Journal of Geochemical Exploration, 3(1974)277—289

MERCURY IN SOME GRANITOID ROCKS OF THE YUKON AND ITS RELATION TO GOLD—TUNGSTEN MINERALIZATION

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(Accepted for publication December 5, 1973)

ABSTRACT

Garrett, R.G., 1974. Mercury in some granitoid rocks of the Yukon and its relation to gold—tungsten mineralization. J. Geochem. Explor., 3: 277—289.

Data for the mean mercury contents of some granitoid rocks of the Yukon are presented. A correlation of high mercury content with plutons postulated to be the sources, or genetically related to the sources, of the alluvial gold deposits of the McQuesten area is established. In addition a relation is indicated between high mercury content in one intrusion and high content in the Palaeozoic shale host rock. A limited amount of data is presented on the mercury content of the Proterozoic and Palaeozoic rocks of the sampled area.

INTRODUCTION

Knowledge of the distribution of mercury in the granitoid rocks of the Canadian Cordillera is sparse and to date no systematic studies have been undertaken. During the summer of 1970 a regional sampling program of the acid plutons northeast of the Tintina Trench in Yukon and adjoining areas of Northwest Territories was carried out. Seventy-four intrusions in the area between 62°40′N and 64°40′N were sampled. During 1971 the sampling was continued to the southeastern extreme of the Cretaceous granitoids northeast of the Tintina Trench through the Nahanni, Flat and Coal River areas. These bodies are considered to be Late Cretaceous in age with K—Ar dates ranging from 74 to 110 m.y. and have intruded rocks of Proterozoic to Cretaceous age. Their composition ranges from quartz diorite to syenite; however, most of the rocks are granodiorites or quartz monzonites.

The samples have been analysed for a wide range of elements with the aim being to correlate the regional geochemistry with features of the regional geology and mineral deposits. Data for the mean molybdenum, tungsten and uranium contents of the plutons have been released and a review has been presented (Garrett, 1971a,b). The data for the base metals have been presented and interpreted in terms of mineral potential, certain regional differences in metal content being noted between different parts of the field area (Garrett, 1973). One of the most striking features of these data lies in the areal distribution of tungsten. Cathro (1969) in a paper on the tungsten mineralization of the Yukon proposed that the scattered tungsten occurrences fell within a contiguous area, which for discussion purposes he named the Selwyn tungsten belt. This extends southeastwards 350 miles from the McQuestern area in the Yukon to the area of the Canada Tungsten mine in Northwest Territories. Bostock (in Little, 1959) had, on the basis of much less data, proposed this same idea earlier. The current regional geochemical work indicates that the belt should be divided into two distinct parts. The Selwyn belt should be restricted to the Selwyn Mountains along the Yukon—Northwest Territories border where it appears to terminate near Keele Peak in the north. An entirely separate area exists in the Mayo—McQuesten area, and it is proposed that this be called the McQuesten belt. Although both these belts contain tungsten mineralization, the form of this mineralization differs. In the Selwyn belt tungsten occurs as scheelite in skarns in Proterozoic to Cambro-Ordovician grits and limestones, the best examples being the Canada Tungsten Mine and the AMAX Mount Allan property. The former in Lower Cambrian limestones and the latter in limestones of possible Lower Cambrian age. In contrast, in the McQuesten belt skarns are less widespread, and the source of the tungsten, as scheelite and to a lesser extent wolframite, is veinlets and pegmatites associated with the granitoids. It is this type of occurrence that has been termed "porphyry tungsten deposits" by Cathro (1969), the best example being Potato Hills. The country rocks intruded by the granitoids are Proterozoic, consisting of schists, quartzites and minor limestones. In detail the mineral associations are also different, in the Selwyn belt scheelite is the most important mineral with some pyrrhotite and minor chalcopyrite. In the McQuesten belt a more complex assemblage consisting of scheelite, gold, cassiterite, galena, jamesonite, arsenopyrite and rarely cinnabar is present. However, some simple scheelite skarns, similar to those in the Selwyn belt, occur in the Proterozoic grits.

Bostock (in Little, 1959) pointed out that many of the gold placer streams of the McQuesten belt, carried some scheelite, with or without associated cassiterite. The geochemical association of high tungsten content of granitoids in the McQuesten belt and areas of alluvial gold production has been pointed out in the three major gold producing areas; Clear, Highet and Haggart Creeks associated with the West Ridge, Scheelite Dome and Potato Hills Stocks (Garrett, 1971b). However, tungsten in the Mayo—McQuesten area did not appear to be a completely reliable indicator of gold potential. There is no record of alluvial gold near the tungsten-rich Two Buttes stock 20 miles southeast of Mayo, and although the lower parts of the Stewart Valley have been glaciated (Bostock, 1966) it is likely that if gold had been present the gold prospectors at the turn of the century would have discovered it. It is possibly significant that the Two Buttes stock is also typified by anomalous molybdenum levels, whereas the tungsten-rich granitoids spatially related to alluvial gold in the McQuesten belt are not. The criterion of low molybdenum associated with high tungsten content in the granitoids was not considered entirely satisfactory, and for that reason the distribution of mercury has been investigated as a possible indicator of potential source granitoids for the alluvial gold.

SAMPLE PREPARATION AND ANALYSIS

Samples of about 2½ pounds each were crushed and ground to minus 10-mesh, and a 40-g split of this material was then ballmilled to minus 100-mesh (Lavergne, 1965). Much concern has been expressed by workers involved in mercury analysis of geological materials as to losses incurred by volatilization during ballmilling, and changes in mercury level as a result of storage in a powdered state. No study has been made of the effects of the particular method of sample preparation used. However, it has been possible to check on the result of storage by an indirect method. Approximately one-third of the samples of one of the plutons, Potato Hills (Fig.1), was collected in 1969 and stored in plastic vials with snap-on tops. The mercury contents of these samples were indistinguishable from samples collected and prepared in 1970.

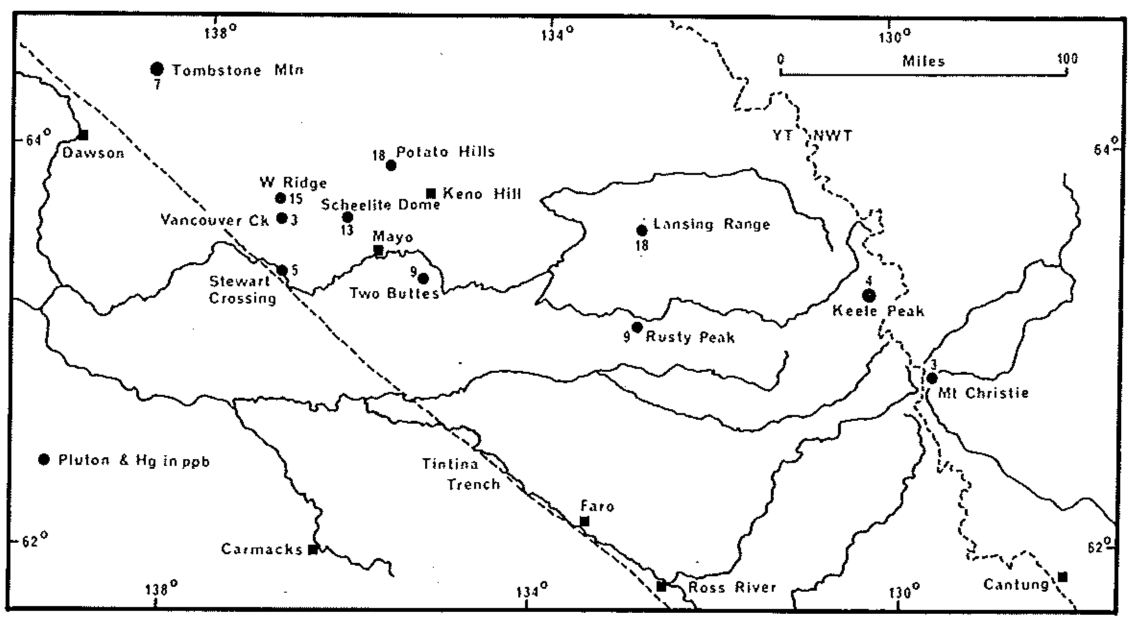

Fig.1. Locations and geometric mean mercury contents of acid plutonic rocks.

The analytical technique is similar to that described by Hatch and Ott (1968), but modified by I.R. Jonasson and J.J. Lynch at the Geological Survey of Canada. Briefly, a 1-g sample is attacked with 50 ml of a solution of 3*M* HNO_3 and 0.5*M* HC1 for 1½ hours at 90°C on a waterbath. After cooling, 10 ml of acidic 10% tin (II) sulphate solution are added, and the

TABLE I

Summary of statistics

Pluton	No. of sample sites (n)	Geometric Mean, (ppb Hg)	Variance in $\log_{10}$ units (σ^2_D)	Combined sampling and analytical variance (σ^2_{SA})	F ratio (σ^2_D/σ^2_{SA})
1 Mount Christie	23	3	0.054	0.051	1.04
2 Keele Peak	17	4	0.024	0.014	1.75
3 Rusty Peak	12	9	0.039	0.029	1.33
4 Lansing Range	11	18	0.062	0.044	1.42
5 Two Buttes	15	9	0.052	0.030	1.72
6 Potato Hills	24	19	0.023	0.006	*3.77*
7 Scheelite Dome	15	13	0.022	0.016	1.42
8 West Ridge	23	15	0.008	0.007	1.12
9 Stewart Crossing	15	5	0.023	0.005	*4.36*
10 Vancouver Creek	15	3	0.043	0.046	0.94
11 Tombstone Mountain	28	7	0.019	0.015	1.27
Total data	198	8	0.108	0.022	*4.85*

Notes: (1) two samples were collected at each site, thus a total of 396 samples were collected and analysed; (2) Values of Fisher's F significant at the 95% confidence level are in italics. The ratio σ^2_D/σ^2_{SA} is evaluated with $n-1$ and n degrees of freedom.

liberated elemental mercury is flushed through a heated 35 cm long absorption cell held in the optical path of a Techtron AA5 atomic absorption spectrophotometer (Jonasson et al., 1973). In this manner contents down to 3 ppb Hg in the rock can be determined. Precision determined by 62 replicate analyses from the total of 396 is ±25% at the 95% confidence level in the range 3—30 ppb. Those samples with values below the detection limit were arbitrarily ascribed values of half the detection limit.

DESCRIPTION AND LOCATION OF PLUTONS STUDIED

Eleven plutons were selected from the 74 sampled in 1970. In addition to those 3 associated with alluvial gold occurrences, 8 others were selected on the basis of rock type and host rock. The granitoids vary in composition from quartz diorite to syenite and the host rocks are both sedimentary and metamorphic ranging from Proterozoic to Cretaceous age.

Mount Christie and Keele Peak, both lie within the Selwyn belt and are respectively quartz monzonitic and granodioritic in composition, though neither is associated with significant tungsten mineralization. The Mount Christie stock was intruded into Devono-Missisippian clastics deposited off the edge of a shelf, the basin being to the west (Douglas, 1970). The Keele Peak stock was intrusive into Proterozoic grits which are covered around the north and east sides of Keele Peak by a thin veneer of Devono-Mississippian shales (Blusson, personal communication, 1970). The Lansing Range stock has a variable composition from quartz diorite to granodiorite and was intruded through Devono-Mississippian black shales and cherts. The Rusty Peak pluton is granodioritic in composition, and intruded Proterozoic shales and grits. Two Buttes is similar in composition to Rusty Peak and was intruded into similar rocks. The Potato Hills, Scheelite Dome, West Ridge and Vancouver Creek plutons all lie within the McQuesten belt and were intruded into Proterozoic schists and grits. All except the last are spatially associated with alluvial gold occurrences and are granodioritic in composition. The Vancouver Creek stock is more quartz monzonitic and contains megacrysts of albitic feldspar. The Stewart Crossing pluton appears to be similar to the Vancouver Creek body but is located on the Tintina Trench and has been considerably sheared. The last pluton chosen for this study is at Tombstone Mountain and it is dominantly syenitic in composition and intruded Cretaceous quartzites (Templeman-Kluit, 1970).

DESCRIPTION OF ANALYTICAL RESULTS

The geometric mean of the mercury contents of the plutons is plotted on Fig.1, and a statistical summary of the data is presented in Table I and Fig.2. The summary statistics (Table I) have been computed with a logarithmic transform for two reasons. Firstly, the errors inherent in the atomic absorption spectrophotometric method are logarithmically distributed, and second-

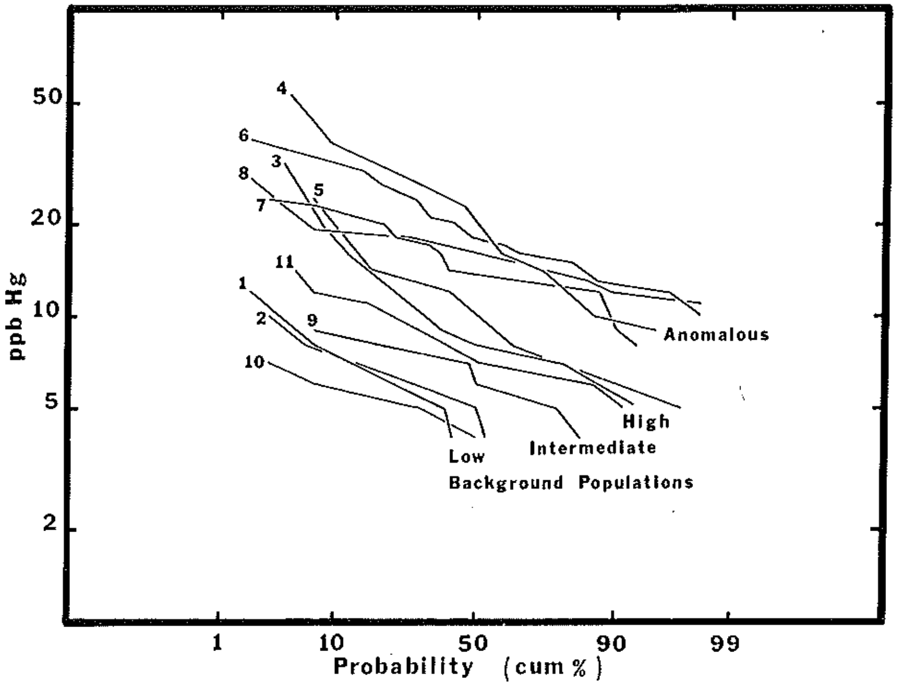

Fig.2. Cumulative frequency plots for the individual plutons.

ly, the data tend to be lognormally distributed. The cumulative frequencies of the mercury data for each pluton are plotted on log-probability paper in Fig.2. These plots should only be regarded as a general indication of the distributions as some are based on as few as 30 determinations. The frequencies have been cumulated downwards so as to better define the high end of the distributions.

To assess the significance of the regional patterns and detect any internal zoning of mercury in the plutons, analyses of variance were carried out; this was made possible by the utilization of a duplicate sampling scheme (Garrett, 1971b). Only in the Potato Hills and Stewart Crossing plutons were the combined sampling and analytical variances significantly lower than over-all pluton variances. Most importantly the overall combined sampling and analytical variance, estimated from 198 duplicate samples covering all the plutons in this study is significantly lower (> 95% level) than the total regional variability. This indicates that regional variations are significantly larger than the sampling and analytical errors, and that the regional variations are due to geological causes.

The Potato Hills stock is known to be zoned with certain inner areas being more felsic than the remainder. During the regional study of the base metal data (Garrett, 1973) a differentiation index was developed for the granitoids with the aid of *R*-mode principle components analysis. Using this index a sympathetic relation, at > 90% confidence level, is indicated between mercury content and the degree of differentiation of the rock, the tendency for higher mercury contents to be related to more felsic rocks has been pointed out by

Jonasson and Boyle (1971). If data from veined and highly altered parts of the pluton are studied there is an obvious correlation between mercury and both copper and lead, this is believed due to the very probable association of mercury with the sulpharsenide-bearing polymetallic veins of the area. During the sampling of the Stewart Crossing pluton it was noted that certain parts of it were intensively sheared and chloritized, possibly due to movements in the Tintina Trench fault system. A review of the data for both the fresh and altered rocks is given in Table II. The mercury content of the altered rocks is some 1.6 times that of the fresh unaltered material. A fixed one-way analysis of variance model (Krumbein and Graybill, 1965) was used to test the hypothesis that the data were drawn from a single population. The analysis of variance model was preferred over a Student's t test as the variances of the data for fresh and altered rocks are significantly different one from the other. This hypothesis is rejected and it therefore seems probable that mercury was introduced during the shearing to lead to higher, and more homogeneous, levels in the altered rocks than in the fresh unaltered material.

TABLE II

Summary of statistics and analysis of variance for the Stewart Crossing pluton

	Geometric mean (ppb)	Variance ($\log_{10}$ units)	No. of sample sites
Total data	5.53	0.02084	15
Fresh rocks	4.27	0.01578	7
Altered rocks	6.93	0.00445	8

Fixed one-way analysis of variance

	Sum of squares	d.f.	Mean sums of squares	F
Between groups	0.16593	1	0.16593	17.14
Within groups	0.12583	13	0.00968	
Total	0.29176	14		

Critical value of $F_{0.95,\ 1,\ 13} = 4.67$. As $F >$ critical value the hypothesis of equality is rejected.

The regional data presented graphically in Fig.3 have been divided into 4 main groups: low, intermediate, and high background, and anomalous. The anomalous group has been subdivided into a black shale association typified by the Lansing Range stock and a gold association as shown at the Potato Hills, Scheelite Dome and West Ridge localities.

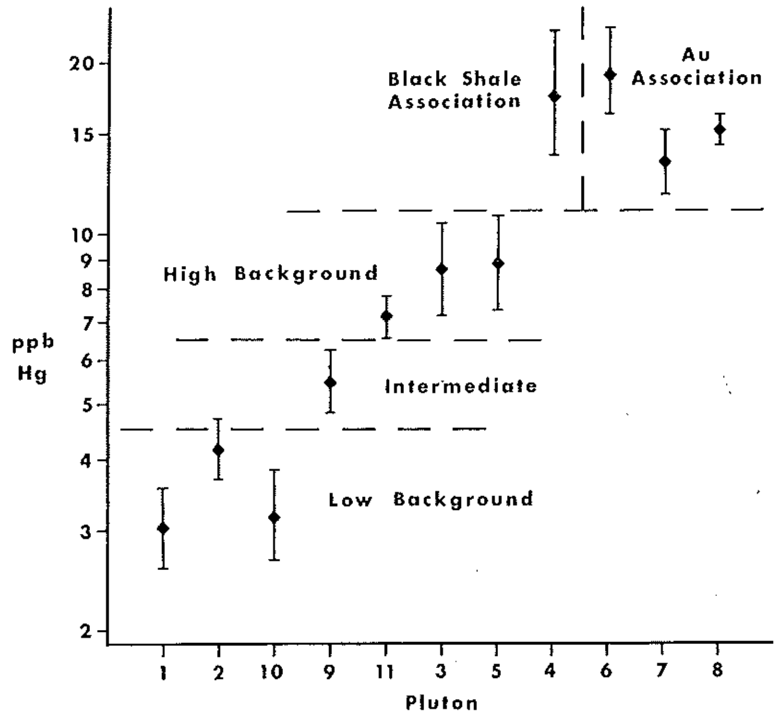

Fig.3. Geometric means and 95% confidence limits of the means of acid plutonic rocks.

DISCUSSION OF RESULTS

The interpretation of the data in the light of present geological information leads to several interesting observations.

Firstly, contrary to expectations and extrapolation from other major linear fault features of the world, where mercury levels are often enhanced in adjacent rocks, the mercury levels in the granitoids show little or no relation to the Tintina Trench. Locally, mercury is higher in content in the sheared rocks of the Stewart Crossing pluton in the Trench; however, in relation to other plutons away from the Trench even these altered rocks locally high in mercury are regionally low.

Secondly, there is no obvious correlation of mercury with igneous rock type; however, there does appear to be some correlation with the type of host rock. Keele Peak and Mount Christie stocks, intruded respectively into Proterozoic grits and Palaeozoic shallow water clastic facies, including black shales, exhibit low contents of mercury. In contrast, the Lansing Range pluton is intruded into Palaeozoic and possibly Mesozoic deep-water facies rocks where black shales form a major part of the section. The actual stratigraphic thicknesses at Mount Christie and the Lansing Range are unknown. The black shales appear similar in both areas and the major difference must be that the Lansing Range area is more distant from the shelf and into the Selwyn basin than the Mount Christie area. It is of note that this intrusion is more mafic

TABLE III

Mercury contents of sedimentary host rocks

		No. of samples	Geometric mean (ppb Hg)	Range (ppb)
Palaeozoic	shales	16	34	5—510
	coarse clastics	7	18	5— 45
Pre-Cambrian	slates and schists	12	23	1— 84
	grits and quartzites	10	10	1— 92

than the others studied and contains mafic clots which are thought to be partially assimilated host rock fragments. Small amounts of chalcopyrite occur in these clots and as disseminated grains in parts of the pluton. The individual high mercury values in the intrusion are associated with the presence of chalcopyrite which, it is postulated, was derived by the assimilation of black shale host rock picked up from much greater depths and entrained in the rising pluton. The geometric mean mercury contents of the four major host rock types of the plutons are given in Table III. These values are based on limited grab sampling and should only be taken as a general indication of mercury levels. The most notable feature of the data are the high mercury contents associated with the Palaeozoic shales. It is through these shales that the Lansing Range pluton has been intruded. Although the mean mercury content of the Rusty Peak stock is not anomalous, erratic high values are found locally (Fig.2). The host rock is Proterozoic and consists of interbedded grits and shales; the peak gets its name from rusty hornfelsic shales in the contact metamorphic aureole. It is possible that the erratic high mercury levels are due to the assimilation of shaley material such as may have occurred on a larger scale in the Lansing Range. The Two Buttes stock was intruded into similar rocks as was the Rusty Peak stock, and although there are a few higher values (> 15 ppb), contamination by mercury from the host rock does not appear to have been an important process at the Two Buttes stock as mafic clots were not observed. The remaining plutons of the Mayo—McQuesten area are all intruded into these same Proterozoic rocks, and the most noticeable feature is the association of high mercury contents with plutons postulated to be the sources of nearby alluvial gold, scheelite and cassiterite. Lastly, the Tombstone Mountain pluton which intruded quartzites of Cretaceous age, exhibits mercury contents similar to other areas where older quartzites were intruded and no erratic high values are observed.

It is especially difficult to compare mercury data from study to study, as is the case with so much trace element data at very low levels. However, some general comparisons can be made after a review of data available on the mercury contents of granitoids.

Jonasson and Boyle (1972) have proposed a clarke of 62 ppb for granitoids, with a range of 7—200 ppb. Turekian and Wedepohl (1961) gave a value of 80 ppb for the average composition of granitic rocks. Vinogradov (1962) also proposed a similar value of 80 ppb, an upward revision of his earlier figure (1956) of 40 ppb. Saukov (1946) compiled data from 24 granitoids from the Northern Hemisphere and computed a mean of 64 ppb. Both Preuss (1940) and Stock and Cucuel (1934) determined mercury in Goldschmidt's composite of 14 German granites and found 100 and 57 ppb respectively. Several studies of individual plutons or groups of plutons have been made in Europe and Asia. Friedrich (1970) presents data for granitoids near the Hermine fluorspar mine in Bayern, W. Germany. Out of the 61 samples analysed 34 fell below the detection limit of 3 ppb, the present author ascribed a value of half the detection limit to these and computed a geometric mean of 7 ppb for the granitoids. Komov and Komova (1972) present limited data for the mercury content of two plutons in the Pamirs, 11 ppb and 20 ppb. In their discussion they state that averages for granitoids in the Western Pamirs range from 10 to 20 ppb, in the Caucasus range from 20 to 30 ppb and average mercury content in granitoids of the Gornyy Altai is 27 ppb. Aydin'yan et al. (1969) studied the distribution of mercury in the Hissar pluton of the Tien Shan; the arithmetic mean contents of the four intrusive phases range from 25 to 40 ppb and they propose an overall mean, weighted by phase abundance of 30 ppb. Golovnya and Volobuyev (1970) in a study of the Proterozoic granitoids of the Yenisey Ridge computed a weighted average for those rocks of 39 ppb.

There are few published data for mercury in granitoids in North America. Webber and Horska (1970) established means of 40 and 26 ppb respectively for the eastern and western granodiorites at Lake Dufault, Quebec. Dodge (1972) presents an arithmetic mean mercury content for the Mesozoic Sierra Nevada batholith. The data was limited, 29 samples being analysed, and ranged from 10 to 260 ppb with a mean of 150 ppb mercury. This value appears high and may be due to samples close to mineralization being included and to the use of an arithmetic mean for data which is probably log-normally distributed. A set of 14 samples of quartz monzonite from the Fremont Lake intrusion south of Sonora Pass in the Central Sierra Nevada yielded a mean of 28 ppb and a range of 22 to 39 ppb. These samples have been stored as powders since 1966 when they were collected in a study made under the sponsorship of NASA through Northwestern University (Garrett, 1967). Sainsbury (1970) presents analyses of 3 composite samples from the Seward Peninsula, Alaska; granite at 40 ppb and granitic dykes at 40 and 90 ppb, the grand mean is 57 ppb.

It would appear that the Yukon granitoids postulated to be unrelated to gold mineralization analysed in this study are remarkably low in mercury, the only similar ones being those investigated by Friedrich (1970). Comparison between laboratories is difficult due to the absence of reliable international standards for mercury (McNeal et al., 1972); even so the results presented are lower than the clarke by a factor of 4 to 6, and it seems probable that the granitoids northeast of the Tintina Trench form a mercury low province.

However, there is now some evidence that the Clarke for mercury in granitoids may be too high due to the excessive influence of data derived from mercuriferous provinces of the earth (I.R. Jonasson, personal communication).

The most important feature of the data is the correlation of high mean mercury plutons (> 12 ppb) with areas of gold mineralization. Cinnabar has been reported by Boyle (1965) and Bostock (in Little, 1959) as being associated with alluvial gold on Canyon Creek, a west bank tributary of the Mayo river 1 mile above the hydro-electric dam. Boyle (1965) determined mercury by a semiquantitative spectrographic method in a gold nugget from Dublin Gulch draining the Potato Hills intrusion. A content of > 1000 ppm was found, but contamination from mercury used for amalgamating fine gold was suspected. More recent work has shown contamination to be unlikely as nuggets from frozen ground in Dublin Gulch and some loamed from soils over the veins to the south of the creek contain 1100 and 3000 ppm respectively (R.W. Boyle and I.R. Jonasson, personal communication, 1971). Although mercury mineralization as such would seem to be rare in the McQuesten belt there is a significant geochemical relationship of mercury with the plutons postulated to be sources of the gold—scheelite—cassiterite placers.

CONCLUSIONS

In terms of the original problem of finding a more refined geochemical tool for indicating source areas of the alluvial gold in the McQuesten belt, the anomalous geochemical coincidence of tungsten and mercury is considered favourable. It may also be that whilst these elements should be high, molybdenum should be low; however, this latter observation has not been established with certainty. The presence of minor molybdenite on joint faces in the Potato Hills stock (Gleeson, 1965) also tempers this statement. From a purely exploration viewpoint it should be sufficient to analyse samples of the granitoids for mercury and then confirm any high level samples with tungsten analyses and heavy mineral studies in the field. The "porphyry tungsten deposits" of the McQuesten belt may become important resources in the future since they contain, or are associated with, multielement mineralization and their physical location makes them suitable for open-pit mining methods. The proposed exploration method would seem to be an efficient way of finding such large bodies.

Finally, it would appear that although mercury is a useful pathfinder element for the gold—tungsten—tin association of the McQuesten belt, the whole area is a mercury poor province when viewed in comparison with the clarke of the element. This fact demonstrates the relative nature of exploration geochemistry where contrast between background and anomalous areas is more important than absolute values of an element.

ACKNOWLEDGEMENTS

The author is indebted to Drs. R.W. Boyle and I.R. Jonasson for their stimulating discussions and suggestions; and to Drs. S.L. Blusson and I.R. Jonasson for critically reading the manuscript.

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