

Geochemistry of the Furnace Magnetite Bed, Franklin, New Jersey, and the Relationship between Stratiform Iron Oxide Ores and Stratiform Zinc Oxide-Silicate Ores in the New Jersey Highlands

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Abstract

The New Jersey Highlands terrane, which is an exposure of the Middle Proterozoic Grenville orogenic belt located in northeastern United States, contains stratiform zinc oxide-silicate deposits at Franklin and Sterling Hill and numerous massive magnetite deposits. The origins of the zinc and magnetite deposits have rarely been considered together, but a genetic link is suggested by the occurrence of the Furnace magnetite bed and small magnetite lenses immediately beneath the Franklin zinc deposit. The Furnace bed was metamorphosed and deformed along with its enclosing rocks during the Grenvillian orogeny, obscuring the original mineralogy and obliterating the original rock fabrics. The present mineralogy is manganiferous magnetite plus calcite. Trace hydrous silicates, some coexisting with fluorite, have fluorine contents that are among the highest ever observed in natural assemblages. Furnace bed calcite has $\delta^{13}\text{C}$ values of -5 ± 1 per mil relative to Peedee belemnite (PDB) and $\delta^{18}\text{O}$ values of 11 to 20 per mil relative to Vienna-standard mean ocean water (VSMOW). The isotopic compositions do not vary as expected for an original siderite layer that decarbonated during metamorphism, but they are consistent with nearly isochemical metamorphism of an iron oxide + calcite protolith that is chemically and mineralogically similar to iron-rich sediments found near the Red Sea brine pools and isotopically similar to Superior-type banded iron formations. Other manganiferous magnetite + calcite bodies occur at approximately the same stratigraphic position as far as 50 km from the zinc deposits.

A model is presented in which the iron and zinc deposits formed along the western edge of a Middle Proterozoic marine basin. Zinc was transported by sulfate-stable brines and was precipitated under sulfate-stable conditions as zincian carbonates and Fe-Mn-Zn oxides and silicates. Whether the zincian assemblages settled from the water column or formed by replacement reactions in shallowly buried sediments is uncertain. The iron deposits formed at interfaces between anoxic and oxygenated waters. The Furnace magnetite bed resulted from seawater oxidation of hydrothermally transported iron near a brine conduit. Iron deposits also formed regionally on the basin floor at the interface between anoxic deep waters and oxygenated shallower waters. These deposits include not only manganiferous magnetite + calcite bodies similar to the Furnace magnetite bed but also silicate-facies deposits that formed by iron oxide accumulation where detrital sediment was abundant. A basin margin model can be extended to Grenvillian stratiform deposits in the northwest Adirondacks of New York and the Mont Laurier basin of Quebec. In these areas iron deposits (pyrite or magnetite) are found basinward of marble-hosted sphalerite deposits, such as those in the Balmat-Edwards district. Whether the iron and zinc precipitated as sulfide assemblages or carbonate-oxide-silicate assemblages depended on whether sufficient organic matter or other reductants were available in local sediments or bottom waters to stabilize H_2S .

Introduction

THE NEW JERSEY HIGHLANDS, an exposure of Middle Proterozoic Grenvillian basement within the Appalachian fold belt, is the site of the well-known Franklin and Sterling Hill zinc-iron-manganese deposits that were mined from the middle of the nineteenth century until 1954 and 1987, respectively (Fig. 1). These deposits are noteworthy because the ore minerals were willemite (Zn_2SiO_4), franklinite (ZnFe_2O_4), and zincite (ZnO) rather than sphalerite. Also noteworthy is the fact that the ores were quite rich, averaging 20 wt percent zinc (Metsger et al., 1958; Frondel and Baum, 1974). The combined production at the two mines was 6.5 million metric tons (Mt) of zinc.

The Highlands also hosts iron oxide deposits that were mined at hundreds of different locations from the late seventeenth

century until the early twentieth century. The deposits were massive magnetite or, rarely, hematite, and although small by today's standard they nonetheless allowed New Jersey to lead the United States in iron production up until the development of the larger Lake Superior deposits in the 1880s. Total production from the New Jersey Highlands deposits was at least 25 Mt of iron (Bayley, 1910; Sims, 1958).

The Franklin and Sterling Hill zinc deposits both occur within the Franklin marble (Fig. 2), a distinctive unit within a supracrustal sequence. The origin of the zinc ores has been extensively debated for many years (e.g., Wolff, 1903; Ries and Bowen, 1922; Tarr, 1929; Palache, 1935; Pinger, 1950; Ridge, 1952; Metsger et al., 1969). However, following the discovery of sea-floor hydrothermal vent deposits in the 1960s, opinion has increasingly swung to the view that Franklin and Sterling Hill were formed by hydrothermal systems operating beneath the floor of the Middle Proterozoic

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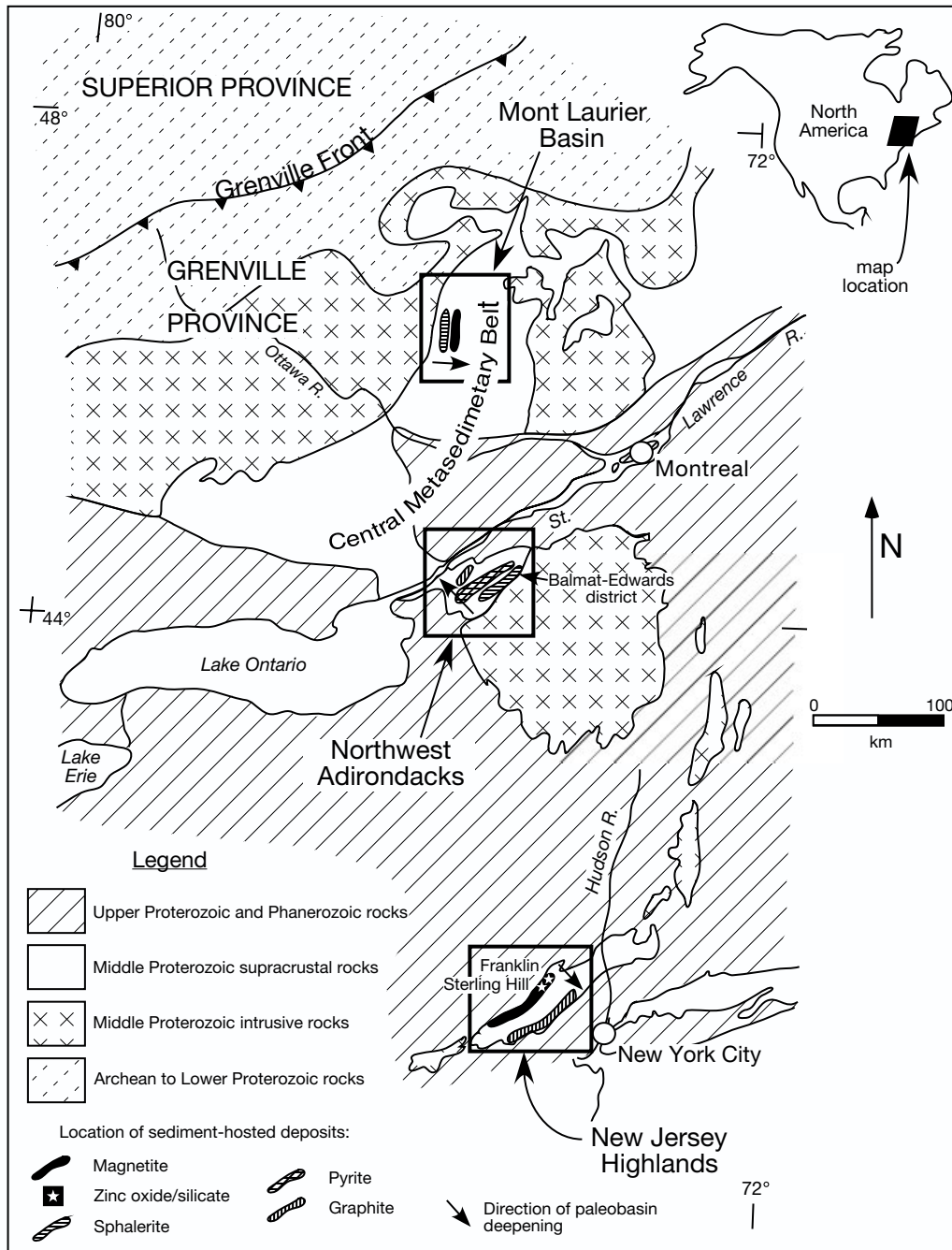


FIG. 1. Map showing the location of the New Jersey Highlands and two other similar terranes that are discussed in this paper, the northwest Adirondacks and the Mont Laurier basin. Geology is generalized after Gauthier et al. (1987) and Rankin et al. (1993).

sea, and that the timing of metal emplacement was either syngenetic or diagenetic (Callahan, 1966; Frondel and Baum, 1974; Squiller and Sclar, 1980; Johnson et al., 1990a; however, see Zheng, 1996, for a synmetamorphic metal emplacement theory). There is strong evidence that the mineral assemblages observed today were produced during high-grade regional metamorphism that accompanied the Grenvillian orogeny (Metsger, 1962; Carvalho and Sclar, 1988) or Ottawa orogeny (Rankin et al., 1993).

The iron deposits stand in contrast to the zinc deposits. They are found within the supracrustal sequence, but they also occur in the underlying gneisses and in granitoids that cut the supracrustal rocks. The host rocks for the iron deposits include paragneisses such as marble and metapelite, quartzfeldspathic lithologies of uncertain origin, and hornblende granite gneisses or amphibolites of likely igneous origin. The origin of the iron deposits, like the zinc deposits, has been controversial (e.g., Buddington, 1966; Collins, 1969a, b; Baker

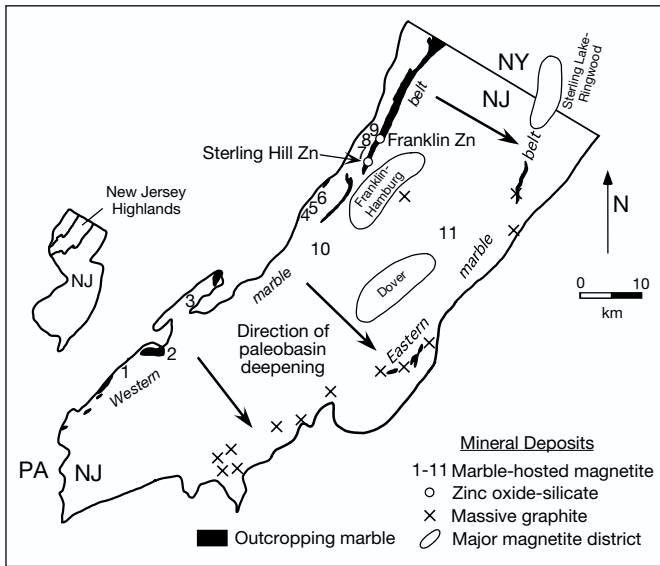


FIG. 2. Outline of Proterozoic rocks of the New Jersey Highlands showing the locations of massive magnetite deposits, zinc oxide-silicate deposits, and graphite deposits. Marble exposures define a western belt (the Franklin marble) and an eastern belt. The numbered magnetite deposits are (1) Schuler, (2) Belvidere group (Ahles, Little, Riddle, Queen, Osmun, Raub), (3) Jenny Jump Mountain group (Smith's, Deats, Hoagland, Stinson, Davis, Albertson, Inshow Exploration, Shaw, Howell Farm), (4) Sulphur Hill, (5) Tar Hill, (6) Longcore, (7) Balls Hill group, (8) Black Hole, Longshore, Pike's Peak, and Furnace, (9) Furnace magnetite bed, (10) Roseville, and (11) Split Rock Pond. After Bayley (1910), Hague et al. (1956), Volkert and Drake (1999), and Volkert et al. (2000b).

and Buddington, 1970; Kastelic, 1980; Foose and McLelland, 1995; Johnson, 1996), but some of the controversy may now be alleviated by the recent proposal (Puffer, 2001) that the Highlands contain multiple types of iron deposits formed during separate events spanning basin development during the Middle Proterozoic, metamorphism of the rocks during

the Grenvillian orogeny, granite plutonism during a period of renewed extension, and rift-basin development during the Neoproterozoic.

The magnetite deposits of the Dover, Franklin-Hamburg, and Sterling Lake-Ringwood districts are several kilometers to tens of kilometers from known zinc deposits (Fig. 2). However, three other groups of magnetite deposits are spatially or stratigraphically close enough to zinc ore that a genetic relationship between the iron and zinc mineralization can be inferred. The related iron deposits are (1) the marble-hosted Furnace magnetite bed immediately beneath the Franklin zinc deposit, plus three similar deposits that extend 250 m along strike (Fig. 3); (2) gneiss-hosted magnetite deposits below the marble-gneiss contact (thin magnetite lenses directly underlie the Furnace magnetite bed, and several larger deposits occurred 450 to 900 m along strike to the southwest [Fig. 3]); and (3) other distal magnetite deposits that occurred within the Franklin marble along the western edge of the Highlands and extended up to 50 km from known zinc mineralization (Fig. 2). The transition from Furnace bed iron mineralization to Franklin deposit zinc-iron-manganese mineralization (or the reverse if the stratigraphy is inverted) is a record of spatial or temporal changes in physicochemical conditions or changes in the hydrothermal metal supply. In either case, the magnetite deposits can potentially provide valuable insights into the origin of the unusual zinc ores. Only sparse information about the iron oxide ores has been available, mainly from regional surveys carried out more than a century ago.

In this paper we report petrologic, geochemical, and stable-isotope data for the Furnace bed and for two underlying gneiss-hosted magnetite occurrences. We use these data to constrain the nature of the protoliths and to establish a genetic link between the iron deposits and the zinc oxide-silicate deposits. We also propose a model in which the iron deposits and the zinc deposits accumulated near the margin of a Middle Proterozoic marine basin. Some aspects of this model

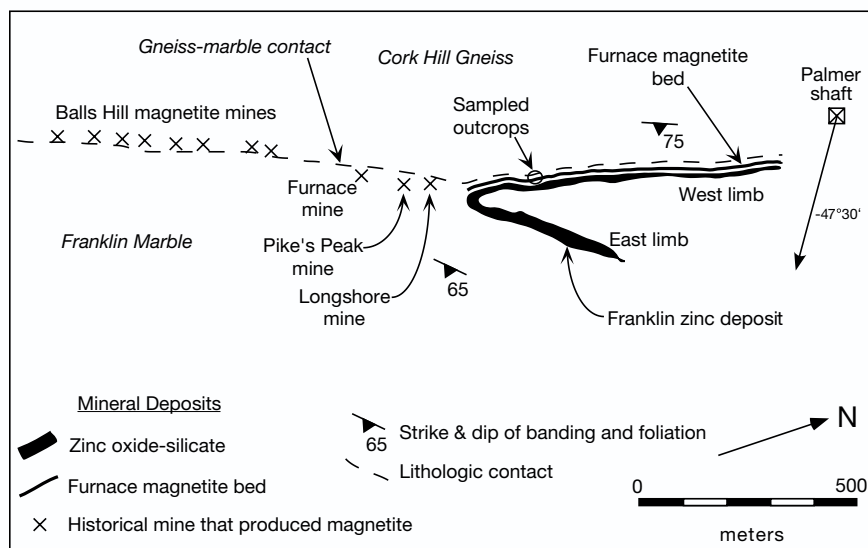


FIG. 3. Map showing the Franklin zinc deposit, the Furnace magnetite bed, and nearby marble-hosted and gneiss-hosted magnetite deposits. The zinc deposit is a north-plunging synform; the Furnace bed underlies its west limb and wraps around its keel at depth. After Palache (1935), Hague et al. (1956), and Dunn (1995).

have been suggested previously by Johnson (2001); this paper, in addition to providing new data, presents a substantial refinement of the model. Because overprinting metamorphism and deformation have obscured the original mineralogy and original fabrics of the rocks, it is not possible for us to distinguish with confidence whether these ores formed syngenetically by settling of metals from the water column or whether they formed diagenetically by replacement of shallowly buried sediments. Nevertheless, our metallogenic model can be extended successfully to stratiform metal deposits found in Grenvillian supracrustal sequences in the Adirondacks of New York, and the Central metasedimentary belt of Ontario and Quebec, and it may provide a useful foundation for zinc oxide-silicate exploration as well as for future genetic investigations.

Geology of the New Jersey Highlands

The New Jersey Highlands, along with the adjoining Reading Prong of Pennsylvania and Hudson Highlands of New York, are part of the Grenville orogenic belt that developed along the southeastern margin of Laurentia during the Proterozoic (Rivers, 1997; Mosher, 1998; Hanmer et al., 2000). The oldest rocks in the Highlands are a group of leucocratic gneisses, charnockite gneisses, and amphibolites comprising the Losee metamorphic suite. These are believed to be remnants of a calc-alkaline magmatic arc that were later deformed, metamorphosed, and partially melted (Puffer and Volkert, 1991).

Overlying the Losee suite is a metamorphosed and isoclinally folded supracrustal section, which has a present-day thickness of at least 2 km and is thought to have accumulated either within a continental rift basin or on a continental margin. Despite multiple folding events and granulite-grade metamorphism in the time period 1.09 to 1.03 Ga (Volkert, 2001), the stratigraphic section can be reconstructed to reveal (1) a basal quartzofeldspathic metasediment-metavolcanic section, (2) a series of calc-silicate gneisses and marbles with stromatolite occurrences and probable evaporite horizons, and (3) an uppermost quartzofeldspathic metasediment-metavolcanic section in which the sediments are less mature than in the basal section and in which the proportion of mafic volcanic rocks is higher (Volkert and Drake, 1999; Volkert, 2001). The transition from shallow-water carbonates to clastic sedimentary rocks and mafic volcanic rocks is thought to reflect the initiation of basin closure.

The New Jersey sequence closely resembles a Middle Proterozoic supracrustal sequence that is exposed in the northwest Adirondacks in that sedimentary lithologies are abundant, two major marble units are present separated by clastic units, and major stratiform zinc deposits are also present (Hague et al., 1956; Rankin et al., 1993). For the New Jersey sequence, it has been suggested that the sedimentary protoliths were deposited between 1.18 and 1.10 Ga (Volkert, 2001), at the same time that the St. Boniface and Flinton groups were being laid down within the Grenville province (Sager-Kinsman and Parrish, 1993; Corrigan and van Breeman, 1997). Correlation with the 1.3 to 1.25 Ga supracrustal rocks of the Frontenac Group (Rivers, 1997; Hanmer et al., 2000) would imply a somewhat older depositional age for the New Jersey rocks.

The Losee metamorphic suite and the supracrustal rocks were intruded by syntectonic granitoids of the Vernon Supersuite during a period of crustal thinning (Volkert et al., 2000a), and also by the posttectonic Mt. Eve granite. Finally, undeformed greenschist-grade clastic and volcanic rocks are preserved in a few locations, mainly in the southwestern Highlands. These rocks are remnants of the Neoproterozoic continental rifting event that marked the opening of the Iapetus Ocean (Drake, 1984).

Previous Work on Magnetite Deposits Spatially Related to Zinc Ore

The magnetite deposits adjacent to the Franklin zinc ores and the more distal marble-hosted deposits were first described nearly two centuries ago (Fowler, 1836, cited by Dunn, 1995), and they have been studied several times since then (Cook, 1868; Nason, 1894; Spencer et al., 1908; Bayley, 1910; Palache, 1935). The only deposit for which there are good surviving maps is the Furnace magnetite bed, which was evaluated as an iron resource when the Franklin zinc mine closed (Stockwell, 1951). The Furnace bed is a layer averaging 2 m thick that lies within the Franklin marble and is situated between the west limb of the Franklin zinc deposit and the underlying Cork Hill gneiss (Fig. 3). The bed diverges from the gneiss contact with depth to wrap around the keel of the synformal zinc deposit, but the extent to which magnetite continues up the east limb of the synform is unknown (Fron- del and Baum, 1974). The mass of the known part of the Furnace bed is estimated to be 0.5 Mt (Stockwell, 1951).

The Furnace bed commonly contains distinct layers oriented parallel to the overall strike of the unit that differ in magnetite-to-calcite ratio (Fig. 4). Textures range from thin

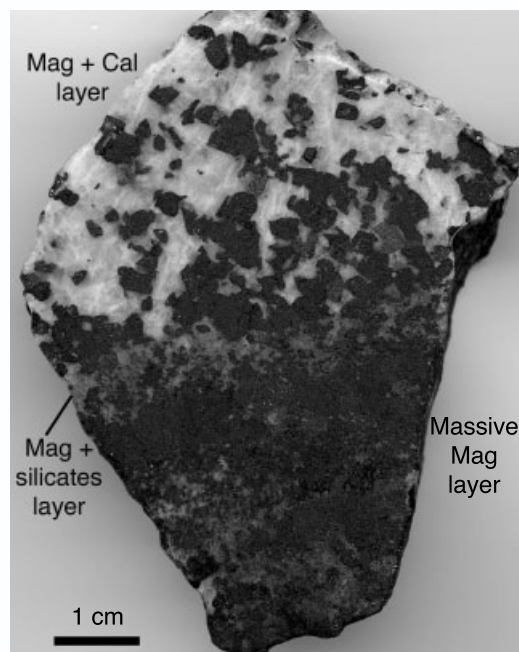


FIG. 4. Hand specimen of the Furnace magnetite bed showing mineralogically distinct layers. The most prominent layering reflects variations in the proportions of magnetite (Mag) and calcite (Cal), but some layers are distinguished by an abundance of silicate minerals.

magnetite disseminations in a matrix of coarse equigranular calcite to massive magnetite. Magnetite grains are subhedral to euhedral and are 1 to 5 mm in diameter.

Sparse analytical data have shown this deposit to be manganeseiferous but essentially zinc free (Cook, 1868; Bayley, 1910; Stockwell, 1951; Dunn, 1995). Magnetite and calcite are the dominant minerals, but graphite and trace pyrite and chalcocopyrite have been reported as well. Pyroxene and garnet appear in the upper levels of the Franklin mine adjacent to crosscutting pegmatite bodies. A partial chemical analysis obtained by Stockwell (1951) is given in Table 1. The bed is rich enough in iron to be a potential ore, but it is lower in silica and much higher in calcium than Superior- or Algoma-type banded iron formations (James, 1992).

Massive magnetite deposits also occurred along the southwestward extension of the Furnace bed. These deposits were exploited at the Black Hole, Longshore, Pike's Peak, and Furnace mines (Fig. 3). Although these mines extended only 250 m from the Furnace bed, no preserved records indicate whether the magnetite deposits were physically contiguous. Trace graphite has been reported in the ores from these mines in addition to manganeseiferous magnetite and calcite (Cook, 1868). The workings are long buried and inaccessible.

Another group of proximal magnetite deposits lies within the Cork Hill gneiss immediately beneath the contact with the Franklin marble (Fig. 3). These deposits were mined 450 to 900 m southwest of the Franklin zinc deposit on Balls Hill (Dunn, 1995), but magnetite lenses several centimeters thick also occur along strike in gneiss immediately beneath the Furnace magnetite bed and the west limb of the Franklin zinc deposit. Wet chemical analyses of Balls Hill ore suggest much lower manganese contents than in the marble-hosted magnetite deposits (Cook, 1868), and a more recent microprobe survey supports this finding (Dunn, 1995).

The distal, marble-hosted occurrences are the Schuler deposit, those of the Belvidere group, including Ahles and smaller deposits that were exploited intermittently, the deposits on Jenny Jump Mountain, the group of deposits farther

north at the Sulphur Hill, Tar Hill, and Longcore mines, the Roseville deposit, and the Split Rock Pond deposit (Fig. 2). Bayley (1910), who studied many of the deposits during or shortly after active mining, demonstrated that these ores were characteristically manganeseiferous and had whole-rock compositions up to 6.5 wt percent MnO. Besides magnetite and calcite, silicate minerals were also observed in some deposits, as were minor sulfides. Analyses by Puffer (1997, 2001) confirm the presence of manganese in the marble-hosted ores and reveal that they are also low in titanium, aluminum, and phosphorous compared with Highlands magnetite deposits in silicate host rocks.

The Furnace magnetite bed is widely considered to be genetically related to the Franklin zinc ores (Fron del and Baum, 1974). However, the magnetite deposits elsewhere in the Franklin marble and those in the Cork Hill gneiss have typically been classified with the more abundant magnetite deposits of the Dover, Franklin-Hamburg, and Sterling Lake-Ringwood districts (Fig. 2). Most workers have concluded that iron was emplaced during the Grenvillian orogeny either by fluids expelled from crystallizing granitic magmas (Hotz, 1953; Sims, 1958; Buddington, 1966; Baker and Buddington, 1970; Foose and McLelland, 1995) or by fluids released during metamorphic devolatilization (Hagner et al., 1963; Collins, 1969a, b). Puffer (1997, 2001) proposed that several different types of magnetite deposit are present in the region, including magmatic-hydrothermal, metamorphic devolatilization, and synsedimentary, as well as a deposit type that formed later within Neoproterozoic rifts (see also Volkert, 2001). Metamorphic decarbonation of sedimentary siderite layers has been proposed for Belvidere group and other Warren County magnetite deposits (Kastelic, 1980). Overall, the sedimentary accumulation hypothesis for the New Jersey iron ores has received less support than the magmatic-hydrothermal or metamorphic devolatilization hypotheses, but the idea was favored early in the debates about genesis (Kitchell, 1857). It was rejuvenated by Baker and Buddington (1970), who acknowledged that some iron deposits in the Franklin-Hamburg area probably represent original sedimentary deposits.

Samples and Analytical Methods

Samples for this study were obtained from the Furnace magnetite bed, from a previously unrecognized magnetite lens within the Franklin zinc deposit, and from gneiss-hosted magnetite lenses beneath the Furnace bed. The Furnace bed was sampled at its only known surface exposure (Fig. 3) and also in diamond drill core that is archived in the Department of Geology and Geophysics at Yale University. Furnace bed intersections were found in holes 5 and 7, which were collared in 1904 on the 750 and 900 levels, respectively, near the Palmer shaft. Massive magnetite also occurs in hole 1, which was collared on the 1050 level near the Palmer shaft. This occurrence is entirely within the zinc orebody, so it is unlikely to be the Furnace bed. However, we include it here because it represents an episode of iron deposition apparently associated with the zinc-depositing hydrothermal system. The gneiss-hosted magnetite samples were obtained from outcrops about 2 m west of the exposure of the Furnace magnetite bed (Fig. 3).

Electron microprobe analyses were obtained at the American Museum of Natural History using an ARL-SEM-Q instrument

TABLE 1. Whole-Rock Chemical Composition of the Furnace Magnetite Bed¹

Constituent	Wt percent	Notes
FeO	60.06	2
MnO	3.17	3
SiO ₂	1.49	
P ₂ O ₅	0.012	
CaO	16.5	4
CO ₂	12.9	4
S	0.197	
C	1.24	
Total	95.6	5

¹ From Stockwell (1951), who collected chip samples across the entire width of the bed in seven separate locations in the Franklin underground workings; this result is an average of the seven analyses

² Calculated from total Fe assuming a valence of +2

³ Calculated from total Mn assuming a valence of +2

⁴ Calculated assuming the difference between the sum of measured constituents and 100 percent is accounted for by calcite; this assumption is supported by petrography

⁵ Does not include the extra oxygen associated with Fe³⁺

and at the U.S. Geological Survey in Denver using a JEOL JXA 8900. At the American Museum, operating conditions were 15 kV accelerating voltage and 5, 15, or 20 nA sample current for carbonates, silicates, and magnetite, respectively. Well-characterized natural minerals were used as standards, including scapolite for Cl and fluorapatite for F. Pulse height analysis was used to eliminate the phosphorous $K\alpha$ contribution to fluorine count rates. Under some circumstances fluorapatite can be a poor F standard owing to diffusion effects (Stormer et al., 1993). However, the fact that the analytical totals meet the generally accepted standard of 100 ± 2 percent for F contents up to 18 wt percent and that fluorite analyses made as a check gave the F levels expected for the beam exposure times that were used (Stormer et al., 1993) suggests that the analyses reported here were not subject to undue error. At the U.S. Geological Survey, operating conditions were 15 kV and 20 nA sample current. Scapolite was used as the Cl standard, and synthetic fluorophlogopite (for silicates) and fluorapatite (for apatite) were used as F standards. Analyses reported in this paper are averages of multiple spots, typically on several different individual crystals. Where they were present, retrograde textures and assemblages were avoided during data collection. Nevertheless, the carbonate and magnetite compositions reported for some samples probably reflect composition changes related to unmixing during postmetamorphic cooling (see below).

Isotopic compositions of carbonates were determined at Yale University or the U.S. Geological Survey by digesting crushed whole rocks in phosphoric acid (McCrea, 1950). The evolved CO_2 gas was purified and analyzed by dual viscous inlet mass spectrometry. The results are reported in δ -notation in units of per mil relative to PDB for carbon and VSMOW for oxygen. Analyses of the NBS 19 ($\delta^{13}\text{C} = 1.92$ per mil, $\delta^{18}\text{O} = 28.65$ per mil) and NBS 18 ($\delta^{13}\text{C} = -5.00\text{‰}$, $\delta^{18}\text{O} = 7.20\text{‰}$) standards gave $\delta^{13}\text{C} = 1.8$ per mil and $\delta^{18}\text{O} = 28.4$ per mil ($n = 4$) and $\delta^{13}\text{C} = -5.0$ per mil and $\delta^{18}\text{O} = 7.1$ per mil ($n = 1$), respectively. Samples were analyzed in duplicate or triplicate; the results typically agreed to within ± 0.1 per mil for carbon and ± 0.5 per mil for oxygen. Graphite was analyzed in crushed material recovered from the phosphoric acid digestion. The material was rinsed, mixed with cupric oxide, and heated to 850°C to produce CO_2 for mass spectrometry. Reproducibility was ± 0.1 per mil.

Results

Mineralogy

Minerals in the Furnace bed and in the magnetite lens within the Franklin zinc deposit include magnetite, calcite, dolomite, diopside, tremolite, phlogopite, chondrodite, norbergite, graphite, and fluorite (Table 2). Minor siderite, pyrite, and chalcopyrite are also present, but they display

TABLE 2. Mineral Assemblages¹

Mineral	Samples from Furnace magnetite bed							Magnetite lens in Franklin Zn deposit	Gneiss-hosted magnetite lenses	
	F5-2.6	F5-2.9	F5-3.2	F7-20	FMB1a	FMB1b ²	FMB2	F1-35.5	LFMB1	LFMB2
Primary mineral										
Magnetite ³	x	x	x	x	x	x	x	x	x	x
Calcite	x	x	x	x	x			x		
Dolomite			x		x	x	x			
Clinopyroxene	x	x	x			x			x	x
Ca clinoamphibole				x		x				
Hornblende										
Biotite						x		x		
Chondrodite ⁴	x	x								
Norbergite ⁵				x						
Graphite				x			x			
Fluorite	x		x							
Plagioclase									x	x
K feldspar									x	x
Apatite										x
Retrograde mineral										
Pyrite	x	x		x				x		
Chalcopyrite	x	x						x		
Dolomite	x	x	x							
Siderite								x		

¹ Drill core samples are labelled by hole number and footage

² Also contains significant amounts of a fluorine-bearing Ca-Mg arsenate that may be tilasite, $\text{CaMgAsO}_4\text{F}$

³ Magnetite abundances determined by point counting (~ 750 points) were F5-2.6, 58.2 percent; F5-3.2, 69.0 percent; FMB1, 45.4 percent; FMB2, 11.8 percent; FMB2 also contains 1.6 percent graphite

⁴ Ideally, $2\text{Mg}_2\text{SiO}_4 \cdot \text{Mg}(\text{OH}, \text{F})_2$

⁵ Ideally, $\text{Mg}_2\text{SiO}_4 \cdot \text{Mg}(\text{OH}, \text{F})_2$

textures suggesting retrograde growth, and the latter two minerals probably replace original pyrrhotite (E. Makovicky, unpub. data, 1987). Some samples contain dolomite blebs that appear to have formed by retrograde unmixing of magnesian calcite. A fluorine-bearing Ca-Mg arsenate in sample FMB-1a may be tilasite ($\text{CaMg}[\text{AsO}_4]\text{F}$). This mineral is subhedral and is intergrown with magnetite and diopside and thus differs from the secondary fault breccia occurrences described at Sterling Hill (Parker and Peters, 1978). Minerals in the gneiss-hosted magnetite lenses include magnetite, hedenbergite, plagioclase, K feldspar, hornblende, and apatite (Table 2). Hercynite occurs as inclusions and lamellae within magnetite consistent with an origin by retrograde exsolution.

Mineral chemistry

Our data (Table 3) show the Furnace bed magnetite to be manganiferous (MnO up to 2.9 wt %) and titanium-poor ($\text{TiO}_2 < 0.04$ wt %) consistent with the findings of Frondel and Baum (1974). By contrast, the gneiss-hosted magnetite is low in manganese (<0.12 wt % MnO) and high in titanium (0.29–0.32 wt % TiO_2), and it also shows higher aluminum (0.77–0.89 wt % Al_2O_3) than the marble-hosted deposits. Thus, despite the fact that the Furnace bed and the gneiss-hosted magnetite lenses are separated by only 2 m of strata, they display the same chemical differences that are evident regionally between marble-hosted and silicate-hosted deposits (Puffer, 1997). The magnetite lens within the Franklin zinc deposit is low in manganese, titanium, and aluminum and thus shows chemical characteristics of both groups.

Silicates in the Furnace bed and in the magnetite lens within the Franklin zinc deposit are magnesium-rich and display Mg/(Mg + Fe) atomic ratios of 0.84 to 0.98 (Tables 4 and

5). The Furnace bed silicates are also manganiferous (e.g., 2 wt % MnO in clinopyroxene). Most unusual, however, are the high fluorine contents of the tremolite, biotite, chondrodite, and norbergite. They represent 66–70, 68, 90–99, and 98 atomic percent, respectively, of the fluorine end-members for these minerals, and they are among the highest fluorine contents ever observed in natural assemblages (cf. Deer et al., 1982; Petersen et al., 1982; Ribbe, 1982).

Silicates in the gneiss-hosted magnetite lenses are intermediate in Mg/(Mg + Fe). The clinopyroxenes are ferrosalites with Mg/(Mg + Fe) values of 0.45 to 0.48, and the hornblende is a ferrohastingsite with Mg/(Mg + Fe) of 0.27. About one third of the hornblende hydroxyl sites are occupied by Cl and about one sixth by F. The F content is high but not particularly unusual for metamorphic hornblendes (cf. Petersen et al., 1982). However, the Cl content is unusually high and is exceeded at only a few other metamorphic localities (cf. Morrison, 1991; Leger et al., 1996).

Furnace bed calcite is manganiferous with MnO contents of 2.5 to 4.6 wt percent (Table 6), whereas calcite in the magnetite lens within the Franklin zinc deposit contains minimal manganese. Specimens 7-20 and 1-35.5 contain calcite and dolomite that appear to be primary. Application of the Ca-Mg-Fe solvus thermometer of Anovitz and Essene (1987) gave 620°C for sample 7-20 but an unreasonably low temperature of 248°C for sample 1-35.5 ($X_{\text{Fe}+\text{Mn}}$ was used for X_{Fe}). The fact that these results are significantly below the $720^\circ \pm 40^\circ\text{C}$ temperature range that has been determined for the regional metamorphism (Volkert, 2001) confirms what is evident from the petrography, namely that the carbonates underwent retrograde unmixing and composition shifts (cf. Essene, 1983). The 620°C temperature obtained for coexisting calcite and dolomite in sample 7-20, and the 602°C temperature minimum that the carbonate solvus implies for magnesian

TABLE 3. Electron Microprobe Analyses of Magnetite¹

	Furnace bed							Gneiss-hosted lenses		Lens in Franklin Zn deposit
	5-2.6	5-2.9	5-3.2	7-20	FMB1a	FMB1b	FMB2	LFMB1	LFMB2	1-35.5
SiO_2	<0.01	<0.01	0.01	0.14	<0.01	<0.01	0.01	0.04	0.04	0.05
TiO_2	0.01	0.03	0.02	0.01	0.01	0.04	0.02	0.32	0.29	0.05
Al_2O_3	0.53	0.83	0.46	0.35	0.28	0.49	0.48	0.89	0.77	0.56
Fe_2O_3	69.17	68.56	69.33	69.33	68.82	68.07	67.78	66.77	67.16	68.46
FeO	27.99	27.91	28.27	31.14	27.02	27.38	29.32	31.16	31.06	31.28
MnO	2.69	2.46	2.80	0.49	2.90	2.76	0.95	0.10	0.12	0.04
MgO	0.44	0.59	0.26	0.08	0.68	0.48	0.30	0.03	0.10	0.05
ZnO	0.02	0.04	0.01	0.02	0.03	0.02	0.06	0.01	0.01	<0.01
Total	100.85	100.42	101.16	101.56	99.74	99.25	98.92	99.34	99.55	100.49
Si	0.000	0.000	0.000	0.005	0.000	0.000	0.000	0.002	0.002	0.002
Ti	0.000	0.001	0.001	0.000	0.000	0.001	0.001	0.009	0.008	0.001
Al	0.024	0.037	0.021	0.016	0.013	0.022	0.022	0.041	0.035	0.025
Fe^{3+}	1.976	1.961	1.978	1.973	1.986	1.975	1.976	1.938	1.945	1.968
Fe^{2+}	0.888	0.887	0.896	0.985	0.887	0.883	0.950	1.005	1.000	0.999
Mn	0.086	0.079	0.090	0.016	0.094	0.090	0.031	0.003	0.004	0.001
Mg	0.025	0.033	0.015	0.004	0.039	0.028	0.018	0.002	0.006	0.003
Zn	0.001	0.001	0.000	0.001	0.001	0.001	0.002	0.000	0.000	0.000

¹Mineral formulas were calculated by normalizing total cations to 3; $\text{Fe}^{3+}/\text{Fe}^{2+}$ was inferred from charge balance assuming no cation vacancies

TABLE 4. Electron Microprobe Analyses of Clinopyroxene¹

	Furnace bed				Gneiss-hosted lenses	
	5-2.6	5-2.9	5-3.2	FMB1	LFMB1	LFMB2
SiO ₂	54.69	54.67	54.51	54.27	50.71	50.71
TiO ₂	0.01	0.01	0.01	<0.01	0.02	<0.01
Al ₂ O ₃	0.12	0.28	0.52	0.67	1.59	1.72
FeO	3.87	3.33	3.85	3.69	17.80	16.37
MnO	2.53	2.26	2.31	2.41	0.54	0.44
MgO	16.64	16.95	16.19	16.09	8.06	8.46
ZnO	0.02	0.03	0.03	- ²	-	-
CaO	23.06	22.92	22.89	22.95	20.97	21.63
Na ₂ O	-	-	-	0.06	0.49	0.42
Total	100.94	100.45	100.31	100.15	100.17	99.75
Si	1.993	1.996	2.001	1.994	1.962	1.962
Ti	0.000	0.000	0.000	0.000	0.000	0.000
Al	0.005	0.012	0.022	0.029	0.073	0.078
Fe	0.118	0.102	0.118	0.113	0.576	0.530
Mn	0.078	0.070	0.072	0.075	0.018	0.014
Mg	0.904	0.922	0.886	0.881	0.465	0.488
Zn	0.000	0.001	0.001	-	-	-
Ca	0.901	0.897	0.900	0.903	0.870	0.897
Na	-	-	-	0.005	0.036	0.031
Mg/(Mg + Fe)	0.884	0.900	0.882	0.886	0.447	0.479

¹ Mineral formulas were calculated by normalizing total cations to 4

² - = not analyzed

calcite without dolomite in sample 5-2.9 provide lower temperature limits for these assemblages.

Apatite in a gneiss-hosted magnetite lens contains substantial F and significant Cl (Table 7). Fluorine is known to partition more strongly into apatite than into biotite and amphibole (Zhu and Sverjensky, 1992). In the limited number of samples available for our study, apatite does not coexist with either silicate mineral. However, the relative F contents of apatite in LFMB-2 and hornblende in LFMB-1 approximate the equilibrium partitioning (Zhu and Sverjensky, 1992), which suggests that fluorine fugacities for the two rocks were similar. The microprobe data also indicate a deficiency in P relative to stoichiometric apatite and give a low total, which suggests that the mineral may contain CO₃²⁻ in solid solution (cf. Binder and Troll, 1989).

Stable isotopes

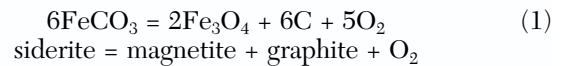
Carbon and oxygen isotope compositions of carbonates and graphite in the Furnace bed are given in Table 8. The carbonate δ¹³C values are essentially uniform at -5.2 ± 0.7 per mil, whereas the carbonate δ¹⁸O values range from 11.5 to 20.1 per mil. Graphite in sample FMB-2 has a δ¹³C value of -8.9 per mil. The 3.9 per mil isotopic difference between dolomite and graphite corresponds to an isotopic equilibration temperature of 728 ± 50°C (fractionations from Shepard and Schwartz, 1970, and Kitchen and Valley, 1995; error is a generous estimate). This result agrees well with the 720 ± 40°C estimate for peak metamorphic temperatures in the region (Volkert, 2001).

Discussion

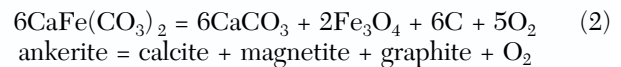
Evidence against metamorphic decarbonation of siderite

Several authors have suggested that the marble- and calc-silicate-hosted magnetite deposits in the Highlands were produced by metamorphic decarbonation of original siderite layers (Fron del and Baum, 1974; Kastelic, 1980; Puffer, 2001). The mineralogic and stable-isotope data given in Tables 2 and 8 provide an opportunity to test this hypothesis for the Furnace bed.

Field studies (Klein, 1983) and laboratory experiments (French, 1971) have shown that siderite decarbonation would occur during prograde heating when the rocks reached temperatures of medium- to high-grade metamorphism, perhaps 450° to 500°C or higher. Because the Furnace bed contains substantial calcite, ankerite (CaFe[CO₃]₂) may be a more likely protolith carbonate mineral (cf. Baur et al., 1985; Beukes et al., 1990). Ankerite also would likely have persisted to relatively high temperatures (Klein, 1983). Decarbonation by carbon-conservative reactions such as

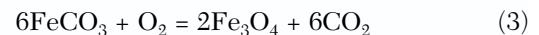


or



would produce rocks containing three molecules of graphite per molecule of magnetite. Graphite does occur locally in the Furnace bed, but its absence from six of eight samples that were examined in our study indicates that reactions (1) and (2) were not the primary pathways for magnetite production.

Alternative pathways are decarbonation reactions such as



or



The CO₂ loss implied by these reactions would be predicted to cause δ¹³C and δ¹⁸O shifts governed by isotopic fractionations between the expelled CO₂ and the rock. For reaction (4), the isotopic shifts have been calculated assuming that decarbonation took place at a temperature of 500°C; the results are shown in Figure 5. Oxygen isotope fractionation between CO₂ and rock was assumed to have been controlled by CO₂-ankerite exchange. Isotopic fractionation factors were taken from Zheng (1999) for oxygen and from Sheppard and Schwartz (1970) and Chacko et al. (1991) for carbon (ankerite was assumed to partition carbon isotopes like its isomorph dolomite). Both batch and continuous (Rayleigh) CO₂ loss mechanisms are illustrated.

The Furnace bed oxygen isotope data are compatible with a Rayleigh decarbonation mechanism but not a batch mechanism, and the reverse is true for the carbon isotopes. For metamorphic decarbonation, both isotope systems would be expected to conform to one of the mechanisms or some intermediate process, but they do not. Assuming that decarbonation took place at temperatures higher than 500°C or by siderite breakdown by means of reaction (3) does not lead to significantly better agreement between the data and

TABLE 5. Electron Microprobe Analyses of Humites, Amphiboles, and Biotite¹

	Chondrodite			Norbergite	Tremolite		Phlogopite	Hornblende
	5-2.6	5-2.9	7-20	7-20	1-35.5	FMB1	FMB1	LFMB1
SiO ₂	32.96	33.01	31.19	27.95	55.60	55.22	43.06	38.42
TiO ₂	<0.01	0.01	0.01	<0.01	0.01	<0.01	0.02	0.08
Al ₂ O ₃	<0.01	<0.01	<0.01	<0.01	1.78	2.49	12.10	12.31
FeO	7.25	7.85	15.09	4.32	5.04	2.52	1.11	25.22
MnO	3.65	3.18	3.23	1.31	0.08	1.33	0.16	0.29
MgO	50.89	51.50	45.94	56.70	22.40	21.85	27.76	5.15
CaO	0.09	0.13	0.20	0.20	13.07	13.10	0.02	11.31
K ₂ O	<0.01	<0.01	<0.01	<0.01	0.14	0.36	10.49	2.53
Na ₂ O	0.02	0.01	0.01	<0.01	0.68	0.27	0.06	1.29
ZnO	0.01	0.03	0.04	0.01	<0.01	- ²	-	-
Cl	<0.01	0.01	<0.01	0.01	0.07	0.03	0.06	2.45
F	9.59	9.93	10.35	18.16	3.06	3.19	6.17	0.46
H ₂ O ³	0.51	0.39	0.03	0.18	0.73	0.65	1.33	1.04
O = F,Cl	4.04	4.18	4.36	7.65	2.61	1.35	2.61	0.75
Total	100.93	101.87	101.73	101.19	101.51	99.66	99.73	99.80
Si	1.954	1.938	1.894	0.952	7.579	7.639	3.021	6.089
Ti	0.000	0.000	0.000	0.000	0.001	0.000	0.001	0.010
Al	0.000	0.000	0.000	0.000	0.286	0.407	1.001	2.300
Fe	0.359	0.386	0.766	0.123	0.574	0.292	0.065	3.343
Mn	0.183	0.158	0.038	0.166	0.009	0.156	0.010	0.040
Mg	4.495	4.507	4.157	2.879	4.550	4.506	2.902	1.218
Ca	0.006	0.008	0.013	0.007	1.909	1.942	0.002	1.922
K	0.000	0.000	0.000	0.000	0.024	0.065	0.939	0.512
Na	0.002	0.001	0.001	0.000	0.180	0.073	0.010	0.399
Zn	0.000	0.001	0.002	0.000	0.000	-	-	-
Cl	0.000	0.001	0.000	0.001	0.016	0.007	0.008	0.660
F	1.798	1.844	1.988	1.957	1.319	1.396	1.369	0.230
OH	0.202	0.155	0.012	0.042	0.665	0.597	0.623	1.110
Mg/(Mg + Fe)	0.926	0.921	0.844	0.959	0.888	0.939	0.978	0.267
F/(F + Cl + OH)	0.899	0.922	0.994	0.978	0.660	0.698	0.684	0.115

¹ Mineral formulas were calculated by normalizing about cations as follows: total cations = 7 for chondrodite, total cations = 4 for norbergite, Ca + Zn + Mg + Mn + Fe + Al + Ti + Si = 15 for tremolite and hornblende, and Zn + Mg + Mn + Fe + Al + Ti + Si = 7 for phlogopite

² - = not analyzed

³ Calculated from stoichiometry

TABLE 6. Electron Microprobe Analyses of Carbonates¹

	Furnace bed					Lens in Franklin Zn deposit	
	Cal 5-2.6	Cal 5-2.9	Cal 5-3.2	Cal 7-20	Dol 7-20	Cal 1-35.5	Dol 1-35.5
CaO	53.41	49.87	52.90	47.75	28.30	54.58	28.92
MgO	1.23	2.57	0.06	2.60	14.79	0.52	17.67
FeO	0.39	0.64	0.02	1.97	6.58	0.34	5.22
MnO	2.56	2.72	4.13	2.54	4.59	0.17	0.24
CO ₂ ²	45.08	44.02	44.15	43.09	45.23	43.71	45.33
Total	102.67	99.82	101.26	97.95	99.49	99.32	97.37
Ca	0.930	0.889	0.940	0.870	0.491	0.980	0.501
Mg	0.030	0.064	0.001	0.066	0.357	0.013	0.425
Fe	0.005	0.009	0.000	0.028	0.089	0.005	0.070
Mn	0.035	0.038	0.058	0.036	0.063	0.002	0.003

¹ Mineral formulas were calculated by normalizing total cations to 1

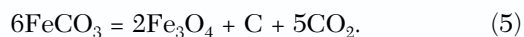
² Calculated from stoichiometry

TABLE 7. Electron Microprobe Analysis of Apatite from Gneiss-Hosted Magnetite Lens¹

Apatite LFMB2	
FeO	0.53
MnO	0.17
CaO	54.73
Na ₂ O	0.00
P ₂ O ₅	39.37
As ₂ O ₅	<0.01
V ₂ O ₃	<0.01
Cl	0.81
F	3.02
H ₂ O ²	0.14
O = F,Cl	1.45
Total	97.32
Fe	0.038
Mn	0.012
Ca	4.950
Na	0.000
P	2.813
As	0.000
V	0.000
Cl	0.116
F	0.806
OH	0.078
F/(F + Cl + OH)	0.806

¹Mineral formula was calculated by normalizing Ca + Fe + Mn to 5²Calculated from stoichiometry

a metamorphic decarbonation model, nor does consideration of reactions involving only partial carbon loss, such as



Including the effects of oxygen exchange between CO₂ and magnetite leads to significantly worse agreement between the data and a metamorphic decarbonation model.

Isotopic exchange between the Furnace bed and externally derived metamorphic fluids might have obscured the isotopic fingerprint of siderite or ankerite decarbonation. For example, exchange could have been promoted by permeability increases associated with the volume reductions that accompany decarbonation (Ferry and Gerdes, 1998). However, evidence suggests that the Furnace bed experienced only limited isotopic exchange with the surrounding rocks or with fluids derived from them. $\delta^{13}\text{C}$ values of carbonate in the Furnace bed are uniformly low ($-5.2 \pm 0.7\text{‰}$) compared with $\delta^{13}\text{C}$ in the Franklin marble that surrounds the bed ($-0.6 \pm$

TABLE 8. Carbon and Oxygen Isotope Compositions of Carbonates and Graphite from the Furnace Magnetite Bed

Sample	Mineral	$\delta^{13}\text{C}$	$\delta^{18}\text{O}$	<i>n</i> ¹
F5-2.6	Calcite	-5.9	11.5	1
F5-3.2	Calcite	-5.9	12.6	2
FMB1	Calcite	-4.6	13.5	2
FMB2	Dolomite	-5.0	20.1	3
FMB2	Graphite	-8.9		2

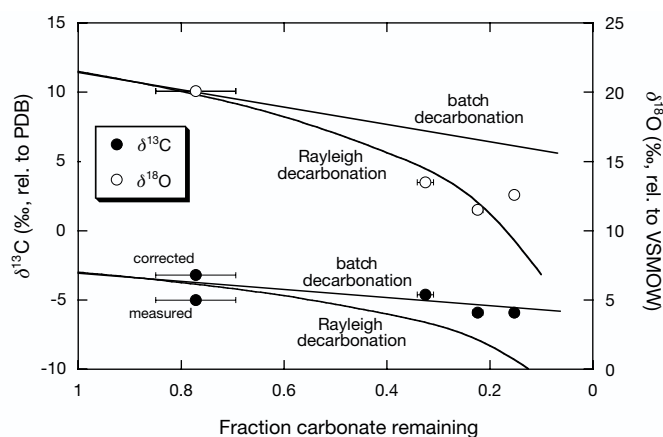
¹Number of replicate analyses

FIG. 5. Graph of Furnace bed stable-isotope data from Table 8 compared with models of metamorphic decarbonation of an ankerite (CaFe(CO₃)₂)-bearing protolith. The oxygen isotope data are compatible with a Rayleigh decarbonation mechanism but not with a batch mechanism, and the reverse is true for the carbon isotopes. For metamorphic decarbonation, both isotopic systems would be expected to conform to one of the mechanisms or some intermediate process, but they do not. Fraction of carbonate remaining was calculated from thin section modes assuming that three moles of CO₂ were lost per mole of magnetite produced (see text for reaction and source of fractionation factors). Two points are plotted for sample FMB-2, the measured $\delta^{13}\text{C}$ value, and the $\delta^{13}\text{C}$ value corrected for metamorphic carbonate-graphite exchange (cf. Kitchen and Valley, 1995).

0.8‰, *n* = 5) or the Franklin zinc ores ($-0.6 \pm 0.9\text{‰}$, *n* = 4) that lie 0 to 2 m above it (C. Johnson, unpub. data, 1990). $\delta^{18}\text{O}$ values of carbonate show a wide range (11.5–20.1‰) more consistent with whole-rock control of mineral isotopic compositions than with metamorphic fluid control. In addition, three of the four Furnace bed samples are significantly lower in $\delta^{18}\text{O}$ than the surrounding Franklin marble ($18 \pm 3\text{‰}$, *n* = 5; Johnson et al., 1990b) more closely resembling the Franklin zinc ores ($12 \pm 3\text{‰}$, *n* = 4; Johnson et al., 1990b). Certainly, metamorphic fluid infiltration cannot be precluded. However, its effects appear to have been limited enough that isotopic characteristics of the protoliths were preserved.

Although the isotopic data provide no evidence that magnetite was produced by decarbonation reactions, small amounts of decarbonation may have caused isotopic shifts that are too small to detect. For example, minor decarbonation likely accompanied the production of diopside, which in most carbonate rocks forms at the expense of dolomite or the dolomite component present in another carbonate mineral by solid solution.

Evidence for nearly isochemical metamorphism of a calcite + iron oxide protolith

If the Furnace bed did not form from an original ferroan carbonate layer, then it is logical to consider calcite + iron oxide assemblages as candidate protoliths. Rocks formed by metamorphism of chemically precipitated mineral assemblages would be expected to show mineral $\delta^{18}\text{O}$ values that vary with mineral proportions (Gregory et al., 1989). Figure 6a shows that the Furnace bed samples lie on a possible mixing line with intercepts of 21 per mil for the pure calcite end member and 7 per mil for the pure iron oxide end member. The 21 per mil intercept would correspond with the average

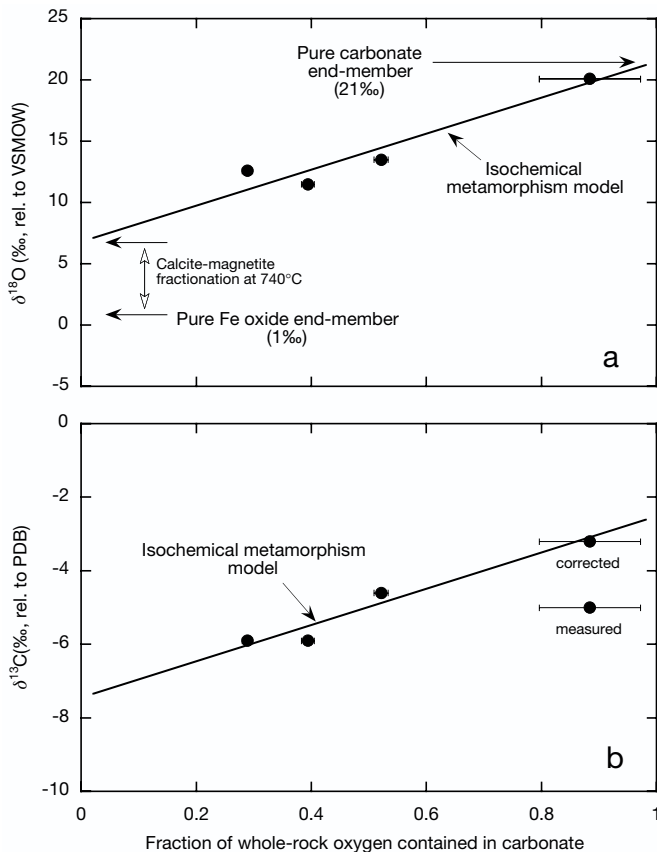


FIG. 6. Graphs of Furnace bed oxygen (a) and carbon (b) isotope data from Table 8 compared with a model involving isochemical metamorphism of chemically precipitated iron oxide + calcite assemblages. The isotopic compositions implied by this model ($\delta^{18}\text{O} = 1\text{‰}$ for the protolith iron oxide, $\delta^{18}\text{O} = 21\text{‰}$ and $\delta^{13}\text{C} = -5 \pm 2\text{‰}$ for the protolith carbonate) are within the ranges observed in Superior-type banded iron formations (see text). The fraction of oxygen contained in carbonate was calculated from modal data (Table 2).

calcite composition in the Furnace bed protolith if metamorphism were isochemical with respect to oxygen. The 7 per mil intercept for the pure iron oxide end member (Fig. 6a) suggests that the $\delta^{18}\text{O}$ value of the protolith iron oxide averaged 1 per mil (the isotopic offset corresponds with the calcite-magnetite fractionation at $720 \pm 40^\circ\text{C}$; Chiba et al., 1989). These inferred $\delta^{18}\text{O}$ values for the protolith minerals fall within the ranges characteristic of carbonates and iron oxides in banded iron formations (Perry et al., 1973; Becker and Clayton, 1976; Perry and Ahmad, 1981; Baur et al., 1985; Beukes et al., 1990; Kaufman et al., 1990; review by Gregory et al., 1989). Many iron formations have experienced secondary resetting of iron oxide $\delta^{18}\text{O}$ values, possibly during conversion of a precursor mineral to magnetite (Gregory et al., 1989). It is impossible to determine from the Furnace bed data whether a similar process has affected these rocks. Nevertheless, the Furnace bed oxygen isotope systematics are similar to those of banded iron formations, diagenetic complications included.

The Furnace bed $\delta^{13}\text{C}$ values show much less variation than the $\delta^{18}\text{O}$ values (Fig. 6b). If the measured $\delta^{13}\text{C}$ for FMB-2 is corrected for the effects of metamorphic isotope exchange between calcite and coexisting graphite (Kitchen and Valley,

1995), the data suggest a small compositional influence on $\delta^{13}\text{C}$; carbonate-rich rocks display $\delta^{13}\text{C}$ values near -3 per mil, and iron oxide-rich rocks display $\delta^{13}\text{C}$ values near -7 per mil.

These $\delta^{13}\text{C}$ values are lower than the values characteristic of marine carbonates of Middle Proterozoic age (Veizer and Hoefs, 1976), but they fall within the range characteristic of banded iron formations (Becker and Clayton, 1972; Perry et al., 1973; Perry and Ahmad, 1981; Baur et al., 1985; Beukes et al., 1990; Kaufman et al., 1990). In addition, the inferred compositional effect on $\delta^{13}\text{C}$ is a feature that has been recognized in Superior-type iron formations in the Transvaal basin of South Africa and the Hamersley basin of Western Australia (Beukes et al., 1990; Kaufman et al., 1990). The Transvaal and Hamersley basin compositions are believed to reflect carbonate precipitation from anoxic bottom waters that contained low $\delta^{13}\text{C}$ dissolved inorganic carbon and a diagenetic history in which carbonate $\delta^{13}\text{C}$ was further lowered by oxidation of organic matter by ferric oxides (Beukes et al., 1990; Kaufman et al., 1990). These same phenomena are plausible explanations for the Furnace bed $\delta^{13}\text{C}$ data.

An exhalative or early diagenetic model for marble-hosted zinc and iron deposits

In a previous study (Johnson et al., 1990a), we showed that the whole-rock chemical and oxygen isotope compositions of a suite of Sterling Hill ore samples are consistent with a model protolith composed of carbonate, clay, and oxyhydroxide minerals that formed at a temperature of $150 \pm 50^\circ\text{C}$. This temperature is significantly higher than expected for either seawater oxidation or subaerial weathering of a preexisting massive sulfide body, which implies that sulfur-poor zincian assemblages precipitated directly from the metal-transporting fluid. Whole-rock zinc-to-silicon ratios in the Sterling Hill ores greatly exceed the ratios of the common zinc silicates found in low-temperature settings, sauconite ($\text{Zn}_3\text{Si}_4\text{O}_{10}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$) and hemimorphite ($\text{Zn}_4\text{Si}_2\text{O}_7(\text{OH})_2 \cdot \text{H}_2\text{O}$), which suggests that a nonsilicate mineral was the main zinc host in the protolith. The isotope modeling suggests that the zinc host was a carbonate, likely smithsonite (ZnCO_3) or hydrozincite ($\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$), that broke down during the Grenvillian metamorphism to give the willemite \pm franklinite \pm zincite assemblages that are observed today (Johnson et al., 1990a).

Possible analogs for the Franklin and Sterling Hill protoliths are hypogene sulfur-poor zinc deposits like those at Vazante, Brazil, and Beltana, Australia (Muller, 1972; Montiero et al., 1999; Groves et al., 2003; Hitzman et al., 2003). The Vazante deposits, however, possess important characteristics that are not shared by the New Jersey deposits. These characteristics include (1) substantial sphalerite present in discrete imbricated sulfide bodies and also coexisting with willemite, (2) widespread silicification in the ores and host rocks suggesting that the ore fluid was silica saturated, and (3) a metamorphic origin for the metal-carrying fluid inferred from $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ values of 11 to 19 per mil (Montiero et al., 1999).

The isotopic and chemical models presented by Johnson et al. (1990a) suggest that the ore-forming fluid at Sterling Hill had a $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ value of 2 ± 4 per mil consistent with a seawater origin and possible ^{18}O enrichment by exchange with

rocks along the hydrothermal flow path. A seawater fluid origin accords with the conclusions of most recent workers that the protolith for the zinc ores formed directly on the Proterozoic sea floor or in shallowly buried sediments (Callahan, 1966; Frondel and Baum, 1974; Squiller and Sclar, 1980; Johnson et al., 1990a). The paucity of sulfide minerals within the deposit is strong evidence that the ore-forming fluid was H_2S poor. Sterling Hill can be viewed as having formed from an oxidized (sulfate-predominant) metalliferous brine similar to the brines that formed McArthur-type sediment-hosted Zn-Pb deposits (Cooke et al., 2000; see also Emsbo, 2000). Oxidized brines develop in sedimentary basins with a predominance of carbonates, evaporites, and hematitic sandstones and shales and a paucity of pyritic or graphitic sandstones and shales. The deposits that they form are characteristically low in barium, gold, and tin owing to the inability of sulfate-bearing fluids to carry significant amounts of those elements. These features are characteristic of the Highlands supracrustal sequence and the New Jersey zinc ores, respectively.

A key characteristic of the New Jersey zinc ores is that metal was deposited in an oxidizing, sulfate-stable environment rather than a reduced, H_2S -stable environment as was the case for the McArthur-type Zn-Pb sulfide deposits (Cooke et al., 2000). The rare metamorphic sulfide occurrences at Sterling Hill are associated with graphite or abundant ferrous silicates (Johnson et al., 1990a), which suggests that, where reducing agents were present, the ambient sulfate was reduced to H_2S that then combined with dissolved metals to form sulfides. Generally, however, conditions were oxidizing enough that sulfate was favored, H_2S concentrations were very low, and the zinc and other metals precipitated as carbonates, oxides, or silicates. Whether these precipitates settled from the water column or whether they formed diagenetically by replacement reactions in shallowly buried sediments remains an open question.

The Furnace bed and other magnetite deposits described in this paper may be metamorphosed equivalents of the ferruginous rocks that are found near sediment-hosted Zn-Pb deposits such as Broken Hill, Australia; Bergslagen, Sweden; Tynagh, Ireland; Bathurst, New Brunswick; and in the Namaqua mobile belt, South Africa (e.g., Goodfellow et al., 1993; Parr and Plimer, 1993; Peter and Goodfellow, 1996). There is some uncertainty whether the iron-rich rocks in these other districts are true syngenetic exhalites or are epigenetic replacements (e.g., Russell, 1975; Hitzman et al., 1995; Cruise, 1996). However, irrespective of the exact timing, there is general agreement that the iron mineralization bears a genetic relationship to the massive sulfides, so these occurrences represent viable analogs for a zinc-iron connection in the New Jersey Highlands.

The closest analog would appear to be the Bergslagen district where manganese iron-oxide rocks are the dominant ferruginous lithology. The fluorite- and fluorapatite-bearing occurrences at Broken Hill (Stanton, 1976; Parr and Plimer, 1993) bear some similarity to the fluorine-rich assemblages in the Furnace bed. However, nowhere in New Jersey have there been found equivalents of the quartz-gahnite rocks that are the common "exhalite" type at Broken Hill. It is important to note that, aside from the results of Puffer (1997, 2001), few

geochemical data are available for the New Jersey iron deposits. Thus, whether they show boron, barium, phosphorous, or other element enrichment known to be characteristic of ferruginous rocks in other zinc districts is unknown.

Recent regional studies of the New Jersey Highlands (e.g., Drake et al., 1996) allow the iron and zinc deposits to be placed in a tectonostratigraphic framework (Fig. 2). The Franklin marble is thought to have accumulated in a marine setting because, removed from iron and zinc mineralization, its oxygen and carbon isotope compositions (Pineau et al., 1976; Valley and O'Neil, 1981; Johnson et al., 1990a) match Middle Proterozoic marine compositions (Veizer and Hoefs, 1976). Two pieces of evidence suggest that the Franklin marble represents the western margin of a marine basin or a marine shelf. The first is the occurrence of stromatolites (Volkert et al., 2000b) and fluoborite-rich probable evaporitic layers (Kearns, 1975, 1977) within the unit. Both features suggest shallow water deposition, and neither has been identified in marbles farther east (see Eastern marble belt in Fig. 2), consistent with deepening water to the east. The second piece of evidence for a west-to-east increase in water depth is the presence of massive graphite deposits within pelitic units in the east and their absence from otherwise similar units farther west. These graphite deposits, which were mined in the late 1800s and early 1900s, likely are metamorphosed sedimentary organic accumulations and may have originated as algal mats (Volkert et al., 2000b). Their preservation is most easily explained by anoxic conditions in basin deep waters.

Iron deposition toward the margin of a stratified basin could be explained by the same model that has been proposed for banded iron formations (James, 1992), in which ferrous iron accumulates in anoxic deep waters and then is oxidized and precipitated at shallower levels at the interface with overlying oxygenated waters. It is unknown whether the iron and manganese in the New Jersey deposits were derived originally from sea floor weathering or from hydrothermal venting, but the occurrence of major stratiform zinc deposits in the region and the presence of intercalated metavolcanic rocks suggest contemporaneous hydrothermal activity.

A stratified basin model would explain a number of features of the New Jersey deposits. The first is their distribution along a 60 km strike length of what appears to be the western edge of the Grenvillian basin (Fig. 2). This distribution might be expected where iron precipitation took place at a chemocline separating anoxic bottom waters and overlying oxygenated waters (cf. Beukes et al., 1990).

Iron deposition close to the zinc ores may have been by a mechanism similar to that operating today in the metalliferous brine pools or "deeps" in axial rifts of the Red Sea (Scholten et al., 2000, and references therein). In the Red Sea, iron oxides and amorphous iron oxyhydroxides form at the anoxic-oxic interface above the ponded brines. Oxides that form over the centers of deeps redissolve as they sink through the reduced brines, but oxides formed around the perimeters where the anoxic-oxic interface intersects the sea floor tend to be preserved (Pottorf and Barnes, 1983). Iron oxide layers also occur in buried sediments beneath the floor of the deeps, having presumably formed at times when there was no static brine pool, and they are also widely distributed on the surrounding sea floor, reflecting dispersal of

the colloidal precipitates in the water column (Bischoff, 1969). The Red Sea ferruginous muds resemble our inferred Furnace bed protolith in that they contain detrital calcite rather than siderite, and in that they are low in silica compared with Superior- or Algoma-type iron formations (Scholten et al., 2000).

The metal endowments are an additional point of similarity between the New Jersey and the Red Sea deposits. The zinc resource contained within the sediments beneath the Atlantis II Deep, one of the larger deeps, is 1.8 Mt of zinc (Nawab, 1994), equivalent to about half the total production at Franklin (4.4 Mt) but very similar to the total production at Sterling Hill (2.2 Mt) (Metsger, 2001).

There are, however, differences between the Atlantis II Deep sediments and the New Jersey ores. For example, although the zinc oxide woodruffite occurs in the Atlantis II sediments (Bischoff, 1969), sphalerite is the dominant zinc host, even in the sulfide-poor facies (Pottorf and Barnes, 1983; Zierenberg and Shanks, 1983). Apparently the environment of metal deposition for the Red Sea deposits was sufficiently sulfidizing to stabilize sphalerite. Also, the Atlantis II resource is an order of magnitude lower in grade (2.06 wt % Zn on a dry, salt-free basis) than the New Jersey ores, and the sediments containing the metals are dominated by detrital silicates (Scholten et al., 2000) rather than by carbonates.

The second feature of the New Jersey iron deposits that can be explained by a stratified basin model is the local presence of sulfide minerals, as at Sulphur Hill, Roseville, and Raub (Bayley, 1910). Sulfides might have formed where an abundance of organic matter led to reduction of seawater sulfate either within bottom sediments or in euxinic bottom waters. The resulting H₂S would have readily reacted with iron and other metals. Fundamentally, the presence or absence of sulfides would reflect variations in biological productivity in the overlying basin waters and variation in organic matter burial rates.

The third feature that can be explained by a stratified basin model is the low $\delta^{13}\text{C}$ relative to normal marine carbonates. Waters that were stratified with respect to oxygen content might also have been stratified with respect to $\delta^{13}\text{C}$ of dissolved inorganic carbon. Beukes et al. (1990) made a strong case for isotopic stratification during deposition of Superior-type iron formations in the Transvaal, giving rise to -5 per mil carbonates associated with the iron formations and 0 per mil carbonates in shallower water deposits. Kaufman et al. (1990) presented isotopic evidence that a similar stratification model may be applicable to Hamersley basin iron formations. The source of the low $\delta^{13}\text{C}$ carbonate cannot be identified with certainty, but likely candidates are hydrothermal fluids venting into the deep waters and methanogenesis in bottom sediments (Beukes et al., 1990; Des Marais, 2001).

The 1.3 to 1.1 Ga time period in which the New Jersey sediments were laid down falls within an interval in which no iron formations of significance were formed globally (James, 1992) and in which surface redox environments, climate, and the global carbon cycle are believed to have been relatively stable (Brasier and Lindsay, 1998). The evidence presented here would suggest that the same redox-controlled iron sequestration processes that operated during Archean, Early Proterozoic, and Phanerozoic time were active during Middle Proterozoic time, although perhaps at smaller scales.

Possible relationship to gneiss-hosted iron deposits in the Highlands

For the Furnace magnetite bed there is strong spatial evidence for a genetic link to the zinc mineralization. The spatial evidence is weaker for the gneiss-hosted magnetite lenses underlying the Furnace bed and the deposits on Balls Hill, because there may have been displacement along the gneiss-marble contact during Grenvillian deformation (cf. Skinner and Johnson, 1987). Nevertheless, a genetic connection between the gneiss-hosted magnetite deposits and the Franklin zinc deposits is certainly suggested.

There are three clear differences between the marble-hosted magnetite deposits and the gneiss-hosted deposits proximal to the Franklin zinc deposit, and all can be explained within the framework of an exhalative or a diagenetic model. Many other magnetite deposits in the Highlands occur in calc-silicate or quartz-K feldspar \pm biotite paragneisses (e.g., Edison deposits in the Franklin-Hamburg district: Baker and Buddington, 1970; Fig. 2) and, to the extent that they resemble the gneiss-hosted magnetite lenses analyzed in this study and those on Balls Hill, they also can be accommodated in an exhalative or a diagenetic model.

The first difference is that the dominant gangue mineral in the marble-hosted deposits is calcite, whereas the gangue in the gneiss-hosted deposits is clinopyroxene, hornblende, and feldspars. This difference can be attributed to iron oxide accumulation across boundaries separating two different sedimentary environments, one characterized by calcite precipitation and the other by abundant siliciclastic sediment. The clastic component is much more abundant in the New Jersey gneiss-hosted deposits than in typical banded iron formations, and there is a closer similarity to the ferruginous deposits in the Red Sea, which are siliciclastic rich (Bischoff, 1969). The absence of quartz in the New Jersey deposits is an additional similarity to the Red Sea iron deposits, which are low enough in chemically precipitated silica that recrystallization gives rise to Fe silicates rather than free quartz (Pottorf and Barnes, 1983).

The second difference is that the marble-hosted magnetites are richer in manganese (as are other minerals in the deposits), and the gneiss-hosted magnetites are richer in titanium and aluminum (Table 3; Puffer, 1997). These features too can be attributed to differences in the sedimentary environments in which iron oxides precipitated. Where carbonate sediments were accumulating, the siliciclastic sediment supply (which would have been the main carrier of titanium and aluminum) would have been low. Manganese, on the other hand, could have been scavenged from seawater during cycling between anoxic and oxic conditions. Recent studies (e.g., Neumann et al., 2002) have shown that manganese accumulated in anoxic bottom waters can precipitate as MnO₂ during flushing by oxygenated waters. A return to anoxic conditions allows for microbial reduction of the MnO₂ and increased alkalinity, both of which favor fixation in the sediment of authigenic Mn carbonate.

The third difference between the marble-hosted and gneiss-hosted magnetite deposits is related to the halogen contents of hydrous minerals (Fig. 7). The marble-hosted deposits have a high fluorine content, whereas the gneiss-hosted

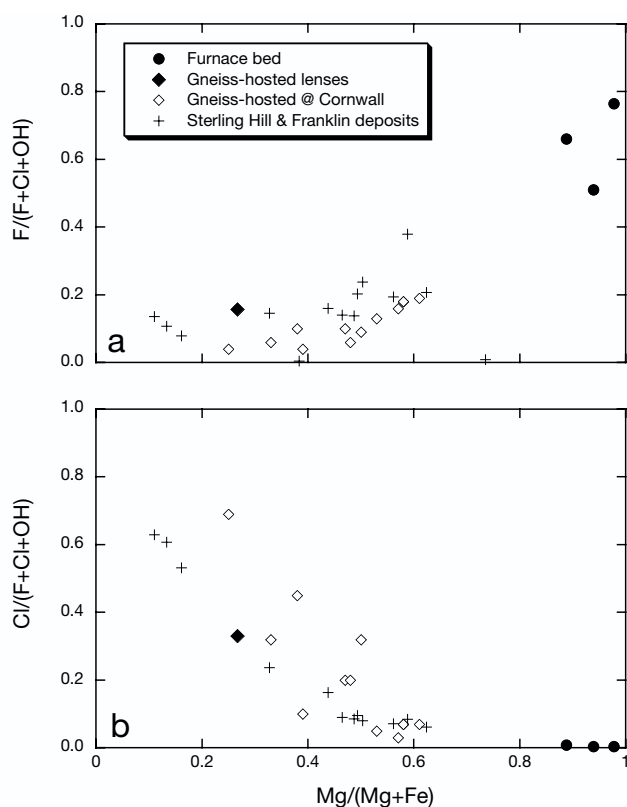


FIG. 7. (a) Plot of $F/(F + Cl + OH)$ versus $Mg/(Mg + Fe)$, and (b) plot of $Cl/(F + Cl + OH)$ versus $Mg/(Mg + Fe)$ for biotite and amphibole from the Furnace magnetite bed, the underlying gneiss-hosted magnetite lenses, other gneiss-hosted magnetite deposits at Cornwall, New York (Leger et al., 1996), and the Sterling Hill and Franklin zinc deposits (Fron del and Ito, 1966; Tracy, 1991). Note the similarity between the gneiss-hosted magnetite deposits and the zinc deposits. Positive slopes in (a) and negative slopes in (b) are due at least partly to Fe-F avoidance (Rosenberg and Foit, 1977).

lenses studied here and one other gneiss-hosted locality for which data are available (at Cornwall, New York; Leger et al., 1996) are both high in Cl. It is noteworthy that in terms of halogen chemistry, the zinc deposits resemble the gneiss-hosted magnetite deposits more than the marble-hosted magnetite deposits despite the fact that the evidence for a zinc-iron link is much stronger for the marble-hosted deposits. Thus, the difference in halogen chemistries between the marble-hosted magnetite deposits and the gneiss-hosted deposits might reflect not different origins, but rather local controls on halogen budgets at the sites of metal deposition, perhaps by fluorine-bearing biogenic sediments in some settings and by marine waters or evaporite assemblages in other settings.

Of the hundreds of individual magnetite deposits that occur in the Highlands, many are contained within lithologies that are clearly metaigneous, such as pegmatite, pyroxenite, and large bodies of granite gneiss (Buddington, 1966; Puffer, 2001). For these deposits, isochemical metamorphism of an original sedimentary deposit is an untenable genetic hypothesis.

Implications for iron and zinc deposits in other Grenvillian terranes

Stratiform zinc and iron deposits are found in other Grenvillian supracrustal sequences exposed in the northwest

Adirondacks of New York and the Central metasedimentary belt of Quebec and Ontario (Fig. 1). In the Adirondacks (Fig. 8), massive sphalerite + pyrite + galena deposits occur within dolomitic marbles in the northeast-southwest-trending Balmat-Edwards district. This district has been a major zinc producer with past production plus reserves of 3.8 Mt of zinc (deLorraine, 2001). Approximately 10 km to the west is a parallel belt of massive pyrite deposits contained in graphitic biotite schists (Prucha, 1957), and still farther west are massive graphite occurrences (Buddington, 1934). In the Mont Laurier basin in southwestern Quebec, which may be the western flank of the same basin represented by the Adirondacks section (Rankin et al., 1993), Gauthier and Brown (1986) and Gauthier et al. (1987) have described dolomitic marble-hosted sphalerite deposits and stratiform magnetite deposits that occur at the same stratigraphic level farther east toward the basin center (Fig. 1; see also fig. 2 of Gauthier and Brown, 1986).

There has been broad agreement that these various deposit types formed either on the Proterozoic sea floor or at shallow levels below the sea floor (Prucha, 1957; Buddington et al., 1969; deLorraine and Dill, 1982; Whelan et al., 1984; Gauthier et al., 1987; deLorraine, 2001). These deposits conform to the same basic regional patterns that are apparent in the New Jersey Highlands, namely carbonate-hosted zinc deposits toward basin margins giving way to iron deposits and then massive organic-rich (graphite) deposits toward basin centers. Genetic connections between zinc and iron mineralization in the Adirondacks and the Central metasedimentary belt have been suggested previously on the basis of geochemical arguments (Gauthier et al., 1987; Whelan et al., 1990). The deposits can be viewed as products of hydrothermal systems that operated beneath the Proterozoic basins. Zinc deposits formed near hydrothermal conduits, and iron deposits formed either near conduits or more regionally at interfaces between anoxic and oxic, or anoxic and euxinic, environments. Whether metals precipitated as carbonate-oxide-silicate assemblages or as sulfide assemblages can be viewed as reflecting redox conditions, and therefore H_2S availability, at the sites of metal deposition. Franklin and Sterling Hill are the only major zinc oxide-silicate deposits that have been found in these Grenvillian terranes; willemite of secondary or uncertain origin has been found at Sulphur Hill, New Jersey (Bayley, 1910) and at Balmat (Brown, 1936). However, the discovery in Quebec of a magnetite occurrence containing 4 percent franklinite component ($ZnFe_2O_4$) in solid solution (Gauthier et al., 1987) suggests that there could be potential for others.

Conclusions

Chemical, mineralogic, and stable-isotope data for the Furnace magnetite bed are consistent with nearly isochemical metamorphism of a calcite + iron oxide protolith that is chemically and mineralogically similar to iron-rich sediments found near the Red Sea brine pools and to ferruginous exhalites associated with massive sulfide deposits at Bergslagen, Sweden, and Broken Hill, Australia. The inferred protolith bears isotopic similarities to Superior-type banded iron formations.

The Furnace bed can be accommodated in a model that we proposed previously for the Highlands zinc oxide-silicate

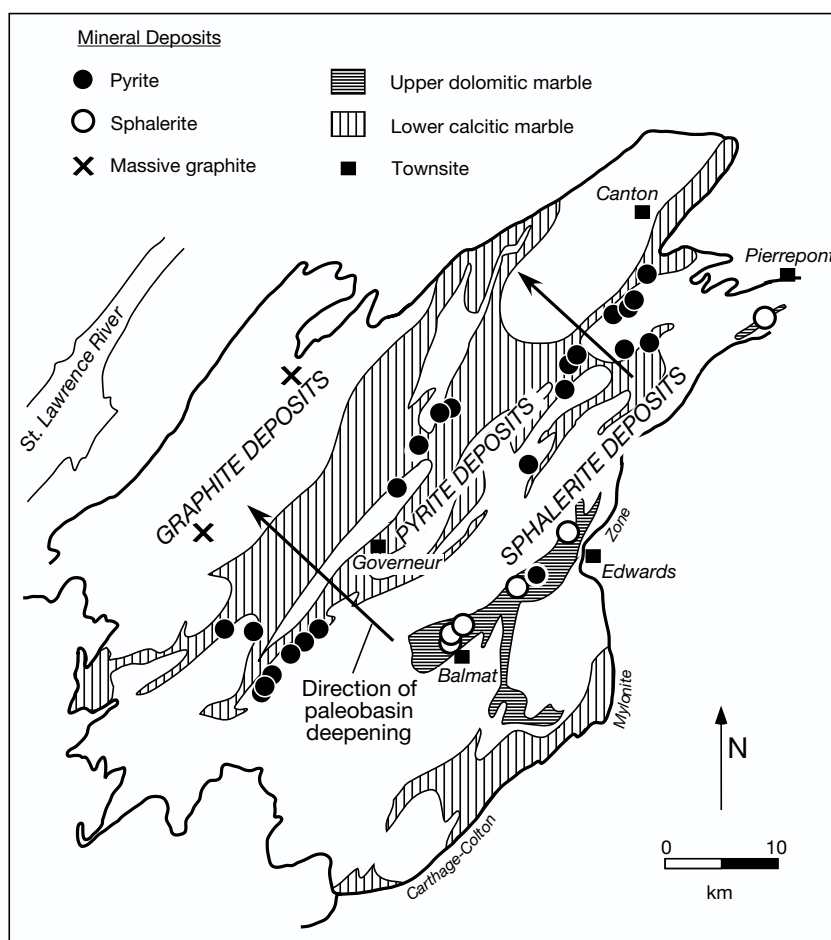


FIG. 8. Map of distribution of Proterozoic rocks of the northwest Adirondacks of New York showing the locations of massive sphalerite deposits of the Balmat-Edwards-Pierrepont district, massive pyrite deposits, and massive graphite occurrences. The deposits define belts along what is thought to be the eastern margin of a Grenvillian depositional basin. After Buddington (1934, 1966) and deLorraine (2001).

deposits in which zinc was transported by sulfate-stable brines, and metals were deposited near the margin of a Proterozoic basin under sulfate-stable conditions as zincian carbonates and Fe-Mn-Zn oxides and silicates. The Furnace bed protolith was formed by seawater-oxidation of hydrothermally transported iron. It is uncertain whether the iron mineralization and the zinc mineralization occurred synchronously, as for example by zinc carbonate replacement of calcitic sediments with accompanying iron venting and iron oxide accumulations on the sea floor. Alternatively, the stratigraphic transition from Franklin deposit zinc mineralization to Furnace bed iron mineralization (or the reverse if the stratigraphy is inverted) could represent temporal changes in metal contents of the hydrothermal fluid.

Other manganeseiferous magnetite + calcite bodies occur at approximately the same stratigraphic position as the Furnace bed along a 60 km length of what was the western edge of a Grenvillian marine basin. This distribution suggests that iron deposits formed not only near hydrothermal conduits but also regionally at the interface between iron-bearing anoxic deep waters and oxygenated shallow waters. Independent evidence for deep water anoxia to the east of the metal deposits sup-

ports the hypothesis that the basin waters were stratified. The finding that the Furnace bed is a sedimentary or hydrothermal iron formation opens the possibility that other Highlands magnetite deposits contained in silicate paragneisses, both those proximal to the Franklin zinc deposit and others that occur regionally, may be facies equivalents of the Furnace bed that formed where siliciclastic detritus was abundant.

The basin-margin metallogenic model can be extended to sediment-hosted zinc and iron deposits in Grenvillian supracrustal sequences in the northwest Adirondacks of New York and the Central metasedimentary belt of Ontario and Quebec. In these terranes, marble-hosted sphalerite deposits give way basinward to iron oxide or iron sulfide deposits. The zinc deposits formed near hydrothermal conduits, and the iron deposits formed at nearby redox boundaries and also along horizons that extended tens of kilometers and marked the intersections of paleochemoclines with the sea floor. Whether metal precipitation was as sulfide assemblages or carbonate-oxide-silicate assemblages can be viewed as reflecting whether or not sufficient organic matter or other reductants were available in sediments or bottom waters to form H_2S from the ambient sulfate.

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REFERENCES

- Anovitz, L.M., and Essene, E.J., 1987, Phase equilibria in the system $\text{CaCO}_3\text{-MgCO}_3\text{-FeCO}_3$; *Journal of Petrology*, v. 28, p. 389–414.
- Baker, D.R., and Buddington, A.F., 1970, Geology and magnetite deposits of the Franklin Quadrangle and part of the Hamburg Quadrangle, New Jersey: U.S. Geological Survey Professional Paper 638, 73 p.
- Baur, M.E., Hayes, J.M., Studley, S.A., and Walter, M.R., 1985, Millimeter-scale variations of stable isotope abundances in carbonates from banded iron-formations in the Hamersley Group of Western Australia: *ECONOMIC GEOLOGY*, v. 80, p. 270–282.
- Bayley, W.S., 1910, Iron mines and mining in New Jersey: Volume VII of the Final Report Series of the State Geologist: Trenton, Geological Survey of New Jersey, 512 p.
- Becker, R.H., and Clayton, R.N., 1972, Carbon isotopic evidence for the origin of a banded iron-formation in Western Australia: *Geochimica et Cosmochimica Acta*, v. 36, p. 577–595.
- 1976, Oxygen isotope study of a Precambrian banded iron-formation, Hamersley Range, Western Australia: *Geochimica et Cosmochimica Acta*, v. 40, p. 1153–1165.
- Beukes, N.J., Klein, C., Kaufman, A.J., and Hayes, J.M., 1990, Carbonate petrography, kerogen distribution, and carbon and oxygen isotope variations in an early Proterozoic transition from limestone to iron-formation deposition, Transvaal Supergroup, South Africa: *ECONOMIC GEOLOGY*, v. 85, p. 663–690.
- Binder, G., and Troll, G., 1989, Coupled anion substitution in natural carbon-bearing apatites: *Contributions to Mineralogy and Petrology*, v. 101, p. 394–401.
- Bischoff, J.L., 1969, Red Sea geothermal brine deposits: Their mineralogy, chemistry, and genesis, in Degens, E.T., and Ross, D.A., eds., *Hot brines and Recent heavy metal deposits in the Red Sea*: New York, Springer-Verlag, p. 368–401.
- Brasier, M.D., and Lindsay, J.F., 1998, A billion years of environmental stability and the emergence of eukaryotes: New data from northern Australia: *Geology*, v. 26, p. 555–558.
- Brown, J.S., 1936, Supergene sphalerite, galena and willemite at Balmat, N.Y.: *ECONOMIC GEOLOGY*, v. 31, p. 331–354.
- Buddington, A.F., 1934, Geology and mineral resources of the Hammond, Antwerp and Lowville quadrangles: *New York State Museum Bulletin* 296, 251 p.
- 1966, The Precambrian magnetite deposits of New York and New Jersey: *ECONOMIC GEOLOGY*, v. 61, p. 484–510.
- Buddington, A.F., Jensen, M.L., and Mauger, R.L., 1969, Sulfur isotopes and origin of northwest Adirondacks sulfide deposits, in *Igneous and metamorphic geology—A volume in honor of Arie Poldervaart*: Geological Society of America Memoir 115, p. 423–451.
- Callahan, W.H., 1966, Genesis of the Franklin-Sterling, New Jersey orebodies [abs.]: *ECONOMIC GEOLOGY*, v. 61, p. 1140–1141.
- Carvalho, A.V., III, and Sclar, C.B., 1988, Experimental determination of the $\text{ZnFe}_2\text{O}_4\text{-ZnAl}_2\text{O}_4$ miscibility gap with application to franklinite-gahnite exsolution intergrowths from the Sterling Hill zinc deposit, New Jersey: *ECONOMIC GEOLOGY*, v. 83, p. 1447–1452.
- Chacko, T., Mayeda, T.K., Clayton, R.N., and Goldsmith, J.R., 1991, Oxygen and carbon isotope fractionations between CO_2 and calcite: *Geochimica et Cosmochimica Acta*, v. 55, p. 2867–2882.
- Chiba, H., Chacko, T., Clayton, R.N., and Goldsmith, J.R., 1989, Oxygen isotope fractionations involving diopside, forsterite, magnetite, and calcite: Application to geothermometry: *Geochimica et Cosmochimica Acta*, v. 53, p. 2985–2995.
- Collins, L.G., 1969a, Host rock origin of magnetite in pyroxene skarn and gneiss and its relation to alaskite and hornblende granite: *ECONOMIC GEOLOGY*, v. 64, p. 191–201.
- 1969b, Regional recrystallization and the formation of magnetite concentrations, Dover magnetite district, New Jersey: *ECONOMIC GEOLOGY*, v. 64, p. 17–33.
- Cook, G.H., 1868, *Geology of New Jersey*: Newark, Daily Advertiser Office, 899 p.
- Cooke, D.R., Bull, S.W., Large, R.R., and McGoldrick, P.J., 2000, The importance of oxidized brines for the formation of Australian Proterozoic stratiform sediment-hosted Pb-Zn (sedex) deposits: *ECONOMIC GEOLOGY*, v. 95, p. 1–18.
- Corrigan, D., and van Breemen, O., 1997, U-Pb constraints for the lithotectonic evolution of the Grenville province along the Maurice transect: *Canadian Journal of Earth Sciences*, v. 34, p. 299–316.
- Cruise, M., 1996, Replacement origin of Crinkill Ironstone: Implications for genetic models of base metal mineralization, central Ireland: *Exploration and Mining Geology*, v. 5, p. 241–249.
- Deer, W.A., Howie, R.A., and Zussman, J., 1982, *Rock-forming minerals*, v. 1A. Orthosilicates—second edition: London, Longman, 919 p.
- deLorraine, W.F., 2001, Metamorphism, polydeformation, and extensive remobilization of the Balmat zinc orebodies, northwest Adirondacks, New York: Society of Economic Geologists Guidebook Series, v. 35, p. 25–54.
- deLorraine, W.F., and Dill, D.B., 1982, Structure, stratigraphic controls, and genesis of the Balmat-Edwards zinc deposits, northwest Adirondacks, New York: Geological Association of Canada Special Paper 25, p. 571–596.
- Des Marais, D.J., 2001, Isotopic evolution of the biogeochemical carbon cycle during the Precambrian: *Reviews in Mineralogy and Geochemistry*, v. 43, p. 555–578.
- Drake, A.A., 1984, The Reading Prong of New Jersey and eastern Pennsylvania: An appraisal of rock relations and chemistry of a major Proterozoic terrane in the Appalachians: Geological Society of America Special Paper 194, p. 75–109.
- Drake, A.A., Jr., Volkert, R.A., Monteverde, D.H., Herman, G.C., Houghton, H.F., Parker, R.A., and Dalton, R.F., 1996, Bedrock geologic map of New Jersey: U.S. Geological Survey Miscellaneous Investigations Series Map I-2540-A, 2 sheets, scale 1:100,000.
- Dunn, P.J., 1995, Franklin and Sterling Hill, New Jersey: The world's most magnificent mineral deposits: Franklin, N.J., The Franklin-Ogdensburg Mineralogical Society, 755 p.
- Emsbo, P., 2000, Gold in sedex deposits: *Society of Economic Geologists Reviews*, v. 13, p. 427–437.
- Essene, E.J., 1983, Solid solutions and solvi among metamorphic carbonates with applications to geologic thermometry: *Reviews in Mineralogy*, v. 11, p. 77–96.
- Ferry, J.M., and Gerdes, M.L., 1998, Chemically reactive fluid flow during metamorphism: *Annual Review of Earth and Planetary Sciences*, v. 26, p. 255–287.
- Foose, M.P., and McLelland, J.M., 1995, Proterozoic low-Ti iron-oxide deposits in New York and New Jersey: Relation to Fe-oxide (Cu-U-Au-rare earth element) deposits and tectonic implications: *Geology*, v. 23, p. 665–668.
- Fowler, S., 1836, Of the white crystalline limestone of Sussex County, N.J., and the minerals and ores connected with it: *New Jersey Geological Survey Report—second edition*, p. 118–122.
- French, B.M., 1971, Stability relations of siderite (FeCO_3) in the system Fe-C-O: *American Journal of Science*, v. 271, p. 37–78.
- Frondel, C., and Baum, J.L., 1974, Structure and mineralogy of the Franklin zinc-iron-manganese deposit, New Jersey: *ECONOMIC GEOLOGY*, v. 69, p. 157–180.
- Frondel, C., and Ito, J., 1966, Hendricksite, a new species of mica: *American Mineralogist*, v. 51, p. 1107–1123.
- Gauthier, M., and Brown, A.C., 1986, Zinc and iron metallogeny in the Maniwaki-Gracefield district, southwestern Quebec: *ECONOMIC GEOLOGY*, v. 81, p. 89–112.
- Gauthier, M., Brown, A.C., and Morin, G., 1987, Small iron-formations as a guide to base- and precious-metal deposits in the Grenville province of southern Quebec, in Appel, P.W.U., and LaBerge, G.L., eds., *Precambrian iron-formations*: Athens, Theophrastus Publications, p. 297–327.

- Goodfellow, W.D., Lydon, J.W., and Turner, R.J.W., 1993, Geology and genesis of stratiform sediment-hosted (SEDEX) zinc-lead-silver sulphide deposits: Geological Association of Canada Special Paper 40, p. 201–251.
- Gregory, R.T., Criss, R.E., and Taylor, H.P., Jr., 1989, Oxygen isotope exchange kinetics of mineral pairs in closed and open systems: Applications to problems of hydrothermal alteration of igneous rocks and Precambrian iron formations: *Chemical Geology*, v. 75, p. 1–42.
- Groves, I.M., Carman, C.E., and Dunlap, J., 2003, Geology of the Beltana willemite deposit, Flinders ranges, South Australia: *ECONOMIC GEOLOGY*, v. 98, p. 797–818.
- Hagner, A.F., Collins, L.G., and Clemency, C.V., 1963, Host rock as a source of magnetite ore, Scott mine, Sterling Lake, N.Y.: *ECONOMIC GEOLOGY*, v. 58, p. 730–768.
- Hague, J.M., Baum, J.L., Herrmann, L.A., and Pickering, R.J., 1956, Geology and structure of the Franklin-Sterling area, New Jersey: Geological Society of America Bulletin, v. 67, p. 435–474.
- Hammer, S., Corrigan, D., Pehrsson, S., and Nadeau, L., 2000, SW Grenville province, Canada: The case against post-1.4 Ga accretionary tectonics: *Tectonophysics*, v. 319, p. 33–51.
- Hitzman, M.W., Earls, G., Shearley, E., Kelly, J., Cruise, M., and Sevastopulo, G., 1995, Ironstones (iron oxide-silica) in the Irish Zn-Pb deposits and regional iron oxide-silica alteration of the Waulsortian Limestone in southern Ireland: Society of Economic Geologists Guidebook Series, v. 21, p. 261–273.
- Hitzman, M.W., Reynolds, N.A., Sangster, D.F., Allen, C.R., and Carman, C.E., 2003, Classification, genesis, and exploration guides for nonsulfide zinc deposits: *ECONOMIC GEOLOGY*, v. 98, p. 685–714.
- Hotz, P.E., 1953, Magnetite deposits of the Sterling Lake, N.Y.-Ringwood, N.J. area: U.S. Geological Survey Bulletin 982-F, p. 153–244.
- James, H.L., 1992, Precambrian iron-formations: nature, origin, and mineralogic evolution from sedimentation to metamorphism, in Wolf, K.H., and Chilingarian, G.V., eds., *Diagenesis, III. Developments in Sedimentology 47*: Amsterdam, Elsevier, p. 543–589.
- Johnson, C.A., 1996, Proterozoic low-Ti iron-oxide deposits in New York and New Jersey: Relation to Fe-oxide (Cu-U-Au-rare earth element) deposits and tectonic implications: *Comment: Geology*, v. 24, p. 475–476.
- 2001, Geochemical constraints on the origin of the Sterling Hill and Franklin zinc deposits, and the Furnace magnetite bed, northwestern New Jersey: Society of Economic Geologists Guidebook Series, v. 35, p. 89–97.
- Johnson, C.A., Rye, D.M., and Skinner, B.J., 1990a, Petrology and stable isotope geochemistry of the metamorphosed zinc-iron-manganese deposit at Sterling Hill, New Jersey: *ECONOMIC GEOLOGY*, v. 85, p. 1133–1161.
- 1990b, Unusual oxygen isotopic compositions in and around the Sterling Hill and Franklin Furnace ore deposits, in Robbins, M., ed., *Character and origin of the Franklin-Sterling Hill orebodies*, proceedings volume, Bethlehem, Pennsylvania, Lehigh University, p. 63–76.
- Kastelic, R.L., 1980, Precambrian geology and magnetite deposits of the New Jersey Highlands in Warren County, New Jersey: U.S. Geological Survey Open-File Report 80-789, 148 p.
- Kaufman, A.J., Hayes, J.M., and Klein, C., 1990, Primary and diagenetic controls of isotopic compositions of iron-formation carbonates: *Geochimica et Cosmochimica Acta*, v. 54, p. 3461–3473.
- Kearns, L.E., 1975, Fluorborite, a new locality: *Mineralogical Record*, v. 6, p. 174–175.
- 1977, The mineralogy of the Franklin marble, Orange County, New York: Unpublished Ph.D. dissertation, Newark, University of Delaware, 211 p.
- Kitchell, W., 1857, Third Annual Report of the Geological Survey of the State of New Jersey: Trenton, New Jersey Geological Survey, 222 p.
- Kitchen, N.E., and Valley, J.W., 1995, Carbon isotope thermometry in marbles of the Adirondack Mountains, New York: *Journal of Metamorphic Geology*, v. 13, p. 577–594.
- Klein, C., 1983, Diagenesis and metamorphism of Precambrian banded iron formations, in Trendall, A.F., and Morris, R.C., eds., *Iron-formation facts and problems*: Amsterdam, Elsevier, p. 417–469.
- Leger, A., Rebbert, C., and Webster, J., 1996, Cl-rich biotite and amphibole from Black Rock Forest, Cornwall, New York: *American Mineralogist*, v. 81, p. 495–504.
- McCrea, J.M., 1950, On the isotope chemistry of carbonates and a paleotemperature scale: *Journal of Chemical Physics*, v. 18, p. 849–857.
- Metsger, R.W., 1962, Notes on the Sterling Hill ore body, Ogdensburg, N.J., in Northern field excursion guidebook: International Mineralogical Association third general congress: Washington, D.C., Mineralogical Society of America, p. 12–21.
- 2001, Evolution of the Sterling Hill zinc deposit, Ogdensburg, Sussex County, New Jersey: Society of Economic Geologists Guidebook Series, v. 35, p. 75–88.
- Metsger, R.W., Tennant, C.B., and Rodda, J.L., 1958, Geochemistry of the Sterling Hill zinc deposit, Sussex Co., N.J.: Geological Society of America Bulletin, v. 69, p. 775–788.
- Metsger, R.W., Skinner, B.J., and Barton, P.B., Jr., 1969, Structural interpretation of the Sterling Hill ore body, Ogdensburg, N.J. [abs.]: Geological Society of America Abstracts with Programs, v. 7, p. 150.
- Monteiro, L.V.S., Bettencourt, J.S., Spiro, B., Graça, R., and De Oliveira, T.F., 1999, The Vazante zinc mine, Minas Gerais, Brazil: Constraints on willemite mineralization and fluid evolution: *Exploration and Mining Geology*, v. 8, p. 21–42.
- Morrison, J., 1991, Compositional constraints on the incorporation of Cl into amphiboles: *American Mineralogist*, v. 76, p. 1920–1930.
- Mosher, S., 1998, Tectonic evolution of the southern Laurentian Grenville orogenic belt: Geological Society of America Bulletin, v. 110, p. 1357–1375.
- Muller, D.W., 1972, The geology of the Beltana willemite deposits: *ECONOMIC GEOLOGY*, v. 67, p. 1146–1167.
- Nason, F.L., 1894, The franklinite-deposits of Mine Hill, Sussex County, New Jersey: American Institute of Mining Engineers Transactions, v. 24, p. 121–130.
- Nawab, Z.A., 1994, Atlantis II Deep, in Collenette, P., and Grainger, D.J., eds., *Mineral resources of Saudi Arabia, not including oil, natural gas, and sulfur*: Directorate General of Mineral Resources Special Publication SP-2: Jiddah, Kingdom of Saudi Arabia Ministry of Petroleum and Mineral Resources, p. 297–301.
- Neumann, T., Heiser, U., Leosson, M.A., and Kersten, M., 2002, Early diagenetic processes during Mn-carbonate formation: Evidence from the isotopic composition of authigenic Ca-rhodochrosites of the Baltic Sea: *Geochimica et Cosmochimica Acta*, v. 66, p. 867–879.
- Palache, C., 1935, The minerals of Franklin and Sterling Hill: U.S. Geological Survey Professional Paper 180, 135 p.
- Parker, F.J., and Peters, T.A., 1978, Tilasite from the Sterling Hill mine, Ogdensburg, New Jersey: *Mineralogical Record*, v. 9, p. 385–386.
- Parr, J.M., and Plimer, I.R., 1993, Models for Broken Hill-type lead-zinc-silver deposits: Geological Association of Canada Special Paper 40, p. 253–288.
- Perry, E.C., Jr., and Ahmad, S.N., 1981, Oxygen and carbon isotope geochemistry of the Drivoy Rog iron formation, Ukrainian SSR: *Lithos*, v. 14, p. 83–92.
- Perry, E.C., Jr., Tan, F.C., and Morey, G.B., 1973, Geology and stable isotope geochemistry of the Biwabik iron formation, northern Minnesota: *ECONOMIC GEOLOGY*, v. 68, p. 1110–1125.
- Peter, J.M., and Goodfellow, W.D., 1996, Mineralogy, bulk and rare earth element geochemistry of massive sulfide-associated hydrothermal sediments of the Brunswick horizon, Bathurst mining camp, New Brunswick: *Canadian Journal of Earth Sciences*, v. 33, p. 252–283.
- Petersen, E.U., Essene, E.J., Peacor, D.R., and Valley, J.W., 1982, Fluorine end-member micas and amphiboles: *American Mineralogist*, v. 67, p. 538–544.
- Pineau, F., Latouche, L., and Javoy, M., 1976, L'origine du graphite et les fractionnements isotopiques du carbone dans les marbres métamorphiques des Gour Oumelalen (Akaggar, Algérie), des Adirondacks (New-Jersey, U.S.A.), et du Damara (Namibie, Sud-Ouest Africain): *Bulletin de la Société Géologique de France*, v. XVIII, p. 1713–1723.
- Pinger, A.W., 1950, Geology of the Franklin-Sterling area, Sussex County, New Jersey, in Dunham, K.C., ed., *The geology, paragenesis, and reserves of the ores of lead and zinc*: International Geological Congress report of the eighteenth session, part VII: Symposium and proceedings of section F: London, Geological Society of London, p. 77–87.
- Pottorf, R.J., and Barnes, H.L., 1983, Mineralogy, geochemistry, and ore genesis of hydrothermal sediments from the Atlantis II Deep, Red Sea: *ECONOMIC GEOLOGY MONOGRAPH 5*, p. 198–223.
- Prucha, J.J., 1957, Pyrite deposits of St. Lawrence and Jefferson counties, New York: New York State Museum and Science Service Bulletin 357, 87 p.
- Puffer, J.H., 1997, Genesis of the New Jersey Highlands magnetite deposits on the basis of geochemical and structural evidence, in Benimoff, A.I., and Puffer, J.H., eds., *The economic geology of northern New Jersey*: Geological Association of New Jersey, annual meeting, 14th, Trenton, Field guide and proceedings, p. 71–96.
- 2001, Origin of five types of Proterozoic magnetite deposits in the New Jersey Highlands: Society of Economic Geologists Guidebook Series, v. 35, p. 103–110.

- Puffer, J.H., and Volkert, R.A., 1991, Generation of trondhjemite from partial melting of dacite under granulite facies conditions: An example from the New Jersey Highlands, USA: *Precambrian Research*, v. 51, p. 115–125.
- Rankin, D.W., Chiarenzelli, J.R., Drake, A.A., Jr., Goldsmith, R., Hall, L.M., Hinze, W.J., Isachsen, Y.W., Lidiak, E.G., McLelland, J., Mosher, S., Ratcliffe, N.M., Secor, D.T., Jr., and Whitney, P.R., 1993, Proterozoic rocks east and southeast of the Grenville front, in Reed, J.C., Jr., Bickford, M.E., Houston, R.S., Link, P.K., Rankin, D.W., Sims, P.K., and Van Schmus, W.R., eds., *The geology of North America*, v. C-2, Precambrian: Conterminous U.S.: Geological Society of America, p. 335–461.
- Ribbe, P.H., 1982, The humite series and Mn-analogs: *Reviews in Mineralogy*, v. 5—second edition, p. 231–274.
- Ridge, J.D., 1952, The geochemistry of the ores of Franklin, New Jersey: *ECONOMIC GEOLOGY*, v. 47, p. 180–192.
- Ries, H., and Bowen, W.C., 1922, Origin of the zinc ores of Sussex County, New Jersey: *ECONOMIC GEOLOGY*, v. 17, p. 517–571.
- Rivers, T., 1997, Lithotectonic elements of the Grenville province: Review and tectonic implications: *Precambrian Research*, v. 86, p. 117–154.
- Rosenberg, P.E., and Foit, F.F., Jr., 1977, Fe²⁺-F avoidance in silicates: *Geochimica et Cosmochimica Acta*, v. 41, p. 345–346.
- Russell, M.J., 1975, Lithochemical environment of the Tynagh basemetal deposit, Ireland, and its bearing on ore deposition: *Transactions of the Institution of Mining and Metallurgy*, v. 84, p. B128–B133.
- Sager-Kinsman, E.A., and Parrish, R.R., 1993, Geochronology of detrital zircons from the Elzevir and Frontenac terranes, Central metasedimentary belt, Grenville province, Ontario: *Canadian Journal of Earth Sciences*, v. 30, p. 465–473.
- Scholten, J.C., Stoffers, P., Garbe-Schönberg, D., and Moammar, M., 2000, Hydrothermal mineralization in the Red Sea, in Cronan, D.S., ed., *Handbook of marine mineral deposits*: Boca Raton, Florida, CRC Press, p. 369–395.
- Sheppard, S.M.F., and Schwartz, H.P., 1970, Fractionation of carbon and oxygen isotopes and magnesium between coexisting metamorphic calcite and dolomite: *Contributions to Mineralogy and Petrology*, v. 26, p. 161–198.
- Sims, P.K., 1958, Geology and magnetite deposits of Dover district, Morris County, New Jersey: U.S. Geological Survey Professional Paper 287, 162 p.
- Skinner, B.J., and Johnson, C.A., 1987, Evidence for movement of ore materials during high grade metamorphism: *Ore Geology Reviews*, v. 2, p. 191–204.
- Spencer, A.C., Kummel, H.B., Wolf, J.E., Salisbury, R.D., and Palache, C., 1908, Franklin Furnace folio: U.S. Geological Survey Atlas 161, 27 p.
- Squiller, S.F., and Sclar, C.B., 1980, Genesis of the Sterling Hill zinc deposit, Sussex County, New Jersey, in Ridge, J.D., ed., *International Association on the Genesis of Ore Deposits Symposium*, 5th, v. 1: Stuttgart, E. Schweizerbart'sche Verlagsbuchhandlung, Proceedings, p. 759–766.
- Stanton, R.L., 1976, Petrochemical studies of the ore environment at Broken Hill, New South Wales: 1. Constitution of "banded iron formation": *Transactions of the Institution of Mining and Metallurgy*, v. 85, p. B33–B46.
- Stockwell, C.H., 1951, Magnetite deposits at Franklin, New Jersey: Unpublished New Jersey Zinc Company report, 26 p.
- Stormer, J.C., Pierson, M.L., and Tacker, R.C., 1993, Variation of F and Cl X-ray intensity due to anisotropic diffusion in apatite during electron microprobe analysis: *American Mineralogist*, v. 78, p. 641–648.
- Tarr, W.A., 1929, Origin of the zinc deposits at Franklin and Sterling Hill, New Jersey: *American Mineralogist*, v. 14, p. 207–221.
- Tracy, R.J., 1991, Ba-rich micas from the Franklin marble, Lime Crest and Sterling Hill, New Jersey: *American Mineralogist*, v. 76, p. 1683–1693.
- Valley, J.W., and O'Neil, J.R., 1981, ¹³C/¹²C exchange between calcite and graphite: A possible thermometer in Grenville marbles: *Geochimica et Cosmochimica Acta*, v. 45, p. 411–419.
- Veizer, J., and Hoefs, J., 1976, The nature of O¹⁸/O¹⁶ and C¹³/C¹² secular trends in sedimentary carbonate rocks: *Geochimica et Cosmochimica Acta*, v. 40, p. 1387–1395.
- Volkert, R.A., 2001, Geologic setting of Proterozoic zinc, iron and graphite deposits, New Jersey Highlands: Society of Economic Geologists Guidebook Series, v. 35, p. 59–73.
- Volkert, R.A., and Drake, A.A., Jr., 1999, Geochemistry and stratigraphic relations of Middle Proterozoic rocks of the New Jersey Highlands: U.S. Geological Survey Professional Paper 1565-C, 77 p.
- Volkert, R.A., Feigenson, M.D., Patino, L.C., Delaney, J.S., and Drake, A.A., Jr., 2000a, Sr and Nd isotopic compositions, age and petrogenesis of A-type granitoids of the Vernon Supersuite, New Jersey Highlands, USA: *Lithos*, v. 50, p. 325–347.
- Volkert, R.A., Johnson, C.A., and Tamashausk, A.V., 2000b, Mesoproterozoic graphite deposits, New Jersey Highlands: Geologic and stable isotopic evidence for possible algal origins: *Canadian Journal of Earth Sciences*, v. 37, p. 1665–1675.
- Whelan, J.F., Rye, R.O., and deLorraine, W., 1984, The Balmat-Edwards zinc-lead deposits: Syndimentary ore from Mississippi Valley-type fluids: *ECONOMIC GEOLOGY*, v. 79, p. 239–265.
- Whelan, J.F., Rye, R.O., deLorraine, W., and Ohmoto, H., 1990, Isotopic geochemistry of a mid-Proterozoic evaporite basin: Balmat, New York: *American Journal of Science*, v. 290, p. 396–424.
- Wolff, J.E., 1903, Zinc and manganese deposits of Franklin Furnace, N.J.: U.S. Geological Survey Bulletin, v. 213, p. 214–217.
- Zheng, Y-F., 1996, Oxygen isotope fractionation of zinc oxides and implications for zinc mineralization in the Sterling Hill deposit, USA: *Mineralium Deposita*, v. 31, p. 98–103.
- 1999, Oxygen isotope fractionation in carbonate and sulphate minerals: *Geochemical Journal*, v. 33, p. 109–126.
- Zhu, C., and Sverjensky, D.A., 1992, F-Cl-OH partitioning between biotite and apatite: *Geochimica et Cosmochimica Acta*, v. 56, p. 3435–3467.
- Zierenberg, R.A., and Shanks, W.C., III, 1983, Mineralogy and geochemistry of epigenetic features in metalliferous sediment, Atlantis II Deep, Red Sea: *ECONOMIC GEOLOGY*, v. 78, p. 57–72.