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COMPOSITIONAL ZONING IN ORE MINERALS AT THE CRAIG MINE, SUDBURY, ONTARIO, CANADA

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ABSTRACT

The Craig mine, located on the North Range of the Sudbury Igneous Complex, in Ontario, is a typical Sudbury-district nickel sulfide deposit with announced reserves of 14.7 million tonnes of ore, grading 2.01% Ni and 0.74% Cu. The ores consist of massive to disseminated pyrrhotite with randomly dispersed veinlets and flames of pentlandite and scattered grains of chalcopyrite and magnetite. Very small quantities of pyrite occur as scattered subhedral to anhedral grains. The physical textures are typical of those of magmatic nickel sulfide deposits and appear to have formed through diffusion of nickel from a pre-existing monosulfide solid-solution during cooling. Chemical textures have been examined using the electron microprobe; element mapping used analysis times up to 12 hours and beam currents up to 1000 nA. The pyrrhotite has been found to contain nickel-depletion zones around pentlandite veinlets and flames; depletion zones also exist around non-nickel-bearing phases. The depletion zones appear to have formed as a result of nickel diffusion, which was arrested at low temperatures. Individual grains of pentlandite within veinlets contain significant inhomogeneities. Representative examples of the scattered grains of pyrite, although showing no physical variation, contain well-defined compositional zoning in terms of cobalt contents; nickel zoning is much less well defined. This zoning presumably resulted from selective loss of cobalt (and, to a lesser extent, nickel) from the monosulfide solid-solution as its compositional range was reduced at low temperatures.

Keywords: pentlandite, pyrrhotite, pyrite, cobalt, nickel, zoning, diffusion, Craig mine, Sudbury, Ontario, Canada.

SOMMAIRE

La mine Craig, située sur le flanc nord du complexe igné de Sudbury, en Ontario, exploite un gisement de sulfure de nickel typique du district; les réserves annoncées totalisent 14.7×10^6 de tonnes de minerai contenant 2.01% Ni et 0.74% Cu. Le minerai contient de la pyrrhotite massive ou disséminée, avec des veinules et des flammes dispersées de pentlandite et des grains disséminés de chalcopyrite et de magnétite. Des quantités infimes de pyrite se présentent sous forme de grains sub-idiomorphes ou xénomorphes épars. Les textures physiques sont tout-à-fait typiques de celles des gisements magmatiques de sulfures de nickel et semblent s'être formées par diffusion du nickel à partir d'une solution solide monosulfurée pré-existante au cours du refroidissement. Les textures chimiques ont été décrites par analyses à la microsonde électronique. Des cartes de répartition d'éléments ont été préparées en 12 heures ou moins à des courants du faisceau jusqu'à 1000 nA. La pyrrhotite possède des zones à plus faible teneur en nickel autour des veinules et des flammes de pentlandite; de telles zones sont aussi présentes autour des minéraux qui ne contiennent pas de nickel. Ces zones semblent s'être formées par diffusion du nickel, figée à faible température. Les grains individuels de pentlandite des veinules sont sensiblement hétérogènes. Des échantillons représentatifs des grains épars de pyrite, qui ne semblent pas varier en propriétés physiques, montrent par contre une zonation compositionnelle marquée, surtout en cobalt. La zonation en nickel est beaucoup plus subtile. Cette zonation résulterait de la perte sélective du cobalt (et, à un degré moindre, du nickel) de la solution solide monosulfurée à mesure que son champ de stabilité diminuait à faibles températures.

(Traduit par la Rédaction)

Mots-clés: pentlandite, pyrrhotite, pyrite, cobalt, nickel, zonation, diffusion, mine Craig, Sudbury, Ontario, Canada.

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INTRODUCTION

The Craig nickel–copper deposit is located in the Onaping–Levack area of the North Range of the Sudbury Igneous Complex, in Ontario. It represents one of a cluster of nickel–copper sulfide orebodies that have been located at the base of the complex over an approximately 10-km-long zone. Nickel mineralization was first recognized in the area in 1888, and the first mine, the Levack, opened in 1913. Claims for the area of the Craig mine were acquired by Falconbridge Nickel Mines in 1935, but the actual ore zones were only defined when encountered in underground drilling from the Onaping mine in the interval 1972–1981. Some development began in 1981, but was halted in 1982. It was reactivated in 1984, and limited production of ore began in 1985. The decision to bring the Craig deposit into full production was made in 1989; this was accomplished by the time of mine commissioning in 1995. The announced reserves in 1995 were 14.7 million tonnes grading 2.01% nickel and 0.74% copper (Moore & Nikolic 1994). The present study was undertaken to test for the presence and nature of heterogeneities that might exist in the major ore minerals of the Craig mine.

GENERAL GEOLOGY

The general geology of the Sudbury Igneous Complex has been extensively described in works such as Hawley (1962), Naldrett (1984, 1989, 1994), Pye *et al.* (1984), and Lightfoot & Naldrett (1994). The regional geology of the North Range has been summarized by Coats & Snajdr (1984), and the local geology of the Craig mine has been described by Moore & Nikolic (1994). The ores of the Craig mine exist in nine discrete zones along and below the sublayer contact extending over a strike length of about 1000 meters at depths between 650 and 1750 meters (Moore & Nikolic 1994).

Coats & Snajdr (1984) summarized six types of mineralization in the North Range deposits. Moore & Nikolic (1994) noted that approximately 75% of all ore at the Craig mine is footwall or granite breccia ore in which sulfides occur as disseminations, blebs, and stringers in a matrix of host breccia. Approximately 15% of the ore occur as massive sulfide, and the remaining 10% occurs as dark norite breccia in which sulfides occur as blebby disseminations, irregular stringers and masses in a noritic matrix. The ore mineralogy is quite characteristic of the Sudbury ores in general. Our observations are identical to those of Moore & Nikolic (1994), who found the ores consisting of pyrrhotite (91% monoclinic variety), pentlandite, and chalcopyrite with accessory magnetite and pyrite.

SAMPLES AND ANALYTICAL METHODS

The present preliminary study is based upon very limited, but very typical, samples of Craig mine ores kindly provided by Falconbridge Limited and the mine geologists. Standard polished sections were prepared (as described in Craig & Vaughan 1994) of each of the major types of ores. Pyrrhotite is invariably the dominant phase, but pentlandite is disseminated throughout as fine exsolution flames and as coarser irregular chains and veins. Chalcopyrite is present as irregular patches ranging from micrometers to millimeters in dimensions. Magnetite is present throughout as 50 to 500 μm grains; most grains are equant and somewhat roundish, but locally the grains are skeletal, suggestive of peculiar initial growth or of partial resorption. Pyrite was found only in samples of the dark norite breccia type of ore, as anhedral grains up to 500 μm across and as smaller but euhedral to subhedral crystals. Hawley (1962) noted that pyrite, though only a minor constituent in the Sudbury ores, occurs in several stages and noted that "its diversity of habit, occurrences and relationships make up in interest for its scarcity". Our samples are too few to clearly indicate where pyrite lies in the paragenesis of the Craig mine ores.

Selected portions of the samples were analyzed using a Cameca SX–50 – SUN 3/160 electron microprobe operating at 25 kV, employing long counting-times (4–12 hours) and high beam-currents (100–1000 nA). Images were prepared using the Fe X-ray intensities to discriminate individual mineral phases; this permitted the isolation of each type of mineral on the basis of the intensity of the iron X-rays. We could then isolate the data from any one type of mineral in which we wished to display a map for cobalt or nickel distribution. This allowed us to then expand the data on cobalt and nickel concentrations in the selected minerals to 256 different levels of intensity for display or plotting. Phases with very much higher or very much lower levels could be isolated and examined where their absolute metal contents could be best evaluated for variations.

RESULTS

Textures of the ores

The samples of ore from the Craig mine were found to contain physical textures characteristic of Sudbury-district nickel–copper ores. The massive ores consist dominantly of coarse-grained pyrrhotite with scattered irregular chains and veinlets of pentlandite ranging from 5 to 20 μm in width. Typical flames of pentlandite are also rather randomly dispersed within the pyrrhotite. The flames (Fig. 1), which are usually 1 to 10 μm in width and 10 to 100 μm in length, commonly occur in clusters of two to 10 lamellae, all with a common orientation. They seem to have nucleated along a fracture, along a grain boundary between pyrrhotite grains, or along a pyrrhotite margin adjacent to another phase. Chalcopyrite is dispersed throughout the pyrrhotite and pentlandite in these samples in grains of very variable size. Within the dark norite breccia type of ore, the sili-

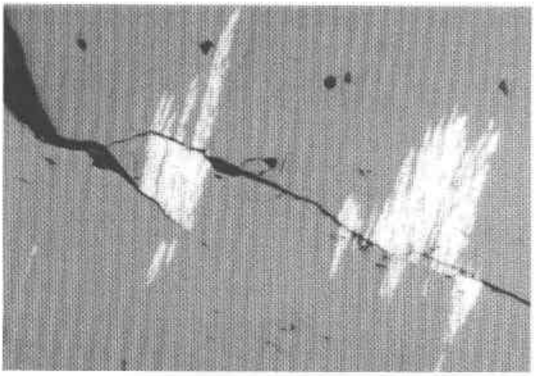

FIG. 1. Typical flame-like exsolution structures of pentlandite within pyrrhotite. These flames commonly occur in families. They appear to have grown from grain boundaries or from small fractures that apparently served as sites of nucleation. The field of view is 0.6 mm.

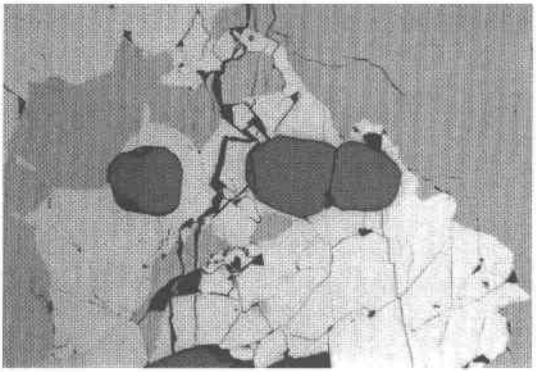

FIG. 2. Typical rounded and equant grains of magnetite of the type dispersed throughout the ores of the Craig mine. The magnetite occurs with pyrrhotite, chalcopyrite, and pentlandite. The field of view is 1.2 mm.

cates, especially along the margins with the sulfides, contain large numbers of small inclusions of pyrrhotite. This type of texture is characteristic of areas where deformation has fractured margins of the crystals and allowed injection of the sulfides before a later stage of overgrowth or annealing of the silicates.

Magnetite occurs dispersed throughout the ores of the Craig mine as roughly equant roundish to subhedral 50 to 200 μm grains (Fig. 2). Numerous additional grains, irregular and arcuate in shape, are interspersed among masses dominated by pyrrhotite and rich in pentlandite and chalcopyrite. Locally, magnetite grains display considerable corrosion, and some contain oriented exsolution-lamellae of ilmenite oriented along the (111) planes of the magnetite. Pyrite is present only locally, and occurs primarily as small (40 to 200 μm) subhedral to euhedral grains dispersed in masses of pyrrhotite in the dark norite breccia ores of the Craig mine (Fig. 3). The pyrite contains scattered small inclusions of pyrrhotite and chalcopyrite but without visible zoning. Etching with hydrogen peroxide for periods of up to one hour revealed no structure within the pyrite grains. Some larger, almost vein-like but highly porous masses of pyrite have been observed. These occur in areas in which the pyrrhotite contains much pressure-induced twinning, a feature absent in most of the pyrrhotite.

Origin of the physical textures

The Sudbury-district nickel–copper ores are generally understood to have formed by the separation of an immiscible sulfide melt from a mafic or ultramafic igneous magma and then to have crystallized more-or-less independently of the silicate magmas (Naldrett 1981). The early experimental studies of Kullerud (1963), Craig *et al.* (1967), and Naldrett *et al.* (1967) have been further refined and expanded in works by Fleet & Pan (1994) and Ebel & Naldrett (1997). These all confirm that the large field of $Fe_{1-x}S$ monosulfide solid-solution (*mss*) would have accommodated all, or nearly all, of the Fe, Ni, Co, Cu, and S in the ores from the time of initial crystallization at greater than 1100°C and then down to less than 600°C. Naldrett *et al.* (1967) examined the compositional limits of the *mss* as temperatures decline in the range 600 to 300°C and documented that pentlandite would exsolve along the S-poor boundary and that pyrite would exsolve along the S-rich boundary. They noted that the exsolution of the pentlandite from the nickeliferous monosulfide solid-solution would be accompanied by the formation of monoclinic pyrrhotite and offered a sample of pentlandite lamellae with

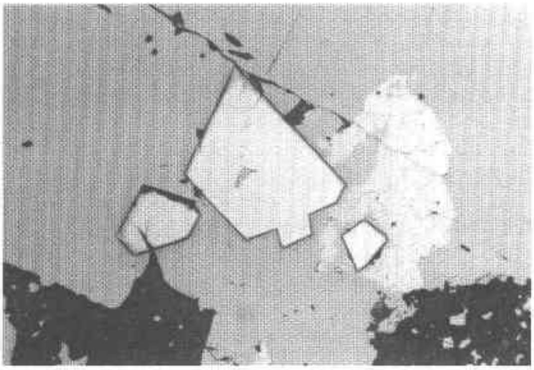

FIG. 3. Typical subhedral grains of pyrite of the type that occur locally in the Craig mine ores. The field of view is 1.2 mm.

coexisting monoclinic pyrrhotite as an example. These studies demonstrated that pentlandite exsolution appears as oriented lamellae within the remaining somewhat Ni-depleted *mss* matrix. Subsequently, Durazzo & Taylor (1982) examined textures developed in cooling experiments and determined that there is a temperature dependency of the individual types of textures; furthermore, they concluded that many of the assemblages observed in ores and most of their textures represent quite low-temperature equilibria. Kelly & Vaughan (1983) examined the mechanisms of pentlandite formation and concluded that changes from heterogeneous to homogeneous nucleation during the cooling path determined the textures. Francis *et al.* (1976) demonstrated that the orientation of exsolved lamellae of pentlandite is controlled by the coincidence of the [111] plane of pentlandite with the [0011] planes of the host hexagonal *mss*.

It has generally been concluded that diffusion of nickel through the *mss* to various nucleation sites created pentlandite lamellae and irregular grains and chains along pyrrhotite grain-boundaries. Continued diffusion and subsequent coalescence of pentlandite resulted in the formation of the relatively coarse veinlets of pentlandite that are commonly seen to be interstitial to pyrrhotite in Sudbury-type ores. Rajamani & Prewitt (1973) demonstrated that pentlandite has an extraordinarily large coefficient of thermal expansion and concluded that the large value, relative to other common sulfides, results in the formation of its characteristic fractured, or "chain-like", texture during cooling. The smaller dispersed flames of pentlandite presumably represent later and lower-temperature diffusion and subsequent exsolution, at a stage when diffusion was too limited to permit coalescence of the pentlandite into larger grains or veins. Although there are few data available, there has been the tacit assumption that both the *mss* interstitial to the pentlandite veins and lamellae, and the pentlandite grains themselves, are homogeneous. Kelly & Vaughan (1983) commented that "pentlandite compositions in the samples analyzed (from the Strathcona and Copper Cliff mines) are remarkably homogeneous". They found no evidence for zoning even within the larger rims of pentlandite or between pentlandite grains of the same sample.

Pyrrhotite is the dominant phase in the ores of the Craig mine, just as it is in all Sudbury-type ores. Moore & Nikolic (1994) have indicated that both forms of the pyrrhotite are present, with the monoclinic variety constituting 91% of the total pyrrhotite present in ores of the Craig mine. This is consistent with the findings in numerous studies of pyrrhotite at Sudbury, but there has been little detailed information on the spatial relationships of the two types of pyrrhotite in the ores. Graham (1969) noted the difficulty of optically determining the amounts of the two types of pyrrhotite because of "the extreme irregularity of certain of the finer intergrowths and the differential effects of orientation of grains upon surface reflectivities (when etchants or stains are used)".

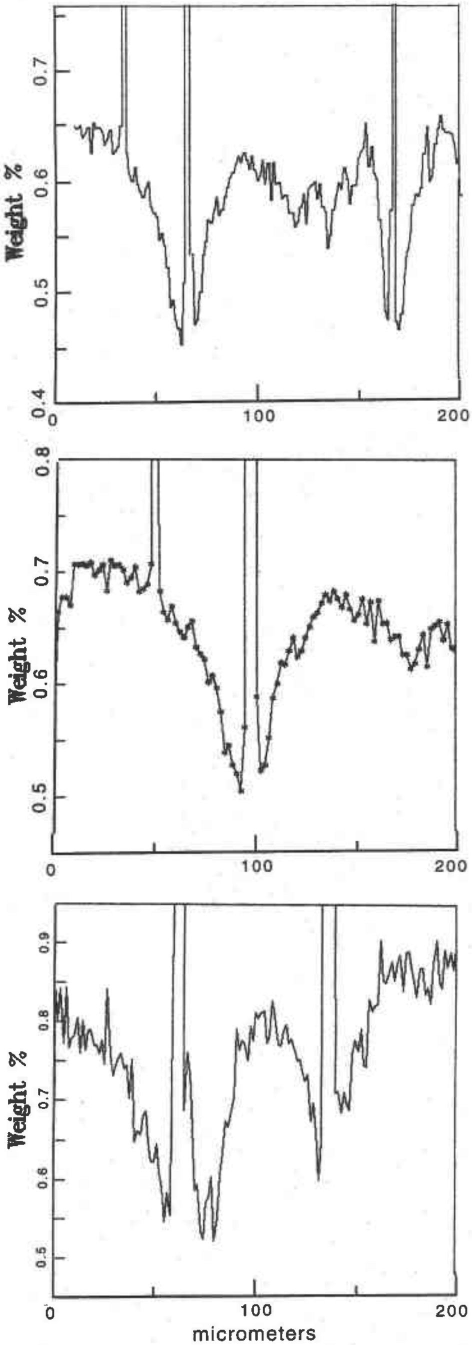

FIG. 4. Profiles showing the nickel depletion in pyrrhotite adjacent to a lamella of exsolved pentlandite. The nickel content of the lamellae is far greater than the vertical axis; hence, the position of the lamellae are shown by the peaks that go off the top of the scale. The zone of depletion is approximately 20 μm in width. Analyses were done at 2 μm intervals.

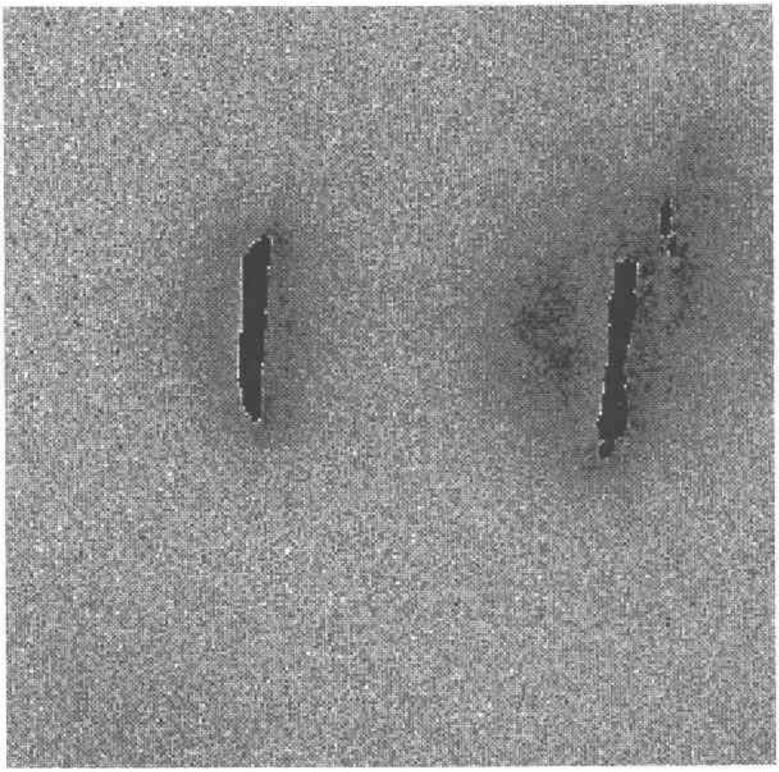

FIG. 5. Nickel X-ray map showing depletion zones (darker zones) that have developed around exsolved lamellae of pentlandite in a matrix of pyrrhotite. Depletion zones exist as concentric zones around every lamella. Because the pentlandite lamellae contain a much higher concentration of nickel than the pyrrhotite, we have eliminated them by using a threshold; hence, they appear black in the image. This approach permitted the discrimination of the variable, but much lower concentrations of the nickel in the pyrrhotite. The field of view is 200 μm.

This situation is also well illustrated by Vaughan *et al.* (1971) and Kelly & Vaughan (1983) where extremely delicate intergrowths of the two types of pyrrhotite are noted in ore samples from the Strathcona mine. Naldrett *et al.* (1967) suggested that the abundance of monoclinic pyrrhotite may well result from the fact that the exsolution of pentlandite drives the composition of the remaining host *mss* toward the somewhat S-enriched Fe_7S_8 composition of the monoclinic phase. Kelly & Vaughan (1983) noted that "the monoclinic phase is concentrated at grain margins, particularly those adjacent to areas of rim pentlandite". They further noted that "flame pentlandite developed within the pyrrhotite grains, whether at fractures or defect-free areas, is invariably enveloped in a thin sheath of monoclinic pyrrhotite which is elongated parallel to the flame".

Pyrite is a minor phase that occurs only locally in the Sudbury-type ores. It has been found in the ores of the Craig mine as irregular anhedral masses up to 2 mm across and as distorted cubes up to about 400 μm across in the dark norite breccia type of ore. The grains are uniform in appearance when viewed in reflected light and occur in intimate association with monoclinic pyrrhotite, pentlandite, chalcopyrite, and magnetite. Craig (1973) determined that pyrite and pentlandite could not stably coexist above about 225°C because of the stability of the *mss*, which spans the system Fe–Ni–S at higher temperatures. It is thus likely that the pyrite–pentlandite coexistence represents a relatively late and low-temperature equilibration of the ores.

Chemical textures

The present study is an outgrowth of the work reported in Craig *et al.* (1998). We initially merely sought to examine the chemical homogeneity of pyrrhotite in the areas adjacent to pentlandite. However, as each analysis and scan provided new data, the study expanded

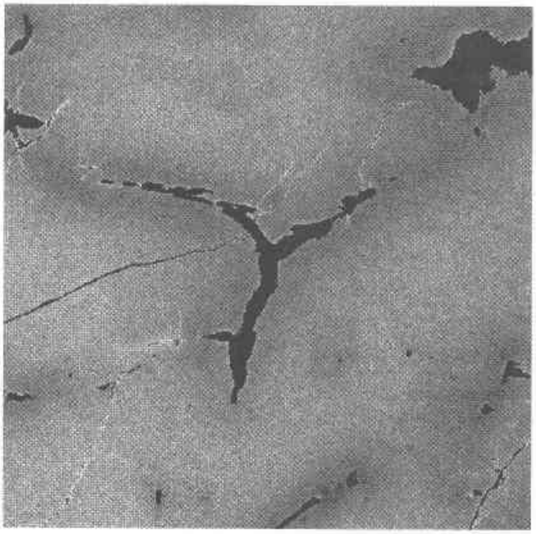

FIG. 6. Nickel X-ray map showing depletion zones in pyrrhotite around pentlandite chains. This map demonstrates that there is nickel depletion adjacent to the margins of the presumably earlier-formed chains of pentlandite as well as around the later-formed lamellae. As in Figure 5, the pentlandite appears black because we have used a threshold to eliminate it and to permit the illustration of the variable nickel contents of the pyrrhotite.The field of view is approximately 500 μm wide.

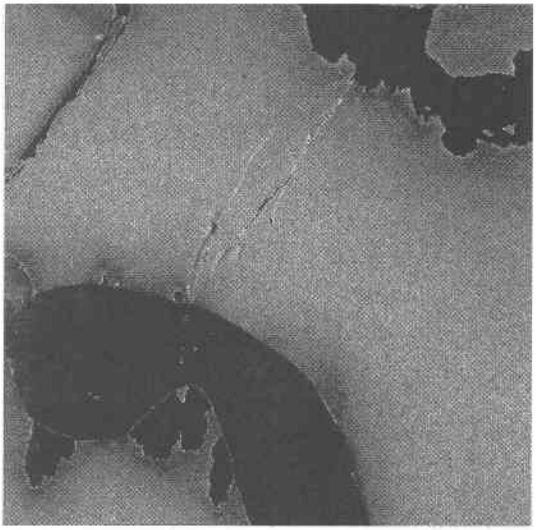

FIG. 7. Nickel X-ray map showing depletion zone developed in pyrrhotite adjacent to a grain of magnetite (rounded grain at lower left) as well as pentlandite (upper right and flame-like structures adjacent to the magnetite). Nickel-depletion zones occur in the pyrrhotite even around non-nickel-bearing phases, probably as grain-boundary diffusion. The pentlandite appears black, as it does in Figures 5 and 6, in order to enhance the differences in the nickel contents of the pyrrhotite. The field of view is approximately 500 μm.

from pyrrhotite to pyrite and on to pentlandite. The bulk composition of the ores of the Craig mine in general, and the samples examined in particular, is very typical of Sudbury-district ores. Moore & Nikolic (1994) reported an average overall grade of 2.01 wt.% nickel and 0.74 wt.% copper and listed values for the sulfide contents of the ore zones ranging from 5.6 to 6.8 wt.% nickel and 0.75 to 2.8 wt.% copper. The cobalt content of the sulfides ranges from 0.14 to 0.21 wt.%. These nickel, copper, and cobalt contents would easily be accommodated within a single homogeneous *mss* phase at temperatures above 600°C as its limits have been defined by experimental studies.

Pyrrhotite

It is generally accepted that the pentlandite lamellae represent products of solid-state diffusion of nickel from an initially homogeneous pyrrhotite to points of nucleation during cooling of the *mss*. Although pentlandite is stable in a high-temperature form up to 865°C (Sugaki & Kitakaze 1998), it is likely that exsolution actually began at much lower temperatures, at which point the compositional limits of the *mss* would have been reduced. It is also generally recognized that pyrrhotite re-equilibrates much more rapidly and to lower temperatures than many other sulfides. Hence the chemical investigation began with a simple scan across an exsolved lamella of pentlandite in an apparently homogeneous matrix of pyrrhotite to determine if there are any variations in the nickel content of the pyrrhotite and, if so, whether they have a relationship to the pentlandite. The result (Fig. 4) revealed that, indeed, there exists a clear zone of nickel depletion up to 80 μm wide on each side of the pentlandite lamella. In this zone, the average nickel content of approximately 0.7 wt.% in areas removed from the pentlandite decreases to as low as 0.5 wt.% immediately adjacent to the pentlandite. Subsequently, elemental mapping of an area containing several lamellae (Fig. 5) revealed that the zone of nickel depletion, as evidenced by the darker shading, exists as a complete concentric zone about the lamellae. These depletion zones are consistent with the expectations of the earlier works of Naldrett *et al.* (1967) and the subsequent speculations of Kelly & Vaughan (1983), who said that "S-enriched and Ni-depleted areas would also occur around pentlandite flames". The next step was to examine the distribution of nickel in pyrrhotite around chains of pentlandite. Despite the general conclusion that the chains represent nickel that had diffused into exsolved phases much earlier and at higher temperatures than in the case of the small lamellae, we found that

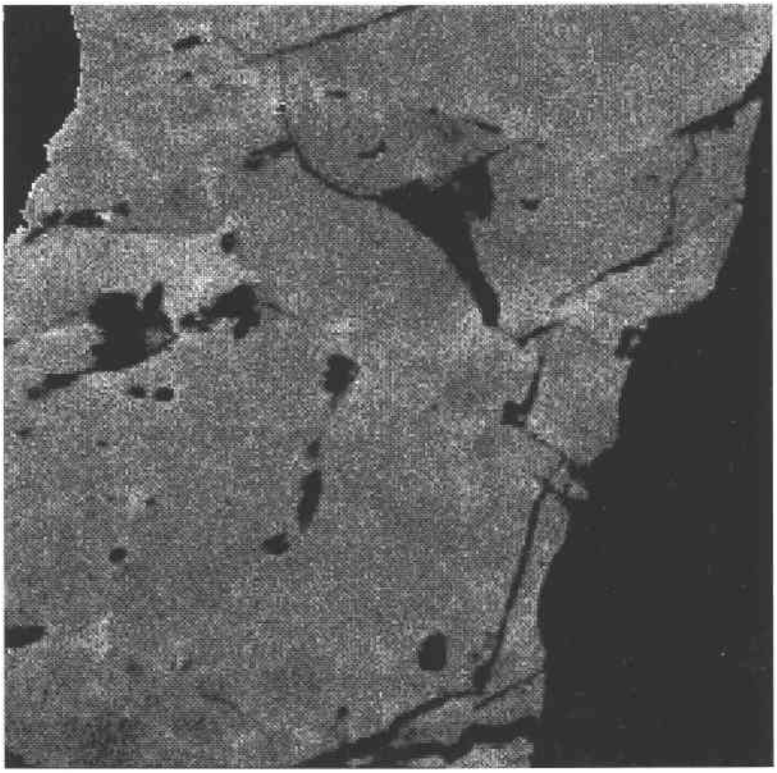

FIG. 8. Nickel X-ray map illustrating compositional variations within a chain of pentlandite. The nickel contents range from 1.5 to 0.7 wt.% in blotchy irregular patterns; the more nickel-rich areas appear lighter in the image. Other phases have been made black in order to enhance the variations of the nickel contents of the pentlandite. The field of view is approximately 100 μm.

there were Ni-depletion zones surrounding the chains just like those around the lamellae (Fig. 6). Thus it appears that the margins of the chains served as nucleation sites to which nickel could diffuse, just as the lamellae.

The depletion zones adjacent to the pentlandite lamellae and chains are very similar to the depletion zones recently documented by Mizuta & Scott (1997) in their study of iron depletion from sphalerite around inclusions of chalcopyrite and pyrrhotite. They concluded that the depletion zones in the sphalerite represented diffusion down to temperatures as low as 245°C. Inasmuch as pyrrhotite readily re-equilibrates more rapidly than sphalerite (Barton & Skinner 1979), and diffusion rates in pyrrhotite are likely much greater than those in sphalerite, it is further likely that the diffusion responsible for the depletion zones shown in this work continued to temperatures far lower than 245°C.

Subsequently, we examined the nature of nickel distribution at the boundaries of pyrrhotite with non-nickel-bearing phases, chalcopyrite and magnetite. As is apparent in Figure 7, there exists a nickel-depletion zone within the pyrrhotite adjacent to those phases just as one exists along the margins of the pentlandite chains and lamellae. In Figure 7, it appears that there may well be a slightly larger nickel-depletion zone adjacent to the pentlandite flames (at the boundaries of the magnetite) than exist around the entire magnetite grains. It is not known whether these depletion zones around the chalcopyrite and magnetite might actually represent areas adjacent to non-visible pentlandite (which were slightly above or below the plane of the polished section or grains too small to be imaged). It is also possible that the margins of the pyrrhotite grains were generally depleted by grain-boundary diffusion of nickel, which now occurs in some of the widespread chains of pentlandite. Certainly, the size of many pentlandite chains requires that there has been considerable movement of nickel, and not all of it from immediately adjacent local areas. We also scanned for cobalt in the pyrrhotite, but the levels of cobalt are below the limits of detection or reveal no recognizable patterns of depletion comparable to those of the nickel.

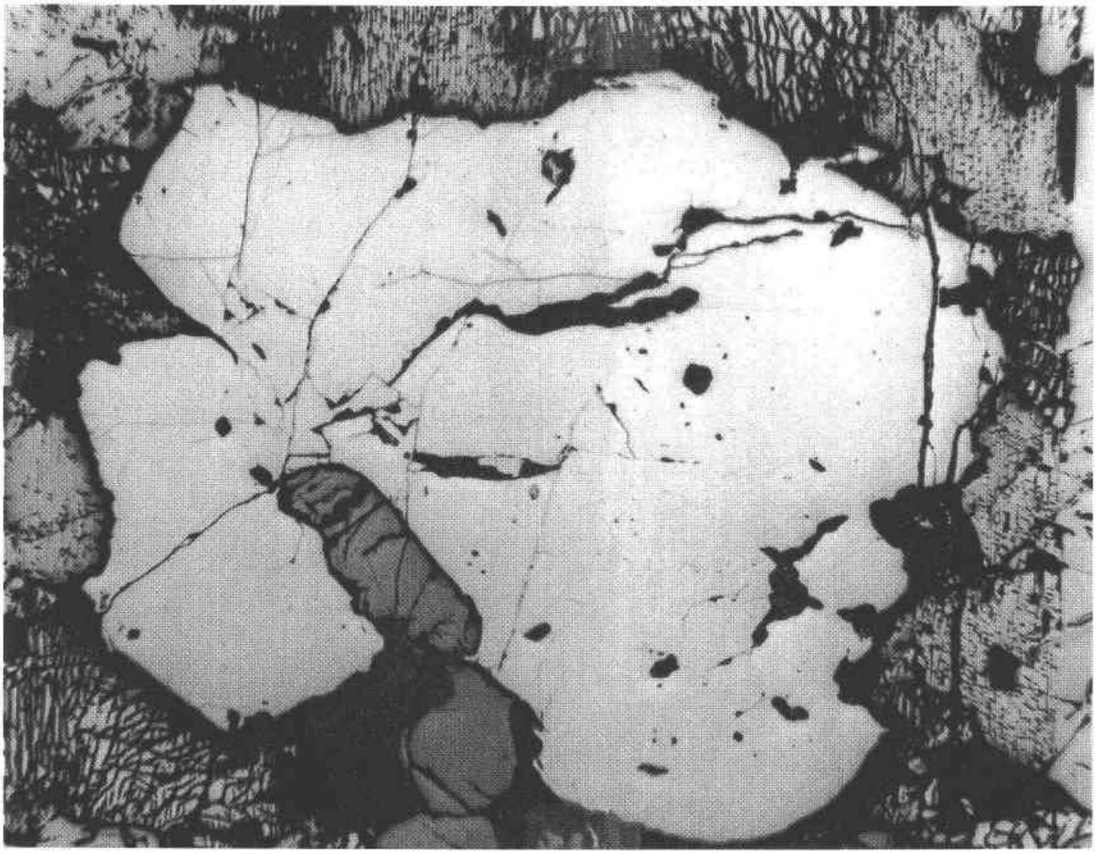

FIG. 9a. Reflected-light image of an anhedral grain of pyrite set in a mass of pyrrhotite and enclosing an elongate grain of magnetite. The field of view is approximately 1.5 mm.

The discovery of the diffusion zones in pyrrhotite around pentlandite lamellae and adjacent to other phases may permit estimation of the rates of diffusion and the temperatures at which diffusion stopped, as has been done by Mizuta & Scott (1997) in sphalerite. Such an investigation would better be carried out using samples whose origins and histories are better known than those examined in the present study.

Pentlandite

There has been the tacit assumption, and published comments, that the composition of pentlandite is essentially constant in individual samples of Sudbury-type ores. It is, of course, well known that pentlandite compositions can range widely in terms of nickel, iron, and cobalt contents between natural ores and compositions in the Co–Ni–Fe–S system (Kaneda *et al.* 1986). We have examined the nickel and cobalt contents of some representative chains of pentlandite and found that there are small but significant variations of nickel in pentlandite (Fig. 8); some spot analyses taken in the highest and lowest nickel zones of the pentlandite images revealed differences in the nickel contents ranging from 0.5 to 1.3 wt.%.

Pyrite

Pyrite occurs only sparingly in Sudbury-type nickel ores, but has been found in many occurrences. Although there are relatively few data on the nickel contents of pyrite from nickel ores, there exist a few data from deposits in Australia and in Canada. Donaldson & Bromley (1981) reported 0.2 wt.% Ni in typical pyrite from western Australia. Hawley (1962) did report a rare nickeloan pyrite, with 5–6% Ni, from the Worthington, Foy, and Milnet deposits at Sudbury, but noted that most contain less than 0.6 wt.% Ni. Cobalt contents in pyrite from the same types of environments range from below 0.1 wt.% (Donaldson & Bromley 1981) to 0.5–1.3 wt.%

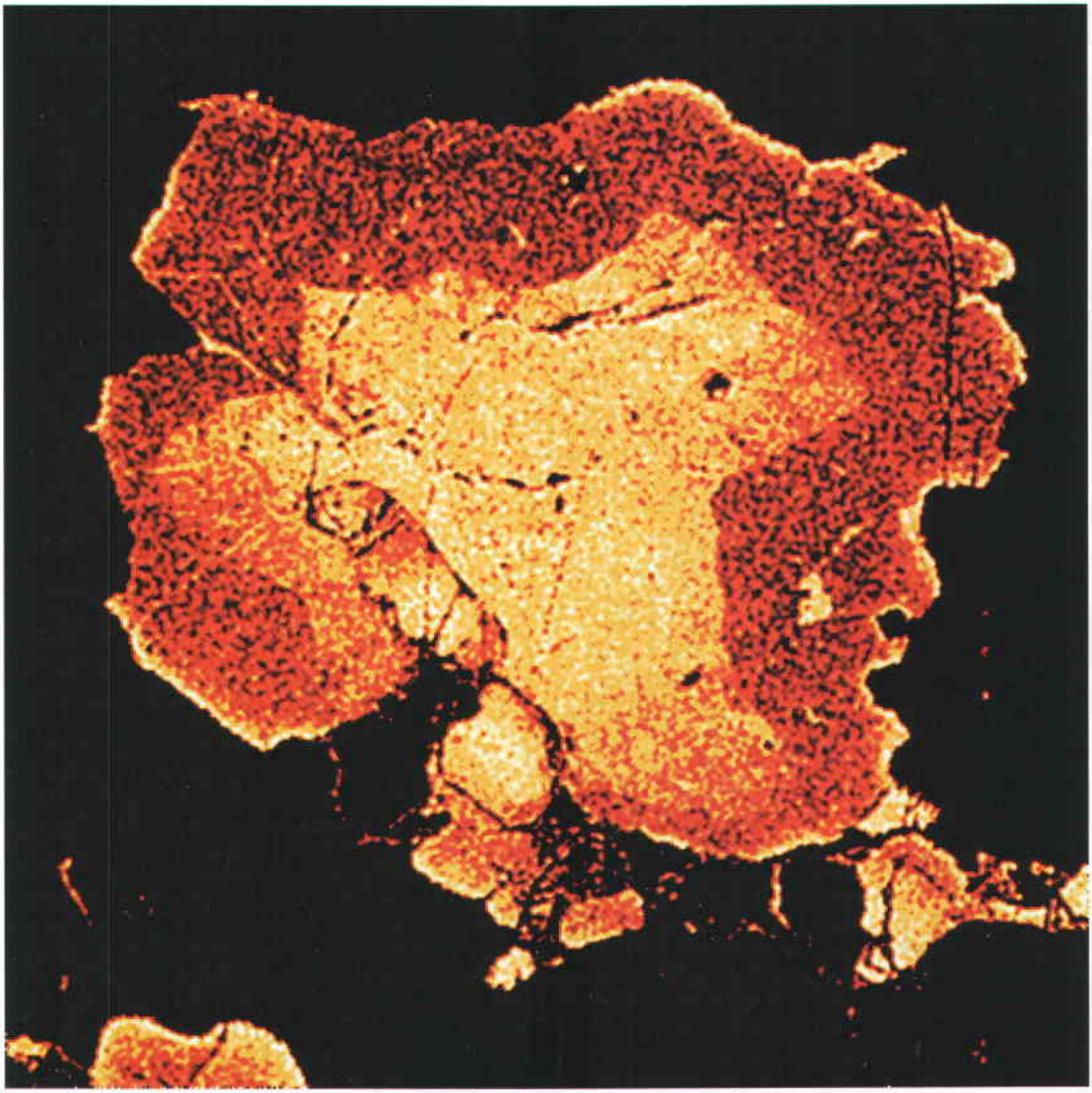

FIG. 9b. Nickel X-ray map of the pyrite grain shown in Figure 9a. There is a slight enrichment in the nickel content in the central area of the pyrite, as indicated by the slightly brighter zone in the image. There is a darker, lower-nickel-content zone extending approximately three-quarters of the way around the core. The nickel content is also shown in profile in Figure 10a. Adjacent phases, including pentlandite, which has a high content of nickel, have been eliminated by use of a threshold.

(Porter & McKay 1981). Hawley (1962) reported the cobalt content of pyrite ranging from 0.2 wt.% to a maximum of 1.7 wt.% in the Fecunis Lake deposit at Sudbury; Naldrett (1984) noted that "a minor amount [of cobalt] is present in the pyrite" from the same area.

Two random, but representative, areas of pyrite were selected for investigation of minor element contents. The first of these (Fig. 9a) is a rather irregular 2-mm-wide grain set in a matrix of pyrrhotite containing small elongate and roundish inclusions of magnetite. There was no evidence of any inhomogeneity using normal optical examination. However, elemental mapping of nickel (Fig. 9b) revealed minor variation, the core region containing very slightly more Ni than the outer parts. In contrast, the cobalt distribution (Fig. 9c) is very complex and generally concentric. The crudely central zone in which Ni contents are slightly elevated contains higher, but rather irregular, zones of higher Co content. Around this, on most sides of the grain, is a zone lower

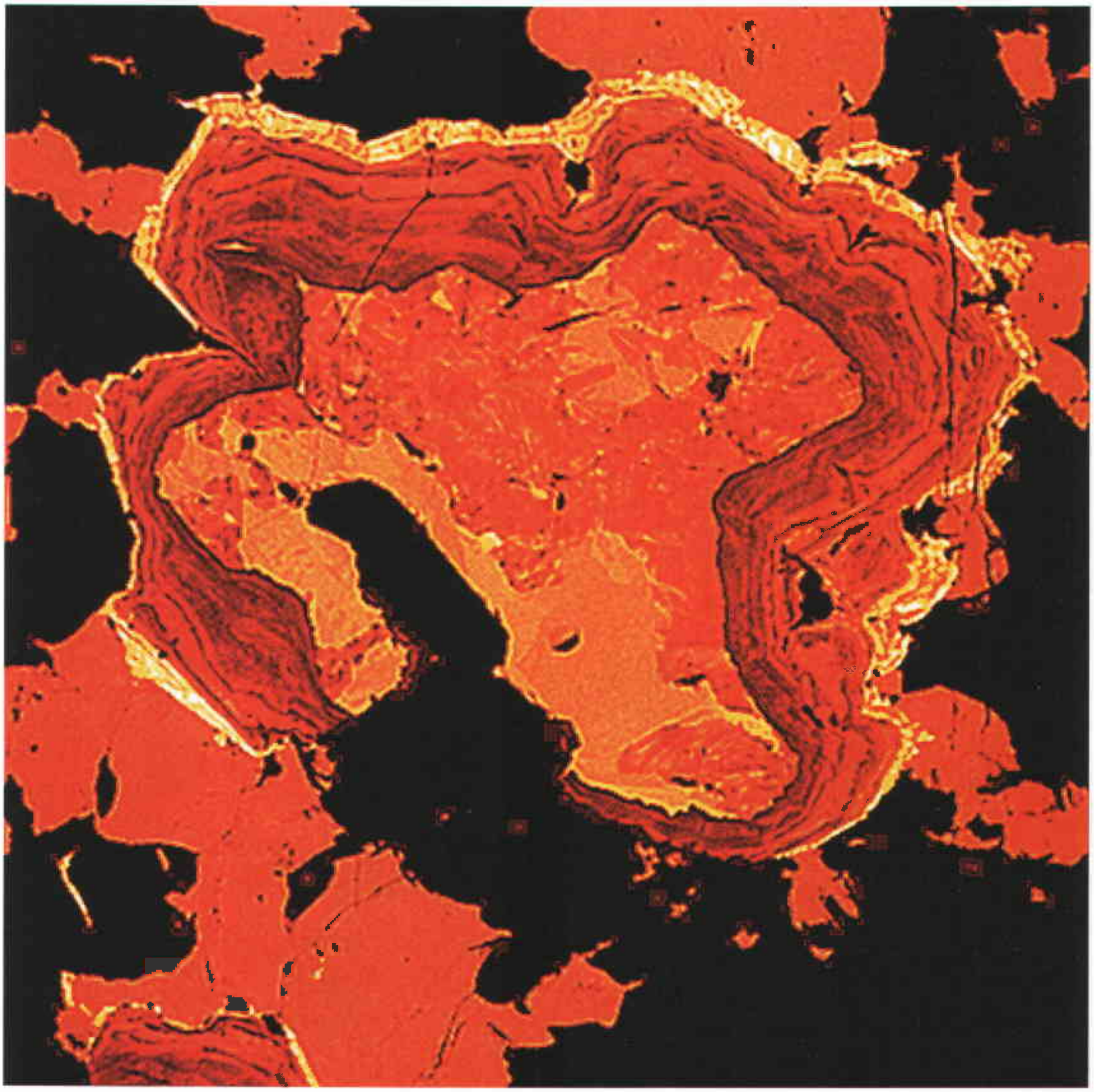

FIG. 9c. Cobalt X-ray map of the pyrite grain shown in Figure 9a. There is a central region with a patchy irregular distribution of cobalt surrounded by a zone that contains concentric zones of variable cobalt content. Higher brightness of an area indicates a higher concentration of cobalt. Thus it is apparent that the outermost zone, presumably the last to form, is the richest in cobalt. The variations of cobalt content are also illustrated in the profile shown in Figure 10b. Other phases have been eliminated by using a threshold.

in Co content. There is, however, within this latter zone, evidence of subtle concentric zones of slightly variable Co content. The very outer zone, brightest in Figure 9c, is very rich in cobalt; careful examination reveals that it also contains subtle zones. Two traverses across the pyrite grain in Figure 9a reveal the higher contents of Ni in the central zone (Fig. 10a) and the zonation in Co (Fig. 10b). The highest cobalt contents, in the outermost zone, reach 3.5 wt.%.

The second occurrence of pyrite consists of two 100-μm euhedral grains (Fig. 11a), one displaying a roughly cubic section, and the other, a nearly triangular section. The cobalt-distribution image (Fig. 11b) reveals a well-developed zonal pattern, with alternating zones of higher and lower values. Figure 11c is a profile across the growth-zoned pyrite shown in Figure 11a. The pattern suggests that the more triangular grain actually consists of two grains, as is indicated by the two triangular zones of cobalt enrichment. Both pyrite occurrences show that same general tendency of a more cobalt-rich core zone surrounded by a cobalt-depleted zone. The only reference reporting a similar type of zoning known to the authors is that of Stekhin (1994), who noted that "pyrite forms zoned crystals showing zones alternately enriched in nickel and cobalt" from the Talnakh ores in Russia. Unfortunately, he did not report any data on the composition of the zones or additional details.

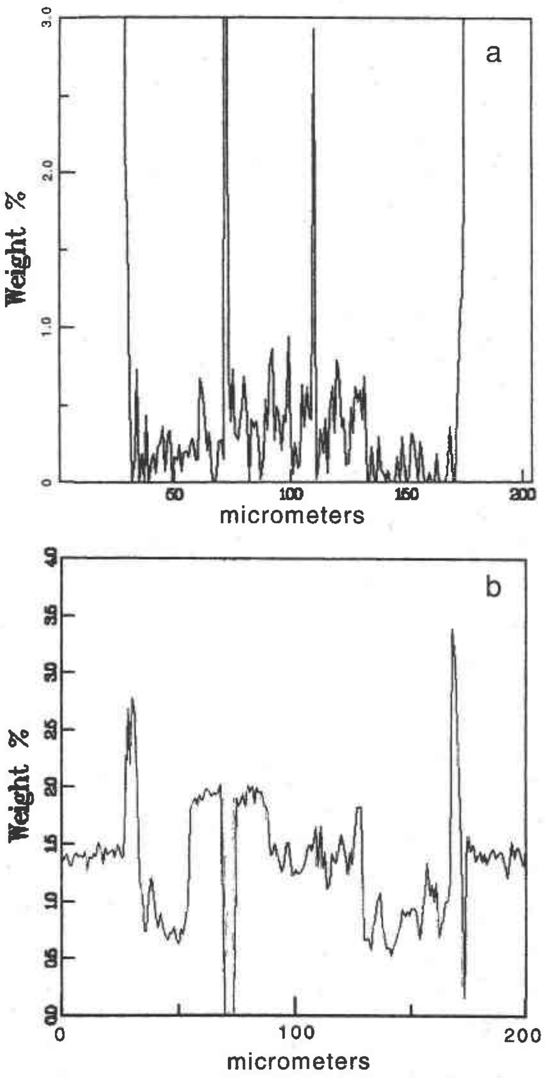

FIG. 10. a. Profile showing the nickel content along a traverse across the pyrite grain shown in Figure 9a. Analyses were made at 5 μm steps and show that the nickel contents in the central portion of the pyrite reach maximum values of approximately 0.7 wt.%. b. Profile showing the cobalt content along a traverse across the pyrite shown in Figure 9a. Analyses were taken at 5 μm steps and show that the cobalt contents vary irregularly in the interior portion of the grain but increase up to more than 3.5 wt.% at the outer margin.

Chalcopyrite

The cobalt and nickel contents of the chalcopyrite grains were not sufficiently high for this technique to reveal any variations.

DISCUSSION AND CONCLUSIONS

The samples available in this investigation and the data derived are too few and limited to permit extensive discussion or to provide sufficient information for sweeping conclusions. They are sufficient, however, to give insights into a few important aspects of the ores of the Craig deposit in particular, and of Sudbury district ores in general.

(1) The ores of the Craig deposit are very typical of Sudbury district ores in their bulk composition and the mineralogy and ore textures.

(2) The dominant ore minerals of the Craig deposit, pyrrhotite, pentlandite, and pyrite are not uniform in composition, as generally believed. Electron-microprobe analysis, analytical profiles, and element-distribution maps reveal significant chemical inhomogeneities.

(3) Grains of pyrrhotite contain zones of nickel depletion adjacent to pentlandite flames and chains. The average nickel content of about 1.1 wt.% in most of the pyrrhotite decreases to about 0.6 wt.% immediately adjacent to the pentlandite along smooth diffusion-controlled boundaries. The pyrrhotite also displays nickel-depletion zones around the margins of grains adjacent to other phases such as magnetite and chalcopyrite.

(4) Pentlandite chains were found to contain local variations in nickel and cobalt contents, but no distinctive patterns were observed.

(5) Pyrite crystals and grains, with no optically visible variations, were found to contain weak nickel zoning but dramatic cobalt zoning. In some euhedral crystals, the zones are parallel to the crystal faces. In other grains, the zones are truncated by sharp disconformities, suggestive of multiple periods of growth or some process that has leached cobalt from pyrite. The sharpness of the boundaries between Co-rich and Co-poor zones suggests deposition under differing conditions of cobalt availability rather than some sort of removal by diffusion.

(6) Chemical zonation in ores such as those from the Craig mine may contain significant information that can be correlated within areas or zones of deposits and that may be interpretable in terms of the origin and cooling history of the ores.

(7) Growth zones are developed within pyrite and provide evidence for sequential removal of nickel and cobalt from the host monosulfide solid-solution during its contraction as the ores cooled.

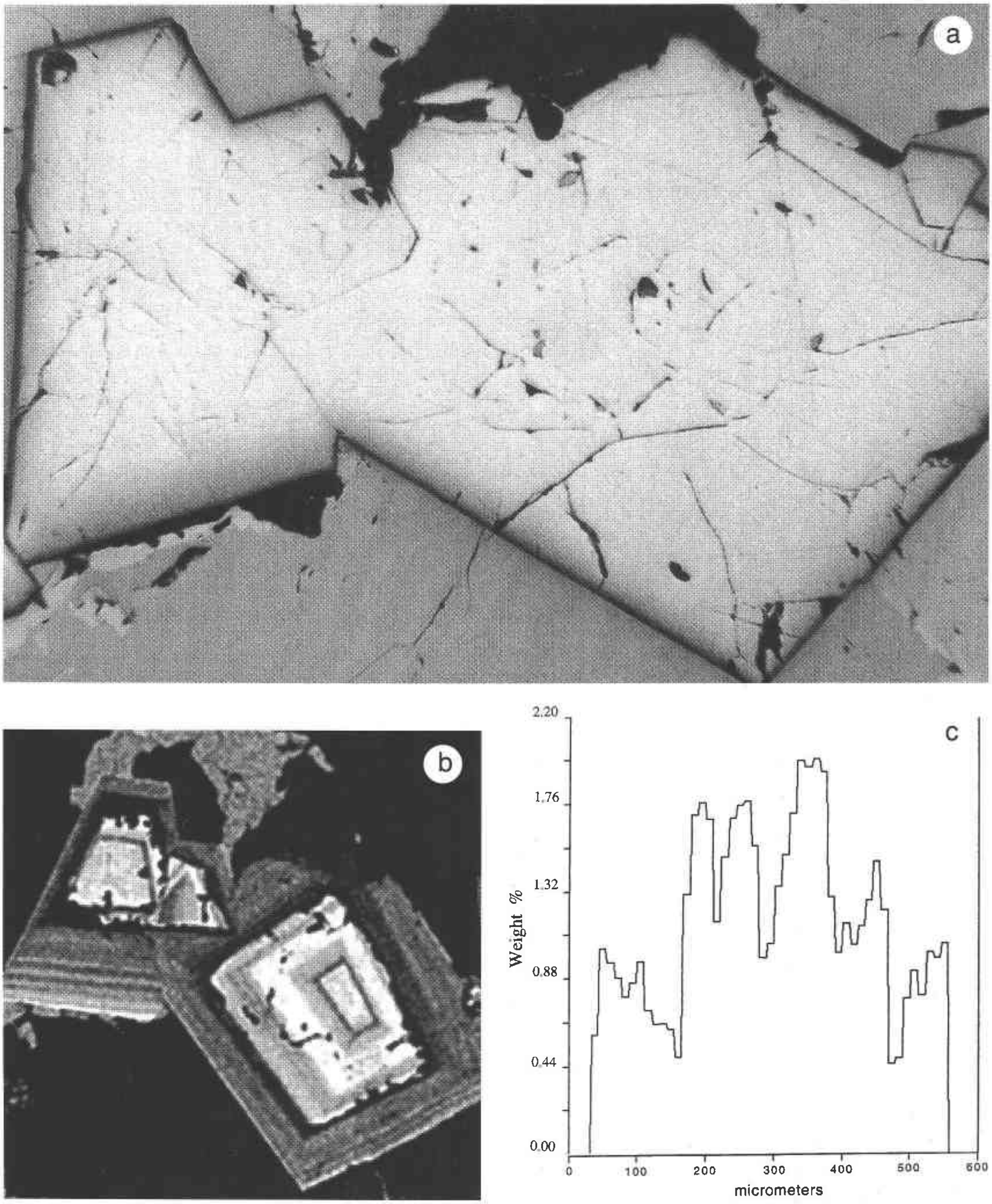

FIG. 11. a. Reflected-light photomicrograph of euhedral grains of pyrite in a matrix of pyrrhotite. The field of view is approximately 1.4 mm across. b. Cobalt X-ray map of the pyrite grains shown in Figure 11a. It is apparent that the cobalt content ranges widely, but the variations define concentric zones parallel to the margins of the crystals and presumably represent growth zones that incorporated variable amounts of cobalt from the surrounding medium during formation. c. Profile showing the cobalt content along a traverse across the larger subhedral grain of pyrite shown in Figure 11a. Analytical points were taken at 5 μm intervals.

(8) Nickel-depletion gradients, resulting from diffusion of nickel from the monosulfide solid-solution, have been preserved as the ores cooled below the point at which the ores were "quenched".

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