follows: (A) hydrothermal (also known as exhalative or volcanogenic) deposits are products of rapid precipitation from hot (100–350 °C) mobile metal-enriched fluids, close to the interface between the ocean and the seafloor. The deposits, commonly forming crusts or lenses of a rather local extent in active tectonic settings, typically consist of major todorokite and birnessite. (B) Hydrogenetic (sometimes referred to as sedimentary) deposits form by slow precipitation at ambient conditions and subsequent sedimentation in rather stable limnic or marine environments. The products are e.g. Fe-Mn crusts and deep-sea nodules (dominated by vernadite and Fe-Mn oxyhydroxides). (C) Diagenetic processes involve precipitation from pore fluids that have interacted with materials at varying levels in a sedimentary column. Mineralogically, the products are diverse (oxides, hydroxides, carbonates, sulphides) and appear in the form of cements, fracture infillings etc. Despite this seemingly clear-cut division, it must be realized that hybrids, where fundamentally different processes have co-operated to form a deposit, commonly exist in nature.

The good separation of the two ore-forming metals at Sjögruvan, illustrated by Mn/Fe ratios ranging from less than 0.001 to over 200 within a rock sequence corresponding to just a few meters, is an important feature of this type of mineralization, and provides definite clues to the origin. It has long been known that Fe and Mn can be effectively fractionated in pH-redox gradients (Krauskopf 1957). During the process of dilution of the reducing hydrothermal fluids with oxygenated seawater, such conditions can be attained. The spectrum of redox conditions encountered in a sedimentary column can contribute to significant fractionation, and Mn/Fe ratios alone cannot thus be used to discriminate between

hydrothermal or diagenetic origins. For most hydroge-
netic deposits the ratio is usually low and show modest
variations (0.3–1.3; Hein et al. 1997). Taking into con-
sideration that metamorphism is expected to result in a
reduction of Mn, and assuming that the present ores
have not suffered from postdepositional supergene
alteration, the high oxidation state of the Sjögruvan Mn
ores suggests an origin unrelated to diagenetic processes
in suboxic or anoxic zones. Braunite-containing assem-
blages are known to have a special capacity to preserve a
high oxidation potential (Robie et al. 1995).

An Si-Al discrimination diagram is sometimes used to
distinguish between hydrothermal and hydrogenetic/re-
sidual (Crerar et al. 1982) Mn deposits. It is based on the
fact that Al is immobile and generally not introduced by
hydrothermal fluxes. The BFM samples have Si/Al < 3,
thus suggesting a detrital or hydrogenetic origin
(Fig. 3c). However, if hydrothermal precipitates are
mixed with detrital particles (e.g. clay minerals) at the
time of settling, a false signature might be obtained in
this simple approach. A good positive correlation be-
tween Al and Ti, as is seen for the present sample pop-
ulation (linear $r=0.95$), is usually taken as an indicator
of detrital input (Barret 1981).

The trace element composition of Mn deposits is of-
ten used to recognize different genetic subtypes. Due to
their slow growth rate and consequently long exposure
times to seawater, in combination with specific adsorp-
tion processes, hydrogenetic Mn deposits are charac-
teristically enriched in certain transition elements, in
particular Co, Ni and Cu. The present data for the
Sjögruvan ores indicate very low contents of these ele-
ments compared to the high levels attained in hydroge-
netic deposits (Usui and Someya 1997). The low total U
and Th concentrations as well as the U/Th ratios fixed at
values close to unity are similar to what Boström et al.
(1979) found for the Långban deposit; they were taken
as evidence for an origin not related to any hydrogenetic
(or supergene) process.

As a rule, hydrogenetic deposits are much more en-
riched in REE than hydrothermal deposits, and the
range shown by the Sjögruvan ores is typical for the

latter kind (Hein et al. 1997). The REE data have been
normalized against PAAS to give an idea of to what
extent the samples are affected with siliciclastic input
(Fig. 4). This approach indicates that the Fe and haus-
mannite ores (the hematite ore has a middle-REE en-
richment which might be related to crystallographic
control) is the part that most closely resembles modern
chemical sediments of hydrothermal origin. Hydroge-
netic Mn deposits show clear positive Ce anomalies
(essentially due to adsorption of Ce^{4+} present in sea-
water), whereas oceanic exhalative deposits normally are
distinctly negative (Nath et al. 1997). Our Ce data for
the hausmannite ore are consistent with a hydrothermal
origin. Although to the greater part possessing a hy-
drothermal REE signature, the BFM association dis-
plays a positive Ce anomaly. The obvious conclusion
from this fact is that some interaction with seawater has
occurred after all.

A look for analogues

Unfortunately, no modern, reliable multicomponent
analyses of the Långban ores are available, a situation
which makes direct comparisons difficult, but the over-
lap in mineralogy, isotope chemistry and internal
structure of the ores are large enough to convince that
Sjögruvan is of the same genetic type. The characteristic
assemblages containing Pb silicates known from other
Långban-type deposits are, however, lacking at Sjögru-
van; this is possibly related to the higher grade of ther-
mal metamorphism in the Långban area (cf. Grew et al.
1994).

Are there any known analogues to the Fe–Mn (Ba–
As–Pb–Sb–W) deposits outside the Bergslagen region? If
close counterparts exist, e.g. fossil deposits in better
preserved areas or modern ones still under formation,
they could provide valuable information not directly
gained at Sjögruvan. Data for some key localities dis-
cussed below are summarized in Table 9. The meta-
morphosed Mn deposits of the Gozaisho Mine, Honshu,
Japan, mimic the Långban-type deposits to some extent.

Table 9 Characteristics of some small, stratiform Mn-(Fe) deposits discussed in the text

	Sjögruvan	Långban	Gozaisho	Val Ferrera	Milos
Mn ore mineralogy	Braunite hausmannite	Braunite hausmannite	Braunite hausmannite	Braunite Mn silicates	Vernadite pyrolusite
Fe ore mineralogy	Hematite + SiO ₂	Hematite magnetite + SiO ₂	Absent	Hematite + SiO ₂	Hematite + SiO ₂
Mn/Fe (maximum)	210	220	High	200	90
Enriched elements	Ba, As, Pb, Sb, W	Ba, As, Pb, Sb, Be, B, W	Ba, As, Sb, Cu, Sr, Be	Ba, V, Sb, As, Be, W	Ba, Zn, As, Pb, Sb, Sr
Host rock	Dolomite/calcite marble	Dolomite marble	Quartz schist	Dolomite marble	Volcaniclastic sandstone
Paleotectonic setting	Back-arc basin?	Back-arc basin?	Volcanic arc	Unknown	Volcanic arc
Type of volcanism	Felsic	Felsic	Felsic	Unknown	Felsic
Depositional environment	Marine	Marine	Terrestrial?	Marine	Marine
Peak metamorphism	Greenschist facies	Amphibolite facies	Amphibolite facies	Blueschist facies	Unmetamorphosed

Here hausmannite and braunite ores associated with Sb and As oxyminerals (långbanite, roméite, manganberzeliite etc.) form thin lenses hosted by quartz schist (Matsubara et al. 1996). They might represent metamorphic equivalents of the minor recent Mn deposits described from Hokkaido (Miura and Hariya 1997), where mainly todorokite and birnessite precipitated from hot-spring waters. The Mn layers here are mixed with volcanic debris and clayey material and sometimes show high concentrations of As, Sb, Zn and Cu. The environment of formation in this case is, however, clearly terrestrial.

The Fe–Mn (Ba–V–Sb–As–Be–W) deposits of Val Ferrera, Switzerland, recently subjected to detailed mineralogical and geochemical studies (Brugger 1996; Brugger and Gieré 1999) are probably the closest related ancient deposits known. Hosted by dolomite marbles of Triassic age, they are typically built up of hematite-quartz-carbonate layers contiguous to braunite-Mn-silicate ores. Minerals bearing the characteristic elements are contained both in rock matrices and in veins and breccias. Once again there is duplication with Sjögruvan in terms of mineral species: among the phases encountered are barylite, långbanite, manganberzeliite and roméite. The Mn ores of Val Ferrera are, however, significantly enriched in V (although it might be noted for the record that very rare pyrobelonite has been observed in fissure material from Sjögruvan) and poor in Pb (<100 ppm). Supported by geological field evidence and geochemical analyses, Brugger (1996) concluded that these deposits were of a syn-sedimentary, exhalative origin.

Geochemical data from other metamorphosed Mn oxide-silicate deposits, inferred to be of marine hydrothermal origin but lacking Långban-type mineralization, sometimes reveal a positive correlation between Mn and As, Sb, Pb and W, albeit at low concentration levels (e.g. Huebner et al. 1992). Slight enrichment has also been seen in many recent hydrothermal Mn deposits, but rarely do all the key elements exceed the trace element level (>1000 ppm). Submarine hydrothermal Mn deposits are commonly associated with a Ba–As anomaly (Nicholson 1992), whereas the appearance of Sb and Pb is more sporadic. An interesting young (Quaternary) formation is the unmetamorphosed Mn–Ba–Zn–As–Pb–Sb deposits of Milos Island (Cyclades) in the Aegean Sea (Hein et al. 1999), where Mn-mineralization (60% MnO), dominated by poorly crystallized vernadite, occurs as thin layers and cement in volcanoclastic sandstone. Separate layers of barite and hematite+silica belong to the same sequence. The contents of characteristic elements mentioned occasionally reach several thousands of ppm in the Mn mineralization, and Sr, W, and Cu are also clearly above background. There is a striking similarity in overall composition with the braunite ore at Sjögruvan, but a carbonate host is missing at Milos. The deposits are believed to have formed from seawater that circulated by convection through volcanic rocks and thereby depleted them in metals (Hein et al. 1999).

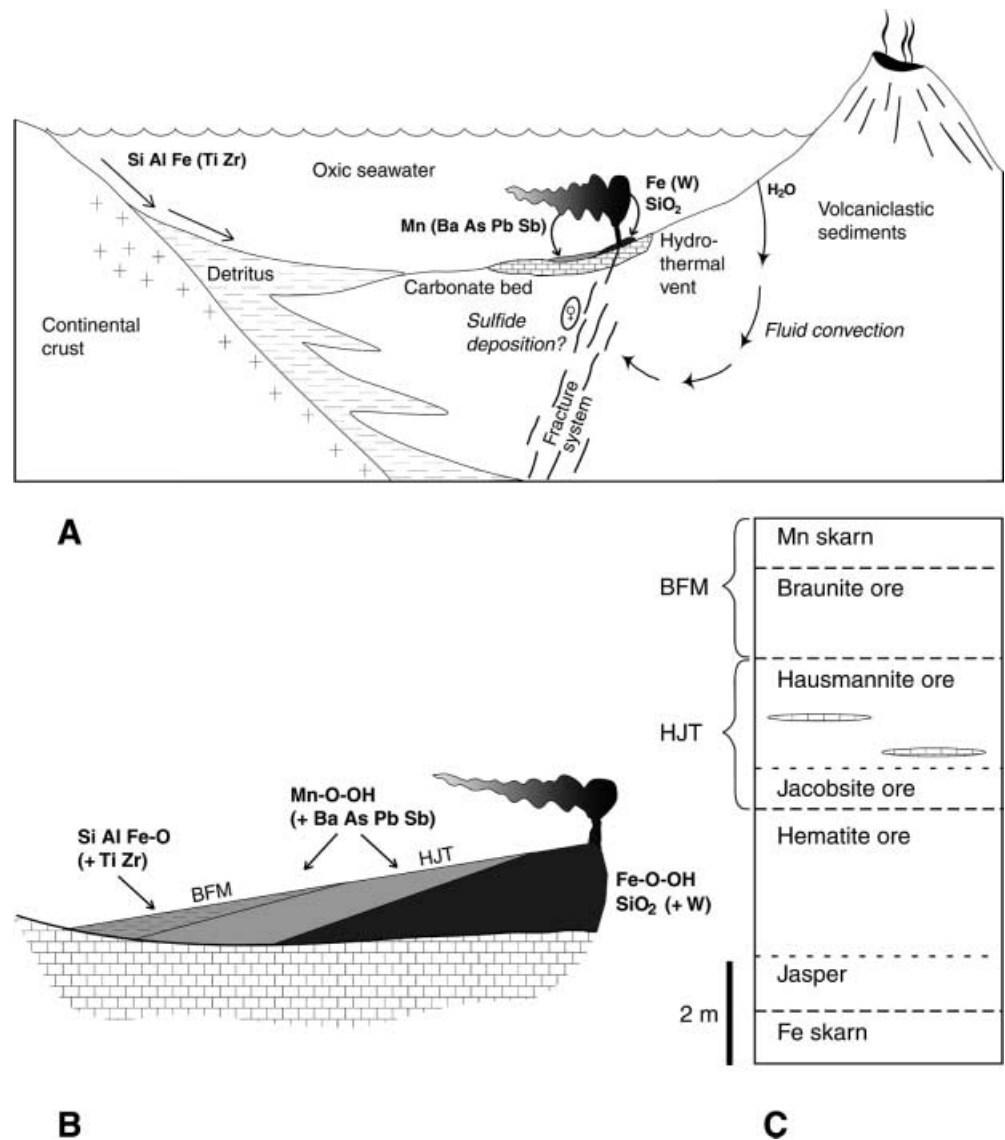
Paleoenvironment of formation and ore progenitors

Although no perfect analogue to Sjögruvan and related deposits in the Bergslagen region has been found, similar mineralizations have certainly formed at other times in the geological record. The low frequency of highly fractionated Fe–Mn oxide deposits in the region compared to pure Fe oxide or massive sulphide deposits points to unusual environments and conditions of deposition. However, submarine exhalative Mn deposits can be seen as the ultimate product of large hydrothermal systems, which have deposited significant amounts of sulphide and Fe oxide at depth (according to the now classical model of a convection cell depicted by Bonatti 1975). The small dimensions and superficial positions of such deposits reduce their chances of becoming preserved, and their likely association with subduction-related settings is of course hazardous.

Bollmark (1999) envisaged the formation of progenitors to the different ore types at the Långban deposit as a result of exhalative processes associated with temporal fluctuations in pH. We are in favour of a model in which spatial variations in primarily the redox conditions in the environments close to hydrothermal vents, corresponding to the mixing zone of hydrothermal fluids and seawater, promoted metal fractionation and deposition (Fig. 7A). Protoliths to the hematite–jacobsonite–hausmannite ores are interpreted as being of a hydrothermal origin, whereas the chemical character of the braunite ore indicates a mixture of hydrothermal and detrital components. This might be a result of slow settling during a waning stage of hydrothermal activity (Fig. 7B). Alternatively, some Mn deposition might have occurred just below the seafloor from fluids that infiltrated siliciclastic sediments. The excellent separation of Fe and Mn at Sjögruvan, however, indicates a rather stable milieu locally, where the hydrothermal fluxes largely were focused to a small number of vents. Although the engine for the hydrothermal convection was heat generated by active volcanism, ore formation of this kind is likely to have taken place during a relatively quiet period. The sand fraction present in metavolcanic rock in proximity with the ores might represent a beach sediment and suggests shallow depth of deposition.

Boström (1973) concluded that the appearance of Långban-type deposits was coupled with mafic volcanism in basically an ocean-floor environment. Our data for Sjögruvan, considering the modern geological picture of the Bergslagen region (and the Grythyttan area in particular; Lundström 1995; Allen et al. 1996) as a fossil caldera back-arc province built on continental crust, demonstrate that the volcanism had a dominantly felsic character at the time of ore formation. The fairly homogeneous Pb isotope signature is consistent with derivation mainly from Svecofennian felsic volcanic rocks (Sundblad 1994), with the addition of a possible minor sedimentary pre-Svecofennian component (Åberg and Charalampides 1986), and the local volcanoclastic sequence was probably the source for all major metals in

Fig. 7 Schematic representation of formation processes and ore layers at the Sjögruvan deposit. **A** Deposition from a hydrothermal plume in a back-arc basin at 1.9 Ga. **B** Waning stage of hydrothermal activity, where the chemical precipitates partly have been mixed with detrital material. **C** Sequence of ores and skarns after metamorphism



the Sjögruvan deposit. The positive Eu anomalies shown by the ores and the carbonate hosts at Sjögruvan, in contrast to the distinctly negative values found for the more altered metavolcanic rocks, supports the view that hydrothermal fluids actually leached the country rocks (or rather, their premetamorphic equivalents) and supplied the bulk of characteristic elements to the present mineralization.

The distinct chemistry of the metavolcanic rock found in proximity with the ore-bearing carbonate, with a depletion in Si and Na but enrichment in most other metals, suggests that it corresponds to the conduit zone of the hydrothermal fluxes. It seems that most small, modern and fossil, hydrothermal Fe-Mn and Mn deposits are spatially associated with (meta-)basalt (Flohr and Huebner 1992), whereas the subgroup under consideration here is normally associated with felsic rocks or sediments. A tempting conclusion is that the mineralogy of the metal source and/or the tectonic setting is critical to their formation. In fact, felsic rocks seems to

be higher in Ba, As, Pb and Sb compared to basalts and thus constitute a potentially more promising source material for this particular set of elements (Reed 1997).

It is far from clear whether the carbonate host rocks were largely derived from hydrothermal fluids or if they have precipitated directly from seawater. The trace element compositions reported here give no direct clues to their origin, but the C isotope data suggest a uniform reservoir of marine rather than hydrothermal character (Hoefs 1997). The contrasting compositions and REE patterns of dolomite and calcite marble probably simply reflect the presence of variable amounts of siliciclastic detritus. Biological activity might have mediated carbonate formation, but in contrast to carbonate from the Mn-skarn deposits containing possible microbial fossils (Oen et al. 1986; De Groot and Sheppard 1988), the Sjögruvan carbonates have $\delta^{13}\text{C}$ values too high to be consistent with derivation of carbon from decomposition of organic matter. Equally unclear as the derivation of the carbonate rocks is their role in ore formation. As

indicated by some of the examples given above, the presence of a carbonate bed does not appear to be instrumental for Mn-(Ba-As-Pb-Sb) deposition, but a sedimentary carbonate rock might have played the role of a "cap", which works as an insulator that enhances the efficiency of the hydrothermal system, and also might contain fractures that provide focused pathways to the seafloor (Scott 1997).

While the composition of the protoliths thus largely survived, the finer sedimentary structures and the primary mineralogy have not (Fig. 7C). Modern hydrothermal Mn deposits are composed of todorokite + birnessite ± vernadite, and these phases have properties that allow them to "scavenge" metals. Large cations like Ba²⁺ and Pb²⁺ are likely to be incorporated in crystallographic "tunnels" whereas highly charged species like As⁵⁺ adsorbs onto crystal faces (Burns and Burns 1979). Although braunite is sometimes found as a primary, nonmetamorphic mineral (Hou 1994), we believe that the braunite ore at Sjögruvan is a metamorphic assemblage. Poorly crystallized, hydrous Mn oxides mixed with volcanogenic debris have been transformed into the present braunite-feldspar-mica assemblage by diagenesis and metamorphism. The hausmannite ore is a metamorphic equivalent of an essentially uncontaminated hydrothermal Mn oxide mineralization, occasionally mixed with carbonate layers. The very high Ba content in these ores suggests that this element in part precipitated as a separate phase (i.e. barite). Si and Fe, which occur at higher concentration levels in the braunite ore, were to some extent introduced as detritus (along with Al, Ti etc.). We do not consider the BFM association as an intermediate between chemical Fe-Si sediments and Mn precipitates because of the order of deposition assumed above. The stratigraphic sequence hematite ore (jasper)-hausmannite ore-braunite ore is clearly not unique to this type (e.g. Ashley 1986).

Because of the extremely low Al/Si ratio in the Fe ore, it is reasonable to assume that the primary source of silica was not detrital in that case. In hydrothermal deposits Fe is often associated with Si, in specific minerals like nontronite or as heterogeneous mixtures of partly amorphous Fe- and Si-rich phases (Damyanov et al. 1998). These formations are usually strongly depleted in trace metals (Hekinian et al. 1993). The present W anomaly associated with the hematite ore is probably related to coprecipitation of W with Fe oxyhydroxides due to effective adsorption on charged crystal surfaces (cf. Kunzendorf and Glasby 1992). Because the concentration of W in seawater is very low, the largest contribution must have been from hydrothermal fluids.

Summary of conclusions

The geochemical signature of the Mn ores at Sjögruvan is distinct from those of hydrogenetic and diagenetic deposits and thus indicates a hydrothermal origin. More

specifically, we believe that the Fe-Mn ore progenitors at Sjögruvan precipitated from fluids that had leached local felsic volcanic rocks, soon after their entrance at the seafloor. The small size of the deposit and the good separation of Fe and Mn suggest that the hydrothermal fluxes were largely restricted to a few vents around which the environment must have been relatively stable. The existence of two Mn ore layers with contrasting mineralogical and chemical compositions (the HJT and BFM associations, respectively) is explained by significant clastic and hydrogenetic contamination of the BFM protolith, which might have settled slowly and was exposed to seawater for longer times.

Field and petrographic relations show that the elements Ba, As, Pb, Sb and W are syngenetic with Mn and Fe, and not introduced by magmatic or late-stage hydrothermal activity. Although Sjögruvan represents a very rare kind of mineralization, there are a few younger deposits in the world that have similar primary geochemical characteristics; some of these have independently been described as being of a syn-sedimentary exhalative origin. A paleoenvironment characterized by felsic volcanism and shallow marine water seems to be another common feature, and is also consistent with the current geological view of the Grythyttan area.

Acknowledgements This study was supported financially by the Swedish Natural Science Research Council (NFR). We thank K. Renman for assistance in the field and C.-E. Gustavsson, the land owner at Sjögruvan, for his courtesy. We also want to thank A.J. Boyce and an anonymous reviewer for their thoughtful comments on the manuscript.

References

- Åberg G, Charalampides G (1986) New lead isotope data from the Långban mineralization, central Sweden. *Geol Fören Stockholm Förhand* 108:243–250
- Allen RL, Lundström I, Ripa M, Simeonov A, Christofferson H (1996) Facies analysis of a 1.9 Ga, continental margin, back-arc, felsic caldera province with diverse Zn-Pb-Ag-(Cu-Au) sulfide and Fe oxide deposits, Bergslagen region, Sweden. *Econ Geol* 91:979–1008
- Ashley PM (1986) An unusual manganese silicate occurrence at the Hoskins mine, Grenfell district, New South Wales. *Aust J Earth Sci* 33:443–456
- Baker D, Fallick AE (1989) Evidence from Lewisian Limestone for isotopically heavy carbon in two-thousand-million-year old seawater. *Nature* 337:352–354
- Barret TJ (1981) Chemistry and mineralogy of Jurassic bedded chert overlying ophiolites in the north Apennines, Italy. *Chem Geol* 34:289–317
- Billström K, Åberg G, Nord AG (1985) Stable isotope data for Bergslagen carbonates and their potential use for sulphide ore prospecting. *Geol Fören Stockholm Förhandl* 107:169–173
- Bollmark B (1999) Some aspects of the origin of the Långban deposit. In: Holtstam D, Langhof J (eds) *Långban. The mines, their minerals, geology and explorers*. Raster Förlag, Stockholm, pp 43–49
- Bonatti E (1975) Metallogenesis at oceanic spreading centers. *Annu Rev Earth Planet Sci* 3:401–431
- Boström K (1973) The origin and fate of ferromanganoan active ridge sediments. *Acta Univ Stockholmiensis Stockholm Contr Geol* 27:149–243

- Boström K, Rydell H, Joensuu O (1979) Långban – an exhalative sedimentary deposit? *Econ Geol* 74:1002–1011
- Brotzen O (1955) Some microstructures in jasper from the Långban mine. *Geol Fören Stockholm Förhand* 77:275–283
- Brugger J (1996) The Fe, Mn, (V, Sb, As, Be, W) deposits of Val Ferrera (Graubünden), Switzerland. PhD Thesis, University of Basel, 257 pp
- Brugger J, Gieré R (1999) As, Sb, Be and Ce enrichment in minerals from a metamorphosed Fe-Mn deposit, Val Ferrera, eastern Swiss Alps. *Can Mineral* 37:37–52
- Burns RG, Burns VM (1979) Manganese oxides. *Min Soc Am Rev Mineral* 6: 1–46
- Crerar DA, Namson J, So Chyi M, Williams L, Feigenson, MD (1982) Manganiferous cherts of the Franciscan assemblage: I. General geology, ancient and modern analogues, and implications for hydrothermal convection at oceanic spreading centers. *Econ Geol* 77:519–540
- Damman AH (1989) Skarn and ore formation in the Gåsborn Area, West Bergslagen, central Sweden: A study of (sub)sea-floor hydrothermal-metamorphic mineral assemblages. PhD Thesis, Free Univ Amsterdam, 183 pp
- Damyantov ZK, Dekov VM, Lisitsyn AP, Bogdanov YA, Aidanliiski G, Dimov VI (1998) Mineralogical features of the near sulfide mound sediments: MIR zone, TAG hydrothermal field (mid-Atlantic Ridge, 26°N). *N Jahrb Mineral Abh* 174:43–78
- Evans BW, Guggenheim S (1988) Talc, pyrophyllite and related minerals. *Min Soc Am Rev Mineral* 19:225–294
- Flohr MJK (1992) Geochemistry and origin of the Bald Knob manganese deposit, North Carolina. *Econ Geol* 87:2023–2040
- Flohr MJK, Huebner JS (1992) Mineralogy and geochemistry of two metamorphosed sedimentary manganese deposits, Sierra Nevada, California. *Lithos* 29:57–85
- Gerstenberger H, Haase G (1997). A highly effective emitter substance for mass spectrometric Pb isotope ratio determinations. *Chem Geol* 136:309–312
- Govindaraju K, Mevelle G (1987) Fully automated dissolution and separation methods for inductively coupled plasma atomic emission spectrometry rock analysis. Application to determination of rare earth elements. *J Analyt Atom Spectrom* 2:615–621
- Grew ES, Yates MG, Belakovskiy DI, Rouse RC, Su S-C, Marquez N (1986) Hyalotekite from reedmergnerite-bearing peralkaline pegmatite, Dara-i-Pioz, Tajikistan and from Mn skarn, Långban, Varmland, Sweden; a new look at an old mineral. *Mineral Mag* 58:285–297
- De Groot PA, Sheppard SMF (1988) Carbonate rocks from W. Bergslagen, Central Sweden: isotopic (C, O, H) evidence for marine deposition and alteration by hydrothermal processes. *Geol Mijnbouw* 67:177–188
- De Groot PA, Baker JH (1992) High element mobility in 1.9–1.86 Ga hydrothermal alteration zones in Bergslagen, central Sweden: relationships with exhalative Fe-ore mineralizations. *Precambrian Res* 54:109–130
- Hein JR, Koschinsky A, Halbach P, Manheim FT, Bau M, Kang J-K, Lubick N (1997) Iron and manganese oxide mineralization in the Pacific. In: Nicholson K, Hein JR, Bühn B, Dasgupta S (eds) Manganese mineralization. Geochemistry and mineralogy of terrestrial and marine deposits. *Geol Soc Spec Publ* 119:123–138
- Hein JR, Dowling J, Stamatakis, MG (1999) Hydrothermal Mn-oxide deposits rich in Ba, Zn, As, Pb, Sb, Milos Island, Greece. In: Stanley et al. (eds) Mineral deposits: processes to processing. Balkema, Rotterdam, pp 519–522
- Hekinian R, Hoffert M, Larqué P, Cheminée JL, Stoffers P, Bideau D (1993) Hydrothermal Fe and Si oxyhydroxide deposits from South Pacific intraplate volcanoes and East Pacific Rise axial and off-axial regions. *Econ Geol* 88:2099–2121
- Hoefs J (1997) Stable isotope geochemistry. Springer, Berlin Heidelberg New York
- Holtstam D, Langhof J, eds (1999) Långban. The mines, their minerals, geology and explorers. Raster Förlag, Stockholm
- Holtstam D (2001) W and V mineralization in Långban-type Fe-Mn deposits: Epigenetic or syngenetic? *GFF* 123:29–33
- Hou B (1994) Primary braunite in Triassic sedimentary deposits of Dounan, Yunnan, China. *Ore Geol Rev* 9:219–239
- Huebner JS, Flohr MJK, Grossman JN (1992) Chemical fluxes and origin of a carbonate-oxide-silicate deposit in bedded chert. *Chem Geol* 100:93–100
- Hughes, CJ (1972) Spilites, keratophyres and the igneous spectrum. *Geol Mag* 109:513–527
- Igelström LJ (1887) Über ein neues Vorkommen von Braunit und Hausmannit bei Sjögrufvan im Kirchspiel Grythyttan, Gouvernement von Oerebro (Schweden), und über die Sjögrube im Allgemeinen. *N Jahrb Miner Abh Geol Palaeontol* 1887(2): 8–11
- Johansson Å, Rickard DT (1985) Some new lead isotope determinations from the Proterozoic sulphide ores of central Sweden. *Miner Deposita* 20:1–17
- Jonsson E, Boyce AJ (1999) Correlation of mineral parageneses with S and O isotopic variation in Pb–Mn–As–Sb-bearing veins at Långban, Sweden. In: Stanley et al. (eds) Mineral deposits: processes to processing. Balkema, Rotterdam, pp 951–954
- Krauskopf KB (1957) Separation of manganese from iron in sedimentary processes. *Geochim Cosmochim Acta* 12:61–64
- Krogh TE (1973) A low-contamination method for hydrothermal decomposition of zircon and extraction of U and Pb for isotopic age determinations. *Geochim Cosmochim Acta* 37:485–494
- Kunzendorf H, Glasby GP (1992) Tungsten accumulation in Pacific ferromanganese deposits. *Miner Deposita* 27:147–152
- Le Maitre RW (ed) (1989) A classification of igneous rocks and glossary of terms. Blackwell, Oxford
- Ludwig KR (1980) Calculation of uncertainties of U–Pb isotope data. *Earth Planet Sci Lett* 46: 212–220
- Lundström I (1995) Beskrivning till berggrundskartorna Filpstad SO och NO. *Sver Geol Undersök Af* 177–185:1–218
- Lundström I, Allen RL, Persson P-O, Ripa M (1998) Stratigraphies and depositional ages of Svecofennian, Palaeoproterozoic metavolcanic rocks in E. Svealand and Bergslagen, south central Sweden. *GFF* 120:315–320
- Magnusson NH (1930) Långbans malmtrakt. *Sver Geol Undersök Ca* 23:1–111
- Matsubara S, Kato A, Shimizu M, Sekiuchi K, Suzuki Y (1996) Romeite from the Gozaisho Mine, Iwaki, Japan. *Min J* 18:155–160
- McCrea JM (1950) On the isotopic chemistry of carbonates and a paleotemperature scale. *J Chem Phys* 18:849–857
- McLennan MC (1989) Rare earth elements in sedimentary rocks: influence of provenance and sedimentary processes. *Min Soc Am Rev Mineral* 21: 169–200
- Miura H, Hariya Y (1997) Recent manganese oxide deposits in Hokkaido, Japan. In: Nicholson K, Hein JR, Bühn B, Dasgupta S (eds) Manganese mineralization. Geochemistry and mineralogy of terrestrial and marine deposits. *Geol Soc Spec Publ* 119:281–299
- Moore PB (1970) Mineralogy & chemistry of Långban-type deposits in Bergslagen, Sweden. *Mineral Rec* 1:154–172
- Nath BN, Plüger WL, Roelandts I (1997) Geochemical constraints on the hydrothermal origin of ferromanganese encrustations from the Rodriguez Triple Junction, Indian Ocean. In: Nicholson K, Hein JR, Bühn B, Dasgupta S (eds) Manganese mineralization. Geochemistry and mineralogy of terrestrial and marine deposits. *Geol Soc Spec Publ* 119:199–211
- Nicholson K (1992) Contrasting mineralogical-geochemical signatures of manganese oxides: guides to metallogenesis. *Econ Geol* 87:1253–1264
- Nysten P, Ericsson T (1994) Fe-rich Långbanite from the Nyberget ore-field, Sweden. *Neues Jahrb Mineral Mon* 1994:557–566
- Nysten P, Holtstam D, Jonsson E (1999) The Långban minerals. In: Holtstam D, Langhof J (eds) Långban. The mines, their minerals, geology and explorers. Raster Förlag, Stockholm, pp 89–183

- Oen IS, de Maesschalck AA, Lustenhouwer WJ (1986) Mid-proterozoic exhalative-sedimentary skarns containing possible microbial fossils, Grythyttan, Bergslagen, Sweden. *Econ Geol* 81:1533–1543
- Ragu A (1994) Helvite from the French Pyrénées as evidence for granite-related hydrothermal activity. *Can Mineral* 32:111–120
- Reed MH (1997) Hydrothermal alteration and its relationship to ore fluid composition. In: Barnes HB (ed) *Geochemistry of hydrothermal ore deposits*. Wiley, New York, pp 303–365
- Robie RA, Huebner JS, Hemingway BS (1995) Heat capacities and thermodynamic properties of braunite (Mn_7SiO_{12}) and rhodnite. *Am Mineral* 80: 560–575
- Roy S (1988) Manganese metallogenesis. *Ore Geol Rev* 4:155–170
- Roy S (1992) Environments and processes of manganese deposition. *Econ Geol* 87:1218–1236
- Scott SD (1997) Submarine hydrothermal systems and deposits. In: Barnes HB (ed) *Geochemistry of hydrothermal ore deposits*. Wiley, New York, pp 797–875
- Stacey JS, Kramers, JD (1975) Approximation of terrestrial lead isotope evolution by a two-stage model. *Earth Planet Sci Lett* 26:207–221
- Sundblad K (1994) A genetic reinterpretation of the Falun and Ammeberg ore types, Bergslagen, Sweden. *Miner Deposita* 29:170–179
- Sundius N (1923) Grythyttfältets geologi. *Sver Geol Undersök* C312:1–354
- Usui A, Someya M (1997) Distribution and composition of marine hydrogenetic and hydrothermal manganese deposits in the northwest Pacific. In: Nicholson K, Hein JR, Bühn B, Dasgupta S (eds) *Manganese mineralization. Geochemistry and mineralogy of terrestrial and marine deposits*. *Geol Soc Spec Publ* 119:177–198
- Valley JW, Bohlen SR, Essene EJ, Lamb W (1990) Metamorphism in the Adirondacks II. *J Petrol* 31:555–596
- Wink BW (1996) Stability relations of antimony and arsenic compounds in the light of revised and extended Eh-pH diagrams. *Chem Geol* 130:21–30