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NICKEL SULPHIDE-ARSENIDE ASSEMBLAGES ASSOCIATED WITH URANIUM MINERALIZATION, ZIMMER LAKE AREA, NORTHERN SASKATCHEWAN

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ABSTRACT

Gersdorffite, millerite, bravoite, pyrite, sphalerite, galena, nickeline, chalcopyrite and hauchecornite accompany pitchblende, hematite and other minerals of U, Cu and Ni in sandstone and conglomerate boulders of the Athabasca Formation. The sulphide and arsenide minerals have been analysed by electron microprobe; they occur as pore fillings and replacements of the sedimentary host. Mineral textures are characterized by simple and complex cores of bravoite and pyrite, rims of millerite and gersdorffite with late uranium minerals. These minerals are interpreted to have precipitated at low temperature in the basal portion of the Athabasca Formation, probably from supergene water.

INTRODUCTION

Texturally and mineralogically complex assemblages of gersdorffite, millerite, bravoite, pyrite, sphalerite, galena, nickeline, chalcopyrite and hauchecornite occur with pitchblende, hematite and various other minerals of U, Cu and Ni in boulders of Athabasca Formation in the Zimmer Lake area, northern Saskatchewan (Fig. 1). The association of nickel, arsenic and uranium is reminiscent of the five-element association of Ni-Co-Bi-U-Ag; classic examples of this type of association are the vein deposits of the Jachymov area, Czechoslovakia (Mrna 1963), Great Bear Lake area (Robinson & Ohmoto 1973) and the Cobalt area (Petruk 1971). In Saskatchewan, major uranium mineralization occurs in the Uranium City, Rabbit Lake, and Cluff Lake areas (Fig. 1, see review by Robertson & Lattanzi 1974); however, only the Nicholson deposits, Uranium City area, are similar to the five-element association (Robinson 1955).

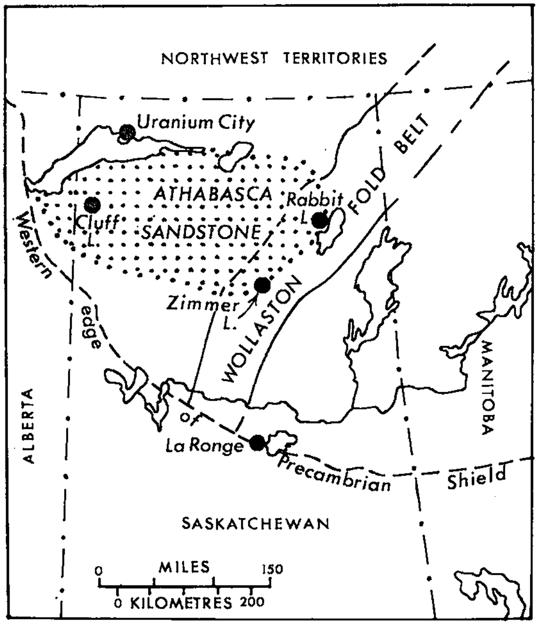

FIG. 1. Location of the Zimmer Lake area, Saskatchewan.

The Zimmer Lake specimens were collected as part of a major study of radioactive occurrences in northern Saskatchewan by INEXCO Mining Co., Ltd. The specimens were documented by petrographic, mineragraphic, *x*-ray diffraction and electron microprobe analyses at Carleton University.

GEOLOGY

The Zimmer Lake area is near the southeasterly limit of the Athabasca Formation. The contact with the underlying Wollaston Fold Belt (Money 1968) is an angular unconformity, but it is not exposed in the Zimmer Lake area because of glacial overburden. The latter is composed dominantly of boulders and sand derived from the Athabasca Formation.

The mineralized boulders are quartz sandstone and quartz-pebble conglomerate; the amount of mineralization appears to be related directly to the former porosity of the sedimentary rocks. The sandstones are poorly sorted, quite pure quartz and compound quartz-grain sandstones; the constituent quartz is fractured and corroded by mineralization in some cases, but most mineralization is restricted to the porous volumes, or to matrix replacement. Quartz-pebble conglomerate has quartz and quartzite pebbles often highly strained and recrystallized in a framework of fine- to medium-grained quartz sandstone. The pebbles are not well-rounded and are only moderately spherical. The quartz is not fractured and has been corroded where in contact with the mineralization.

MINERALOGY AND TEXTURES

The minerals encountered in this study are listed in Table 1 and their textures are illustrated in Figures 2 and 3.

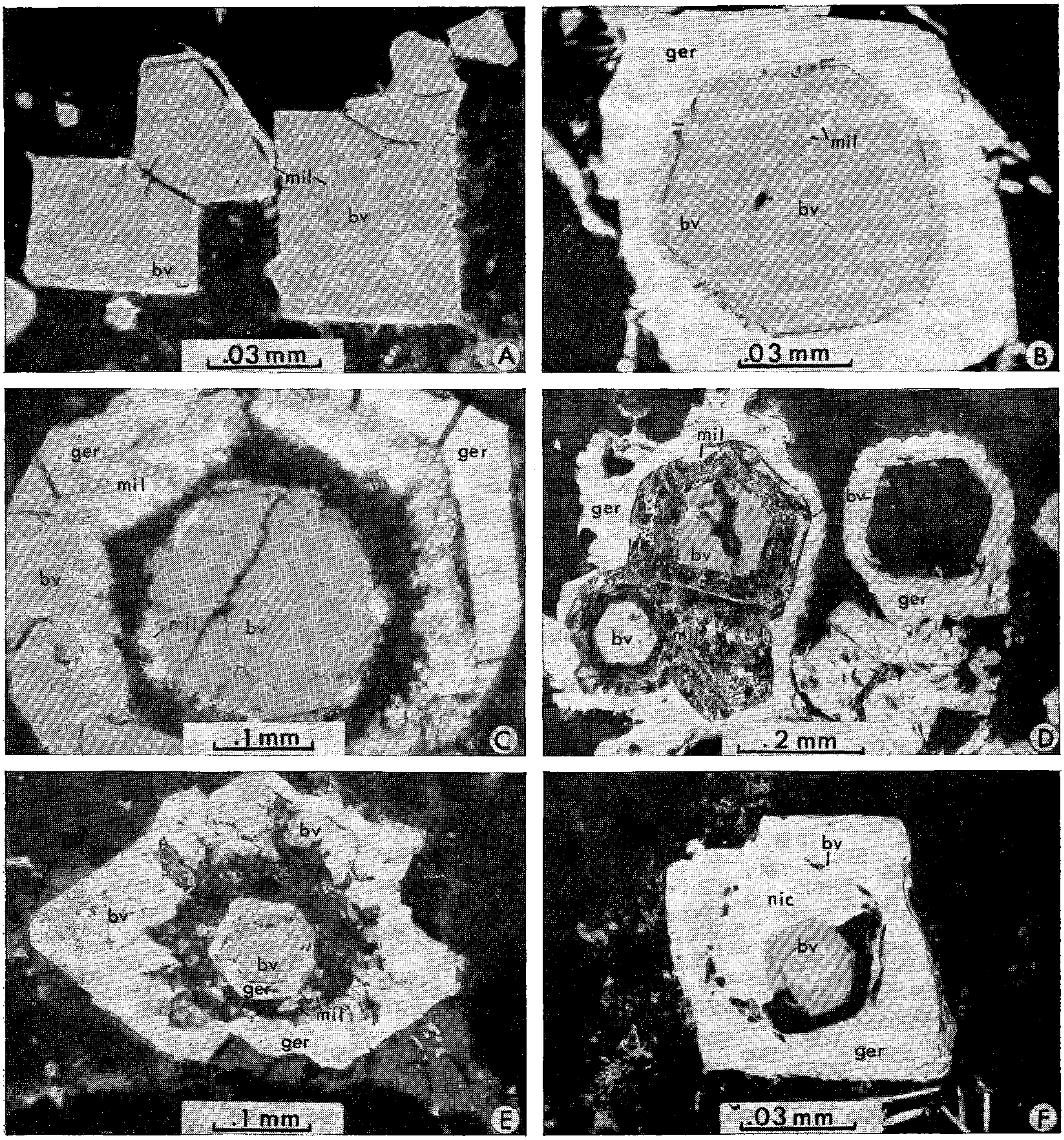

FIG. 2. Photomicrographs of polished sections; bv-bravoite, gal-galena, ger-gersdorffite, mil-millerite, nic-nickeline, sph-sphalerite. a) Bravoite squares (grey) partly rimmed by millerite (white) surrounded by bravoite and thin outer rim of millerite. b) Delicate oscillatory zoning in bravoite with gersdorffite rim. c) Zoned bravoite core with partial millerite rim, black matrix, millerite (mottled), bravoite and gersdorffite. Partly crossed polarizers. d) Pentagonal and hexagonal bravoite cores, surrounded by millerite and black matrix, then gersdorffite. e) Bravoite-gersdorffite core surrounded by black matrix and millerite triangles, all enveloped by bravoite then gersdorfffite. Outer matrix contains triangular millerite and dark grey uranium mineral. f) Zoned bravoite hexagon partly enclosed by nickeline, then bravoite and black matrix and finally gersdorffite. Outer matrix contains acicular millerite.

TABLE 1. MINERALOGY OF THE ZIMMER LAKE SPECIMENS

Sulphide-arsenide minerals		Uranium materials	
gersdorffite	NiAsS	pitchblende	UO_2
millerite	NiS	coffinite	$U(SiO_4)_{1-x}(OH)_{4x}$
galena	PbS	sklodowskite	$Mg(UO_2)_2(SiO_3)_2(OH)_2 \cdot 5H_2O$
bravoite	$(Fe,Ni)S_2$	uranophane	$Ca(UO_2)_2(SiO_3)_2(OH)_2 \cdot 5H_2O$
pyrite	FeS_2	rutherfordine	$(UO_2)(CO_3)$
hauchecornite	$Ni_9Bi_2S_8$	metanovacekite	$Mg(UO_2)_2(AsO_4)_2 \cdot 8H_2O$
chalcopyrite	$CuFeS_2$	Other minerals	
nickeline	NiAs	hematite	Fe_2O_3
sphalerite	ZnS	annabergite	$Ni_3As_2O_8 \cdot 8H_2O$
		brochantite	$Cu_4SO_4(OH)_6$

Sulphide and arsenide minerals

Gersdorffite is the most abundant nickel-bearing mineral and it occurs in the pore space between quartz grains in sandstones and conglomerates or as massive material. Numerous small gersdorffite grains are also integrown with uranium minerals. It occurs in single grains or aggregates with maximum size of the former being about 0.4 mm. There are numerous areas of minute gersdorffite grains that give the matrix a cloudy appearance. Gersdorffite tends to envelope other sulphide and some uranium minerals (Figs. 2,3c).

Millerite is the second most abundant nickel mineral, occurring mainly as extremely thin needles, (Fig. 2e, f), often triangular in section, with a maximum length of about 0.1 mm. These needles occur singly or in sheaf-like radiating bundles (Fig. 3c), either in the matrix or projecting into quartz grains. Larger anhedra and composite aggregates may be associated or intergrown with galena (Fig. 3d) often in laths related to cubic crystallographic directions in galena. Irregular and lath-shaped millerite occurs in both sphalerite and in hauchecornite. Some cores of gersdorffite grains are single grains of millerite or delicate intergrowths with siliceous matrix. In some cores millerite has partly replaced bravoite, leaving only islands of bravoite.

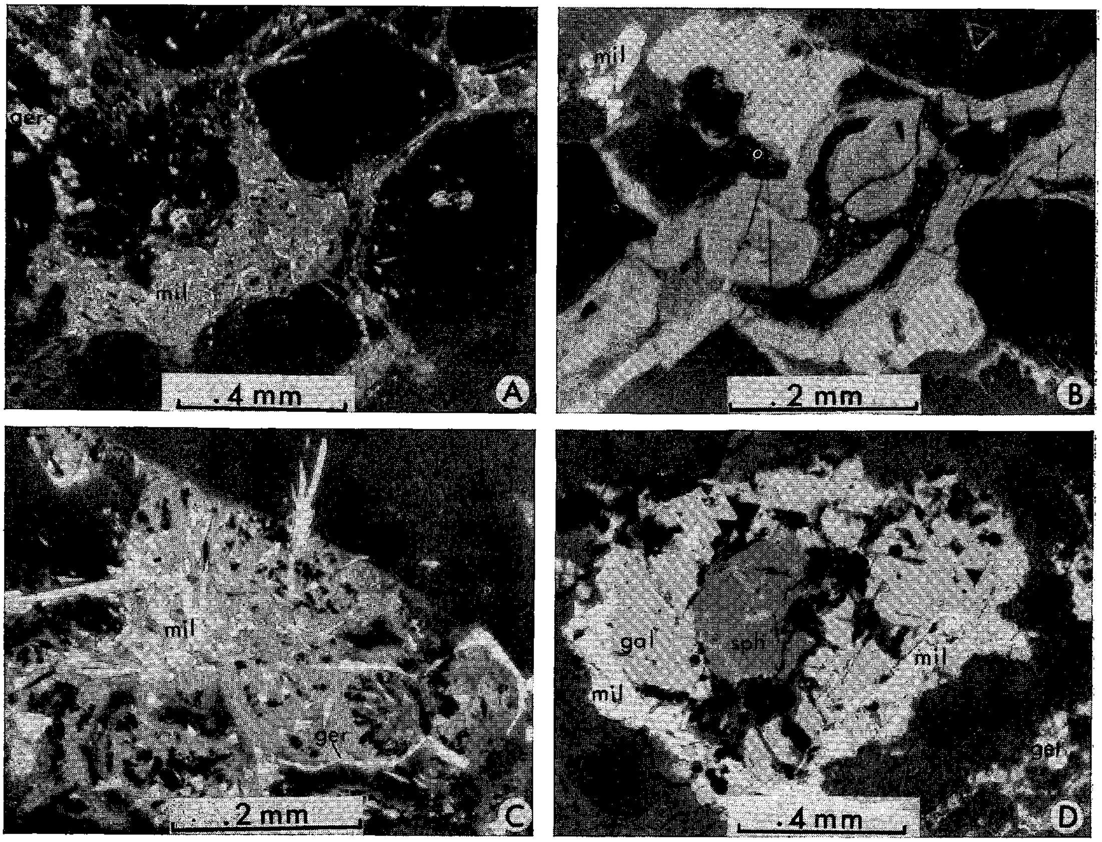

FIG. 3. a) Quartz grains enclosed and invaded by millerite (white needles and triangles) grey uranium minerals and white polygonal gersdorffite. b) Colloform pitchblende and weathering-type uranium minerals with millerite interstitial to quartz grains. c) Uranium minerals (light and dark grey) intergrown with millerite and partly enclosed by gersdorffite. d) Sphalerite-gersdorffite core rimmed by intergrown galena and millerite.

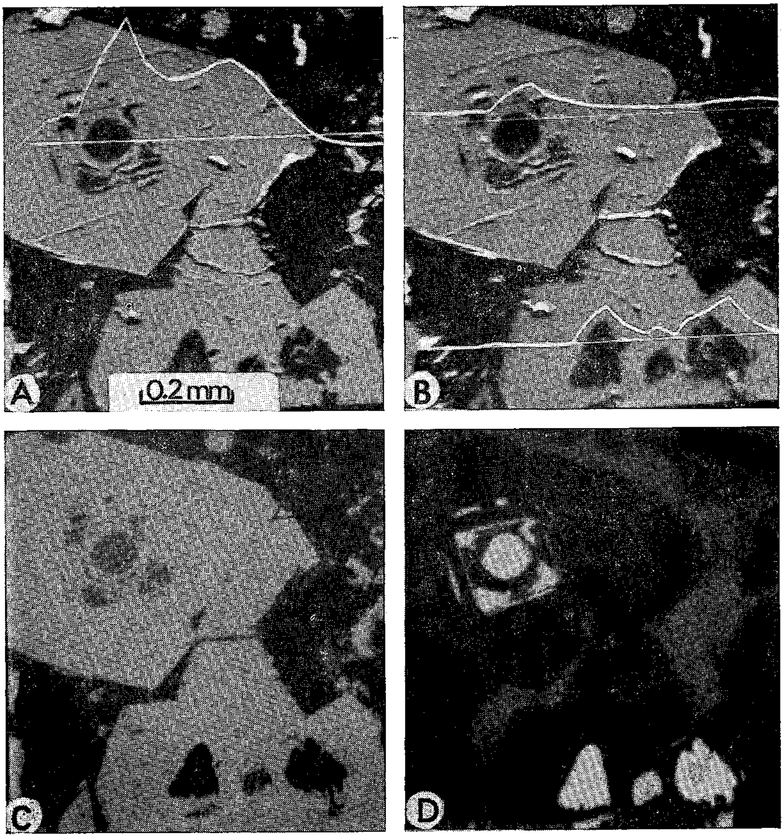

FIG. 4. Electron microprobe scans of gersdorffite with intricate core of bravoite (upper grain) and pyrite cores (bottom grain).
(a) Reflected electron image with trace of Ni distribution along horizontal line. (b) Reflected electron image with trace of Fe distributions along horizontal lines. (c) Ni$K\alpha$ x-ray image. (d) FeKα x-ray image.

Bravoite does not occur as discrete single-phase grains but always as cores or as parts of complex cores of gersdorffite and millerite grains. The cores are most commonly euhedral with square, pentagonal, hexagonal or octagonal outlines (Figs. 2, 4); hexagons are the most common. Bravoite was found in contact only with gersdorffite, millerite, pyrite and nickeline. The most diagnostic feature of bravoite is its delicate color zonation (Figs. 2a, b, c). Much of this cannot be resolved in the photomicrographs. Low-nickel bravoite is similar to pyrite, usually occurring in the central core, whereas higher-nickel varieties are pinkish-brown and occur toward the margins of cores. The geometrical outline of the core zonation often changes during the growth process (Fig. 4). Numerous examples of similarly zoned bravoite are described by Ramdohr (1969).

Galena occurs as parts of large (3.0 mm) composite grains with millerite. These often have sphalerite cores. Sphalerite also occurs in the matrix as large single anhedra.

A nickel-bismuth sulphide occurs as single grains in the matrix or as compound grains with millerite. It is light brownish-yellow, more brownish-pink than millerite and moderately anisotropic with weak reflection pleochroism. On the basis of its optical properties and chemical composition (Table 2) it has been tentatively identified as hauchecornite.

Nickel-bearing pyrite occurs as simple euhedral to anhedral cores and parts of complex cores within gersdorffite (Fig. 4).

Nickeline is rare and occurs with millerite or bravoite (Fig. 2f) as part of complex cores in gersdorffite grains. Chalcopyrite is also rare, occurring with millerite, enclosed in gersdorffite.

Brochantite and annabergite were found as coatings on some specimens.

TABLE 2. ELECTRON MICROPROBE ANALYSES

	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.	12.	13.
Fe	0.33	0.72	1.68	0.43	0.46	30.97	28.73	26.74	43.61	42.73	0.22	4.96	--
Co	0.19	0.19	0.10	0.28	0.20	0.56	0.87	0.54	0.15	0.13	0.66	0.01	--
Ni	63.63	62.14	59.68	35.81	35.79	13.67	16.04	18.65	0.96	2.22	45.85	0.53	0.25
Cu	--	--	0.56	--	--	--	--	0.75	--	0.29	--	--	--
Zn	0.26	--	--	0.13	--	--	--	--	0.28	--	--	59.85	--
Pb	--	0.42	--	--	--	--	0.13	--	--	--	0.01	--	87.80
As	0.22	0.89	1.34	45.56	46.11	1.20	1.62	0.67	0.63	1.58	0.72	0.02	--
S	35.39	35.31	33.74	18.97	19.17	51.28	52.34	51.49	54.07	51.03	22.46	33.33	12.37
	100.02	99.67	97.10	101.18	101.73	97.68	99.73	98.84	99.70	97.98	97.68	98.71	100.43

1. Millerite A-33-1; average of 4 grains except Zn (1 grain)
2. Millerite A-33-B1; 5 grains except Pb (2 grains)
3. Millerite A-67-1; one grain
4. Gersdorffite A-33-1; 5 grains
5. Gersdorffite A-33-B-1; 2 grains, Pb not detected
6. Bravoite A-33-1; 2 grains, Zn not detected
7. Bravoite A-33B1; 3 grains
8. Bravoite A-67-1; 3 grains
9. Pyrite A-33-1; 2 grains
10. Pyrite A-67-1; 2 grains
11. Hauchecornite(?) A-33-B-1; 2 grains. Total includes 27.76% Bi.
12. Sphalerite A-33-B-1; 1 grain
13. Galena A-33-B-1; 1 grain, Co, Fe and As not detected.

Uranium minerals

Pitchblende or uraninite and coffinite are interpreted to be primary minerals in the sulphide-arsenide assemblages. They occur as fillings of pore space and as irregular coatings on quartz. Large massive grains are usually highly fractured, altered, and rimmed by "secondary" uranium minerals.

Polished sections of most large pitchblende grains have a mottled appearance: pitchblende occurs in various shades of grey and contains disseminated white grains, some of which have been identified as gersdorffite, but others may be galena formed from radiogenic lead released on alteration of primary pitchblende. The size of these grains is generally too small for identification. Botryoidal, reniform and colloform textures (Fig. 3b) are not common.

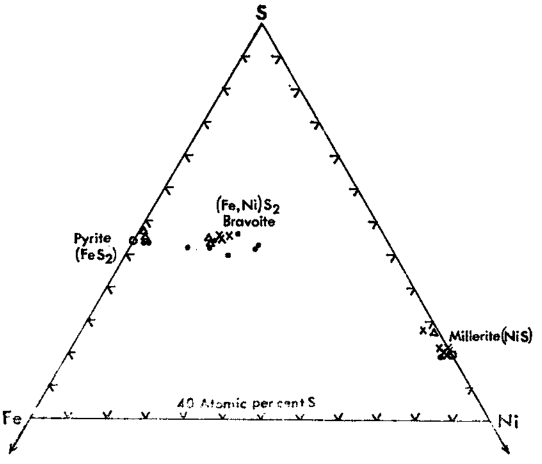

FIG. 5. Projection of mineral analyses onto the composition join Fe-Ni-S. Four analyses from A-33 coincident with the millerite composition are omitted for clarity. O-theoretical composition, X-A33B, △-A33, ●-A67.

Uranium minerals formed by weathering occur as replacements of pitchblende, as fillings in small fractures in quartz, as coatings on quartz, and as pore fillings. They have not been studied in detail, but *x*-ray diffraction has revealed sklodowskite, uranophane, rutherfordine and metanovacekite. Sklodowskite is fairly common as pistaccio-green crystals and masses coating some specimens.

Hematite is locally abundant, especially with the above uranium minerals, but does not occur consistently with the sulphide-arsenide assemblages.

MINERAL CHEMISTRY

Minerals from five specimens were quantitatively analyzed using a Cambridge MK 5 electron microprobe. Standards used were the synthetic compounds NiS for Ni, $CoAs_2$ for Co and As, PbS for Pb, CuS for Cu; natural pyrite for Fe and S, sphalerite for Zn; native metals for U, Th and Bi. The *x*-ray data were computer-corrected using the program EMPADR 7 (Rucklidge & Gasparrini 1969). The sulphide-arsenide data are presented in Table 2 and illustrated in Figures 4 and 5. Zoning of bravoite is evident in Figure 2 and the bravoite Ni and Fe analyses are thus averages of highly variable values (Fig. 5). For example, ranges were 24.66-31.38 weight % Fe, 13.24 - 23.71 wt. % Ni and 0.21 - 1.19 wt. % Co. The high and low cobalt data were from one specimen. The range of values is probably much greater than these because analyses were made only where the thicknesses of zones were in excess of about 10 μm to permit return to the same spot when performing analyses for other batches of two elements. Pyrite has rather uniform Co but a range of 0.92 - 2.39 wt. % Ni.

Pitchblende analyses were highly variable; in specimen A-60 the approximate range of PbO was 1.7 - 14.6 wt. %. In specimens A-50 the range was 9.1 - 11.6 (average 10.9) wt. % PbO from six different grains. No Th was detected in the pitchblende. Complete analyses were not attempted on the uranium minerals that formed by weathering.

DISCUSSION AND CONCLUSIONS

The mineral assemblages in the Zimmer Lake specimens are not conducive to extensive phase equilibrium interpretation because there is no assurance that any mineral was in equilibrium with the others. This is suggested by the banded and irregular nature of pitchblende, differing reflectivity and chemical composition, the oscillatory zoning of bravoite and multiple mineral zoning. The assemblage gersdorffite - millerite - nickeline, however, does suggest low-temperature deposition especially because gersdorffite is stoichiometric (Ni:As:S = 1:1:1) and has no exsolution textures (Yund 1962).

Bravoite cores in complex assemblages further suggest that deposition occurred at very low temperatures. Preliminary data on bravoite stability (Clark & Kullerud 1963) suggested an upper temperature limit of 137 ± 6°C for bravoite. However, Shimazaki (1971) has shown that there is no confirmation of thermochemically stable bravoite with fixed composition below 137°C, and he concluded that all bravoite is probably metastable under normal geological conditions.

Thus in Zimmer Lake material the coexistence of pyrite and millerite with bravoite may not be significant as far as stable equilibrium is concerned. The occurrence of these assemblages (Fig. 5) rather than assemblages with violarite is attributed by Misra & Fleet (1974) to metastability of pyrite + millerite (and bravoite) at low temperature.

The low thorium content in pitchblende from the Zimmer Lake specimens is similar to that of uranium-bearing minerals from veins and replacements which are interpreted to be of low-temperature origin. This is generally believed to be the result of separation of uranium as an oxidized complex from thorium which is not readily oxidized during solution of uranium-thorium minerals. This suggests that the transportation of the metals and nonmetals to the Zimmer Lake and other similar deposits was in a low-temperature oxidized aqueous phase probably of supergene origin. Solutions may have leached material from gneisses of the Wollaston fold belt, basal units of the Athabasca Formation, or from regolith formed at their unconformity. Deposition of minerals could have been accomplished by any of the usual variety of proposed mechanisms for breaking down complexes in solution, but probably reduction by carbonaceous or pre-existing sulphide material may have been important. However, there is no evidence that sulphides forming the cores of the mineral assemblages in the Zimmer Lake specimens (usually bravoite or pyrite) were foreign to the uranium-bearing solutions; the common association of Ni-Fe-As-S minerals with uranium mineralization suggests that they are compatible elements.

A supergene-type of model for deposition of uranium minerals has been proposed by Knipping (1974) for the origin of the nearby Rabbit Lake deposit. The differences in mineralogy of the low-temperature vein and replacement-type deposits such as Rabbit Lake and Cluff Lake in Saskatchewan (see review by Roberston & Lattanzi 1974) may thus reflect differences in precipitation mechanisms and nature of the ore solution but equally likely it may be a function of the composition of the leached rocks.

ACKNOWLEDGEMENTS

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