# The Sterling Mine, Antwerp, New York A New Look at an Old Locality

S. C. Chamberlain

Institute for Sensory Research, Syracuse University, Syracuse, NY 13210

### INTRODUCTION

The Sterling mine was the first American locality for the nickel sulfide, millerite. In the last hundred years it has produced many fine specimens of that mineral, including some that many regard to the the finest examples of the species ever found. In the past several years George Robinson at the National Museums of Canada and I have reexamined the geology, mineralogy, and origin of this landmark locality (Robinson and Chamberlain, 1984). Our interest was stimulated by our finding that much of the crystallized hematite in the ore had been reduced to magnetite and that some of the millerite had altered to the rather rare nickel silicate, pecoraite. The following pages summarize the history, geology, mineralogy, and paragenesis of this locality.

#### LOCATION

The Sterling Mine is in Jefferson County, New York, along US Route 11 between Watertown and Gouverneur (Fig. 1). The water-filled open pit (Fig. 2) and surrounding dumps may be reached by foot via a farm lane which runs east from US Route 11 at a point 3.75 miles north of the intersections of Routes 11 and 26 in the village of Antwerp. The mine appears on contemporary topographic maps of the Antwerp quadrangle as a small pond surrounded by low hills between Route 11 and Hawkins Creek. The property is owned by Mr. Raymond Villeneuve whose farm is 0.6 miles south of the entry lane on the east side of Route 11. Permission to collect must be secured before visiting the mine.

The Sterling Mine lies within a band of hematite deposits (Fig. 3) known as the Antwerp-Keene belt. According to Smock (1889) the occurrences from southwest to northeast were the Colburn, Ward, Dickson, White, and Old Sterling Mines owned by the Jefferson Iron Company; The Keene, Caledonia, and Kearney Mines owned by the Rossie Iron Works; and the Clark and Pike Mines owned by the Gouverneur Iron Ore Company. The Sterling and Caledonia mines were the largest of the group, were the only ones studied in any detail by the geologists of the time, and were the only producers of any quantity of mineral specimens.



Figure 1. Location of the Sterling Mine.



Figure 2. Looking east at the northern end of the Sterling Mine open pit in September, 1983. The two islands are topped by remnants of the cap of Potsdam sandstone. Photo by S. Chamberlain.

#### HISTORY

The Caledonia Mine, located about a mile southeast of Somerville in St. Lawrence County, was the first working mine in the district (Hough, 1853). Operations began in 1812, and by 1815 the Caledonia was furnishing ore to the Parish Iron Works in Rossie (Durant and Pierce, 1878). Between 1825 and 1835 the other deposits of the belt were discovered. One such deposit lay on an island surrounded by upland swamp on the farm of Hopestill Foster. In 1836, David Parish sold this property to James Sterling for \$200, marking the beginning of the Sterling Mine (Hough, 1854; Haddock, 1895).

James Sterling, the "Iron King of Northern New York," formed the Sterling Iron Company in 1837. Ore was first hauled to his furnace at Sterlingville and later to Sterlingburgh. Pig iron was wrought using a charcoal, cold-air blast at the rate of about 12 tons per week. Horses were used to pump the water and raise the ore from the Sterling Mine pit. Later a hot-air blast was introduced and the Philadelphia Iron Company was organized. The Sterling Mine was operated during the late 1850's by Samuel G. Sterling (James' brother) and from 1859 onward by James' son A. P. Sterling. In 1869 the mine was sold to the Jefferson Iron Company of Antwerp (Emerson, 1898). Smock (1889, page 45) gives the following account of the operations under the Jefferson Iron Company:

The open pit at the north-east is 115 feet deep, and approximately, 500 by 175 feet. The underground workings are south and south-west of it, and the ore has been followed for a distance of 900 feet, and to a depth of 185 feet. This deposit lies between the gneissic rocks on the south-east, 400 feet distant, and the sandstone (Potsdam) on the west side of the mine, but no walls have as yet been reached in the mine. A serpentine rock occurs with the ore, apparently without any order in its relations to it. The ore varies from a specular ore of metallic lustre and steel-gray shade of color to amorphous, compact masses of deep red. The crushed powder answers well as a point, and stains deeply all with which it comes in contact. The ore stands up well, and, by leaving pillars, with arched roof in the galleries and drifts, no timbering is necessary. There is comparatively little water in the mine. The serpentine is not so firm as the ore, and is full of slickensided surfaces. Small mine cars are used on the narrow gauge tramways in the mine drifts. A skip track runs to the bottom of the open pit. A branch railroad three miles long connects this mine and the Dickson with the main line of the R.W. & O. R.R., near Antwerp...

By the 1880's the local furnaces had been largely abandoned and most of the ore was shipped to Pennsylvania for smelting. Competition from the Mesabi Range in Minnesota and a depressed economy gradually forced the closure of the mines in the belt. The Sterling Mine was last worked between 1904 and 1911 and was the last operating mine in the district (Newland, 1921). Buddington (1934) estimates the production of the Antwerp-Keene belt as 2.5 million tons, of which the Sterling Mine and adjacent Dickson Mine accounted for more than 750,000 tons (Smock, 1889).

The Rossie Iron Ore Company launched a brief, small-scale venture for making iron oxide pigments in 1942. In 1948, the Republic Steel Corporation conducted a diamond drilling program on the Caledonia and Sterling Mine properties, but concluded that further development was unwarranted.

#### GEOLOGY

The Sterling Mine ore body is bounded by Grenville marble to the northwest and gneissic granite to the southeast. It is locally overlain unconformably by an outlier of the Potsdam sandstone (Fig. 3). The rock immediately adjacent to the ore is heavily chloritized and slickensided and forms an irregular and intimate contact with it (Emmons, 1842; Hough, 1853; Smyth, 1894a,b). The ore itself contains many open cavities with marked evidence of stalactitic and botryoidal deposition of iron oxyhydroxides with subsequent crystallization or recrystallization of quartz and iron oxides, carbonates, and silicates.

Figure 4 shows a schematic longitudinal section through the ore body. The ore lies within a distinct unit of granitic gneiss locally rich in phlogopite, pyrite, and pyrrhotite. The unit is bounded on the hanging wall by crystalline marble and on the foot wall, by a garnetiferous, biotitic, granitic gneiss.

Although Emmons (1842) originally described the dark green rock associated with the ore as serpentine, and Shepard (1851) proposed it to be a new mineral species, dysyntribite, the best modern evidence suggests that it is a chloritized granite gneiss. Smyth (1894a,b) reported that in the operating mine, it was possible to observe areas in the footwall where the green rock graded gradually and completely into unaltered granite gneiss.



Figure 3. Geological map of the Antwerp-Keene belt of hematite deposits showing the location of the Sterling and other mines operated to exploit specular hematite (adapted from Buddington, 1934 and Newland, 1921).



Schematic cross-section through the pit at the Sterling Mine based on drill core data from the Republic Steel exploration of 1948. The section represents the view looking northeast along the strike. Figure 4.

161

Buddington (1934) studied Smyth's thin sections and concluded that "the evidence all confirms Smyth's conclusions as to the origin of the chlorite and sericitic schists through alteration and replacement of gneiss or granite." Reexamination of the core logs and geologists' reports by W. M. Sirola and E. F. Fitzhugh, Jr. from the Republic Steel's diamond drilling program revealed clear evidence of complete and gradual chloritization of granite (Robinson and Chamberlain, 1984). Thus the ore body lies in a chloritized granite gneiss at its contact with the Grenville marble. The origin of the deposit will be discussed in greater detail under paragenesis below.

#### MINERALOGY

The majority of the minerals found at the Sterling Mine contain iron. Those of greatest interest to collectors occur in cavities in the hematite/quartz ore. These cavities range in size from a few millimeters to over 25 cm across. Hough (1853, page 683) gives the following description:

These red ores impart their color to whatever comes in contact with them, giving a characteristic tinge to every person and object about the premises. They are never crystallized, but occur in every variety of lamellar, slaty, botryoidal, and pulverulent forms, and in some cases, cavities are found lined with beautiful and peculiar crystallizations of carbonate of lime, spathic iron, heavy spar, aragonite, quartz, iron pyrites, and more rarely cacoxene or chalcodite, and millerite, the latter being the rarest and most beautiful of its associates. It occurs in brilliant needle shaped crystals, radiating from a centre like the fibres of a thistledown, having the color and brilliancy of gold. Groups of crystalline specimens of these minerals, often form objects of great beauty...

No doubt the finest specimens were collected more than a century ago. Today, however, there are extensive dumps which have not been heavily dug and it is still possible to collect many of the species listed below, at least as microscopic crystals. Millerite and pecoraite are rather difficult to find, although hundreds of specimens have been found since 1979. Siderite, dolomite, quartz, stilpnomelane, and magnetite pseudomorphs after hematite are readily available.

The mineral descriptions which follow include only those species

found in the crystallized cavities in the hematite ore. Species found in the marble, granitic gneiss and chloritic rock such as graphite, phlogopite, chlorites, micas, etc, will not be further discussed. These descriptions are based on the examination of several hundred hand specimens<sup>1</sup> and extensive field work at the locality, but in general, only the more common habits and associations are described.

**Apatite:** A member of the apatite group, almost certainly carbonate apatite, occurs sparingly as microscopic tan, pink, or brown crystals associated with quartz and magnetite pseudomorphs after hematite (Fig. 5). The crystal forms observed are the hexagonal prism and basal pinacoid, rarely modified by the hexagonal dipyramid.

**firagonite:** Aragonite occurs as clear to white crystals up to 1 millimeter in length. The crystals appear late in the paragenetic sequence. SEM photomicrographs show them to be relatively simple combinations of orthorhombic pyramids, pinacoids, and prisms (Fig. 6).

**Calcite:** At least three generations of crystallized calcite can be observed in cavities in the ore. The earliest is preserved as encrustation pseudomorphs of stilpnomelane after calcite scalenohedra, and is rarely encountered. The second generation consists of translucent, milky crystals of rhombohedral habit, described in detail by Whitlock (1910) (Fig. 7). The third generation is typically of the "nailhead" habit (Fig. 7). In addition, some cavities are partially or completely filled with a milky white, coarsely crystalline calcite. Whether this represents a continuation of one of these three generations, or an additional one is unknown.

**Chalcopyrite:** Chalcopyrite is uncommon at the Sterling Mine. Crystals up to a centimeter across are known, but most are only a few millimeters. The crystal forms observed include combinations of positive and negative disphenoids, [hhl] and [hhl]; two sets of tetragonal scalenohedra, [hkl]; and the tetragonal prism, [110]. Most specimens have a bright, metallic luster with occasional irridescence. A specimen in the Burridge collection at Harvard University, shows millerite needles protruding from a mass of chalcopyrite crystals with darkened surfaces and covered with minute sprays of acicular malachite. Similar specimens of malachite-covered chalcopyrite have recently been collected from the dumps.

<sup>&</sup>lt;sup>1</sup>Specimens were examined from the following collections: Mineralogical Museum, Harvard University; Department of Geology, Hamilton College; National Display Collection, National Museums of Canada; Department of Geology, Cornell University; Geological Museum, Rutgers University; Department of Geology, Vassar College; New York State Museum; Ron Waddell, Syracuse, NY; Steve Chamberlain, Syracuse, NY; George Robinson, Ottawa, Canada; and Georgia and Everett Shaw, Cortland, NY.



Figure 5a. Pink tabular carbonate apatite crystals. The field of view of about 1mm. Collection of Ron Waddell, Syracuse, NY. Photo by S. Chamberlain.

Figure 5b. Carbonate apatite crystals. The magnification of the SEM photomicrograph is about 300x. Photo by G. Robinson.



Figure 6. Aragonite crystals. The magnification of the SEM photomicrograph is about 400x. Photo by G. Robinson.



Figure 7. Crystal forms of calcite from the Sterling Mine. The second generation is shown in **d**, **e**, and **f**. The third generation is shown in **a**, **b**, and **c**. Modified from Whitlock (1910).

**Dolomite:** Dolomite is a relative common mineral at the Sterling Mine. It occurs as white, creamy, saddle-shaped crystals up to 5 mm, and as spherical aggregates of curved rhombohedra up to 1.5 cm in diameter (Fig. 8). Microprobe analyses show that this dolomite is actually a ferroan dolomite of composition  $Ca(Mg_{62}Fe_{31}Ca_{02})(CO_3)_2$ .



Figure 8. Spherical arrays of dolomite crystals with millerite, stilpnomelane, quartz, and magnetite pseudomorphs after hematite. The millerite spray is about 1 cm long. Oren Root Collection, Hamilton College, #H183. Photo by S. Chamberlain.

Commonly, dolomite crystals are epitaxially overgrown by light tan to dark reddish brown siderite, resulting in zoned crystals. Microprobe analyses of such zones crystals give  $Ca(Mg_{.66}Fe_{.30}Ca_{.02}Mn_{.02})(CO_3)_2$  for the ferroan dolomite cores,  $(Fe_{.75}Mg_{.16}Ca_{.08}Mn_{.01})CO_3$  for the light tan siderite overgrowths, and  $(Fe_{.81}Mg_{.10}Ca_{.08}Mn_{.01})CO_3$  for the dark reddish brown siderite overgrowths

Ankerite is commonly listed in the literature as occurring at the Sterling Mine (e.g. Buddington, 1934; Palache et al., 1951; Roberts et al., 1974; Jensen, 1978). Neither X-ray diffraction nor electron microprobe studies revealed any ankerite at this locality. It seems likely that earlier wet chemical analyses of dolomite/siderite zoned crystals are the source of this misidentification.

**Goethite:** Goethite is relatively uncommon at the Sterling Mine, usually occurring as microscopic tufts of acicular golden crystals (Fig. 9) which

formed relatively early in the paragenetic sequence. More rarely goethite occurs as crystalline botryoidal coatings on hematite crystals or as an alteration of magnetite pseudomorphs after hematite crystals. Massive brown "limonite" is not uncommon in the dump material.



Figure 9. Golden sprays of acicular goethite on quartz crystals. The field of view is about 2 mm. Collection of Georgia and Everett Shaw, Cortland, NY. Photo by S. Chamberlain.

**Hematite:** Hematite was the principal ore mined, and as might be expected is common. Mostly it occurs as earthy, red masses. Steel-grey massive hematite and botryoidal (Fig. 10) and specular forms are less common. Unaltered crystals of hematite are rarely encountered because most of what appears to be hematite has been altered to magnetite.

**Magnetite:** Virtually all of what appears to be specular hematite is actually a replacement of hematite by magnetite. These pseudomorphs are typically small, flattened rhombohedra with black, lustrous faces Figs. 11 and 12). Although they appear to be hematite, they are strongly magnetic, have a black streak, and their X-ray diffraction pattern clearly shows strong magnetite lines.

**Millerite:** This is the species for which the locality is justly famous. Millerite was discovered at the Sterling Mine by Franklin B. Hough, a noted scientist, historian, and collector who lived in the nearby village of Somerville. Hough's original description (Hough and Johnson, 1850, page 287) includes:

It was first noted by the writer about two years since, and

attracted his attention for its delicate capillary appearance, brilliant lustre and the difference of its crystalline form from that of sulphuret of iron, which in color and association it so nearly resembles. It occurs mostly in radiating tufts of exceedingly minute and slender crystals of brass-yellow color, and a very brilliant lustre, which when highly magnified present the appearance of flattened hexagonal prisms with striated faces, the striae being parallel with the principal faces of the prism ... They occur in geode-like cavities of the iron ore, which are lined with crystallizations of spathic iron, specular iron, quartz, calcite, cacoxene, and sulphuret of iron; from among these crystals the tufts proceed, attached generally to the spathic iron, more rarely to the crystals of iron. It is not an abundant mineral; only perhaps one or two dozen specimens have been procured since its discovery... In a specimen which the writer procured of a miner,... a crystal was found completely transfixing a rhomb of spathic iron, and supporting it in air, at a distance of 1/8 inch above the inner surface of the cavity.



Figure 10. Red botryoidal hematite. The specimen is 15 cm in width. #H268, Oren Root Collection, Hamilton College. Photo by S. Chamberlain.

Sprays of acicular millerite crystals range from microscopic to about 3 cm in largest dimension. Individual crystals may be relatively sturdy and longitudinally striated (Figs. 8 and 13), delicate and curved, or spiraled. Occasionally smaller sprays are observed to radiate from a single thicker



Figure 11. Black pseudomorphs of magnetite after rhombohedral crystals of hematite with pink carbonate apatite crystals. The magnification of the SEM photomicrograph is about 200x. Photo by 6. Robinson.



Figure 12. Black magnetite pseudomorphs after rhombohedral crystals of hematite with pink carbonate apatite crystals. The magnification of the SEM photomicrograph is about 200x. Photo by G. Robinson.

crystal in a habit resembling a broom (Fig. 14).

**Pecoraite:** Some millerite at the Sterling Mine is altered to a light yellow to dark green secondary minerals. The degree of alteration ranges from thin, partial coatings to complete replacement (Fig. 15). Work on such alteration products is often difficult because they are not well crystallized. By combinations of X-ray diffraction, electron microprobe analysis, and TGA-EGA analysis, Robinson has concluded that the alteration product is largely pecoraite (Robinson and Chamberlain, 1984). The measured composition is  $(Ni_{5.87}Mg_{.16})(Si_{3.76}Fe_{.30})O_{10}(OH)_8$  in excellent agreement with the theoretical composition  $Ni_6Si_4O_{10}(OH)_8$ .



Figure 13. Millerite crystals on tan siderite crystals. The millerite spray is nearly 2 cm. \*H281, Oren Root Collection, Hamilton College. Photo by C. A. Smith.

Figure 14. Millerite "broom" on magnetite pseud. after hematite crystals. Gore Collection, Harvard University. Photo by S. Chamberlain.

**Pyrite:** Pyrite is uncommon at the Sterling Mine. Usually it occurs as small cubes or octahedra rarely exceeding 1 or 2 mm on edge. The most interesting pyrite specimens are parallel growths of octahedral crystals on tan siderite (Fig. 16).

**Quartz:** Quartz is common in vugs as druses of clear crystals which rarely exceed 1 cm across. Stalactitic growths and ferruginous crystals are occasionally encountered. Some individual crystals have attenuated prism faces and resemble hexagonal dipyramids, while others have more complex morphology (Fig. 17). Quartz also occurs in the massive ore as yellow and brown jasper.

**Siderite:** Siderite is common at the Sterling Mine. Two color varieties are present. One is a light tan color (Fig. 16) and has a composition of  $(Fe_{.77}Mg_{.13}Ca_{.10})CO_3$ . The other is dark red to reddish brown and has a composition of  $(Fe_{.81}Mg_{.10}Ca_{.08}Mn_{.01})CO_3$ . Both types occur with about equal frequency as rhombohedral crystals up to 5 mm or as parallel groups up to several centimeters. The light tan crystals are occasionally observed to be impaled on millerite needles as described by Hough above.



Figure 15. Pecoraite pseudomorph after millerite crystal. The SEM photomicrograph is about 1000x. Photo by G. Robinson. Figure 16. Pyrite crystals on light tan siderite crystals. The field of view is about 1 cm. New York State Museum Collection, Albany, NY. Photo by S. Chamberlain.

**Sphalerite:** Sphalerite is rare at the Sterling Mine. Figure 18 shows a 6 mm, complex, twinned crystal from the Root Collection. This crystal occurs in a cavity with siderite, dolomite, calcite, chalcopyrite, quartz, and magnetite pseudomorphs after hematite.

**Stilpnomelane:** This species was originally identified as cacoxenite (Emmons, 1842; Beck, 1842; Hough and Johnson, 1850). It was put forth as the new species chalcodite by Shepard in 1852. A few years later, Brush (1858) finally correctly suggested that chalcodite was stilpnomelane. Both X-ray diffraction and electron microprobe analyses confirm its identity as stilpnomelane. It occurs as velvety golden-brown, green-brown, and green coatings, and small isolated spheres. Close examination shows arrays of micaceous crystals (Fig. 19) up to 2 mm across. It commonly fills fractures

in the ore and the chloritic rock, and is usually found in crystal-lined cavities in the ore. It also occurs more rarely as encrustation pseudomorphs after calcite scalenohedra and an unknown orthorhombic mineral, perhaps anhydrite (Fig. 20).



Figure 17. Colorless quartz crystals with pink carbonate apatite crystals. The magnification of the SEM photomicrograph is about 250x. Photo by G. Robinson.



Figure 18. Twin crystals of dark brown sphalerite. The crystals are 6 mm on edge. #H228, Oren Root Collection, Hamilton College. Photo by S. Chamberlain.



BC-6

Figure 19. Stilpnomelane with quartz. The magnification of the SEM photomicrograph is about 225x. Photo by G. Robinson.



Figure 20. Encrustation pseudomorph of stilpnomelane after an unknown mineral, possibly anhydrite, with siderite. The pseudomorph is about 1 cm. \*2435, Steve Chamberlain Collection, Syracuse, NY. Photo by S. Chamberlain.

**Talc:** An iron-rich talc has been found at the Sterling Mine. It occurs as gray, clay-like masses in the walls of some cavities in the ore, and as spheroidal aggregates of off-white microscopic crystals (Fig. 21) in others. It is most commonly associated with quartz, stilpnomelane, and magnetite pseudomorphs after hematite. Less commonly, striated molds of an unknown minerals, possibly anhydrite, are observed in the massive talc. A composite formula for this talc, based on electron microprobe, TGA, and wet chemical analyses, is  $(Mg_{1.90}Fe(11)_{.78}Fe(111)_{.26}Al_{.02})Si_{4.04}O_{10.06}(OH)_{2.23}$  in excellent agreement with the general talc formula (Mg,Fe)<sub>3</sub>Si<sub>4</sub>O<sub>10</sub>(OH)<sub>2</sub>. Note that the when iron-rich talcs are synthesized (Forbes, 1969) ferric iron substitutes for Si, but in this iron-rich talc, both ferrous and ferric iron are substitution for Mg.



Figure 21. Creamy white aggregates of iron-rich talc crystals. The magnification of the SEM photomicrograph is about 700x. Photo by G. Robinson.

# PARAGENESIS

The origin of this deposit now appears to have been quite complex, with a number of stages spanning an unknown period of geologic history. Before presenting a summary paragenesis, I shall review several topics which bear directly on this deposit's origin.

1. The deposit sits on a boundary between Grenville marble and granite gneiss. Smyth (1894b) and Buddington (1934) have shown that the

BC-6

bulk of the chloritized rock in the ore body is an altered granite. Smyth suggested that the chloritization resulted from the action of iron-rich, acidic solutions arising from surficial weathering of pyritic gneisses or schists.

2. The basic structure of the ore itself is stalactitic, such as occurs from the precipitation of iron oxyhydroxides from aqueous solution at or near the surface. Furthermore, the voids or cavities in this basic stalactitic structure although subsequently mineralized, were never subjected to sufficient pressure to collapse them.

**3.** Thin sections of the overlying Potsdam sandstone clearly show that, contrary to the conclusions reached by Smyth from field observations, the phase of mineralization which included specular hematite, quartz, and stilpnomelane occurred after the deposition of the Potsdam. The bottom of the overlying Potsdam sandstone was mineralized from below. We believe Smyth mistakenly identified mineralized boulders in the Potsdam as pieces of detrital ore. Thin sections clearly show this is not the case.

**4**. Fluid inclusion studies of the quartz crystals suggest that the quartz and specular hematite was deposited at the somewhat elevated temperature of 150°C,

5. An oxidation-reduction reaction occurred sometime after the deposition of the specular hematite. These crystals have been largely reduced to magnetite. Furthermore, the reduction appears to have proceeded from the cavities outward into the walls. The major portion of the massive hematite was not affected. Both stilpnomelane and talc can be implicated in this reaction. Analyses of the degree of hematite reduction and the color and ferric/ferrous ratios of associated stilpnomelane show a clear correlation. Generally the greener stilpnomelane has  $Fe_2O_3/FeO = 2.5$  and is associated with magnetite-poor vugs. The golden brown stilpnomelane has  $Fe_2O_3/FeO = 16.3$  and is associated with magnetite-rich vugs. It is generally thought that stilpnomelane forms as stilpnomelane-Fe(III) and may be subsequently oxidized to stilpnomelane-Fe(III) (Zen, 1960; Brown, 1967, 1971; Hutton, 1938). Thus the association of stilpnomelane rich in ferric iron with vugs rich in magnetite suggests the coupled redox reaction:

hematite + Fe(II) stilpnomelane » magnetite + Fe (III) stilpnomelane + 02

Likewise, our finding that in the iron-rich talc, the ferric iron substitutes for magnesium rather than for silicon suggests that the talc formed as ferroan talc and was subsequently partially oxidized to ferrian talc.

6. Although pecoraite is presently much more common on the dumps than it is in collections assembled while the mine was operating, some "old time" specimens show the alteration of millerite to pecoraite, and some specimens have been found with pecoraite pseudomorphs after millerite completely embedded in calcite. Thus, while the formation of pecoraite represents a late stage weathering, it may not exclusively be a phenomenon occurring on the dumps.

With this introduction, the paragenesis of the minerals can now be considered in three parts: 1) the minerals remaining from the original marble; 2) those remaining from the original granite gneiss; and 3) those formed during and after the deposition of the ore. Minerals remaining from the original marble include flakes of graphite and phlogopite found in a calc-silicate rock that has been partially replaced by hematite. Minerals remaining from the original granite gneiss are found as grains and plates in the green, chloritic rock and include quartz, feldspar, phlogopite, and minor tourmaline. The paragenesis of the minerals found in the cavities in the ore has been determined from examination of numerous hand specimens and while not exhaustive, should be indicative of the general pattern (Fig. 22). The observed sequence of mineral formation coupled with the observations above suggest the following five paragenetic stages: 1) stalactitic deposition; 2) ferric mineral deposition; 3) ferrous mineral deposition; 4) coupled oxidation-reduction; and 5) late deposition and weathering.

Stage 1 - Stalactitic Deposition: It is obvious that open spaces must have existed in order to have formed the crystals observed in the vugs. These voids may have resulted from the attack of the marble by acidic solution derived from decomposing sulfides or meteoric water with dissolved carbon dioxide. Some may simply have existed as fractures. The change in volume resulting from the chloritization process may have produced openings in or around the altered gneiss. Regardless of their origin, the fact remains that open spaces must have been present for solutions to enter and deposit botryoidal and stalactitic hematite. Ocherous and botryoidal hematite is a universal feature of cavity walls, and thin sections of stalactitic aggregates of later formed minerals often show a core of this hematite phase. The original precipitates may have been amorphous ferric hydroxides or oxyhydroxides that gradually recrystallized as hematite, possibly after passing through an intermediate goethite phase. This stage of deposition may well have occurred at or near surface conditions in late Precambrian time.

Stage 2 - Ferric Mineral Deposition: The minerals of this stage include

#### BC-6

PARAGENESIS of the STERLING MINE					
HEMATITE (botryoidal) QUARTZ HEMATITE (specular) GOETHITE CARBONATE APATITE ANHYDRITE (?) CALCITE TALC [Fe(II)] TALC [Fe(II)] STILPNOMELANE [Fe(II)] STILPNOMELANE [Fe(II]] MILLERITE DOLOMITE SIDERITE PYRITE MAGNETITE PECORAITE	]	TITI	T I I III	III	II II ŀ?ł
STAGE	1	2	3	4	5
1STALACTITIC DEPOSITION2FERRIC MINERAL DEPOSITION3FERROUS MINERAL DEPOSITION4COUPLED OXIDATION-REDUCTION5LATE DEPOSITION AND WEATHERING					

Figure 22. Paragenesis diagram for the major species occurring at the Sterling Mine. The vertical divisions between the stages represent unknown time periods.

quartz, specular hematite, carbonate apatite, crystallized goethite, calcite, and anhydrite(?). Fluid inclusion studies indicate an elevated temperature (150°C) during this phase of mineralization. The first two minerals to form were hematite and quartz. The walls of many cavities are a banded mixture of these two minerals. Often hematite crystals are embedded in guartz crystals and the quartz is encrusted with hematite, suggesting a simultaneous or alternating crystallization. The few specimens of carbonate apatite that were available for study suggest that this mineral also formed at this time. The next mineral to form appears to have been goethite, since delicate golden sprays of acicular crystals often lay partially within the terminations of quartz crystals. The anhydrite (?) laths and calcite scalenohedra that formed during this stage were subsequently dissolved away leaving crystals molds in later formed minerals. Since these minerals certainly did not form under surface conditions, considerable time may have elapsed between stages 1 and 2.

**Stage 3 - Ferrous Mineral Deposition:** After the final deposiiton of quartz, specular hematite, and goethite, a new association of minerals began to be deposited, starting with talc and stilpnomelane. As discussed above, there is good reason to believe that both these silicates formed initially as ferrous iron species, marking the beginning of a new stage in the paragenesis. After stilpnomelane, a second generation of calcite of predominantly rhombohedral habit formed, followed in order by millerite, dolomite, siderite, and pyrite. Thin sections of the overlying Potsdam sandstone clearly show replacement by hematite, carbonates, and stilpnomelane, which strongly suggests that stages 2 and 3 occurred in the Paleozoic after the formation of the sandstone.

**Stage 4 - Coupled Oxidation-Reduction:** The nearly universal reduction of the hematite crystals in the cavities to magnetite appears to have been a major event in the paragenesis. The evidence presented above suggests that a coupled oxidation-reduction reaction occurred in the open cavities between hematite and stilpnomelane (and talc). This reaction may have been triggered by an elevation in temperature and pressure subsequent to the deposition of the minerals involved, as stilpnomelane is a typical indicator of low grade metamorphic conditions. In the conversion of stilpnomelane rich in ferrous iron to stilpnomelane rich in ferric iron, electrons were made available to reduce some of the ferric iron in hematite to ferrous iron and produce magnetite. We have placed stage 4 at this point in the paragenesis based upon the observations that in specimens where the cavities were completely filled with calcite from stage 5, the hematite was reduced to magnetite, but in a few specimens where the cavities were

completely filled with dolomite from stage 3, the hematite was not reduced.

**Stage 5 - Late Deposition and Weathering:** Late in the paragenesis, a third generation of "nailhead" calcite was deposited. Some finely crystallized talc also appears to have formed very late in the sequence. Small amounts of hematite, acicular goethite, and aragonite were also deposited. The remainder of events in this stage involve the alteration of earlier minerals. Malachite formed from chalcopyrite; pecoraite, from millerite; and goethite, from pyrite, magnetite, and siderite. These alterations can take place under atmospheric conditions and may still be occurring in the dumps today. At some point or points in this final stage, some vugs were completely filled with calcite, or more rarely with calcite and gypsum. As noted above, pecoraite pseudomorphs after millerite pseudomorphs after hematite crystals.

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#### ACKNOWLEDGEMENTS

I am indebted to many for their assistance and forbearance in the conduct of the work reported here. I am most grateful to my collaborator, Dr. George Robinson, for permission to use his photomicrographs herein and for contributing at least half of the substance! We are also happy to acknowledge the assistance and support of Drs. Neal O'Brien and Brad Van Diver, SUNY Potsdam; Dr. William Elberty, St. Lawrence University; Dr. Peter Roeder and Mr. David Kempson, Queen's University; Mr. Robert Ramik and Miss Terri Ottaway, Royal Ontario Museum; Dr. Stephen Guggenheim, University of Illinois; Mr. Ian Wainwright and Mr. Greg Young, Canadian Conservation Institute; Dr. Fred Chandler, Geological Survey of Canada; Mr. Louis Moyd, National Museums of Canada; Dr. John Prucha, Syracuse University; and Mr. Patrick Farrell, Republic Steel Corporation. Finally we thank the Villeneuve family for their continued cooperation in granting permission to visit and collect specimens at the Sterling Mine.