PLATINUM METALS IN SOME CANADIAN URANIUM AND SULPHIDE ORES

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Abstract

A spectrographic method has been developed for the quantitative analysis of the platinum metals in fire-assay beads obtained from both sulphide and some uranium ores to which gold is added as a collector. Beads are incorporated in lead buttons and analyzed using lead as a variable internal standard.

Results are given for several nickeliferous sulphide ores from both Canada and South Africa (Insizwa), for an exceptional type of uranium ore, and for non-nickeliferous copper sulphide ores of both Precambrian and post-Cambrian age. The amounts of Pd, Pt, Rh, Ru, Ir, and Os are given in ppm, and ratios of these are compared with those noted by Rankama & Sahama for a composite of magmatic sulphides. A comparison is also made of the distribution of the platinoids in different metallic minerals.

Spectrographic investigation of the platinum metal content of various Canadian ores was initiated some time ago in order to complete mineralogical studies of nickeliferous ores in Canada. A technique involving the use of fire-assay beads and the incorporation of these in mercury-gold beads for spectrographic analysis, using gold as an internal standard, has been previously described. (Hawley, Lewis & Wark, 1951). Further investigation of this method uncovered difficulties in the uniform mixing of platinum and rhodium "black" and of bismuth in the gold amalgam which in turn gave rise to the development of a new technique by which fire assay beads of precious metals are dissolved in lead, a method to be described in detail elsewhere.[1]

This spectrographic method has now been applied to the study of platiniferous uranium ores, following a suggestion by Dr. G. S. Hume, Department of Mines and Technical Surveys, in 1950, and the study has been extended, first to include the nickeliferous sulphides of the Sudbury district and the non-nickeliferous sulphides which occur in scattered deposits between Sudbury and Sault Ste Marie, Ontario, with the thought in mind of attempting in this way to delimit metallogenic provinces characterized by the platinum metals. The study was later expanded to include other nickeliferous and non-nickeliferous sulphide ores, as well as samples from gold and mixed, base-metal ores of both Precambrian and post-Cambrian age. Though by no means complete, the results obtained to date are presented herewith and some tentative conclusions are given.

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[1] Trans. Can. Instit. Mining & Metal., vol. 56, pp. 19–26, 1953.

LEAD BEAD METHOD OF SPECTROGRAPHIC ANALYSIS OF PRECIOUS METALS AND BISMUTH

Since this method is being described elsewhere in greater detail, only a summary will be included here.

Fire-assay beads are made from one assay ton, or a fraction thereof, of the selected ore or ore minerals. In those samples which do not contain much if any gold or silver, pure gold is added to the sample as a collector prior to assaying, the amount of which may be varied from 1 to 10 mg., particularly to insure the production of a weighable bead. Losses on assaying, due to volatilization and absorption in cupels, have so far not been corrected.

Resultant precious metal beads are then fused with chemically pure lead with a blowpipe on charcoal[1] and the weight of lead actually added is determined from the total weight less the known weight of assay bead. The amount of lead used is within the ratio of 9 to 9.9 parts of lead to 1 to 0.1 part of precious metal bead. Lead buttons so formed, depending on their size, may be used in whole or in part. These are then soldered on the top of 2 inch lengths of 1/16″ to 1/4 dia. copper electrodes. Where increased sensitivity is required, two such electrodes are prepared as anode and cathode: otherwise hemispherical-tipped graphite counter electrodes have been used.

Samples are then sparked with a high voltage condensed spark (ca 15,000 v.) supplied by a Hilger unit, for 1 minute. Slit −60 microns, Gap −2 mm., Transmission −100%, Film type—Spectrum Analysis #1.

In order to prepare working curves, standards were made up containing Pd, Au, Ag, Pt, Rh, Ru and Ir as well as Bi since the latter is almost invariably present. As gold and silver may be major constituents compared with the other precious metals, in most samples standards of these were prepared covering a range of 0.001 to 10% Au or Ag/%Pb and working curves were established using four different gold and silver lines.

Throughout lead is used as an internal standard and intensity ratio of *element line/lead line* is plotted against the calculated ratio of *% Element/% lead*, a method referred to as the "Mutual Standard" method by Churchill & Russell (1945) and discussed by Harvey (1950), and Coulliette (1943).

Having determined the ratios of percentage of each element to percentage of lead, (from the working curves) the percentage lead is then calculated according to

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[1] An alternative method recently used is to carry out the fusion in graphite cups ininserted in a small furnace under hydrogen with maximum loss of 0.1% lead.

$$\% \text{Pb} = \frac{100}{1 + \frac{\% \text{Au}}{\% \text{Pb}} + \frac{\% \text{Ag}}{\% \text{Pb}} + \frac{\% \text{Pd}}{\% \text{Pb}} + \frac{\% \text{Bi}}{\% \text{Pb}} + \text{etc.}}$$

The figure for %Pb should check the actual known amount of lead added. A slightly higher percentage may be present if any lead has been left in the original precious metal assay bead, but on the whole excellent checks have been obtained.

Knowing accurately the percentage lead, the percentage of the sought-for element is then found by simply multiplying

$$\frac{\% \text{Element}}{\% \text{Pb}} \times \% \text{Pb}$$

Percentage element may then be stated in terms of milligrams per assay ton or troy ounces per ton, knowing the weight of the lead plus precious metals button. In this paper results are stated in terms of grams per metric ton or parts per million, except where noted. Since this work was completed Treadwell, Amrein & Bodmer (1952) have reported spectrochemical analysis of silver in lead over the ranges of 0.001% to 1.6% with deviations of 5% or less. Ageing of the lead silver alloys over a period of six weeks has shown that original homogeneous solid solutions ex-solve silver crystals along grain boundaries and yield less dense lines on excitation with an interrupted spark discharge. This is clearly a feature which requires consideration, not only for silver but for the other metals included in the present investigation and is undergoing further study.

Some measure of the accuracy obtained by this method is given by the following results on gold and silver beads in which only traces of the platinum metals were found by dc arc qualitative methods:

TABLE 1

	Gold		Silver		% Difference	
	mg. Assay	mg. Spectro	mg. Assay	mg. Spectro	Au	Ag
Q-1	11.81	11.89	3.1	2.37	0.7	20.
Q-2	11.98	11.93	2.65	2.70	0.45	1.9
P-1	476.00	515.40	1658.43	1622.50	8.3	2.5
P-2	476.05	477.20	1658.43	1658.20	0.3	0.1
P-3	476.01	477.60	1658.43	1653.07	5.37	0.3
C-1	18.10	16.45	57.55	57.01	9.0	1.0
C-3	17.345	14.16	64.45	64.96	18.0	0.8
C-4	17.185	18.18	64.45	62.80	5.7	2.5

Though no analyzed samples containing the platinum metals have been available, prepared standards were made independently and with different dilutions in lead, and found to check satisfactorily the working curves previously established. In addition special lead beads were made by evaporating, in lead cups, solutions containing known amounts of Pd, Pt, and Rh. Table 2 gives a comparison of spectrographic determinations with actual amounts of the metals in a prepared standard.

TABLE 2

	Pd	Pt	Rh
Amount in Standard—mg.	0.021	0.0350	0.0210
Amount determined spectrographically—mg.	0.021	0.0330	0.0214

The range covered by our analytical curves for the platinum metals is from 0.00056% to 3% and for gold and silver up to 10% of the lead beads.

According to this technique there is theoretically almost no limit to the lower limit of detectability of platinum metals since by concentrating these from several assay tons the actual amount may be eventually brought up to a level which is detectable spectrographically. Practically, however, if the gold or silver present, or added as a collector, increases too greatly, the platinum metals may be diluted too much for actual detection. Detectability of platinum, in terms of the final lead bead is 0.00175%, and of palladium and rhodium 0.0005%. Using one assay ton of mineral or ore, and a lead bead of 10 mg. these percentages give a detectability of platinum of about 0.003 ppm. and of palladium and rhodium of 0.0008 ppm.

Curves for ruthenium and iridium, in contrast to the others cover only the range from 0.2% to 2.0% in lead beads. These metals were only determined in a few cases in the later stages of the investigation by concentrating them in smaller lead beads than were used for determining the other platinoids. Amounts recorded in three samples fall below the above limit and hence will require further checking. Amounts of osmium given are only approximations based largely on the fact that its sensitivity is recorded as equal to iridium. Since both ruthenium and osmium form volatile oxides, our results must be regarded as tentative, awaiting more accurate techniques for their concentration by wet methods rather than by fire-assay.

PLATINUM METALS IN URANIUM ORES

Table 3 gives the analyses of platinum metals in two uranium ores, one a phenomenal type from Lake Athabasca, the other from Great Bear Lake, for comparison.

In the ore from Athabasca exceptional concentrations of the platinum metals are present, the ratio of Pd:Pt: Rh approximating 6:1:0.01. Due to lack of unground specimens it has not been possible to separate individual minerals for analysis, but there does appear to be some correspondence between the amount of gold and amounts of platinum metals as indicated by the low and high values, given. This confirms an opinion by S. C. Robinson,[1] who identified the following minerals in this ore: —pitchblende, tiemannite, galena, pyrite, chalcopyrite, niccolite and gold.

As a matter of curiosity following the above determinations, concentrates of niccolite, cobalt arsenides (skutterudite and safflorite) and a composite sample consisting largely of pitchblende from a deposit at Great Bear Lake were analyzed in a similar manner, but only the very small amounts of palladium and rhodium indicated were found.

Though considerable quantities of palladium are known in mixed arsenides at Sudbury (see p. 469) there is obviously no constant association of these metals with such minerals. Furthermore no data are available to indicate any direct relation between the platinum metals and the uranium oxides in such ores.

TABLE 3. PLATINUM METALS IN URANIUM ORES

Grams per Metric Ton

Deposit	Minerals	Palladium	Platinum	Rhodium	Others
Athabasca (Nicholson)	Ore	0.10–443.	.02–73.	.006–.67	Au—25–2242. Ag—17–209. Ru—0.35* Ir—0.43 Os—0.33 (?)
Great Bear Lake Area	Niccolite (calcined)	.03–.045	tr	tr	Ag—56–74.
	Cobalt Arsenides (calcined)	.05	tr	.037	Ag—245.
	Composite Ore (calcined)	tr	—	—	Ag—2543.

* Ru, Ir, Os, determined approximately on only one sample, but show in three separate beads of this sample.

PLATINUM METALS IN NICKELIFEROUS SULPHIDE ORE MINERALS

The results of spectrographic analyses of selected minerals in nickeliferous ores are given in Table 4. In all cases the specimens contained no visible platiniferous minerals, thus the results do not indicate maximum

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[1] Written communication.

amounts of such elements in the ores as a whole. Several of the analyses do show, however, an erratic distribution of palladium and platinum which may best be accounted for by inclusion of discrete mineral particles of these elements, as in chalcopyrite, pentlandite and arsenides.

Samples analyzed consist of concentrates from various localities along the south range of the Sudbury basin, from the base metal ore of the Treadwell-Yukon, within the basin, and from chalcopyrite associated with pyrrhotite and pentlandite in the Springer deposit of Baldwin township on the west. In addition are given results on samples of the recently discovered nickeliferous sulphides at the base of the Duluth gabbro, Minnesota and of samples from Lynn Lake, Manitoba, Rankin Inlet on the west coast of Hudson's Bay, and of a suite of samples obtained from the magmatic deposit at Insizwa, South Africa. For comparison, similarly stated ratios given by Rankama & Sahama (1949) are presented for a composite of magmatic sulphides.

The occurrence of the platinoids in ores from Sudbury is, of course, well known and these will be further discussed. The presence of the three platinum metals in the Treadwell-Yukon sample containing chiefly pyrite with minor galena and sphalerite, may be taken as a very likely indication of a genetic relation between this ore and those on the margins of the Sudbury basin. Scattered sulphide deposits west of Sudbury fall into two categories, those with pentlandite and those without. The Springer deposit in Baldwin township and the Shakespeare mine, west of Sudbury are both nickeliferous and carry the platinum metals. Others, which are non-nickeliferous are reported with such ores later (see p. 472).

Deposits farther afield, such as those of the Duluth gabbro, Lynn Lake, Rankin Inlet, and Insizwa again illustrate the association of these metals with nickeliferous ores and give an approximation at least of the relative quantities present.

With few exceptions all of the samples analyzed show one or more parts per million of palladium and in many cases much more. Platinum and rhodium[1] are usually lower. Though chalcopyrite on the whole shows more of the platinoids, particularly palladium, this is not always the case, both pentlandite and pyrrhotite, as well as mixed arsenides, being locally richer in this respect. There is thus no very clear relation between the amounts of platinum metals, particularly of palladium and platinum, and the order of introduction of the common sulphides, though analyses to date do suggest ruthenium, iridium and osmium may possibly be concentrated more in pyrrhotite, usually the earliest of the three sulphides.

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[1] *Rhodium* was not determined in several samples due to use of a different technique employed at the time.

TABLE 4. PLATINUM METALS IN NICKELIFEROUS SULPHIDE ORES
Grams per Metric Ton

Sudbury	Mineral	Palladium	Platinum	Rhodium	Others
South Range	Pyrrhotite	0.45	0.18	0.10	Ru 0.35–0.04
		0.75	0.85	0.45	Ir 0.33–0.02
					Os 0.37 (?)
South Range	Chalcopyrite	1.17	1.30	.27	
Falconbridge[1]	Chalcopyrite	34.28	1.54	nd	
Falconbridge	Chalcopyrite	1.61	3.77	nd	
Falconbridge	Pentlandite	17.50	29.8	nd	
Falconbridge		12.65	34.2+		
Falconbridge	Pyrrhotite	34.2+	15.6	nd	
		0.13	0.170		
Falconbridge	Arsenides	246.8	tr	nd	
Falconbridge	Pyrite	0.31	0.37	nd	
Nickel Offsets	Pentlandite & Pyrr.	2.00	2.68	0.10	
Treadwell-Yukon	Py. Ga. Sp.	1.92	0.61	1.73	
Springer-Baldwin	Chalcopyrite	0.03		0.04	
Duluth Gabbro	Pyrrhotite	1.47	0.11	0.07	
Lynn Lake Man.	Pyrrhotite	1.36	0.18	0.018	
Rankin Inlet	Pyrrhotite	3.79	1.26	0.55	
N. W. T.	Pyrrhotite	4.45	2.40	.30	Ru 1.6, Ir 1.03
	Pyrr. Pent. Cpy.[3]	5.15	2.71	0.58	Ru 2.12, Ir 1.03
					Os 1.0 (?)
Insizwa, S. Africa	Chalco-cubanite	13.75	2.06	0.057	Ru .09
	Pyrrhotite-Pent.	0.38	0.48	0.38	Ru .41, Ir .51
					Os .34 (?)
Magmatic[2]	Sulphides	4.0	2.0	0.3	Ru 1.0
					Ir 0.4
					Os 0.1

[1] After Hawley, Lewis & Wark, Econ. Geol. **46**, pp. 149–161, 1951.

[2] Noddack, Ida & Walter, Zeit. Physik. Chem. A. **154**, 207, and Rankama & Sahama-Geochemistry, 1949, pp. 692.

[3] Sample dominantly pyrrhotite with minor pentlandite and chalcopyrite.

Abbreviations—Py pyrite, Pyrr. pyrrhotite, Ga galena, Sp sphalerite, Pent. pentlandite, nd Not determined.

Little information is available regarding the ratios of the various platinum metals, one to another, in ores from which they have been recovered. Actual recovery is of course not necessarily the same as actual occurrence in the ores and individual minerals, so basic data on the ratios of these metals in the ore minerals themselves are badly needed. Analyses of a composite of magmatic sulphides, from various localities, in part Norwegian, were made by Noddack & Noddack (1931) and are quoted by Rankama & Sahama (1950). In these the ratio of Pd:Pt:Rh, in parts per million is 4.0:2.0:0.3, and that of Ru:Ir:Os is 1.0:0.4:0.1.

It is not possible to arrive at an average ratio from our figures for the Sudbury area, though it may be noted that for nine pyrrhotite samples from the south range, the Pd:Pt:Rh ratio is 4.0:2.0:1.3. Actual quantities are lower than given by Rankama, but the Pd:Pt ratio agrees with his, while that of rhodium is somewhat higher.

Attention may also be called to the close similarity between the relative amounts of Pd, Pt, and Rh in the pentlandite-pyrrhotite ores of Rankin Inlet and the composite given by Rankama & Sahama, an average of the three samples from this locality giving a ratio of Pd:Pt:Rh of 4.16:2.0:0.4.

The magmatic ores of Insizwa, described and classified by Scholtz (1936) are divided into three groups, massive chalcopyrite-rich ore containing much cubanite, massive pyrrhotite-rich ore with intergrown pentlandite, and disseminated ore. Samples from the first two were analyzed for individual platinum metals and the totals are compared in Table 5 with recalculated assays on two and three samples respectively, given by Scholtz.

TABLE 5. TOTAL PLATINOIDS INSIZWA ORE
Grams per Metric Ton

	Spectrographic	Scholtz—Assays
Pyrrhotite ore.	2.5	6.85– 7.71 (2)
Chalcopyrite ore.	17.01	11.15–46.3 (3)

Our results thus fall within the range given by Scholtz for the chalcopyrite-rich ore, but are lower than his for pyrrhotite.

A study of our results, given in Table 4, shows in addition to the fact that more platinoids are concentrated in the Insizwa chalcopyrite, that chalcopyrite contains between three and four times as much palladium and platinum as the pyrrhotite ore and about seven times as much silver. The pyrrhotite ore, however, contains about six times as much rhodium and over four times as much ruthenium as found in the chalcopyrite. Iridium and likely an equal amount at least of osmium are also present in the pyrrhotite but were not detected at all in chalcopyrite ore.

Ratio of Pd:Pt:Rh in Insizwa pyrrhotite ore is about 1 and in chalcopyrite, about 14:2:0.06. An average of the two ores (though it is not clear that they are present in equal amounts) gives a ratio for these metals of about 10:2:0.3 in which Pd is much higher than given by Rankama & Sahama, but, surprisingly, the figures for platinum and rhodium are identical with theirs. It is apparent however, that to obtain dependable ratios of these metals for various types of nickeliferous ores many more analyses are required.

Only in our more recent work have results been obtained on the distribution of what are normally thought of as the somewhat rarer platinoids, namely ruthenium, iridium and osmium. As is well known, the platinum metals fall in *two* groups according to their atomic numbers and properties, Ru, Rh, and Pd, and Os, Ir, and Pt, and one might expect some such association in nature. So far however, this cannot be clearly demonstrated. For instance, in the Insizwa ore high palladium in chalcopyrite is not accompanied by high ruthenium, and in *one* sample of pyrrhotite of the same ore, low platinum is accompanied by relatively high iridium as well as ruthenium and rhodium.

On the other hand, as will be seen later, in Table 6 of the non-nickeliferous ores, some samples contain both rhodium and palladium, members of one triad, but no platinum.

In Table 4, of the nickeliferous ores, ruthenium, iridium and osmium were only determined in three different ores. Results of the Insizwa ore have already been mentioned. In the other two, again Ru, Ir and Os are present as at Insizwa, in pyrrhotite-rich ores. Rankama & Sahama give the ratio and parts per million of these metals as Ru:Ir:Os = 1.0:0.4:0.1, for a composite of magmatic sulphides apparently from Norway. In contrast, our results for both Sudbury pyrrhotite and Insizwa pyrrhotite-rich ore show more nearly equal quantities of these three metals though about the same total of slightly over 1 ppm. The Rankin Inlet sample on the other hand, shows a total of over 4 ppm, with ruthenium about double that of iridium and of osmium. Again, much further study is required as well as different concentration techniques to satisfactorily arrive at reliable ratios for these metals.

PLATINUM METALS IN NON-NICKELIFEROUS SULPHIDE ORES

Spectrographic analyses of minerals in non-nickeliferous sulphide ores of Precambrian age are given in Table 6. These include chiefly copper ores in Quebec, Ontario, Manitoba, two gold deposits, as well as arsenides from the native copper deposits of Michigan.

In view of the fact that research on the platinum metals in their nearly pure state was carried out in our laboratory at the same time as this work, the possibility of contamination of samples was carefully examined. As a check against several of our determinations, qualitative analyses of gold beads prepared from several of the ores here described, were kindly undertaken by Dr. B. J. Stallwood, Mines Branch, Dept. of Mines and Technical Surveys, and confirmation was obtained of the presence of Pd, Pt, Rh, and Ir and Ru in several of these.

In the northwestern Quebec area the related deposits of Noranda, Quemont, Waite, Aldermac and Normetal almost all contain some of the platinum metals in determinable amounts, with palladium in excess of platinum. In two instances, rhodium is in excess of palladium. In the Noranda and Aldermac ores palladium increases with the order of paragenesis, namely pyrite, pyrrhotite, chalcopyrite, though in both the Normetal and Flin Flon (Man.) deposits amounts of this metal are about the same in both pyrrhotite and chalcopyrite. In the latter, rhodium is again slightly in excess of palladium.

TABLE 6. PLATINUM METALS IN NON-NICKELIFEROUS SULPHIDE ORES

Grams per Metric Ton

Deposit	Mineral	Palladium	Platinum	Rhodium	Others
Quebec					
Noranda	Chalcopyrite	.025–.018	tr	tr—.055	Ru—tr
	Pyrrhotite	.017			
	Pyrite	.012	tr	tr	
Waite	Pyrrhotite	.016	tr	tr	
Quemont	Chalcopyrite	tr	tr	tr	Ru-Ir-Os—tr
Aldermac	Chalcopyrite	1.03	.09	tr	
	Pyrrhotite	.02		.06	
	Pyrite	tr		.003	
Normetal	Chalcopyrite	.004		.003	
	Pyrrhotite	.004			
Opemisca	Chalcopyrite	.02			
Powell-Rouyn	Pyrite	tr	tr	tr	
Manitoba					
Flin Flon	Chalcopyrite	.055		.07	
	Pyrrhotite	.056			
Ontario					
North Shore					
Lake Huron—					
Bruce Mines	Chalcopyrite	.019	tr	.021	
Bi-Ore	Chalcopyrite	tr	tr	.13	
Bald Dome	Chalcopyrite	tr	tr	.08	
Eckett	Chalcopyrite				
Rock Lake	Chalcopyrite	.033	tr	tr	
Porcupine Dist					
Hollinger	Pyrrhotite	.006		.03	
Michigan					
Keweenaw Pen.	Cu Arsenides	.068	.041		

tr = trace, found on qualitative analysis.

In chalcopyrite from the scattered, small, non-nickeliferous deposits along the north shore of Lake Huron, platinum metals are also present in either traces or detectable amounts with one exception. Again palladium is in excess of platinum and rhodium in excess of palladium. Total amounts of the platinoids in these ores, where pentlandite is absent is very much less than in those ores containing even small amounts of nickel.

The occurrence of traces of these metals in pyrite from the Powell-Rouyn gold vein, near Noranda, and of minute amounts of palladium and rhodium in pyrrhotite from the Hollinger gold deposits are of interest in showing their rather ubiquitous character. Similarly the presence of palladium and platinum in a concentrate of algodonite from the Keweenaw peninsula, Michigan, in which nickel and cobalt are also prominent as trace elements, suggests these metals are by no means as rare as might be supposed. Whether they are of genetic significance, however, is still a question, but attention is called to the results already given for nickeliferous sulphides at the base of the Duluth gabbro, an intrusive believed similar to gabbro to which the Keweenawan copper ores have been ascribed.

On the whole, though it was first thought that the presence of platinum metals in various copper ores both in Quebec and Ontario might indicate a genetic relation to the Sudbury ores, both the decidedly lower concentrations in non-nickeliferous ores and the demonstrated ubiquitous character of the metals in even unrelated gold deposits, precludes the drawing of any such conclusions at this time. Since nickel is so much more readily determined, the delineation of any nickeliferous and platiniferous metallogenic provinces can obviously be made more simply by determination of nickel.

PLATINUM METALS IN POST-CAMBRIAN SULPHIDES

As a sequel to the above studies a few analyses have been made on chalcopyrite concentration from post-Cambrian (Palaeozoic) ores in Newfoundland and the Eastern townships, Quebec. These are given in Table 7.

In these ores the presence of only traces of palladium in Newfoundland

TABLE 7. PLATINUM METALS IN POST-CAMBRIAN CHALCOPYRITE
Grams per Metric Ton

	Palladium	Platinum	Rhodium
Newfoundland			
Buchans	.026	tr	tr
Quebec			
Ascot	1.82	.041	tr
Ascot	1.61	.062	
Moulton Hill	0.16	tr	tr
Weedon	0.65	.410	tr
Weedon	0.34	tr	

chalcopyrite and of both palladium and platinum in the Quebec deposits is noted. In the latter palladium averages nearly 1 pm and the ratio of Pd:Pt averages 9:1, a somewhat higher ratio of palladium than in Precambrian ores. The absence of rhodium may also be a characteristic difference of such ores, but again more detailed studies will be required to determine reliable ratios of the platinoids in post-Cambrian sulphides of other areas.

Summary and Conclusions

By means of fire-assay beads in which gold is used as a collector, a satisfactory spectrographic technique has been established for the determination of the platinum metals quantitatively in both uranium and sulphide ores and ore minerals. Beads are diluted in lead, mounted on copper electrodes, and with a high voltage condensed spark, ratios of percentage precious metals to percentage lead are determined by the "Mutual Standard" method. Gold, silver and bismuth may be similarly determined. By controlling the amount of gold and lead and varying the fractions or number of assay-ton samples used the method may be applied to minerals with a wide range of concentrations of the precious metals.

Uranium ore from one locality in the Lake Athabasca area contains remarkable concentrations of the platinum metals which appear to bear a rough relation to the amount of gold present. In this ore the ratio of Pd:Pt:Rh is 6:1:0.01; while Ru, Ir, and Os are present in about equal proportions and in amounts up to 0.3 ppm. each. Tests on uranium ore from Great Bear Lake indicate three to four hundredths of a part per million of Pd and Rh in nickel and cobalt arsenides.

Analyses of nickeliferous sulphides from various areas in Canada are compared with the platinoids in similar ore from South Africa and with ratios of these given by Rankama and Sahama for a composite of magmatic sulphides.

All nickeliferous ores tested indicate the presence of platinoids. All contain 1 or many ppm. palladium and usually platinum and rhodium in lower quantities. Of the sulphides, chalcopyrite is the richest in platinum metals, but pentlandite and pyrrhotite may be equally so. There is a suggestion that ruthenium, iridium and osmium are concentrated more in the earlist mineral, pyrrhotite.

Though no definite ratios of Pd:Pt:Rh can be given for Canadian ores as a whole, the Pd:Pt ratio of some Sudbury pyrrhotite is the same as given by Rankama and Sahama though amounts are less, while rhodium is greater. Ratios for the three metals in an average of Rankin Inlet ore are almost identical with figures given by Rankama and Sahama as are the parts per million.

In the Insizwa magmatic ore Pd and Pt appear concentrated in chalcopyrite while Rh, Ru, Ir and possibly Os are more abundant in pyrrhotite.

The average ratio of Pd:Pt:Rh of this ore shows more Pd but similar amounts of Pt and Rh, compared with the ratio given by Rankama and Sahama.

In non-nickeliferous copper-iron sulphides of Precambrian deposits palladium, rhodium and in a few cases, platinum are present in amounts ranging from 4/1000 to one ppm. Palladium is invariably present in larger amounts than platinum, but in several cases, peculiarly, rhodium is in excess of palladium. In chalcopyrite of base metal ores of Palaeozoic age, palladium and platinum have both been detected, ranging from about 3/100 to nearly 2 ppm. with palladium always in excess of platinum.

The much greater affinity of these metals for nickeliferous ores is amply borne out by the data presented. Since the determination of nickel is less difficult than of the platinoids, delineation of metallogenic provinces can be made most easily by the former.

Though, according to Goldschmidt's geochemical classification of elements, all the platinoids are noted as *siderophile* in character (most readily soluble in molten iron and nickel), and Pd, Pt, and Ru are classified also as being concentrated but to a lesser extent with the chalcophile elements (having an affinity for sulphur, Rankama & Sahama 1949, p. 88), rhodium, iridium and osmium may likewise be so classified in view of their frequent presence in pyrrhotite. The persistence of traces of the platinum metals in pyrite of hydrothermal gold deposits is also shown.

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