# ELECTRON MICROPROBE INVESTIGATIONS OF PLATINUM METAL MINERALS FROM ONTARIO

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## ABSTRACT

Minute grains of minerals containing significant concentrations of the platinum metals Pd, Pt, Rh and Ir have been found associated with nickel ores from Werner Lake, Strathcona, and Falconbridge, Ontario. These grains have been analysed by electron probe methods and three species with the formulae $(Pd,Ni,Pt)(Te,Bi)_2$, RhAsS and IrAsS have been identified. The presence of major amounts of Ni in the first distinguishes it from other bismuthotellurides of the platinum metals. The latter two phases may be identified as hollingworthite and irarsite, both of which have only recently been described from South Africa. Between the two intergrown sulpharsenide phases all of the Pt metals are found, with the heavier ones concentrated in irarsite, and the lighter in hollingworthite. The presence of Ni in the platinoid bismuthotellurides may have genetic implications.

## INTRODUCTION

The past two or three years have seen increasing interest in defining the mode of occurrence of the platinum metals in the ultrabasic rocks and ore bodies around the world. Stumpfl in particular has been active in this field and has described with the use of the electron probe microanalyser, several new platinum metal minerals (Stumpfl 1961, Stumpfl & Clark 1965a, 1965b). These usually occur in grains so small that only the rough chemical compositions and optical properties may be determined, while it has not been possible to make *x*-ray diffraction or density measurements. A mineral so described is hollingworthite, a rhodium platinum palladium sulpharsenide which was found in platinum concentrates from the Driekop Mine, Transvaal, South Africa. Russian workers (Genkin, *et al.* 1966) have also been active in this field and have reported several new platinum metal minerals such as a platinum bismuthotelluride, moncheite, and an iridium sulpharsenide, irarsite. They have also found new and better occurrences of minerals which were earlier described only in terms of their chemistry, for example hollingworthite, and have succeeded in making *x*-ray powder measurements on these minute grains. This work has established that the sulpharsenides of iridium and rhodium (irarsite and hollingworthite) are isostructural with the cobaltite group of minerals, rather than with the sperrylite group as once suggested. To date, these minerals have only been found in South Africa.

## EXPERIMENTAL METHODS

An ARL type EMX electron probe was used in this investigation. *X*-ray intensities were converted to element concentrations by the correction procedures described by Rucklidge (1967). Because of the small sizes of the mineral grains studied, extreme care was necessary in positioning the electron probe. A method was developed where the *x*-ray intensity of the major element in the phase was continuously monitored while recording the counts from the other elements. This way, it was possible to be certain that measurements were made wholly within the grain under examination.

## PLATINOID SULPHARSENIDES

This work concerns the occurrence of the platinum metals in a few Canadian localities. In a section of drill core through massive sulphides at Werner Lake, Ontario, several grains with high concentrations of the platinum metals have been found. In particular two distinct minerals have been characterised: sulpharsenides of iridium and rhodium respectively. These are undoubtedly to be identified as irarsite and hollingworthite, though there are considerable differences in the relative proportions of the various metals. The minerals occur as fine grains, the largest being about 20 microns across. The iridium-rich phase is invariably enveloped by the rhodium-rich, consequently the iridium-rich areas are very small indeed. The description of the Onverwacht, South Africa, occurrence by Genkin *et al.* (1966) is identical. To quote "Irarsite constantly occurs in intergrowth with ruthenian hollingworthite . . ." and ". . . irarsite is only small deposits in crystalline grains of ruthenian hollingworthite." The optical properties are similar, inasfar as one can judge in such small grains. In reflected light, both phases are grayish white, isotropic. Irarsite has a characteristic bluish tint and lower reflectivity than hollingworthite. In Fig. 1 two overgrowths of hollingworthite on irarsite are shown. Figure 2 shows, in *x*-ray scanning photographs taken on the electron probe microanalyser, the distribution of the various elements in these two phases. The main partition of iridium and rhodium between the inner and outer phases is well seen, but the distribution of the other elements Pt, Pd, Ru, Os is not so obvious. However all these elements do occur in significant amounts, along with a little Co and Ni. The complete analyses of these phases are given in Table 1.

Genkin has described the co-existence of hollingworthite and irarsite at Onverwacht in what appears to be an identical intergrowth to the

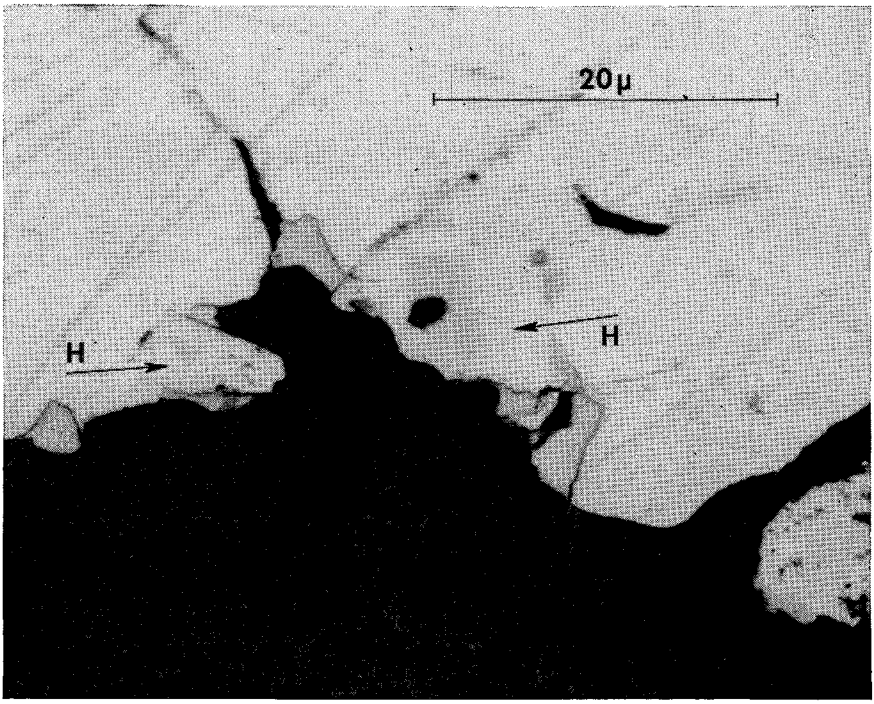

FIG. 1. Two grains of hollingworthite with irarsite cores, Werner Lake, Ontario. Reflected light.

present case. Stumpfl (1965b), in his description of hollingworthite did not identify irarsite with it (it was not described at that time) but he did mention that the original hollingworthite was intergrown with a phase he called "rhodium sperrylite," where platinum was present slightly in excess of the next most abundant metal, iridium. The reflectivity of the rhodium sperrylite is slightly higher than that of hollingworthite. The analysis of this phase, reproduced in Table 2 shows that "rhodium sperrylite" is a sulpharsenide similar in many respects to irarsite, but that it contains considerably more platinum and rhodium, and less iridium.

There are now three documented occurrences of hollingworthite. In each case this phase is intimately associated, usually as an overgrowth, with another sulpharsenide rich in the heavy platinum metals, principally iridium or platinum. It seems reasonable to consider the rhodium sperrylite of Stumpfl as a platinum-rich version of irarsite. It may be instructive to draw attention to the fact that these two minerals have only been found together. Table 2 compares the compositions of the

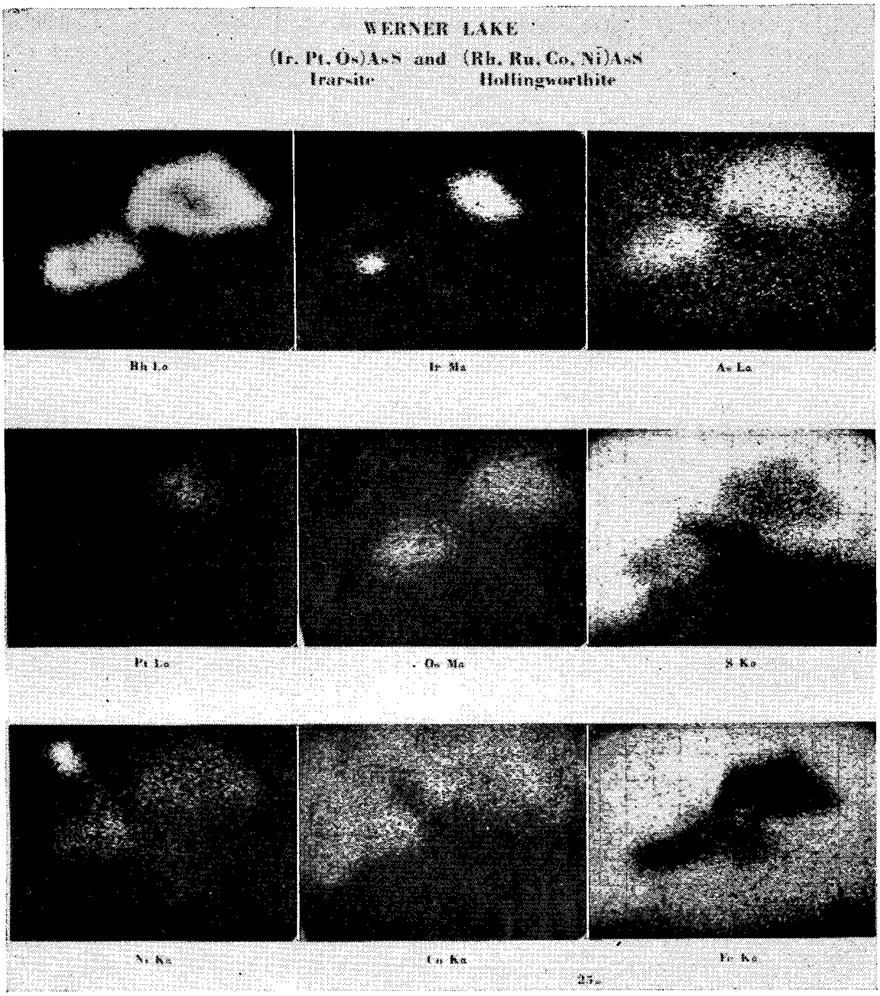

FIG. 2. *X*-ray scanning photographs showing the distribution of Ir, Pt, Os, Rh, Ni, Co, Fe, As and S in the field shown in Fig. 1.

three occurrences of hollingworthite with the associated iridium-platinum sulpharsenides. There are considerable differences, but the pattern appears to be consistent. The Werner Lake examples show almost complete partition of the heavy and light platinum metals between the core phase and the rim phase, while in the other examples the separation is not so sharp. Perhaps this is due to different conditions of formation, though one might wonder if the earlier analyses of Genkin and Stumpfl

TABLE 1. ELECTRON MICROPROBE ANALYSES OF IRARSITE AND HOLLINGWORTHITE FROM WERNER LAKE, ONTARIO

| | Irarsite | Hollingworthite |
|---|---|---|
| Ir | 44.8 | 0.22 |
| Pt | 7.8 | .61 |
| Os | 2.2 | 00.00 |
| Rh | 3.8 | 41.3 |
| Pd | 1.2 | 0.85 |
| Ru | 0.0 | 2.8 |
| Ni | 0.19 | 1.3 |
| Co | 1.4 | 2.5 |
| As | 24.7 | 33.3 |
| S | 12.3 | 16.4 |
| Total | 98.4 | 99.2 |

Irarsite $(Ir_{3.27}Pt_{0.56}Rh_{0.52}Co_{0.34}Pd_{0.17}Os_{0.15})_{5.06}As_{4.64}S_{5.36}$.
Hollingworthite $(Rh_{4.21}Co_{0.44}Ru_{0.28}Ni_{0.23}Pd_{0.08}Pt_{0.03})_{5.29}As_{4.65}S_{5.34}$.

TABLE 2

| | Irarsite | | 'Rh Sperrylite' | Hollingworthite | | |
|---|---|---|---|---|---|---|
| | Rucklidge | Genkin | Stumpfl | Rucklidge | Genkin | Stumpfl |
| Ir | 44.8 | 23.0 | 17.8 | 0.22 | 1.4 | 3.1 |
| Pt | 7.8 | 12.6 | 23.8 | 0.61 | 18.4 | 10.3 |
| Os | 2.2 | | | 0.00 | | |
| Rh | 3.8 | 7.2 | 11.6 | 41.3 | 24.6 | 30.8 |
| Pd | 1.2 | | 2.1 | 0.85 | | 8.7 |
| Ru | 0.0 | 9.4 | | 2.8 | 12.8 | |
| Ni | 0.19 | | | 1.3 | | |
| Co | 1.4 | | | 2.5 | | |
| As | 24.7 | 34.5 | 30.7 | 33.3 | 34.0 | 32.6 |
| S | 12.3 | 11.6 | 10.8 | 16.4 | 13.0 | 13.9 |
| Total | 98.4 | 98.3 | 96.8 | 99.2 | 104.2 | 99.4 |

completely resolved the two phases, as this was found to be difficult in the present work.

It should be mentioned that Stumpfl & Clark (1966) spoke briefly of the occurrence of a sulpharsenide of iridium from southeast Borneo. This phase containing 53% of iridium is probably irarsite, but no details of its paragenesis are given.

Genkin *et al.* (1966) proposed a nomenclature for the sulpharsenides, to be named on the basis of the principal metal. At present hollingworthite is used for the rhodium member and irarsite for the iridium member. The platinum-rich, in which iridium is also a major component, has only been referred to as "rhodium sperrylite," but on this basis would become a separate species. However, the constant association of sulpharsenides of the light platinum metals, Rh, Pd (with Pt) with the sulpharsenides of the heavy platinum metals, Ir, Pt (with Rh) suggests that platinum metal sulpharsenides occur in two series which concentrate the light and heavy metals respectively. It would be premature to define new mineral names until the extent of variation of these phases is established.

Synthetic work of Hulliger (1963) has shown the existence of semiconducting compounds RhAsS and IrAsS, both having the cobaltite structure and very similar cell dimensions of 5.780 and 5.791 Å respectively. The reason for the distinct separation of these phases in the natural occurrences is not immediately apparent. From considerations of cell parameters and atomic radii, one might expect that complete solid solution should exist between these two phases. Perhaps the association is not due to unmixing or insolubility, but simply an overgrowth of the later lighter phase on the heavier early formed phase. This would explain why irarsite is never seen without an overgrowth of hollingworthite, but hollingworthite, the later phase to form, may grow without an irarsite nucleus.

## PLATINOID BISMUTHOTELLURIDES

Besides the association of the platinum metals with sulphur and arsenic, these elements also occur combined with tellurium and bismuth (Wright & Fleischer, 1965). Table 3 shows the compositions and names of known minerals relevant to this study. The bismuth tellurium association with platinum metals seems to be restricted to the elements platinum and palladium.

TABLE 3. BISMUTHOTELLURIDES AND BISMUTHIDES OF PLATINUM METALS

| | | | |
|---|---|---|---|
| $(Pt\,Pd)(Te,Bi)_2$ | Moncheite | $Pd(Te,Bi)_{1-2}$ | Kotulskite |
| $(Pd,Pt)(Te,Bi)_2$ | Merenskyite | $PdBi_2$ | Froodite |
| $Pd_{.75}Pt_{.25}BiTe$ | Michenerite | $(Pd,Ni,Pt)(Te,Bi)_2$ | This study |

In this study, where polished sections of massive sulphides from different Canadian nickel deposits have been examined, several grains of bismuthotellurides have been encountered. In samples from three separate localities, Werner Lake, Falconbridge and Strathcona, three examples with the general formula $(Pd,Ni,Pt)(Te,Bi)_2$ have been found. The analyses of these phases are shown in Table 4. There appears to be an almost complete solid solution series from $(Ni,Pd)(Te,Bi)_2$ to $(Pd,Ni)(Te,Bi)_2$ with minor platinum. Optically the material has high reflectivity, estimated from 60–65%, is strongly anisotropic, and varies from cream colour in the low nickel member to white with higher nickel content.

TABLE 4. ELECTRON MICROPROBE ANALYSES OF $(Ni,Pd)(Te,Bi)_2$

| | Werner Lake, Ont. | Strathcona, Ont. | Falconbridge, Ont. |
|---|---|---|---|
| Ni | 5.9 | 11.3 | 17.1 |
| Pd | 18.3 | 7.4 | 2.1 |
| Pt | .37 | 3.7 | 1.5 |
| Te | 65.6 | 65.2 | 72.5 |
| Bi | 10.8 | 14.4 | 9.1 |
| Total | 101.0 | 102.0 | 102.3 |

Werner Lake $(Ni_{0.35}Pd_{0.61}Pt_{0.01})_{0.97}(Te_{1.82}Bi_{0.18})_2$.
Strathcona $(Ni_{0.66}Pd_{0.24}Pt_{0.07})_{0.97}(Te_{1.76}Bi_{0.24})_2$.
Falconbridge $(Ni_{0.95}Pd_{0.07}Pt_{0.02})_{1.04}(Te_{0.86}Bi_{0.14})_2$.

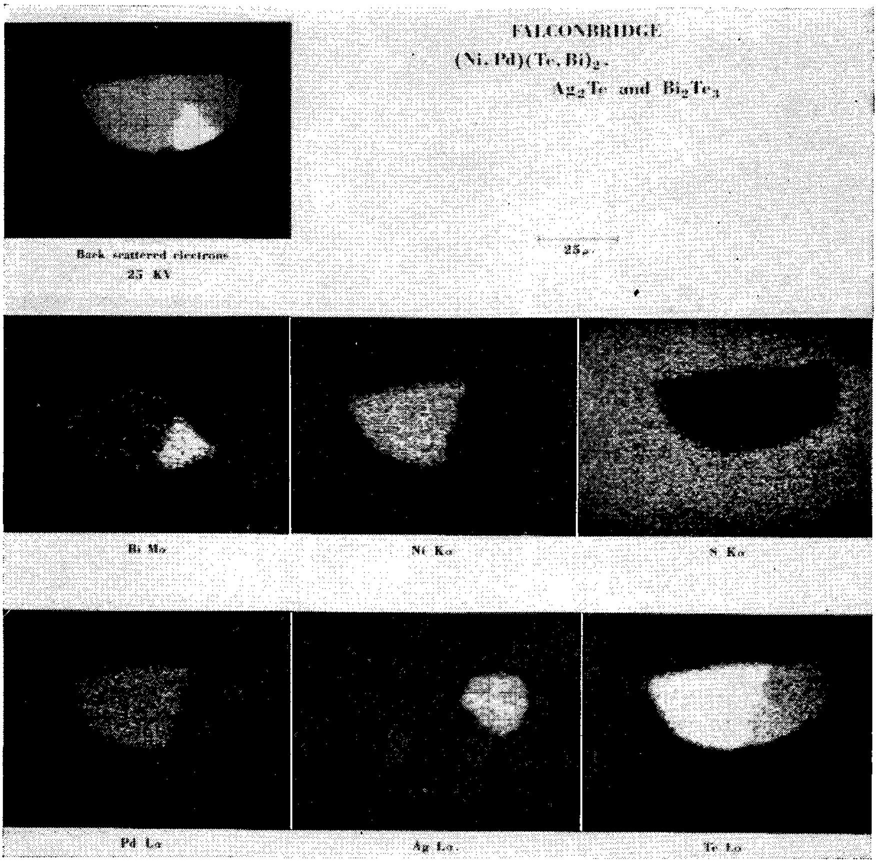

FIG. 3. *X*-ray scanning photograph showing the distribution of Pd, Ag, Te, Bi, Ni and S in a composite grain of palladium bismuthian melonite, hessite and tellurbismuth from Falconbridge, Ontario.

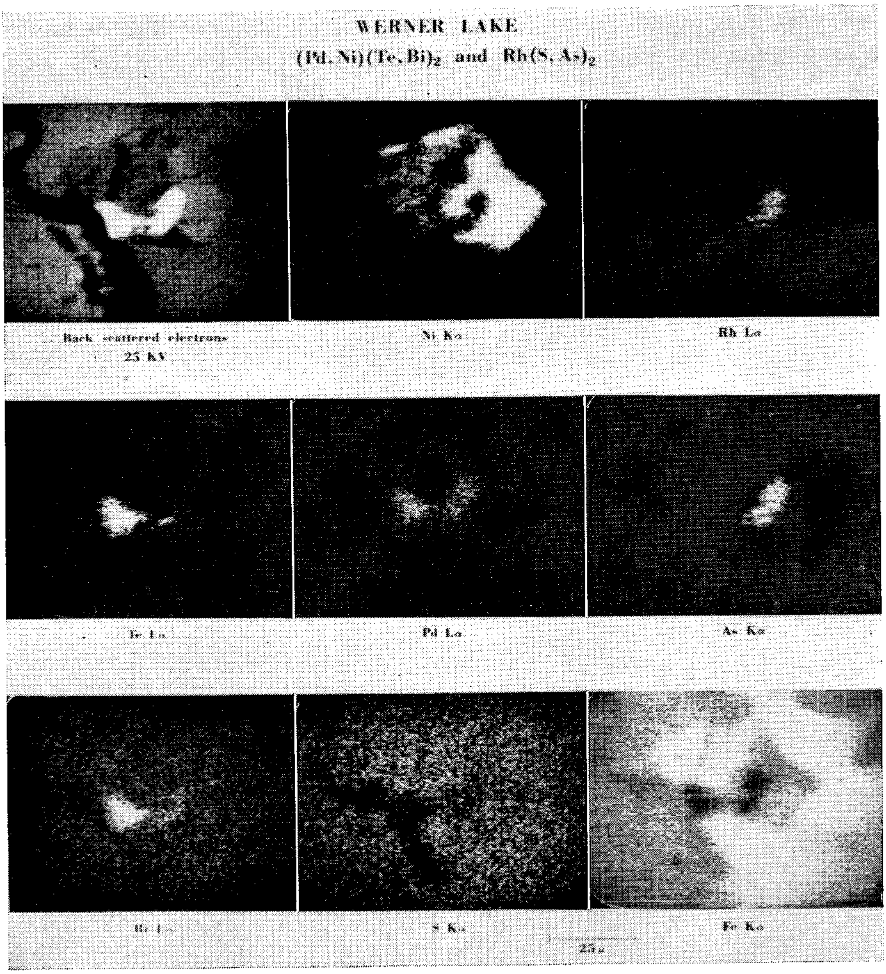

FIG. 4. $X$-ray scanning photographs showing the distribution of Pd, Rh, Te, Bi, Ni, Fe, As and S in grains of nickeloan merenskyite and hollingworthite from Werner Lake, Ontario. The apparent concentration of Pd in hollingworthite is due to the overlapping of Rh L$\beta$, and Pd L$\alpha$ radiations.

Figures 3, 4 and 5 show $x$-ray scanning pictures of grains from these three localities. The example from Falconbridge is part of a composite grain where the other components are hessite ($Ag_2Te$) and tellurbismuth ($Bi_2Te_3$). The grain is surrounded by pyrrhotite, but chalcopyrite and pentlandite are plentiful throughout the rock. The Strathcona example occurs in relatively large grains, up to 100 microns, associated with chalcopyrite and millerite. At Werner Lake a grain of hollingworthite

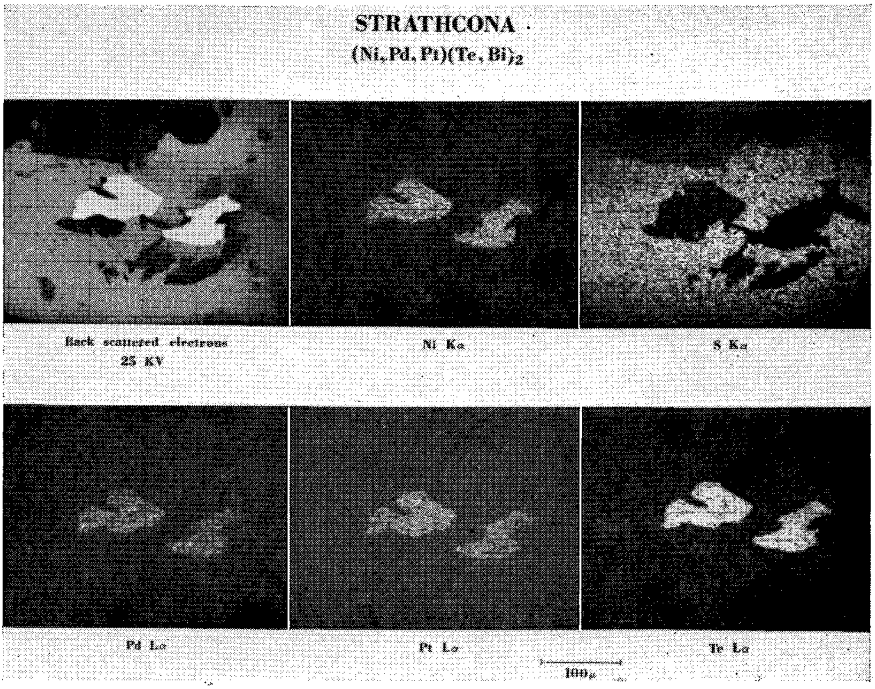

FIG. 5. *X*-ray scanning photographs showing the distribution of Pt, Pd, Te, Ni and S in nickeloan merenskyite from Strathcona, Ontario.

occurs in close proximity to a grain of palladium nickel bismuthotelluride. This rock consists of massive pyrrhotite and pentlandite, with minor pyrite and chalcopyrite.

Despite the extremely small grains in which this mineral occurs, and the extreme rarity of the occurrences, Mr. R. Buchan of Falconbridge Research laboratories, was able to extract from the Strathcona sample enough of sufficient purity for a recognisable *x*-ray powder pattern to be obtained. This pattern, while containing contaminating lines of chalcopyrite, contains distinctive lines of the palladium mineral. Most of the lines may be indexed on a hexagonal cell with $a = 3.909$ Å and $c = 5.272$ Å, Table 5. This cell is similar to, and slightly larger than that of melonite, which may be considered to be the nickel tellurium end member of the series. It was not possible to obtain *x*-ray data on the other samples.

In view of the fact that the *x*-ray data show this mineral to be isostructural with melonite, differing only in the degree of substitution of Pd for Ni, and of Bi for Te, there is no justification for naming a new mineral species. The three examples may be considered to represent a

TABLE 5. PALLADIAN MELONITE: *x*-RAY POWDER DATA
Locality: Strathcona. Analysis in Table 4. CoK radiation 1.7889 Å
Hexagonal $a = 3.909$ Å, $c = 5.272$ Å

| *I* | *d*(meas) | *d*(calc) | *hkil* | *I* | *d*(meas) | *d*(calc) | *hkil* |
|---|---|---|---|---|---|---|---|
| 3 | 5.30 Å | 5.272 Å | 0001 | 5 | 1.954 | 1.954 | $11\bar{2}0$ |
| 2 | 3.38 | 3.385 | $10\bar{1}0$ | 1 | 1.612 | 1.611 | $20\bar{2}1$ |
| 10 | 2.85 | 2.848 | $10\bar{1}1$ | ½ | 1.428 | 1.424 | $20\bar{2}2$ |
| 1 | 2.71 | — | | ½ | 1.324 | 1.318 | 0004 |
| 1 | 2.53 | — | | ½ | 1.240 | 1.243 | $21\bar{3}1$ |
| 5 | 2.08 | 2.080 | $10\bar{1}2$ | | | | |

solid solution series extending from merenskyite to melonite, with the Strathcona occurrence approximately in the middle of the series. The Falconbridge sample is a palladium bismuthian melonite, and that from Werner Lake a nickeloan merenskyite.

The simultaneous revelation of three members of a new solid solution series seems to be rather remarkable, and one is forced to reflect on the reasons for this. The presence of nickel is the common factor which distinguishes these three examples from the other platinoid bismuthotellurides. Nickel is known to substitute for platinum and palladium in braggite (Pt,Pd,Ni)S and vysotskite (Pd,Ni,Pt)S. The latter is a fairly new mineral described by Genkin & Zvyagintsev (1962) from Noril'sk. Nickel, in a platinum or palladium bismuthotelluride, would seem to be a reasonable substitution. Why has it not been observed before if it is common enough to be found in what amounts to a fortuitous selection of samples?

The principal occurrences of platinoid bismuthotellurides outside Canada are from the Merensky Reef, Rustenburg, in the Bushveld (Kingston, 1966) and from Monchegorsk, USSR (Genkin *et al.* 1963), both of which are copper nickel deposits. In Canada, michenerite and froodite were described by Hawley and Berry (1958) from concentrates from arsenic- and lead-copper-rich ores of the Frood Mine, Sudbury. The ubiquity of nickel at all these localities makes it seem unlikely that the nickel in the platinoid bismuthotellurides described here is a direct consequence of the nickel concentration in the surrounding rocks. Kingston (1966) has shown a photograph of nickel-free moncheite intergrown with a grain of pentlandite from Rustenburg. He has reported some analyses of moncheite containing undifferentiated Fe, Cu, Ni up to 8%, but he noted that these analyses were unsatisfactory, while the single reliable analysis contained no Fe, Cu or Ni.

In general the platinoid bismuthotellurides of Merensky Reef and

Monchegorsk are associated with chalcopyrite, and pentlandite is only a minor constituent, in contrast to the present occurrences where pentlandite is a major phase. Both Genkin *et al.* (1963) and Kingston (1966) argue that the platinoid bismuthotellurides were the latest minerals to form, in a "pegmatite" phase. At this stage little nickel would be available, so the tellurides would be nickel free. The platinoid sulphides, which may form in an earlier stage, about the same time as the pentlandite, contain high concentrations of nickel, presumably because its activity is high at this stage of the paragenesis. From crystal chemical considerations, one might expect nickel to substitute for palladium as easily in a telluride phase as in a sulphide phase. Two possible explanations may account for the presence of the nickel in the examples under discussion.

The nickel may enter the structure because nickel is a major component of the rock. An abundance of nickeliferous phases was not emphasised as being associated with the platinoid bismuthotellurides at the Rustenburg, Monchegorsk or Frood occurrences. In the present account, a nickel sulphide phase, pentlandite is an important constituent of the rock and is closely associated with the platinoid minerals. Nickel may simply be partitioned between sulphide and telluride to give the observed compositions.

On the other hand, the presence of nickel in the telluride phase may imply a high activity of nickel, and hence that the telluride formed earlier than is suspected at the other deposits. Further speculations on the genetic implications are unjustified with the present paucity of data.

## ACKNOWLEDGMENTS

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## COBALT–GOWGANDA ISSUE

A Cobalt–Gowganda issue is currently being prepared by Dr. W. Petruk, Mines Branch, and Dr. J. L. Jambor, Geological Survey of Canada. This issue will be edited by the co-authors and others in the Department of Energy, Mines and Resources, Canada, and will be published by the Canadian Mineralogist as a special issue about 1970. Information on research being conducted on the Cobalt–Gowganda ores, and copies of manuscripts that could be included in this issue are invited. Please forward all information and manuscripts to Dr. W. Petruk, Mines Branch, 555 Booth Street, Ottawa 4, Ontario.