

Petrology and Stable Isotope Geochemistry of the Metamorphosed Zinc-Iron-Manganese Deposit at Sterling Hill, New Jersey

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Abstract

The Sterling Hill deposit is an isoclinically folded sequence of zinc-, iron-, and manganese-rich strata surrounded by the Franklin Marble. The most metal-rich layers are composed of combinations of willemite, franklinite, zincite, and calcite; other layers contain calc-silicate minerals and calcite. Structural, petrologic, and geochronologic evidence indicates that the deformation and mineral assemblages observed today were produced during granulite-grade Grenville metamorphism of the deposit at about 1.0 Ga.

In general, the oxygen isotope and chemical compositions of individual minerals vary from lithologic layer to lithologic layer but are uniform within layers which suggests that mineral compositions were controlled by the bulk compositions of the rocks. Important exceptions to this rule occur near faults and fractures where the deposit was infiltrated by retrograde metamorphic fluids. In these areas, the rocks commonly contain hydrous minerals which have replaced anhydrous assemblages, and the minerals have been exchanged to larger $\delta^{18}\text{O}$ values.

Willemite and zincite are stable at higher $f_{\text{O}_2}/f_{\text{S}_2}$ than pyrite and pyrrhotite which implies that the ores are not chemically equilibrated with the surrounding Franklin Marble but are higher in oxidation state and/or lower in sulfidation state. The deposit also contrasts with the surrounding marble in oxygen isotope composition. Bulk $\delta^{18}\text{O}$ values for ore layers range from about 6 to 13 per mil, and thin marble layers interbedded with the ores are consistently about 15 per mil. The Franklin Marble is 20 to 25 per mil.

Models for the protolith are presented in which the bulk oxygen isotope compositions and bulk chemical compositions of the rocks are assumed to reflect protolith compositions modified by metamorphic devolatilization. The mineralogy of the protolith is inferred from the bulk chemical compositions of the rocks and by analogy with the mineralogy of other metal-rich oxidized rocks, and the minerals are assumed to have equilibrated isotopically with the fluid which formed them. The application of the models which require the fewest assumptions is to the marbles interbedded with the ore layers. Their isotopic compositions appear to require either equilibration with ^{18}O -depleted meteoric water at the earth's surface temperatures, or equilibration with a more ^{18}O -enriched water at temperatures characteristic of hydrothermal or metamorphic processes. Application of the models to the ore layers suggests that the last fluid-dominated event took place at $150^\circ \pm 50^\circ\text{C}$ rather than at the earth's surface temperatures. Structural features of the deposit also support the higher temperature formation in that they appear to be incompatible with an origin by weathering.

Exposure to seawater is the most plausible alternative to subaerial weathering for producing the high oxidation state-low sulfidation state of the protolith. An extremely large volume of seawater would have been required to oxidize the entire metal inventory of the deposit. Thus, the formation of the oxidized protolith is best inferred to have taken place on the Proterozoic sea floor or in shallowly buried sediments which were well irrigated by seawater. The closest modern analogues for Sterling Hill, and by analogy the nearby Franklin Furnace deposit, are the sulfide-poor strata in the metalliferous sediments beneath the Red Sea brine pools. There are, however, significant differences between the two occurrences.

Introduction

THE Sterling Hill deposit, and its nearby and similar relative at Franklin Furnace, consist of metal-rich strata which are extraordinary in several ways. First, they are extremely high grade. The overall compo-

sition of Sterling Hill, for example, was 20 wt percent zinc, 16 wt percent iron, 8 wt percent manganese, and substantial portions of the deposit contained greater than 40 wt percent zinc. Second, the strata have unique mineralogical makeups, and they constitute one of the most unusual mineralogical provinces of the world. The zinc ore minerals are willemite (ideally Zn_2SiO_4), franklinite (ZnFe_2O_4), and zincite (ZnO) rather than sulfide minerals which are the common constituents of other zinc deposits. In ad-

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dition, there is a great diversity of minerals at the deposits; 333 different mineral species have been identified from the deposits and associated rocks (Anonymous, 1990). Of those minerals, 65 were recognized first at Sterling Hill or Franklin, and 33 have no other known occurrence. The deposits are important sources of minerals for studying zinc and manganese in a wide variety of crystal structures (e.g., Dunn, 1985a; Essene and Peacor, 1987).

A third feature which makes the deposits noteworthy is the controversy surrounding their genesis. No other deposit is known with the same assemblage of ore minerals and the same chemical composition ($Zn > Fe > Mn$, essentially free of Pb, Cu, and S). It has been difficult, if not impossible, to offer defensible genetic arguments by drawing analogies with other more common classes of deposits. Arguments for the origin of the deposits have ranged considerably since the first discussions on the topic (Rogers, 1836) covering a variety of both epigenetic and syngenetic hypotheses. Some workers argued that the ores were favorable horizons in the Franklin limestone which were replaced by a reaction with magmatic fluids (Spencer, 1908; Ries and Bowen, 1922; Pinger, 1950; Ridge, 1952). Others favored a syngenetic timing for mineralization, with metals being deposited on the floor of an ancient sea or in shallowly buried sediments, either as sulfides which were later subjected to oxidation (Wolff, 1903; Tarr, 1929; Palache, 1935) or as zinc-iron-manganese-rich sediments (Callahan, 1966; Metsger et al., 1969; Squiller and Sclar, 1980). Frondel and Baum (1974) suggested that the metals were volcanically derived.

A major obstacle to understanding the origin of the deposits is the fact that they, along with the rocks which enclose them, were deformed and metamorphosed at approximately 1.0 Ga during the Grenville orogeny. Although the question has been raised whether mineralization predated or postdated the metamorphism, it is now clear that the metals were in place prior to the peak of metamorphism. The evidence supporting this conclusion comes from structural studies which indicate that the Sterling Hill orebody is composed of continuous strata with the same isoclinal folding and mineral lineations as the host rocks (Metsger, 1962; Metsger et al., 1969) and mineralogical studies which indicate that at least some of the minerals in the deposits formed at high temperatures characteristic of granulite facies metamorphism (Mason, 1947; Carvalho and Sclar, 1988). It is clear that the mineralogy of the ores and the rock fabrics within the ore zone result from the regional metamorphism and do not bear directly on the process which concentrated the metals prior to metamorphism.

In fact, a number of workers have proposed that the metamorphism itself is responsible for the unusual chemical and mineralogical composition of the ores.

Guilbert and Park (1986) and Tracy et al. (1987) have proposed that the ores were produced by metamorphic oxidation of a protolith composed mainly of zinc, iron, and manganese sulfide minerals. Wolff (1903), Frondel and Baum (1974), and Squiller and Sclar (1980) have proposed that the ores were produced by metamorphic decarbonation of a protolith composed mainly of zinc, iron, and manganese carbonate minerals. The metamorphic process is postulated by some authors to have stripped any lead and copper that was originally present.

Because the Franklin Furnace mine has been closed for three decades, data for the present study were collected only from the Sterling Hill deposit. Underground workings at the deposit were accessible for all but the final stages of the project. Conclusions of the study, however, can be applied to both deposits because they are closely similar.

In addition to addressing the genesis of the Sterling Hill and Franklin Furnace deposits, this paper addresses the topic of the effects of fluids and fluid-aided processes on mineral deposits as they undergo metamorphism. Such effects have long been of interest to economic geologists because fluids have the potential for redistributing the constituents of preexisting deposits, either enhancing metal grades or tonnages (e.g., Sangster, 1971; Rye and Rye, 1974; Pederson, 1980) or dispersing metals (e.g., DeVore, 1955; Vokes, 1971; Skinner and Johnson, 1987). Sterling Hill and Franklin Furnace are deposits whose chemical compositions may have been radically changed during metamorphism, either by oxidation or by decarbonation, to give rise to the high-grade ores observed today.

Geologic Setting and Deposit Geology

Sterling Hill occurs within a belt of Proterozoic rocks 30 to 40 km wide that extends from eastern Pennsylvania to western Connecticut. The belt, referred to as the Reading prong in Pennsylvania and New Jersey and the Hudson Highlands in New York, is composed of high-grade metamorphic and igneous rocks and represents an inlier of Grenville rocks exposed through a window in the Paleozoic cover (Drake, 1984). The oldest rocks in the northern New Jersey portion of the belt comprise a plagioclase-rich suite of gneisses, granulites, pegmatites, and amphibolites referred to as the Losee metamorphic suite. The Losee has been interpreted by Drake (1984) to be a metamorphosed and partially melted volcanic pile composed originally of quartz keratophyre and spilite with associated trondhjemite intrusions. Overlying the Losee is a series of quartzofeldspathic and calcareous gneisses and amphibolites. The gneisses have been interpreted as metamorphosed detrital and carbonate sediments (Drake, 1984). Hague et al. (1956) recognized relict pillow structures in some amphibolite exposures which indicates that basaltic volcanism

accompanied sedimentation. Both the Losee suite and the gneisses are intruded by plutonic rocks, the majority of which are granitic in composition. Several of the plutonic units have been grouped in the Byram suite. The emplacement of the plutons appears to have accompanied Grenville deformation, and Drake (1984) and Volkert and Drake (1986) have proposed that they are products of partial melting during the Grenville metamorphism.

The tectonic environment represented by the protoliths for the Losee suite, the gneisses, and the amphibolites is not known with certainty. Drake (1984) and Volkert and Drake (1986) have suggested that the protoliths formed on a Proterozoic continental margin, and that the gneiss sequence was originally a clastic wedge which overlay sodium-rich ocean-floor basalts. There is evidence in more recent work, however, that the rocks formed in an extensional environment. Gundersen (1985) has proposed a back-arc spreading basin as the tectonic setting and Drake (1990) a rift basin at the margin of the North American craton.

The dominant structures in the area are westward-verging isoclinal folds with north-northeast-trending axial traces. Volkert et al. (1986) have identified fold interference patterns and crosscutting foliations which suggest that the rocks were subjected to at least two separate folding events. Hypersthene occurs in some orthogneisses (Baker and Buddington, 1970; Drake, 1984) which indicates that the rocks are granulite facies. Metamorphic temperatures are estimated to have reached 700° to 800°C (Mason, 1947; Hewins and Yersak, 1977; Carvalho and Sclar, 1988). Metamorphic pressures, based on the sphalerite-pyrite-pyrrhotite and plagioclase-garnet-aluminosilicate-quartz barometers, were 4 to 5 kbars (Hewins and Yersak, 1977; Johnson, 1990) which indicates that the rocks were buried to a depth of at least 11 to 14 km.

The paragneisses contain two populations of zircon (Eckelmann, 1963; Aleinikoff et al., 1982) which represent 1,550- to 1,790-Ma detrital grains and ~1,000-Ma Grenville metamorphic grains and overgrowths (Aleinikoff et al., 1982). The syntectonic Canopus pluton yields an Rb-Sr whole-rock isochron of $1,068 \pm 40$ Ma (Ratcliffe et al., 1972, recalculated in Rankin et al., 1983) which may indicate that plutonism was broadly synchronous with the metamorphism. However, as Grauch and Aleinikoff (1985) have pointed out, the Grenville orogeny in the Reading prong-Hudson Highlands may have included multiple thermal events which have not yet been resolved. Post-tectonic pegmatites in the northern Reading prong contain zircons which give dates in the range 965 to 1,023 Ma (Aleinikoff et al., 1982).

The $^{40}\text{Ar}/^{39}\text{Ar}$ release spectra for hornblendes and biotites from the area typically show well-developed plateaus consistent with closure of the minerals during

cooling after the Grenville thermal peak. The K-Ar dates for samples with flat release spectra are in the ranges 937 to 876 and 830 to 782 Ma for hornblendes and biotites, respectively (Dallmeyer et al., 1975). Dates quoted here have been recalculated using the decay constants in Steiger and Jager (1977). Assuming that the difference in Ar closure temperature for the two minerals is approximately 300°C (Berger and York, 1981), the data are consistent with—as are the K-Ar data of Long and Kulp (1962)—slow cooling at a rate of about 3°C/Ma. The $^{40}\text{Ar}/^{39}\text{Ar}$ release spectra show no evidence of reheating during the Ordovician Taconian orogeny in contrast with spectra from hornblendes and biotites from rocks farther north in the Hudson Highlands which indicate an Ar loss at ~480 Ma (Dallmeyer and Sutter, 1976).

The Sterling Hill and Franklin Furnace deposits are located within the Franklin Marble, which is a unit contained in the gneiss sequence. The marble is nearly pure with trace amounts of graphite, silicate minerals (forsterite, diopside, phlogopite, humites), and sulfide minerals (usually pyrrhotite or pyrite). Both deposits occur near the contact with the structurally underlying Cork Hill Gneiss. Sterling Hill and Franklin Furnace lie approximately 180 and 1 m, respectively, from the contact (Hague et al., 1956).

Sterling Hill is a sequence of strata with the form of a northeast-plunging synform (Fig. 1). Individual strata are chemically and mineralogically distinct, and they range from centimeters to meters in thickness. Metsger et al. (1958, 1969, in prep.) have established the lateral continuity of the strata by tracing distinctive bands, including a thin fluorite-bearing band, some 600 m down the plunge of the synform; and by establishing that the deposit has a macroscopic stratigraphy which continues through both limbs of the synform. The stratigraphic sequence from bottom to top is (1) a willemite + franklinite + zincite + calcite unit, (2) a willemite + franklinite + calcite unit, (3) a calc-silicate unit composed of calcite \pm pyroxene \pm garnet \pm other calc-silicate minerals, and (4) a horizon of angular fragments of biotite and hornblende gneiss encased in marble. Mineral abbreviations are found in Table 1. In the fragmental unit, which is referred to as black rock, gneissic banding varies in orientation from one fragment to another indicating that the fragments were rotated after the development of the banding. Metsger et al. (1969) have proposed that the horizon was originally a continuous stratum which was brecciated as the metal-rich strata were folded, and possibly as they sank in an inverted diapirlike fashion, during the Grenville metamorphism. This interpretation implies that the contact between the zincite-bearing unit and the surrounding Franklin Marble (Fig. 1), and possibly other contacts as well, are synmetamorphic faults. Thus trace element and stable isotope halos which have been observed in the wall rock (Buis et al., 1988; this work) may reflect

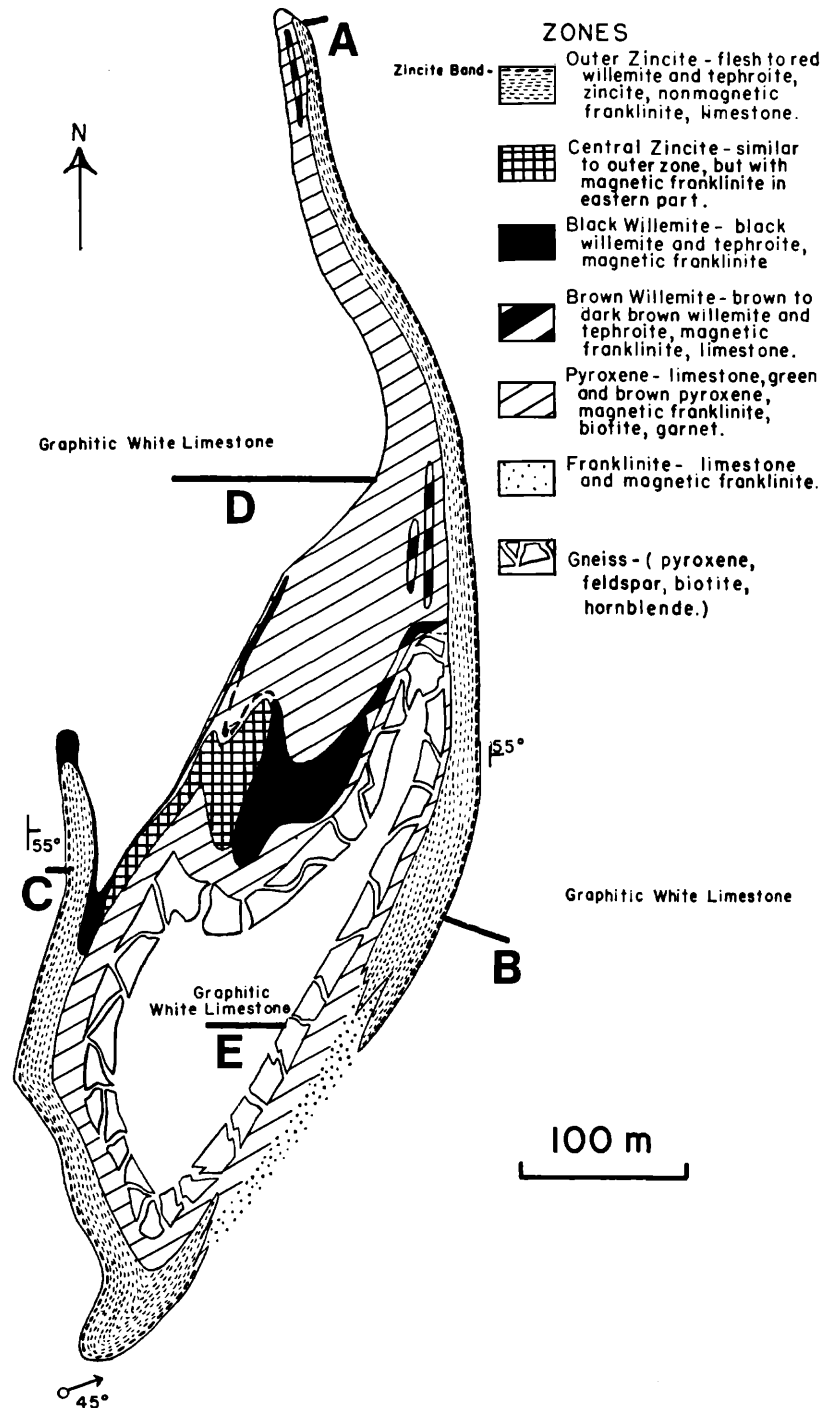


FIG. 1. Geologic map of the Sterling Hill orebody (after Metsger et al., 1958). Traverses A through E mark the locations of Franklin Marble host rock analyzed in this study.

partial equilibration of the ores and the wall rock during metamorphism rather than hydrothermal alteration of the wall rock during premetamorphic metal deposition.

The synform which comprises the deposit extends

about 400 m along strike and is about 200 m wide; it extends from the surface to a depth of 760 m where it is severed by Phanerozoic faults. A portion of the deposit was removed by erosion in Pleistocene and Recent times and, possibly, in Cambrian time as well

TABLE 1. Mineral Abbreviations

Ap	Apatite	Mag	Magnetite
Bt	Biotite	Phl	Phlogopite
Cal	Calcite	Po	Pyrrhotite
Cam	Ca clinoamphibole	Py	Pyrite
Chn	Chondrodite	Qtz	Quartz
Chu	Clinohumite	Sil	Sillimanite
Cpx	Clinopyroxene	Sp	Sphalerite
Crn	Corundum	Spl	Hercynite-gahnite spinel
Di	Diopside	Spn	Sphene
Dol	Dolomite	Srp	Serpentine
Ep	Epidote	Tlc	Talc
Fo	Forsterite	Tp	Tephroite
Fr	Franklinite	Tr	Tremolite
Gah	Gahnite	Wt	Willemite
Grt	Garnet	Wo	Wollastonite
Hem	Hematite	Zc	Zincite
Hu	Humite		

(the Cambrian Hardyston Quartzite which unconformably overlies the Grenville rocks in the area contains detrital franklinite derived from the Franklin mine, R. W. Metsger, pers. commun.). The original size of the deposit is therefore unknown. Total ore production at Sterling Hill was about 11×10^6 metric tons and the entire mineralized mass, including the subore-grade calc-silicates, was about 48×10^6 metric tons. Production from Franklin was about 22×10^6 metric tons.

Although the vast majority of the rocks within the Sterling Hill deposit are free of sulfide minerals, the few sulfide occurrences have important genetic implications, and they warrant description here. The most common occurrence is along faults and fractures which cut the deposit in a number of locations. For example, nearly pure, colorless sphalerite is common within a major east-dipping normal fault zone, the Nason fault, which offsets ore strata by several meters. Similar occurrences of sulfide minerals are associated with minor fractures which have no apparent offset. A variety of sulfide minerals, including galena, chalcopyrite, and sphalerite, occurs in the black rock horizon along the contacts between gneiss fragments and marble (Metsger et al., 1958; in prep.). Coarse amphibole, biotite, garnet, and gahnite also occur at the contacts, and they have been interpreted by Metsger et al. (1958; in prep.) as reaction zones that developed during the Grenville metamorphism. A third occurrence of sulfide minerals, mainly sphalerite, is in the matrix of a breccia located near the keel of the synform in the deeper levels of the mine. An apparent fossil hash has been identified in the matrix of the breccia (R. W. Metsger, pers. commun.) which indicates that breccia emplacement took place in Phanerozoic time and that fragments were derived from the lower Paleozoic limestones which overlie the Grenville rocks in the region. Elsewhere within the breccia, the matrix is composed of a fine-grained

mixture of willemite, franklinite, and calcite. The fourth occurrence of sulfide minerals is a small volume of ore, measuring a few tens of cubic meters, within the transverse portion of the deposit. The sulfide mineral present is colorless sphalerite which occurs as coarse grains disseminated in a calcite + willemite + franklinite + loellingite + graphite rock. Finally, R. W. Metsger et al. (in prep.) describe a thin, laterally continuous calcite + phlogopite + pyrrhotite + chondrodite + graphite layer within the limits of the orebody which is unrelated to faults and fractures.

Sampling and Analytical Techniques

Samples were collected throughout the deposit for this study (see Johnson, 1990, for locations). The majority are from systematic traverses across the ore layers and the enclosing Franklin Marble (Fig. 1) and were obtained from surface outcrops, underground exposures, and drill core. Polished thin sections were used for petrographic and microprobe analysis. For many of the ore samples, polished slabs were used for modal analysis.

Microprobe analyses were obtained using an Acton Laboratories (Cameca) MS64 equipped with a Tracor Northern solid state detector and TN2000 multi-channel analyzer. Operating conditions were 15 kV accelerating voltage and 5.0 nA sample current measured on brass. For carbonates, the sample current was reduced to 0.5 nA and the beam diameter enlarged to $\sim 10 \mu\text{m}$. Spectra were collected for 200 s which permitted detection of heavy elements ($Z > 9$) present at concentrations greater than about 0.1 wt percent. For carbonates, spectra were collected for 100 s. Unknown and standard spectra were compared using a least squares deconvolution technique; K ratios were corrected using alpha factors (Albee and Ray, 1970).

Microprobe standards were selected for their similarity to unknowns. This was particularly important for zinc-rich minerals because zinc imparts a bimodal appearance to the spectrum of background radiation. Failure to select standards for major elements with similar background spectra resulted in poor quality peak deconvolution results. The standards used for analysis of oxide and silicate phases were wollastonite, forsterite, fayalite, zincian rhodonite, willemite, gahnite, corundum, and rutile; for carbonate phases the standards used were calcite, periclase, pyrolusite, hematite, and gahnite. Four or more analyzed points (in some cases on more than one grain) were averaged to obtain each analysis.

Analyses were normalized about cations to obtain mineral formulas. Hydroxyl in hydrous minerals and CO_2 in carbonates were inferred from stoichiometry. Iron and manganese are expressed as FeO and MnO in all mineral and bulk-rock analyses, and the excess oxygen associated with trivalent iron and manganese

is not included in the totals. For franklinite and magnetite, therefore, perfectly accurate analyses will give totals of about 93 wt percent. For bulk rocks, perfectly accurate analyses of franklinite- and magnetite-free samples will total 100 wt percent, whereas totals for samples with 50 percent franklinite will be about 97 wt percent.

Samples were prepared for isotopic analysis by crushing and sieving or by using a fine dental drill. To obtain CO₂ gas from calcites, aliquots of crushed rock containing 10 to 20 mg calcite were reacted with H₂PO₄ at 25°C (McCrea, 1950). Willemite, tephroite, franklinite, and zincite were separated by magnetic techniques and handpicking. The separates were inspected with a binocular microscope and estimated to be >98 percent pure which ensures that error due to impurities is <0.1 per mil. Franklinite inclusions are present in many Sterling Hill willemites (Metsger et al., 1958) and they were present in willemite from sample J8523. Point counting revealed that the inclusions made up 1 to 2 vol percent of the mineral and therefore did not significantly affect the isotopic ratio measurement.

Oxygen was obtained from silicate and oxide separates by reacting ~10-mg aliquots with BrF₅ for 10 to 12 h (Clayton and Mayeda, 1963). Willemite and tephroite were reacted at 550°C; franklinite and zincite were reacted at 650°C. Franklinite, particularly samples with a substantial magnetite component in solid solution, and zincite did not always react completely and for some analyses the separates were ground with mortar and pestle prior to reaction in order to increase the oxygen yield. For neither mineral did the isotopic composition of the liberated O₂ vary systematically with yield, which indicates that no significant fractionation took place as a result of partial reaction and that the measured values reflect the true compositions of the minerals.

Isotopic ratios were measured using a Finnegan MAT 251 or a Nuclide 6-60; some samples were measured on both instruments. Differences between the results for gas samples run on both instruments were never more than 0.1 per mil in δ¹⁸O. The δ¹⁸O and δ¹³C values for calcite were reproducible to within ±0.1 per mil. The δ¹⁸O values for silicates and oxides were generally reproducible to within ±0.2 per mil. Replicate analyses of some samples spanned larger ranges up to 0.9 per mil suggesting that those samples may be isotopically heterogeneous. Aliquots of the NBS 28 oxygen isotope standard were periodically reacted with BrF₅ and analyzed over the course of the experiments. The δ¹⁸O results (six measurements) ranged from 9.52 to 9.63 and averaged 9.56 per mil. Oxygen isotope data are herein reported relative to the V-SMOW standard; carbon isotope data are reported relative to the PDB standard.

The K-Ar measurements were carried out on biotite

separated from three samples. The procedures used were described by Seidemann (1978).

Petrographic and Chemical Characteristics

The minerals in Sterling Hill rocks are generally coarse grained and euhedral to subhedral. Grain boundaries commonly meet at triple junctions which suggests that the minerals are equilibrated metamorphic assemblages. The ores, which is the term used throughout this paper to refer to the most zinc-rich units lowest in the lithologic sequence, contain combinations of calcite, willemite, franklinite, tephroite, and zincite. The assemblages in individual samples reflect bulk chemical composition. Rocks that contain significant silica, as most do, have willemite and/or tephroite as part of the assemblage. Rocks that are high in zinc relative to silica also contain zincite, and rocks that are high in magnesium contain magnesian tephroite in addition to, or instead of, willemite. The calc-silicate units contain calcite and a wide variety of minerals of which clinopyroxene and franklinite or magnetite are most common (Metsger et al., 1958). Units that are high in aluminum commonly contain hercynite-gahnite spinel or garnet. Units that contain H₂O have amphibole, biotite, or humite minerals as part of the assemblage. Modes and mineral compositions for representative samples are given in Tables 2-6, and the assemblages are illustrated in Figures 2 and 3.

From stratum to stratum within the deposit, the modal abundances and chemical compositions of the minerals vary widely (note the ranges in Tables 2-6). Within an individual stratum, however, modal abundances and chemical compositions are generally uniform (compare samples J858 and J859 which were separated by 1.8 m in stratigraphic height within the same lithologic unit).

There are important exceptions to this rule where

TABLE 2. Modal Analyses of Ore Samples
(Measurements were carried out on polished slabs and/or on several petrographic sections)

Sample no.	Cal	Wt	Tp	Fr	Zc
J844	76.5	16.6		6.9	
J858	55.5		12.4	19.1	13.1
J859	59.8		10.1	22.5	7.6
J8523	54.1	32.4		13.5	
J8524	77.8	7.2		15.0	
J8525	56.3	26.0		17.7	
J8528	65.9		26.9	7.2	
J867	27.5	48.2		24.3	
J871	9.7	3.0		47.7	39.6
SU112	30.9	12.2		16.7	40.2
SU115	53.7	22.8		23.5	
SU121	52.6	28.9		16.2	2.2
M9	5.2	68.1		26.6	

Mineral abbreviations in Table 1

TABLE 3. Modal Analyses of Calc-Silicate Samples (Measurements were carried out on petrographic sections)

Sample no.	Cal	Grt	Cpx	Tr	Bt	Fr	Mag
SH124-19	21.6		70.2			8.1	
SH124-36	59.2		5.8			35.0	
SH124-126	49.5		44.8	0.4	5.3		tr
SH124-155	32.6	40.0	22.3				5.0

Mineral abbreviations in Table 1; tr = trace

the deposit is crosscut by north-northeast-trending faults and fractures. In these areas, the ore strata are locally cut by calcite or willemite veins (Fig. 4). Vein calcite is commonly less pure than the disseminated calcite which occurs elsewhere in the same stratum (Fig. 5); it is readily apparent under ultraviolet illumination because it is nonfluorescent in contrast to the common calcite in the deposit in which manganese induces red fluorescence (Fig. 4). Vein willemite is commonly more pure than the willemite disseminated in the strata in which fayalite and/or forsterite are minor components (Fig. 6). Like vein calcite, vein willemite is commonly apparent under ultraviolet illumination because it fluoresces bright green in contrast to disseminated willemite in which the fluorescence is suppressed somewhat by impurities (Metsger et al., 1958). Vein willemite can phosphoresce as well which may indicate trace amounts of arsenic (R. W. Metsger, pers. commun.).

The rocks affected by crosscutting fractures also show evidence of mineral replacement reactions. The reactions produced a wide variety of assemblages which vary as a function of the original mineral assemblage in the stratum and the location within the deposit. Replacement textures which have been observed in the ores are (1) willemite after tephroite (Fig. 7) and (2) hematite + serpentine minerals after willemite. Furthermore, zincite has locally been removed from strata in the vicinity of fractures. Good examples of this phenomenon were observed in the outer zincite band in the east limb of the deposit.

Replacement textures which have been observed in calc-silicate and marble units are (1) tremolite after diopside, (2) tremolite + biotite + sphalerite after diopside, (3) epidote after garnet, (4) biotite + amphibole after hercynite-gahnite spinel + clinopyroxene, and (5) complex intergrowths of clinohumite + humite after forsterite (Fig. 8). Microprobe analyses of replacement minerals in representative samples are given in Table 7.

Bulk chemical compositions have been computed for representative ore and calc-silicate samples from microprobe analyses of minerals and modal data. The data show a considerable range of compositions (Table 8). In general, the lithologic sequence established by Metsger et al. (1958) corresponds to a chemical sequence of (1) silica-poor ores with $Zn > Fe > Mn$

(outer zincite band), (2) ores richer in silica (willemite + franklinite + calcite band), and (3) silica-rich carbonates with $Fe > Mn \sim Zn$ (calc-silicate band). Overlying the silica-rich carbonates are the black rock fragments. The interiors of the gneiss fragments contain no more than trace amounts of zinc; none was observed in 200-s energy dispersive microprobe spectra of the minerals. However, minerals at the margins of the fragments, which are inferred to be metamorphic reaction zones, contain zinc-rich amphibole, mica, and spinel.

Isotopic Characteristics and Zonation

Oxygen and carbon isotopes in ore and gangue minerals

Oxygen and carbon isotope analyses were carried out on separated minerals from ten samples of ore (Table 9). The data constitute the first reported analyses of the minerals willemite, tephroite, franklinite, and zincite. Individual minerals vary in $\delta^{18}O$ values from sample to sample spanning the ranges 12 to 18, 7 to 11, 6 to 9, 3 to 11, and 4 to 6 for calcite, willemite, tephroite, franklinite, and zincite, respectively. The ^{18}O partitioning is $Cal > Wt \sim Tp > Fr > Zc$ which indicates that the partitioning behavior of tephroite is similar to its isomorphs, forsterite and fayalite, and that of franklinite is similar to magnetite (cf. Friedman and O'Neil, 1977). These latter two minerals are both spinel structures, although they are not strictly isomorphous because franklinite has a normal distribution of cations among octahedral and tetrahedral sites whereas magnetite has an inverse distribution. Zincite is significantly depleted in ^{18}O compared with coexisting franklinite. The mineral has an unusually strong tendency to concentrate ^{16}O , more so, apparently, than any rock-forming mineral yet analyzed (cf. Hattori and Halas, 1982). For six samples, isotopic compositions and modal data were combined to give bulk $\delta^{18}O$ values. The values range from 6.1 to 12.5 per mil (Table 9).

Calcites from additional ore samples were also analyzed. The $\delta^{18}O$ values range from 11 to 18 per mil, much the same as the results in Table 9. The $\delta^{13}C$ values are -1 to +3 per mil. Some of the samples were collected along traverses perpendicular to the ore strata (e.g., Fig. 9), and the data illustrate that the oxygen isotope composition of calcite can vary markedly from one stratum to another, whereas compositions within an individual stratum are generally uniform.

Oxygen and carbon isotopes in calcite in wall rocks

Figure 1 shows the locations of five traverses along which samples of wall rock were collected for isotopic analysis. Traverses A, B, and C begin where willemite + franklinite + zincite + calcite ore abuts marble and

TABLE 4. Microprobe Analyses

Sample no.	J844		J858			J859			J8523		J8524		J8525	
	Fr	Wt	Fr	Tp	Zc	Fr	Tp	Zc	Fr	Wt	Fr	Wt	Fr	Wt
SiO ₂	0.3	28.0	0.1	34.1		0.4	33.8		0.3	27.0	0.1	26.8	0.2	27.0
TiO ₂	0.0		0.1			0.1			0.1		0.1		0.1	
Al ₂ O ₃	1.3		1.0			0.9			1.7		1.0		1.3	
ZnO	21.4	68.5	23.0	8.1	97.3	22.4	7.5	98.6	23.6	71.5	22.2	68.2	21.7	65.6
FeO	63.2	0.3	58.6	0.0	0.1	56.7	0.2	0.2	66.3	1.4	63.1	0.7	63.5	0.9
MnO	8.3	3.8	10.9	37.8	1.3	10.6	37.8	1.6	0.8	0.3	8.0	5.3	8.1	4.6
MgO	0.0	0.0	0.8	19.1	0.0	0.9	19.0	0.0	0.1	0.0	0.0	0.0	0.3	1.8
Total	94.5	100.6	94.5	99.1	98.7	92.0	98.3	100.4	92.9	100.2	94.5	101.0	95.2	99.9
Si	0.012	1.024	0.004	1.017		0.016	1.017		0.012	0.997	0.004	0.978	0.008	0.978
Ti	0.000		0.003			0.003			0.003		0.003		0.003	
Al	0.059		0.046			0.042			0.079		0.046		0.059	
Zn	0.612	1.849	0.655	0.178	0.984	0.654	0.167	0.980	0.687	1.950	0.636	1.837	0.614	1.756
Fe	2.045	0.009	1.890	0.000	0.001	1.876	0.000	0.002	2.186	0.043	2.048	0.021	2.036	0.027
Mn	0.272	0.118	0.356	0.955	0.015	0.355	0.964	0.018	0.027	0.009	0.263	0.164	0.263	0.141
Mg	0.000	0.000	0.046	0.849	0.000	0.053	0.852	0.000	0.006	0.000	0.000	0.000	0.017	0.097

Mineral abbreviations in Table 1

extend outward into barren Franklin Marble. Traverses D and E begin where calc-silicate rocks abut marble and extend inward toward the core of the synform. Calcite makes up at least 95 percent of all the samples; the oxygen isotope compositions of the calcites are shown in Figure 10.

The Franklin Marble is depleted in ¹⁸O near the zinc-iron-manganese-rich rocks, and it increases in ¹⁸O away from the deposit to $\delta^{18}\text{O}$ values typical of Proterozoic marine limestones (Veizer and Hoefs, 1976). The ¹⁸O-depleted halo is asymmetrical; it is a few tens of centimeters wide, and erratic, where it borders the outer zincite band, and is some 20 to 30 m wide adjacent to the calc-silicate unit (Fig. 10). The ¹⁸O depletions are coincident with a zone of graphite-free marble which surrounds the deposit extending approximately 1 m from the outer zincite band (Metsger et al., 1958; Metsger, 1962).

Oxygen and carbon isotopes in calcite associated with crosscutting fractures

Calcites lining and adjacent to fractures were analyzed, and the results are shown in Figure 6. The data from a single hand sample can cover the same range of $\delta^{18}\text{O}$ values as the data from calcites collected at random in the deposit (Table 9). In the examples shown in Figure 4, calcite lining fractures has $\delta^{18}\text{O}$ values of 17 to 18 per mil; calcite in the adjacent rocks is 13 to 14 per mil. The asymmetrical pattern in Figure 6a is an artifact of sampling, and the boundaries between ¹⁸O-enriched and ¹⁸O-depleted calcite are probably sharper than shown. The $\delta^{13}\text{C}$ value is constant across the fractures at 0 to 1 per mil.

There is some evidence, although the data are few, textures contain calcite with $\delta^{18}\text{O}$ values near the upper end of the observed range. Calcites in samples

SH12478 and SH124145 (Table 7), both of which contain hydrous minerals after clinopyroxene, have $\delta^{18}\text{O}$ values of 16.0 and 16.1 per mil, respectively.

Age Dating

Coarse biotite was separated from three rocks for K-Ar age dating. Samples SU36 and SU39 (Table 10) are from the transverse portion of the deposit; biotite in the samples occurs as rims on gahnite-hercynite spinel (Fig. 8d). Energy dispersive microprobe spectra reveal that the biotite in SU36 is zinc rich and resembles biotite from Franklin described by Evans and Strens (1966) and Frondel and Ito (1966). Sample SU94 (Table 10), on the other hand, is from the interior of a biotite + hornblende + plagioclase gneiss fragment in the black rock horizon. Zinc was not observed in a 200-s energy dispersive spectrum which indicates that the zinc concentration is less than ~0.1 wt percent. The biotite is low in Al^{VI} and high in Ti (Johnson, 1990) which is typical of biotites in granulite-grade metaluminous rocks (Guidotti, 1984).

The K-Ar dates (Table 10) range from 883 ± 35 to 908 ± 36 Ma. There appears to be no difference in age between the two biotite types. The dates are somewhat older than the range reported by Dallmeyer et al. (1975) for biotites collected elsewhere in the region but are within the range reported by Long and Kulp (1962). The 883 ± 35 -Ma date for the black rock fragment is somewhat older than the 808 ± 32 -Ma date for a similar black rock sample analyzed by Long and Kulp (1962).

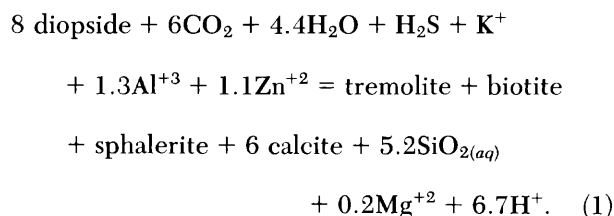
Secondary Characteristics and Processes

In portions of the deposit crosscut by fractures, the rocks have clearly had their mineralogy and chemical

of Ore Silicates and Oxides

J8528		J867		J871			SU112			SU115		SU121	
Fr	Tp	Fr	Wt	Fr	Wt	Zc	Fr	Wt	Zc	Fr	Wt	Fr	Wt
0.3	33.5	0.3	27.8	0.2	29.1		0.5	27.9		0.4	25.3	0.4	27.2
				0.1			0.0			0.0		0.0	
		0.4		0.8			2.1			0.8		1.7	
26.0	11.2	22.0	65.2	16.7	70.2	100.4	27.3	67.2	99.4	21.4	67.3	23.8	67.3
58.7	1.2	63.2	0.3	57.4	0.0	0.1	58.9	0.3	0.3	64.0	0.3	62.4	0.7
6.2	32.4	8.8	5.4	17.7	2.4	1.6	5.3	3.0	1.0	7.8	5.7	5.9	4.0
0.7	21.4	0.0	0.0	0.0	0.0	0.0	0.4	1.1	0.0	0.0	0.0	0.2	0.9
93.9	99.7	94.7	98.7	92.9	101.7	102.1	94.5	99.5	100.7	94.4	98.6	94.4	100.1
0.012	0.984	0.012	1.032	0.008	1.052		0.019	1.021		0.016	0.948	0.016	0.992
0.000		0.003		0.003			0.000			0.000		0.000	
0.092		0.018		0.037			0.096			0.037		0.078	
0.746	0.243	0.630	1.788	0.483	1.874	0.981	0.781	1.816	0.985	0.614	1.862	0.681	1.814
1.907	0.030	2.049	0.009	1.881	0.000	0.001	1.907	0.009	0.003	2.078	0.009	2.021	0.021
0.204	0.806	0.289	0.170	0.588	0.074	0.018	0.174	0.093	0.011	0.256	0.181	0.194	0.124
0.040	0.937	0.000	0.000	0.000	0.000	0.000	0.023	0.060	0.000	0.000	0.000	0.012	0.049

compositions changed. In ores, minerals which are absent or very rare elsewhere in the deposit, such as hematite and sphalerite, are present as replacements. In calc-silicates, hydrous minerals commonly occur as replacements of anhydrous minerals. Attempts to write reactions using the minerals observed in the rocks reveal that either some reactant phases were invariably entirely consumed, or a fluid phase supplied or removed H₂O, silica, reduced sulfur, and/or alkalis. For example, the sample shown in Figure 8a contains diopside, tremolite, sphalerite, biotite, and calcite. The textures indicate that diopside is breaking down to a tremolite + sphalerite + biotite assemblage. It is unclear whether calcite is a reactant or a product. There is no reaction capable of producing the observed texture given only the phases observed in the rock. However, the following reaction, which employs a fluid phase as the carrier of H₂O, H₂S, potassium, aluminum, and silica, can give rise to the texture:



The apparent solubility of aluminum may be a result of complexing with alkalis, a phenomenon which has been described by Anderson and Burnham (1983). Further, the extreme insolubility of zinc in the presence of H₂S suggests that the zinc may have been derived locally and was never transported for significant distances in solution along with H₂S.

The petrographic evidence that sphalerite, biotite,

and tremolite were produced where fluids infiltrated along fractures suggests that at least some of the sulfide minerals and hydrous minerals which have been reported from the deposit (e.g., Dunn, 1985a; Tracy et al., 1987) are products of secondary metasomatism which introduced H₂O and sulfur to the deposit. Such an interpretation is compatible with several of the occurrences of sulfide minerals described above. R. W. Metsger et al. (in prep.), however, have established that the deposit does contain some primary metamorphic hydrous and sulfide minerals in a phlogopite + pyrrhotite-bearing marble layer which occurs within the limits of the orebody unrelated to faults or fractures.

The variation in replacement mineralogy from one place to another within the deposit suggests that the concentration of solutes in the fluid was influenced by dissolution and precipitation reactions as it passed through the rocks. At some point, the fluid clearly carried sulfide which precipitated as sphalerite and other sulfide minerals; the source of the zinc may well have been zincite which appears from textural evidence to have been locally dissolved. Elsewhere, dissolved iron was oxidized to produce hematite. The occurrence of willemite and calcite in veins is evidence that the fluid was locally supersaturated with respect to the two minerals. Further evidence for changing solute concentrations is the variation in the chemical composition of calcite precipitated in veins (Fig. 6).

Figure 6 shows that the calcite within and adjacent to veins is enriched in ¹⁸O. An enrichment in ¹⁸O is evident also in the suite of representative ore samples that was selected for detailed isotopic analysis (Table 9). The compositions of coexisting calcites and franklinites fail to define an array on a δ-δ diagram with

TABLE 5. Microprobe Analyses of Minerals from Calc-Silicates

Sample no.	SH12419		SH12436		SH12478		SH124103			SH124126			SH124145		SH124155		J8638		
	Cpx	Fr	Cpx	Fr	Cpx	Mag	Cpx ¹	Crt ²	Mag ²	Cpx	Tr	Bl ³	Mag	Cah	Cpx	Mag		Wo	Spn
SiO ₂	53.3	0.3	53.1	0.2	55.5	0.0	46.6	37.12	0.02	53.9	57.1	40.0	0.2	0.1	37.5	50.3	0.4	50.3	30.5
TiO ₂	0.1	0.6	0.0	0.0	0.0	0.0	0.3	0.10	0.04	0.0	0.1		0.1	0.0	0.1	0.0	0.2	0.1	35.7
Al ₂ O ₃	0.7	3.1	0.2	2.3	0.0	0.1	3.1	13.70	0.04	0.0	0.2	1.1	0.1	57.0	12.5	1.5	0.1	0.0	4.3
ZnO	3.5	19.6	2.9	13.6	0.4	0.1	1.5	0.11	0.77	0.4	0.3	0.7	2.5	33.3	0.1	0.7	2.0	0.2	0.0
FeO	4.3	60.2	4.4	66.0	3.4	92.9	18.4	18.87	91.85	3.8	2.5	3.1	88.3	5.3	17.6	14.3	90.6	0.3	0.5
MnO	8.3	6.2	9.7	7.6	0.6	0.1	1.0	4.27	0.25	1.0	0.5	0.2	0.8	0.2	4.7	1.4	0.4	0.1	0.0
MgO	9.4	0.1	8.9	0.0	16.8	0.0	4.6	0.20	0.00	15.7	21.9	24.2	0.1	2.8	0.2	7.7	0.1	0.1	0.1
CaO	21.3	0.0	21.2	0.1	24.9		22.7	26.11		24.3	13.3	0.1	0.0	0.1	26.2	23.2	0.1	48.4	29.4
H ₂ O											2.1								
Total	100.9	90.1	100.4	89.8	101.6	93.2	98.2	100.48	92.97	99.1	98.0	92.1	92.1	98.8	99.1	93.9	99.5	100.5	100.5
Si	2.051	0.012	2.061	0.008	2.003	0.000	1.890	2.937	0.001	2.009	8.000	3.468	0.008	0.003	3.027	1.977	0.015	0.984	0.974
Ti	0.003	0.018	0.000	0.000	0.000	0.000	0.008	0.006	0.001	0.000	0.010		0.003	0.000	0.006	0.000	0.006	0.002	0.857
Al	0.032	0.147	0.009	0.109	0.000	0.005	0.150	1.278	0.002	0.000	0.033	0.112	0.005	2.000	1.190	0.070	0.004	0.000	0.161
Zn	0.100	0.582	0.083	0.403	0.010	0.002	0.044	0.007	0.022	0.011	0.031	0.045	0.072	0.732	0.006	0.020	0.056	0.003	0.000
Fe	0.138	2.024	0.143	2.217	0.104	2.991	0.623	1.249	2.966	0.118	0.293	0.224	2.880	0.132	1.188	0.470	2.895	0.005	0.013
Mn	0.270	0.211	0.319	0.259	0.019	0.002	0.034	0.286	0.008	0.032	0.059	0.015	0.026	0.005	0.321	0.047	0.013	0.002	0.000
Mg	0.539	0.006	0.515	0.000	0.901	0.000	0.276	0.024	0.000	0.872	4.573	3.126	0.006	0.124	0.024	0.451	0.006	0.004	0.003
Ca	0.867	0.000	0.870	0.004	0.963		0.976	2.214		0.958	1.971	0.009	0.000	0.003	2.238	0.965	0.004	1.001	0.992
OH											2.000								

¹ Cores of large grains² Wavelength dispersive analysis using Camebax instrument at State University of New York at Stony Brook³ This Bt contains substantial Ba and probably Ti; the measurements reported constitute only a partial analysis

Mineral abbreviations in Table 1

TABLE 6. Microprobe Analyses of Carbonates

Sample no.	SH124-															
	J844	J858	J859	J8523	J8524	J8525	J8528	J867	J871	SU112	SU115	SU121	19	36	126	155
ZnO	0.3	0.1	0.0	0.0	0.2	0.0	0.1	0.2	0.2	0.6	0.2	0.3	0.1	0.0	0.0	0.1
FeO	0.5	0.2	0.2	1.2	0.6	0.4	0.2	0.2	0.4	0.3	0.8	0.3	0.2	0.3	0.3	0.4
MnO	13.7	9.5	9.5	2.7	13.4	13.1	4.8	9.8	9.4	19.8	18.0	9.1	5.1	3.9	1.1	0.6
MgO	1.9	1.7	1.9	1.7	2.0	1.6	0.8	1.2	1.8	3.5	2.1	0.7	0.2	0.3	1.4	0.2
CaO	39.2	45.3	44.4	50.0	40.6	42.0	50.5	45.4	44.7	34.0	36.7	46.4	50.3	52.1	53.5	55.4
CO ₂	41.4	43.5	43.0	43.5	42.4	43.1	43.2	42.8	42.8	43.2	42.5	43.0	43.0	43.8	44.3	44.4
Total	97.0	100.3	99.0	99.1	99.2	100.2	99.6	99.6	99.3	101.4	100.3	99.8	98.9	100.4	100.6	101.1
Zn	0.003	0.002	0.000	0.000	0.002	0.000	0.002	0.003	0.002	0.008	0.003	0.004	0.001	0.000	0.000	0.001
Fe	0.008	0.003	0.003	0.017	0.008	0.006	0.003	0.002	0.006	0.005	0.011	0.004	0.003	0.004	0.004	0.006
Mn	0.205	0.137	0.139	0.039	0.196	0.194	0.069	0.142	0.137	0.286	0.263	0.132	0.074	0.056	0.016	0.008
Mg	0.050	0.044	0.049	0.043	0.052	0.023	0.020	0.031	0.046	0.090	0.054	0.017	0.005	0.008	0.035	0.005
Ca	0.733	0.814	0.809	0.901	0.742	0.777	0.906	0.822	0.809	0.612	0.668	0.843	0.916	0.932	0.945	0.980

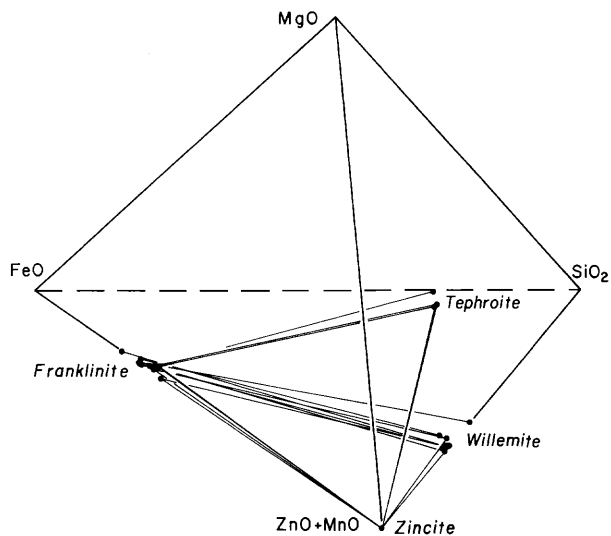


FIG. 2. Mineral assemblages in samples of common ore projected from calcite. Data from Table 4.

slope equal to one (Fig. 11), as they would if they had retained oxygen isotope fractionations established during granulite facies metamorphism. (The equilibrium fractionation between calcite and magnetite at 750°C (Matthews et al., 1983; Clayton et al., 1989) is shown in Figure 11 as an estimate of the peak metamorphic fractionation.) The data instead define an arcuate disequilibrium array which suggests that ¹⁸O-depleted ores were exchanged and enriched in ¹⁸O and that the kinetics of exchange were more favorable for calcite than for franklinite. Gregory and Criss (1986) have ascribed similar arrays at other localities to exchange with infiltrating fluids. The infiltration interpretation is further supported by the bright and

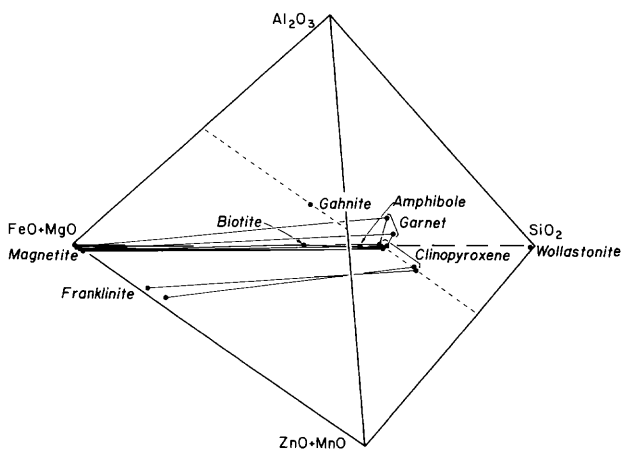


FIG. 3. Mineral assemblages in representative calc-silicate samples projected from calcite, CaO, K₂O, and H₂O. Data from Table 5.

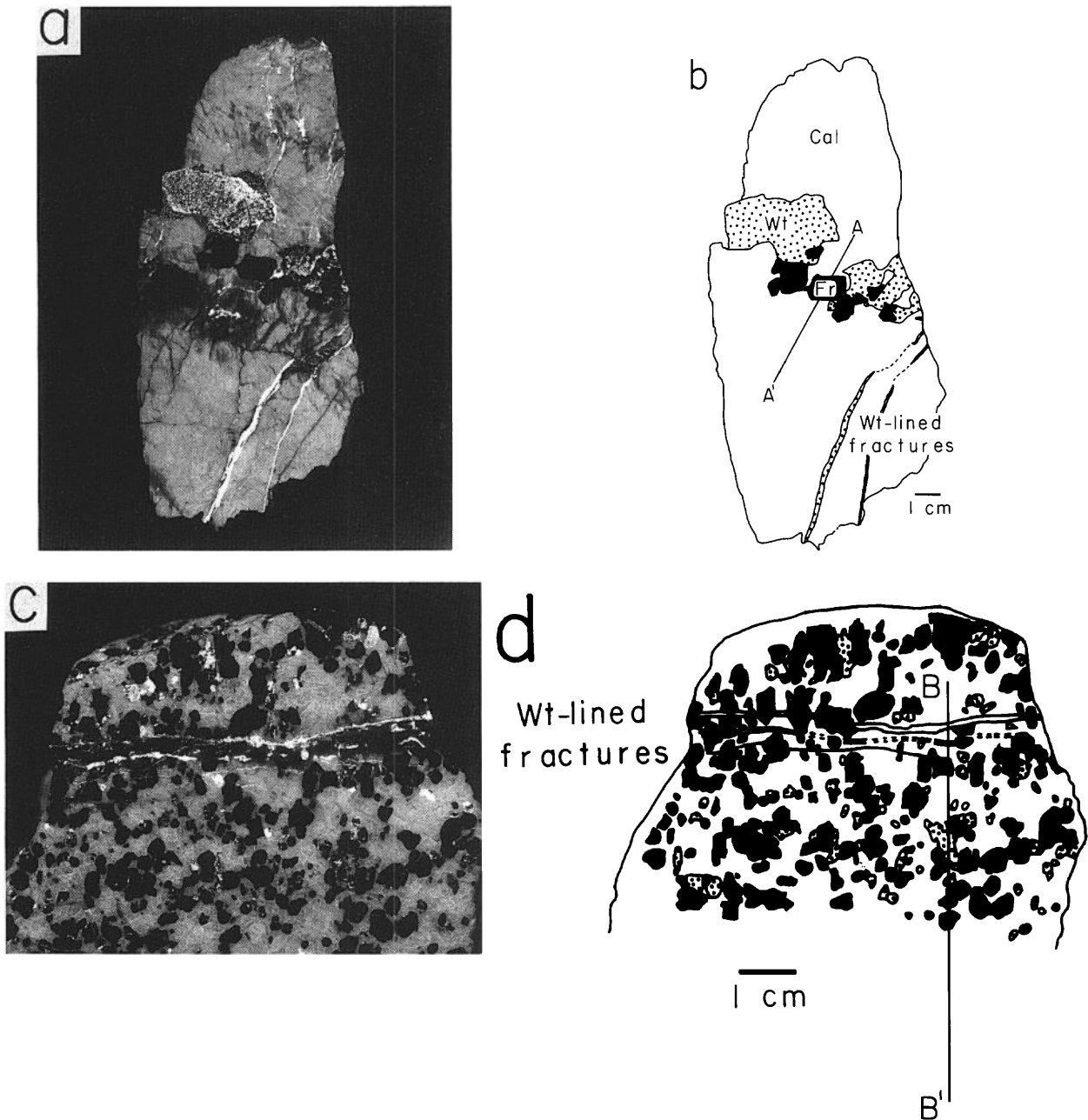


FIG. 4. (a) Fluorescence of coarse-grained ore under shortwave ultraviolet illumination. Bright areas are green-fluorescing willemite which occurs as veins and large intergrown crystals with patchy and irregular fluorescence. Next brightest areas are red-fluorescing calcite. Dark areas are franklinite and calcite which have been altered by retrograde metamorphic fluid. b. Same specimen as in (a). c. Fluorescence of calcite + tephroite + franklinite specimen cut by willemite-lined fracture under shortwave ultraviolet illumination. Brightest areas are green-fluorescing willemite which occurs as veins and replacements of tephroite near the vein. Next brightest areas are red-fluorescing calcite. Dark areas are franklinite and, near the vein, calcite which has been altered by retrograde metamorphic fluid. d. Same specimen as in (c). Stippled pattern represents tephroite, black represents franklinite. A-A' and B-B' are traverses along which microprobe and isotopic data were collected (Fig. 6).

homogeneous fluorescence of willemite in samples which plot on the upper end of the array. Bright fluorescence is known to be characteristic of willemite

which reacted with the fracture-related fluids, and the observation suggests that ^{18}O -enriched rocks experienced infiltration, despite the fact that they do

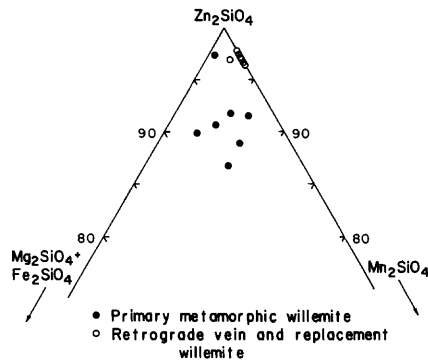


FIG. 5. Compositions of Sterling Hill willemite (energy dispersive microprobe analyses). Vein and replacement occurrences are essentially devoid of iron and magnesium unlike primary metamorphic occurrences.



FIG. 7. Photomicrograph showing willemite pseudomorphous after tephroite within a few centimeters of a willemite-lined fracture. Field of view is about 0.5 mm, crossed polars.

not always contain obvious veins. Reaction of willemite with fracture-related fluids may be partly responsible for the crossing tielines in Figure 2.

The timing of brittle fracturing and fluid flow is only approximately known. The fractures crosscut the isoclinal folds which appear to represent the final phase of deformation associated with the ~1,000-Ma Grenville metamorphism. They resemble, in some respects, retrograde shear zones which have been described elsewhere in the region (Hull et al., 1986) and are inferred to have formed when the terrane had cooled some 200° to 300°C from the Grenville thermal maximum of 700° to 800°C. If the mean cooling rate of the rocks was 3°C/Ma, fracturing would have occurred in the interval 900 to 933 Ma, some 67 to 100 Ma after the thermal maximum. The K-Ar measurements reported in Table 10 are consistent with such a conclusion. Biotites which formed by replacement reactions give the same date for Ar closure, about 900 Ma, as foliated primary biotite from a

nearby gneiss fragment. Because the dates represent closure of the minerals to Ar diffusion at about 300° to 350°C (e.g., Berger and York, 1981), the data give a lower age limit for the fluid-driven reactions of 900 Ma.

In principle, the oxygen isotope data in Figure 11 give the temperature, and therefore the point on the retrograde metamorphic path, at which infiltration took place. Mineral pairs which plot on the upper end of the array of data, if they have equilibrated with the fluid, reveal the temperature of exchange in their isotopic fractionation. In practice, the data permit only an approximation. It is uncertain that the minerals in sample J8523 (Table 9) fully equilibrated with the fluid; their fractionation therefore gives only a lower bound for the temperature. If one accepts that franklinite fractionates oxygen isotopes like magnetite, then the lower limit for the temperature of infiltration is 670°C.

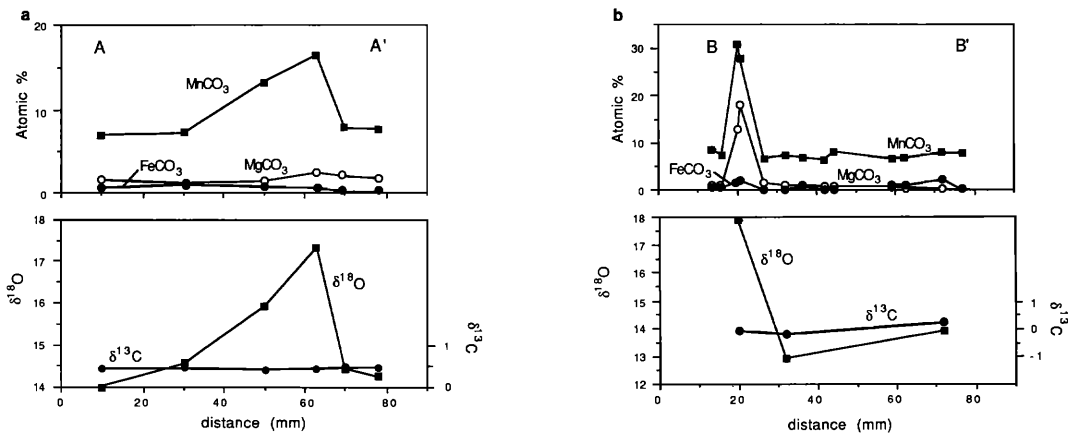


FIG. 6. Isotopic and chemical compositions (energy dispersive microprobe analyses) of calcite along traverses crossing retrograde metamorphic fractures. a. Traverse A-A' is marked in Figure 4b. Traverse B-B' in Figure 4d.

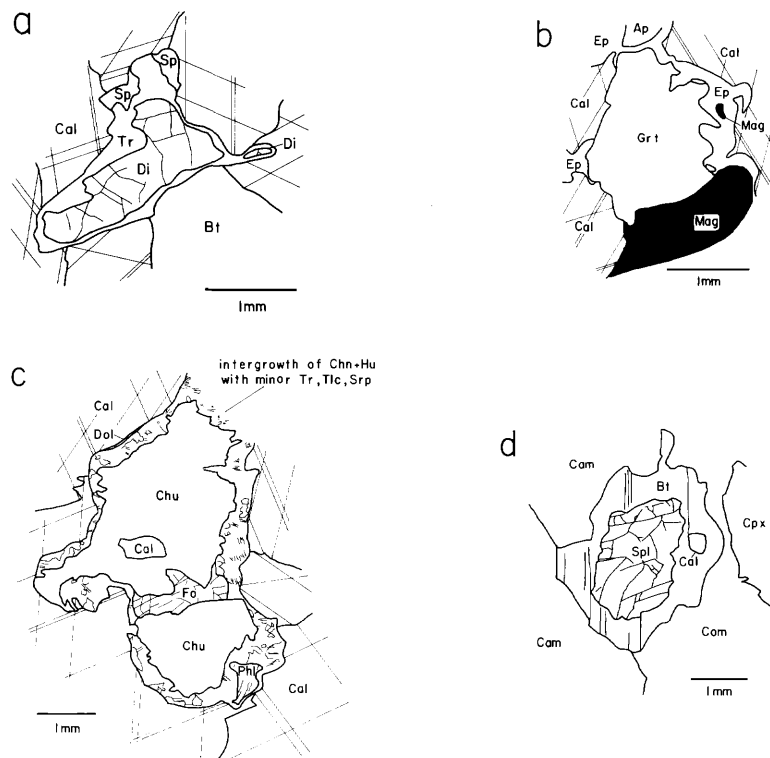


FIG. 8. Examples of rimming mineral textures observed in samples of ore, calc-silicate, and wall rock. a. Calc-silicate sample SH12478. b. Calc-silicate sample SH124103. c. Wall-rock sample J8511. d. Calc-silicate sample SU34. Abbreviations are in Table 1.

The fractionation of oxygen isotopes between calcite and H_2O changes relatively little, from 3 to 0 per mil, between 400° and 700°C (O'Neil et al., 1969). Thus, despite the uncertainty in the temperature of infiltration, the $\delta^{18}O_{H_2O}$ value of the infiltrating fluid is constrained to the range 15 to 18 per mil. The large value suggests that the fluid was derived from, or had exchanged oxygen extensively with, pelites and possibly carbonates within the metamorphic pile prior to the time that it infiltrated the deposit.

Primary Characteristics and Processes

Rocks isolated from crosscutting fractures are free of veins and other mineralogic evidence of retrograde fluid infiltration, and they represent the best record of the last fluid-dominated process to have affected the ores. It is the nature of this process, whether it was metal deposition under oxidizing conditions or the secondary oxidation—potentially weathering—of a preexisting sulfide deposit, which is the critical genetic issue at Sterling Hill.

With respect to the secondary oxidation hypothesis, it is instructive to estimate the amount of H_2O which would have been required to entirely strip the sulfur from a preexisting sulfide body. A sulfide deposit with the same quantity of zinc, iron, and manganese as

Sterling Hill would contain at least 2.6×10^9 kg sulfur. Complete oxidation of the body would produce 7.9×10^9 kg sulfate ion which would require a large flux of H_2O for its removal. For waters flowing through calcite-bearing rocks or sediments, the sulfate-carrying capacity would probably be limited by the solubility of gypsum or anhydrite. At 1 bar and 25°C, the solubility of gypsum in H_2O is 0.017 mole/l (Holland and Malinin, 1979). In order to remove the sulfur from the hypothetical protolith under these conditions, a minimum of 4.8 km^3 H_2O would be required to pass through the deposit. The solubility of calcium sulfate (gypsum is the stable phase below 57°C, and anhydrite above) decreases with increasing temperature and increases with increasing pressure and NaCl concentration (Holland and Malinin, 1979). However, at the temperatures, pressures, and NaCl concentrations to be expected at the land surface, on the sea floor or during diagenesis, the solubility is unlikely to exceed 0.1 mole/l which implies that a minimum H_2O volume of 0.82 km^3 would be required to strip the body of its sulfur. This corresponds to a volumetric H_2O /rock ratio of about 50/1.

The formation of Sterling Hill, like any hydrothermal ore deposit, must have involved a large volume of H_2O so that the zinc, iron, and manganese could be transported, and the H_2O flow must have been

focused at the depositional site for the metals. The secondary oxidation hypothesis would require that a second large H₂O volume flowed through the exact same site. The probability of such an occurrence while the deposit was overlain by any significant thickness of sediment is extremely remote. Thus secondary oxidation, if it occurred, must have been a surficial process involving either ground water or seawater.

Primary features of the protolith

An important characteristic of the deposit is the variation in chemical and isotopic compositions of individual minerals between lithologic strata and the generally uniformity of compositions within a stratum. The isotopic data from coexisting calcite and franklinite can be used to establish that the variation is a primary feature of the minerals rather than a product of retrograde fluid infiltration.

Figure 12, an expansion of Figure 11, shows isotopic data from the rocks lacking obvious petrologic evidence for retrograde infiltration. The data indicate isotopic disequilibrium (i.e., they fail to define a line with slope equal to one), although their departure from equilibrium is less extreme than the most ¹⁸O-enriched assemblages shown in Figure 11. The disequilibrium may have resulted from exchange with small amounts of infiltrating fluid, the net effect of which would have been to shift calcites to slightly larger $\delta^{18}\text{O}$ values while leaving franklinites unchanged. The exchange paths that the samples would have taken from the inferred peak metamorphic fractionation line are shown as vertical lines in Figure 12. Alternatively, the departure from equilibrium could have resulted from exchange of oxygen among minerals in the rocks during retrograde metamorphic cooling. Evidence of such exchange is common in high-grade rocks (e.g., Deines, 1977). The closed-system retrograde path that each sample would have followed was reconstructed using modal and isotopic data (Tables 2 and 9) and the methodology of Gregory and Criss (1986). All minerals in the assemblages were assumed to have exchanged oxygen, and all mineral-mineral fractionations were assumed to approach zero as temperature approaches infinity. The results are shown in Figure 12 as sloping lines joining the data points with their inferred starting points. Combinations of the two processes, infiltration and closed system retrograde exchange, would have shifted the samples along trajectories between the two end-member cases within the shaded triangles corresponding to each datum (Fig. 12). It is clear that, no matter what the relative importance of the two processes, the primary isotopic compositions of franklinite and calcite varied by at least 3 per mil within the deposit. The conclusion is not sensitive to the position of the peak metamorphic fractionation line and is

therefore valid despite the fact that the calcite-franklinite fractionation has been approximated by using calcite-magnetite.

The presence of isotopic and chemical variation in a given mineral from one layer to another indicates that mineral compositions were not controlled by a pervasive fluid but rather that they reflect, at least in part, the bulk isotopic and chemical compositions of the rocks. Thus the fluid-dominated process which established the bulk compositions of the ores must have occurred prior to the growth of the willemite + franklinite \pm zincite + calcite assemblages. The layer-to-layer variation in mineral composition resulted from isotopic and elemental partitioning among the metamorphic minerals within individual strata.

A second important characteristic of the deposit is its ¹⁸O-depleted bulk composition compared to the Franklin Marble which, at 20 to 25 per mil, has a composition typical of Proterozoic marine limestone. Willemite-, franklinite-, or zincite-bearing strata range from 6.1 to 12.5 per mil. Nearly pure marble bands interbedded with ore layers have isotopic compositions in the narrow range of 15 to 16 per mil, as does the marble wall rock adjacent to the calc-silicate units (Figs. 9 and 10).

The uniform isotopic compositions of the interbedded marbles is not likely to have resulted from oxygen exchange with the retrograde fluid because infiltration affected the deposit only locally along crosscutting fractures. The uniform compositions are also unlikely to have resulted from exchange between marbles and adjacent lithologic units during high-grade metamorphism. Calcite in the ore layers varies widely in $\delta^{18}\text{O}$ from unit to unit (Table 9, Fig. 9) and oxygen exchange across lithologic contacts would have produced a range of $\delta^{18}\text{O}$ values in the marble layers approaching that observed in other units rather than the narrow range of 15 to 16 per mil. It appears most reasonable to attribute the isotopic compositions to exchange between the marble layers and a large fluid reservoir during the last fluid-dominated process to have affected the rocks. The isotopic composition of the marble wall rock adjacent to the calc-silicate unit may have been established by the same process. However, it is also possible that the compositions result from infiltration of the wall rocks by fluids derived from metamorphic decarbonation of the calc-silicates. Rye et al. (1976) observed similar ¹⁸O depletions in high-grade marbles where they are in contact with pelitic schists, and they attributed them to infiltration of the marbles by metamorphic fluids derived from the schists. Moreover, Metsger et al. (1969) suggested that the ore-host rock contacts may in fact be faults which, if correct, would cast doubt on the interpretation of the ¹⁸O depletion in the footwall of the east limb as wall-rock alteration produced during the metal-depositing event.

TABLE 7. Microprobe Analyses of Representative

Sample no.	SH12478			J8515					
	Bt ¹	Tr	Cal	Di(p) ²	Tr	Cal	Dol	Fo(p)	Chu
SiO ₂	41.4	55.6		56.1	57.1			38.2	36.2
TiO ₂	1.5	0.0		0.0	0.1			0.0	0.1
Al ₂ O ₃	13.2	1.3		0.0	1.3			0.0	0.0
ZnO	0.3	0.2	0.0	0.0	0.1	0.0	0.1	9.1	7.7
FeO	5.2	4.4	0.3	0.1	0.3	0.1	0.2	4.7	3.5
MnO	0.1	0.5	0.8	0.0	0.2	0.0	0.1	0.8	0.8
MgO	23.2	20.7	0.7	18.6	24.4	0.9	21.9	45.5	49.4
CaO	0.0	13.2	54.5	26.0	13.7	55.9	29.7	0.0	0.0
H ₂ O		2.1			2.2				2.7
CO ₂			44.1			44.9	47.4		
Total		98.0	100.4	100.8	99.4	101.8	99.4	98.3	100.4
Si	2.979	7.838		2.005	7.770			0.976	3.951
Ti	0.079	0.000		0.001	0.011			0.000	0.012
Al	1.111	0.223		0.000	0.208			0.000	0.000
Zn	0.014	0.019	0.000	0.001	0.009	0.000	0.001	0.172	0.620
Fe	0.312	0.519	0.004	0.004	0.034	0.001	0.001	0.100	0.320
Mn	0.008	0.061	0.011	0.001	0.019	0.000	0.001	0.017	0.070
Mg	2.497	4.346	0.016	0.992	4.955	0.023	0.504	1.735	8.024
Ca	0.000	1.996	0.969	0.996	1.994	0.977	0.492	0.000	0.002

¹ Partial analysis² p = primary mineral in the assemblage, r = rim composition

TABLE 8. Bulk Chemical Compositions

Sample no.												SH124-				
	J844	J858	J859	J8523	J8524	J8525	J8528	J867	J871	SU112	SU115	SU121	19	36	126	155
Oxides (wt %)																
SiO ₂	6.2	4.4	3.6	8.2	2.6	8.3	10.9	13.8	0.7	3.2	6.7	9.2	37.4	2.9	29.4	28.0
TiO ₂	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.0	0.0	0.0	0.1	0.0	0.0	0.0
Al ₂ O ₃	0.2	0.3	0.3	0.5	0.3	0.3	0.2	0.1	0.4	0.4	0.3	0.4	0.9	1.2	0.1	6.0
ZnO	17.9	26.8	19.9	27.9	12.1	26.1	6.8	39.6	52.5	63.1	25.2	31.9	5.0	7.3	0.2	0.4
FeO	8.0	16.5	19.2	18.6	16.5	17.6	7.7	20.8	28.7	12.0	22.8	15.6	10.9	35.2	2.2	18.0
MnO	10.8	12.0	12.0	1.4	11.3	9.2	14.0	7.3	10.7	5.6	11.3	6.3	7.4	6.3	1.0	2.6
MgO	1.3	3.4	2.3	0.8	1.3	1.3	7.4	0.2	0.1	0.9	0.8	0.6	6.7	0.6	9.9	1.9
CaO	25.7	18.2	19.6	20.9	26.5	17.8	28.1	8.2	2.2	6.2	14.4	18.0	23.6	24.0	35.8	31.0
H ₂ O	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.2	0.0
CO ₂	27.1	17.4	19.0	18.1	27.7	18.3	23.9	7.7	2.1	7.9	16.8	16.8	7.4	19.2	19.5	11.3
Total	97.2	99.0	95.9	96.4	98.3	98.9	99.0	97.7	97.5	99.3	98.3	98.8	99.4	96.7	98.3	99.2
Cations (atomic %)																
Si	6.1	4.6	3.8	8.7	2.5	8.6	10.1	16.0	0.9	3.8	7.1	9.7	36.3	3.0	25.8	26.9
Ti	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.0	0.0	0.0	0.1	0.0	0.0	0.0
Al	0.2	0.4	0.2	0.6	0.2	0.2	0.2	0.2	0.6	0.6	0.4	0.6	1.0	1.4	0.0	6.8
Zn	12.9	20.5	15.5	21.9	8.7	20.0	4.7	33.8	49.4	55.6	19.8	24.8	3.6	5.6	0.2	0.3
Fe	6.6	14.3	16.8	16.5	13.4	15.3	6.0	20.0	30.5	12.0	20.4	13.8	8.9	30.2	1.6	14.5
Mn	9.0	10.5	10.7	1.3	9.3	8.1	10.9	7.2	11.6	5.6	10.2	5.7	6.2	5.5	0.7	2.1
Mg	1.8	5.2	3.7	1.3	1.9	2.0	10.3	0.4	0.2	1.5	1.3	1.0	9.7	0.9	13.0	2.6
Ca	27.0	20.1	22.0	23.5	27.5	19.8	27.8	10.2	3.1	8.0	16.5	20.4	24.6	26.4	33.8	32.0
H	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1.4	0.0
C	36.4	24.5	27.1	26.2	36.6	25.9	30.2	12.2	3.7	13.0	24.4	24.2	9.8	27.0	23.5	14.9

Replacement Minerals

J8511				SH124103			SH124145			
Dol	Cal	Chn	Hu	Cpx(r) ²	Ep ³	Cal	Mag	Hu	Cal	Dol
		31.7	35.1	50.9	37.44		0.3	36.0		
		0.0	0.1	0.3	0.02		0.0	0.0		
		0.0	0.0	0.4	22.24		0.2	0.0		
0.7	0.1	9.5	7.1	1.2	0.02	0.0	2.5	0.8	0.0	0.0
0.8	0.2	3.8	3.7	14.3	13.67	0.4	89.5	4.5	0.1	0.6
0.6	0.3	0.8	0.8	1.3	0.18	0.8	1.3	1.0	0.5	1.0
21.1	1.6	47.6	51.3	8.1	0.01	0.2	1.4	55.3	1.6	21.4
30.6	53.1	0.1	0.1	23.8	24.59	54.4	0.0	0.0	54.2	30.7
		4.9	3.6		1.90			3.7		
48.3	43.8					43.7			44.6	48.4
102.1	99.1	98.4	101.8	100.3	100.07	99.5	95.2	101.3	101.0	102.1
		1.953	2.907	1.981	2.957		0.011	2.912		
		0.000	0.007	0.009	0.001		0.000	0.000		
		0.000	0.000	0.018	2.070		0.009	0.000		
0.008	0.001	0.433	0.432	0.034	0.001	0.000	0.069	0.048	0.000	0.000
0.010	0.003	0.193	0.256	0.465	0.903	0.006	2.792	0.304	0.001	0.008
0.008	0.004	0.043	0.056	0.043	0.012	0.011	0.041	0.068	0.007	0.013
0.476	0.040	4.370	6.333	0.470	0.001	0.020	0.078	6.667	0.040	0.485
0.497	0.952	0.008	0.010	0.980	2.054	0.963	0.000	0.000	0.952	0.494

³ Wavelength dispersive analysis using the Camebax instrument at State University of New York at Stony Brook
Mineral abbreviations in Table 1

TABLE 9. Isotopic Compositions of Minerals and Computed Whole-Rock Values

	Cal		Wt		Tp		Fr		Zc		Whole rock
	$\delta^{13}\text{C}$	$\delta^{18}\text{O}$	Yield (%)	$\delta^{18}\text{O}$	Yield (%)	$\delta^{18}\text{O}$	Yield (%)	$\delta^{18}\text{O}$	Yield (%)	$\delta^{18}\text{O}$	$\delta^{18}\text{O}$
J844	0.5	14.0	91	9.6			93	5.5			12.5
	0.6	14.1	94	9.5			93	5.7			
J8444	0.5	15.8					96	7.5			
J859	0.6	12.1			95	6.9	87	6.1	76	5.1	9.6
	0.7	11.9			93	7.3	63	6.3	48	5.5	
					97	6.8					
J8523	0.9	17.5	97	11.0			93	11.1			
	1.1	17.6	98	11.4							
J8524	0.4	11.8	100	9.4			98	5.2			10.4
	0.3	11.7	101	8.6			97	4.5			
							96	4.6			
J8528	1.0	12.8			86	8.5	98	6.0			11.1
	0.7	12.9									
J867	-0.2	15.7	100	11.3			97	6.3			
	-0.4	15.8					96	6.6			
J871 ¹	-1.0	14.1	66	7.4			92	6.1	91	4.0	6.1
			114	7.6			98	5.8	48	3.9	
			117	7.6							
M9	0.6	12.8	94	9.0			93	3.5			7.8
	0.6	12.8									
G12	0.0	14.8	98	8.2			48	6.9	102	5.6	
	0.0	14.7	100	8.8							

¹ Wt in this sample is largely replaced by secondary minerals (note the apparent surplus oxygen yield), and the reported composition may not reflect the primary Wt value. Wt is a minor phase, however, and the computed whole-rock value is not significantly different from the value that would have been obtained if a pure separate had been analyzed

Mineral abbreviations in Table 1

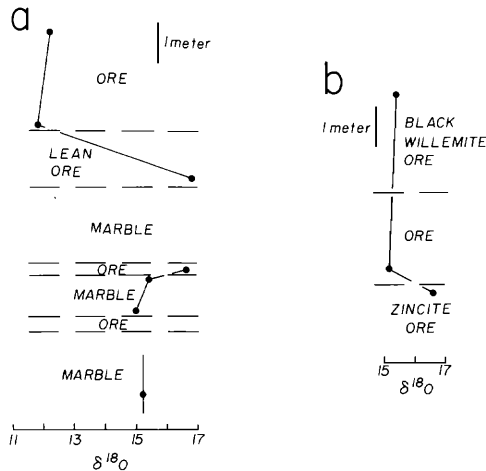


FIG. 9. Stratigraphic variation in the oxygen isotope composition of calcite. a. A section in the transverse portion of the deposit. b. A section in the west limb.

The interbedded marble compositions place an important constraint on the metal depositing-oxidizing fluid. Because the oxygen isotope fractionation between calcite and H_2O depends only on temperature, the $\delta^{18}O_{H_2O}$ value and temperature of the fluid from which the calcites precipitated are related by the equation:

$$\delta^{18}O_{H_2O} = -2.78 \times 10^{-6}T^{-2} + 17.89 \quad (2)$$

(O'Neil et al., 1969). The possible combinations of $\delta^{18}O_{H_2O}$ and temperature are illustrated in Figure 13. Some potential sources of the fluid based solely on oxygen isotope composition are also indicated.

A third important characteristic of the deposit is its oxidation and sulfidation state. The stability limits of phases in the systems Fe-S-O, Zn-Al-Si-S-O, and Mn-Si-S-O can be used to constrain f_{O_2} and f_{S_2} , and the limiting reactions have been calculated using the equation:

$$-\Delta G_{298}^{\circ} = \Delta V_{298}^{\circ} \Delta P + RT \ln f_{O_2}^x f_{S_2}^y + RT \ln K, \quad (3)$$

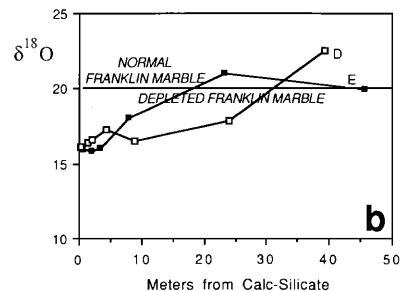
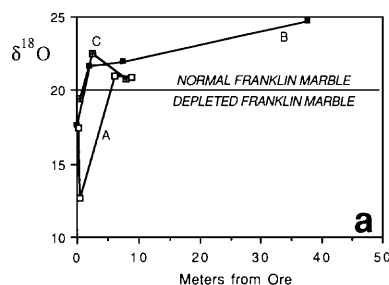


FIG. 10. Oxygen isotope composition of wall-rock calcite along traverses A-E shown in Figure 1. a. Traverses outward from ore. b. Traverses inward toward the core of the synform. Distances were measured in a horizontal plane approximately perpendicular to the contact.

TABLE 10. Biotite K-Ar Analytical Data

Sample	Biotite occurrence	K (wt %) ¹	cc ⁴⁰ Ar/gm ($\times 10^{-6}$)	Date (Ma) ²
SU36	Rimming	7.32	324.2	884 \pm 35 ³
SU39	Rimming	6.95	318.7	908 \pm 36
SU94	Primary metamorphic	7.86	347.6	883 \pm 35

¹ Measured by atomic absorption

² Calculated using decay constants in Steiger and Jager (1977)

³ Uncertainty reported is 2 sigma, the standard error on the mean of multiple analyses

where ΔV_{298}° is the volume change of the solid phases at 1 bar and 298K, ΔP and T are the conditions of metamorphism, 5,000 bars and 1,000K, R is the gas constant, x and y are the coefficients for O_2 and S_2 , respectively, in a given reaction, and K is the equilibrium constant for the solid phases. The results are shown in Figure 14a to c, and a summary diagram is given in Figure 14d. Free energy data were taken from the compilations of Robie et al. (1978) and Essene and Peacor (1987), and from Schaefer (1982; Mn_3O_4 , Mn_2O_3), Schaefer (1983; $MnSO_4$), Robie et al. (1982; Mn_2SiO_4), Robie and Hemingway (1985; MnO_2), and Mills (1974; MnS_2). Molar volumes were taken from Robie et al. (1978).

The most common assemblage in the ore layers is willemite + franklinite + calcite. In these rocks franklinite generally contains at least 10 mole percent magnetite in solid solution, and the magnetite component can be used to constrain the range of f_{O_2} over which the mineral is stable. Dilution of magnetite by franklinite will shift the magnetite-wustite equilibrium to lower f_{O_2} and the magnetite-hematite equilibrium to higher f_{O_2} . The shifts in f_{O_2} have been calculated using equation (3), assuming $a_{Mag} = X_{Mag}$, and the results are shown by dashed lines in Figure 14a and d. The f_{O_2} value corresponding to these rocks is in the range $10^{-19.4}$ to $10^{-6.8}$, and the f_{S_2} value, based on the presence of nearly pure willemite rather than

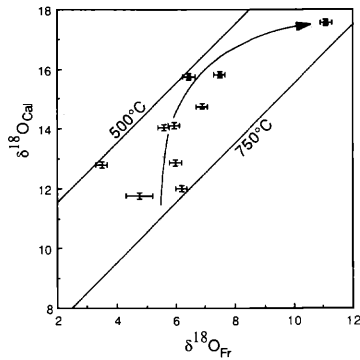


FIG. 11. Oxygen isotope compositions of coexisting calcite and franklinite from ten Sterling Hill ore samples. Calcite is the most ^{18}O -enriched mineral in all samples; franklinite is the most ^{18}O -depleted mineral in all but two samples which contain zincite. Equilibrium fractionations at 750° and 500°C are taken from the system calcite-magnetite (see text). Samples with bright and homogeneously fluorescent willemite are indicated with filled circles. The arrow shows the effect on the rocks of exchange with the infiltrating retrograde fluid.

sphalerite + quartz or zinc sulfate + quartz, is below $10^{-1.9}$ (Fig. 14b and d).

Franklinite in zincite- or tephroite-bearing ores generally contains little or no magnetite in solid solution, and the magnetite-wustite and magnetite-hematite equilibria cannot, therefore, be used to constrain f_{O_2} . The absence of a magnetite component does not necessarily mean that the rocks formed at an f_{O_2} at which magnetite is unstable; the component may have been destabilized by the higher bulk zinc and manganese contents of the rocks. The presence of

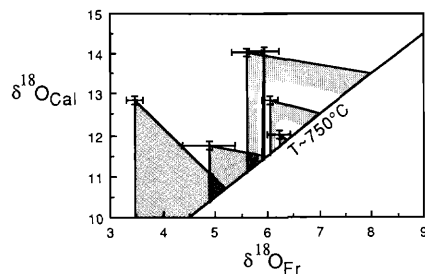


FIG. 12. Oxygen isotope compositions of coexisting calcite and franklinite from the rocks which were least affected by retrograde infiltration. Each datum is at the vertex of a shaded triangle, one leg of which is the locus of inferred starting points for the sample at the metamorphic thermal peak ($T \sim 750^\circ\text{C}$). The vertical legs of the shaded triangles represent retrograde exchange with the infiltrating fluid; the negatively sloped (with one exception) legs represent retrograde exchange among the minerals present in each sample. Any given sample has a range of possible starting points on the $T \sim 750^\circ\text{C}$ line reflecting the degree to which exchange involved the infiltrating fluid. Whether or not the fluid participated in the retrograde exchange, franklinite and calcite $\delta^{18}\text{O}$ values in the deposit must have originally spanned a range of at least 3 to 4 per mil.

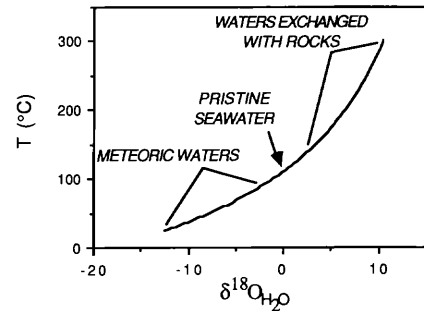


FIG. 13. Possible combinations of temperature and $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ for the metal depositing-oxidizing fluid. The curve was derived from the calcite- H_2O fractionation of O'Neil et al. (1969) assuming that the fluid was in isotopic equilibrium with 15 per mil marble. Some possible sources for the fluid, based solely on oxygen isotope composition, are shown.

zincite and tephroite provide broad limits on f_{O_2} and f_{S_2} values (Fig. 14b and c). Whereas the zincites are relatively pure, tephroites are commonly diluted by other components (Table 4). The displacement of the end-member tephroite reactions corresponding to 50 percent dilution by other components, assuming $a_{\text{T}_p} = X_{\text{T}_p}^2$, is shown in Figure 14d.

The sphalerite + calcite + willemite + franklinite + loellingite + graphite rock which occurs in a small volume in the transverse portion of the deposit (see Geologic Setting section) represents an environment of lower f_{O_2} and/or higher f_{S_2} than zincite-bearing ores (Fig. 14d). If the assemblage is primary rather than a product of retrograde metamorphic fluid infiltration, then it suggests layer-to-layer variation in f_{O_2} and/or f_{S_2} within the deposit. Otherwise, the stability fields delineated above all overlap, and the equilibria considered here neither demonstrate nor preclude layer-to-layer variations.

The Franklin Marble surrounding the deposit contains pyrrhotite and pyrite, and it is an environment lower in $f_{\text{O}_2}/f_{\text{S}_2}$ than the ores and related rocks. The fact that willemite and zincite are stable at higher $f_{\text{O}_2}/f_{\text{S}_2}$ than iron sulfides was pointed out previously by Essene and Peacor (1987). The possibility that the contrast in $f_{\text{O}_2}/f_{\text{S}_2}$ across the ore-host rock contact is a product of a metamorphic process is extremely remote. It is more likely that it is a feature inherited from the protolith for the deposit, and that metal deposition, or the alteration of a preexisting sulfide body, took place in an environment higher in $f_{\text{O}_2}/f_{\text{S}_2}$ than marine carbonate sediments.

Mineralogy of the protolith

The main minerals in the protoliths for the ore layers can be reconstituted through analogies with oxidized sphalerite deposits and the oxidized facies of metalliferous sediments such as those beneath the Red Sea brine pools. Mineral assemblages in such envi-

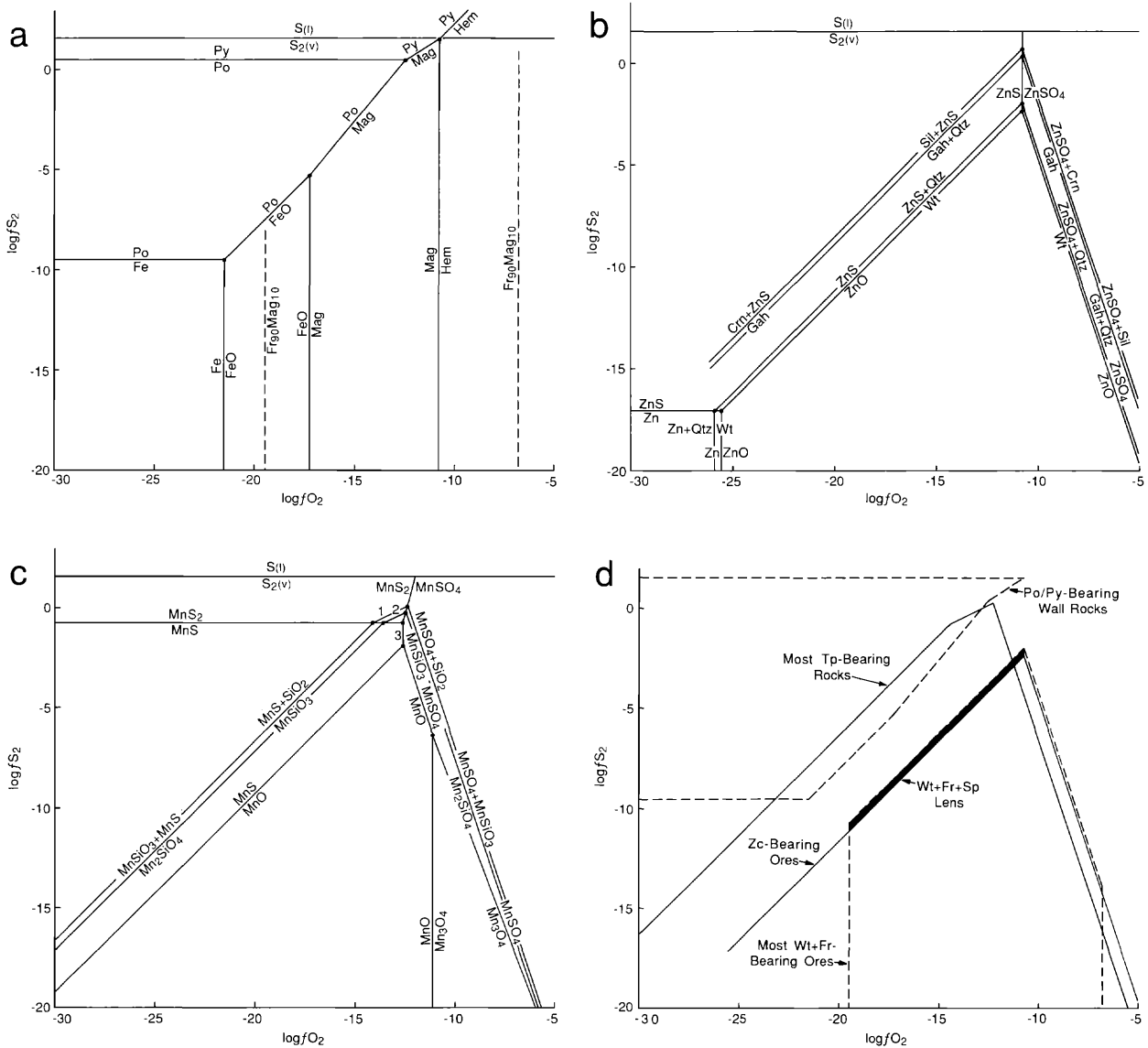


FIG. 14. Stability of phases at 5 kbar and 1,000K in the systems Fe-S-O (a), Zn-Al-Si-S-O (b), and Mn-Si-S-O (c), and a summary diagram showing the stability fields of common assemblages at Sterling Hill (d). Note that willemite and zincite cannot coexist stably with pyrrhotite or pyrite which implies that the ores and the host rocks are not equilibrated chemically. The ores are an environment higher in f_{O_2}/f_{S_2} . See text for sources of thermochemical data; mineral abbreviations are in Table 1. Numbered reactions in (c) are: (1) $2MnSiO_3 + 2S_2 = 2MnS_2 + 2SiO_2 + O_2$, (2) $2Mn_2SiO_4 + 2S_2 = 2MnSiO_3 + 2MnS_2 + O_2$, and (3) $MnS + 2O_2 = MnSO_4$.

ronments generally contain carbonates, smectite-type clays, iron-manganese oxides and hydroxides of varying crystallinity, quartz, and less commonly, hemimorphite ($Zn_4Si_2O_7(OH)_2 \cdot H_2O$) and hydrozincite ($Zn_5(CO_3)_2(OH)_6$) (e.g., Takahashi, 1960; Bischoff, 1969; Singer and Stoffers, 1987).

Calcite, or a calcium-bearing carbonate, can reasonably be assumed to have been present in the protoliths for the ores because calcite is present in all

ore strata and it is the dominant mineral in many strata. The remaining minerals in the protolith can be determined using bulk chemical data. Figure 15 illustrates bulk zinc and zinc + iron + manganese versus silicon for representative samples of ore and calc-silicate along with the ratios characteristic of several minerals which may have occurred in the protoliths. It is clear that zinc is far too abundant to have been contained solely in silicates. Whereas sauconite

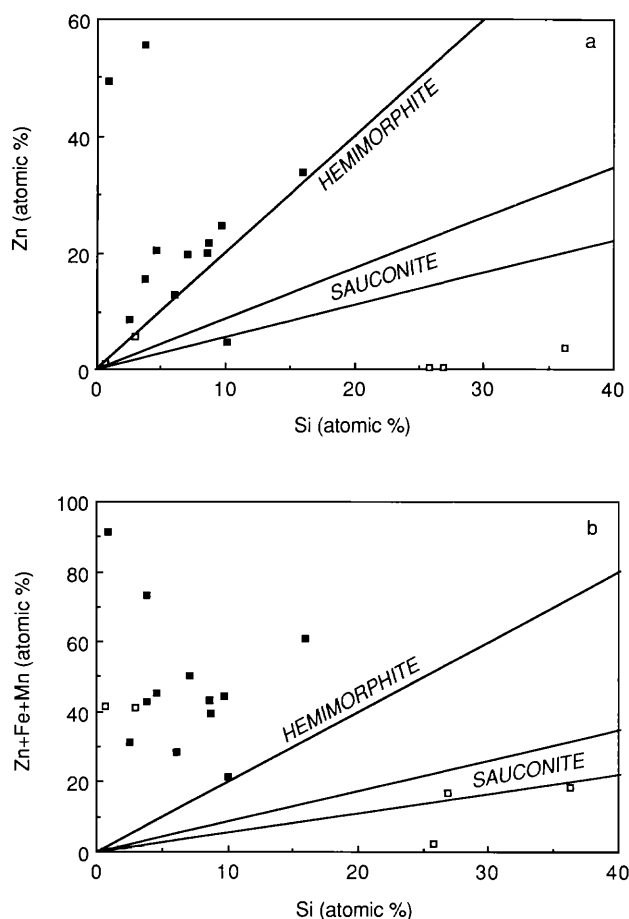


FIG. 15. Bulk cations in ores (filled squares) and calc-silicate rocks (open squares) compared with the cation ratios characteristic of potential protolith minerals. a. Zn versus Si for the rocks compared with Zn/Si ratios characteristic of the zincian smectite sauconite (Ross, 1946; Deer et al., 1962) and the Zn/Si ratio characteristic of hemimorphite. Hemimorphite is shown as a line rather than a field because natural occurrences conform closely to the ideal 2/1 ratio (Phillips and Griffen, 1981). b. Zn + Fe + Mn versus Si for the same rocks. Data from Table 8.

(zincian smectite) and hemimorphite may have been present in the protoliths for the ores, a nonsilicate mineral or minerals must have carried significant amounts of zinc. The same conclusion applies to iron and manganese. Analogy with weathered sphalerite deposits suggests that the minerals were carbonates and/or hydroxides; candidates for the zinc carriers are smithsonite, or smithsonite solid solution in the calcium-bearing carbonate, and hydrozincite. Wulfingite ($\text{Zn}(\text{OH})_2$) is a third candidate although it is rare in nature (Schmetzer et al., 1985) and must be regarded as less likely to have been present. It should be pointed out that the metal depositing-oxidizing process at Sterling Hill may have taken place at temperatures higher than that of weathering where hy-

droxide minerals are unstable relative to oxide minerals.

Calc-silicate units, on the other hand, contain sufficient silicon to have accommodated zinc in a smectite mineral (Fig. 15). In fact, the high silicon concentrations in some samples suggest that a metal-poor silicate, possibly quartz, was present in the protolith for some of the rocks.

Characteristics of the metal depositing-oxidizing fluid

Given these minerals as the main constituents of the ore layers, the temperature and $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ value of the metal depositing-oxidizing fluid can be determined subject to certain conditions. The methodology takes advantage of the fact that the minerals in the protolith would in all likelihood have equilibrated isotopically with the fluid; the bulk $\delta^{18}\text{O}$ values of the ores would then have varied with the relative proportions of the constituent minerals. For example, carbonate minerals partition ^{18}O more strongly than smectite, hydroxide, or oxide minerals. Strata in the protolith which were rich in carbonate, therefore, would have had larger bulk $\delta^{18}\text{O}$ values than those which contained less carbonate. The relationship between the modal abundance of minerals in the protolith, which can be determined by calculating normative minerals from bulk chemical data by methods described below, and bulk isotopic composition can be quantified and then used to determine temperature and $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ value.

The validity of this approach depends on the degree to which the ore layers acted as closed systems since the last fluid-dominated event, in other words whether they have retained their original bulk chemical and isotopic compositions. Metamorphic devolatilization and fluid infiltration are two processes which could have perturbed the compositions. The effects of devolatilization can be estimated by calculating the isotope fractionation which would have accompanied dehydration or decarbonation (e.g., Matthews and Kolodny, 1978). The effects of fluid infiltration are more difficult to assess. In some metamorphic terranes, infiltration appears to have been common, particularly in impure carbonates where permeability may have been enhanced by decarbonation reactions (e.g., Rye et al., 1976; Rumble et al., 1982). In other terranes, there is little evidence for the process in similar lithologies (Valley and O'Neil, 1984). Several observations at Sterling Hill, which are presented below, suggest that the effects of metamorphic fluid infiltration on the chemical and isotopic compositions of the ores is sufficiently small to justify the modeling.

Two different methods for calculating normative minerals were employed. In the first case, the pro-

toliths were presumed to be mixtures of smectite, carbonate, and hydroxide minerals. The procedure for calculating the norms was to assign all silica and a corresponding amount of magnesium, iron, manganese, or zinc to smectite and to assign all trivalent manganese and trivalent iron to a hydroxide mineral (in the common ore assemblages, only franklinite contains significant amounts of trivalent cations). The remaining metals were assigned to a carbonate mineral. Norms calculated by this method produce a model protolith in which the majority of the zinc is contained in the carbonate mineral; the calculation permits CO_2 and a small amount of H_2O to be added to the rock.

In the second case, the protoliths were presumed to be mixtures of the same three minerals. Silica was assigned to smectite, and the carbonate component was calculated from the amount of CO_2 . All the calcium was assigned to the carbonate component as were small amounts of iron, manganese, or zinc which were always required to balance CO_2 . The remaining iron, manganese, and zinc were assigned to the hydroxide component. Most of the zinc in this case is contained in hydroxide minerals; the calculation permits H_2O to be added to the rock.

Carbonate minerals were assumed to have partitioned oxygen isotopes like calcite (O'Neil et al., 1969). If other carbonate minerals were present in the protolith, their isotopic compositions would probably have differed from calcite by only a few per mil (e.g., O'Neil et al., 1969), and the approximation is sufficiently accurate. The smectite- H_2O and hydroxide- H_2O fractionations were taken from Yeh and Savin (1977) and Yapp (1987), respectively. Solid solution in these two mineral groups affects their partitioning behavior (e.g., Lawrence and Taylor, 1972); however, the magnitude of the effect is small compared with the differences in partitioning between carbonate, silicate, and hydroxide minerals, and it was ignored. Yapp (1990) has shown that the goethite- H_2O and hematite- H_2O fractionations are similar at temperatures near the breakdown of goethite to hematite. Thus, whether the protolith contained ferric or manganic hydroxide, or ferric or manganic oxide, the oxygen isotope composition of the bulk rock would have been about the same.

The results of the modeling are shown in Figure 16. The diagrams represent ternary mixtures of smectite, carbonate, and hydroxide minerals, and they are contoured for bulk isotopic composition assuming that the minerals equilibrated with an aqueous fluid. The fluid $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ values were taken from equation (2), and results for the two model mineralogies are shown at 25° and 150°C.

The data points represent the normative compositions of six ore samples which appear to have escaped infiltration by retrograde metamorphic fluids.

For each data point, an isotopic composition is given. The values are the measurements in Table 9 corrected for the effects of metamorphic decarbonation in the case where zinc is contained mainly in carbonate and metamorphic dehydration in the case where zinc is contained mainly in hydroxides. Harker and Hutta (1956) and Roy and Mumpton (1956) have shown that smithsonite, sauconite, hemimorphite and, possibly, $\text{Zn}(\text{OH})_2$ become unstable at relatively low temperatures; the minerals would probably have devolatilized at an early point during prograde metamorphic heating. The corrections were carried out assuming that fluid loss was episodic rather than continuous and that it occurred at 200°C. For the case in which zinc resided in carbonate, the corrected values are 1 to 5 per mil larger than the measured values; for the case in which zinc resided in hydroxides, they are within one per mil of the measured values.

The model in which zinc is contained in hydroxide minerals corresponds poorly with the corrected measurements. The correspondence is better for the model in which zinc is in carbonate, particularly for the higher temperature fluid. The isotopic compositions predicted by the 150°C model agree within one per mil with the corrected measurements.

The modeling suggests, then, that the last fluid-dominated event to have affected the ores involved temperatures more characteristic of hydrothermal processes or prograde metamorphism than surficial processes. Given the constraint imposed by equation (2), the fluid would have had a $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ value several per mil larger than zero and may have been seawater, or some other fluid, which had circulated through and exchanged with crustal rocks. This conclusion, however, is subject to the condition that the ore layers were not significantly altered chemically and mineralogically by infiltrating fluids since the time of the metal depositing-oxidizing event, and this condition is the subject of the next section.

The possibility of fluid infiltration during prograde metamorphism

A number of studies have shown that infiltration of lithologically stratified sequences by fluids during metamorphism leads to equilibration of oxygen isotopes across lithologic contacts (Rye et al., 1976; Rumble et al., 1982; Wickham and Taylor, 1985). In cases where a particular mineral occurs in more than one stratum, infiltration tends to produce uniform isotopic compositions for that mineral throughout the stratigraphic sequence. Rumble et al. (1982) and Rumble and Spear (1983) have documented the effect and have illustrated how it is diagnostic of fluid infiltration.

On the other hand, wide variation in the isotopic composition of a given mineral from stratum to stratum suggests that fluid infiltration was of little im-

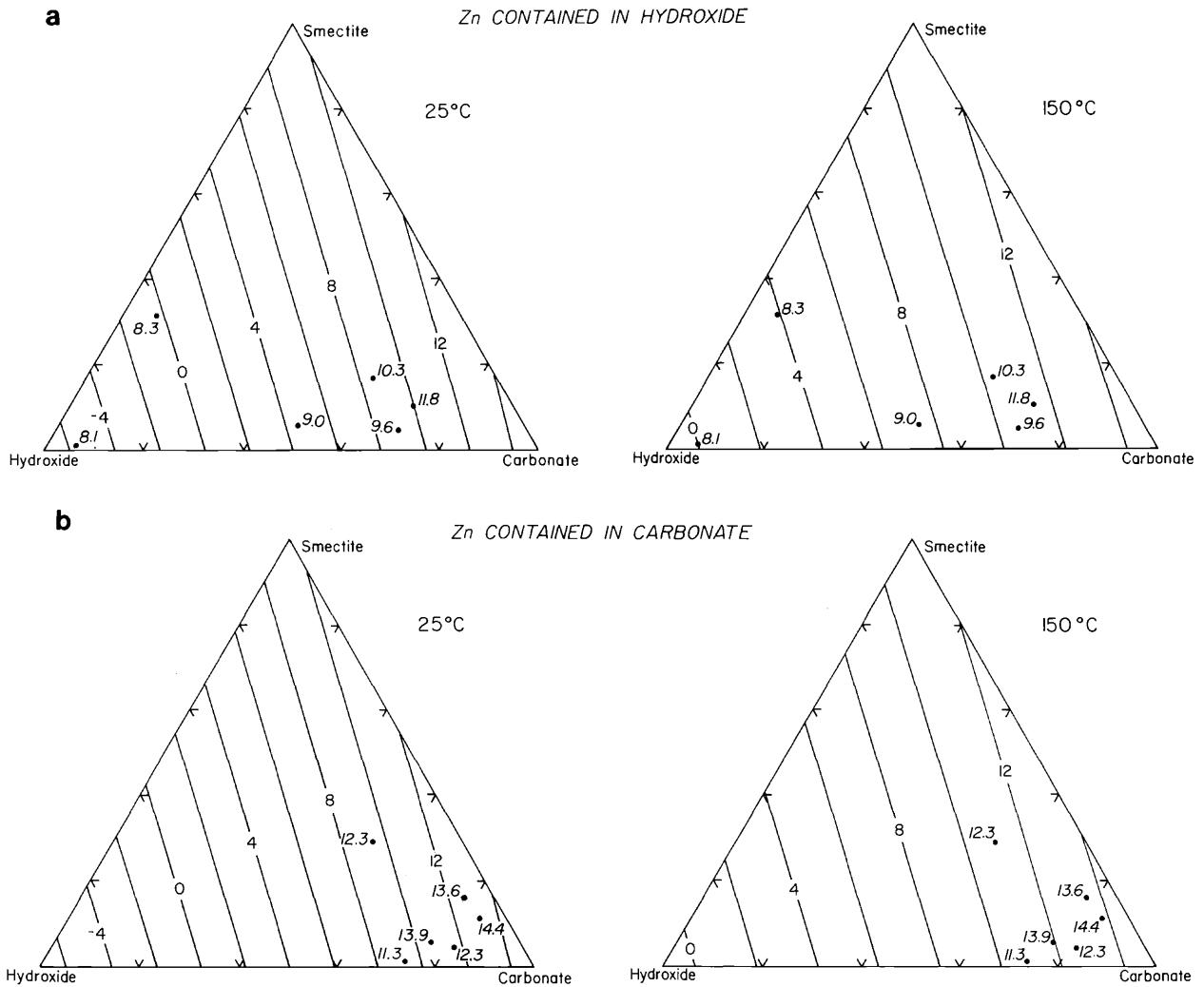


FIG. 16. Bulk $\delta^{18}\text{O}$ values expected of a model smectite + hydroxide + carbonate protolith formed at 25° and 150°C (contour lines) compared with the compositions of Sterling Hill ores (data points). The measured compositions have been corrected for the effects of metamorphic devolatilization. Normative mineral components for the ores were calculated assuming that zinc was contained mainly in a hydroxide mineral (a), and mainly in a carbonate mineral (b). The best correspondence is for a model protolith which formed at hydrothermal or low-grade metamorphic temperatures in which zinc was contained mainly in a carbonate.

portance in establishing the isotopic compositions of metamorphic rocks (e.g., Rumble et al., 1982; Rumble and Spear, 1983). A number of workers have shown that the extent of infiltration is controlled by rock permeability which can be enhanced by devolatilization reactions or by fracturing.

At Sterling Hill, calcite is common to nearly all lithologic layers. The isotopic composition of the calcite can vary dramatically from layer to layer; Figure 9 illustrates a section in which compositions span a range of some six per mil. Thus, the calcite compositions suggest that fluid infiltration was of minor importance during metamorphism.

It is difficult, however, to rule out infiltration entirely. First, fluid infiltration might have been confined strictly to specific layers in which case oxygen might not have exchanged across lithologic contacts, and layer-to-layer variation in the isotopic composition of calcite might remain. Ferry (1987) has inferred fluid flow of this type during metamorphism of pelitic schists in south-central Maine.

Second, infiltration could plausibly have occurred during the earliest stages of, or prior to, metamorphism at a time when the mineral assemblages in the ores were different from what they are now. The growth of metamorphic minerals during continued

prograde heating might have caused oxygen isotopes to be partitioned among the minerals differently in different layers such that the fluid-controlled compositions of the calcites were not preserved.

Some general observations, however, suggest that either scenario, although possible, may be unlikely. The first observation is that most fluids circulating in the crust would have been far from chemical equilibrium with the ores, and they would have led to some distinctive chemical alterations which are not observed. The retrograde metamorphic fluid which was discussed in a preceding section is an example. The fluid appears on the basis of its oxygen isotope composition to have been derived from, or to have circulated through, pelitic units in the region and possibly carbonate units as well. Pelites and carbonates commonly contain sulfide minerals and can also contain graphite; Dallmeyer and Dodd (1971) and Drake (1984) have confirmed this to be the case in the Hudson Highlands-Reading prong belt. Thus one would expect the fluid to have been sufficiently reducing that it could coexist with graphite, and sufficiently sulfidating that it could coexist with pyrite or pyrrhotite. On encountering the high oxidation-low sulfidation state ores, the fluid would have driven redox and sulfidation reactions, and this is in fact what occurred. Ores which were infiltrated contain sulfide minerals produced by reaction of sulfide in the fluid with zinc and iron in ore minerals. Elsewhere they contain hematite which was produced by oxidation of dissolved ferrous iron. Apart from these retrograde metamorphic alterations, there is little evidence that the ores were ever sulfidated or reduced by pervasive or lithologically controlled infiltration. Two exceptions are a small volume of graphite-bearing ore in the transverse portion of the deposit (see Geologic Setting section), and a thin, laterally continuous layer which contains abundant ferrous iron in phlogopite and sulfur in pyrrhotite (R. W. Metsger et al., in prep.).

The second observation which suggests that the ores underwent little infiltration is that willemite and zincite display little evidence of redistribution within or between strata. The retrograde fluid, again, provides an example of the effects which would be expected if the ores had been infiltrated. As was discussed in a preceding section, there is ample evidence that the fluid locally dissolved and removed the two minerals; in some cases willemite was redeposited elsewhere in veins or as replacements. There is little evidence of similar primary redistributions. The integrity of willemite- and zincite-bearing units is well illustrated by the outer zincite band which can be traced for over a kilometer along strike (Fig. 1).

In spite of these observations, the absence of infiltrating fluids cannot be proven. In particular, infiltra-

tion by meteoric water or seawater in the near-surface environment, which is where the ores resided prior to burial and metamorphism, would be difficult to identify. Meteoric water or seawater would have neither reduced nor sulfidized the ores, and the waters may have infiltrated prior to the growth of willemite and zincite during prograde metamorphism. Nevertheless, it is clear that some granulite-grade carbonate rocks have retained their premetamorphic oxygen isotope compositions (e.g., Valley and O'Neil, 1984). One can easily imagine that the ores at Sterling Hill might have been protected from infiltration, at least at deep crustal levels, by the low permeability of the Franklin Marble which surrounds them. However, considering that the deposit may be allochthonous (Metsger et al., 1969), it is difficult to argue against fluid infiltration during prograde metamorphism on the basis of its current surroundings. Consequently, the preservation of primary bulk chemical and isotopic compositions required by the models must remain as an assumption.

Genetic Hypotheses

The primary features of the Sterling Hill deposit, particularly the high f_{O_2}/f_{S_2} character of the ore assemblages and the small bulk $\delta^{18}O$ values of ore layers and interbedded marbles, are consistent with two genetic hypotheses. The first is that the deposit was produced by subaerial weathering of a preexisting sulfide body. The oxidizing agent would have been meteoric water, and the ^{18}O -depleted composition of the meteoric waters would have established the small $\delta^{18}O$ values of the rocks. A $\delta^{18}O_{H_2O}$ value of about -13 per mil would have been required to produce the 15 to 16 per mil compositions observed in the marble layers interbedded with the ores.

The second hypothesis is that the deposit formed on the sea floor either by precipitation directly from a hydrothermal fluid or through seawater oxidation of an already-formed sulfide body. The oxidizing agent in this case would have been seawater, and the oxygen isotope compositions of the rocks would have been established by the ambient mixture of hydrothermal fluid and seawater or by seawater alone. Mixing of a hydrothermal fluid and seawater could have taken place in the subsurface or in a ponded brine pool. The ambient fluid is unlikely to have been ^{18}O depleted as -13 per mil, thus the small bulk $\delta^{18}O$ values of the rocks would have been established by isotopic equilibration between fluid and minerals at high temperatures. A generous estimate of the range of $\delta^{18}O_{H_2O}$ values to be expected in a sea-floor hydrothermal system is -10 to $+10$ per mil (Franklin et al., 1981; Gustafson and Williams, 1981) which would require temperatures for Sterling Hill in the range 43° to $320^\circ C$. The bulk isotopic compositions of the

ore layers suggest that the ambient fluid had $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ a few per mil larger than seawater and was approximately 150°C . The conclusions based on the ore layers, however, are subject to the assumption that the bulk isotopic compositions are unaltered; the uncertainties are $\pm 50^\circ\text{C}$ and ± 4 per mil at best.

If the ores were formed by seawater oxidation of a preexisting sulfide body, then the seawater must have been hot. The isotopic compositions observed in the marble layers suggest that, if the seawater had a normal isotopic composition, its temperature was about 120°C .

Structural features of the ore layers favor the sea-floor hypothesis rather than the weathering hypothesis in that they appear to be incompatible with an origin by subaerial weathering. Portions of the deposit have been shown to be stratified on a centimeter scale, and the strata can be traced over tens or hundreds of meters. In addition, the general map units shown in Figure 1 are continuous through both limbs and the keel of the synform, a distance of a kilometer. These features are not characteristic of weathered carbonate-bearing rocks in which beds are brecciated and fragmented by dissolution of carbonate minerals and subsequent collapse. Furthermore, an origin by weathering would require a highly fortuitous circumstance in which oxidation corresponded exactly to the volume of rock containing sulfides. There is no significant sulfide portion of the deposit as there would be if it had been only partially oxidized, and there is no sulfide-free Franklin Marble as there would be if weathering had affected some of the surrounding host rock. In addition, there is a thin, continuous pyrrhotite-bearing stratum within the deposit (see Geologic Setting section) which is unlikely to have escaped oxidation during weathering.

The best model for the origin of Sterling Hill protolith, then, appears to be either metal deposition on the ocean floor or in well-irrigated, shallowly buried sediments where redox conditions were controlled by seawater, or oxidation of an already-deposited sulfide body by hot seawater. The closest modern chemical analogue to the deposit is the metalliferous sediment beneath the Red Sea brine pools. The brine pools are formed by hot, saline waters which emerge from depth and discharge into depressions on the sea floor (see Degens and Ross, 1970, for a review). The waters develop their high salt content, and thereby their ability to dissolve and transport metals at high concentrations, by dissolving Miocene evaporites as they circulate beneath the sea floor. The emerging brines are more dense than normal seawater, and they pond within the depressions. Sediments beneath the pools are stratified, and many of the strata are sulfide poor. In these units, the manganosiderite facies, iron-montmorillonite facies and goethite-amorphous facies of

Bischoff (1969), metal deposition occurred under oxidizing conditions. Oxygen was derived from the overlying Red Sea water which mixed periodically with the brines.

The mineralogy inferred for the Sterling Hill protolith—carbonates, hydroxides, and smectite—is similar to the mineralogy of the sulfide-poor units (Bischoff, 1969). Furthermore, the temperature and isotopic composition of the metal depositing-oxidizing fluid at Sterling Hill, although they have been determined here only approximately, are compatible with a Red Sea-type model. The Red Sea brines, which are thought to be the metal-carrying fluids, are currently about 60°C (Schoell and Hartmann, 1978) and metal precipitation is inferred to have occurred in the temperature range 150° to 250°C (Shanks and Bischoff, 1977; Pottorf and Barnes, 1983). Craig (1966) and Schoell and Faber (1978) have shown that the brines have $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ values 1 to 3 per mil larger than seawater. The brine is supposed to have originally been seawater which was enriched in ^{18}O by evaporation in a restricted basin (Craig, 1966) and may have been further enriched by exchange of oxygen at high temperatures with rocks along the flow path (Shanks and Bischoff, 1977). If the fluid at Sterling Hill had a similar isotopic composition, then equation (2) suggests that temperatures were in the range 125° to 150°C . If it had a salinity like that of the Red Sea brine, a fluid of this temperature would have been denser than the overlying seawater and might have ponded (Sato, 1972; Turner and Gustafson, 1978).

Although no anhydrite-bearing units have been recognized in the Reading prong, Kearns (1977) has described boron-rich zones within the Franklin Marble and has pointed out the possibility that they are remnants of evaporite facies. Similar boron-rich zones occur in Grenville marbles in the northwest Adirondack Mountains, New York, where their interpretation as evaporites is strengthened by the presence of bedded anhydrite in the stratigraphic sequence (Brown and Engel, 1956). In any case, evaporites may not be a critical component of the ore-forming process because there are other potential sources of dissolved salts. The metal-carrying fluid at the Red Sea, and plausibly at Sterling Hill, was seawater, and its salt content may have been enhanced by the hydration of rocks along its flow path (cf. Von Damm et al., 1985).

An important difference between the inferred Sterling Hill protolith and the sulfide-poor strata in the Red Sea is zinc content. The major zinc concentrations in the Red Sea sediments are the sulfide facies which contain sphalerite (Bischoff, 1969); sulfide-poor facies are much lower in zinc. In spite of the absence of smithsonite from the Red Sea sediments, its inferred presence in the Sterling Hill protolith is entirely consistent with studies of zinc solubility in

the earth's surface environments. In natural waters lacking reduced sulfur, smithsonite, hydrozincite, and zinc hydroxide are known to be important controls of zinc solubility (e.g., Takahashi, 1960; Sangameswar and Barnes, 1983; Zachara et al., 1989). Smithsonite appears to be the stable phase, or the kinetically favored phase, in many such environments.

Another distinctive feature of Sterling Hill is the extreme enrichment of zinc relative to copper and lead. The atomic ratios Zn/Cu and Zn/Pb in the ores are approximately 10^5 (R. W. Metsger, pers. commun.). The ratios in the overlying calc-silicate units are unknown, although the presence of lead-bearing feldspars and other lead minerals in calc-silicate lithologies at Franklin Furnace (Fron del et al., 1966; Dunn, 1985b) opens the possibility that the zinc enrichment in the calc-silicates at Sterling Hill is less than in the ores. The Zn/Pb in calc-silicate units at Franklin is about 10^2 (Fron del and Baum, 1974). For comparison, Zn/Cu and Zn/Pb in the sulfide-poor Red Sea strata are about 10 and 10^2 , respectively (Bischoff, 1969).

Whatever the cause of the zinc enrichment, the feature is to a degree characteristic of stratiform base metal deposits throughout the Grenville province and related terranes. In their review of Grenville deposits, Sangster and Bourne (1982) point out that, although galena is an important constituent of a few deposits (e.g., New Calumet), the majority of the numerous stratiform zinc deposits in the Grenville are low in both lead and copper. Sterling Hill appears to be at the extreme end of the observed zinc-to-lead and zinc-to-copper enrichments. Whether metal abundances in the deposits reflect metal extraction or transport processes that occurred in the source rocks, and whether local precipitation conditions caused further separation of zinc from lead and copper are questions that will require further study.

It is not uncommon for metals to precipitate under oxidizing conditions where hydrothermal fluids discharge onto the sea floor. There are well-documented examples associated with both fossil and active oceanic spreading ridges including the umbers within the Troodos massif in Cyprus (Robertson, 1975), the manganese-rich cherts in the Franciscan assemblage, California (Crerar et al., 1982), and the laterally extensive iron- and manganese-rich deposits which have been identified on the ocean floor near active spreading ridges (e.g., Bonatti and Joensuu, 1966; Edmond et al., 1979). There are also examples in continental rift environments including portions of the Red Sea metalliferous sediments (Bischoff, 1969) and the deposits in the Afar depression (Bonatti et al., 1972). The lithologic package in the Reading prong appears to have formed in an extensional tectonic environment (Gundersen, 1985; Drake, 1990) which further sug-

gests that the aforementioned deposits may be appropriate analogues for Sterling Hill.

In sum, Sterling Hill and, by analogy, Franklin Furnace owe their uniqueness to the combination of three factors, none of which is particularly unusual in its own right: (1) the deposits were rich in zinc and poor in lead and copper, (2) the metals occurred as carbonate, hydroxide, and silicate minerals rather than sulfide minerals, and (3) the deposits were metamorphosed to the granulite facies. If these conclusions are correct, then there is no reason, a priori, why other deposits with similar mineralogy and chemical composition might not be discovered. Given the abundance of zinc-rich stratiform deposits, and the abundance of stratiform deposits which appear to have formed in oxidizing environments (C. A. Johnson, 1990; in prep.), other Grenvillian supracrustal terranes are the obvious places to search.

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