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

CRAIG A. JOHNSON†

U.S. Geological Survey, Box 25046, MS 963, Denver, Colorado 80225

AND BRIAN J. SKINNER

Department of Geology and Geophysics, Yale University, New Haven, Connecticut 06520

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 δ18O values of −5 ± 1 per mil relative to Pee Dee belemnite (PDB) and δ13C 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 shallow 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 H2S.

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 (Zn2SiO4), franklinite (ZnFe2O4), 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 supraclastul 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; Finger, 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
sea, and that the timing of metal emplacement was either syn-
genetic 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 assem-
blages observed today were produced during high-grade re-
gional metamorphism that accompanied the Grenvillian
orogeny (Metsger, 1962; Carvalho and Sclar, 1988) or Ot-
tawan 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 in-
clude paragneisses such as marble and metapelite, quartz-
feldspathic 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. 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).
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

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
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 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 are later deformed, metamorphosed, and partially melted (Puffer and Volkert, 1991).

Overlying the Losee suite is a metamorphosed and isoclinically 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 Bree- man, 1997). Correlation with the 1.3 to 1.25 Ga supracrustal rocks of the Frontenac Group (Rivers, 1997; Hamner 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
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 manganiferous 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 chloropyrite 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 southwest 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 manganiferous 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 Franklin zinc deposit. Wet chemical analyses of Balls Hill ore suggest much lower manganese contents than in the marble-hosted magnetite and calcite (Cook, 1868). The workings are long buried and inaccessible.

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 manganiferous 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 (Frondel 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-SEMQ instrument

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Wt. percent</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeO</td>
<td>60.06</td>
<td>2</td>
</tr>
<tr>
<td>MnO</td>
<td>3.17</td>
<td>3</td>
</tr>
<tr>
<td>SiO₂</td>
<td>1.49</td>
<td></td>
</tr>
<tr>
<td>P₂O₅</td>
<td>0.012</td>
<td></td>
</tr>
<tr>
<td>CaO</td>
<td>16.5</td>
<td>4</td>
</tr>
<tr>
<td>CO₂</td>
<td>12.9</td>
<td>4</td>
</tr>
<tr>
<td>S</td>
<td>0.197</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>1.24</td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>95.6</td>
<td>5</td>
</tr>
</tbody>
</table>

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 Kα 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 fluorphlogopite (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 CO₂ 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 (δ¹³C = 1.92 per mil, δ¹⁸O = 28.65 per mil) and NBS 18 (δ¹³C = −5.00‰, δ¹⁸O = 7.20‰) standards gave δ¹³C = 1.8 per mil and δ¹⁸O = 28.4 per mil (n = 4) and δ¹³C = −5.0 per mil and δ¹⁸O = 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 CO₂ 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>
<thead>
<tr>
<th>Table 2. Mineral Assemblages¹</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Mineral</strong></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>Primary mineral</td>
</tr>
<tr>
<td>Magnetite³</td>
</tr>
<tr>
<td>Calcite</td>
</tr>
<tr>
<td>Dolomite</td>
</tr>
<tr>
<td>Clinopyroxene</td>
</tr>
<tr>
<td>Ca clinopyroxene</td>
</tr>
<tr>
<td>Hornblende</td>
</tr>
<tr>
<td>Biotite</td>
</tr>
<tr>
<td>Chondrodite⁴</td>
</tr>
<tr>
<td>Norbergite⁵</td>
</tr>
<tr>
<td>Graphite</td>
</tr>
<tr>
<td>Fluorite</td>
</tr>
<tr>
<td>Plagioclase</td>
</tr>
<tr>
<td>K feldspar</td>
</tr>
<tr>
<td>Apatite</td>
</tr>
<tr>
<td>Retrograde mineral</td>
</tr>
<tr>
<td>Pyrite</td>
</tr>
<tr>
<td>Chalcopyrite</td>
</tr>
<tr>
<td>Dolomite</td>
</tr>
<tr>
<td>Siderite</td>
</tr>
</tbody>
</table>

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, CaMgAsO₄F
³ Magnetite abundances determined by point counting (~750 points) were F5-2.6, 55.2 percent; F5-3.2, 69.0 percent; FMB1, 45.4 percent; FMB2, 11.8 percent; FMB2 also contains 1.6 percent graphite
⁴ Ideally, 2MgSiO₄·Mg(OH,F)₂
⁵ Ideally, Mg₂SiO₄·Mg(OH,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 mag-
nesian calcite. A fluorine-bearing Ca-Mg arsenate in sample
FMB-1a may be tilasite (CaMg[AsO4]F). This mineral is
subhedral and is intergrown with magnetite and diopside
and thus differs from the secondary fault breccia occur-
rences described at Sterling Hill (Parker and Peters, 1978).
Minerals in the gneiss-hosted magnetite lenses include mag-
netite, hedenbergite, plagioclase, K feldspar, hornblende,
and apatite (Table 2). Hercynite occurs as inclusions and
lamellae within magnetite consistent with an origin by ret-
rograde exsolution.

Mineral chemistry

Our data (Table 3) show the Furnace bed magnetite to be
manganiferous (MnO up to 2.9 wt %) and titanium-poor
(TiO2 <0.04 wt %) consistent with the findings of Frondel
and Baumi (1974). By contrast, the gneiss-hosted magnetite is low in manganese (<0.12 wt % MnO) and high in titanium
(0.29–0.32 wt % TiO2), and it also shows higher aluminium
(0.77–0.89 wt % Al2O3) 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 de-
positions (Puffer, 1997). The magnetite lens within the Franklin
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 dis-
play 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 con-
tents ever observed in natural assemblages (cf. Deer et al.,
1982; Petersen et al., 1982; Ribbe, 1982).

Silicates in the gneiss-hosted magnetite lenses are interme-
mediate 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 particu-
larly 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. Mor-
rison, 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 mag-
netite lenses 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 temper-
ature of 248°C for sample 1-35.5 (XFe+Mn was used for XFe).
The fact that these results are significantly below the 720° ±
40°C temperature range that has been determined for the re-
gional metamorphism (Volkert, 2001) confirms what is evi-
dent from the petrography, namely that the carbonates un-
derwent 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 tempera-
ture minimum that the carbonate solvus implies for magnesian

<table>
<thead>
<tr>
<th>Furnace bed</th>
<th>Gneiss-hosted lenses</th>
<th>Lens in Franklin Zinc deposit</th>
</tr>
</thead>
<tbody>
<tr>
<td>5-2.6</td>
<td>5-2.9</td>
<td>5-3.2</td>
</tr>
<tr>
<td>SiO2</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>TiO2</td>
<td>0.01</td>
<td>0.03</td>
</tr>
<tr>
<td>Al2O3</td>
<td>0.53</td>
<td>0.83</td>
</tr>
<tr>
<td>Fe2O3</td>
<td>60.17</td>
<td>68.56</td>
</tr>
<tr>
<td>FeO</td>
<td>27.99</td>
<td>27.91</td>
</tr>
<tr>
<td>MnO</td>
<td>2.69</td>
<td>2.46</td>
</tr>
<tr>
<td>MgO</td>
<td>0.44</td>
<td>0.59</td>
</tr>
<tr>
<td>ZnO</td>
<td>0.02</td>
<td>0.04</td>
</tr>
<tr>
<td>Total</td>
<td>100.85</td>
<td>100.42</td>
</tr>
</tbody>
</table>

1Mineral formulas were calculated by normalizing total cations to 3; Fe3+/Fe2+ was inferred from charge balance assuming no cation vacancies.
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 CO$_3^-$ 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 $\delta^{13}C$ values are essentially uniform at $-5.2 \pm 0.7$ per mil, whereas the carbonate $\delta^{18}O$ values range from 11.5 to 20.1 per mil. Graphite in sample FMB-2 has a $\delta^{13}C$ value of $-9.9$ per mil. The 3.9 per mil isotopic difference between dolomite and graphite corresponds to an isotopic equilibration temperature of 728 \pm 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 \pm 40°C estimate for peak metamorphic temperatures in the region (Volkert, 2001).

Table 4. Electron Microprobe Analyses of Clinopyroxene

<table>
<thead>
<tr>
<th></th>
<th>Furnace bed</th>
<th>Gneiss-hosted lenses</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>5-2.6</td>
<td>5-2.9</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>54.69</td>
<td>54.67</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>0.12</td>
<td>0.28</td>
</tr>
<tr>
<td>FeO</td>
<td>3.87</td>
<td>3.33</td>
</tr>
<tr>
<td>MnO</td>
<td>2.53</td>
<td>2.26</td>
</tr>
<tr>
<td>MgO</td>
<td>16.64</td>
<td>16.95</td>
</tr>
<tr>
<td>ZnO</td>
<td>0.02</td>
<td>0.03</td>
</tr>
<tr>
<td>CaO</td>
<td>23.96</td>
<td>22.92</td>
</tr>
<tr>
<td>Na$_2$O</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Total</td>
<td>100.94</td>
<td>100.45</td>
</tr>
</tbody>
</table>

$^1$ Mineral formulas were calculated by normalizing total cations to 4
$^2$ = not analyzed

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 (Frondel 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 ($\text{CaFe(CO}_3\text{)}_2$) 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

$$6\text{FeCO}_3 = 2\text{Fe}_2\text{O}_3 + 6\text{C} + 5\text{O}_2$$

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

$$6\text{FeCO}_3 + \text{O}_2 = 2\text{Fe}_2\text{O}_3 + 6\text{CO}_2$$

The CO$_2$ loss implied by these reactions would be predicted to cause $\delta^{13}C$ and $\delta^{18}O$ shifts governed by isotopic fractionations between the expelled CO$_2$ 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 CO$_2$ and rock was assumed to have been controlled by CO$_2$-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) CO$_2$ 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 Biotite

<table>
<thead>
<tr>
<th></th>
<th>Chondrodite</th>
<th>Norbergite</th>
<th>Tremolite</th>
<th>Hornblende</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>5-2.6</td>
<td>5-2.9</td>
<td>7-20</td>
<td>7-20</td>
</tr>
<tr>
<td>SiO₂</td>
<td>32.96</td>
<td>33.01</td>
<td>31.19</td>
<td>27.95</td>
</tr>
<tr>
<td>TiO₂</td>
<td>&lt;0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>FeO</td>
<td>7.25</td>
<td>7.85</td>
<td>15.09</td>
<td>4.32</td>
</tr>
<tr>
<td>MnO</td>
<td>3.65</td>
<td>3.18</td>
<td>3.23</td>
<td>1.31</td>
</tr>
<tr>
<td>MgO</td>
<td>50.89</td>
<td>51.50</td>
<td>45.94</td>
<td>56.70</td>
</tr>
<tr>
<td>CaO</td>
<td>0.09</td>
<td>0.13</td>
<td>0.20</td>
<td>0.20</td>
</tr>
<tr>
<td>K₂O</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.02</td>
<td>0.01</td>
<td>0.01</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>ZnO</td>
<td>0.01</td>
<td>0.03</td>
<td>0.04</td>
<td>0.01</td>
</tr>
<tr>
<td>Cl</td>
<td>&lt;0.01</td>
<td>0.01</td>
<td>&lt;0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>F</td>
<td>9.59</td>
<td>9.93</td>
<td>10.35</td>
<td>18.16</td>
</tr>
<tr>
<td>H₂O ± Cl</td>
<td>0.51</td>
<td>0.39</td>
<td>0.03</td>
<td>0.18</td>
</tr>
<tr>
<td>Mg/(Mg + Fe)</td>
<td>0.926</td>
<td>0.921</td>
<td>0.844</td>
<td>0.959</td>
</tr>
<tr>
<td>Zn/(Zn + Mg + Fe + Al + Ti + Si)</td>
<td>0.024</td>
<td>0.001</td>
<td>0.000</td>
<td>0.000</td>
</tr>
</tbody>
</table>

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 Carbonates

<table>
<thead>
<tr>
<th></th>
<th>Furnace bed</th>
<th>Lens in Franklin Zn deposit</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cal</td>
<td>Cal</td>
</tr>
<tr>
<td></td>
<td>5-2.6</td>
<td>5-2.9</td>
</tr>
<tr>
<td>CaO</td>
<td>53.41</td>
<td>49.57</td>
</tr>
<tr>
<td>MgO</td>
<td>1.23</td>
<td>2.57</td>
</tr>
<tr>
<td>FeO</td>
<td>0.39</td>
<td>0.64</td>
</tr>
<tr>
<td>MnO</td>
<td>2.56</td>
<td>2.72</td>
</tr>
<tr>
<td>CO₃²⁻</td>
<td>45.08</td>
<td>44.02</td>
</tr>
<tr>
<td>Total</td>
<td>102.67</td>
<td>99.52</td>
</tr>
<tr>
<td>Ca</td>
<td>0.930</td>
<td>0.890</td>
</tr>
<tr>
<td>Mg</td>
<td>0.030</td>
<td>0.064</td>
</tr>
<tr>
<td>Fe</td>
<td>0.005</td>
<td>0.009</td>
</tr>
<tr>
<td>Mn</td>
<td>0.035</td>
<td>0.038</td>
</tr>
</tbody>
</table>

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 Lens

<table>
<thead>
<tr>
<th>Element</th>
<th>FeO</th>
<th>MnO</th>
<th>CaO</th>
<th>Na2O</th>
<th>P2O5</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.53</td>
<td>0.17</td>
<td>54.73</td>
<td>0.00</td>
<td>39.37</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mineral</th>
<th>δ13C</th>
<th>δ18O</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>F5-2.6</td>
<td>Calcite</td>
<td>-5.9</td>
<td>11.5</td>
<td>1</td>
</tr>
<tr>
<td>F5-3.2</td>
<td>Calcite</td>
<td>-5.9</td>
<td>12.6</td>
<td>2</td>
</tr>
<tr>
<td>FMB1</td>
<td>Calcite</td>
<td>-4.6</td>
<td>13.5</td>
<td>2</td>
</tr>
<tr>
<td>FMB2</td>
<td>Dolomite</td>
<td>-5.0</td>
<td>20.1</td>
<td>3</td>
</tr>
<tr>
<td>FMB2</td>
<td>Graphite</td>
<td>-8.9</td>
<td>-</td>
<td>2</td>
</tr>
</tbody>
</table>

\[6\text{FeCO}_3 = 2\text{Fe}_3\text{O}_4 + \text{C} + 5\text{CO}_2.\] 

FIG. 5. Graph of Furnace bed stable-isotope data from Table 8 compared with models of metamorphic decarbonation of an ankerite \((\text{CaFe(CO}_3)\text{)}_2\)-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 δ13C value, and the δ18O value corrected for metamorphic carbonate-graphite exchange (cf. Kitchen and Valley, 1995).

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

\[2\text{FeCO}_3 = \text{Fe}_3\text{O}_4 + \text{C} + 4\text{CO}_2.\] 

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. δ13C values of carbonate in the Furnace bed are uniformly low (–5.2 ± 0.7‰) compared with δ13C in the Franklin marble that surrounds the bed (–0.6 ± 0.8‰, \(n = 5\)) or the Franklin zinc ores (–0.6 ± 0.9‰, \(n = 4\)) that lie 0 to 2 m above it (C. Johnson, unpub. data, 1990). δ18O 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 δ18O than the surrounding Franklin marble (18 ± 3‰, \(n = 5\); Johnson et al., 1990b) more closely resembling the Franklin zinc ores (12 ± 3‰, \(n = 4\); 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 isochronal 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 δ18O 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...
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 δ¹⁸O value of the protolith iron oxide averaged 1 per mil (the isotopic offset corresponds with the calcite-magnetite fractionation at 720 ± 40°C; Chiba et al., 1989). These inferred δ¹⁸O values for the protolith minerals fall 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).

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 (δ¹⁸O = 1‰ for the protolith iron oxide, δ¹⁸O = 21‰ and δ¹³C = –5 ± 2‰ 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).  

The Furnace bed δ¹³C values show much less variation than the δ¹⁸O values (Fig. 6b). If the measured δ¹³C 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 δ¹³C; carbonate-rich rocks display δ¹³C values near –3 per mil, and iron oxide-rich rocks display δ¹³C values near –7 per mil.

These δ¹³C 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 δ¹³C 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 δ¹³C dissolved inorganic carbon and a diagenetic history in which carbonate δ¹³C 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 δ¹³C 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 Franklin Hill ore samples are consistent with a model protolith composed of carbonate, clay, and oxyhydroxides that formed at a temperature of 150 ± 50°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 zinc and iron oxide assemblages precipitated directly from the metal-transporting fluid. Whole-rock zinc-to-silicon ratios in the Franklin Hill ores greatly exceed the ratios of the common zinc silicates found in low-temperature settings, saucnite (Zn₅Si₄O₁₀(OH)₂·4H₂O) and hemimorphite (Zn₃Si₂O₇(OH)₂·H₂O), which suggests that a nonsilicate mineral was the main zinc host in the protolith. The isotopic modeling suggests that the zinc host was a carbonate, likely smithsonite (ZnCO₃) or hydrozincite (Zn₂(CO₃)₂(OH)₃), that broke down during the Grenvillian metamorphism to give the willemite ± franklinite ± 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 δ¹⁸Owater 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 δ¹⁸Owater value of 2 ± 4 per mil consistent with a seawater origin and possible ¹⁸O 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$_2$S 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 Ensmbo, 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$_2$S-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$_2$S that then combined with dissolved metals to form sulfides. Generally, however, conditions were oxidizing enough that sulfate was favored, H$_2$S 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 diagenerically 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 theNamaqua 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 manganiferous 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 fluorspar-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 basal 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, 1953; 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 H$_2$S 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 $\delta^{13}$C relative to normal marine carbonates. Waters that were stratified with respect to oxygen content might also have been stratified with respect to $\delta^{13}$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 carbonate 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 $\delta^{13}$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 ± 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 MnO$_2$ during flushing by oxygenated waters. A return to anoxic conditions allows for microbial reduction of the MnO$_2$ 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
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 metagneous, 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 Baldmat-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 H2S 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 (ZnFe2O4) 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 exhales 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 proposed previously for the Highlands zinc oxide-silicate
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 manganiferous 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 supports 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 supraclast 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 $\text{H}_2\text{S}$ from the ambient sulfate.
Acknowledgments

We thank R. Metsger, J. Puffer, and R. Volkert for helpful discussions and expert guidance in the field, Amy Bern for assistance with the USGS microprobe, and John Gianculli of the Franklin Mineral Museum for providing a copy of Stockwell (1951). Also appreciated are invitations to participate in excellent field trips organized by the Geological Association of New Jersey (1997), the University of Arizona Center for Mineral Resources (1995), and the Society of Economic Geologists (2001). M. Gauthier, J. Peter, D. Sangster, C. Taylor, and J. Whelan provided thorough and helpful reviews. Our initial work on Grenville metallogenesis was supported by NSF grant EAR-8417445; continuing support is from the USGS Mineral Resources Program.

REFERENCES


Cruise, M., 1996, Regional recrystallization and the formation of magnetite concentrations, Dover magnetite district, New Jersey: ECONOMIC GEOLOGY, v. 64, p. 17–33.

Cruice, M., 1996, Regional recrystallization and the formation of magnetite concentrations, Dover magnetite district, New Jersey: ECONOMIC GEOLOGY, v. 64, p. 17–33.

Cruice, M., 1996, Regional recrystallization and the formation of magnetite concentrations, Dover magnetite district, New Jersey: ECONOMIC GEOLOGY, v. 64, p. 17–33.

Cruice, M., 1996, Regional recrystallization and the formation of magnetite concentrations, Dover magnetite district, New Jersey: ECONOMIC GEOLOGY, v. 64, p. 17–33.


Kearns, L., 1975, Fluoborite, a new locality: Mineralogical Record, v. 6, p. 261–263.


