

# Indium-bearing chalcopyrite and sphalerite from the Gåsborn area, West Bergslagen, central Sweden

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## Abstract

In the Gåsborn area, West Bergslagen, central Sweden, Fe-rich, indium-bearing (0.1–2.0 wt.% In) sphalerite is replaced by Fe-poor sphalerite containing minute inclusions of chalcopyrite, roquesite and an unnamed In–Zn-rich phase. Fe-rich, In-bearing sphalerite is primary; indium occurs as a roquesite molecule in solid solution. Fe-poor sphalerite, roquesite, chalcopyrite and the unnamed In–Zn-rich phase were formed from In-bearing sphalerite by secondary processes, characterized by the so-called ‘chalcopyrite disease’.

**KEYWORDS:** sphalerite, indium, chalcopyrite disease, Gåsborn, Sweden.

## Introduction and geological setting

INDIUM-bearing sphalerite associated with roquesite and In-bearing stannite or sakuraiite has previously been described from only a few localities (Kato and Shinohara, 1968; Sutherland and Boorman, 1969; Oen *et al.*, 1980; Burke and Kieft, 1980; Shimizu *et al.*, 1986; Johan, 1988). This paper describes the petrogenesis of a new occurrence. Evidence is presented that secondary processes, such as those associated with the formation of ‘chalcopyrite disease’ (Barton and Bethke, 1987; Eldridge *et al.*, 1988), were responsible for the transformation of In-bearing, Fe-rich sphalerite, containing up to 3.3 mole % roquesite in solid solution, into a mixture of Fe-poor sphalerite, chalcopyrite, roquesite and an unnamed In–Zn-rich phase. Moreover, an unnamed mineral of the kesterite–sakuraiite series was formed by exsolution from chalcopyrite.

The volcano–sedimentary sequence in the Gåsborn area consists of acid metavolcanics with intercalated marbles, metacherts, metamorphosed basic lavas and a metamorphosed manganeseiferous iron ore horizon (Damman, 1988*a*), belonging to the upper leptite and slate group of the Bergslagen supracrustal series (Oen *et al.*, 1982; Oen, 1987). During their deposition these rocks have been intruded by the Ostra Höjden granite (Damman, 1988*b* (Fig. 1); Damman, 1989) of the Bergslagen older granite suite (Åberg *et al.*, 1983 *a,b*; Oen *et al.*, 1984; Baker, 1985).

Under the influence of hydrothermal fluids associated with the Ostra Höjden granite, marbles are locally altered into pyroxene–garnet skarns, containing minor sphalerite, scheelite, molybdenite, Pb–Bi–Ag- and Pb–Bi–Cu-sulphosalts, galena, cassiterite, arsenopyrite, löllingite, pyrrhotite, chalcopyrite, pyrite, cubanite, native Pb, native Bi, and native Sn (Damman and Kieft, 1989).

## Description of sphalerite and associated minerals

Two types of sphalerite occur in skarns in the Gåsborn area: In-poor (<0.1 wt.% In) and In-bearing (0.1–2.0 wt.% In) sphalerite. The In-poor type occurs in skarns from the outer parts of the Gåsborn area; the In-bearing type only occurs in skarns in the area of hydrothermal veining associated with the Ostra Höjden granite, (Fig. 1 in Damman, 1988*b*; Damman and Kieft, 1989).

Indium-poor sphalerite is dark-reddish brown in transmitted light. It is characterized by high contents of Fe (up to 13 wt.%), variable Cd contents (0.1–5.0 wt.%) and minor Mn (up to 0.6 wt.%) (Table 1*a*). In-poor sphalerite is locally rimmed by a mantle of an opaque sphalerite, showing a weak abnormal anisotropism, which is crowded with minute (<5 µm) chalcopyrite inclusions. Chemical analyses from core and rim show that the Fe, Cd and Mn contents decrease and the Cu content increases from core to rim (Table 1 *a,b*). In-poor sphalerite is frequently surrounded by large chalcopyrite crystals, suggesting

Table 1. Compositions of sphalerite in wt.%, atomic ratios and molecular percentages  
 a) Da 368-primary sphalerite; b) Da 368-altered sphalerite; c, d) St 188II-1-primary In-bearing sphalerite; e-j) St188II-1, In-, Cu-enriched altered sphalerite

	a	b	c	d	e	f	g	h	i	j
S	33.10	32.76	33.00	32.40	32.30	31.55	31.78	31.81	30.91	30.00
Mn	0.08	0.02	0.44	0.20	0.12	0.03	-	-	-	-
Fe	9.70	5.45	11.68	11.45	6.77	6.74	7.07	7.54	7.64	7.46
Cu	0.54	5.40	1.04	2.06	7.31	9.27	11.33	12.31	15.02	15.22
In	<0.05	<0.05	0.50	1.92	2.16	4.53	8.02	9.34	14.38	15.43
Zn	55.04	54.65	50.86	49.30	48.30	44.65	39.54	37.47	29.84	28.68
Cd	1.12	0.61	2.01	2.29	2.04	2.35	2.14	2.21	1.88	1.99
Ag	-	-	-	-	0.39	0.40	0.22	0.40	0.55	0.79
Total	99.59	98.92	99.53	99.62	99.39	99.52	100.10	101.08	100.22	99.57
Atomic ratios										
Mn	0.15	<0.05	0.80	0.35	0.20	0.05	-	-	-	-
Fe	16.80	9.50	20.25	20.00	11.95	12.05	12.30	13.40	14.00	13.75
Cu	0.80	8.30	1.60	3.15	11.15	14.10	17.90	19.25	24.20	24.65
Zn	81.30	81.60	75.10	72.85	72.70	67.50	60.70	56.95	46.75	45.20
Cd	0.95	0.55	1.75	2.05	1.80	2.05	1.90	1.95	1.70	1.80
In	<0.05	<0.05	0.50	1.60	1.85	3.90	7.00	8.10	12.80	13.85
Ag	-	-	-	-	0.35	0.35	0.20	0.35	0.55	0.75
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Molecular percentages										
2 x CuInS <sub>2</sub>	-	-	1.0	3.2	3.7	7.8	14.0	16.2	25.6	27.7
2 x CuFeS <sub>2</sub>	1.6	16.6	2.2	3.1	19.3	21.1	22.2	23.0	23.9	23.1
ZnS	98.4	83.4	96.8	93.7	77.0	71.1	63.8	60.8	50.5	49.2
FeS	16.3	1.4	19.5	20.7	3.0	2.1	2.0	3.1	4.0	4.5
in sphal.										

Instrument: Cambridge Instrument Microscan IX.

Operating Conditions: Acceleration voltage 15 kV; current on faraday cage 40 nA.

Standards: ZnS (Zn, S), FeS (Fe, S), rhodonite (Mn), chalcocopyrite (Cu, S), CdS (Cd) and InSe (In).

ZAF program: online.

that sphalerite formation was followed by that of chalcocopyrite. Chalcocopyrite contains minute, occasionally star-shaped exsolution bodies of sphalerite.

Indium-bearing sphalerite is also dark-reddish brown in transmitted light and contains minute (<5 $\mu$ m) inclusions of chalcocopyrite. The composition of In-bearing sphalerite (Table 1 c, d) is similar to that of In-poor sphalerite (Table 1a), apart from higher contents of In and Cu. These two elements are present in amounts up to 2 wt.% (Table 1 c, d). Fig. 1 shows the relation between In, Cu, Fe and Zn (Fig. 1, left side). There is a positive correlation between In and Cu, commonly with an excess of Cu above the atomic ratio Cu/In = 1:1. There is no apparent relationship between In and Fe; however, a slight negative correlation between In and the irregular Mn content exists (Table 1), suggesting that the solubility of In in sphalerite is hampered by the presence of Mn.

Along its outer rim and along cracks In-bearing sphalerite is replaced by an opaque black mass, consisting of sphalerite, crowded with minute inclusions of other phases. These phases are too small for quantitative analysis. Therefore, an

attempt was made to characterize them by bulk chemical analysis of the host sphalerite together with its inclusions. One rim contains between 2 and 16 wt.% In (Table 1, e-j). In this rim, In shows a positive correlation with Cu (Johan, 1988), while Cu shows a negative correlation with Zn (Fig. 1). The Fe content remains approximately constant (Fig. 1), but there is clearly less Fe than in In-bearing sphalerite. The Cd content is about the same as in the In-bearing type (compare analyses c and d with e-j, Table 1). Ag, which was not detected in In-bearing sphalerite, occurs in amounts up to 1 wt.% (Table 1, e-j).

The above data indicate that the obtained analyses most probably correspond to a mixture of chalcocopyrite, Fe-poor sphalerite and roquesite (Table 1, e-j).

In another grain the X-ray image shows that chalcocopyrite inclusions in Fe-poor sphalerite are intergrown with an unidentifiable In-Zn-rich phase of <2 $\mu$ m diameter.

Indium-bearing sphalerite, similar to In-poor sphalerite, is frequently surrounded by large chalcocopyrite crystals. This chalcocopyrite contains small amounts of In (up to 0.09 wt.%) and Ag (up to 0.03 wt.%), and also small elongate In- and Zn-

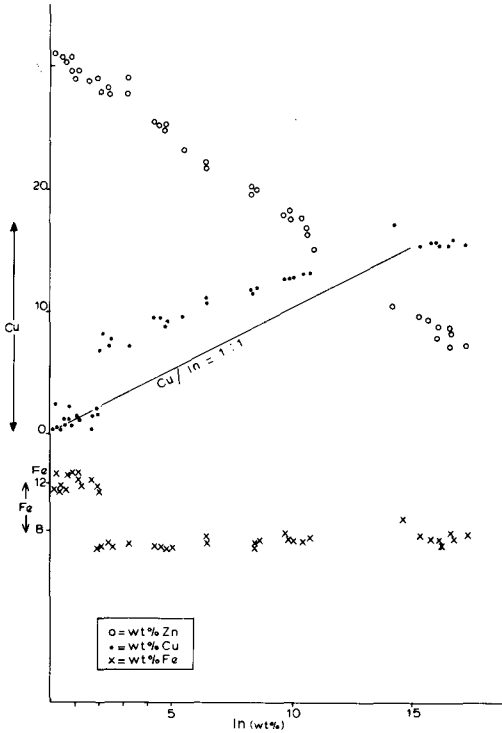


FIG. 1. Relationships of wt.% In with Zn, Cu and Fe in Fe-rich sphalerite and In- and Cu-enriched sphalerite. Open circles—wt.% Zn; closed circles—wt.% Cu; crosses—wt.% Fe.

rich inclusions. The dimensions of these inclusions are too small for quantitative analyses; compositions obtained correspond to mixtures of chalcopyrite and the In-Zn-rich phase. In order to avoid inaccuracies, only 2 elements, one on each spectrometer, were measured in one determination. Special attention was given to the element pairs In-Cu, In-Fe and In-Zn. From the analyses presented in Fig. 2 it is evident that 2 Fe + 1 Cu (both from chalcopyrite) are approximately replaced by 2 Zn + 1 In, suggesting that the In-Zn phase is about  $CuZn_2InS_4$ , the end-member of the series kesterite  $[Cu_2(Zn,Fe)SnS_4]$ -sakuraiite  $[(Cu,Fe,Zn)_3(In,Sn)S_4]$  (Shimizu *et al.*, 1986) or  $(Cu,Fe,Zn,In,Sn)_4S_4$  (Kissin and Owens, 1986)— $Cu_1(Zn \gg Fe)_2In_1S_4$ . This phase with a small content of Fe substituting for Zn, has also been described by Ohta (1980, 1983).

In several samples chalcopyrite shows characteristic intergrowths with secondary pyrite, marcasite and/or Fe-hydroxides, suggesting replacement of the chalcopyrite. Minute In concentrations, apparently S-free, are found together with pyrite, marcasite and Fe-hydroxides.

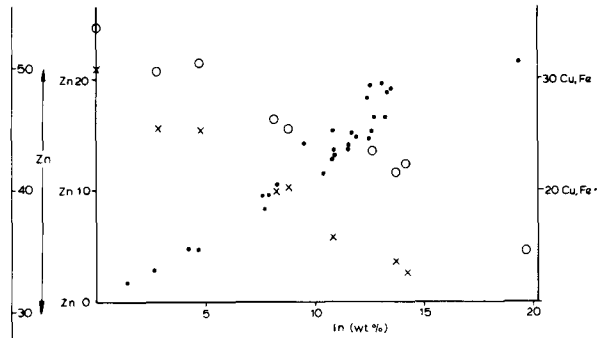


FIG. 2. In- and Zn-rich inclusions in chalcopyrite. Partial analyses (in wt.%) of In-Zn, In-Cu and In-Fe pairs; closed circles—In-Zn; open circles—In-Cu; crosses—In-Fe.

Discussion

Data presented in this paper show that Fe-rich, In-bearing sphalerite is replaced by a mixture of Fe-poor sphalerite, chalcopyrite, roquesite and an unnamed In-Zn-rich phase. Microscopic observations and analyses by electron microprobe show that chalcopyrite is present as small inclusions in Fe-rich, In-bearing sphalerite, but there is no separate In-rich phase visible, suggesting that roquesite most probably occurs in solid solution in Fe-rich sphalerite (Johan, 1988). The fact that Fe-rich sphalerite contains <2wt.% In (=3.3 mole % roquesite; Table 1d), suggests that 2wt.% In is likely to be the upper limit of solubility of In in Fe-rich sphalerite.

The change from Fe-rich, In-bearing- to Fe-poor sphalerite, chalcopyrite, roquesite and the In-Zn-rich phase is characterized by a strong decrease in Fe-content and a strong increase in Cu- and In-contents (compare Table 1, c, d with Table 1, e-g). This suggests that the formation of chalcopyrite, roquesite and the unnamed In-Zn-rich phase may be due to the so-called chalcopyrite 'disease' (Barton and Bethke, 1987; Eldridge *et al.*, 1988), caused by introduction of Cu from later hydrothermal solutions from which chalcopyrite surrounding the In-bearing sphalerite was deposited as well. This chalcopyrite locally contains small amounts of In and Ag and small exsolution bodies of an In, Zn-rich phase, suggesting that some In, Zn and Ag may at one time have been present in solid solution.

In-poor, Fe-rich sphalerite (Table 1a) is locally mantled by opaque In-poor, Cu-rich material, consisting of Fe-poor sphalerite and fine chalco-

pyrite inclusions (Table 1*b*), suggesting a mode of formation by chalcopyrite disease similar to that proposed for the replacement of In-bearing sphalerite.

Pyrite, marcasite and/or Fe-hydroxides that were formed after sphalerite and chalcopyrite occur together with small amounts of an S-free, In-rich phase, suggesting that this phase is formed during alteration of sphalerite and chalcopyrite.

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