Canadian Mineralogist
Vol. 14, pp. 58-61 (1976)

Pt, Pd, Au AND Ir CONTENT OF KELLEY LAKE BOTTOM SEDIMENTS

J. H. CROCKET AND Y. TERUTA
Department of Geology, McMaster University, Hamilton, Ontario L8S 4M1

ABSTRACT

Three samples of Kelley Lake (Sudbury district, Ontario) bottom sediment average (in ppm) 1.8 Pt, 0.2 Pd, 0.3 Au, and 0.03 Ir. These concentrations are in excess of the noble-metal concentrations of common rocks by factors of 100 to 1000. It is unlikely that rock weathering in the drainage basin or input of glacial sediment is a significant contributor of noble metals at these levels. Comparison of the average noble-metal content of Sudbury Irruptive sulfide ores with Kelley Lake sediment does not support normal weathering of the ore deposits as a major source of noble metals. Evidence from nickel content versus lake sediment core depth indicates that the Ni levels in Kelley Lake bottom sediment reflect human activity. Such is also probably the most reasonable explanation for the high noble-metal levels. An analysis of a stack particulate sample showed significantly higher noble-metal content for all four metals than Kelley Lake sediment. The possible significance of atmospheric loading as a contributor of noble metals to Kelley Lake bottom sediment is briefly considered.

RÉSUMÉ

Trois échantillons de sédiments du fond du lac Kelley (région de Sudbury, Ontario) ont une moyenne, en ppm, de 1.8 Pt, 0.2 Pd, 0.3 Au et de 0.03 Ir. Ces concentrations dépassent, dans une proportion de 100 à 1000, le taux habituel de concentration en métaux précieux qui prévaut dans des roches ordinaires. Il ne semble pas que ce soit la décomposition rocheuse dans le bassin de drainage ou l'entrée de sédiments glaciaux qui procurent, de façon significative, ces niveaux de métaux précieux. Une comparaison entre le contenu moyen de métaux précieux des minerais de sulfure du Sudbury Irruptive et les sédiments du lac Kelley n'appuie pas l'hypothèse qui veut que la source majeure des métaux précieux soit la décomposition normale des dépôts de minerais. La preuve obtenue en comparant le contenu de nickel avec la profondeur des carottes de sédiments du lac, indique que les niveaux de Ni dans les sédiments du fond du lac Kelley sont la manifestation d'activité humaine. Telle est aussi la plus raisonable explication des niveaux élevés de métaux précieux. Les résultats d'analyse d'un échantillon de particules de cheminée indiquaient un contenu significativement plus élevé en métaux précieux pour tous les quatre métaux que pour les sédiments du lac Kelley. On considère brièvement le fait que le chargement atmosphérique contribue au contenu de métaux précieux dans les sédiments du lac Kelley.

(Traduit par le journal)

INTRODUCTION

This study presents preliminary data on the concentrations of four noble metals, Pt, Pd, Au and Ir, in bottom sediments from Kelley Lake and particulate collected from the International Nickel Company's (INCO) 1250-foot (417m) smoke stack at Copper Cliff, Ontario. Kelley Lake is in Waters and Broder Townships and partly in the city of Sudbury. It is approximately 2.5 miles (4 km) SSW of the 1,250-foot (417 m) stack at Copper Cliff and about 4.5 miles (7.2 km) SW of the center of the city of Sudbury. Noble metals occur as trace constituents of the Ni-Cu sulfide ores of the Sudbury Irruptive. Their concentrations are usually in the ppb range in ore although their distribution is irregular and ppm levels are characteristic of relatively small portions of some deposits. Through floatation concentration and smelting, matte containing ppm levels of noble metals is produced. Although background levels of the noble metals analyzed in this study are known, with the exception of gold, only moderately well, it is highly probable that common rocks and most soils contain noble metals in the range 0.01 to 10 ppb. Noble metals are, therefore, potentially sensitive indicators of human activity involving metallurgical processes which produce a product containing ppm or 100 ppb levels of these metals. The objective of our study was to characterize Kelley Lake bottom sediment with respect to noble-metal content, and to qualitatively evaluate possible sources of these metals.

SAMPLE DESCRIPTION

The Kelley Lake samples are dredged bottom sediments taken from eastern, central, and western stations in the lake. Sampling was conducted by the Ministry of the Environment (Ontario) and the analyses for Cu and Ni reported in Table 1 were performed in Ministry of the Environment Chemical Laboratories. The

TABLE 1. NOBLE-METAL CONTENT (IN PPM) OF KELLEY LAKE BOTTOM SEDIMENTS AND PARTICULATE FROM THE INCO 1250-FOOT STACK

Sample	Pt	Pd	Au	Ir	Cu	Ni	Ni/Cu	Pt/Pd	Pt/Au	Pt/Ir
K.L-1 Kelley Lake, east location	1.0	0.11	0.13	0.014	1,016	1,590	1.6	9.1	7.7	71
K.L-2 Kelley Lake, central location	1.7	0.20	0.27	0.020	9,060	20,000	2.2	8.5	6.3	85
K.L-3 Kelley Lake, west location	2.8	0.23	0.40	0.056	5,525	10,100	1.8	12.2	7.0	50
INCO 1250-foot stack particulate (4 June, 1973)	11	2.5	0.77	0.250				4.4	14.3	44
INCO 1250-foot stack particulate, average of 10 samples (8 June - 13 July, 1973)					32,056	23,530	0.7			
Kelley Lake Average	1.8	0.2	0.3	0.03	5,200	10,560	2	10	7	70
Stack particulate/Kelly Lake average	6	14	3	8	6	2				

sediment samples were provided by Dr. J. R. Kramer, McMaster University.

The stack particulate sample was collected from INCO's 1250-foot (417 m) stack at Copper Cliff, Ontario. The sample was taken at an elevation of 267 feet (89m) in the stack. It is a composite of 88 individual sampling points from which 0.7354 gms were obtained. The sample was taken on June 4th, 1973 by INCO in collaboration with the Air Management Branch, Ministry of the Environment. Details on compositional characterization of similar samples are presented in the Interim Report on the INCO 1250 Foot Stack Emission Study, Air Management Branch, Ministry of the Environment, Ontario (1973). The sample was provided by Dr. J. R. Kramer, McMaster University.

ANALYTICAL PROCEDURE

The noble metals were determined by neutron-activation analysis using a method described by Crocket *et al.* (1968) with certain modifications as described below.

Irradiation — Samples of approximately 100 mg were irradiated in the McMaster Nuclear Research Reactor for a period of three days. After cooling (decaying) for eight days the samples were re-irradiated for 12 hours, cooled a further 12 hours and then processed chemically. In the first irradiation, 2.69-day Au^{198} and 74-day Ir^{192} activities were induced. The second irradiation was necessary to produce 13.5-hr. Pd^{109}.

Method — Relative to the procedure noted above, two main modifications were involved.

1) The steps for Os and Ru were omitted. Because of this, the initial peroxide fusion cake from Step 1 could be dissolved in a mixture of HCl and HNO_3 acids rather than water.

2) Due to the high Pt/Au ratios of these samples it was feasible to determine platinum from the 158 KeV γ of Au^{199}. This photopeak appears in the gold γ-spectrum due to the reaction Pt^{198} (n, γ) $Pt^{199} \xrightarrow[30\text{ mins.}]{\beta^-} Au^{199}$.

Thus, a specific Pt separation was not required and Step 8 was omitted.

Counting — Beta radiation from Pd^{109} was counted on a low background Geiger-Muller counter as described by Crocket *et al.* (1968). Au and Pt were counted from the 158 and 412 KeV photopeaks of Au^{198} and Au^{199} respectively with a gamma spectrometer employing a Ge(Li) detector with a resolution of 3.3 KeV and peak-to-compton efficiency of 11:1. Ir^{192} was counted with the same spectrometer using the 316 KeV γ photopeak.

RESULTS

The noble-metal contents of Kelley Lake sediment and the stack particulate are presented in Table 1. Data for Cu and Ni on the Kelley Lake samples and comparative Cu, Ni data on other stack particulates are also included in Table 1. The stack particulate data for Cu and Ni are the average of 10 samples collected over the period June 8th, 1973 to July 13th, 1973.

Table 2 presents various averaged values for the noble metals, copper and nickel content of rocks, soils and Sudbury nickel-copper ores. Although the noble-metal data are limited and in some cases highly uncertain, they serve to indicate the unusual nature of the noble-metal levels of Kelley Lake bottom sediments.

DISCUSSION

Two aspects of the noble-metal data on Kelley Lake bottom sediments are worthy of note: (1) noble metals in Kelley Lake sediments exceed the averages for igneous rocks by factors of 100 to 1000; (2) the proportions of noble metals in the three samples analyzed are very consistent. For any one set of metal ratios, say Pt/Ir, the maximum difference between the three samples is about 40%. These observations place certain restrictions on the probable sources of noble metals in Kelley Lake sediments.

Relevant comparison with noble-metal concentration levels in other lake sediment is pre-

TABLE 2. ABUNDANCE ESTIMATES FOR NOBLE METALS AND CU, NI IN COMMON ROCKS AND SUDBURY ORES

	Pt (ppb)	Pd (ppb)	Au (ppb)	Ir (ppb)	Cu (ppm)	Ni (ppm)
Acid Rocks (mainly granite, rhyolite, granodiorite)	<0.5(2)[f]	<0.5(2)[f]	2.2(878)[c]	0.03[*,d]	9(6669)[h]	15[g]
Basic Rocks (basalt, gabbro)	4(3)[f]	6(26)[b]	4.1(1276)[c]		75(2764)[h]	130[g]
Shales and Carbonate rocks	--	--	2.3(48)[c]	--	27(5782)[h]	68[g] shale 20[g] carb.
Soils	--	--	--	--	25(855)[h]	40[a]
Sudbury Irruptive Ores	--	1060±2780(55)[e]	90±300(54)[e]	31±56(55)[e]		

*Crustal abundance estimate based on 65 analyses. Figure in parenthesis is the number of samples.
Reference" (a) Andrews-Jones (1968); (b) Crocket (1970); (c) Crocket (1974); (d) Greenland et al. (1974); (e) Keays & Crocket (1970); (f) Rowe & Simon; (g) Turekian & Wedepohl (1961); (h) Wedepohl (1974).

cluded by the complete lack of such data. It is apparent, however, that a very significant increase in noble-metal concentration levels is shown by Kelley Lake sediments relative to ordinary igneous and sedimentary rocks. Although rock-abundance data are incomplete, approximate levels of 5 to 0.05 ppb are suggested by the averages in Table 2 for noble-metal abundance in common igneous and sedimentary rocks. The Kelley Lake averages (Table 1) exceed these levels by 100 to 1000 times. The implication of this comparison is that the weathering of ordinary rocks in the Kelley Lake drainage basin or input of glacial sediment derived from such rocks is unlikely to be a significant contributor to noble-metal concentrations at the levels present in Kelley Lake.

Rather than a general source, localized sources of high noble-metal content are probably much more relevant. The Sudbury-Cobalt Sheet 2188 (Ontario Dept. of Mines Geological Compilation Series) records numerous metalliferous deposits in the district, but only the nickel-copper sulfide deposits of the Sudbury Irruptive are known to contain high levels of noble metals. It is difficult to estimate average noble-metal content of these ores due to the very irregular distribution of the noble metals in the Sudbury ores. The averages presented in Table 2 are computed from the data of Keays & Crocket (1970, Table 2) and represent the Creighton, Frood, Falconbridge and Strathcona deposits, although about one-half the analyses are from Strathcona. The averages presented are arithmetic means. They are higher than the corresponding geometric means or modes due to the influence of two or three samples of very high noble-metal content. The variability of noble metals is reflected in the large standard deviations associated with the averages.

Weathering of Nickel Irruptive sulfide deposits with subsequent collection and precipitation of soluble species is an unlikely mechanism to account for the noble-metal levels in Kelley Lake sediment. The average gold content of these sediments is four times higher than average Irruptive ore and the Ir contents are approximately the same. Thus, unrealistic constraints are placed on Kelley Lake as a catchment basin for weathering products from the Irruptive in respect to Au and Ir. Although the average Pd levels in the Irruptive ores are approximately five times that of Kelley Lake sediment, other evidence argues cogently against a significant influence from weathering of Irruptive sulfide deposits. Thus, Allan (1974) obtained a very high nickel content from a surface dredge sample only (11,050 ppm Ni), whereas much lower Ni values prevailed at sediment depths of 5 to 25 cm (4 samples taken at successively deeper 5-cm intervals in core gave 1746, 99, 59, and 56 ppm Ni). These data imply that the high heavy-metal values are recent in origin. Possible mechanisms noted by Allan (1974) whereby human activity in the form of mining operations might cause high metal levels in lake sediments include introduction of tailings or tailing leachates, mine effluents, or smelter airborne particulate.

We shall consider the final factor, airborne particulate, in the light of the particulate data from Table 1. If we consider the stack particulate as a potential airborne fallout contributor, then noble-metal concentrations in excess of those in Kelley Lake sediment are required to accommodate dilution by normal rock-fragment detritus. As indicated by the comparison of Kelley Lake metal averages and stack particulate, the latter material is 3 to 14 times higher in noble metals than the sediments. Other stack particulates are also considerably higher in both Cu and Ni than the sediment. Thus, stack particulate does represent a concentrated noble-metal source which could sustain dilution by normal sedimentary detritus and still yield the high noble-metal levels observed in Kelley Lake sediment.

A further significant point is that the proportions of metals in the three sediment samples are fairly consistent. The variation in Pt/Pd, Pt/Au and Pt/Ir ratios is 30%, 18% and 41%, respectively, over the three samples in each set. Further, the concentrations of all four noble metals in any one sediment sample are either higher or lower than all four metals in any other sample. Thus, K.L.-3 contains the highest Pt, Pd, Au and Ir values whereas K.L.-1 is characterized by the lowest values for the four metals. These observations tentatively suggest a source of rather uniform noble-metal content as might be expected from smelter matte. It is, however, important to emphasize that no direct analytical verification of the homogeneity of stack particulate is available, our evaluation of stack particulate being based on one sample. Further, Kelley Lake noble-metal ratios differ appreciably from stack particulate metal ratios. Thus, the Pt/Pd and Pt/Ir ratios in stack particulates are approximately one-half those of average Kelley Lake sediment whereas the Pt/Au ratio of stack particulate is approximately double that of the sediments. These differences may be generated by reaction of particulate with lake waters, and may reflect largely the relative solubilities of the mineral components of the particulates in the rather acidic Kelley Lake waters.

Conclusions

The noble-metal levels in Kelley Lake sediments are too high to be explained by weathering and erosion of rocks in the drainage basin or even Nickel Irruptive ores. Human activity is a more plausible agency. Some properties of the noble-metal content of stack particulate support atmospheric loading as a significant contributory factor. Specifically, the noble-metal concentrations of stack particulate are suitably high. The differences in noble-metal ratios of stack particulate and Kelley Lake sediment suggest that such particulate is modified by reaction with Kelley Lake water, or that multiple high-level noble-metal sources are involved in the heavy-metal loading of Kelley Lake sediment, or that stack particulates are rather variable with respect to noble-metal content.

References

Allan, R. J. (1974): Metal contents of lake sediment cores from established mining areas: an interface of exploration and environmental geochemistry. *Geol. Surv. Can. Paper* 74-1 Part B, 43-49.

Andrews-Jones, D. A. (1968): The application of geochemical techniques to mineral exploration. *Colorado School Mines Mineral Ind. Bull.* 11, 31 p.

Crocket, J. H. (1971): Neutron activation analysis for noble metals in geochemistry. Proc. NATO Advanced Study Inst. *Activation Analysis in Geochemistry and Cosmochemistry* (eds. A. O. Brunfelt & E. Steinnes), 339-351. Oslo: Universitetsforlaget.

——— (1974): Gold. *Handbook of Geochemistry* (K. H. Wedepohl, ed.), II/4. Springer-Verlag, Berlin.

———, Keays, R. R. & Hsieh, S. (1968): Determination of some precious metals by neutron activation analysis. *J. Radioanal. Chem.* 1, 487-507.

Greenland, L. P., Gottfried, D. & Tilling, R. I. (1974): Iridium in some calcic and calc-alkalic batholithic rocks of the western United States. *Chem. Geol.* 14, 117-122.

Keays, R. R. & Crocket, J. H. (1970): A study of precious metals in the Sudbury Nickel Irruptive ores. *Econ. Geol.* 65, 438-450.

Rowe, J. J. & Simon, F. O. (1971): Determination of platinum and palladium in geological materials by neutron-activation analysis after fire-assay preconcentration. *Talanta* 18, 121-125.

Turekian, K. K. & Wedepohl, K. H. (1961): Distribution of the elements in some major units of the earth's crust. *Bull. Geol. Soc. Amer.* 72, 175-192.

Wedepohl, K. H. (1974): Copper. *Handbook of Geochemistry* (K. H. Wedepohl, ed.), II/4. Springer-Verlag, Berlin.

Manuscript received July 1975, emended November 1975.