

NATIVE ARSENIC IN NEWFOUNDLAND

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ABSTRACT

Native arsenic has been found in the Whalesback and Little Bay copper mines on the Springdale Peninsula, Newfoundland. The largest mass, 3 feet long and 2 inches thick, fills a fracture in an altered basic dyke on the 1500 level of the Little Bay mine. The host-rocks are Ordovician basic volcanics cut by numerous dykes.

The main arsenic mass is crudely layered, with a rough colloform texture. One specimen contains small spherical inclusions of ramellbergite. Loellingite occurs locally as thin rims and as impregnations of brecciated wall-rock. The arsenic contains less than 0.3 per cent Sb; $a = 3.758 \pm 0.001 \text{ \AA}$, $c = 10.544 \pm 0.003 \text{ \AA}$; $D(\text{meas.}) = 5.741 \pm 0.023$, $D(\text{calc.}) = 5.786$.

The following origin of the native arsenic is proposed: A basic dyke intruded a minor concentration of arsenopyrite. (Pyrite-arsenopyrite veins are known in the vicinity). When heated to about 600° C, arsenopyrite broke down giving off an As-rich vapour which was free to migrate (as gas, in solution or in colloidal suspension) and deposit metallic arsenic in favourably located fractures.

INTRODUCTION

Small grains of native arsenic in thin calcite veins have been found occasionally during recent exploration and development work in the Whalesback and Little Bay mines on Springdale Peninsula, Newfoundland. In the spring of 1966, a mass of native arsenic weighing over ten pounds was discovered on the 1500 level of the Little Bay mine.

The discovery of this relatively substantial quantity of a mineral not previously recognized in Newfoundland, together with its somewhat unusual setting, warrant a detailed description of the occurrences.

DESCRIPTION

The Whalesback mine (British Newfoundland Expl.) and the Little Bay mine (Atlantic Coast Copper Corp.) are producing copper mines situated about 4 miles apart on the Springdale Peninsula, Notre Dame Bay, Newfoundland. (49°35' N, 56°00' W). The ore consists essentially of stringers and disseminated grains of pyrite and chalcopyrite with minor pyrrhotite and sphalerite, forming steeply dipping lenticular bodies in altered basic volcanics of Ordovician age.

Whalesback mine

Only one specimen of native arsenic is known from the Whalesback mine. The mineral was found (by Mr. J. Drover) in a drill-hole located on

the 975 mine level, in the footwall of the ore zone. The arsenic-bearing veinlet was intersected about 140 feet southeast of the main shaft. The wall-rock is a greenish grey altered rock of basaltic composition.

The arsenic forms a granular mass about 10 mm thick in a thin (15 mm) veinlet of light greenish calcite. The boundaries of the arsenic, as seen in the drill-core, are sharply angular, indicating that the surface of the aggregate consists of idiomorphic crystals. The mineral is deeply tarnished. On a broken surface, it shows good platy cleavage; changes in orientation of the cleavage planes indicate that the arsenic mass consists of interlocking grains about 1–2 mm in diameter.

The arsenic is bordered by a hair-thin (0.05 mm) discontinuous rim of a silvery white mineral identified by *x*-rays as loellingite, FeAs_2 . The loellingite band consists of idiomorphic lath-like and diamond-shaped crystals; it lies very close to, but not always in direct contact with, the arsenic. The thin calcite band between the arsenic and the wall-rock contains small (0.01–0.03 mm) elongated crystals of pyrrhotite partly altered to marcasite; a few of these, close to the arsenic, are intergrown with euhedral crystals of loellingite. Several equally small crystals and grains of loellingite are scattered along the contact of the calcite veinlet and the wall-rock.

Little Bay mine, 1150 level

The first specimen of arsenic in the Little Bay mine was found in an exploratory drill-hole which intersected a thin calcite veinlet at the elevation of the present 1150 mine level. The vein contains a brecciated mass of arsenic about 10 mm wide, broken into a number of small angular fragments cemented by white calcite. The wall-rock, a fine-grained greenish grey rock rich in leucoxene, contains coarse granular pyrite adjacent to the carbonate vein.

When the approximate location of the arsenic veinlet was reached by underground workings, Mr. G. Johnson, mine geologist, found there a thin calcite vein containing small and widely scattered grains of arsenic. The vein, 10–25 mm thick and nearly vertical, cuts an altered basic dyke. It consists of coarse-grained light greenish grey calcite and contains small (1–4 mm) angular fragments of a highly altered greenish wall-rock. The arsenic appears as black, angular and pitted grains from 0.5 to 5.0 mm in diameter, probably widely separated fragments of a larger mass. Some of the wall-rock fragments contain very small crystals of loellingite.

Little Bay mine, 1500 level

The largest mass of native arsenic in the area was discovered by Mr. Y. J. Lepinis during development work on the 1500 level. The arsenic

forms a band about 3 feet long and 1–2 inches wide, slightly concave upward, localized in a relatively narrow shear-zone dipping flatly to the north. The shear intersects at this point a steeply dipping, dark, fine-grained dyke of olivine diabase now strongly altered. The dyke is about 6 feet wide; both walls consist of a dark schistose chloritic rock grading into altered basic volcanics. According to Y. J. Lepinis (personal communication), the relatively thin and discontinuous arsenic-bearing fracture is a small part of a major fault-zone which cuts and to some extent displaces the ore body on the 1500 level.

The arsenic band filling part of the fracture has a crudely layered appearance; locally it forms rough colloform crusts with a typical fibrous internal structure. The mineral, deeply tarnished to a black colour, is strongly pitted and corroded; it contains numerous elongated cavities (solution pits?) of irregular shape, parallel to or cross-cutting the banding. The arsenic vein is bordered on both sides by a whitish clayey gouge; the dyke rock immediately above the vein is strongly fractured and altered to a soft, light greenish mass crumbling easily under a pick. The clayey gouge contains several broken fragments of arsenic, showing that movement on the fracture continued after the deposition of the mineral. Examination of a carefully washed, pitted surface of the arsenic shows that the mineral is in places overgrown by small (0.5 mm or less) euhedral crystals of quartz. Many of the deep surface pits contain aggregates of very small octahedral crystals of arsenolite, As_2O_3 . The gouge reacts strongly with dilute HCl, indicating the presence of abundant calcite.

One of the arsenic specimens contains numerous very small inclusions of rammelsbergite, NiAs_2 . The rammelsbergite forms small rounded grains, many almost perfectly circular in section (Fig. 1), others partly coalescing, arranged in slightly diverging lines which resemble streaks of spherical bubbles. Most of the grains are 0.02–0.03 mm in diameter, some are much smaller; the largest, a composite equidimensional grain, is about 0.3 mm across.

A narrow zone located about 30 feet east of the arsenic vein in the south wall of the drift is impregnated with numerous very small crystals of loellingite, FeAs_2 . The crystals are subhedral to euhedral, about 0.01 mm long and diamond-shaped in cross-section; some show well-developed star-shaped trillings. The rock consists of a very fine-grained aggregate of quartz, albite, minor very pale chlorite and carbonate; it is strongly brecciated and cemented with calcite. A thin-section shows that the loellingite is concentrated predominantly, though not entirely, in the calcite filling between rock fragments and in calcite grains partly replacing the rock.

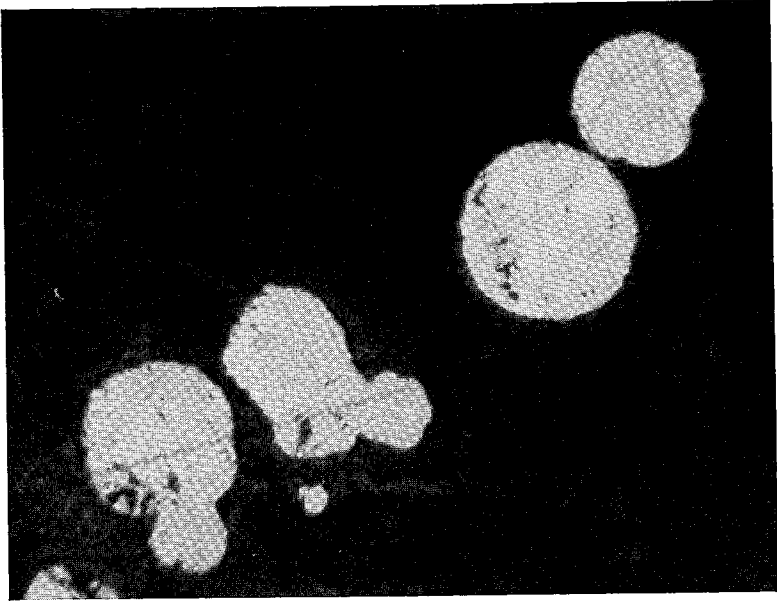


FIG. 1. Globules of rammelsbergite (white) in native arsenic (dark grey, tarnished). Main arsenic vein, 1500 level, Little Bay mine. The largest globule is about 0.03 mm in diameter.

Chemical and physical properties

The original specimen of native arsenic from the Whalesback mine was analyzed by spectrographic and x -ray fluorescence methods by Dr. G. R. Webber of McGill University, who reported the following results:

0.2–0.3 per cent :Sb

Trace: Mn, Cu, Ag, (possibly) V

Looked for but not found: Ba, Be, Cd, Co, Cr, Ca, Ge, Hg, Mo,
Ni, P, Pb, Nb, Sn, Sr, Ta, Th, Ti.

Using x -ray fluorescence the writer found traces of Sb, Cu, Fe and Ni in arsenic from the 1500 level of the Little Bay mine. The specimen containing rammelsbergite showed in addition a trace of Co. On comparing the arsenic to several artificial mixtures of arsenic and antimony in known proportions, it was found that the Little Bay arsenic contained less than 0.3 per cent Sb.

The arsenic from both mines was then examined by x -ray diffractometer. Two smear-mounts were made from each of three specimens, two

from Little Bay and one from Whalesback. Arsenic lines (003) and (110) were measured; As (105) was found to interfere to some extent with the otherwise preferable As (006). Lines (111) and (220) of NaCl ($a = 5.64028 \text{ \AA}$) were used as internal standard. All peaks were located by the counting method, traversing the peaks in steps of 0.02° and refining the area of the peak by a repeated traverse in steps of 0.01° . Comparison of the arsenic peaks relative to the NaCl lines both in the duplicates from the same hand specimen and in the three different specimens shows that the position of the As lines varies on the average by less than 0.01° , no variation being greater than 0.02° . This confirms that the arsenic from the two mines is virtually identical in composition.

The calculated cell edges (for a hexagonal cell) are close to those given by Skinner (1965) for pure arsenic:

	$a \text{ \AA}$	$c \text{ \AA}$
This study	3.758 ± 0.001	10.544 ± 0.003
Skinner (1965)	3.760 ± 0.001	10.555 ± 0.003

The density of the Little Bay arsenic was measured on a Berman balance using 16 chips from 3 different specimens, and calculated from the above cell dimensions (assuming 100 per cent As) with the following results:

$$D (\text{Meas.}) = 5.741 \pm 0.023; D (\text{Calc.}) = 5.786$$

ORIGIN OF THE NATIVE ARSENIC

Arsenic is known to be a common though minor constituent of volcanic gases and sublimates (*e.g.* Onishi & Sandell, 1955), and thus may have originated in the volcanic rocks themselves, or it may have been added to the country rocks during the intrusion of the numerous dykes, ranging from basic to acid in composition, that are common on the Springdale Peninsula. (Although no acid intrusive rocks are known in the two mines, it should be noted that a medium-grained granodiorite was intersected in a few deep drill-holes 1200–1500 feet below the surface in the vicinity of the Whalesback mine.) However, the occurrence of a relatively substantial quantity of arsenic in its native state within 100 feet of a massive concentration of iron and sulphur—the pyrite-chalcopyrite orebody—calls for an explanation.

The native arsenic was clearly deposited later than the ore, which is itself a complex product of folding, shearing and simultaneous or subsequent mobilization of several elements. It is therefore unlikely that any arsenic originally present in the lavas and repeatedly forced to migrate

could have attained—or remained in—its elemental state throughout the complex tectonic history of the host rocks. A similar objection may be raised against a genetic connection of the native arsenic with acid intrusive rocks. Although arsenic mineralization is commonly associated with granitic and intermediate intrusives, the element, present in minor quantities, normally has ample opportunity to combine with iron and sulphur to form complex deposits of arsenopyrite associated with pyrite and other minerals. This may well be the origin of the pyrite-arsenopyrite veins in Little Bay Head which appear related to rhyolite porphyry dykes (MacLean, 1947), and possibly those of the Hearn prospect (only one-half mile from the mine) where acid rocks were not seen on the surface.

Thus it appears more probable that the native arsenic was produced at a relatively late stage by some secondary process from a preexisting arsenic-bearing mineral, possibly arsenopyrite.

According to Clark (1960), arsenopyrite melts incongruously at 702° C to pyrrhotite, loellingite and an arsenic-rich liquid. The assemblage arsenopyrite-pyrite becomes unstable at 491° C, giving pyrrhotite and liquid or pyrrhotite and an As-rich vapour. Strathdee & Pidgeon (1961) measured the vapour pressure and determined the composition of the vapour phase during a distillation of arsenopyrite and an arsenopyrite-pyrite assemblage. They report that at temperatures between 540° and about 650° C, "the dissociation pressure of arsenic over arsenopyrite is much higher than that of sulphur over pyrite. Thus during distillation of the ore arsenic is predominant in the vapour phase." The vapour condenses to metallic arsenic and an arsenic sulphide, leaving a residue consisting essentially of pyrrhotite.

Thus an As-rich vapour can be produced by heating arsenopyrite to about 600° C. In nature, such conditions could be produced by a basic dyke intruding an arsenopyrite-bearing mineral deposit. The arsenic would then be free to move through fractures in the rock, partly as gas, partly in solution, in part perhaps in colloidal suspension, to be deposited in favourable areas of lower temperature. Although the exact source of the arsenic at Little Bay cannot be identified with certainty, all the postulated materials and agents are present in the vicinity and the theory appears plausible.

The presence of rammelsbergite in one of the specimens may serve as additional evidence. According to Yund (1961), rammelsbergite inverts to pararammelsbergite at 598° C. As the inversion temperature appears to be greatly affected by the presence of other elements (Co, S etc.), it cannot be used as a reliable geothermometer; however, the presence of the high-temperature polymorph of NiAs_2 indicates that the minerals

were deposited at an elevated temperature, perhaps in the order of 400–500° C (Yund, 1961, p. 1294).

The external form and the internal structure of the arsenic veins clearly indicate that the mineral was deposited in a colloidal state. This is not unusual for native arsenic and has been described from several localities. For example Stevenson (1943) described an occurrence of colloform arsenic in British Columbia, suggesting that the mineral was transported in solution and that it flocculated in the presence of CaCO_3 . This is an interesting idea in view of the abundant calcite in the arsenic veins of Newfoundland.

The almost perfectly spherical shape of the nickel arsenide globules contained in the arsenic suggests that the nickel was originally present in solution and that it eventually formed an emulsion in the arsenic gel. The well-developed streaky alignment of the rammelsbergite globules may be due to some movement of the arsenic gel before consolidation and crystallization. The small amount of nickel involved may be derived either from the postulated basic dyke which had produced the original arsenic vapour or from the diabase dyke in which the arsenic is deposited; the nickel content of the volcanic wall-rocks seems to be too low to contribute any significant amounts by leaching. (Unpublished reports, British Newfoundland Exploration.)

While the small grains of arsenic on the 1150 level of the Little Bay mine are probably derived from the same source as the main arsenic vein 400 feet below, the occurrence of native arsenic at the Whalesback mine, four miles distant, indicates that the same sequence of events may have occurred at several localities in the area and that other pockets of arsenic may be present.

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