Zoned hollingworthite from the Two Duck Lake intrusion, Coldwell complex, Ontario

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ABSTRACT
Hollingworthite from a deposit rich in copper sulfides in olivine gabbro of the Two Duck Lake intrusion, Coldwell complex, Ontario, is complexly zoned. There are two main compositional trends: Ir- and As-rich hollingworthite is progressively zoned to pure hollingworthite (RhAsS) followed by partial dissolution, replacement, and overgrowth; the processes have caused the replacement of up to half of the Rh atoms by Os and Ru and, in one of the grains, of 0.4 of the As atoms by S. This type of zoning cannot result from simple exsolution of hollingworthite from interstitial magmatic sulfide; it is interpreted to reflect the effects of fluids that may have transported and precipitated different proportions of the Pt-group elements at different times.

INTRODUCTION
Hollingworthite (RhAsS), defined by Stumpfl and Clark (1965), was found in Pt concentrates from the Driekop mine, South Africa. Other data on hollingworthite are derived from specimens from the same area (Tarkian and Stumpfl, 1975) and the Onverwacht mine, South Africa (Genkin, 1968). Hollingworthite is also associated with copper nickel sulfides at Noril'sk, USSR (Genkin, 1968; Genkin and Evstigneeva, 1986); Werner Lake, Canada (Rucklidge, 1969); Rathbun Lake, Canada (Rowell and Edgar, 1986); Kambalda, Australia (Hudson, 1986), and Siikakämä, Finland (Hänninen et al., 1986). Other occurrences are from Pt-group mineral (PGM) parageneses with magnetite and pentlandite interstitial to chromite in the Bird River Sill, Canada (Cabri and Laflamme, 1988); in chromite from Osthammeren, Norway (Nilsson, 1990); in alpine-type ultramafic rocks (Distler et al., 1986); and in ophiolitic complexes (Tarkian and Prichard, 1987; Thalhammer and Stumpfl, 1988).

In the Coldwell complex, hollingworthite was found in close association with chalcopyrite in coarse-grained to pegmatitic gabbroic rocks. The purpose of this paper is to elucidate the zoning of the hollingworthite crystals with respect to the whole paragenesis of the sulfide-bearing gabbroic host rock.

GEOLOGICAL SETTING AND SAMPLE DESCRIPTION
The Coldwell alkaline complex, Ontario (Puskas, 1967; Mitchell and Platt, 1982), located on the north shore of Lake Superior (48°47'N, 86°30'W), is a Proterozoic (1.1 Ga) composite intrusion of silica-saturated and undersaturated plutonic rocks. It was emplaced into Archean metasedimentary, metavolcanic, and granitic rocks of the Superior Province. In the eastern part of the complex, the arcuate belt of layered gabbroic rocks, the “Eastern Gabbro,” is regarded as the earliest unit (Currie, 1980) and is host to disseminated copper nickel sulfides (Wilkinson, 1983). A Pt-group element (PGE) and copper deposit was outlined through recent exploration by Fleck Resources Ltd. (Dahl et al., 1986; Watkinson et al., 1986) in the Two Duck Lake intrusion that was emplaced into the contact area of the Eastern Gabbro with the Archean metavolcanic rocks. The host unit contains abundant inclusions of both rock types.

A disseminated pyrrhotite + chalcopyrite + pentlandite + cubanite assemblage enriched in PGE occurs in coarse-grained to pegmatitic gabbroic rocks. In sample 85-13-109.5, zoned hollingworthite occurs in a very coarse-grained sulfide-bearing olivine gabbro (Fig. 1A) composed of cumulus plagioclase (An80,0003-004x/91/0910-1694$02.00 1694 10-1694$02.00) and biotite, apatite, and oxides. The sulfides are pyrrhotite, pentlandite, and chalcopyrite. The habit of the sulfides, the reaction textures, the plagioclase...
pseudomorphs, and the existence of Cu-rich minerals in cracks are compatible with late stage metasomatic replacement from a circulating Cu-rich fluid (Watkinson and Dahl, 1988).

The most common PGM are kotulskite and sperrylite. Kotulskite may be enriched in Bi or in Pb. The Pb-rich kotulskite is associated with zvyaginsteite and Au-bearing atokite. The Pd minerals are also present as complex intergrowths of palladoarsenide–nickel–merteite II–majakite associated with Pd-bearing nickeline and unknown Pd$_2$(Sb,As).

**Fig. 1.** Photomicrographs of sulfide-bearing olivine gabbro: (A) hollingworthite 1 (50 × 65 μm) and (B) hollingworthite 2 (30 × 30 μm). Abbreviations: pl, plagioclase; cpx, clinopyroxene; bi, biotite; ap, apatite; mte, magnetite; po, pyrrhotite; cpy, chalcopyrite; cc, calcite; chl, chlorite; hol, hollingworthite.

**TABLE 1.** Representative analyses of hollingworthite (wt%)

<table>
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<th></th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
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<th>8</th>
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<th>10</th>
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<td>Os</td>
<td>0.00</td>
<td>0.36</td>
<td>7.00</td>
<td>4.00</td>
<td>3.08</td>
<td>9.38</td>
<td>10.07</td>
<td>1.07</td>
<td>1.16</td>
<td>2.05</td>
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<tr>
<td>As</td>
<td>34.04</td>
<td>34.69</td>
<td>29.28</td>
<td>31.01</td>
<td>34.12</td>
<td>28.10</td>
<td>26.74</td>
<td>39.11</td>
<td>35.01</td>
<td>34.41</td>
<td>33.05</td>
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<td>Ir</td>
<td>0.70</td>
<td>2.50</td>
<td>0.36</td>
<td>0.39</td>
<td>2.46</td>
<td>0.23</td>
<td>0.57</td>
<td>2.59</td>
<td>4.46</td>
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<tr>
<td>Cu</td>
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<td>0.08</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Ru</td>
<td>0.00</td>
<td>0.01</td>
<td>4.17</td>
<td>2.47</td>
<td>1.07</td>
<td>5.61</td>
<td>6.41</td>
<td>0.00</td>
<td>0.00</td>
<td>0.17</td>
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<td>Rh</td>
<td>44.54</td>
<td>40.31</td>
<td>28.52</td>
<td>34.90</td>
<td>35.39</td>
<td>25.02</td>
<td>24.89</td>
<td>35.06</td>
<td>34.31</td>
<td>38.78</td>
<td>28.67</td>
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<td>Pt</td>
<td>3.91</td>
<td>7.36</td>
<td>13.43</td>
<td>11.16</td>
<td>9.30</td>
<td>13.05</td>
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<td>Pd</td>
<td>1.30</td>
<td>0.50</td>
<td>0.05</td>
<td>0.17</td>
<td>0.42</td>
<td>0.03</td>
<td>0.06</td>
<td>0.73</td>
<td>1.36</td>
<td>0.28</td>
<td>1.51</td>
</tr>
<tr>
<td>Fe</td>
<td>0.40</td>
<td>0.54</td>
<td>1.38</td>
<td>0.73</td>
<td>1.01</td>
<td>2.14</td>
<td>1.12</td>
<td>0.51</td>
<td>0.27</td>
<td>0.42</td>
<td>0.30</td>
</tr>
<tr>
<td>Ni</td>
<td>0.18</td>
<td>0.14</td>
<td>0.05</td>
<td>0.06</td>
<td>0.09</td>
<td>—</td>
<td>—</td>
<td>0.15</td>
<td>0.22</td>
<td>0.05</td>
<td>0.20</td>
</tr>
<tr>
<td>Total</td>
<td>99.99</td>
<td>100.58</td>
<td>100.38</td>
<td>99.78</td>
<td>100.53</td>
<td>99.28</td>
<td>100.79</td>
<td>99.45</td>
<td>99.74</td>
<td>100.99</td>
<td>100.59</td>
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</table>

**Formulas**

| Os | 0.000 | 0.004 | 0.082 | 0.047 | 0.036 | 0.108 | 0.119 | 0.013 | 0.014 | 0.024 | 0.006 |
| As | 0.975 | 1.023 | 0.872 | 0.928 | 1.024 | 0.821 | 0.804 | 1.189 | 1.086 | 1.032 | 1.052 |
| S  | 0.998 | 0.949 | 1.117 | 1.041 | 0.953 | 1.184 | 1.182 | 0.835 | 0.900 | 0.964 | 0.926 |
| Ir | 0.008 | 0.029 | 0.004 | 0.005 | 0.029 | 0.005 | 0.007 | 0.001 | 0.002 | 0.003 | 0.004 |
| Cu | 0.000 | 0.000 | 0.003 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| Ru | 0.000 | 0.000 | 0.092 | 0.055 | 0.024 | 0.121 | 0.143 | 0.000 | 0.000 | 0.004 | 0.001 |
| Rh | 0.528 | 0.866 | 0.618 | 0.760 | 0.773 | 0.532 | 0.545 | 0.776 | 0.775 | 0.847 | 0.685 |
| Pt | 0.043 | 0.083 | 0.154 | 0.128 | 0.107 | 0.146 | 0.144 | 0.115 | 0.122 | 0.097 | 0.101 |
| Pd | 0.026 | 0.019 | 0.001 | 0.004 | 0.009 | 0.001 | 0.001 | 0.016 | 0.030 | 0.006 | 0.034 |
| Fe | 0.015 | 0.021 | 0.055 | 0.029 | 0.041 | 0.084 | 0.045 | 0.021 | 0.011 | 0.017 | 0.013 |
| Ni | 0.007 | 0.005 | 0.002 | 0.002 | 0.003 | 0.000 | 0.000 | 0.006 | 0.009 | 0.002 | 0.008 |

**Note:** Analyses 1–7 correspond to grain 1 of hollingworthite, 8–11 to grain 2.

**Analytical methods**

All analyses were performed on the CNRS–BRGM–University of Orleans Camebax electron microprobe with wavelength dispersive spectrometers and LiF, TAP, and PET analyzing crystals. Hollingworthite was analyzed with an acceleration voltage of 25 kV, a 20-s counting time, and a reference current of 40 nA using OsLβ, IrLα, RuLα, RhLα, PtLα, PDLβ, AsLβ, CuLα, FeKα, NiKα, and BiMα on metals standards. For SKα, pyrite was used as a standard. The correction of the overlap of RuLβ and RhLα
observed for Ru-rich minerals (Ohnenstetter et al., 1986) was not deemed necessary for the low to very low Ru zones of hollingworthite. All data were corrected with the ZAF program MBXCOR of Henoc and Tong (1978). Backscattered images were performed on Cambridge Stereoscan 200 SEM at the BRGM and at the Geological Survey of Canada, and the X-ray scanning was performed on the Camebax microbeam. To compare the X-ray scanning with the probe data, 137 analyses were performed on a 50 × 65 μm zoned euhedral hollingworthite and 80 on a second hollingworthite (30 × 30 μm). Typical compositions of hollingworthite are listed in Table I and illustrated in Figures 2–6; all data are reported by Ohnenstetter (1990).

**Hollingworthite zoning**

Hollingworthite is isometric with a cobaltite structure (Hulliger, 1963), as are irarsite (IrAsS) and platarsite (PtAsS). Osarsite (OsAsS) and ruarsite (RuAsS) are monoclinic (Snetsinger, 1972) with arsenopyrite-type structure (Hulliger, 1964). No Pd equivalent is known. The different crystal structures of the MeAsS minerals and the similar sizes of the relevant atoms indicate that Ir and Pt could substitute for Rh more easily than would Os and Ru in hollingworthite. Laurite (RuSr) and erlichmanite (OsSr) have the same Pa3 space group as does hollingworthite but with the pyrite structure (Leonard et al., 1969; Snetsinger, 1971).

As with other hollingworthite (Cabri, 1981), that from the sulfide-bearing olivine gabbro at Coldwell is marked by zoning as shown by contoured diagrams (Figs. 2 and 3). Growth zoning is modified by late dissolution and
replacement along cracks and at the edges of the grains. Nearly pure hollingworthite replaces Ir-rich zones in the center of the crystals. Both may be replaced by late Pt-enriched hollingworthite, especially along cracks. It appears that after these two major replacement stages, which exist in both grains, a new influx of Pt followed by Os and Ru influxes modified the previous minerals especially at the rims of hollingworthite I (Fig. 2).

In hollingworthite I, the core has low contents of Fe (0.0-0.5%), Ni (0.1-0.3%), and Pd (2-3%) with Ir content as high as 23 wt%. Pt values (2-4%) are also low and no Os and Ru were detected. In the Pt-enriched zones, Fe
increases slightly (0.5–1%), whereas Rh decreases. This stage is marked by overgrowth of a Pt-enriched zone (up to 13.8%) followed by Os- (up to 10%) and Ru- (up to 9.2%) enriched zones, whereas Pd, Ni, As (20–32%), and Rh (<30 wt%) decrease. The composition of the thin rims is generally modified by analytical border effects that cause low totals of the analyses (95–97%). Close to chalcopyrite, an apparent increase in Fe and Cu in the rim results from contamination from the surrounding mineral. In the second hollingworthite (Fig. 3), the core is Ir rich (22.9 wt%) with Ni and Fe values about 0.3%. However, Pt content is high (near 8%), whereas Ru and Os are less than 2%. Partway to the edge, Pt-enriched zones have lower Ir and Rh contents, and Fe and Ni values are similar to those in the core area. The rim is enriched in Pt (about 9%) and poor in Ni (<0.1 wt%).

Three major stages of crystallization may be pointed out in the two hollingworthite crystals (Fig. 4): (1) crystallization of Ir- and As-rich hollingworthite (close to the irarsite composition), (2) partial resorption of this phase and precipitation of nearly pure hollingworthite, and (3) resorption along the edges of the grain and in cracks to generate Pt- and Fe-enriched hollingworthite as well as enrichment in Pd along the main transverse cracks, growth of an outer rim enriched in Pt, or in Os and Ru, or in all three, and depletion in Pd and Ni.

**Substitution in hollingworthite**

Two main substitutions in hollingworthite are defined (Figs. 5 and 6). The first, observed in both grains, is irarsite-hollingworthite substitution with replacement of Ir by Rh coupled with an increase of the S-As ratio. The transition is clear in Figure 5 from a composition that is Ir rich toward nearly pure RhAsS (Begizov et al., 1976). The second, observed toward the rim of one grain, corresponds to the substitution of laurite-erlichmanite for hollingworthite. The Ru and Os enrichments are also accompanied by an increase in S (Fig. 4). Our data indicate a wide range of solution between hollingworthite and laurite marked by the replacement of 0.4 formula units of As by S (Fig. 4) and half the Rh by Ru and Os (Fig. 5). The As-S substitution covers a range from MeAs$_{1.40}$S$_{1.60}$ to MeAs$_{1.15}$S$_{0.85}$, with most of the analyses close to the line MeS$_2$-MeAs$_2$. The three analyses that plot outside the general trend on the left part of Figure 4 are contaminated by chalcopyrite; they fall on the trend after

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Fig. 6. Rh-Pt-Ir and Rh-(Pt + Ir)-(Ru + Os) triangular plots after Tarkian (1987) for the two hollingworthite grains (atomic percent). Symbols are as those in Figure 4.
chalcopyrite subtraction (arrows). The As-S substitution is characterized by a strong S depletion. The highest As value in hollingworthite (Me$_{3}$S$_{8}$As$_{S}$) is from Feather (1976). Irsarsite and osarite from the Witwatersand may have similarly high As values (Feather, 1976). However, there is little or no As substitution exhibited either by the Me$_{3}$S$_{8}$ series [laurite-erlichmanite (Cabri, 1981), IrS$_{2}$ (Ren and Deng, 1973), and RhS$_{2}$ (Feather, 1976)] or by the Me$_{3}$S$_{8}$ series [irarsite (Harris, 1974), andouite (Yu and Chou, 1979), osmeite (Ren et al., 1978), and sperrylite (Feather, 1976; Cabri et al., 1977)]. Cabri and Laflamme (1988) have also described an overgrowth of laurite on hollingworthite.

**CONCLUSION**

The precipitation of highly zoned hollingworthite is clearly later than the crystallization of sulfide-bearing magma in the Two Duck Lake intrusion, Coldwell complex. Hollingworthite is spatially related to veins and alteration assemblages of iron chloride + epidote + actinolite + calcite, as are other PGM in the Two Duck Lake rocks, and it is characterized by compositional variation in response to the chemical change of fluid with time. Two successive main substitutions are defined between irarsite or Ir-rich hollingworthite and hollingworthite and between laurite-erlichmanite and hollingworthite. During these events, As decreased more than 0.4 formula units, whereas S increased in response to an increase of f$_{s}$ with time. Variations in hollingworthite compositions thus reflect variations in the composition of fluid, perhaps as saline fluid became enriched in S by the breakdown of pyrrhotite; they cannot be readily explained by exsolution of PGM from magmatic sulfides. Fluids caused a different alteration of original silicates and oxides, modified the original magmatic sulfides through replacement of the Fe minerals by chalcopyrite, and precipitated Pt-group minerals (Watkinson and Dahl, 1988).

**ACKNOWLEDGMENTS**

Fleck Resources Ltd. kindly made available its drill core and gave us access to all pertinent data; in this regard, we thank John McGoran in particular. We also thank Z. Johan, M. Ohnenstetter, C. Gilles, J. Breton, I. Jonasson, and P.C. Jones for their help in this research. We thank L.J. Cabri and J.M. Hughes for helpful reviews. The opportunity to work at CRSCM and BRGM during sabbatical leave is especially appreciated by D.H.W. Partial financial support was provided through NSERC grant A7874 to D.H.W. and through BRGM grant RM 15 to D.O.

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Manuscript received August 13, 1990
Manuscript accepted May 14, 1991