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**PETROLOGY AND CRYSTALLIZATION HISTORY OF MULTI-  
PHASE SULPHIDE DROPLETS IN A MAFIC DYKE FROM  
URUGUAY: IMPLICATIONS FOR THE ORIGIN OF  
CU-NI-PGE-SULPHIDE DEPOSITS**

**H. M. PRICHARD , D. HUTCHINSON and P. C. FISHER**

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by

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# **PETROLOGY AND CRYSTALLIZATION HISTORY OF MULTI-PHASE SULPHIDE DROPLETS IN A MAFIC DYKE FROM URUGUAY: IMPLICATIONS FOR THE ORIGIN OF CU-NI-PGE-SULPHIDE DEPOSITS**

## **ABSTRACT**

Sulphide blebs in a mafic dyke from the Uruguayan Dyke Swarm replicate, in miniature, many of the features observed in other world-class platinum-group element-enriched nickel-copper-sulphide deposits, such as at Sudbury and Noril'sk. The blebs crystallized from droplets of immiscible sulphide-oxide liquid to form ~ 1 cm-wide ovoid structures with a geopetal morphology – pyrrhotite and pentlandite are found at the base, chalcopyrite and cubanite at the top and titaniferous magnetite at the margins. Titaniferous magnetite crystallized first, which subsequently exsolved titanium in the form of microscopic ilmenite laths. This was followed by a nickel-poor iron-rich monosulphide solid solution (MSS) phase, which sank to the bottom of the droplets to form pyrrhotite with orientated laths of olivine. Pentlandite crystallized from the residual Ni- and Cu-rich sulphide liquid, while the remaining copper-rich liquid in the upper part of the droplets formed an intermediate solid solution (ISS) phase from which chalcopyrite and cubanite subsequently exsolved. On cooling, excess nickel in the pyrrhotite exsolved from to form Ni-rich pyrrhotite along the contacts to the pentlandite and chalcopyrite. The residual, extremely evolved Cu-, Fe-, S-rich, Pd-, Sn-, Pb-, Mo-, Ag-, Bi-, Te- and Sb-bearing liquids were expelled along brittle, radially orientated fractures in the magnetites to form 10-20  $\mu\text{m}$ -wide chalcopyrite veinlets, many of which terminate as 100  $\mu\text{m}$ -wide sulphide globules where they exit the magnetites. Such features indicate a direction of veinlet filling, which was away from the blebs. Textural evidence suggests that the sulphide droplets sank during crystallization of the dyke (a distance of less than 1 mm relative to the adjacent silicate) into already partially crystallized silicates and the earlier formed magnetite crystals, which consequently, led to their partial resorption. An assemblage of quartz-plagioclase symplectite and amphibole at the top of the blebs represents the products of crystallization of a highly evolved silicate melt that was drawn into the space above the droplets as they sank. The radial nature of the magnetite fracture patterns and their filling by late-stage, evolved, Cu-rich sulphide liquids, indicate that the fracture mechanisms were related to the crystallization processes rather than later tectonic events. Furthermore, the Bi, Te and Sb in the chalcopyrite veins have a late magmatic origin associated with crystallization of the immiscible sulphide-oxide liquids rather than being introduced later via hydrothermal fluids.

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# **PETROLOGY AND CRYSTALLIZATION HISTORY OF MULTI-PHASE SULPHIDE DROPLETS IN A MAFIC DYKE FROM URUGUAY: IMPLICATIONS FOR THE ORIGIN OF CU-NI-PGE-SULPHIDE DEPOSITS**

## **INTRODUCTION**

It is well known that Pt and Pd are chalcophile and siderophile with very high partition coefficients between sulphide and silicate melts (Bezmen *et al.*, 1994) and so are concentrated by immiscible sulphide liquids (*e.g.*, Cabri, 1981). These sulphide melts separate from silicate magmas and crystallize to form platinum-group element (PGE) - enriched and base metal-rich sulphide deposits (*e.g.*, Naldrett, 1981; Campbell and Barnes, 1984). The immiscible sulphide liquids fractionate as they cool, producing a cumulate Ni-, Fe-rich monosulphide solid solution (MSS) and leaving a Cu-rich liquid that subsequently crystallizes to form an intermediate solid solution (ISS). Iridium, Ru and Rh are extracted from the sulphide liquid early and are incorporated into the cumulate MSS, whereas Pt, Pd and Au are concentrated in the remaining Cu-rich liquid (Hawley, 1965; Kullerud *et al.*, 1969; Ewers and Hudson, 1972; Naldrett *et al.*, 1982; Fleet *et al.*, 1993, 1996; Li *et al.*, 1996; Barnes *et al.*, 1997). Pyrrhotite and pentlandite exsolve from the MSS during subsolidus cooling (Naldrett *et al.*, 1967), although recent experimental evidence suggests that, in Ni-rich systems, pentlandite can coexist with the sulphide liquid in peritectic relations and therefore much of the coarse pentlandite observed in sulphide ores may represent a primary magmatic texture (Sugaki and Kitakaze, 1998). Pentlandite may also form at the contact between chalcopyrite and pyrrhotite. Chalcopyrite, cubanite, mooihoekite, haycockite and talnakhite exsolve from the ISS (Cabri, 1973; Craig and Scott, 1974; Naldrett, 1989). Thus major PGE-enriched Ni-Cu-sulphide deposits are often zoned into pyrrhotite-pentlandite-rich ores and chalcopyrite-rich ores. Such zoning has been described from the North Range deposits at Sudbury (Li *et al.*, 1992; Naldrett *et al.*, 1994a) where Cu-rich offshoot ores spread out away from and beneath the massive cumulate MSS. Also in the Noril'sk deposits, for example in the Oktyabr'sk deposit, the lower and marginal ores are pyrrhotite-rich whereas the central overlying ores are often Cu-rich (Distler *et al.*, 1977; Zientek *et al.*, 1994; Naldrett *et al.*, 1994b). Many PGE-enriched Ni-Cu-sulphide deposits such as in Sudbury, Noril'sk, Jinchuan in China and deposits associated with komatiites, such as Raglan in northern Quebec (Barnes *et al.*, 1982) and Kambalda in western Australia (Groves *et al.*, 1986), have been overprinted by regional metamorphic and tectonic events and subjected to later hydrothermal alteration. Therefore it is difficult to distinguish the original precious, base metal and trace element composition of the magmatic immiscible sulphide liquid from that produced by introduction and removal of elements due to later metamorphism or hydrothermal circulation, especially in terms of minor elements such as the volatile elements Bi, Te, Sb and As.

There are a number of early magmatic features of these deposits that are not always easily recognized. For example the effects of differential volume changes during the crystallization of minerals of different densities, such as silicates and sulphides, or the build up of volatile pressures during primary crystallization are rarely preserved in a form where they can be distinguished from the products of later tectonic disruption. The different structural competence of massive sulphides and adjacent silicate rock may concentrate subsequent fracturing and fluid flow in these areas, obscuring primary relationships. Such post magmatic disruption also makes it difficult to determine how the immiscible sulphide liquid and silicate magma behaved during crystallization.

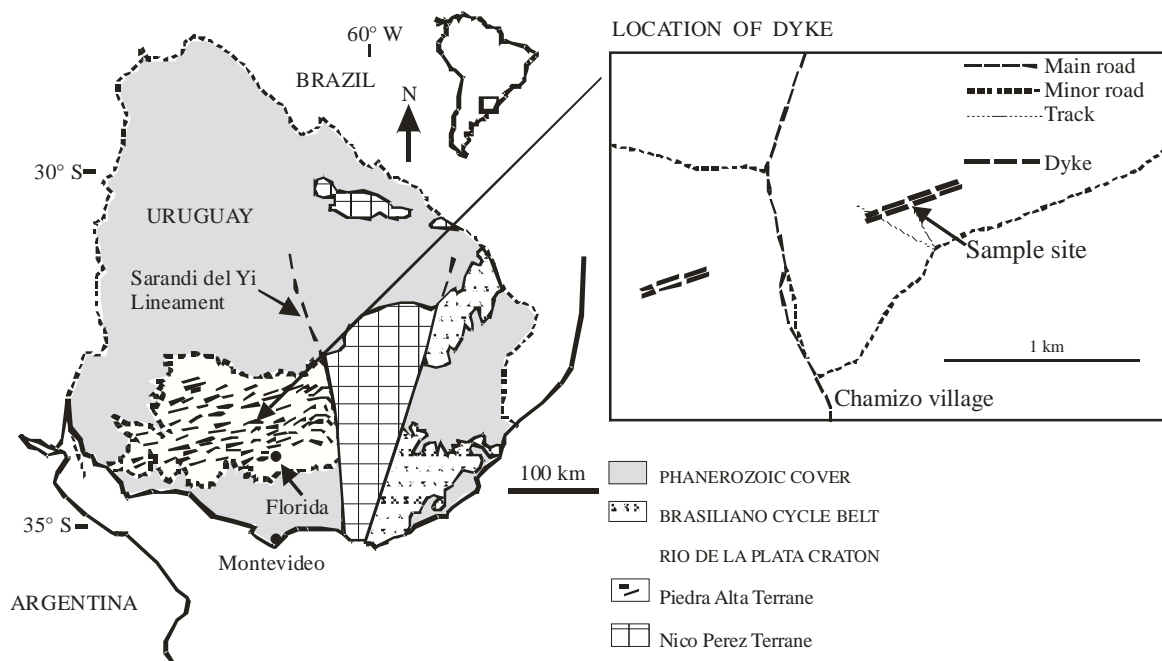
In this paper we examine the mineralogy and textures of an unusual occurrence of sulphide blebs hosted in one mafic dyke belonging to the Uruguayan Dyke Swarm to illustrate and to further understand the processes of formation of primary magmatic concentrations of PGE-bearing Ni-Cu-sulphides. The 1 cm-diameter blebs in the dyke are surrounded by silicate rock in all directions for a distance of 5m. This creates an environment within and immediately adjacent to the blebs in which it is very likely that the distribution and concentration of the trace elements have been isolated from fluids external to the igneous system during post intrusion events. The small size of the blebs also means that there were likely to have been few complications from later tectonic disruption, metamorphism or hydrothermal overprints. Features such as base metal zoning, internal fracturing and evidence for the stages of escape of fractionated immiscible sulphide liquid from the droplet into the partially crystallized surrounding silicate rock and movement of the sulphide droplet relative to the silicate host are preserved.

Sulphide blebs similar to those described here, composed of segregations of chalcopyrite and pyrrhotite with pentlandite, are quite common and typically are associated with and located above massive PGE-enriched Ni-Cu-sulphide deposits. Lightfoot *et al.* (1984) describe sulphide globules from olivine gabbro sills at the Insizwa Complex and similar textures are also reported in PGE-enriched Ni-Cu-sulphide deposits in Noril'sk (Czamanske *et al.*, 1992) and in Sudbury (Naldrett, 1984). Sulphide blebs have been described in oceanic basalt by Czamanske and Moore (1977) and Distler *et al.* (1983). However, detailed mineralogical studies of these blebs are rare.

### **Geology of the host dyke**

The southern portion of the Brazilian Shield has three major Precambrian geotectonic units in Uruguay (Fig.1). These are: (1) the Paleoproterozoic Piedra Alta Terrane; and (2) the Nico Perez Terrane, which together constitute the Rio de la Plata Craton in the west, and (3) the younger Cuchilla Dionisio Neoproterozoic mobile belt (Brasiliano Cycle belt) in the east (Hartmann *et al.*, 2001). The Piedra Alta Terrane lies to the west of the Nico Perez Terrane and consists of granitoids and gneisses of 2.2-1.9 Ga (Rivalenti *et al.*, 1995). It is cross-cut by thousands of ENE-WSW dykes that form the Uruguayan Dyke Swarm which marks a transcontinental intra plate episode within South America which occurred shortly after the Transamazonian orogeny (Teixeira *et al.*, 1999). This swarm is about 100 km wide and almost 250 km long. At its eastern end, the swarm is truncated against the dextral Sarandi del Yi fault which separates the Piedra Alta Terrane from the Nico Perez Terrane, and the dyke swarm has not been found east of the fault (Halls *et al.*, 2001). The swarm is open-ended at its western end where it becomes covered by Phanerozoic strata.

The dykes vary from 0.5 to 80 metres in width but rarely exceed 20-30 metres and are typically 1 km long. Many are up to 5 km long, and individual dykes can be traced for 20 km. The dykes generally strike approximately N70°E, and they are mostly vertical but may dip up to 70° to the south (Bossi *et al.*, 1993; Teixeira *et al.*, 1999). They are generally straight, parallel, have planar walls, chilled margins, sharp contacts with the host rocks, and are undeformed except for displacements caused by local faulting. They are unmetamorphosed and have a grain size of up to 1-2 mm in the center of the thickest dykes. The composition of the dykes is tholeiitic and they have either high or low (less than 1.05 wt %) Ti and are described as andesite or andesitic basalt, respectively (Bossi *et al.*, 1993). The current best estimate for the age of the dykes, based on the Rb-Sr method on 17 whole rock samples from dykes



**Figure 1.** Map showing the location of the sulphide bleb-bearing dyke adapted from Hartmann *et al.* (2001). Quarry site is at 56°40'01"W and 34°09'06"S.

representing both high- and low-Ti types, is  $1766 \pm 124$  Ma (Teixeira *et al.*, 1999), and this combines new data points with those from Bossi *et al.* (1993). More recently a U-Pb age on baddeleyite from one high Ti dyke gave an age of  $1790 \pm 5$  Ma (Halls *et al.*, 2001), and the dykes may have been intruded over a considerable period of time.

The initial sampling of the dyke hosting the sulphide blebs was carried out in 1991 when several dykes within the Uruguayan Dyke Swarm were visited and examined for sulphides. Only one dyke was observed in the field to be sulphide-bearing, and the sulphide blebs described in this study were collected from this dyke in a quarry that lies to the north of Montevideo at 56°40'01"W and 34°09'06"S near the small village of Chamizo (Fig. 1). The dyke is a low-Ti andesite and has an undeformed and unmetamorphosed igneous texture. Mineralogically, the dyke is composed of plagioclase and clinopyroxene with minor ilmenite, biotite, tremolite-ferroactinolite, alkali feldspar, and quartz. The primary igneous silicate minerals are very fresh, although most of the feldspars show minor alteration to clay minerals and the pyroxenes are slightly uralitized. Micrographic and symplectic intergrowth textures between the feldspars and minor quartz are common.

## ANALYTICAL METHODS

Samples of the sulphide-bearing dyke were analyzed for major and trace elements using a Philips PW1400 XRF, and PGE concentrations were determined using a Ni-collection fire assay technique followed by ICP-MS analysis at Genalysis in Perth, Western Australia. Representative major and trace element concentrations in samples of approximately 0.3 kg size from the dyke hosting the sulphide blebs are given in Table 1. Samples UR1 and UR2 host sulphide blebs but the parts of these samples analyzed for major and trace elements were selected to avoid the sulphide blebs. UR7 and UR8 are barren of sulphide blebs. UR1a and

**Table 1 Major and trace element analyses of the dyke containing the blebs**

|                                | UR1  | UR2  | UR7   | UR8   |
|--------------------------------|------|------|-------|-------|
| <b>Major elements (wt %)</b>   |      |      |       |       |
| SiO <sub>2</sub>               | 54.0 | 53.7 | 54.3  | 56.2  |
| Al <sub>2</sub> O <sub>3</sub> | 15.6 | 15.8 | 15.1  | 13.2  |
| Fe <sub>2</sub> O <sub>3</sub> | 10.6 | 10.4 | 11.7  | 14.7  |
| MnO                            | 0.1  | -    | 0.2   | 0.2   |
| MgO                            | 6.6  | 6.9  | 5.7   | 3.0   |
| CaO                            | 9.6  | 9.8  | 9.3   | 6.9   |
| Na <sub>2</sub> O              | 1.5  | 1.3  | 1.6   | 2.1   |
| K <sub>2</sub> O               | 1.0  | 1.0  | 1.2   | 1.9   |
| TiO <sub>2</sub>               | 0.7  | 0.6  | 0.8   | 1.6   |
| P <sub>2</sub> O <sub>5</sub>  | 0.1  | 0.1  | 0.1   | 0.2   |
| LOI                            | -    | 0.1  | -     | -     |
| Total                          | 99.8 | 99.7 | 100.0 | 100.0 |

**Trace elements (ppm)**

|    |     |     |     |     |
|----|-----|-----|-----|-----|
| Pb | -   | 6   | 4   | 4   |
| Ba | 222 | 211 | 289 | 487 |
| Sn | -   | 13  | -   | -   |
| Zn | 61  | 59  | 71  | 82  |
| Cu | 67  | 72  | 77  | 117 |
| Ni | 72  | 74  | 77  | 21  |
| Cr | 96  | 102 | 59  | 33  |
| S  | 155 | 165 | 442 | 491 |
| Cl | 102 | 98  | 93  | 127 |
| Ce | 79  | -   | 69  | 83  |
| Nd | -   | -   | 34  | 47  |
| Ga | 15  | 16  | 15  | 16  |
| V  | 162 | 146 | 185 | 297 |
| Co | 38  | 34  | 168 | 22  |
| Rb | 30  | 30  | 36  | 48  |
| Sr | 164 | 170 | 160 | 168 |
| Y  | 15  | 14  | 16  | 25  |
| Zr | 96  | 88  | 97  | 156 |
| As | -   | -   | -   | -   |
| Mo | -   | 4   | -   | -   |
| Te | -   | 7   | -   | -   |
| Sb | 4   | 3   | -   | -   |
| Ag | -   | -   | -   | -   |
| Cd | 4   | -   | 6   | -   |
| Bi | -   | -   | -   | -   |

**Platinum-group elements (ppb)**

|    | UR1a | UR2b | UR7 | UR8 |
|----|------|------|-----|-----|
| Ru | -    | 2    | -   | 2   |
| Rh | 1    | 2    | 2   | 1   |
| Pd | 14   | 32   | 16  | 14  |
| Os | -    | -    | -   | -   |
| Ir | 2    | -    | 2   | 2   |
| Pt | 12   | 12   | 16  | 14  |

**Foot notes to Table 1**

UR1 and UR2 are samples hosting sulphide blebs; UR7 comes from the centre of the dyke; UR8 comes from the dyke margin, and both are free of sulphide blebs. For major and trace element analysis (excluding samples for PGE analysis) portions of the sample were chosen so as to avoid inclusion of sulphide blebs in the material analyzed. For the PGE analysis portions of samples UR1 and UR2 were chosen to include sulphide blebs. - = not detected. Detection limit is approximately 0.01 wt % for major elements, 2 ppm for trace elements except for 5 ppm for As, Ag and Bi and 2 ppb for PGE.



UR2a, which were analyzed for PGE, were selected from the parts of samples UR1 and UR2 that contain sulphide blebs.

To interpret the mineralogical textures of the sulphide blebs we qualitatively identified the major silicate and sulphide minerals using conventional optical microscopy and a Cambridge Instruments (now Leo) S360 scanning electron microscope (SEM). Quantitative analyses of the sulphide minerals and larger PGM were obtained using the SEM with an Oxford Instruments AN10000 EDX analyzer (Table 2). Operating conditions for the quantitative analyses were 20 kV, with a specimen calibration current of ~1 nA and a working distance of 25 mm. A cobalt reference standard was regularly and frequently analyzed, in order to check for any analytical drift. A comprehensive set of standards, used to calibrate the EDX analyzer, was obtained from Micro Analysis Consultants Ltd. (St Ives, Cambridgeshire). ZAF corrections were performed using an AN 10000 software program ZAF4-FLS. Images were obtained using a four quadrant back scattered detector operating at 20 kV, a beam current of ~500 pA, and a working distance of 13 mm, under which conditions magnifications up to 15000 x are possible. Most of the minor phases and platinum-group minerals (PGM) were too small for quantitative analysis and were identified qualitatively.

**Table 2 Analyses of sulphides and accessory minerals in weight per cent**

|       | 1    | 2    | 3    | 4     | 5    | 6    | 7    | 8    |
|-------|------|------|------|-------|------|------|------|------|
| Fe    | 59.7 | 55.1 | 29.8 | 30.6  | 40.5 | 45.8 | 36.4 | 2.2  |
| Ni    | -    | 7.2  | 34.6 | -     | -    | -    | 17.9 | -    |
| Co    | 0.4  | 0.4  | 1.6  | -     | -    | -    | -    | -    |
| Cu    | -    | -    | -    | 34.0  | 23.4 | -    | -    | -    |
| Ag    | -    | -    | -    | -     | -    | -    | 12.2 | 59.2 |
| Te    | -    | -    | -    | -     | -    | -    | -    | 35.9 |
| S     | 38.4 | 35.6 | 32.8 | 35.4  | 35.6 | 53.2 | 31.1 | -    |
| Total | 98.5 | 98.3 | 98.8 | 100.0 | 99.5 | 99.0 | 97.6 | 97.3 |

1. Pyrrhotite ( $\text{Fe}_{0.89}\text{Co}_{0.01}$ )<sub>0.9</sub>S
  2. Ni-pyrrhotite ( $\text{Fe}_{0.89}\text{Ni}_{0.11}\text{Co}_{0.01}$ )S
  3. Pentlandite ( $\text{Fe}_{4.2}\text{Ni}_{4.6}\text{Co}_{0.2}$ )<sub>9</sub>S<sub>8</sub>
  4. Chalcopyrite  $\text{Cu}_{0.97}\text{Fe}_{0.99}\text{S}_2$
  4. Cubanite  $\text{Cu}_{0.96}\text{Fe}_2\text{S}_3$
  5. Pyrite  $\text{Fe}_{0.99}\text{S}_2$
  6. Argentopentlandite ( $\text{Fe}_{5.37}\text{Ni}_{2.46}\text{Ag}_{0.97}$ )<sub>8.8</sub>S<sub>8</sub>
  7. Silver telluride ( $\text{Ag}_{1.95}\text{Fe}_{0.15}$ )<sub>2.1</sub>Te
- = not detected

## GEOCHEMISTRY AND MINERALOGY

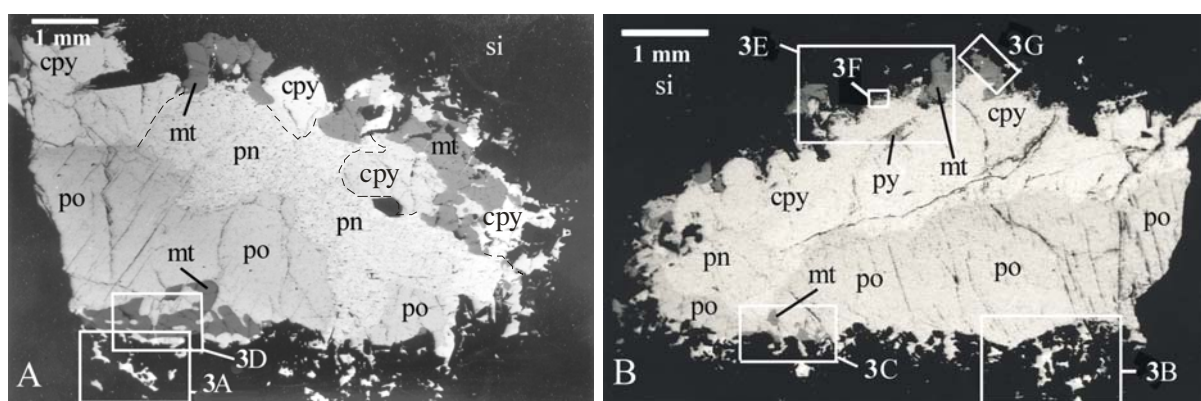
### Sulphide blebs

The sulphide blebs occur in a small irregular patch approximately 2m x 2m near the center of the dyke and the blebs weather to rusty patches on exposed rock surfaces. Visible sulphides and sulphide blebs are rare in the remainder of the dyke exposed in the quarry containing the sampled outcrop. Within the patch they make up less than one percent of the dyke. The blebs

are composed of sulphide minerals, and in hand specimen the blebs are clearly divided into a chalcopyrite-rich half and a pyrrhotite- and pentlandite-rich half. The blebs sometimes show flattening parallel to the junction between the pyrrhotite and pentlandite half and chalcopyrite-rich half and typically have a maximum diameter of 1 cm and a minimum diameter of 0.5 cm. Locally, the blebs are aligned parallel to each other or in en echelon arrays. Owing to difficulties in sampling the precise orientation of the blebs in the dyke could not be determined.

### Mineralogy of sulphide blebs

The blebs consist largely of magnetite, pyrrhotite, pentlandite, chalcopyrite and cubanite. Representative analyses of sulphides and accessory minerals are given in Table 2, and the distribution of the minerals within two blebs is shown in Figure 2 a and b. Magnetite occurs at the margins of each bleb and contains ilmenite laths. Each bleb is divided internally into a lower zone of predominantly pyrrhotite and pentlandite and an upper zone of predominantly



**Figure 2** (A) and (B) Back-scattered electron photomicrographs of oriented sulfide blebs surrounded by silicates (si). Magnetite (mt) occurs around the edges of the sulfide blebs. The blebs are divided into an upper part composed of a cubanite-bearing chalcopyrite (cpy), a central zone of pentlandite (pn), and a lower part of pyrrhotite (po) crossed by magnetite and a Fe-silicate (subvertical lines from bottom left to top right in A and from bottom right to top left in B). In B, a small inclusion of pyrite (Py) occurs within cubanite in the top center. Locations of Fig. 3 A-G are indicated by boxes. The left hand edge of the bleb in A and the right hand edge of the bleb in B runs along the edge of the polished block. The orientation is thought to be approximately upright.

chalcopyrite intergrown with laths of cubanite. These represent original zones of MSS and ISS respectively, from which the observed minerals formed by subsolidus reaction. The pyrrhotite is compositionally homogeneous but may contain long acicular subparallel laths of magnetite. Pentlandite generally forms subrounded crystals either within pyrrhotite or between pyrrhotite and chalcopyrite. Nickel is present not only in pentlandite but also in Ni-pyrrhotite which forms flames in chalcopyrite. These are especially abundant at the contact between chalcopyrite and both pyrrhotite and pentlandite. The Ni-pyrrhotite also occurs with cubanite laths and at the contact of the chalcopyrite with the silicate host minerals. Cubanite laths are most common in the massive zones of chalcopyrite which also locally contain pyrite with tiny inclusions of chalcopyrite.

## **Upper and lower bleb margins**

The margin of the lower pyrrhotite-rich zone with the underlying silicate minerals is strikingly different from the margin of the upper chalcopyrite-rich zone with the overlying silicate minerals. The lower margin is sharp, and the interlocking igneous texture of the pyroxene and plagioclase crystals at the contact with the pyrrhotite is similar to that of the background dyke rocks. The silicate minerals penetrate into the blebs along their lower contacts (Fig. 3a and b). Just above the lower contact of the bleb, magnetite occurs within and is surrounded by the pyrrhotite and commonly has smooth curved crystal edges (Fig. 3c and d).

In contrast, the upper contact of the blebs with the silicate host is irregular, with a granular texture that consists of a mixture of sulphide and silicate minerals (Fig. 3 e and f). A thin (approximately 0.5 mm) zone of silicate minerals above and in contact with the sulphide consists of amphiboles with quartz and feldspar showing a graphic intergrowth texture that differs from the dominant interlocking bladed texture of the surrounding pyroxene and plagioclase of the host dyke. Magnetite occurs within the silicate minerals rather than being enclosed by sulphide minerals and is commonly only in contact with the chalcopyrite along the lower edge of magnetite grains (Fig. 3e).

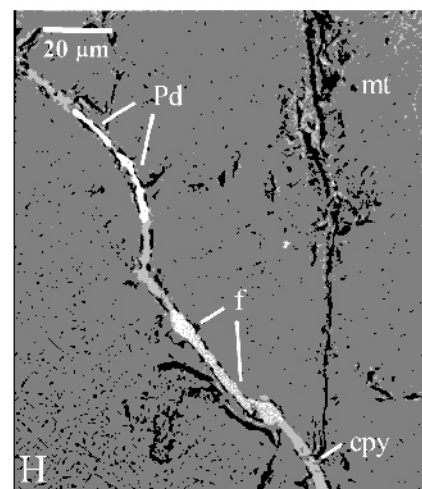
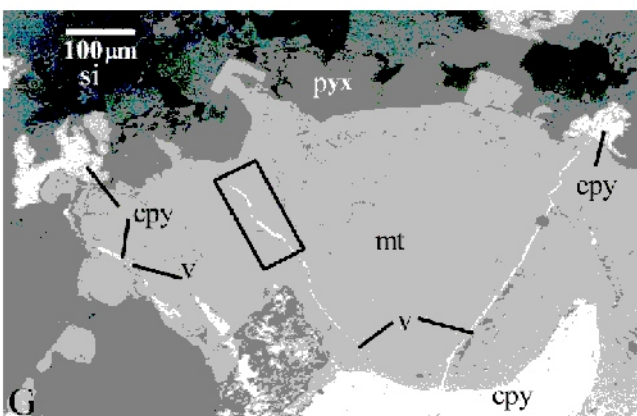
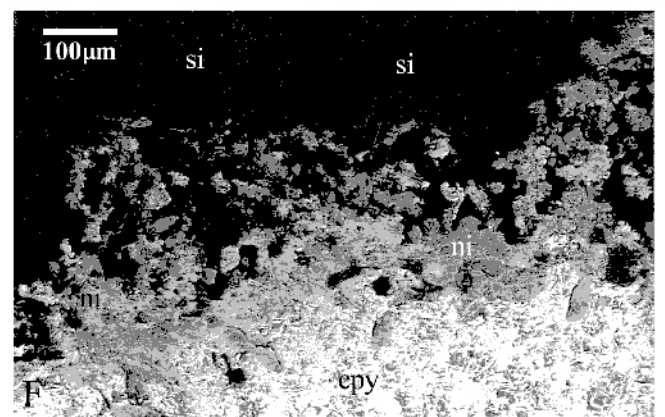
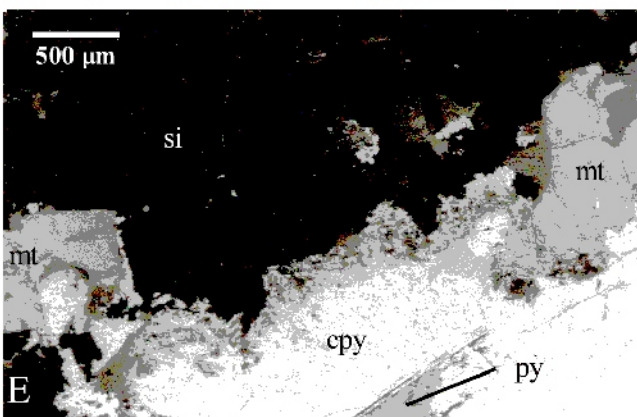
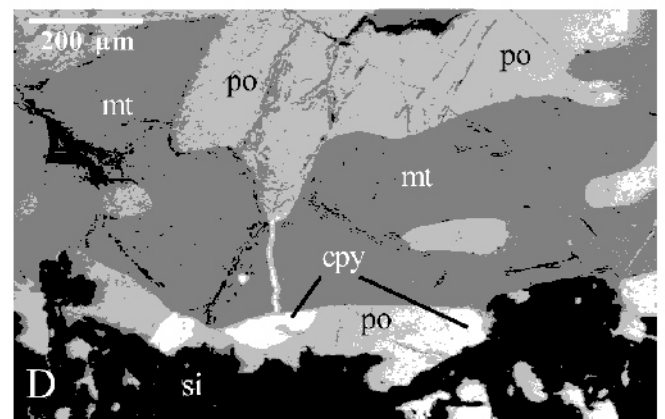
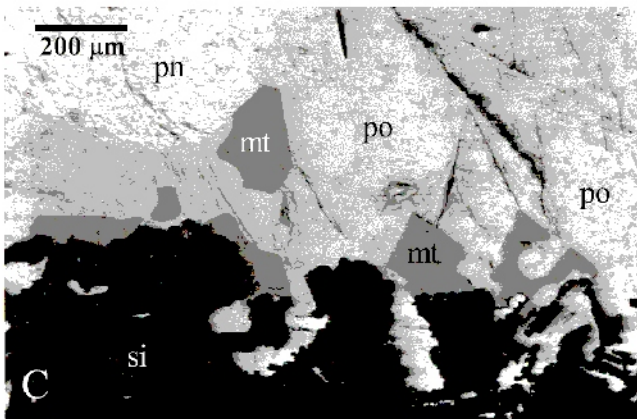
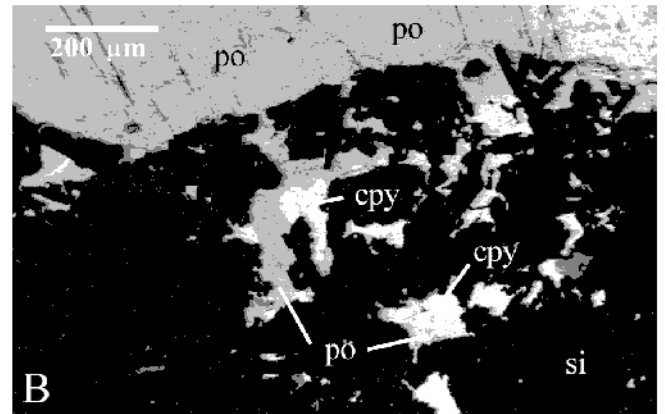
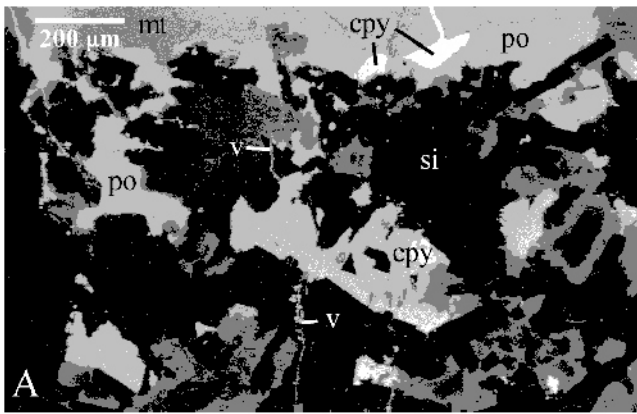
Euhedral feldspar laths, especially at the sides of the blebs, in some cases penetrate the sulphide blebs where they are surrounded by sulphide minerals and are commonly thinner than the feldspar crystals in the host dyke. This suggests that the feldspars impinging on the sulphide bleb margins have been isolated from the supply of silicate melt and so did not grow as fast as feldspars within the rest of the dyke. In a few cases the feldspar laths are replaced by sulphide minerals, producing pseudomorphs of the feldspar laths.

## **Late chalcopyrite fracture fillings**

At both the upper and lower margins of the blebs the magnetite grains are commonly fractured, and these fractures are filled by chalcopyrite. The veinlets also contain the majority of the accessory minerals in the blebs. The veinlets extend from the interior of the blebs to the outer edge of the blebs, cutting through the magnetite grains and terminating at the outer margin of the magnetite in contact with the silicate rock minerals. Homogeneous globules of chalcopyrite commonly occur at the terminations of the fractures where they meet the silicate host especially at the top of the blebs (Fig. 3 d and g).

## **Sulphides external to the blebs**

Sulphide minerals also occur outside the blebs in small patches (much smaller than the blebs) filling spaces interstitial to the silicate minerals. These tend to be concentrated in a zone below the blebs (Fig. 3b). The patches are commonly dominated by chalcopyrite but may be subdivided into chalcopyrite-rich upper parts and pyrrhotite-rich lower parts, mimicking the mineral distribution within the blebs. In addition, fractures sometimes extend from the main blebs for distances of at least 1 mm into the surrounding silicate host. These discontinuous, irregular fractures, often subparallel to each other, are filled with chalcopyrite (Fig. 3a).



**Figure 3.** (A) Close up of Figure 2A. The base of the sulphide bleb appears at the top of the photomicrograph showing enclosed magnetite (mt) and is adjacent to underlying silicates (plagioclase and pyroxene) (si). Chalcopyrite (cpy) occurs as patches within the silicates. Irregular but approximately parallel veinlets of chalcopyrite (v) extend from the base of the bleb and through the silicates as vertical discontinuous lines crossing the left and center of the photomicrograph. (B) Close up of Figure 2B. The lower part of the bleb composed of pyrrhotite appears at the top of the photomicrograph (po) and below this are smaller sulphide patches filling interstitial spaces between silicates (si). These small patches mimic the textures within the main bleb consisting of chalcopyrite (cpy) and pyrrhotite (po) segregations. (C) Close up of Figure 2B. Lower part of the bleb showing curved and rounded grains of magnetite (mt) within the pyrrhotite (po). A patch of pentlandite occurs in the top left hand part of the photomicrograph (pn). Silicate beneath the bleb is shown at the base of the photograph (si). (D) Close up of Figure 2A showing the base of the bleb with magnetite grains displaying subrounded and curved edges (mt) within the pyrrhotite (po) adjacent to silicate (si). A veinlet of chalcopyrite crosses the magnetite and a semicircular area of chalcopyrite (cp) occurs at the end of the veinlet closest to the margin of the bleb. (E) Close up of the upper edge of the bleb shown in Figure 2B. This reveals a granular texture of the contact between the silicates (si) and the chalcopyrite (cpy). Two grains of magnetite (mt) also are located at the contact. A grain of pyrite (py) with two parallel grain boundaries (a possible pseudomorph of feldspar) occurs within a cubanite-bearing chalcopyrite zone at the base of the photograph. (F) Close up of Figure 3E, position shown in Figure 2B, showing the granular texture at the contact of the silicate (si) with the chalcopyrite and cubanite (cpy). Ni-rich pyrrhotite (ni) occurs at the contact. This contrasts with the sharp contact between the silicates and sulphides at the base of the blebs shown in Figures 3A-D. (G) Close up of Figure 2B showing a magnetite grain at the top of the bleb at the junction of the silicates (si) and chalcopyrite (cpy). A rim of pyroxene (pyx) occurs above the magnetite grain. Chalcopyrite fills fractures (v) that cross the magnetite. The veinlets contain globules with irregular outlines composed of chalcopyrite where they reach the top of the bleb. The chalcopyrite veinlets also contain Pd-Bi-Sb and Ag-tellurides. (not shown) The box in G shows the location of Figure 3H. (H) Close up of Figure 3G showing one of the chalcopyrite (cpy) veinlets in magnetite. The veinlet contains an elongate grain of (froidite)  $\text{PdBi}_2$  (f) and smaller elongate grains of Pd-Bi-Sb (Pd). Note the needles of ilmenite exsolving from the magnetite.

### Accessory minerals associated with the sulphide blebs

Minor minerals within the blebs include baddeleyite ( $\text{ZrO}_2$ ) enclosed in chalcopyrite, a rare grain of rhenium sulphide in pyrrhotite, apatite between pyrrhotite and pentlandite, and molybdenite ( $\text{MoS}_2$ ) and argentopentlandite both enclosed in pentlandite. Argentopentlandite also occurs as small grains hosted by a nickeliferous pyrrhotite (Table 2).

Many accessory minerals, including PGM and Bi-Sb- and Te-bearing phases, occur in the chalcopyrite-rich veinlets (Fig. 3 g and h) which cross-cut magnetite grains on the edges of the blebs. In these veinlets, PGM are associated with Bi-Te phases. The largest PGM grain is 3 x 35 microns, which contains 19.7 wt percent Pd and 79.7 wt percent Bi, is interpreted to be froodite ( $\text{PdBi}_2$ ), as described in Cabri and Laflamme (1976). Other PGM, too small for quantitative analysis, include Pd-bearing Sb-Bi phases, a Pd-bearing Bi-Sn phase and a Pd-

bearing Sn phase, possibly paolovite. Silver telluride (hessite,  $\text{Ag}_2\text{Te}$ , Table 2) and silver telluro-bismuthides are also present in the veinlets, and one veinlet is composed largely of galena. Galena and silver telluride also are present in the silicate host near the chalcopyrite-rich edge of the blebs.

### **PGE distribution**

The PGE concentrations in the dykes are low. Four samples from the dyke were analyzed for all six PGE (Table 1), and Pt and Pd values are an order of magnitude higher than the other PGE. Palladium is most enriched in the sulphide-bleb bearing sample UR2a, having a maximum concentration of 32 ppb. The presence of Pd-bearing minerals in late veinlets in the sulphide blebs indicates initial concentration of the Pd into the immiscible sulphide droplets and then a further concentration into the most fractionated liquid filling fractures in the magnetite grains. Here the abundance of Pd is sufficient to form PGM.

## **PETROLOGICAL IMPLICATIONS OF THE TEXTURES OF THE BLEBS**

### **Sequence of mineral formation in the blebs**

The sequence of crystallization of sulphide minerals in the blebs is summarized in Figure 4. Magnetite crystallized early around the edges of the immiscible liquid, accompanied by crystallization of MSS, removal of Fe and Ni from the sulphide liquid, and fractionation to produce a more Cu-rich liquid. The fractionated liquid then crystallized to ISS. The final residual liquid was not only Cu-rich but also enriched in metals such as Pb, Sn, Ag and Mo, as well as Pd, Bi, Te, Sb. This is indicated by the presence of galena, Pd-Cu-Sn-Bi-Te-bearing PGM and hessite in late veinlets. Pyrrhotite and pentlandite then exsolved from MSS during subsolidus cooling, and chalcopyrite and cubanite with Ni-pyrrhotite and minor pyrite exsolved from ISS.

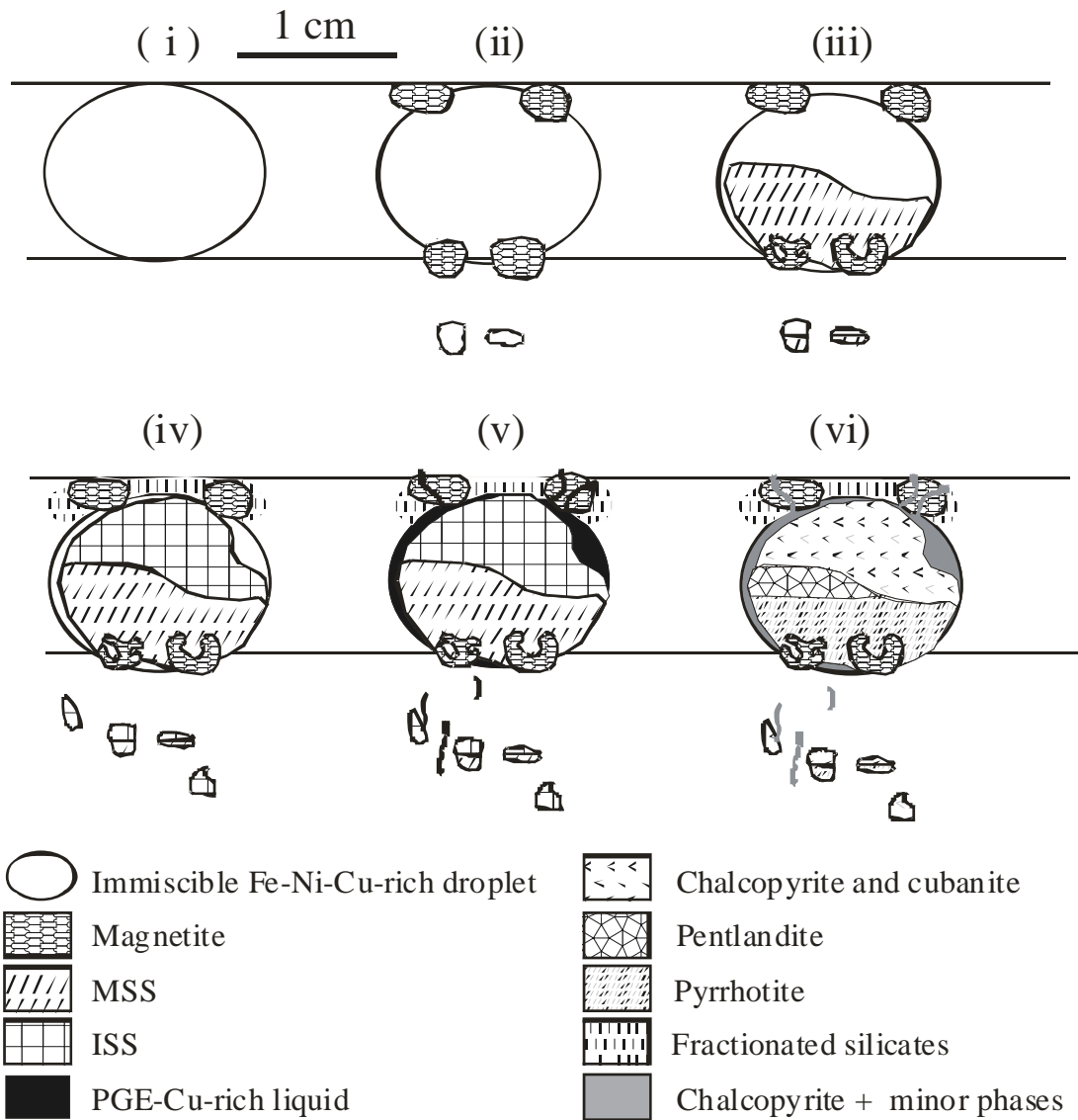
### **Early magnetite**

Magnetite occurs around the edges of the blebs, shows partial resorption in contact with pyrrhotite, and is crossed by fractures filled by chalcopyrite. The magnetite, therefore, appears to have crystallized prior to the formation of the major sulphide components of the blebs.

Resorption of magnetite has been observed elsewhere, for example, in the massive sulphides from Voisey's Bay (Lightfoot and Naldrett, 1999). Hawley (1962) also described titaniferous magnetite replaced and cross-cut by sulphides in the Sudbury ores and concluded that this titaniferous magnetite formed early. The magnetite in the blebs described here always contains abundant exsolved ilmenite and so originated as titaniferous magnetite. The  $\text{TiO}_2$  was probably derived from the silicate melt, as the immiscible sulphide liquid is  $\text{TiO}_2$ -poor. This agrees with Hawley's (1962) observations that magnetite grains at the edges of sulphide blebs in the Sudbury ores are Ti-rich, whereas those within sulphides are generally Ti-poor.

Naldrett (1969) examined the Fe-S-O system in detail and suggested that pyrrhotite should be joined by magnetite as the magnetite - pyrrhotite cotectic is reached during crystallization of an isolated sulphide liquid. However, he concluded that for a sulphide liquid enclosed by a silicate magma, oxygen will be lost to the silicates and the sulphide liquid will crystallize only





**Figure 4.** Model for the formation of the textures observed in the sulphide blebs. (i) Oval representing the boundary between the immiscible sulphide liquid and the surrounding silicate melt. (ii) Crystallization of magnetite at the rim of the immiscible sulphide droplet. (iii) Dense immiscible liquid surrounds the basal magnetite grains and resorbs them as crystallization of MSS occurs at the base of the droplet on a substrate of already crystallized silicates. Immiscible sulphide liquid leaks from the droplet and fills spaces interstitial to the silicates and MSS. A space or pressure low begins to form above the droplet as it shrinks and leaks. (iv) Crystallization of ISS occurs above the MSS in the droplet and from the sulphide liquid in the underlying interstitial spaces. More immiscible sulphide liquid of a Cu-rich composition leaks into spaces below the droplet and crystallizes. Fractionated silicate magma fills the space above the droplet. (v) The last and most fractionated immiscible sulphide liquid enriched in Cu, PGE, Bi, Te, Sb, Pb, Mo, Ag and Sn crystallizes filling fractures in the silicate and in magnetite and extruding into the still only partially crystallized fractionated silicate above the droplet. (vi) The droplet is fully crystallized and forms a complex bleb of the type seen in the Uruguayan example. Subsidiary re-equilibration occurs with MSS converting to pyrrhotite and pentlandite and ISS converting to chalcopyrite and cubanite. Parallel lines are drawn to emphasize the sinking of the sulphide bleb relative to the host silicate as the bleb crystallizes.

pyrrhotite rather than pyrrhotite followed by pyrrhotite and magnetite. As pyrrhotite begins to crystallize an increase of oxygen fugacity causes diffusion of  $\text{Fe}_2\text{O}_3$  outward to the margins of the immiscible sulphide where it can react with FeO and  $\text{TiO}_2$  in the silicate magma to form titaniferous magnetite at the sulphide silicate contact (Naldrett, 1969). Thus Ti-rich magnetite could have crystallized early during a period in which the sulphide liquid was saturated only with respect to MSS and under oxygen fugacity conditions that were buffered by the enclosing silicates. Alternatively the Ti-rich magnetite may have nucleated on the surface of the immiscible sulphide droplets. J. Brenan (pers. commun., 2003) has shown that a 'necklace' of chromite forms on the two liquid interface between Fe-sulphide melt and silicate liquid at a temperature above the sulphide liquidus, and a similar process may lead to the formation of early magnetite. Hawley (1965) observed similar magnetite rims around the edges of silicate inclusions within immiscible sulphides from Sudbury. Both conditions lead to the formation of early titaniferous magnetite.

### **Blebs as geopetal features**

Sulphide blebs in the Uruguayan dyke form geopetal structures with pyrrhotite and pentlandite in the lower part of the blebs overlain by chalcopyrite, similar to those observed in blebs above massive ore in major PGE enriched Ni-Cu-sulphide deposits (Lightfoot *et al.* 1984; Czamanske *et al.*, 1992). Other textural features that suggest the sulphide blebs are geopetal include leakage of the sulphide liquid into the silicates below the pyrrhotite and pentlandite, engulfing of the magnetite at the base of the bleb in the pyrrhotite, isolation of the magnetite above the chalcopyrite and filling of the void above the chalcopyrite by more evolved silicate magma. These observations suggest that the immiscible sulphide droplets sank through the silicate melt during crystallization, with sulphide liquid percolating down below them.

Adjacent to and below the pyrrhotite/pentlandite of the main blebs there often are several smaller patches of base metal sulphide in the host silicate. These are sometimes composite grains (chalcopyrite, pyrrhotite and pentlandite) or they may be formed only of chalcopyrite. These patches are thought to have formed by leakage of immiscible sulphide liquid into interstitial spaces in the underlying silicate minerals as crystallization proceeded. The patches are absent in the silicate host adjacent to and above the chalcopyrite part of the blebs. Ebel and Naldrett (1996) noted in their experiments that high-temperature sulphide melts exhibit important wetting properties against the experimental capsules. Rose and Brenan (2001) also concluded that under certain conditions, olivine crystals can be wetted by sulphide liquids. This is supporting evidence that sulphide melts can be mobile and leak into the adjacent partially crystallized host silicate below the blebs where they may adhere to crystal surfaces.

There is also good evidence that the immiscible sulphide liquid droplets sank under gravity a short distance (*ca.* 0.5 mm) relative to the host silicate and early magnetite as they cooled and crystallized (Fig. 4). The distance the droplets sank was just sufficient to leave the magnetite grains at the top of the bleb surrounded on three sides by the silicate host but still in contact with chalcopyrite at their base. The texture of magnetite surrounded by pyrrhotite at the bottom of the bleb suggests that these early magnetite grains were resorbed as the droplets sank and magnetite grains were engulfed by the descending sulphide liquid.

The silicates just above the blebs are products of the final stages of crystallization of the silicate magma consisting of eutectic quartz and feldspar intergrowths and amphiboles. There are also minor phases such as galena and silver telluride. The mineral assemblage crystallized



immediately above the blebs may indicate the presence of a volatile phase associated with the final stages of crystallization of both the silicate and the immiscible sulphide liquids. It is likely that at a late stage, highly fractionated silicate liquid was drawn into the space created above the immiscible sulphide droplets as they leaked, crystallized and sank.

### **Late fracturing of the blebs**

Fractures that cross-cut magnetite grains at the top and base of the blebs, and that extend away from the blebs into the silicate host rock were filled by late Cu-rich liquid enriched in Pd, Pb, Sn, Mo, Ag, and volatile elements such as Bi, Te, and Sb. The sharp margins of the fractures in the silicate host and their cross cutting nature suggest that they were brittle fractures that may have developed by over-pressuring due to a build up of volatiles in the late stage liquid trapped between the surrounding crystallized sulphide minerals, magnetite and host silicate minerals. Alternatively the late fracturing may be related to thermal expansion during crystallization of pentlandite which, for example, has been suggested as the cause of cracking of silica glass tubes during experimental studies of the Fe-Ni-S system (Sinyakova *et al.*, 1999).

### **Relationships between crystallization of the silicate host and immiscible sulphide liquid**

The near spherical shape of the sulphide blebs indicates that immiscible sulphide liquid droplets were formed in the magma prior to silicate mineral crystallization. Similarly, the uninhibited growth of plagioclase indicates that the silicate minerals crystallized at a time when the immiscible sulphide was still liquid. The presence of sulphide minerals in the interstices between the silicate minerals below the blebs also indicates migration of the immiscible sulphide liquid downwards and away from the base of the blebs prior to solidification of the silicate melt.

That the space above the blebs is now filled with silicate minerals that are more evolved than the silicate mineralogy of the host dyke indicates that the silicate magma was still crystallizing at the time of formation of the sulphides. The irregular granular texture of the sulphides and silicates at the upper contact of the blebs appears to indicate that the silicates and sulphides were crystallizing simultaneously.

The final stage of crystallization of the immiscible sulphide liquid and silicate melt is recorded by injection of Cu-rich sulphide liquid into fractures that cross-cut the magnetite and pooled at the contact between the magnetite and the silicate host minerals. The presence of the globules of chalcopyrite at the end of some of these fractures indicates that some of the final immiscible Cu-rich sulphide liquid was expelled from the blebs at a time when the silicate melt itself was still only semi-solid and did not restrict the growth of the globules.

### **Other occurrences of sulphide blebs**

A few of the features displayed in the blebs from the dyke in the Uruguayan Dyke Swarm have been described in sulphide blebs from Noril'sk in Siberia and the Insizwa complex in South Africa. In sulphide blebs from Noril'sk, Czamanske *et al.* (1992) suggested that MSS was crystallizing at the same time as the silicates indicated by the highly irregular margins of the blebs that are inter-fingered with the adjacent silicates. P. Lightfoot (pers. commun., 2003) noted that there is a thin cusped accumulation of a white silicate mineral at the upper margin of the sulphide blebs from Insizwa. This is perhaps similar to the zone of more evolved silicate immediately adjacent to the chalcopyrite part of the blebs in the dyke in the samples from this

study in which evolved silicate melt is interpreted to have filled the space left as the blebs sank. We also examined sulphide blebs in a number of samples from Noril'sk, Sudbury, and Insizwa. All of these blebs are of a similar size and, in each case, the blebs are divided into zones that are pyrrhotite/pentlandite-rich and zones that are chalcopyrite-rich with magnetite grains around the bleb margins. In our samples from Noril'sk we observed small stringer veinlets of chalcopyrite filling fractures in magnetite extending from the chalcopyrite within the bleb outwards to the silicate host, as in the blebs from the Uruguayan dyke. We also found the blebs from Noril'sk to be PGM-bearing with platinum and palladium tellurides and bismuthides in pyrrhotite, pentlandite and chalcopyrite, one grain of sperrylite in pentlandite, and a Pt-Pd-Sn-bearing PGM and several galena grains in chalcopyrite. Although the blebs from these other localities, as described in the literature and from our own studies, individually may display one or two of the characteristics described from the Uruguayan samples, the sulphide blebs from the Uruguayan dyke each show many more of the features associated with the sequence of crystallization. The reason for this is uncertain but may be related to the particular composition of the immiscible silicate and liquids, the cooling rate of their host dyke and the lack of metamorphism and deformation that helped to preserve the textures in these sulphide blebs.

## **COMPARISON WITH NI-CU-PGE SULPHIDE DEPOSITS**

### **The distribution of magnetite**

The textural relations in the sulphide-bearing samples from the dyke belonging to the Uruguayan Dyke Swarm indicate that magnetite grains formed at an early stage during the crystallization of the sulphide liquid. The magnetite grains were resorbed by the sulphide liquid at the base of the blebs and partially surrounded by silicate minerals at the top of the blebs, indicating that the sulphide liquid sank relative to the magnetite.

On the scale of major ore deposits, magnetite layers have been observed at the basal and upper contacts of massive sulphide orebodies (*e.g.* at the basal contact of a komatiite flow in the Juan complex, in Kambalda, Western Australia : Marston and Kay, 1980). Magnetite at the base of the flows is typically surrounded by sulphide and at the top of the flow it is located at the contact of the silicate rock and the underlying sulphide ores. Marston and Kay (1980) proposed that the magnetite formed as a result of late, low-temperature metamorphic oxidation of the sulphide ore. However, the sulphide blebs described here indicate that magnetite can form early as a selvage on the crystallizing immiscible sulphide liquid. Similar processes may have operated on a larger scale in Kambalda.

### **Origin of the volatiles and Bi, Te and Sb in PGE-enriched Ni-Cu-sulphide deposits**

Large PGE-enriched Ni-Cu-sulphide deposits often contain hydrous minerals including biotite, phlogopite, amphibole, chlorine-rich minerals such as apatite and PGE- and Ag-bearing tellurides, bismuthides, antimonides and arsenides and lead- and tin-bearing phases. There is controversy concerning the origin of the hydrothermal fluids which formed these assemblages. The hydrothermal fluids may have originated in the immiscible sulphide melt which separated from the silicate magma, the aqueous phase being concentrated into the latest, most fractionated portions of the melt. Alternatively, the hydrothermal fluids may have been introduced into the massive sulphide deposits from external sources adjacent to the magmatic intrusion.

In Sudbury the majority of the PGE-bearing minerals are Pt-, Pd-bearing tellurides, bismuthides, antimonides and arsenides, associated with Sn and Ag (Cabri, 1981). It has been argued for a long time that the Sublayer PGE-enriched Ni-Cu-sulphide ores at Sudbury formed by magmatic processes with segregation of a Cu-rich liquid to form footwall dykes (Naldrett and Kullerud, 1967; Keays and Crocket, 1970; Hoffman *et al.*, 1979; Naldrett *et al.*, 1982; Li *et al.*, 1992, 1993; Ebel and Naldrett, 1996). Chlorine and alkali geochemical halos in footwall breccia are interpreted to result from the interaction of residual magmatic fluids with host rocks (McCormick *et al.* 2002). Li and Naldrett (1993a, b) and Jago *et al.* (1994) suggested that the footwall deposits formed from halogen-rich fluids in a highly evolved sulphide liquid as it approached the solidus. Szentpéteri *et al.* (2002) noted that in the Lady Violet deposit in Sudbury hydrous silicates are restricted to the vicinity of the sulphide blebs implying the presence of a locally generated aqueous fluid. Farrow and Watkinson (1997, 1999) suggested that the metals in the footwall ore deposits in the Sudbury Igneous Complex were scavenged by ground waters from deep formational brines circulating from the basement into the Sudbury Igneous Complex and this flow was driven by heat from the Main Mass as it cooled. They suggested that complex H-O-Cl-S-Fe-Cu-Ni-Te-Se-Bi-As-rich fluids were responsible for the variability in the composition of the ores in different parts of the Sudbury footwall deposits and favor a late hydrothermal system rather than a late magmatic origin. In Sudbury several hydrothermal phases have been identified and later metamorphism and deformation have overprinted earlier processes (Dressler, 1984; Rousell, 1984; Magyarosi *et al.* 2002) making it difficult to resolve this controversy.

In the Noril'sk deposits, Genkin and Evstigneeva (1986) suggested that the Pt, Pd, Sn, Te, Pb, As, Sb and Bi were concentrated magmatically in a Cu-rich liquid that accumulated in pockets along the upper contacts of the orebodies or filled veins cross-cutting the massive base metal sulphides. In the Baula Complex, in Orissa State, India, Augé *et al.* (2002) favored a late magmatic fluid origin for the PGE associated with Te, Sb, Bi, As, Hg, and Sn rather than a later hydrothermal origin. Similar arguments have been made for komatiite hosted PGE-enriched Ni-Cu-sulphide deposits. Barnes and Naldrett (1986, 1987) favoured immiscible sulphide liquid fractionation to explain the compositional variations in the Alexo deposit in Canada, whereas at Kambalda in Western Australia, Keays *et al.* (1981) and Leshar and Keays (1984) proposed a later remobilization and hydrothermal transport of ores into the footwall.

The late cross-cutting Cu-rich veinlets in the sulphide blebs from the Uruguayan dyke described in this paper have a complex mineralogy, including apatite and PGE- and Ag-bearing tellurides, bismuthides, antimonides and arsenides and lead- and tin-bearing phases similar to that described at Sudbury (*e.g.*, Farrow and Watkinson, 1997) and to the Pd-bearing minerals at Noril'sk (Kozyrev *et al.* 2002). The sulphide blebs described in this study represent an isolated system in that they are small and surrounded by an effectively infinite silicate host compared with the size of the blebs. Therefore it seems unlikely that the PGE- and Ag-bearing minerals were introduced by external hydrothermal fluids. The background levels of, for example, the volatile elements Bi, Te and Sb and metals such as Ag, Pb, Sn and Mo in the silicate host dyke are very low (Table 1). It appears likely that all the trace elements required to form the minor minerals were concentrated into the immiscible sulphide liquid droplet as it separated from the silicate magma and were subsequently partitioned into the most fractionated Cu-rich liquid. Whether this also occurs at a larger scale is uncertain, but the example described in this study supports the suggestion that PGE and volatile element components of PGE-Ni- and Cu-rich sulphide deposits can form from the fractionation of immiscible sulphide liquids without the

introduction of elements or modification of the ores by external hydrothermal processes (cf. Ebel and Naldrett, 1996).

### **Late fractures**

The presence of late Cu-rich veinlets radiating from the blebs and cross-cutting the adjacent silicates in the Uruguayan examples suggests that Cu-rich liquids may have been under a sufficiently high pressure to cause fracturing of magnetite grains, MSS and host silicate minerals. The brittle nature of the fractures indicates that this occurred at moderately low temperatures and possibly as part of the crystallization process. In major PGE-enriched Ni-Cu-sulphide deposits the late injection of fractionated Cu-rich liquid is commonly observed and can be directed upwards or downwards from the already crystallized MSS. If injection is downwards this can result in an upside down sulphide stratigraphy with the copper-rich ore below the Ni-rich ore, as for example described at Frood Mine in the Sudbury Igneous Complex by Hawley (1965). It is interesting to speculate whether a build up of pressure during crystallization, as indicated by the textures in the sulphide blebs in the dyke from the Uruguayan Dyke Swarm, could occur on a much larger scale causing fracturing of the adjacent rocks or whether on a larger scale the pressure might be somehow dissipated.

## **CONCLUSIONS**

Internal textures of sulphide blebs from the dyke belonging to the Uruguayan Dyke Swarm indicate a consistent order of crystallization of the minerals. Early crystallization produced titaniferous magnetite at the margins followed by cumulate MSS. The final stages of crystallization took place as ISS crystallized and Cu- and -fluid-rich liquid filled fractures in magnetite grains, the MSS and surrounding silicate. Some of these fractures contain the PGM. Subsolidus recrystallization produced the mineralogy observed in the blebs.

The sulphide textures also indicate that the sulphide droplet was sinking through its host silicate melt and that immiscible sulphide liquid was leaking from the droplet during fractionation into spaces between silicate crystals below the droplet. Late-stage formation of chalcopyrite-filled fractures radiating out from the blebs may reflect pressure build up, perhaps by volatiles, at the end of immiscible sulphide crystallization, causing internal fracturing.

The blebs are isolated from other blebs and the dyke margins by the silicate host, and all of the components of the immiscible sulphide liquid are preserved in and around them. Minor elements such as those contained in PGM-bearing bismuthides, antimonides and tellurides, locally including tin, hessite, argentopentlandite, galena and molybdenite, are thought to have been derived entirely from fractionation of the immiscible sulphide liquid rather than introduction by later hydrothermal activity. The evidence provided by the sulphide blebs in the dyke from the Uruguayan Dyke Swarm strengthens the case for the origin of these minor phases in larger sulphide accumulations by magmatic fractionation rather than by later hydrothermal deposition.

Large, economic PGE-enriched Ni-Cu-sulphide deposits commonly are zoned with Ni-Fe-rich sulphides forming first, followed by Cu-Fe-rich sulphides and a final PGE-rich volatile-rich phase. In these large deposits the products of the later stage fractionated liquids often cross-cut earlier phases in a manner similar to that observed in the sulphide blebs from this study. These observations may also have implications for the crystallization of small volumes of sulphide

minerals in mafic and ultramafic complexes such as in the PGE-rich sulphide-bearing Merensky Reef of the Bushveld Complex (*e.g.*, Barnes and Maier 2002).

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