MINERALOGICAL MAGAZINE, MARCH 1986, VOL. 50, PP. 101-10

Conditions of formation of the iron-containing minerals, Hällefors silver mines, Bergslagen, Sweden

A. W. JASIŃSKI*

Institute of Earth Sciences, Free University, De Boelelaan 1085, 1007 MC Amsterdam, The Netherlands

ABSTRACT. The Hällefors silver deposit is regarded as a volcanogenic-exhalative iron ore deposit with dispersed amounts of Ag-Pb-Zn (±Cu) which has undergone secondary remobilization leading to the concentration of sulphides and sulphosalts. Based on data from the iron oxides and sulphides, the sulphide-sulphosalt mineralization is believed to have been formed in two stages. The first is characterized by the ranges 573-473 K and 2.25-1.5 kbar, higher gradient of changes of $\log a_{S_2}$ with temperature and mostly sulphide precipitation; the second by the ranges 473-443 K, lower gradient of changes of $\log a_{S_2}$ and mainly sulphosalt deposition. Assuming the precipitation was from fluids and aqueous solutions, possible conditions of formation of some of the iron minerals have been determined.

KEYWORDS: iron oxides, iron sulphides, Hällefors mine, Bergslagen, Sweden.

THE area under investigation is located in the northern part of the Grythyttan-Hällefors-Filipstad region of Bergslagen in the Central Swedish Svecofenides. The lithologies and age determinations were given by Sundius (1923), Welin *et al.* (1981), and Moorman *et al.* (1982). The ore deposits of the Hällefors silver mines are restricted chiefly, but not exclusively, to felsic pyroclastic rocks (Jasiński, 1983).

Recently Oen *et al.* (1982) proposed a model of continental rifting involving widespread subseafloor metamorphism and hydrothermal alteration to account for the formation and metamorphism of Fe-Mn and sulphide ores located in the 1.9-1.8 Ga Bergslagen Supracrustal Series. The rocks described in this paper belong to the Upper-Leptite-Hälleflinta-Slate Group of Oen *et al.* (1982) and were affected by low-grade greenschist facies metamorphism (Sundius, 1923), which occurred during the post-rift stage major phase of tectonic compression and regional metamorphism (Oen *et al.*, 1982).

Geological descriptions of the mineralized area were given by Tegengren (1924), Sundius (1923), Sundius *et al.* (1966) and Nugteren (1978).

Mineralization. The Bergslagen metallogenic province has more than 2000 iron and more than 200 base metal (predominantly of the Ag-Pb-Zn ±Cu type) deposits and is a producer of Mn, Co, W, Mo, Au, Bi, Ce, Hg, and Se. The Hällefors silver deposit could be considered as an original volcanogenic-exhalative iron ore deposit, in the sense proposed by Large (1977) and by Zakrzewski (1982). It is presumed to have contained dispersed amounts of Ag-Pb-Zn-(±Cu); subsequently, secondary mobilization of metals occurred due to an increase in temperature and to a lesser extent pressure, followed by the precipitation of sulphides and sulphosalts with decreasing temperature and changes of sulphur and oxygen activities.

Descriptions of the mineralization and the paragenetic sequence may be found in Nugteren (1978), Nugteren and Zakrzewski (1984), Sundius *et al.* (1966), and Jasiński (1983).

Samples were examined by means of a microscope and an electron-microprobe (Nugteren, 1978; Nugteren and Zakrzewski, 1984; Jasiński, 1983), and chemically analysed by Boliden Metal AB.

Thermodynamic calculations. Thermodynamic calculations were made using the data of Robie *et al.* (1978), Craig and Barton (1973), Helgeson *et al.* (1978), Vaughan and Craig (1978), Garrels and Christ (1965), Table I. ΔG_r, $\log a_{S_2}$ and $\log a_{O_2}$ were calculated in the same way as in Jasiński (1983). In order to estimate the lower stability limit of an aqueous fluid on $\log a_{S_2}$-$\log a_{O_2}$ diagrams, the following assumptions were made:

1. A fluid (for simplicity containing $X_{CO_2} = 0.3$ and $X_{H_2O} = 0.7$, excluding other components, e.g. H_2 or CH_4 etc.; fugacity coefficients of H_2O gas

---

* Present address: Technical University of Wrocław, Institute of Inorganic Chemistry and Metallurgy of Rare Elements, 50-370 Wrocław, Wybrzeże Wyspiańskiego 27, Poland.

TABLE I. Thermodynamic data used in calculations **

mineral	ΔG_f^o 298	ΔH^o298	ΔS^o298	V mol. solid
	cal/mole	cal/mole	cal/mole deg.	cm^3
Pyrite FeS_2	-38296	-41000	12.65	23.94
Troilite FeS	-24219	-24130	14.42	18.2
Iron Fe			6.52	7.092
Sulphur S_2	18910	30710	54.53	
Gudmundite FeSbS	-24600	-24300	25.3	30.10
Berthierite $FeSb_2S_4$	-64100	-64380	57.74	91.46
Antimony Sb			10.88	18.178
Tetrahedrite* $Cu_{10}Fe_2Sb_4S_{13}$	-226528	-197795	330.98	332.96
Freibergite * $Cu_4Ag_6Fe_{1.5}Zn_{0.5}Sb_4S_{13}$	-207436	-177880	348.95	348.64
Magnetite Fe_3O_4	-242009	-266665	34.93	44.524
Hematite Fe_2O_3	-177505	-197094	20.89	30.274
Arsenopyrite FeAsS	-26200	-25200	25.9	26.23
Arsenic As			8.53	12.963
Chalcocite Cu_2S	-20565	-18226	31.31	35.11
Water H_2O (l)	-56678	-68315	16.72	18.069
H_2O (g)	-54618	-57792	45.10	
Oxygen O_2			49.03	
Hydrogen H_2			31.23	
Sphalerite ZnS	-48398	-49450	14.02	23.83
Silver Ag			10.17	10.272
Stibnite Sb_2S_3	-37424	-37080	43.5	73.41
Chalcopyrite $CuFeS_2$	-44850	-44453	30.96	42.83
Copper Cu			7.92	7.113

* - entropy calculated using the assumption of an ideal solution and "$n_{mix.}$ = 1"

** all references in the text

taken from Helgeson and Kirkham, 1974) represented in Table II by equation 12′b;

2. A fluid as above with $X_{H_2O} = 1$ (Table II, equation 12′a);

3. Pure liquid water (Table II, equation 12′w, a reasonable approximation of natural solutions at relatively low temperature and pressure).

Ore-formation temperatures of Coolen (pers. comm.) have been confirmed by my unpublished studies of fluid inclusions (560–440 K, higher in some cases). Nugteren's pressure approximations using the sphalerite geobarometer (Hutchinson and Scott, 1980) have been invalidated (Hellingwerf, 1984; Kalogeropulos, 1983), but recent fluid inclusion studies reveal that for 473 K and the CO_2 isochore 0.925, the pressure should be about 1.5 kbar. Assuming the same isochore for 573 K, the pressure should not exceed 2.25 kbar and for 443 K about 1.2 kbar. Taking into account the type of mineralization, its relation to tectonics and the decrease of pressure to the west, the pressure gradient for the 473–443 K range was assumed to be higher (500 bar/30 K) than it appeared from the CO_2 isochore (300 bar/30 K). The pressure gradient for the 573–473 K range (750 bar/100 K) was used in the calculations.

In a previous paper (Jasiński, 1983) calculations were made using pressure values of up to 5 kbar. Recalculations using the more realistic pressures mentioned above resulted in the same mineral sequence, suggesting that pressure does not significantly influence the mineral equilibria. The basic assumption made was that precipitation of sulphides and sulphosalts took place from an aqueous fluid that later, and at lower temperatures and pressures, behaved more like pure water. Temperature limits of the stabilities of minerals coexisting with probable mother solutions can be fixed on a $\log a_{O_2}$-$\log a_{S_2}$ diagram (fig. 1) by the intersection of the reaction lines expressing limits of mineral stability with stability limits for aqueous fluid or water (12b, w). The possible upper temperature of precipitation of pyrrhotite accompanied by magnetite is the intersection of lines 12w, 2 and 3 (or 1, 2, 3, and 12w); namely *T* ~ *560 K*, $\log a_{O_2} \sim -35.3$ and $\log a_{S_2} \sim -12.7$ (with water treated as a pure liquid). If this deposition is from an aqueous fluid with $X_{H_2O} = 1$ these values are *T* ~ *620 K*, $\log a_{O_2} \sim -30.9$ and $\log a_{S_2} \sim -9.8$; and for $X_{H_2O} = 0.7$: *T* ~ *670 K*, $\log a_{O_2} \sim -27.5$ and $\log a_{S_2} \sim -7.9$.

Parameters for the initiation of gudmundite formation along with pyrrhotite and magnetite are fixed on a $\log a_{S_2}$-$\log a_{O_2}$ diagram by the intersection of lines corresponding to equations 2, 7, and 12 in Table II. This point, in the case of precipitation from water, occurs at $T \sim 510$ K, $\log a_{O_2} \sim -40.8$ and $\log a_{S_2} \sim -15.6$. If precipitation takes place from the aqueous fluid with $X_{H_2O} = 1$, the values are as follows: $T \sim 540$ K, $\log a_{O_2} \sim -38.1$ and $\log a_{S_2} \sim -14.2$: if $X_{H_2O} = 0.7$ then $T \sim 565$ K, $\log a_{O_2} \sim -35.9$ and $\log a_{S_2} \sim -13.1$. Fig. 4 shows a graphical method for the determination of the $\log a_{S_2}$ and $\log a_{O_2}$ ranges over which sulphide and sulphosalt precipitation with pyrrhotite is possible.

In figs. 2, 3, and 4, the lines labelled 12a, b, w are defined by the sets of $\log a_{S_2}$ and $\log_{O_2}$ values from

TABLE II. Results of thermodynamic calculations

Line	Reaction, ΔG reaction (ΔG_r), log a_{S_2}, log a_{O_2}
1a	$2Fe + S_2 = 2FeS$ $\Delta Gr = -74992 + 29.08T + 0.531\ (P-1)$ $\log a_{S_2} = -16388/T + 6.35 + 0.116\ (P-1)/T$
1	$2FeS + S_2 = 2FeS_2$ $\Delta G_r = -64450 + 58.07\ T + 0.278\ (P-1)$ $\log a_{S_2} = -14084/T + 12.69 + 0.061\ (P-1)/T$
2	$3FeS + 2\ O_2 = Fe_3O_4 + 3/2\ S_2$ $\Delta G_r = -148210 + 24.5\ T - 0.241\ (P-1)$ $\log a_{S_2} = 21592/T + 1.333 \log a_{O_2} + 0.035(P-1)/T - 3.57$
3	$3FeS_2 + 2\ O_2 = Fe_3O_4 + 3S_2$ $\Delta G_r = -51535 - 62.51\ T - 0.65\ (P-1)$ $\log a_{S_2} = 0.667 \log a_{O_2} + 3754/T + 4.55 + 0.047\ (P-1)/T$
4	$2FeS_2 + 3/2\ O_2 = Fe_2O_3 + 2S_2$ $\Delta G_r = -53674 - 31.10T - 0.426\ (P-1)$ $\log a_{S_2} = 5880/T + 3.41 + 0.75 \log a_{O_2} + 0.046\ (P-1)/T$
5	$4Fe_3O_4 + O_2 = 6Fe_2O_3$ $\Delta G_r = -115904 + 59.78\ T + 0.086\ (P-1)$ $\log a_{O_2} = -25329/T + 13.06 + 0.019\ (P-1)/T$
6	$4/3\ Sb + S_2 = 2/3\ Sb_2S_3$ $\Delta G_r = -55430 + 40.10\ T + 0.59\ (P-1)$ $\log a_{S_2} = -12113/T + 8.76 + 0.13\ (P-1)/T$
7	$2/3\ FeSbS + 2/3\ Sb + S_2 = 2/3\ FeSb_2S_4$ $\Delta G_r = -57403 + 39T + 0.686\ (P-1)$ $\log a_{S_2} = -12544/T + 8.52 + 0.150\ (P-1)/T$
8	$2FeAsS + S_2 = 2FeS_2 + 2As$ $\Delta G_r = -62310 + 63.97T + 0.51\ (P-1)$ $\log a_{S_2} = -13617/T + 13.98 + 0.112\ (P-1)/T$
9	$5/3\ Cu_2S + 2/3\ FeS + 4/3\ Sb + S_2 = 1/3\ Cu_{10}Fe_2Sb_4S_{13}$ $\Delta G_r = -55430 + 31.83T + 0.7\ (P-1)$ $\log a_{S_2} = -12113/T + 6.86 + 0.153\ (P-1)/T$
10	$0.44\ Cu_2S + 1.333\ Ag + 0.333\ FeS + 0.111\ ZnS + 0.889\ Sb$ $+ S_2 = 0.222\ Cu_4Ag_6Fe_{1.5}Zn_{0.5}Sb_4S_{13}$ $\Delta G_r = -50896 + 24.42T + 0.64\ (P-1)$ $\log a_{S_2} = -11122/T + 5.34 + 0.14\ (P-1)/T$
11	$3/2\ Fe + O_2 = 1/2\ Fe_3O_4$ $\Delta G_r = -133332 + 41.35T + 0.28\ (P-1)$ $\log a_{O_2} = -29137/T + 9.04 + 0.061\ (P-1)/T$
12′a	$1/2\ O_2 + H_2 = H_2O$ (gas) $(X_{H_2O} = 1)$ $\Delta G_r = -57795 + 10.65T + 4.576T \log P_{H_2O}^{p} \cdot 1$ $\log a_{O_2} = 2\Delta G_r/4.576T$
12′b	$\Delta G_r = -57795 + 10.65T + 4.576T \log P_{H_2O}^{p} \cdot 0.7$ $\log a_{O_2} = 2\Delta G_r/4.576T$ $(X_{H_2O} = 0.7)$
12′w	$1/2\ O_2 + H_2 = H_2O$ (1) $\Delta G_r = -68315 + 39.02\ T + 0.432\ (P-1)$ $\log a_{O_2} = -29858/T + 17.06 + 0.189\ (P-1)/T$

the intersection points of the 2 and 12a, b, w lines on fig. 1. The FeS-FeS_2-Fe_3O_4 and FeS_2-Fe_3O_4-Fe_2O_3 lines are defined by the sets of log a_{S_2} and log a_{O_2} values from the intersection points of the lines labelled 1 and 2 and 3 and 5 respectively, on fig. 1. The areas between the 12a, b, w and FeS-FeS_2-Fe_3O_4 lines define probable ranges of log a_{S_2} values for sulphide and sulphosalt precipitation accompanied by pyrrhotite. A superposition of the gudmundite line 7 on the FeS-Fe_3O_4-H_2O line gives the values mentioned above for the conditions of formation of this mineral. In order to illustrate the changes of temperature, log a_{S_2} and log a_{O_2} during the formation of ores from the Hällefors mines, the T-log a_{S_2}-log a_{S_2} diagram for the Fe-S-O-H_2O system is presented in fig. 2.

Discussion. This work was undertaken to define the conditions of ore mineral formation in the Hällefors deposit, particularly conditions involving iron, the most abundant metal. It supplements a previous study into the paragenetic sequence of precipitation of silver minerals in the Hällefors mines (Jasiński, 1983). Mineralogical observations, together with calculations point to several stages in the formation. A probable sequence of events is as follows:

1. Iron oxides were initially formed, starting with hydroxycompounds and then hematite and magnetite. Increasing temperature and possibly pressure due to metamorphic events caused a release of metals from these compounds, and, to a lesser extent, their precipitation. This stage of meta-hydrothermal fluid circulation and interaction could not have been important because of the rather low activities of the components (relatively small amounts of an aqueous fluid, relatively high temperature, and high stability of soluble, charged and neutral metal complexes and in consequence their low activity coefficients, and high stability constants for complexes in such an aqueous solution).

2. The second stage occurred when mixing took place of the first hydrothermal solution with heated sea water. It is generally accepted by most workers (e.g. Large, 1977; Seyfried and Mottle, 1982) that sea water is a significant component of many ore-forming fluids. The evidence for alteration of felsic volcanics by hydrothermal solutions in which sea water was the major component, resulting in Mg-rich alteration zones 20 km east of Hällefors mines, includes (Baker and de Groot, 1983): (i) the progressive alteration of the pyroclastic textures through hydrolysis of the feldspar and grain-size increases in the matrix due to quartz recrystallization; (ii) the discordant nature of the lensoid zones aligned along old fault systems; (iii) the similar radiometric ages obtained for the emplacement and

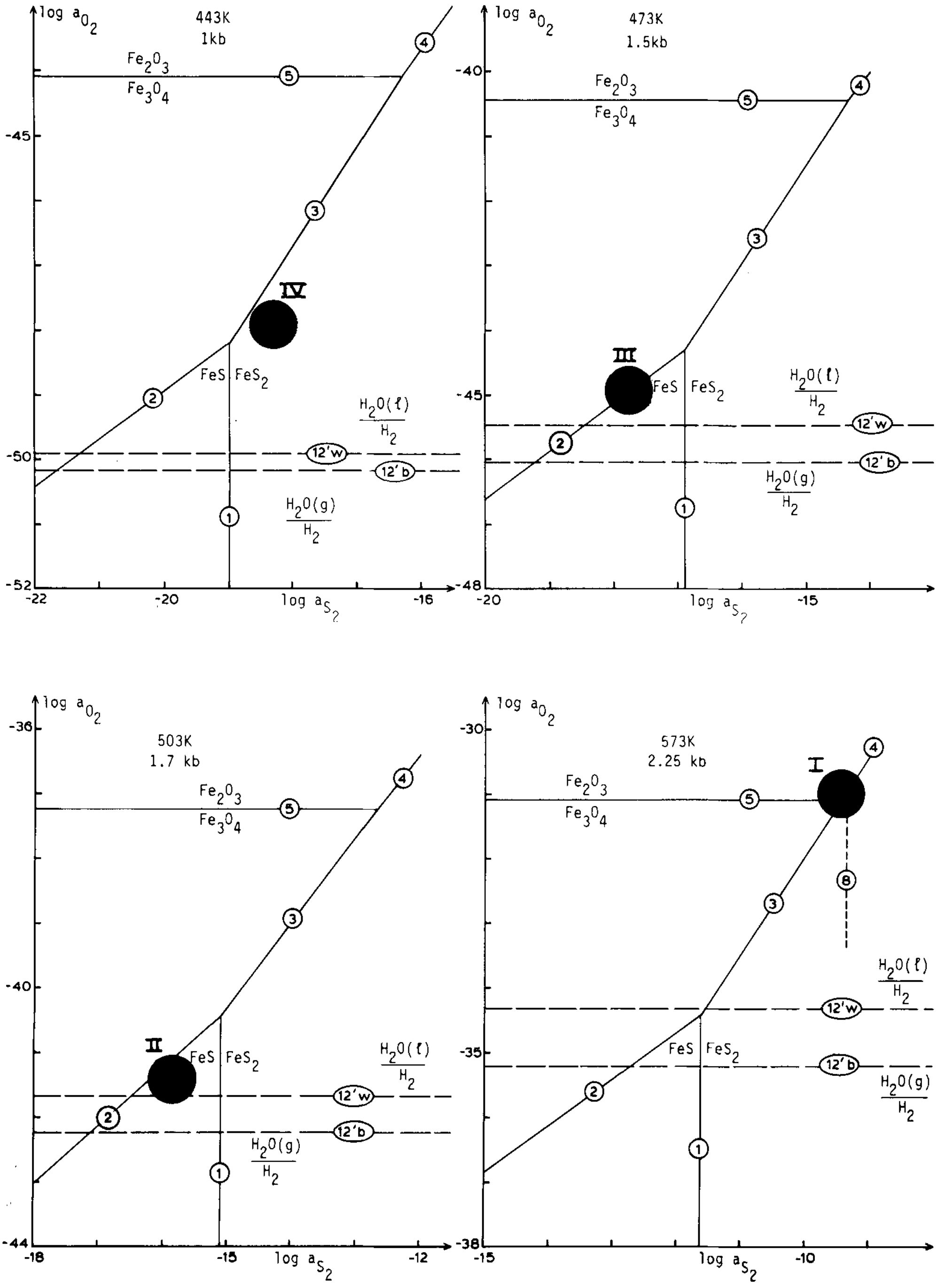

FIG. 1. Log a_{O_2}–log a_{S_2} diagrams at various temperatures and pressures for the Fe–S–O–H_2 system. Numbers marked on the lines are the same as the numbers of reactions in Table II. I, II, III, and IV show the probable calculated conditions of the mineral assemblages at Hällefors during the mineralization process.

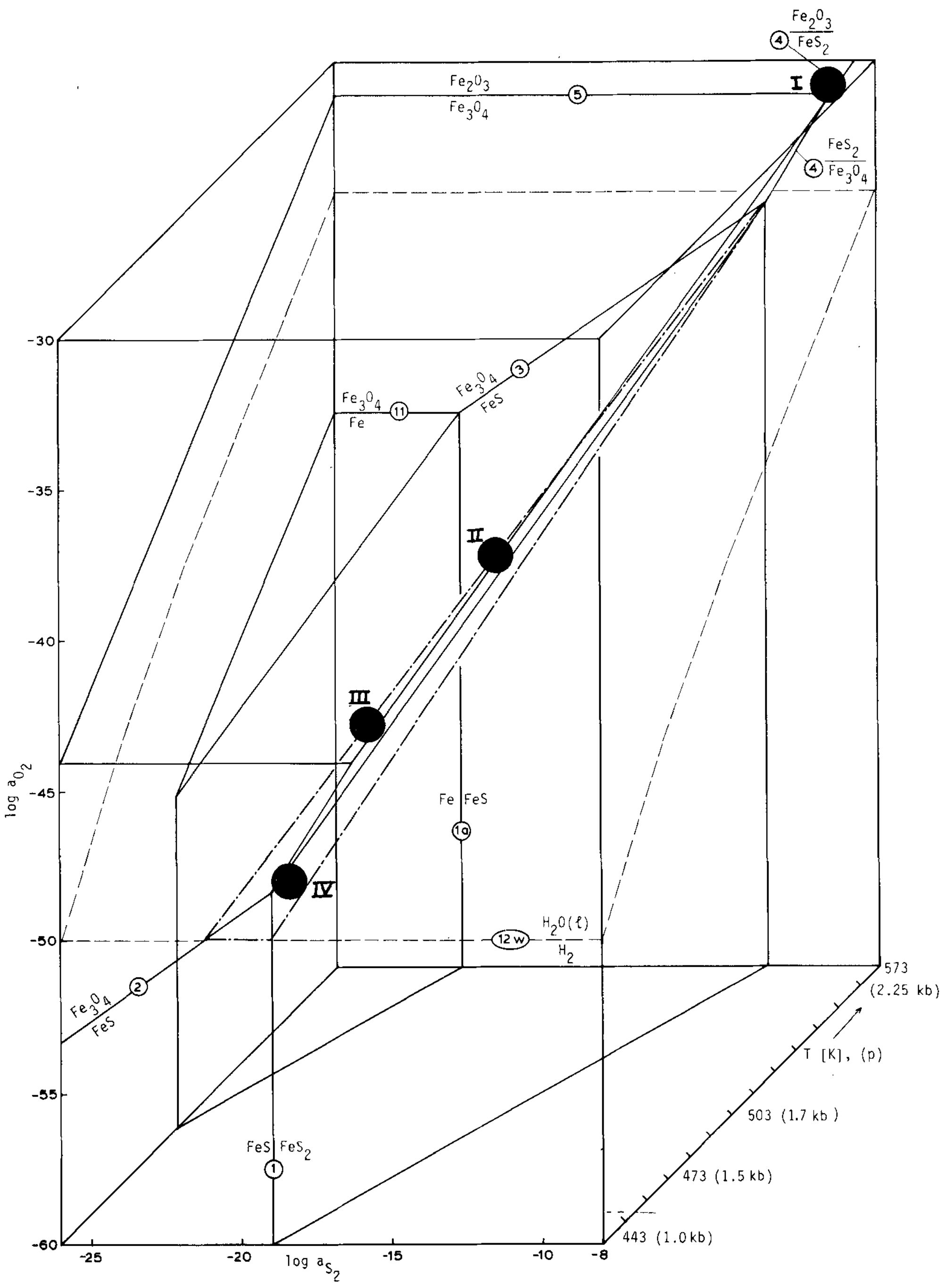

FIG. 2. Log a_{S_2}-log a_{O_2}-T diagram for the Fe-O-S-H_2 system. Other symbols as in fig. 3.

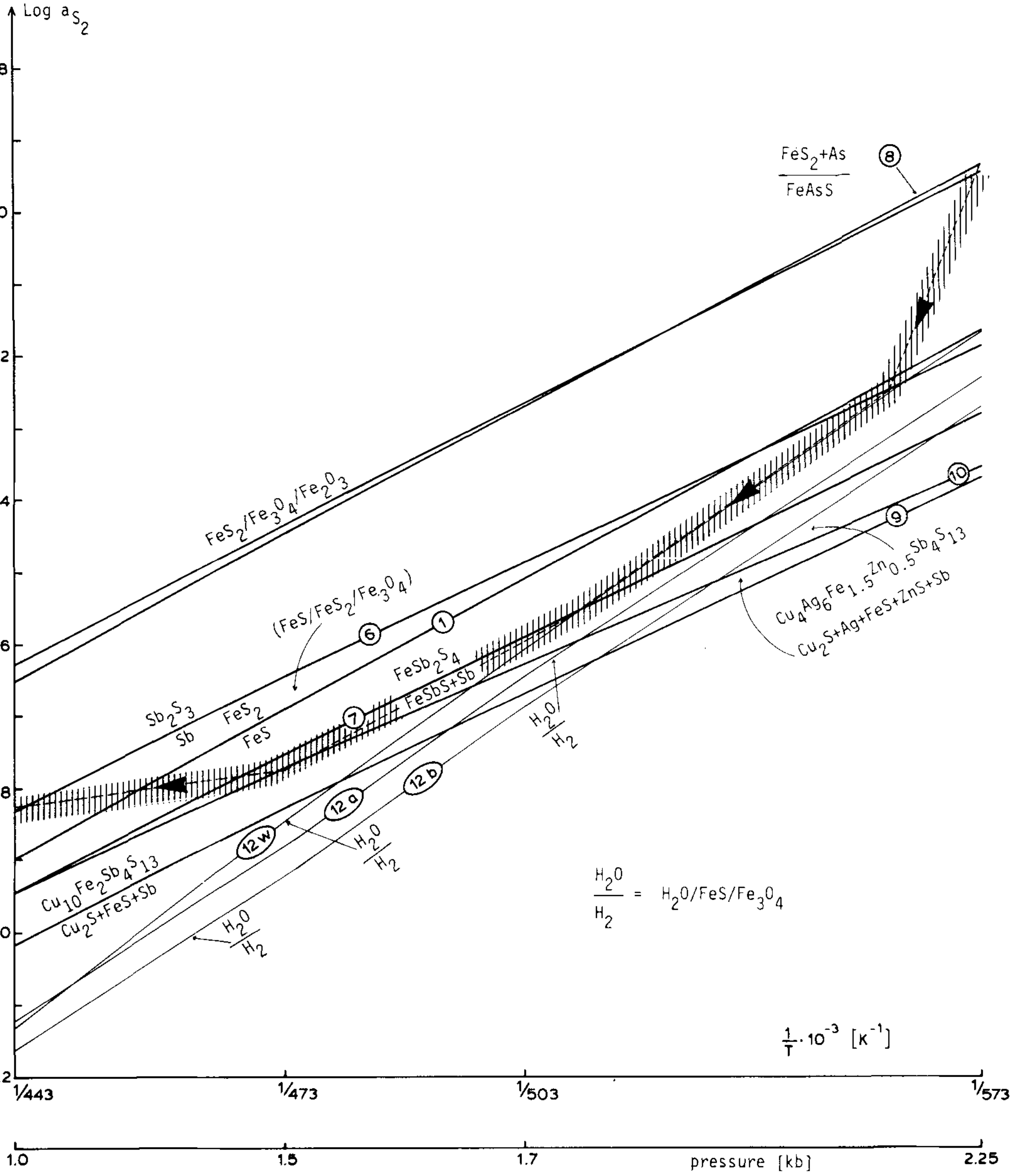

FIG. 3. Log a_{S_2}-$1/T$ diagram. Dashed line—the path showing probable changes in the chemistry of metal-bearing fluids; solid lines—the lower limits of aqueous fluid (12a: $X_{H_2O} = 1$; 12b: $X_{H_2O} = 0.7$) and water (12w). Numbers marked on the lines are the same as the numbers of reactions in Table II. The FeS_2-FeS-Fe_3O_4 and FeS_2-Fe_3O_4-Fe_2O_3 curves are defined by the sets of log a_{S_2} and log a_{O_2} values for the intersection points of the curves numbered 1 and 2, and 3 and 5 respectively, on fig. 1.

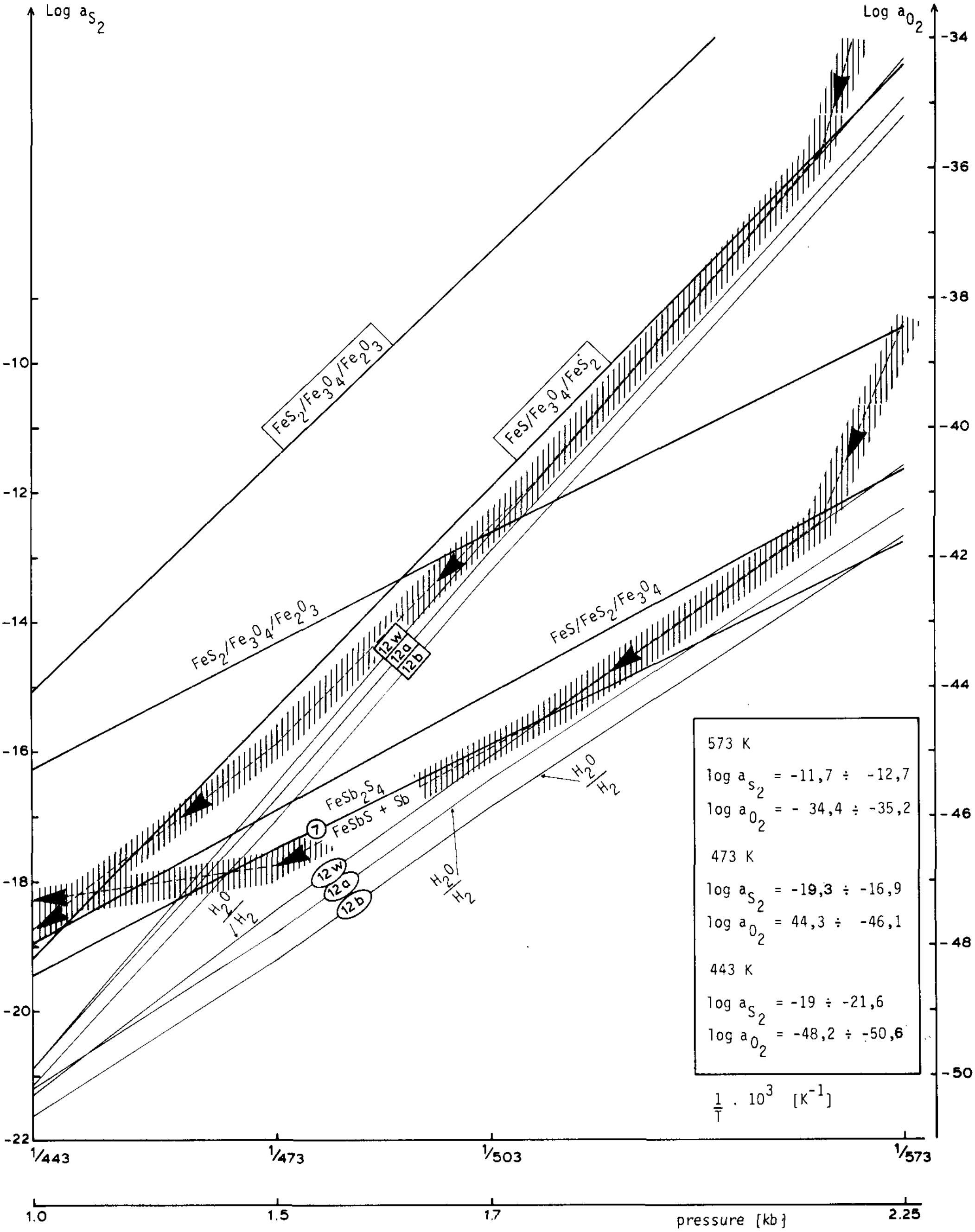

FIG. 4. A combined $\log a_{S_2}$–$1/T$ and $\log a_{O_2}$–$1/T$ diagram (numbers and symbols in rectangles) illustrating the determination of $\log a_{S_2}$ and $\log a_{O_2}$ ranges (see the inset) of sulphide and sulphosalt precipitation with pyrrhotite. Other symbols as in fig. 3.

the metamorphism of the meta-volcano-sedimentary sequence; and (iv) the enrichment in magnesium contained in sheridanite (the magnesium chlorite).

During the mixing stage the solution chemistry ($\log a_{O_2}$, $\log a_{S_2}$, pH, T, P, velocity of transport, etc.) would be changed not only due to mixing but also due to interactions with the surrounding rocks. In the Hällefors region the most important interactions between hydrothermal fluids and host rocks would have occurred along contacts with carbonates of the eastern part, and shales of the western area. The conditions of formation indicated by microscopic and thermal studies on samples from the Hällefors mines have been confirmed by the thermodynamic calculations presented here. Analysing $\log a_{O_2}$-$\log a_{S_2}$ diagrams (fig. 1), and the equations in Table II, it can be concluded that pyrite and automorphic arsenopyrite precipitated from an aqueous fluid under higher temperature regimes of about 573 K with $\log a_{S_2} < -9.3$ (below line 4). The values given by lines 3, 4, and 8 point to precipitation of arsenopyrite with pyrite and hematite, very close to the upper limit of the magnetite stability field (573 K, $\log a_{S_2} \sim -9.4$, $\log a_{O_2} \sim -31.1$). This could well explain the apparent antipathetic relationship between arsenopyrite and magnetite observed in this region of Bergslagen. During cooling, $\log a_{S_2}$ and $\log a_{O_2}$ decreased and precipitation of pyrrhotite took place (precipitation started under conditions when, with decreasing temperature, line 12′w covers the point of intersection of lines 1, 2, 3 which takes place for $\log a_{O_2} \leqslant -35.3$ and $\log a_{S_2} \leqslant -12.7$ on a $\log a_{O_2}$-$\log a_{S_2}$ diagram as on fig. 1 for $T \leqslant 562$ K). A further drop in temperature, with $\log a_{O_2}$ and $\log a_{S_2}$ below the values where pyrrhotite coexists with some sulphides and sulphosalts (Jasiński, 1983), then took place with conditions indicated by line 12 and the FeS-FeS_2-Fe_3O_4 lines (figs. 1-4). The beginning of gudmundite deposition may be characterized by $T < 510$ K, $\log a_{S_2} < -15.6$, $\log a_{O_2} < -40.8$. Occurrences of secondary pyrite, marcasite, and arsenopyrite could also be explained by a decrease in the steepness of the $\Delta \log a_{S_2}$-$\Delta 1/T \times 10^3$ gradient in the log a_{S_2}-$1/T$ diagram (fig. 3), underlining the existence of two phases of ore formation. The first phase over the T range 573-473 K would have been generally characterized by a higher $\Delta \log a_{S_2}$-$\Delta 1/T \times 10^3$ gradient (fig. 3) and by sulphide (pyrite, arsenopyrite, pyrrhotite, chalcopyrite) and some sulphosalt (tetrahedrite) formation. This stage is characterized by the formation of minerals the constituents of which are abundant in a chloride complex solution, and by strong sulphur consumption. The second stage, with a less steep $\Delta \log a_{S_2}$-$\Delta 1/T \times 10^3$ gradient and strong Sb consumption, would have been the stage of sulphosalt and secondary sulphide formation (FeS-FeS_2 line 1 is crossed once more).

One possible explanation for such a change in the $\Delta \log a_{S_2}$-$\Delta 1/T \times 10^3$ gradient could be the ore-forming solution coming into contact with carbonates in the eastern part of the Hällefors mines. Rapid cooling, a rise in pH, decrease in velocity of complex transport and the participation of carbonate-containing ligands in complexing processes would have caused a reconstruction of metal complexes and deposition of metal compounds. A second possible explanation for a change of complex stabilities and a phase of precipitation could be cooling and a release of pressure in an open fissure system of shales in the western part of the area.

As and Sb stages are clearly separated. The As stage is linked only to arsenopyrite formation while the Sb stage started with gudmundite and tetrahedrite precipitation.

These considerations confirm the author's conclusions in previous studies (Jasiński, 1983) that the proposed order of precipitation is: arsenopyrite, pyrite → pyrrhotite, chalcopyrite → sphalerite → gudmundite, galena → tetrahedrite → (meneghinite) → (bournonite) → freibergite → pyrargyrite → stephanite. This corresponds to precipitation from the systems: Fe-As-S, Fe-S → Cu-Fe-S → Zn-S, Pb-S, Fe-Sb-S → (Cu, Ag)-(Fe, Zn)-Sb-S, Cu-Pb-Sb-S → Pb-Sb-S → (Pb-Ag-Sb-S) → Ag-Sb-S.

Conclusions. Zakrzewski (1982) proposed a geochemical facies model to account for the distribution of different ore types at Hällefors relative to their position in the stratigraphy with oxide-silicate-carbonate and sulphide facies corresponding to levels in a Na-leptite-K-leptite-sediment sequence. He also proposed that all the ores had a common mafic volcanogenic origin. Oen *et al.* (1982) suggested that the ore deposits located in the Bergslagen Supracrustal Series were formed by exhalative-sedimentary and sea-floor hydrothermal processes related to both felsic and mafic magmatism, in connection with various stages of continental submarine rifting. Postrifting deformation, metamorphism and post-deformational recrystallization are considered to have modified these ores. The Hällefors silver mines deposit could be considered as consisting of an original volcanogenic-exhalative iron deposit, presumed to have contained dispersed amounts of Ag-Pb-Zn-(Cu), which was then affected by secondary remobilization and concentration of sulphides and sulphosalts.

Iron and other metals which occur in the Hällefors silver deposits were probably transported out of a volcanic system as a metalliferous brine of low alkaline pH and relatively high a_{S_2}. High density brines, discharged from fumarolic outlets in this manner may travel along the sea floor in a similar fashion to turbidity currents and may easily become trapped in sea-floor depressions. In such cases precipitation of hydrolitic metal compounds, in particular iron, could take place. Iron colloids with their large active surface area could be an adequate reservoir for adsorbed base metal ions. A reducing environment would have been possible in a depression if the brine which formed the Hällefors deposit was in contact with graphitic sediments of the Hällefors syncline. Initially this may have been insufficient to cause precipitation of all metals as sulphides; pyrite being the notable exception. During diagenesis, further reduction of SO_4^{2-} to S^{2-}, HS^- and H_2S, an increase of temperature and pressure enabled the remobilization of adsorbed ions to take place. Hydrolitic iron colloids could have been changed to hematite and then to magnetite when the oxygen fugacity was low enough. As a result of sedimentation of iron compounds and their subsequent diagenesis, a banded iron formation probably developed, this process accounting for the first stage of iron-ore formation of the Hällefors deposit. Temperature and pressure variations accompanying metamorphism would have caused the release of water from hydrated minerals and the remobilization of ions previously adsorbed on the surface of iron colloids. Crystallization of iron compounds from colloids together with recrystallization of other Fe-minerals and related magnetite formation would have caused a decrease in the active surface area and capacities of minerals for isomorphic substitution. Previously precipitated base metal compounds (e.g. sulphides) would then be dissolved. The final aqueous fluid would have been characterized by a relatively high concentration of reduced sulphur forms $[\Sigma S_r = \Sigma(H_2S + HS^- + S^{2-})]$ with a low $a_{SO_4^{2-}}/a_{\Sigma S_r}$ ratio and a weakly acidic or neutral pH. The pH could have been changed to higher values due to interaction with carbonates such as those in the eastern part of the Hällefors mines. Recent studies of Baker and de Groot (1983) on Mg-chlorite formation in neighbouring regions point to mixing of the metahydrothermal fluid described above with sea water, bringing about an increase in a_{O_2}, $a_{\Sigma S}(\Sigma S = S_r + SO_4^{2-})$, a_{Cl^-}, $a_{Mg^{2+}}$, a_{Na^+} and a decrease in T, P, and pH or, where the fluid came in contact with carbonate, stabilization of pH. Coolen's (pers. comm.) fluid inclusion studies indicate the presence of chlorides in fluid inclusions in minerals from the Hällefors mines suggesting that metal ions were probably transported mainly as chloride complexes.

In this way, metalliferous fluids ran westwards following the pressure gradient in the Hällefors silver mines area, profiting from fissure systems, and finally metals were precipitated due to changes of T, P, pH, $a_{\Sigma S}$, transport velocity or metal complexing forms. These changes may have resulted from the interaction of high-temperature, acidic, chloride-complex-bearing fluids, transported relatively fast via fissures, with carbonates (lacking such fissures) from the eastern sector. Due to the drop in temperature and increase of pH, much slower velocity of transport and higher activities of S^{2-} and HS^- at the expense of H_2S, precipitation of iron and other metal sulphides (together with some sulphosalts) took place. Some ions were probably transported further westwards not only as chlorides but also hydroxyl and carbonate complexes (which are less stable, and of lower mobility). When the solutions reached the cracked hälleflintas and the slate zone in the western part of the area, sulphides and sulphosalts were deposited, mainly due to a drop in temperature and pressure in an open fissure system.

In the overall process, two stages can be distinguished. The first one is characterized by higher temperatures 573–473 K and higher $\Delta \log a_{S_2}$–$\Delta 1/T \times 10^3$ gradients, resulting mainly in sulphide and, to a lesser extent, sulphosalt precipitation. The mineral succession for this stage is as follows: arsenopyrite ($T > 573$ K, $\log a_{S_2} < -9.3$, $\log a_{O_2} < -30.9$, pyrite → pyrrhotite ($T < 562$ K, $\log a_{S_2} < -12.7$, $\log a_{O_2} < -35.3$), chalcopyrite → sphalerite → gudmundite ($T < 510$ K, $\log a_{S_2} < -15.6$, $\log a_{O_2} < -40.8$), galena → tetrahedrite.

The second stage is characterized by lower temperatures ($T < 473$ K) and lower $\Delta \log a_{S_2}$–$\Delta 1/T \times 10^3$ gradients, and mainly sulphosalt precipitation (Jasiński, 1983).

Acknowledgements. I am indebted to Drs D. J. Vaughan, J. H. Baker, E. A. J. Burke, and M. A. Zakrzewski for their helpful suggestions and critical reading of the manuscript.

REFERENCES

Baker, J. H., and de Groot, P. A. (1983) *Contrib. Mineral. Petrol.* **82,** 119–30.

Craig, J. R., and Barton, P. B. (1973) *Econ. Geol.* **68,** 493–506.

Garrels, R. M., and Christ, C. L. (1965) *Solutions, Minerals and Equilibria*, Harper and Row, 450 pp.

Helgeson, H. C., and Kirkham, D. H. (1974) *Am. J. Sci.* **274,** 1089–261.

——Delany, J. M., Nesbitt, H. W., and Bird, D. K. (1978) Ibid. **278-A,** 229 pp.

Hellingwerf, R. H. (1984) *Econ. Geol.* **79,** 696–715.

Hutchison, M. N., and Scott, S. D. (1980) *Norges Geol. Unders.* **360,** 59–71.

Jasiński, A. W. (1983) *Mineral. Mag.* **47,** 507–14.

Kalogeropulos, S. J. (1983) *Neues Jahrb. Mineral. Monatsh.* 89-96.

Large, R. R. (1977) *Econ. Geol.* **72,** 549-72.

Moorman, A. C., Andriessen, P. A. M., Boelrijk, N. A. J., Hebeda, E. H., Oen, J. S., Priem, H. N. A., Verdurmen, E. A. T., Verschure, R. H., and Wiklander, U. (1982) *Geol. För. Förh.* **104,** 1-9.

Nugteren, H. W. (1978) *The silver mines of Hällefors, Central Sweden.* M.Sc. thesis, Free University of Amsterdam.

—— and Zakrzewski, M. A. (1984) *Can. Mineral.* in press.

Oen, J. S., Helmers, H., Verschure, R. H., and Wiklander, U. (1982) *Geol. Rund.* **71,** 182-94.

Robie, R. A., Hemingway, B. S., and Fischer, J. R. (1978) *U.S. Geol. Survey Bull.* no. 1452, 456 pp.

Seyfried, W. E., and Mottle, M. J. (1982) *Geochim. Cosmochim. Acta,* **46,** 985-1002.

Sundius, N. (1923) *Sver. Geol. Undersökning,* ser. C, **312,** 354 pp.

—— Parwel, A., and Rajandi, B. (1966) Ibid. **614,** 20 pp.

Tegengren, F. (1924) Ibid. ser. Ca, **17,** 406 pp.

Vaughan, D. J., and Craig, J. R. (1978) *Mineral chemistry of metal sulfides,* Cambr. Univ. Press, 493 pp.

Welin, E., Wiklander, U., and Kähr, A. M. (1981) *Geol. För. Förh.* **102,** 269-72.

Zakrzewski, M. A. (1982) *Geol. Rund.* **71,** 195-205.

[*Manuscript received 15 November 1984;
revised 28 May 1985*]