SPHALERITE AND ARSENOPYRITE AT THE BRUNSWICK NO. 12 MASSIVE-SULFIDE DEPOSIT, BATHURST CAMP, NEW BRUNSWICK: CONSTRAINTS ON P–T EVOLUTION

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Abstract

Sphalerite and arsenopyrite from a transposed and recrystallized feeder stockwork to the Brunswick No. 12 massive-sulfide deposit, in the Bathurst camp of northern New Brunswick, are typically associated with an assemblage of pyrite, pyrrhotite, chalcopyrite, quartz, and Fe-rich chlorite. Textural and compositional analyses of sphalerite and arsenopyrite enclosed in metamorphic pyrite coexisting with pyrrhotite indicate a significant variation in syngenetic through to early D_1/M_1 pressures and temperatures. The X_{FeS} of sphalerite, ranging between 11.4 and 15.2 mole %, is consistent with pressures of 770 to 440 MPa, which is interpreted as peak to late-D_1 pressure, respectively. The local preservation of skeletal arsenopyrite–pyrite intergrowths, discrete zoning in some arsenopyrite crystals, together with a high As:S ratio (31.5 to 33.9 atom % As; 375–475°C), and high Co (0.5 to 10 atom %) and Ni (0.1 to 1.4 atom %) in the intermediate to core zone of many arsenopyrite crystals, could reflect subseafloor epigenetic conditions. Recrystallization during metamorphism yields a lower As:S ratio (29 to nearly 32 atom % As; <425°C) and usually lower Ni and Co contents in arsenopyrite. The compositional variation in sphalerite and arsenopyrite is consistent with evidence of varying degrees of textural preservation and local compositional re-equilibration during a complex P–T metamorphic evolution.

Keywords: sphalerite, arsenopyrite, textural relics, compositional re-equilibration, Bathurst No. 12 deposit, Bathurst camp, New Brunswick.

Sommaire

La sphalérite et l'arsénopyrite d'un système hydrothermal nourricier associé au gisement de sulfures massifs de Brunswick No. 12 (camp minier de Bathurst, Nouveau-Brunswick), maintenant transposé et recristallisé, sont typiquement associées à un assemblage de pyrite, pyrrhotite, chalcopyrite, quartz, et une chlorite ferrifère. Les résultats d'analyses texturales et chimiques de la sphalérite et l'arsénopyrite incluses dans la pyrite métamorphique en coexistence avec la pyrrhotite indiquent une variation importante en pression entre les conditions épigénétiques, précoces, et celles de la recristallisation au début de l'événement D_1/M_1. La teneur de la sphalérite en X_{FeS}, variant entre 11.4 et 15.2% (base molaire), concorde avec une pression de 770 à 440 MPa, qui représenterait la pression maximale et la pression à un stade tardif de l'événement D_1, respectivement. La préservation locale d'une intercroissance squelettique d'arsénopyrite et de pyrite, une zonation claire dans certains cristaux d'arsénopyrite, ainsi qu'un rapport As:S élevé (entre 31.5 et 33.9% As, base d'atomes; 375–475°C), et des teneurs élevées en Co (entre 0.5 et 10%) et Ni (entre 0.1 et 1.4%) dans la zone intermédiaire ou centrale de plusieurs cristaux d'arsénopyrite, pourrait bien témoigner de conditions épigénétiques dans le socle sub-océanique. La recristallisation au cours du métamorphisme a mené à une réduction du rapport As:S (dans l'intervalle de 29 à presque 32% As; <425°C) et, en général, une diminution des teneurs en Ni et en Co de l'arsénopyrite. La variation en composition de la sphalérite et de l'arsénopyrite concorde avec les degrés variables de préservation texturale et de ré-équilibrage local en composition au cours de l'évolution métamorphique complexe en termes des conditions P–T.

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Mots-clés: sphalérite, arsénopyrite, reliques texturales, ré-équilibrage des compositions, gisement Bathurst No. 12, camp minier de Bathurst, Nouveau-Brunswick.

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INTRODUCTION

The Brunswick No. 6 and 12 deposits are large Cu–Pb–Zn–Ag massive-sulfide deposits (12 Mt and 137 Mt, respectively, averaging 13% combined Zn+Pb+Cu+Ag) in the Bathurst Camp, New Brunswick (Lentz 1999a); the deposits are interpreted as being synvolcanic and exhalative. These deposits have well-developed cogenetic stringer-sulfide stockwork systems formed beneath the basal copper-rich massive zones (Luff *et al.* 1992), which supports a proximal, autochthonous accumulation of sulfides (Jambor 1979, Luff *et al.* 1992). Intense deformation of these deposits has obliterated many of the primary features, particularly within the massive-sulfide bodies (van Staal & Williams 1984, van Staal 1985, Lentz & van Staal 1995), such that little is known about the primary conditions under which they formed.

Although the overall layering in both these deposits and associated capping and laterally extensive iron formation are consistent with an exhalative origin, the mesoscopic and microscopic layering is, for the most part, tectonically and metamorphically enhanced (van Staal 1985). There is also considerable thickening of the massive sulfides in the hinge zones of F_1 and F_2 folds, with extensive thinning on the limbs and considerable transposition of the stockwork veins parallel to the composite S_1S_2 fabric (Lentz 1999b). Coincident with the deformation, multiple stages of metamorphic growth and cataclastic deformation affected the massive-sulfide bodies, which is particularly evident from morphology and zoning of pyrite and arsenopyrite.

This study of sphalerite and arsenopyrite focuses mainly on the epigenetic stockwork of sulfide veins at this deposit, although several massive-sulfide samples were included. The mineralogy is dominated by pyrite, pyrrhotite, quartz, and chlorite, with subordinate sphalerite, chalcopyrite, arsenopyrite, galena, and siderite (Luff *et al.* 1992). The S buffer assemblage, pyrite and pyrrhotite, associated with arsenopyrite and sphalerite in the stockwork zone, allows P and T to be characterized. The apparent preservation of primary vein textures within competent silicified zones thus allows assessment of the relationships among sulfide veins, host rock, and tectonic elements of the fabric. Near the Brunswick deposits, the rocks have undergone conditions of middle to upper greenschist-grade regional metamorphism (M_1 and M_2), involving a fairly high pressure (700 to 1000 MPa), an inference based on the development of D_1 blueschists approximately 7 km west of the orebodies, between the Tetagouche Group and the Fournier Group (van Staal *et al.* 1990, Currie & van Staal 1999).

ANALYTICAL METHODS

Chemical analyses of sulfides for As, S, Fe, Co, Ni, Sb, Cu, and Zn were made at the Geological Survey of Canada using a Cameca SX50 electron microprobe (wavelength-dispersion spectrometry) at an accelerating voltage of 15 kV and a beam current of 30 μA, with 10-s integration times. Natural arsenopyrite, löllingite, pyrite, and sphalerite were used as As, S, Fe, and Zn standards, and synthetic sulfides were used for the other metals, with data manipulated using the SESULF program. The complete set of data acquired can be obtained from the Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Ontario K1A 0S2, Canada.

SULFIDE PETROLOGY

Sampling and analysis

Stockwork sulfide veins were sampled mostly from diamond drill holes (A1 and A3) and a few from the underground workings at Brunswick No. 12, particularly the 850 and 475 m levels, with a few additional samples from Brunswick No. 6 and Austin Brook deposits. The samples usually have some evidence of F_1 or F_2 folding of the veins or transposition into the S_1 fabric, in order to establish conditions as early as possible in the deposit (van Staal 1985). The sulfide vein relationships are consistent with a primary origin and have some evidence of mylonitic quartz ribbons within the stringer veins, indicating that they were probably pre-D_1 deformation. Preservation of the irregular nature of the stockwork veins within competent silicified and chloritic altered footwall rocks is not uncommon with veins up to 20 cm wide (Fig. 1).

Background information

The composition of sphalerite (Scott & Barnes 1971, Scott 1973, 1983, Lusk & Ford 1978, Hutchinson & Scott 1981, Lusk *et al.* 1993) and arsenopyrite (Clark 1960, Kretschmar & Scott 1976, Scott 1983, Sharp *et al.* 1985) coexisting with pyrite and pyrrhotite can shed light on the conditions of formation or metamorphism of undeformed or deformed hydrothermal systems. The idioblastic morphology and refractory nature of arsenopyrite and pyrite may be retained even under upper greenschist conditions (Scott 1983, Sharp *et al.* 1985, Craig & Vokes 1992).

As suggested by Hutchinson & Scott (1981), Scott (1983), and Sundblad *et al.* (1984), textural and intermineral relationships were considered in the selection of sphalerite and arsenopyrite phases for chemical analysis. The ductile sulfides (pyrrhotite, chalcopyrite, sphalerite, and galena) and silicates (chlorite and quartz) have been remobilized and recrystallized to variable degrees in the veins during the prograde and early retrograde dynamic metamorphism (Kalliokoski 1961, van Staal & Williams 1984, van Staal 1985), as well as locally during the latest very low-grade events involving dynamic strain.

FIG. 1.   Anastomosing stockwork containing the assemblage pyrite – pyrrhotite – sphalerite – chalcopyrite (± quartz), hosted in chloritic footwall metasedimentary rocks parallel to the S_1S_2 foliation at the southwestern end of the Brunswick No. 12 deposit (475 m level) (sample LPA–262). Coarse-grained pyrite porphyroblasts are hosted in a pyrrhotite-rich matrix. The composite S_1S_2 fabric is almost parallel to the face.

Sphalerite

The sphalerite compositions presented in this study were obtained to assess the general "locked-in" pressure conditions for these deposits. Sphalerite is generally free of fine-grained chalcopyrite inclusions, but locally is fractured and hosts ductile sulfides. Within the deposit, rotated pyrite porphyroblasts are recognized (van Staal 1985), indicating the variability in grain-size (from a few millimeters to several centimeters) resulting from growth and cataclasis, with infillings or pressure shadows of the ductile sulfide phases, such as pyrrhotite, chalcopyrite, and lesser proportions of sphalerite and galena. For the most part, primary variations in the $f(S_2)$ recorded in sphalerite have been destroyed during metamorphism; the presence of pyrite or pyrrhotite (or both) may not be reliable, as dynamic metamorphism has mechanically mixed these phases. The mole fraction of FeS, X_{FeS}, in sphalerite coexisting with hexagonal pyrrhotite, which would have been the dominant pyrrhotite phase during conditions of higher-grade metamorphism (>300°C), and pyrite, readily changes in response to pressure so long as the diffusion rate is high enough to facilitate re-equilibration to prevailing local P–T conditions of metamorphism. The diffusion of iron in sphalerite should be sufficiently high to approach equilibrium during prograde metamorphism (high T), although more sluggish on the retrograde P–T path (low T) (Mizuta 1988). This is an important factor

in estimating the peak conditions of pressure that should have been preserved near the peak conditions of temperature. If retrograde metamorphic equilibration proceeded below 300°C, the change from disordered to ordered hexagonal pyrrhotite could affect the calculated temperatures (Scott 1983). The formation of monoclinic pyrrhotite can have a profound affect in decreasing the X_{FeS} content of sphalerite (Scott & Kissin 1973, Lusk *et al.* 1993). Therefore, sphalerite crystals isolated in metamorphic quartz and pyrite, with pyrrhotite and pyrite (S buffer) present in the system, were analyzed (see Scott 1983); sphalerite inclusions in quartz and pyrite were buffered by pyrite–pyrrhotite during porphyroblastic growth and entrapment by sphalerite. The core of the largest sphalerite grains (>0.5 mm; *cf.* Mizuta 1988) usually was analyzed, although the rim compositions were found to be essentially identical to those of the core (Tables 1, 2).

The mean composition of the sphalerite (X_{FeS} = 13.3 ± 1.9, n = 40; Fig. 2) is consistent with compositions equilibrated with hexagonal pyrrhotite at high pressures and temperatures above 300°C (Table 2). Excluding the three samples with X_{FeS} greater than 15.0, Figure 2 illustrates that sphalerite associated with, or hosted in, pyrite or arsenopyrite contains less iron (X_{FeS} = 12.0 to 13.5, 770 to 600 MPa) than samples associated with pyrrhotite or pyrrhotite and pyrite (X_{FeS} = 13.0 to 14.5, 500 to 650 MPa). These estimates of high pressure may indicate that either the iron content of sphalerite was

unbuffered when associated with pyrite or, more likely, that pyrite growth and recrystallization at higher temperatures and pressures modified the textural relationships such that X_{FeS} of sphalerite was shielded from further exchange with pyrrhotite. Those samples of sphalerite in direct contact with pyrrhotite have slightly higher X_{FeS} contents, which is consistent with high-temperature (>300°C) re-equilibration in the presence of hexagonal pyrrhotite and pyrite on the retrograde path, during uplift. The sphalerite with the highest X_{FeS} is hosted within pyrrhotite and may not have been buffered by the pyrite–pyrrhotite assemblage, or it may represent further equilibration at decreasing temperatures (<300°C) and decreasing pressure (500 to 300 MPa).

No compositional effect was noted in sphalerite as a result of proximity to chalcopyrite, except where Cu was detected as irregular inclusions or along grain boundaries of sphalerite. Although the presence of chalcopyrite should not affect the X_{FeS} characteristics of sphalerite (Hutchinson & Scott 1981), sphalerite intergrown with chalcopyrite was avoided. McNulty (1981) also found no difference in X_{FeS} contents of sphalerite in the presence or absence of chalcopyrite at Brunswick No. 12. The Mn content of the sphalerite is less than 0.1 wt.%.

In previous studies of the sphalerite from the Brunswick deposits, Benson (1960) and Kalliokowski (1961) found X_{FeS} contents slightly different from those in this study. In both studies, their analytical method was sufficiently imprecise so as not to warrant integration of their results. From several ore samples, Sutherland & Halls (1969) found an average sphalerite composition of 12.9 ± 0.1 mole % FeS. McNulty (1981) determined

an average composition of 13.6 ± 0.7 mole % FeS for sphalerite coexisting with pyrite (± pyrrhotite) in the No. 12 deposit, East Ore Zone. Using two samples from the West Ore Zone and two from the Main Ore Zone, van Staal (1985) found a compositional range from 12.3 to 13.4 mole % FeS in sphalerite with pyrrhotite and pyrite present. He also noted that the sphalerite inclusions in the core of a rotated porphyroblast of pyrite had the highest X_{FeS} (17.2 mole % FeS).

A sample from Austin Brook deposit has a range (12.3 to 13.5 mole % FeS, van Staal 1985) similar to that found in Brunswick No. 12 samples, whereas as five samples from Brunswick No. 6 range from 15.2 to 17.5 mole % FeS (240 to 440 MPa, Table 2, Fig. 2), with a mean near 16.5 mole % FeS (van Staal 1985). Interestingly, the range in samples from Brunswick No. 6 is similar to that in a few samples that equilibrated with pyrrhotite and pyrite from Brunswick No. 12, suggesting that there was a greater degree of low-P re-equilibration at Brunswick No. 6. This inference is consistent with a slightly higher temperature at Brunswick No. 6, as is evident by the local presence of spessartine-rich garnet in compositionally favorable (Mn-enriched) rocks subjected to early D_2 metamorphism associated with the early phase of uplift (M_2) (van Staal 1985, Lentz 1999b).

Arsenopyrite

There is considerable evidence of partial to complete metamorphic recrystallization of arsenopyrite and pyrite, such as inclusion trails, although cataclastic textures in pyrite and associated grain-size reduction are also evident, with ductile sulfides remobilized throughout the ores. Local preservation of quartz ribbons infilling fractured pyrite and mylonitic quartz in stockwork veins indicates that recovery and recrystallization of quartz were incomplete. The fine-grained, skeletal pyrite–arsenopyrite intergrowths investigated in this study seem to be primary features within the stockwork veins at Brunswick No. 12 (Figs. 3a, b, c), the FAB zone, and at Brunswick No. 6, but are usually in minor abundance. This stockwork-related texture resembles skeletal features associated with growth from supersaturated fluids.

If enclosed in pyrite or quartz, zoned arsenopyrite re-equilibrated compositionally to variable degrees, while locally preserving the bulk As/S value. If associated with pyrrhotite or sphalerite, chemical re-equilibration of arsenopyrite seems to occur with a homogeneous As/S (weak zoning) consistent with the metamorphic conditions. Back-scattered electron images of pyrite shows multiple episodes of growth, brecciation, and regrowth within these veins, with sharp to diffuse growth-induced interfaces developed. As Sutherland (1967) had found, the As content of pyrite from the stockwork zone is low (<0.25 wt.%), but does increase up to 2 wt.% immediately beneath the copper-rich basal

TABLE 1. AVERAGE COMPOSITION OF SPHALERITE
FROM STOCKWORK SULFIDE MINERALIZATION
AT THE BRUNSWICK NO. 12 MASSIVE-SULFIDE DEPOSIT

Sample	5A	19	25	46	54	69	148	257
n	7	2	6	2	2	9	3	12
S wt.%	32.10	31.73	31.62	31.50	31.41	31.96	32.00	31.79
As	0.20	0.00	0.02	0.06	0.00	0.05	0.08	0.13
Zn	58.45	59.02	59.23	56.72	57.08	58.70	59.97	58.96
Fe	8.36	7.60	7.64	9.45	9.21	7.69	6.98	7.29
Cd	0.11	0.01	0.03	0.13	0.13	0.15	0.15	0.23
Mn	0.04	0.02	0.01	0.09	0.03	0.02	0.03	0.03
Cu	0.09	0.03	0.20	0.04	0.21	0.04	0.12	0.04
Co	0.06	0.01	0.03	0.01	0.04	0.02	0.04	0.02
Sum	99.6	98.6	98.9	98.0	98.2	99.0	99.5	98.5
S atom %	48.75	48.72	48.49	48.54	48.39	48.86	48.77	48.87
As	0.13	0.00	0.01	0.04	0.00	0.03	0.05	0.08
Zn	43.55	44.45	44.54	42.87	43.14	44.02	44.80	44.45
Fe	7.28	6.71	6.72	8.36	8.18	6.75	6.11	6.43
Cd	0.05	0.00	0.02	0.06	0.06	0.07	0.06	0.06
Mn	0.05	0.02	0.01	0.08	0.02	0.02	0.02	0.02
Cu	0.07	0.02	0.16	0.04	0.17	0.03	0.10	0.03
Co	0.05	0.02	0.02	0.01	0.03	0.01	0.04	0.01

n: number of spot analyses in average. Datafile of all analytical data obtained on arsenopyrite is deposited with CISTI (see text).

TABLE 2. SUMMARY OF PROPORTION OF FeS IN SPHALERITE
FROM THE BRUNSWICK NO. 12 DEPOSIT

Sample	Mole %	MPa	Relationship	Location	Host rock
005A-1D	14.3	520	rim in po w asp	750 m level	veins in silicified & chloritized FW sediment
005A-1E	13.6	590	core in po w asp	750 m level	veins in silicified & chloritized FW sediment
005A-1H	13.3	620	core in po w asp	750 m level	veins in silicified & chloritized FW sediment
005A-1I	21.1	0-0.2	core in po w asp	750 m level	veins in silicified & chloritized FW sediment
005A-2D	13.1	640	rim in po w asp	750 m level	veins in silicified & chloritized FW sediment
005A-2H	13.1	640	core in po w asp	750 m level	veins in silicified & chloritized FW sediment
005A-2I	12.7	690	core in po w asp	750 m level	veins in silicified & chloritized FW sediment
019-1B	13.6	590	core in py w po	750 m level	veins in silicified FW sediment
019-2D	13.2	630	core in po w py	DDH A1-331'	veins in silicified FW sediment
025-1B	12.8	680	core in py w po & ccp	DDH A1-447'	veins in chloritized CT
025-1C	12.7	690	core in py w po & ccp	DDH A1-447'	veins in chloritized CT
025-1D	12.4	720	core in py w po & ccp	DDH A1-447'	veins in chloritized CT
025-2A	13.7	580	core in po & py	DDH A1-447'	veins in chloritized CT
025-2B	13.9	560	core in po & py	DDH A1-447'	veins in chloritized CT
025-2C	13.9	560	core in po & py	DDH A1-447'	veins in chloritic CT
046-2A	16.5	320	core in asp	DDH A1-1193'	brecciated massive-sulfides
046-2B	16.4	330	core is py	DDH A1-1193'	brecciated massive-sulfides
054-1B	15.8	380	core in py w po	DDH A1-1209'	silicified FW sediment
054-1C	16.5	320	core in py w po	DDH A1-1209'	silicified FW sediment
069-1A	12.8	680	core in py & qtz w po	DDH A3-607'	veins in chloritized & silicified FW sediment
069-1B	12.9	665	rim in py & qtz w po	DDH A3-607'	veins in chloritized & silicified FW sediment
069-1C	13.0	650	int. in py & qtz w po	DDH A3-607'	veins in chloritized & silicified FW sediment
069-2B	13.8	570	core w py & po	DDH A3-607'	veins in chloritized & silicified FW sediment
069-2B	14.6	490	core in py & qtz w po	DDH A3-607'	veins in chloritized & silicified FW sediment
069-2C	13.6	590	core in qtz & py w po	DDH A3-607'	veins in chloritized & silicified FW sediment
069-2E	13.4	610	core in py w po	DDH A3-607'	veins in chloritized & silicified FW sediment
069-2F	13.0	650	core w py & po	DDH A3-607'	veins in chloritized & silicified FW sediment
069-2G	14.3	520	core w py & po	DDH A3-607'	veins in chloritized & silicified FW sediment
148-1A	12.0	770	core in py & ccp w po	DDH A81-310'	sulfide-bearing IF
148-1B	12.6	700	int. in py & ccp w po	DDH A81-310'	sulfide-bearing IF
148-1C	11.6	810	rim in py & ccp w po	DDH A81-310'	sulfide-bearing IF
257-1D	12.6	700	core w asp & py	475 m level	veins in chloritized FW sediment
257-1E	12.6	700	core w asp & py	475 m level	veins in chloritized FW sediment
257-1F	12.6	700	core in py & asp	475 m level	veins in chloritized FW sediment
257-1O	12.4	720	core in py	475 m level	veins in chloritized FW sediment
257-1P	13.6	590	core in py	475 m level	veins in chloritized FW sediment
257-1Q	13.4	610	core in py	475 m level	veins in chloritized FW sediment
257-2E	12.1	750	core w py & asp	475 m level	veins in chloritized FW sediment
257-2G	13.1	640	core w py & asp	475 m level	veins in chloritized FW sediment
257-3B	12.9	665	core w asp	475 m level	veins in chloritized FW sediment
257-3F	12.8	680	core w po & py	475 m level	veins in chloritized FW sediment
257-3H	12.4	720	core w po & py	475 m level	veins in chloritized FW sediment
257-3I	13.0	650	core w po & py	475 m level	veins in chloritized FW sediment

Several samples with minor contents of As and Cu had appropriate amounts of FeS (in arsenopyrite and chalcopyrite) deducted from the listed values. The mean mole % FeS = 13.3 ± 1.0 (n = 34, sample 005A-1I excluded). P is pressure. P = 42.3 − 32.1 log mole % FeS. FW: footwall, CT: crystal tuff, IF: iron formation.

sulfide zone (Table 3). In one example, As-poor pyrite (0.14 wt.%) seems to have metamorphically overgrown cataclastic As-rich pyrite (1.6 to 2.4 wt.% As). The cobalt content of pyrite is typically less than 0.15 wt.%. Based on a few X-ray-diffraction determinations by van Staal (1985), most samples of pyrrhotite at the Brunswick No. 6 deposit are hexagonal, whereas most are monoclinic at the Brunswick No. 12 deposit.

Arsenopyrite was analyzed from the Brunswick No. 12 deposit, as well as in a few samples previously studied by van Staal (1985) from the Brunswick No. 6 and Austin Brook deposits (Table 4). For the most part, these samples coexist directly with pyrite, pyrrhotite and sphalerite. In a few samples, pyrrhotite and sphalerite were not directly evident or paragenetically associated; thus their presence is only inferred based on the com-

mon presence of pyrrhotite within the stockwork veins. Of the grains examined, only a few have very complex internal textural features that are difficult to interpret. Figure 4a shows arsenopyrite occurring in a remobilized sulfide vein in the hanging wall. Most idiomorphic crystals, however, are subtly zoned, with an As-rich core and a S-rich rim (Figs. 4a, b) such that they may be primary. Most seem to have a relatively homogeneous outer zone that mimics the inner idiomorphic outline of the core (Fig. 4c), whereas most other crystals preserve some evidence of diffuse replacement of the inner arsenic-rich core (Figs. 4d, e). In a few cases, the rim of the arsenopyrite is cobalt-rich, causing an apparent reversal in the typical As–S zoning pattern (Fig. 4f) in the back-scattered image. In the author's opinion, the outer zones for most crystals are of metamorphic origin where
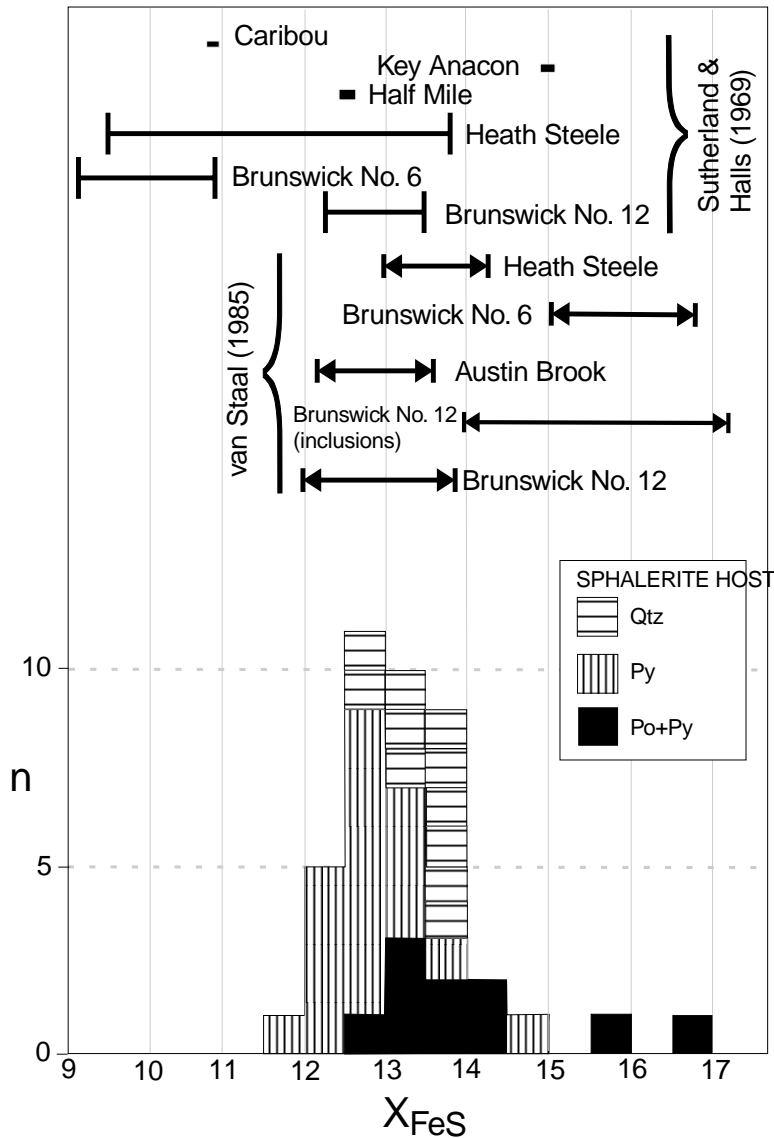
FIG. 2.   Mole % FeS in sphalerite from the stockwork mineralization at the Brunswick No.
12 deposit (this study), compared with data from other areas of the Bathurst Camp
(Sutherland & Halls 1969, van Staal 1985).

hosted with pyrrhotite, sphalerite, and possibly quartz. The discrete complex zoning in some arsenopyrite grains resembles that in hydrothermal arsenopyrite deposited in vein systems, although it may be partially due to metamorphic re-equilibration and growth as well.

The samples show a considerable As–S variability from 28.4 to 34.7 atom % As, but most fall between 31.4 and 33.4 mole % As (Fig. 5a). As observed petro-graphically, the core tends to have the highest As contents, although there is considerable compositional overlap with middle and rim compositions as well. There is also a large range in cobalt contents (up to 10.2 atom % in sample 181–2 rim; Fig. 4f), with the highest values typically associated with compositions having between 31.4 and 33.4 atom % As, but most samples contain less than 4 atom % Co, with an average of less than 0.5
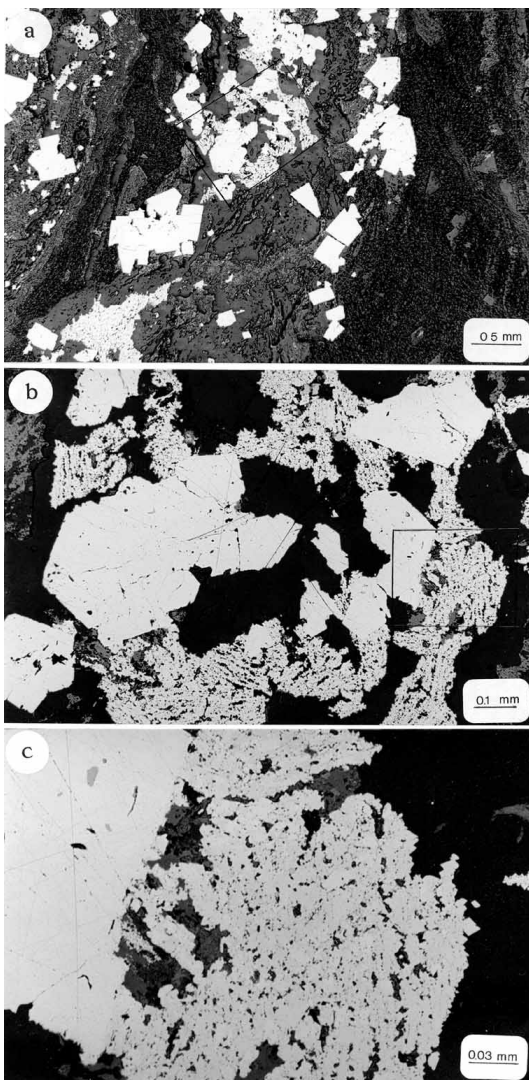
FIG. 3. a) Stockwork sulfide veinlet hosted in altered (carbonaceous) mudstones (dark grey) and quartzitic siltstones (lighter grey) of the Miramichi Group that is infolded close to the basal part of the deposit (sample 031, DDH A1 – 203.6 m; photomicrograph, reflected light). b) Euhedral porphyroblasts of pyrite with skeletal arsenopyrite–pyrite intergrowth hosted in quartz; closeup of a) (rectangular outline). c) Skeletal pyrite–arsenopyrite intergrowth with quartz inclusions coexisting with euhedral pyrite with small inclusion(s) of pyrrhotite. Minor inclusions of chalcopyrite and sphalerite hosted in, and mantling?, or being replaced by, idiomorphic pyrite porphyroblasts; closeup of b) (rectangular outline).

atom % (Fig. 5b). However, there is not a consistent relationship with respect to arsenopyrite zoning. Ni is elevated (0.05 to 0.35 atom %, Fig. 5c) within the same range of As contents, but locally is up to 1.4 atom %. Sb content is irregular, but averages about 0.1 atom %, with values greater than 0.5 atom % (0.5 to 1.15 atom % Sb, Fig. 5d) associated with As contents greater than 32 atom %.

The estimated pressure effect on the As–S content of arsenopyrite is relatively small (see also Clark 1960, Kretschmar & Scott 1976, Sharp *et al.* 1985); unfortunately, only the 33 atom % As isopleth was evaluated for 500 MPa (5 kbar). Overall, the arsenopyrite geothermometer provides a rudimentary basis for evaluating the peak T conditions of metamorphism in these deposits, if textural evidence suggests that the arsenopyrite composition reflects these conditions. The arsenic liberated during metamorphic equilibration of arsenopyrite with the host assemblages will either i) react with pyrrhotite or the FeS in sphalerite to form metamorphic arsenopyrite, ii) modify existing arsenopyrite compositions depending on P–T conditions, or iii) be mobilized out of the local system (Lentz 1999b).

Arsenopyrite containing more than 0.5 atom % Co, Ni, Mn, and Sb was not used for geothermometric purposes, because trace amounts of these elements may affect the As/S value of arsenopyrite (Scott 1983, Sharp *et al.* 1985). The irregular compositional nature of the outermost zone with respect to the inner zones may be a function of metamorphic re-equilibration with the host assemblages, as with sphalerite. The marked decrease in As/S is consistent with metamorphic re-equilibration of the outermost zones, but at what stage this happened is uncertain. The high As/S values in the core of many crystals is compatible with a primary origin, particularly those that are cobaltiferous. Using the equilibria established by Kretschmar & Scott (1976), the very high As contents (32.5 to 33.4 atom % As) of some of the cores may be interpreted as a sign of high-temperature deposition of sulfide (430° to 490°C, Fig. 6). However, most compositions fall between 31.5 and 33 atom % As, which corresponds to temperatures between 350° and 450°C (Fig. 6). The highest inferred temperatures for the original stockwork assemblage seem too high when compared together with known exhalative hydrothermal systems. Alternatively, the aS_2 is unbuffered, if some arsenopyrite deposition is paragenetically very early. This early paragenesis would be favored at low aS_2 and high aH_3AsO_3 (*cf.* Heinrich & Eadington 1986), *i.e.,* preceding pyrite deposition. This scenario is reasonable, considering that the pyrite – pyrrhotite ± magnetite assemblage in the stringer sulfide zone is indicative of low-aS_2 conditions (Luff *et al.* 1992), and its saturation would be paragenetically later.

Rim compositions are typically between 30 and 32 atom % As, but extend up to 33 and down to 28 atom % As. If formed in the 500 MPa (5 kbar) pressure range, the typical crystal of metamorphic arsenopyrite would
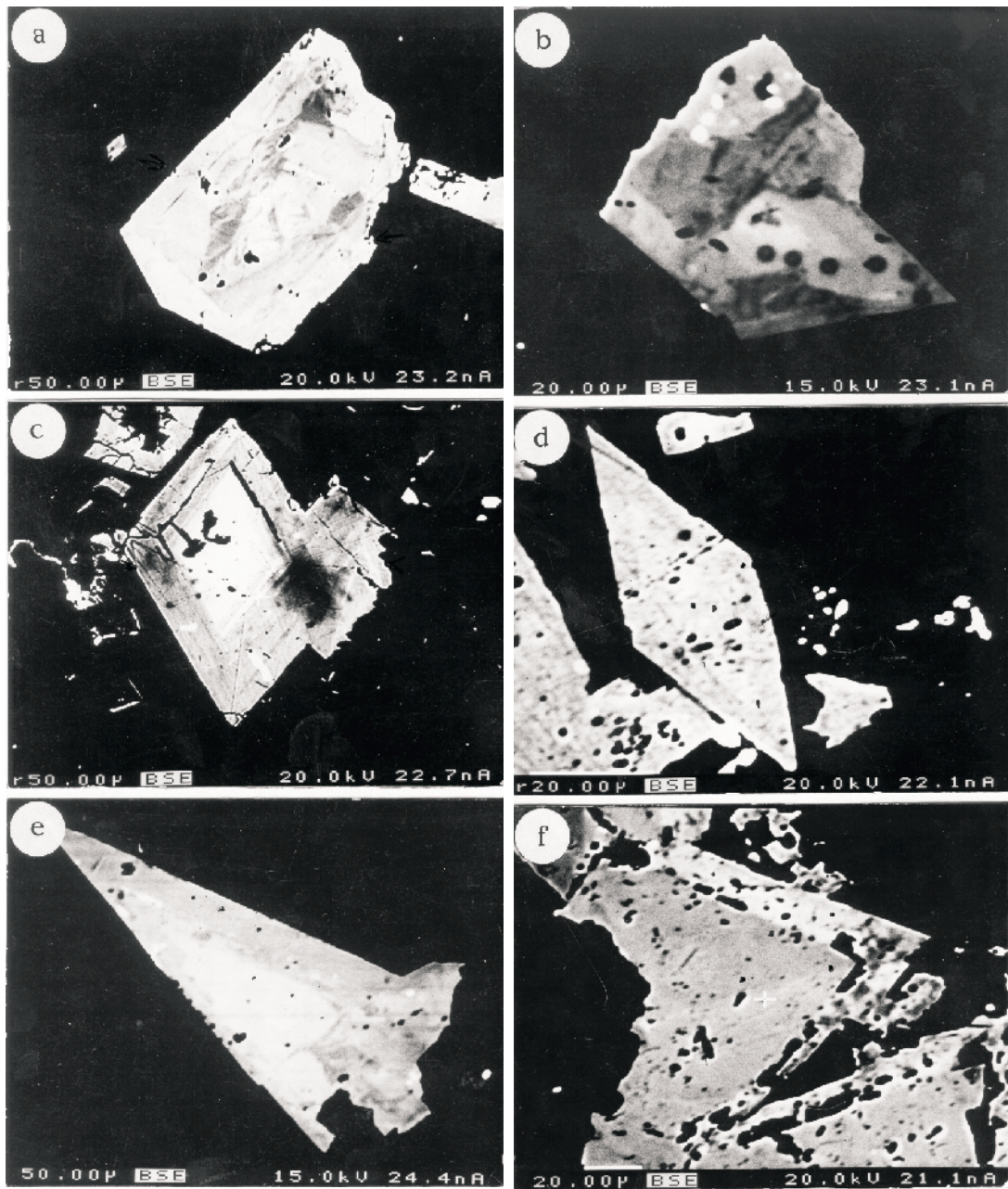
FIG. 4.   Back-scatter electron image of arsenopyrite crystals from samples (a) LPA–014 (Brunswick No. 12), (b) LPA–049 (Brunswick No. 12), (c) 373 (Austin Brook), (d) 373 (Austin Brook), (e) LPA–049 (Brunswick No. 12), and (f) LPA–181 (Brunswick No. 12). Scanning electron microscopy.

have formed between 300° and 425°C (Fig. 6). This range is consistent with the fluid inclusion and S isotopic evidence presented by Lusk & Krouse (1997).

It is uncertain if low contents of Co are typical of metamorphic arsenopyrite. If so, then cobalt-rich rim compositions could be interpreted as a primary feature.

TABLE 3. COMPOSITION OF PYRITE FROM STOCKWORK SULFIDE MINERALIZATION
AT THE BRUNSWICK NO. 12 MASSIVE SULFIDE DEPOSIT

Sample	158	158	158	158	144	257	019	021	025	042	043	049
n	1	1	1	1	1	1	4	5	11	15	10	1
S wt.%	51.81	51.43	51.82	51.68	53.49	52.91	51.76	53.57	53.19	53.62	53.12	52.25
As	0.14	0.01	0.11	0.12	0.00	0.28	0.08	0.10	0.22	0.46	0.96	0.06
Zn	0.06	0.02	0.00	0.00	0.02	0.25	0.20	0.01	0.02	0.02	0.03	0.00
Fe	47.44	47.95	47.68	47.84	46.99	46.75	47.76	45.83	45.65	45.91	45.41	47.24
Cd	0.00	0.09	0.02	0.00	0.03	0.00	0.03	-	-	-	-	-
Mn	0.02	0.01	0.03	0.02	0.02	0.03	0.02	0.01	0.01	0.02	0.01	0.01
Cu	0.03	0.01	0.00	0.00	0.03	0.02	0.02	-	-	-	-	-
Co	0.03	0.02	0.04	0.04	0.11	0.05	0.06	0.12	0.21	0.08	0.05	0.04
Sum	99.5	99.5	99.7	99.7	100.7	100.3	99.9	99.6	99.3	100.1	99.5	99.6
S atom %	65.41	65.08	65.31	65.20	66.39	66.07	65.21	66.96	66.77	66.80	66.66	65.77
As	0.08	0.00	0.06	0.07	0.00	0.15	0.04	0.05	0.12	0.25	0.52	0.03
Zn	0.03	0.00	0.00	0.00	0.00	0.15	0.12	0.01	0.01	0.01	0.02	0.00
Fe	34.39	34.83	34.49	34.65	33.48	33.51	34.54	32.89	32.90	32.83	33.51	34.14
Cd	0.00	0.03	0.01	0.00	0.01	0.00	0.01	-	-	-	-	-
Mn	0.03	0.00	0.02	0.02	0.02	0.02	0.01	0.01	0.01	0.01	0.01	0.01
Cu	0.02	0.00	0.00	0.00	0.02	0.01	0.01	-	-	-	-	-
Co	0.02	0.02	0.03	0.03	0.07	0.04	0.04	0.05	0.14	0.05	0.03	0.03

n: number of analyses. Samples with $n > 1$ are averages that were previously reported by Lentz & Goodfellow (1993a).

TABLE 4. SELECTED COMPOSITIONS OF ARSENOPYRITE
FROM STOCKWORK SULFIDE MINERALIZATION
AT THE BRUNSWICK NO. 12 MASSIVE-SULFIDE DEPOSIT

Sample	49	49	49	49	49	49	373	373
Area	1C	1D	1E	1F	1G	1H	x	x
Location	core	int	int	int	int	rim	core	rim
Host	py-qtz	py-qtz	py-qtz	py-qtz	py-qtz	py-qtz	ms	ms
S wt.%	19.05	18.94	19.41	19.64	19.51	19.92	18.08	19.88
As	45.16	45.38	44.67	44.77	44.12	42.92	45.64	43.37
Fe	34.35	35.03	35.67	35.52	35.48	35.66	33.31	33.90
Sb	0.17	0.10	0.00	0.00	0.00	0.18	1.91	0.59
Mn	0.00	0.02	0.00	0.02	0.00	0.00	0.02	0.02
Ni	0.45	0.41	0.22	0.13	0.15	0.03	0.06	0.03
Co	0.89	0.21	0.09	0.07	0.05	0.09	0.05	0.06
Zn	0.00	0.03	0.00	0.05	0.00	0.00	0.36	0.67
Pb	0.00	0.08	0.00	0.08	0.00	0.00	0.08	0.09
Sum	100.1	100.2	100.1	100.3	99.3	98.9	99.6	98.6
S atom %	32.51	32.33	32.78	33.09	33.13	33.82	31.57	34.21
As	33.00	33.10	32.30	32.30	32.10	31.20	34.08	31.94
Fe	33.67	34.32	34.70	34.35	34.60	34.76	33.37	33.49
Mn	0.01	0.01	0.00	0.02	0.00	0.00	0.02	0.02
Co	0.83	0.20	0.08	0.06	0.05	0.08	0.05	0.05
Ni	0.42	0.38	0.20	0.13	0.14	0.03	0.06	0.03
Sb	0.08	0.05	0.00	0.00	0.00	0.01	1.91	0.59

Selected compositions obtained on a Cameca electron microprobe (WDS) at the Geological Survey of Canada using arsenopyrite and metal standards for calibration (SESULF program). The samples were analyzed for Se, although spectral interferences with As were not fully evaluated. Typical results were 0.10 to 0.30 ppm Se. Sample 373 (van Staal 1985): averages of probe traverse for core ($n = 8$) and rim ($n = 12$) and includes a few inclusions (Zn + Pb contamination). Datafile of all analytical data obtained on arsenopyrite is deposited with CISTI (see text).

The idiomorphic nature and development of symmetrical outer zones of most crystals of arsenopyrite postdate the most intense phase of ductile deformation. In contrast, van Staal (1985) detected no zoning, but a variable composition (32.5 ± 0.7 mole % As), which he interpreted as evidence for metamorphic recrystallization. It is possible though that the As/S was affected by high Sb contents in those samples analyzed or formed at a higher T (sample 373, Table 4).

DISCUSSION

There are several detailed studies that successfully utilized sphalerite geobarometry of Scott & Barnes (1971) and arsenopyrite geothermometry of Kretschmar & Scott (1976) in massive-sulfide settings (*e.g.*, Ethier *et al.* 1976, Berglund & Ekström 1980, Sundblad *et al.* 1984). The presence of the appropriate sulfide assemblages and structural control from vein–host relationships make stockwork veins optimal for mineral–chemical geothermometric and geobarometric determinations of deformed VMS deposits. Recrystallization of sulfides during syngenetic hydrothermal activity and later metamorphism, in many cases, expels inclusions, particularly during grain growth. The mantling of primary skeletal pyrite–arsenopyrite intergrowths on coarser-grained euhedral pyrite (Fig. 3) supports the assertion that syngenetic processes of hydrothermal recrystallization are responsible for sulfide coarsening to some degree. The low-As outer zones of pyrite and arsenopyrite represent metamorphic overgrowths and replacements of cores of possibly primary origin. The higher levels of arsenic and cobalt in the remnant core of arsenopyrite and pyrite grains are consistent with a relatively higher temperature of formation of the Cu-rich stringer zone compared to the exhalative sulfides (Lentz & Goodfellow 1993a). The As content of a few pyrite crystals analyzed exceeds the determined limit of solubility, 0.53% As at 600°C (Clark 1960); metastable substitution of As for S in
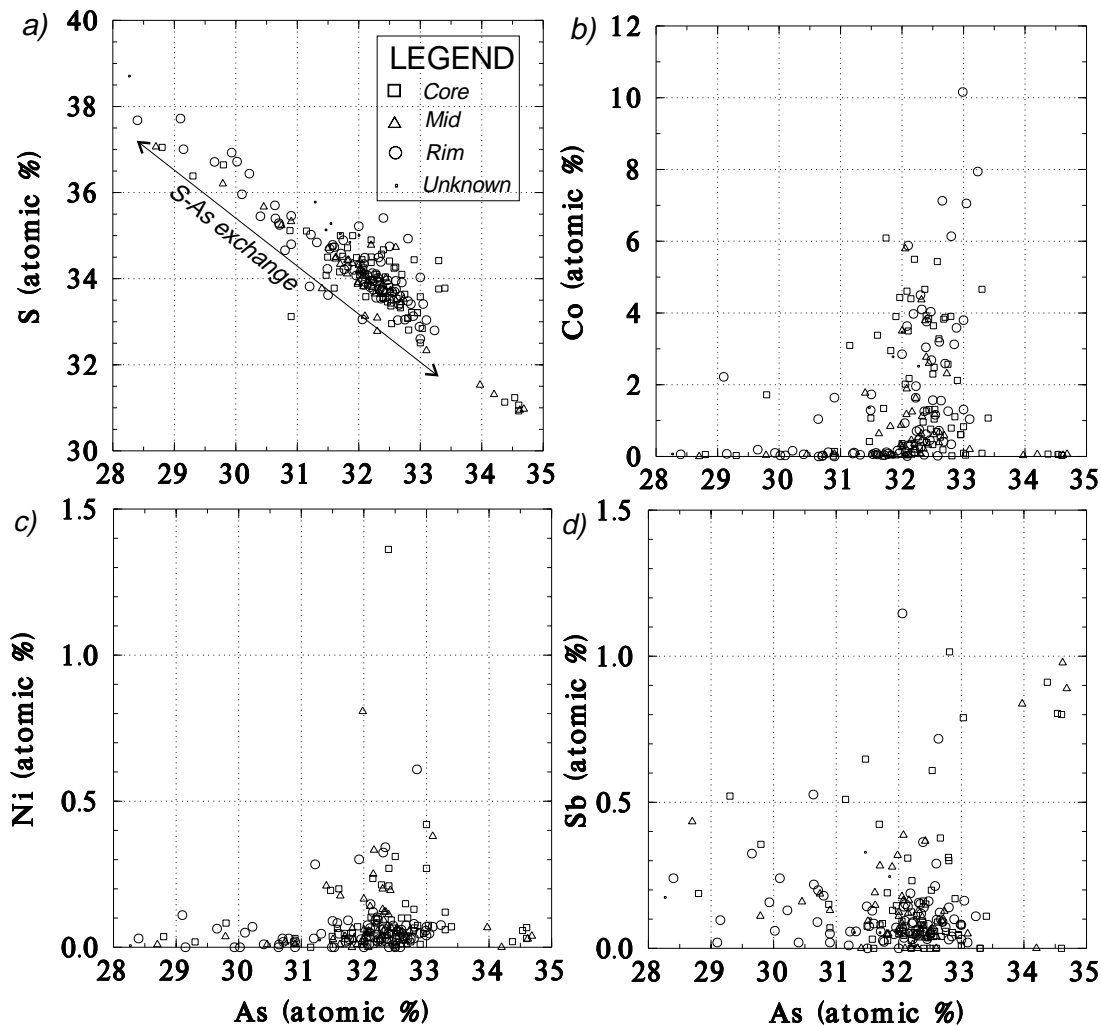
FIG. 5.   Concentrations of arsenic *versus* sulfur (a), cobalt (b), nickel (c), and antimony (d) (in atom %) in arsenopyrite from stockwork and massive-sulfide mineralization from the Brunswick Belt deposits.

pyrite is possibly related to supersaturation. The lack of complex zoning evident within the inner As-rich zones of pyrite and arsenopyrite, except in one example, presumably associated with dynamic deposition from fluid, indicates that these minerals were thoroughly recrystallized and homogenized during hydrothermal activity or possibly during early metamorphic recrystallization. Interestingly, it is not uncommon to have elevated arsenic, cobalt, and nickel in pyrite associated with vein systems, and probably in arsenopyrite as well, in contrast to those of sedimentary origin. On the basis of the few results from Sutherland (1967), the Co and Ni contents of pyrite from exhalative sulfide deposits in the

Bathurst Camp are less than 1000 and 80 ppm, respectively; unfortunately, the detection limits of Ni by EMPA were not sufficient to obtain reasonable results for pyrite and pyrrhotite.

In the Bathurst Camp, there are few estimates of pressure based on sphalerite from deposits other than those along the Brunswick Belt. The inferred pressures of sphalerite crystals hosted in inclusions (600 to 770 MPa) at Brunswick No. 12 are consistent with results from the phengite geobarometer (Lentz & Goodfellow 1993b), which seems to record the late M_1 development of the fabric (S_1S_2). The higher X_{FeS} of sphalerite hosted in the core of rotated porphyroblasts (van Staal 1985) is
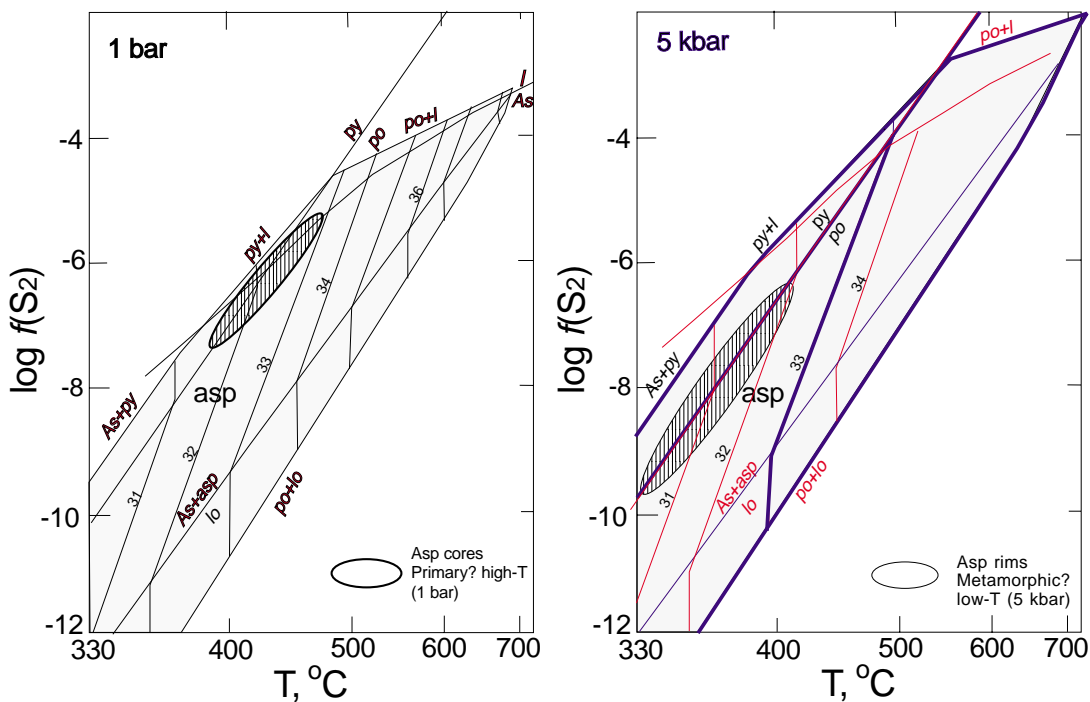
FIG. 6. Plot of $f(S_2)$ *versus* T with As–S–Fe phase boundaries and As isopleths for arsenopyrite (modified from Kretschmar & Scott 1976, Sharp *et al.* 1985). The general fields for primary (?) and metamorphic arsenopyrite from stockwork and massive-sulfide mineralization from the Brunswick deposits are shown.

inconsistent with this interpretation, although it may record early prograde M_1 (low P) pressures. The lower pressures inferred from the matrix sphalerite in contact with pyrrhotite and pyrite were probably achieved by re-equilibration to 500 to 650 MPa, early in the M_2 up-lift event (Lentz 1999b). At the Brunswick No. 12 deposit, the rare presence of biotite and sparse evidence of post-M_1 overgrowths suggest that peak thermal metamorphism was coincident with development of the S_2 fabric (D_1). In contrast, the Brunswick No. 6 area has abundant post-D_1 porphyroblasts (early M_2), with spessartine and biotite most diagnostic of slightly higher-temperature conditions (van Staal 1985) than at Brunswick No. 12; this finding, together with the lower inferred pressures from sphalerite geobarometry (240 to 440 MPa) at No. 6, which would have re-equilibrated at the higher temperatures, suggest that post-D_1 thermal metamorphism occurs during D_2 uplift (M_2). Overall, the sphalerite textural relations and metamorphic compositions of the arsenopyrite are consistent with the P–T path for the autochthonous Brunswick Belt based on metamorphic textural relationships inferred using silicate assemblages (van Staal 1985, Lentz 1999b).

CONCLUSIONS

1. The stockwork (stringer-sulfide) feeder veins within the hydrothermally altered footwall rocks associated with the Brunswick massive-sulfide deposits were transposed parallel to the composite S_1S_2 fabric, as well as extensively metamorphosed and recrystallized. In spite of extensive recrystallization during metamorphism, local preservation of syngenetic textures is evident, *e.g.,* the skeletal pyrite–arsenopyrite inter-growths. The metamorphic assemblage in the stockwork veins is pyrite, pyrrhotite, sphalerite, chalcopyrite, arsenopyrite, quartz, and chlorite and, more rarely, accessory sulfides, carbonate, and silicate phases. Therefore, stockwork veins are potentially favorable for studying syngenetic to metamorphic paragenetic relationships within the setting of deformed massive-sulfide deposits. The combined textural analysis and determination of the compositional range of sphalerite and arsenopyrite both indicate variable degrees of textural preservation and compositional re-equilibration during tectono-metamorphic evolution of the eastern Bathurst Camp.

2. Sphalerite readily re-equilibrates and recrystallizes at the middle greenschist P–T conditions experi-

enced by the rocks of the Brunswick Belt, with compositional preservation where hosted within inert metamorphic phases, like pyrite and quartz or, if coexisting with pyrrhotite, where diffusion (thermally induced) is too limited to affect composition. Sphalerite compositions enclosed in metamorphic quartz and pyrite have the lowest X_{FeS} content (12.0 to 13.5 mole % FeS), suggesting locked-in prograde metamorphic pressures up to 770 MPa. Sphalerite associated with pyrite and pyrrhotite displays compositions in the range 13.0 to 14.5 mole % FeS (500 to 650 MPa), which is consistent with equilibration to lower pressures during the late- to post-D_1 uplift that is also coincident with peak thermal metamorphism (M_1) at Brunswick No. 12; even lower pressures are noted at Brunswick No. 6.

3. Preservation of primary intergrowths with discrete zoning in some arsenopyrite crystals is reminiscent of syn-hydrothermal textures related to stockwork vein development. The high As:S values (31.5 to 33.9 atom % As; 325–475°C), cobalt (0.5 to 10 atom %), and nickel contents (0.1 to 1.4 atom %) of the intermediate to core zone of many arsenopyrite crystals are consistent with a syngenetic origin. Partial metamorphic recrystallization and homogenization of arsenopyrite during metamorphism yield lower As:S values (29 to nearly 32 atom % As) and usually lower trace-element contents, both consistent with a peak metamorphic T of less than 425°C at the Brunswick deposits, or possibly with re-equilibration to those conditions from a higher temperature, *i.e.,* a minimum estimate of temperature.

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