Stable Isotope and Petrologic Evidence for the Origin of Regional Marble-Hosted Magnetite Deposits and the Zinc Deposits at Franklin and Sterling Hill, New Jersey Highlands, United States

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Abstract

Mesoproterozoic marble in the New Jersey Highlands hosts small magnetite deposits that occur in discrete groups along linear trends and are concentrated mainly in the western part of the region. Magnetite also forms a layer structurally beneath the Zn-Fe-Mn orebody at the Franklin mine. Marble host rocks are interlayered at Fe and Zn-Fe-Mn deposits with bimodal metavolcanic rocks (amphibolite and rhyolitic gneiss) that were deposited synchronously in a back-arc basin developed on the eastern margin of Laurentia between 1.3 and 1.25 Ga. Magnetite in the deposits ranges from massive to disseminated and is characterized by low Ti, variable Mn, and locally high S. Concentrations of As, V, Sb, and Zn are enriched in magnetite compared to marble host rocks and associated metavolcanic rocks. Carbon and oxygen isotope ratios of the marbles are consistent with water-rock interaction between the marble protolith and a mixture of igneous fluids and seawater. Regional geology, petrology, and isotope data indicate that Fe was introduced into the carbonate protolith as low-temperature Fe oxides and hydroxides via hydrothermal fluids discharged along basinal fracture zones on the sea floor. Related marble-hosted Zn-Fe-Mn deposits at Franklin and Sterling Hill contain the assemblage willemite + zincite + franklinite. Stable isotope compositions of the Zn deposits are consistent with alteration of host rocks by water-rich fluids, preserving protolith carbon isotope ratios. Stable isotope modeling suggests that Zn silicate + oxides or hydroxides represent an appropriate protolith for the high-grade Zn ores.

Alteration of metavolcanic rocks at the Fe deposits, combined with the isotope data and other petrologic and geochemical evidence, document the presence of an extensive hydrothermal system of Grenville age centered in the western Highlands. Metals precipitating from this hydrothermal system were responsible for Fe in the marble-hosted magnetite deposits and Zn in the deposits at Franklin and Sterling Hill from the same or a related hydrothermal system. Underplating of the back arc by mafic magma provided the heat to melt the lower crust and drive the hydrothermal system, resulting in carbonate-hosted Fe and Zn ore deposits and associated bimodal volcanism.

Introduction

ROCKS of Mesoproterozoic age in the New Jersey Highlands host more than 400 magnetite deposits, most of which occur in granite and gneiss, but a small group located mainly in the western Highlands is hosted by marble. These metamorphosed marble-hosted deposits, worked mainly during the middle 19th century, are small and collectively yielded <1 million metric tons (Mt) of low Ti magnetite ore. They are not as easily studied as the larger and more voluminous granite- and gneiss-hosted deposits because they are poorly exposed, lack preserved drill core, and are only briefly discussed in the historic literature (Bayley, 1910), with limited emphasis on the geologic relationships of the deposits. Possibly for these reasons, prior research on the marble-hosted Fe deposits has been meager, especially compared to the marble-hosted Zn-Fe-Mn deposits at the Franklin and Sterling Hill mines, which have been studied by numerous workers for more than two centuries (e.g., Dunn, 1995). The limited amount of previous work on the Fe deposits was undertaken for unrelated reasons, such as the U.S. Bureau of Mines to evaluate them for strategic Fe reserves (Kerns, 1944; Lynch, 1947; Neumann, 1952; Sims and Leonard, 1952), for graduate thesis

work (Kastelic, 1979), or to genetically classify the deposits in relationship to those hosted by gneiss or granite (Puffer, 1997, 2001). More recently, Johnson (1997) and Johnson and Skinner (2003) studied an occurrence of marble-hosted magnetite (Furnace magnetite bed), structurally beneath the west limb of the Zn orebody at the Franklin mine, that was discussed previously by Frondel and Baum (1974), to evaluate the genetic relationship between marble-hosted Fe and Zn oxide mineralization.

The present study was undertaken to expand on previous work on the marble-hosted Fe deposits by utilizing carbon and oxygen isotopes to evaluate their origin. Isotope data were interpreted in the context of new geochronologic data that permit a refined tectonic synthesis for the Mesoproterozoic rocks, as well as new mineralogic and geochemical data, and the further recognition of an extensive Grenville-age hydrothermal system centered in the western Highlands (Peck et al., 2006; Volkert, 2006). The results provide new insights on potential protoliths for Fe in the deposits, the sedimentary environment of the host carbonate, and the physical and chemical conditions during formation of the ores. Moreover, they allow the relationship between the marble-hosted Fe and Zn deposits to be evaluated further.

In addition, data are reported here for samples collected along a traverse through the Zn deposit at Franklin. These data complement the work of Johnson et al. (1990) at Sterling

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Hill, who favor hydrothermal alteration of protolith rocks by seawater to explain oxygen and carbon isotopes of this deposit. These results permit a comparison of the stable isotope signature of the two Zn deposits and an evaluation of potential protoliths for the high-grade Zn ore.

Regional Geologic Setting

The New Jersey Highlands, and contiguous Hudson Highlands in southern New York and Reading Prong in eastern Pennsylvania, constitute one of the largest Grenville terranes that extend along eastern North America. Mesoproterozoic rocks in the New Jersey Highlands are in fault contact along their eastern border with Late Triassic to Early Jurassic rocks of the Newark basin. Along the western border of the Highlands, Mesoproterozoic rocks are nonconformably overlain by, or in fault contact with, a passive margin sequence of clastic and carbonate shelf rocks of Cambrian and Ordovician age. The Highlands are separated into western and eastern segments by downfaulted Paleozoic cover rocks of the Green Pond Mountain region (Fig. 1).

The New Jersey Highlands are underlain by a heterogeneous assemblage of Mesoproterozoic rocks, most of which were metamorphosed to the granulite-facies at temperatures of ~760°C and pressures of 410 to 500 MPa by 1020 Ma during the Ottawan orogeny (Volkert, 2004; Peck et al., 2006).

These rocks include the Losee Suite, a regionally widespread assemblage of 1.28 to 1.25 Ga (Aleinikoff et al., 2007) calc-alkaline magmatic-arc plutonic (diorite, quartz diorite, and tonalite) and volcanic (basalt, andesite, dacite, and minor rhyolite) rocks formed along the eastern Laurentian continental margin (Volkert, 2004). The Losee Suite is spatially associated with a supracrustal succession of metasedimentary gneisses, quartzite, marble, and bimodal volcanic rocks all of which predominate in the western Highlands where they are as much as 2,100 m thick. The supracrustal succession is interpreted as having formed in a back-arc basin inboard of the Losee arc above thinned and extended crust (Volkert, 2004). Evidence supporting this interpretation includes the occurrence of bimodal volcanic rocks and their geochemical compositions.

Supracrustal metavolcanic rocks consist of foliated, medium-grained, grayish-black amphibolite composed of clinopyroxene + hornblende + plagioclase (interpreted as metabasalt) and foliated, medium-grained, pinkish-gray, quartz + K-feldspar + plagioclase ± biotite gneiss, which is likely to be a metarhyolite (Volkert, 2004; Volkert and Aleinikoff, 2007). Rhyolitic gneiss layers intercalated with Franklin Marble yielded U-Pb SHRIMP ages of 1.29 to 1.25 Ga (Aleinikoff et al., 2007) that are coeval with magmatism and arc development of the Losee Suite. Marble is a volumetrically minor but important part of the supracrustal succession. It is thickest in the western
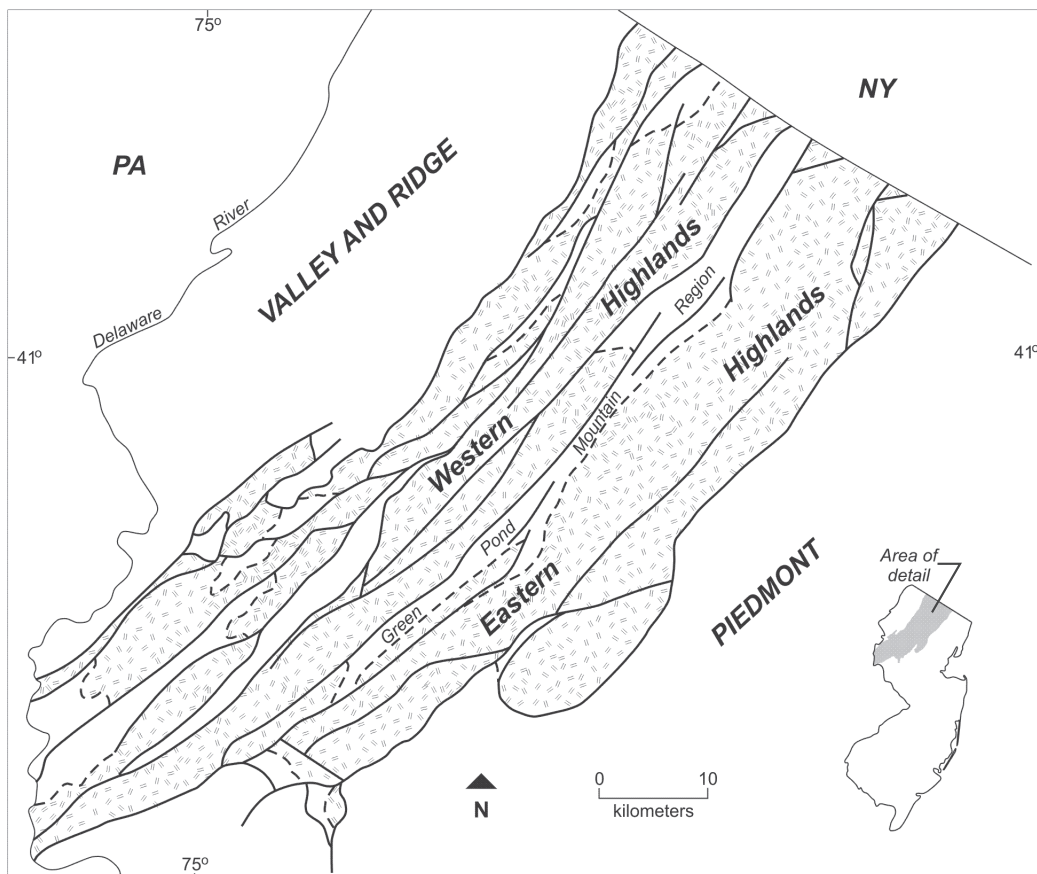

FIG. 1. Simplified geologic map showing the distribution of Mesoproterozoic rocks (cross-hatched) in the western and eastern New Jersey Highlands. Unpatterned areas within the Highlands are underlain by Paleozoic rocks. Solid lines are faults; dashed lines are unconformities.

Highlands where it is divided into the stratigraphically lower 335- to 457-m-thick Franklin layer, which hosts the Franklin and Sterling Hill Zn oxide deposits, and the stratigraphically higher ~91-m-thick Wildcat layer in which Zn mineralization has not been found (Hague et al., 1956; Fig. 2). Marble in the Franklin and Wildcat layers is white to light gray, foliated, medium to coarse grained, and calcitic to locally dolomitic. Common accessory minerals include graphite, phlogopite, norbergite, calcic amphibole, and clinopyroxene. Separating the two marble layers is the Cork Hill Gneiss zone of Hague et al. (1956), which is interpreted as a sequence of metasedimentary gneisses of marine origin and bimodal volcanic rocks (Volkert and Drake, 1999; Volkert and Aleinikoff, 2007). Marble in the eastern Highlands occurs as discontinuous bands no thicker than 30 m that lack graphite but commonly contain serpentine minerals.

There is general agreement that the protolith of marble is a marine carbonate. Evidence supporting this includes the carbon isotope data (Johnson et al., 1990; Peck et al., 2006), recognition of relict stromatolites in the Franklin layer and possible organic structures in the Wildcat layer (Volkert, 2004), and the geochemical composition of paragneisses interlayered with marble (Volkert and Drake, 1999; Volkert, 2004). Thin marble layers in the eastern Highlands also preserve marinelike carbon isotope values (Volkert, 2004), and these marbles are intercalated with, and grade along strike into, graphitic paragneisses (Fig. 3) that represent deeper water marine deposits (Volkert et al., 2000b; Johnson and Skinner, 2003).

The Losee Suite and supracrustal rocks were intruded by widespread A-type granite and related rocks of the 1.18 Ga Byram and Lake Hopatcong Intrusive Suites (Volkert et al., 2000a; Aleinikoff et al., 2007) and various postorogenic felsic intrusive rocks dated at 1019 to 986 Ma (Drake et al., 1991; Volkert et al., 2005).

Tectonic Setting

Based on field relationships and geochemical considerations, the supracrustal rocks are interpreted as a thick succession of intercalated metasedimentary and bimodal metavolcanic rocks that were formed in a back-arc basin on extended
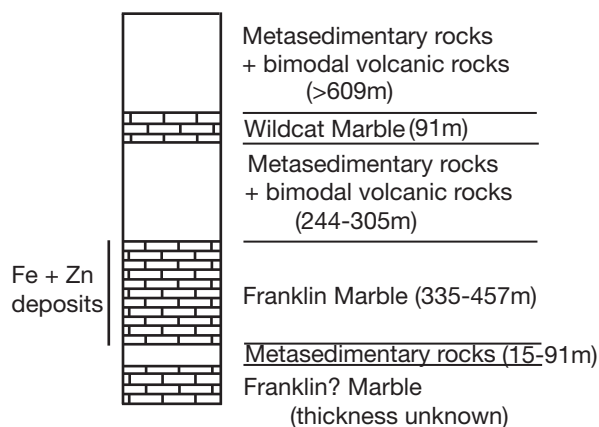

FIG. 2. Generalized stratigraphic column of supracrustal rocks compiled mainly for the western Highlands. Thickness of column blocks and symbols are not to scale. Modified from Hague et al. (1956) and Volkert (2004).

continental crust and inboard of a continental margin magmatic arc (Volkert, 2004). Supracrustal rhyolitic gneisses reflect a distinct change from arc-related magmatism of the Losee Suite generated above a subduction zone to potassic magmatism formed through partial melting of a felsic crustal source distally from the arc. They are geochemically distinct from barren, unmineralized arc-related metarhyolites of the Losee Suite (Fig. 4). Supracrustal rhyolitic gneisses have an A-type granite affinity and low Zr/Y ratios of 4 to 7 that correlate to increasing Y, similar to mineralized rhyolites from continental back-arc environments (Lesher et al., 1985; Lentz, 1998), implying a change from magmatism in a compressional to an extensional setting. Rhyolitic gneisses have low Ba/Ta (~500) and Ba/Th (<200) compared to the arc-related metarhyolites of the Losee Suite (Ba/Th >800), suggesting significant crustal involvement during magma formation but little to no involvement of subduction zone fluids. Amphibolites are locally pillowed and have mixed MORB and arc-like geochemical compositions that are unlike arc-related amphibolites of the Losee Suite, but that are compatible with formation in a back-arc environment (Volkert, 2004). Rocks of intermediate composition are absent in the supracrustal succession, consistent with emplacement of bimodal volcanic rocks in an extensional environment rather than as part of an arc-related magmatic series.

In the western Highlands, metasedimentary gneisses interlayered with marble represent metaclastic rocks of marine affinity that were receiving detritus from a continental sediment source based on ratios of immobile elements such as Ti/Zr and other elements using discriminant function analysis (Volkert, 2004). Marble in the western Highlands reflects deposition in a shallow-marine environment on the continental margin side of the back arc, thus providing an important constraint on the depositional setting of Fe and Zn mineralization.

Overlapping ages of 1.29 to 1.25 Ga from arc-related rocks of the Losee Suite and from supracrustal rhyolitic gneisses intercalated with Franklin Marble (Aleinikoff et al., 2007) are consistent with coeval pluton emplacement in the magmatic arc and sedimentation plus bimodal volcanism in the back arc. Bimodal volcanic rocks are most voluminous in the northwest Highlands, from the Andover group mines northward to the New York border, implying proximity there to a volcanic center (Volkert, 2004).

Magnetite Deposits

Geologic relationships

Marble-hosted magnetite deposits occur at 21 mines in the western Highlands over a distance of 45 km, and at three mines in the eastern Highlands over a distance of 16 km, but that also extend northward another 14 km into the southern New York Hudson Highlands (Fig. 3). Mines in the western New Jersey Highlands occur intermittently along linear trends in four discrete groups: (1) the Franklin group (Furnace bed, and Hill vein); (2) Andover group (Sulphur Hill, Tar Hill, and Longcore mines); (3) Jenny Jump group (Smiths, Hoagland, Deats, Albertson, Stinson, Davis, Inshow Exploration, Howell Farm, and Shaw mines); and (4) Belvidere group (Ahles, Raub, Little, Riddle, Queen, and
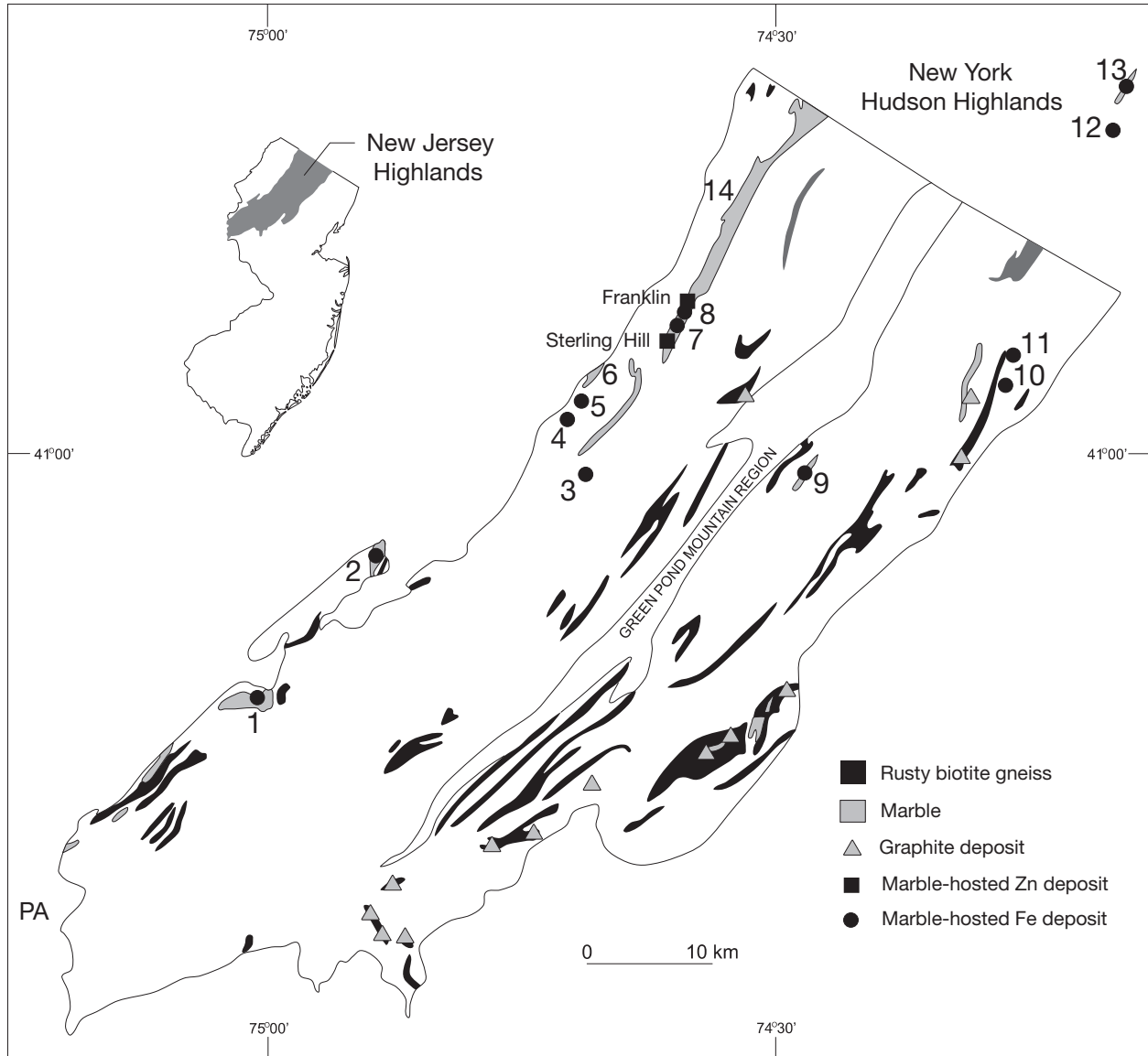
Fɪɢ. 3. Distribution of marble-hosted magnetite deposits in the western and eastern New Jersey Highlands and adjacent New York Hudson Highlands. Magnetite mines, and locations sampled for this study are as follows: 1 = Belvidere Group mines; 2 = Jenny Jump Group mines; 3 = Roseville mine; 4 = Sulphur Hill mine; 5 = Tar Hill and Longcore mines; 6 = Limecrest quarry; 7 = Hill vein; 8 = Furnace bed; 9 = Splitrock mine; 10 = Kanouse mine; 11 = Unnamed prospect; 12 = Bradley mine; 13 = Twin Lakes calcic skarn; 14 = Hamburg quarry. Zinc deposits at Franklin and Sterling Hill are unnumbered. Also shown are locations of graphite deposits.

Osmun mines; Fig. 3). Mines in the Andover and Franklin groups are hosted by the Franklin Marble layer, but other host-rock marbles are unable to be correlated with certainty to the Franklin Marble. The solitary Roseville mine is located southeast of the Andover group. Mines in the eastern Highlands are discrete occurrences along a linear trend that includes the Kanouse mine, an unnamed prospect, and Splitrock mine in the New Jersey Highlands and the Bradley mine and Lower Twin Lake occurrence in the New York Hudson Highlands (Fig. 3).

Magnetite orebodies have mainly tabular to lenticular shapes that locally pinch and swell along strike. Widths of orebodies range from 0.6 to 17 m and average about 4 m (Bayley, 1910).

Ores generally maintain structural conformity with metamorphic foliation in host marble and adjacent country rocks and share complex fold geometries with enclosing host rocks. At all of the deposits massive to granular magnetite ores grade into disseminated magnetite in hanging wall and footwall marble and then into unmineralized marble over a distance of less than a meter (Fig. 5). Volkert (2001) presented evidence suggesting that Fe was present in the host rocks prior to high-grade metamorphism during Grenvillian orogenesis based on the following: (1) the structural conformity of the deposits; (2) plunge of the deposits parallel to the regional axis of folds; (3) scarcity of postmetamorphic replacement features; (4) equilibration of ore and country rock at comparable metamorphic
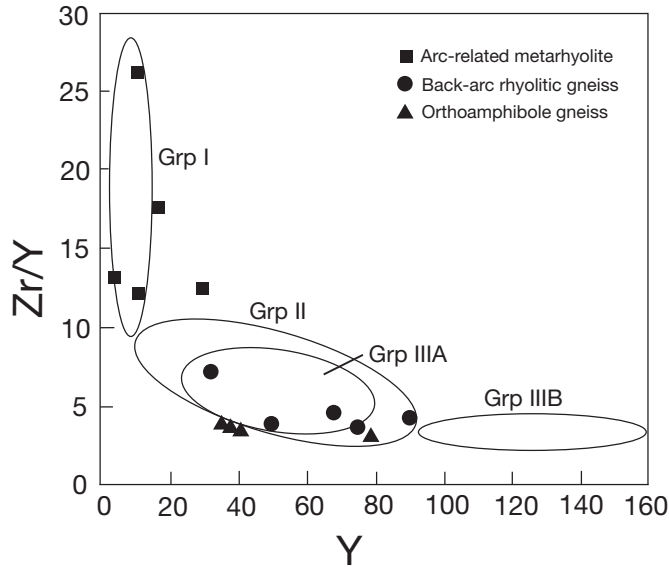
FIG. 4. Diagram of Y vs. Zr/Y for felsic volcanic rocks (after Lesher et al., 1985, and Lentz, 1998). Fields are as follows: Group I = unmineralized island arc-related volcanics; Group II = occasionally mineralized continental arc-related volcanics; Groups IIIA and IIIB = commonly mineralized volcanics from rift-related back-arc environments. Note the affinity of arc-related metarhyolite of the Losee Suite to Group I and of supracrustal back-arc rhyolitic gneisses and orthoamphibole gneiss to Group III. Sample data are from Drake and Volkert (1999) and Volkert (2006).

temperatures; and (5) absence of reaction rims between magnetite and adjacent silicate phases. Retrograde minerals in the ores are rare, and the deposits exhibit a lack of brittle fracturing or discordant, postmetamorphic veins mineralized by magnetite, indicating a high temperature of formation for the deposits.

All of the marble-hosted magnetite mines occur within the supracrustal rocks. Ores in the Jenny Jump, Belvidere, and Andover groups, and New York Hudson Highlands are spatially associated with calc-silicate gneiss composed of plagioclase + diopside ± quartz ± titanite and bimodal metavolcanic rocks (amphibolite and rhyolitic gneiss). Skarnlike assemblages composed mainly of clinopyroxene and garnet formed in mines in the Andover group and a few mines in the Jenny Jump group and New York Hudson Highlands. The term "skarn" has been used here in a descriptive sense to refer to rocks that are garnet and pyroxene rich, rather than in a petrogenetic sense implying the influence of contact metamorphism or magmatic fluids from plutonic rocks in the formation of the magnetite ores. Skarnlike mineral assemblages are absent at the rest of the mines and magnetite occurs entirely within marble. Common lithologic associations at these mines are calc-silicate gneiss, composed of diopside + quartz + plagioclase ± titanite, amphibolites, and quartzite. The Ca-rich nature of the mineral assemblages at all of the mines, and the paucity of magnesian minerals, indicate that the premetamorphic carbonate protolith was predominantly calcitic.

FIG. 5. Hammer rests on contact between granular magnetite ore on the right and sparsely mineralized marble from a deposit in the Franklin group. This style of mineralization is characteristic of most marble-hosted deposits in the New Jersey Highlands.

Sparse amounts of granite and syenite pegmatite are observed on mine dumps and in outcrop at some mines where they discordantly intrude marble and calc-silicate rocks. The pegmatites are undeformed and contain small xenoliths of country rock, indicating they postdate the regional high-grade metamorphism and formation of the magnetite deposits. Plutonic rocks are otherwise absent from the deposits, although considerable volumes of granite occur 1 km or more from some of the mines.

Mineralogy and geochemistry

Prograde mineral assemblages of the marble-hosted magnetite deposits are grossly similar and include calcite + magnetite ± garnet ± clinopyroxene; calcic amphibole, biotite, and titanite occur locally. Trace amounts of Mn minerals, observed by scanning electron microscopy, include Fe-Mn oxide in samples from the Howell Farm mine and an unnamed mine dump between the Howell Farm and Shaw mines, Mn-Ti oxide from the Furnace bed, and marokite (?) from the Stinson mine. In addition, Modreski (2008) describes Fe-Pb-Al and Mn-Fe-Ti oxides associated with Pb- and Ba-rich orthoclase from Sulphur Hill. Retrograde minerals include quartz, epidote, chlorite, K-feldspar, sulfide minerals, serpentine, and limonite. Mines in the Belvidere group are unique in having considerable alteration at the top of the orebody that has some of the characteristics of a gossan. There, magnetite has been oxidized to limonite, and at the Ahles mine limonite contains nodules of pyrolusite and masses of cherty quartz (Bayley, 1910). The alteration postdates the regional high-grade metamorphism associated with the Ottawan orogeny.

Calcite is the principal mineral in the host rocks where it consists of white to light gray, medium crystalline grains and aggregates of grains that form concordant folia and share grain boundaries with coexisting silicates and magnetite. Locally, coarse calcite grains form small, unfoliated pods and lenses adjacent to some of the ore zones. Sparse amounts of graphite that coexist with calcite are found at a single location in between the Howell Farm and Shaw mines in the Jenny Jump group.

Clinopyroxene occurs as dark green grains in calc-silicate wall rocks and the assemblage diopside + calcite enveloping the ore zones, and less commonly with garnet in the ore zones. Electron microprobe analyses of pyroxenes from Andover group deposits are homogeneous and unzoned diopside with compositions of (Hed $_{29-32}$Di$_{66-70}$Jh$_1$; abbreviations from Kretz, 1983). However, more work is necessary to determine if there are systematic compositional variations within or between deposits. Pyroxenes from Andover group deposits have F contents of 158 to 264 ppm and Zn contents of 516 to 3,200 ppm that overlap the composition of clinopyroxenes from the Franklin-Sterling Hill area (Essene and Peacor, 1987).

Garnet occurs in the assemblage garnet + calcite + magnetite in ore zones and grades outward into the assemblage garnet + clinopyroxene + calcite. The garnet in each type is dark reddish-brown and consists of discrete grains or clusters of grains in a matrix of calcite. Electron microprobe analyses of Andover group garnets are andradite (Adr$_{45-53}$ Grs$_{41-51}$ Sps$_{2-4}$Pyp$_{1-2}$Alm$_{0-7}$). Analyzed garnets have Zn contents of 93 to 456 ppm and F that ranges from 2,100 to 2,400 ppm. Rare pale green apatite has been observed with garnet in dump material at the Sulphur Hill mine.

Sulfides postdate the formation of magnetite and garnet skarn at the Sulphur Hill deposit (Neumann, 1952). They follow the paragenetic sequence: pyrite → pyrrhotite → sphalerite (ferroan variety marmatite) → chalcopyrite → galena (Sims and Leonard, 1952). Molybdenite is locally abundant in garnet-pyroxene skarn along with pyrite (Neumann, 1952) but is typically absent from the ore zones.

Magnetite is texturally massive to granular and grades into disseminated grains outward from the ore zones. Magnetite is typically free of silicates and coexists with calcite. Magnetite is characterized by low Al$_2$O$_3$ (avg 1.61 wt %), TiO$_2$ (avg 0.11 wt %), and P$_2$O$_5$ (avg 0.10%), and locally high S (avg 0.46 wt %; Table 1). The Mn content of magnetite is quite variable (0.18–3.3 wt %) and exceptionally high values in magnetite from Ahles and Raub are due to alteration of Paleozoic or younger age. The Andover group is exceptional in having only ~0.24 wt percent MnO. Data are unavailable for the Roseville mine or from mines in the eastern Highlands.

Zinc is locally abundant in magnetite from the Sulphur Hill mine (1,800–3,000 ppm), the Franklin group at the Hill Vein (1,160–1,200 ppm; Table 2) and the Furnace bed (80–500 ppm; Johnson and Skinner, 2003). The source of zinc in the magnetite is not known, but it may be due to finely disseminated sphalerite that is present in minor amounts as discrete grains at the Raub mine in the Belvidere group and the Sulphur Hill mine. Abundances in ppm of As, V, Sb, and Zn are high in magnetite from the Sulphur Hill and Hill vein deposits (Table 2) compared to Franklin Marble that has As = 5, V = 7, Sb = 1, and Zn = 59 ppm and upper crustal values of 1.5, 60, 0.2, and 71 ppm, respectively (Taylor and McLennan, 1995).

Zinc Deposits

Geologic relationships

Excellent summaries of the geologic relationships of the 22 Mt Zn-Fe-Mn deposit at Franklin are given in Spencer et al. (1908), Ries and Bowen (1922), Frondel and Baum (1974), and of the 11 Mt Zn-Fe-Mn deposit at Sterling Hill in Metsger et al. (1958), Metsger (2001), and Johnson (1990, 2001). Both of the deposits are folded, penetratively deformed, and are entirely within the Franklin layer, although at different stratigraphic positions (Hague et al., 1956). The Franklin deposit is folded into a hook-shaped synform that plunges 25° toward the northeast and was mined to a depth of 370 m (Frondel and Baum, 1974). The deposit consists of a sequence of lenslike bodies rich in zinc minerals (ore) and calc-silicate (skarn) rocks (Frondel and Baum, 1974). The 0.9- to 2.4-m-thick, marble-hosted Furnace magnetite bed is structurally beneath the west limb of the Zn deposit at Franklin. Directly beneath, and in conformable contact with the Furnace magnetite bed, is a 0.3-m-thick magnetite band hosted by amphibolite. Whether these are continuous with the marble- and amphibolite-hosted magnetite of the Hill vein about 600 m to the southwest continues to be disputed (e.g., Frondel and Baum, 1974).

The Sterling Hill deposit occurs lower in the Franklin layer than the Franklin deposit and structurally above amphibolite

TABLE 1. Bulk-Ore Composition of Marble-Hosted Magnetite from Highlands Mines[1]

Mine	Fe[2]	Mn	Ti	P	S
Belvidere group					
Little	37.94–68.60	0.77–0.90	trace	0.02–0.10	0.08–0.10
Riddle	34.72	0.34–0.35	0.19–0.31	0.008–0.04	0.38–0.54
Queen	54.35–55.29	1.26	trace	0.23–1.52	0.0
Osmun	55.73–58.30	1.08	trace	0.03–0.06	0.0
Ahles	35.75–57.01	2.35–8.73	0.017–0.12	0.0–0.17	0.04–4.25
Raub	33.80–63.87	0.51–5.81	trace	0.11–0.19	0.0
Jenny Jump group					
Albertson	55.60	3.30	0.0	-[3]	-
Howell Farm	50.72–58.50	0.50–2.09	0.0	0.05–0.37	0.18–2.14
Inshow	51.40	0.79	0.0	0.17	-
Stinson	49.79–63.12	0.40–2.74	0.0	trace-0.02	trace
Shaw	54.80–59.10	-	-	0.0	0.90
Andover group					
Sulphur Hill[4]	61.16–68.48	0.07–0.25	0.08–0.24	0.02–0.24	0.27–2.29
Tar Hill	53.30	-	0.0	trace	1.10
Franklin group					
Furnace bed	33.15–57.19	0.18–2.71	trace-0.02	0.0–0.03	0.19–0.44
Hill vein[4]	67.86	0.27	0.17	0.01	trace
Other mines					
Roseville	50.61–53.92	-	-	0.0–0.03	0.01–0.40
Split Rock	63.39	-	0.0	0.01	0.07

[1] Data sources: Sulphur Hill and Hill vein (Volkert, unpub.); Furnace bed (Bayley, 1910; Johnson and Skinner, 2003); all other mines (Bayley, 1910)
[2] All analyses in wt percent
[3] - = not analyzed
[4] Analyses of massive magnetite by ICP-MS (SGS Laboratories, Ontario, Canada)

and foliated, medium-grained calc-silicate gneiss composed of plagioclase + diopside ± quartz ± titanite (Fig. 2). The deposit, mined to a depth of 564 m, is folded into a synform that plunges 45° toward the northeast and exhibits more complex internal deformation than the Franklin deposit (Metsger, 2001). The Sterling Hill deposit is distinguished by a "cross member" of ore linking the east and west limbs and a western limb truncated by Paleozoic-age faulting (Metsger, 2001).

Mineralogy and geochemistry

The mineralogy of the Zn-Fe-Mn deposits at both Franklin and Sterling Hill is remarkably similar (willemite + franklinite + zincite + tephroite, with accessory carbonate and silicates), as is the geochemistry of the ore that contains 20+ percent Zn, 16 to 17 percent Fe, and 7 to 9 percent Mn (Frondel and Baum, 1974; Metsger, 2001). The Franklin deposit has a more varied mineralogy than Sterling Hill, due to minerals associated with abundant late pegmatites and more common garnet-clinopyroxene-feldspar calc-silicate units at Franklin (Dunn, 1995).

The sulfide-free assemblage in the Zn ore deposits reflects a higher f_{O_2}/f_{S_2} compared to the pyrrhotite-pyrite assemblages of the Franklin Marble elsewhere regionally (Essene and Peacor, 1987; Johnson et al., 1990). Lower f_{O_2}/f_{S_2} characterized local environments at Sterling Hill and resulted in the local occurrence of sphalerite in parts of the orebody. Except for a few rare localities, the Zn ore is graphite free, as is the

Franklin marble within about 2 m of the ore (Metsger, 2001). Elevated metal contents (e.g., Mn, Fe, Zn, Mg, Cd, and Pb) extend as much as 40 m from orebodies in the Franklin marble (Buis, 1987).

Carbon and Oxygen Isotope Data

Analytical methods

Samples for this study were collected from marble-hosted magnetite deposits between 2006 and 2007, with the sample suite dominated by silicate-poor magnetite deposits from the western Highlands (Fig. 3). Magnetite-bearing samples were collected where possible, but some deposits are represented by host skarn or marble samples (Table 3). To test for variability in the metasedimentary sequence, a barren calcitic marble in pyroxene skarn from Hamburg quarry was also sampled, as was a sequence of calcite-diopside calc-silicate from the Limecrest quarry, structurally above the Franklin band of marble (Table 4). In addition, for comparison to existing data from the Sterling Hill deposit (Johnson et al., 1990), we collected samples along a traverse through the north end of the west limb of the Franklin Zn orebody (Table 5).

Samples for carbon and oxygen isotope analysis were crushed, washed, and handpicked for purity. Powdered calcite and dolomite mineral separates were dissolved using phosphoric acid in off-line reaction vessels after the method of McCrea (1950). Calcite samples were reacted at 25°C and

TABLE 2. Trace Element Composition of Marble-Hosted Magnetite[1]

Location	Sulphur Hill		Hill vein
Ba[2]	27	14	20
V	149	202	265
Cr	207	75	27
Co	33	45	30
Ni	31	20	37
Cu	27	30	0.7
Zn	1820	3020	1210
As	8	5	6
Sn	67	87	–[3]
Sb	25	2	0.2
Pb	10	4	236
B	-	-	45
La	2.9	0.54	1.1
Ce	5.6	0.9	2.2
Pr	0.75	0.15	0.26
Nd	2.8	0.56	1.0
Sm	0.63	0.1	0.2
Eu	0.148	0.032	<0.05
Gd	0.7	0.1	0.11
Tb	0.12	0.01	<0.05
Dy	0.78	0.07	0.12
Ho	0.18	0.02	<0.05
Er	0.62	0.05	<0.05
Tm	0.096	0.006	<0.05
Yb	0.72	0.05	0.1
Lu	0.102	0.023	0.09
Total REE	45.53	6.97	16.01
Eu/Eu^*_{CN}[4]	0.69	0.99	0.95
Ce/Ce^*_{SN}[5]	0.87	0.71	0.96
$(Ce/Pr)_{SN}$	0.82	0.65	0.96

[1] Data from Volkert (unpub.); analysis of magnetic separates of massive magnetite by ICP-MS (SGS Laboratories, Ontario, Canada)

[2] All elements in parts per million

[3] - = not analyzed

[4] Chondrite normalized ratio of Eu/[Sm+Gd/2]; normalization values from Masuda et al. (1973)

[5] Shale normalized ratio of Ce/(0.5La + 0.5Pr); PAAS normalization values from Taylor and McLennan (1985)

dolomite samples were reacted at 40°C overnight. Evolved CO_2 was cryogenically purified and was analyzed in dual-inlet mode using a Thermo Finnigan Delta Plus Advantage mass spectrometer at Colgate University (Peck et al., 2005). Calcite standards and samples were corrected using the sealed vessel phosphoric acid fractionation factor of Swart et al. (1991), and dolomite samples were corrected using Rosenbaum and Sheppard (1986). Eight analyses of NBS-19 averaged $\delta^{13}C$ = 2.04 ± 0.02 per mil (PDB) and $\delta^{18}O$ = 28.58 ± 0.04 per mil (SMOW). An internal calcite lab standard (CCA1) was analyzed on each of the ten analysis days. CCA1 averaged $\delta^{13}C$ = –18.36 ± 0.02 per mil and $\delta^{18}O$ = 8.92 ± 0.08 per mil (*n* = 25), and daily averages were within 0.04 per mil of the average for $\delta^{13}C$ and 0.06 per mil for $\delta^{18}O$. Daily reproducibility averaged $\delta^{13}C$ = 0.02 ± 0.01 per mil and $\delta^{18}O$ = 0.03 ± 0.03 per mil. Duplicated samples had reproducibility equal to or better than analyses of CCA1.

Results

Results are shown in Tables 3 through 5 and in Figures 6 and 7. Oxygen isotope values from ore deposits range from $\delta^{18}O$ = 9.7 to 24.5 per mil, and, in general, most samples have lower isotope ratios than barren Franklin Marble (Peck et al., 2006). Carbon isotope values through the Franklin Zn-Fe-Mn orebody have a more limited range ($\delta^{13}C$ = –0.8 ± 1.5‰) than $\delta^{13}C$ values from marble-hosted magnetite deposits (0.8 to –4.8‰). The lowest $\delta^{13}C$ values (–4.4 to –5.9‰) occur in Furnace bed calcite (Johnson and Skinner, 2003). Because of the poor exposure at most magnetite deposits, much of the data in Table 3 is represented by ore host rocks (marble or skarn). These rocks have similar oxygen and carbon isotope ratios to magnetite-bearing samples (this study; Johnson and Skinner, 2003) but are distinct from isotope ratios in marble away from the ore deposits (Peck et al., 2006) and are interpreted here to be representative of the ore-forming hydrothermal system.

Discussion of Isotope Data

Preservation of protolith isotope ratios in ores

Johnson et al. (1990) presented several lines of evidence for essentially closed-system metamorphism of the orebody at Sterling Hill. Most important are layer to layer variability and sharp contrast with host marbles for both f_{O_2}/f_{S_2} and mineral $\delta^{18}O$, indicating a lack of pervasive fluid flow during metamorphism (see also Essene and Peacor, 1987). A stable isotope sampling traverse was made across the Franklin orebody for comparison to values recorded at Sterling Hill. Our data from Franklin are similar to those from Sterling Hill: ~8 per mil steps in $\delta^{18}O$ (Cal) are observed, with marble on either side of the orebody averaging 20.7 ± 0.7 per mil (*n* = 7) and orebody samples averaging 12.4 ± 2.5 per mil (*n* = 7; Fig. 6). In comparison, calcite from orebody samples at Sterling Hill average 14.3 ± 1.8 per mil (*n* = 41; Johnson, 1990). Interestingly, $\delta^{13}C$ values are identical for Franklin and Sterling ores and marble host rocks (Fig. 6; Johnson et al., 1990). Our traverse through the orebody at Franklin suggests that it shares both the unusual mineralogy and general carbon and oxygen isotope characteristics of the orebody at Sterling Hill.

The Furnace magnetite bed also has a stable isotope contrast with host marble, similar to the adjacent Franklin Zn deposit. Johnson and Skinner (2003) documented a ~4.5 per mil step in $\delta^{13}C$ between magnetite ore and host marble, and variable $\delta^{18}O$ (Cal) suggestive of closed-system metamorphism of iron-bearing protoliths with slightly different compositions. Other marble-hosted magnetite deposits in the New Jersey Highlands are more poorly exposed, preventing detailed comparison of isotope ratios between host marble and ore deposit lithologic units, except for the skarn-hosted Inshow Exploration (Fig. 7; Table 3). At Inshow, there is a difference in $\delta^{18}O$ (Cal) of ~1.4 per mil between host marble and the center of the skarn zone, which is accompanied by a difference in $\delta^{13}C$ of ~0.5 per mil. This argues against significant metamorphic fluid flow, at least across this marble-skarn contact. These steps in isotopic composition within ore deposit lithologic units, and the preserved heterogeneity between premetamorphic veins and host marble at the Roseville deposit, suggest preservation of isotope ratios from the peak of metamorphism. Preservation of premetamorphic stable isotope ratios is common in granulite-facies marbles in the absence of fluid infiltration during metamorphism (Valley and O'Neil, 1984; Cartwright and Valley, 1991). This feature

TABLE 3. Stable Isotope Compositions of Carbonate from Marble-Hosted Magnetite Deposits, New Jersey Highlands

Sample no.	Lithology	δ^{13}C(PDB)	δ^{18}O(SMOW)	Major Minerals
		Western New Jersey Highlands		
Ahles mine (40°48' 58"N, 75°00' 34"W) silicate-poor magnetite				
BVD-133A	Marble	–1.52	17.01	Cal+Ksp+Mt
Davis mine (40°55' 13"N, 74°54' 17"W) silicate-poor magnetite				
BVD-154A	Marble	–1.12	15.18	Cal+Ol+Mu+Mt
Furnace bed (41°06' 56"N, 74°35' 17"W) silicate-poor magnetite				
FB-1	Marble	–4.39	12.38	Cal+Di+Qtz+Op
Hamburg quarry (41°10' 02"N, 74°34' 39"W) barren skarn				
HAM-827	Skarn	–2.25	10.59	Cal+Di
Howell Farm mine (40°55' 14"N, 74°53' 22"W) silicate-poor magnetite				
BLR-349A	Marble	0.35	16.64	Cal+Ol+Mu+Bt+Gr+Op
BLR-349B	Marble	–0.65	16.13	Cal+Ol+Bt+Spl
Inshow Exploration (40°53' 44"N, 74°55' 33"W) skarn-hosted magnetite				
AM-03	Marble (0 m[1])	–1.15	15.19	Cal
AM-04	Marble (0.4 m)	–1.26	15.14	Cal+Di
AM-05	Marble (0.6 m)	–1.28	15.19	Cal+Di
AM-08	Skarn (1.1 m)	–1.27	15.19	Cal+Di
AM-11	Skarn (1.6 m)	–1.71	14.18	Cal+Di
AM-12	Skarn (1.6 m)	–1.92	13.73	Cal+Di+Grt
AM-16	Skarn (2.8 m)	–1.90	13.86	Cal+Di+Grt
AM-18	Marble (9.3 m)	0.10	15.32	Cal+Di
AM-19	Marble	–0.45	15.50	Cal+Mt
AM-21	Marble	0.10	15.71	Cal+Di
BLR-326	Marble	–2.02	15.71	Cal+Di
Pikes Peak mine (Furnace Bed) (41°06' 35"N, 74°35' 29"W) silicate-poor magnetite				
FR-1	Marble	–0.04	16.28	Cal+Mt
Roseville mine (40°58' 09"N, 74°41' 50"W) silicate-poor magnetite				
AM-02A	Vein	–2.90	13.13	Cal+Mu+Bt
AM-02B	Marble	–1.34	13.91	Cal
ST-31A	Marble	–1.37	12.30	Cal+Ol+Mt
ST-31B	Vein	–3.38	11.69	Cal+Grt+Qtz
Shaw mine (40°55' 06"N, 74°53' 32"W) silicate-poor magnetite				
BLR-354A	Marble	–0.01	15.45	Cal+Ol+Mu+Bt+Ks+Mt
BLR-354B	Marble	0.10	15.83	Cal+Ks+Gr+Mt+Op
Stinson mine (40°54' 26"N, 74°55' 00"W) silicate-poor magnetite				
BLR-335A	Marble	–2.69	15.56	Cal+Ol+Mt
BLR-335B	Ore	–2.59	17.00	Cal+Mt
Sulphur Hill mine (41° 0' 26"N, 74° 44'0"W) skarn-hosted magnetite				
SH-3	Skarn	–3.5	14.2[2]	Cal+Di+Py
SH-5	Skarn	–4.2	12.9[2]	Cal+Grt+Pl+Py+Sp+Gl
SH-18	Skarn	–3.5	12.7[2]	Cal+Di+Grt+Py
Tar Hill mine (41°00' 45"N, 74°43' 30"W) skarn-hosted magnetite				
NE-1258A	Skarn	–4.80	13.37	Cal+Grt+Qtz+Op
NE-1258B	Skarn	–4.86	13.42	Cal+Di+Grt+Op
Unnamed mine dump between Howell Farm and Shaw mines (40°55' 06"N, 74°53' 32"W) silicate-poor magnetite				
BLR-353	Marble	–0.90,–1.00	14.39, 14.14	Cal+Ol+Bt+Mt
Marble with disseminated magnetite (40°54' 46"N, 74°53' 26"W)				
BLR-379	Marble	0.72	18.38	Cal+Mt
		Eastern New Jersey Highlands		
Splitrock mine (40°59' 38"N, 74°26' 15"W) silicate-poor magnetite				
BN-718	Marble	0.31	24.51	Cal+Ol+Spl
Unnamed mine, Wanaque quadrangle (41°04' 26"N, 74°16' 52"W) silicate-poor magnetite				
WQ-1233	Marble	–0.21	22.25	Cal+Ol+Mt
		Hudson Highlands, NY		
Bradley mine (41°16' 35"N, 74°06' 02"W) skarn-hosted magnetite				
PL-1	Marble	–0.75	16.84	Cal+Ol+Spl+Mt
Lower Twin Lake mine (41°18' 52"N, 74°04' 41"W) skarn-hosted magnetite				
PL-2	Marble	0.80	13.78	Cal+Di+Qtz+Op

Abbreviations: Bt = Biotite, Cal = Calcite, Di = Diopside, Gl = Galena, Gr = Graphite, Grt = Garnet, Ksp = K-feldspar, Mt = Magnetite, Mu = White mica, Ol = Olivine, Op = Other opaques, Pl = Plagioclase, Py = Pyrite, Qtz = Quartz, Sp = Sphalerite, Spl = Spinel

[1] Traverse distance is given in meters across strike (Inshow Exploration, from south to north)

[2] Isotope data from Meredith et al. (2003)

TABLE 4. Stable Isotope Compositions of Carbonate from
Limecrest Quarry Calc-silicates, New Jersey Highlands

Sample no.	Lithology	δ^{13}C(PDB)	δ^{18}O(SMOW)	Major Minerals
AM-46	Calc-silicate (1.2 m)	–4.33	14.44	Cal+Di
AM-47A	Calc-silicate (1.4 m)	–4.52	14.51	Cal+Di
AM-47B	Calc-silicate (1.8 m)	–4.22	14.61	Cal+Di
AM-48	Marble (5.8 m)	–4.56	13.16	Cal+Di
AM-49	Calc-silicate (7.6 m)	–3.38	13.49	Cal+Di+Bt
AM-50	Calc-silicate (8.7 m)	–4.51	12.86	Cal+Di+Bt
AM-51	Calc-silicate (10.2 m)	–4.10	12.87	Cal+Di+Bt
AM-52	Marble (18.5 m)	–3.47	12.87	Cal+Di
AM-53	Marble (19.4 m)	–3.77	13.34	Cal+Di
AM-54	Marble (19.9 m)	–3.01	13.15	Cal+Di

Notes: Bt = Biotite, Cal = Calcite, Di = Diopside; traverse distance is given in meters across strike (from west to east) in the calc-silicate sequence structurally above the Franklin Marble layer.

TABLE 5. Stable Isotope Compositions of Carbonate from a Transect across the Franklin Zn-Fe-Mn Orebody, New Jersey Highlands

Sample no.	Lithology	δ^{13}C(PDB)	δ^{18}O(SMOW)	Major Minerals
AM-24	Marble (–1.0 m)	–0.79	20.69	Dol+Di
AM-25	Marble (0 m)	–0.23	14.39	Dol+Di+Grt
AM-26	Ore (0.2 m)	–0.54	14.74	Dol+Wm+Fr
AM-27	Ore (0.4 m)	0.91	11.18	Dol+Wm+Fr
AM-28	Ore (1.5 m)	0.83	9.72	Dol+Wm+Fr
AM-29	Ore (1.5 m)	0.75	10.29	Dol+Wm+Fr
AM-31	Ore (3.4 m)	0.82	10.67	Dol+Wm+Fr
AM-32	Marble (6.9 m)	0.52	21.41	Dol
AM-33	Marble (8.4 m)	–0.21	20.07	Dol
AM-34	Marble (12.2m)	–0.65	20.75	Dol
AM-35	Marble (15.1m)	0.34	21.28	Dol+Grt
AM-36	Marble (19.8m)	0.29	19.98	Dol
AM-37	Marble (24.9m)	0.64	20.02	Dol+Gr
AM-40	Ore	1.52	16.05	Dol+Wm+Fr
AM-45	Marble	0.66	21.81	Dol

Notes: Di = Diopside, Dol = Dolomite, Fr = Franklinite, Gr = Graphite, Grt = Garnet, Wm = Willemite; traverse distance is given in meters across strike (from west to east)

allows the calculation of protolith isotope ratios once the effects of metamorphic devolatilization are taken into account (see below).

Peck et al. (2006) presented carbon isotope evidence for closed-system metamorphism of unmineralized Franklin Marble. Values of Δ^{13}C (Cal-Gr) = 3.31 ± 0.25 (n = 34) and Δ^{13}C (Dol-Gr) = 3.07 ± 0.30 (n = 6) are consistent with equilibrium at granulite-facies temperatures and do not correlate with δ^{18}O or δ^{13}C in calcite. This shows that carbon isotopes (and probably oxygen isotopes) are reflective of values at the
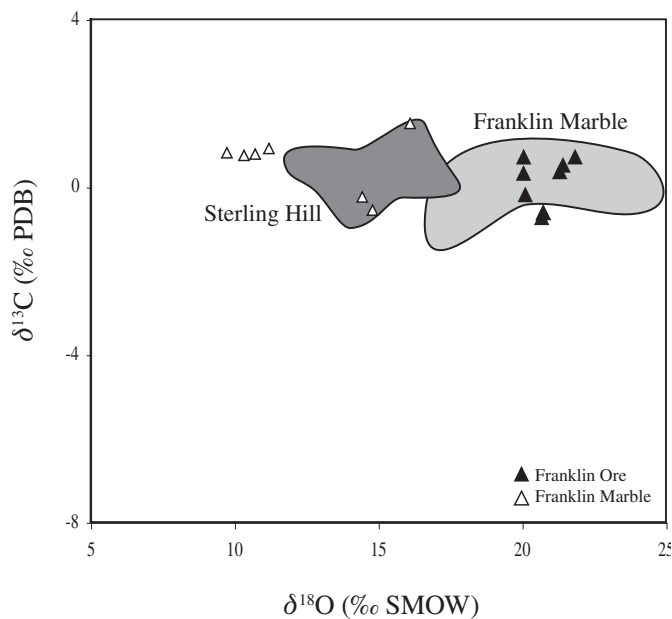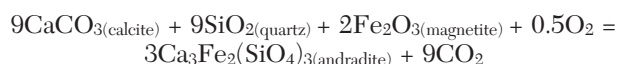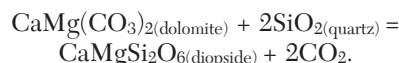

FIG. 6. Oxygen and carbon isotope ratios of analyzed samples from the Buckwheat open cut, Franklin Zn-Fe-Mn orebody, and host Franklin Marble. Franklin Marble field is from Peck et al. (2006), Sterling ore field from Johnson (1990) and Johnson et al. (1990).

peak of metamorphism for these rocks. Peck et al. (2006) interpreted the restricted range of δ^{13}C (Cal) in marbles across the New Jersey Highlands (Fig. 7) to reflect preservation of carbon isotope ratios reflecting a common depositional environment for these rocks.

Effects of metamorphic devolatilization on protolith isotope ratios

Loss of volatiles during metamorphism has predictable effects on isotope ratios of the remaining rock (e.g., Valley, 1986). In the Franklin Marble, associated calc-silicate, and marble-hosted magnetite deposits, the main influence on isotope ratios will be decarbonation during pyroxene and garnet formation. These reactions were modeled by:

$$9CaCO_{3(calcite)} + 9SiO_{2(quartz)} + 2Fe_2O_{3(magnetite)} + 0.5O_2 = 3Ca_3Fe_2(SiO_4)_{3(andradite)} + 9CO_2$$

and

$$CaMg(CO_3)_{2(dolomite)} + 2SiO_{2(quartz)} = CaMgSi_2O_{6(diopside)} + 2CO_2.$$

Granulite-facies oxygen and carbon isotope fractionation factors between rock and CO_2 from Valley (1986) were used with modal mineralogies estimated from thin sections and hand samples. Raleigh, as opposed to batch fractionation was calculated, because Raleigh fractionation causes the largest shifts in isotope ratios for extreme decarbonation. Franklin Marble typically has <10 percent silicate minerals, the formation of which would result in <0.1 per mil shifts in oxygen and carbon isotope ratios of the remaining rock during decarbonation reactions. Calc-silicates from the Limecrest quarry contain ~15 percent diopside, which would result in shifts from protolith values to lower isotope ratios of about 0.3 and 0.5 per mil in δ^{13}C and ^{18}O, respectively (Fig. 8). Comparable effects are calculated for skarn samples from Hamburg, the Inshow Exploration, the Sulphur Hill and Tar Hill deposits, and other silicate-rich (>20%) marble samples that have δ^{13}C shifts of –0.3 to 4.1 per mil and δ^{18}O shifts of 0.7 to 5.2 per mil.
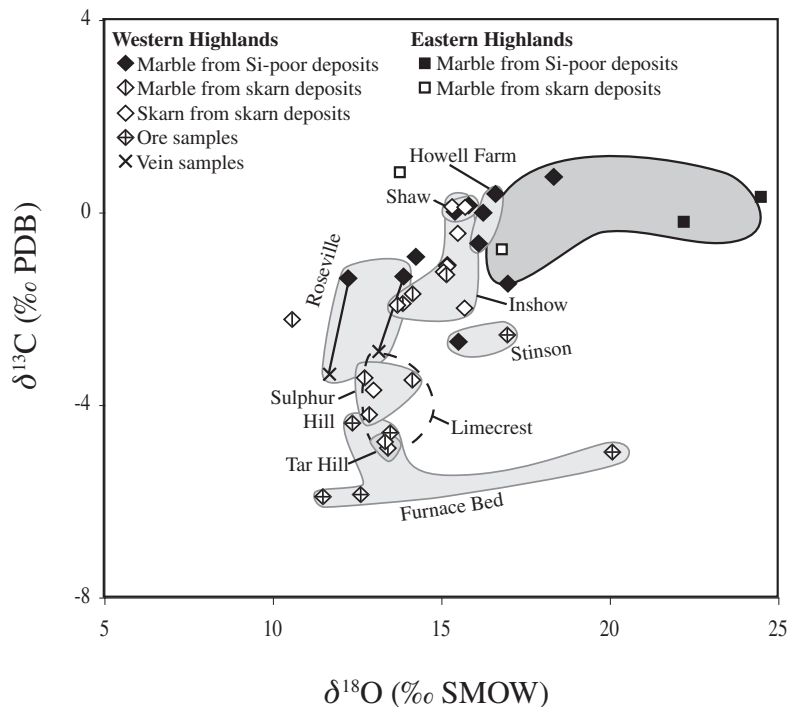
FIG. 7. Oxygen and carbon isotope ratios from analyzed samples of marble-hosted Fe ore deposits and calc-silicates in the western and eastern New Jersey Highlands and adjacent New York Hudson Highlands. Samples from the Roseville deposit are shown with a tie-line to hosted recrystallized veins, and the field for calc-silicate samples from the Limecrest quarry is shown as a dashed circle. Franklin Marble field is from Peck et al. (2006).

Siderite has been proposed to be an important component of the protolith of New Jersey magnetite ores (Collins, 1969; Frondel and Baum, 1974; Kastelic, 1979; Puffer, 2001). This genetic model requires a reaction such as the following:

$$6FeCO_{3(siderite)} = 2Fe_2O_{3(magnetite)} + C_{(graphite)} + 5CO_2,$$
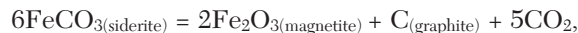
which would affect $\delta^{13}C$ and $\delta^{18}O$ of ores in a similar fashion to the calc-silicates and skarns. Johnson and Skinner (2003)

presented calculations for the Furnace bed, demonstrating that the modal abundances of magnetite and carbon and oxygen isotope values in these rocks cannot be explained by decarbonation, making iron carbonates unlikely protoliths. Magnetite formation via siderite decomposition has been documented elsewhere (e.g., Gauthier and Brown, 1986; van Zuilen et al., 2003), and in these rocks magnetite coexists with reaction products graphite + Mg carbonate (presumably representing Mg substitution in original siderite). Graphite is present in small amounts in Furnace bed samples (Johnson and Skinner, 2003), and graphite and Mg carbonates are rare in the rest of the New Jersey marble-hosted magnetite deposits (Bayley, 1910; this study). Note that if magnetite formed from siderite by oxidation reactions graphite would not be a product, but isotope effects caused by devolatilization would be even larger, a relationship which is not observed in samples from the same deposit with different magnetite contents.

Discussion

Advances in ore processing and understanding of nonsulfide zinc deposits have renewed interest in this class of ore
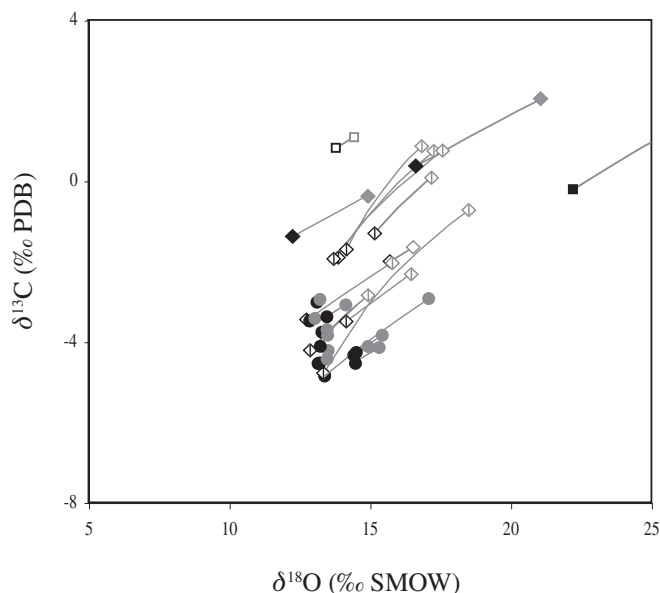
FIG. 8. Modeled effects of decarbonation reactions and hypothetical protoliths of skarn and silicate-rich carbonate-hosted iron deposits and calc-silicates. Symbols are as in Figure 7—black symbols are measured values, gray symbols are calculated protoliths (see text for discussion). Carbonate $\delta^{18}O$ values are used as a proxy for whole-rock values.

deposits (e.g. Sangster, 2003; Gilg et al., 2008), of which the Franklin and Sterling Hill deposits are among the most enigmatic examples. These deposits have some similarities to other hypogene sediment-hosted metal deposits but are distinctive in their Pb-poor and oxidized chemistry. For example, Hitzman et al. (2003) proposed that Franklin and Sterling Hill may represent a kind of intermediate submarine exhalative (SEDEX) environment, showing characteristics of both Broken Hill-type deposits (which contain Pb-Zn sulfides and are Mn rich) and Långban-type Mn-Fe oxide deposits. These similarities extend to marble-hosted magnetite deposits in the New Jersey Highlands, which have been compared to other Fe-rich facies associated with sediment-hosted Pb-Zn deposits and have been linked genetically to the Franklin and Sterling Hill Zn-Fe-Mn orebodies (Johnson and Skinner, 2003; Gauthier and Chartrand, 2005). Here we focus on constraining the genesis of the Fe and Zn-Fe-Mn deposits and comparing their carbon and oxygen isotope systematics to data from other carbonate-hosted ore deposits and to published ore deposit models.

Premetamorphic hydrothermal origin of marble-hosted deposits

Callahan (1966) was among the first to propose that Zn-Fe-Mn in the deposits at Franklin and Sterling Hill originated through sea-floor volcanism. Subsequent workers also advocated a hydrothermal sea-floor hypothesis for the origin of these Zn deposits (e.g., Frondel and Baum, 1974; Squiller and Sclar, 1980; Johnson et al., 1990; Johnson and Skinner, 2003). While the idea of a sea-floor hydrothermal origin is not new, its influence was not recognized beyond the deposits at Franklin and Sterling Hill. More recent work (Peck et al., 2006; Volkert, 2006; Volkert and Aleinikoff, 2007) has documented a far more extensive sea-floor hydrothermal system of Grenville age centered in the western Highlands based on the following evidence. High Mg orthoamphibole gneisses occur structurally between the Franklin Marble and bimodal volcanic rocks, midway between the Andover and Franklin group mines. Based on their geochemistry, Volkert (2006) interpreted these gneisses to have formed through localized hydrothermal alteration of basalt to a chlorite-rich rock by heated Mg-rich seawater on or beneath the Proterozoic sea floor. Subsequent metamorphism during the Ottawan orogeny produced the current assemblage in orthamphibole gneiss. In addition, bimodal volcanic rocks in the northwestern Highlands exhibit geochemical evidence of a progression from relatively unaltered compositions distal to magnetite deposits, to intensely altered rocks proximal to the deposits along a trend reflecting breakdown of feldspars and replacement by chlorite, sericite, and pyrite (Volkert and Aleinikoff, 2007; Fig. 9).

Compared to host marble, magnetite is enriched in As, V, Sb, B, and Zn (Table 2) that we propose were introduced via hydrothermal fluids during precipitation of the Fe. Enrichment of these elements during submarine hydrothermal activity in back-arc basin settings is well documented (e.g., Fouquet et al., 1993; Glasby and Notsu, 2003) in which they readily adsorb onto Fe and Mn oxyhydroxides that scavenge them from seawater (Zantop, 1981; Marchig et al., 1982, Cronan and Hodkinson, 1997). Abundances of Co and Ni are low in carbonate-hosted magnetite, as is the Co/Zn ratio that

ranges from 0.015 to 0.025, characteristic of hydrothermal deposits which have a mean value of 0.15, but not of hydrogenous deposits which have Co/Zn ratios >2.5 (Toth, 1980). Fe and Mn from hydrothermal sources typically undergo considerable fractionation with Fe precipitating rapidly upon mixing with seawater, thus producing high Fe/Mn ratios compared to hydrogenous deposits that have Fe/Mn ratios ~1 (Nicholson, 1992; Mills et al., 2001). Fe/Mn ratios of magnetite average ~300 and are comparable to the Fe/Mn ratios of Fe oxyhydroxide deposits of hydrothermal origin (e.g., Pichler and Veizer, 1999). Carbonate-hosted magnetite has low total rare earth element abundances (7–45 ppm), slightly to moderately negative Ce anomalies (Ce/Ce* = 0.75–0.97), and shale-normalized Ce/Pr ratios <1 (Table 2), all of which are characteristic of submarine hydrothermal deposits (e.g., Hein et al., 1994; Kuhn et al., 1998; Pichler and Veizer, 1999). The high abundance of F in the deposits at Franklin, the Furnace magnetite bed (Johnson and Skinner, 2003), and the Sulphur Hill mine is also characteristic of marine hydrothermal systems and their metamorphosed equivalents (e.g., Rajavuori and Kriegsman, 2002). Some magnetite deposits in the Belvidere and Jenny Jump groups are intercalated with tourmaline-rich quartzites that may represent meta-exhalative horizons.

Johnson et al. (1990) proposed that protoliths for the Zn ore were altered by hydrothermal fluids at ~150° by water-rich fluids with value of $\delta^{18}O \approx 2 \pm 4$ per mil to explain the oxygen and carbon isotope compositions at Sterling Hill. In light of the isotopic similarities between the two Zn deposits (Fig. 7), this model can be generalized to include both Franklin and Sterling Hill. Seawater, or a mixture of seawater and water with an igneous component at these temperatures, would lower the $\delta^{18}O$ of the ores from protolith values but leave $\delta^{13}C$ unaffected as seen at Franklin and Sterling Hill.
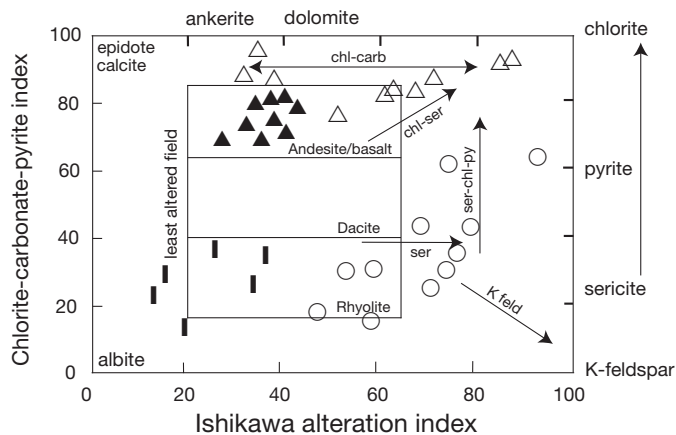

FIG. 9. Alteration box diagram after Large et al. (2001b), showing trends for hydrothermal alteration (solid arrows). Inset box shows the field of least altered felsic, intermediate, and mafic volcanic rocks. Bimodal volcanic rocks from magnetite deposits in the western Highlands plot along a trend characterized by moderate to severe sericite-chlorite-pyrite hydrothermal alteration, while metavolcanic rocks distal to the deposits are relatively unaltered. Symbols: filled circles = unaltered rhyolitic gneisses; open circles = altered rhyolitic gneisses; filled triangles = unaltered amphibolites; open triangles = altered amphibolites (data from Volkert and Drake, 1999; Volkert, unpub.). Axes: AI = 100(K₂O + MgO)/(K₂O + MgO + Na₂O + CaO) and CCPI = 100(MgO + FeOT)/(MgO + FeOT + Na₂O + K₂O), where FeOT is total iron as FeO.

Marble-hosted magnetite deposits have a similar range in values of $\delta^{18}O$ to marble at Franklin and Sterling Hill, but $\delta^{13}C$ values are distinctly lower and have a correlation with lower $\delta^{18}O$ values. Coupled trends in depletion of $\delta^{18}O$ and $\delta^{13}C$ from protolith values are typical in carbonates that have experienced fluid-rock interaction (e.g. Valley, 1986; Bowman, 1998; Fig. 10). This trend is clear in the uncorrected data (Fig. 7) and is improved slightly when the likely maximum effects of metamorphic devolatilization are removed (Fig. 8). Unmineralized calc-silicates from the Limecrest quarry were collected from a sequence of layered rocks structurally above the main Franklin Marble layer. These rocks are not spatially related to igneous rocks, although postorogenic felsic intrusions are present lower in the quarry. The Limecrest calc-silicates have similar carbon and oxygen isotope ratios to samples from magnetite deposits and may have been part of the same or a similar hydrothermal system. In general, oxygen and carbon isotope trends of New Jersey marble-hosted magnetite deposits are similar to those in other deposit types that formed from hydrothermal alteration and replacement of carbonate rocks (Fig. 10).

Modeling of water-rock interaction was calculated using the method of Zheng and Hoefs (1993). Initial carbonate isotope ratios of $\delta^{18}O = 25$ per mil SMOW and $\delta^{13}C = 0.2$ per mil PDB were used because these are representative of the most primary values of the Franklin Marble (Peck et al., 2006). Average fluid temperature of 150°C and $\delta^{18}O = 2$ per mil calculated by Johnson et al. (1990) for hydrothermal alteration of the Sterling Hill deposit was used in our calculations. A fluid $\delta^{13}C = -7$ per

mil was chosen as representative of typical sea-floor hydrothermal systems (Shanks, 2001). This is consistent with the lowest $\delta^{13}C$ values observed in the Fe deposits and could represent either igneous fluids or a mixture of seawater carbonate and organic carbon. The effect of carbon speciation (i.e., H_2CO_3 vs. HCO_3^-) on carbon isotope fractionation is negligible at this temperature (Ohmoto and Rye, 1979), and slightly lower starting $\delta^{18}O$ (such as modeled by Johnson et al., 1990, for the fractionation between zinc ore whole rocks and calcite) does not change the overall exchange trajectory. Figure 11 shows the results of hydrothermal alteration at different ratios of water/rock and $X(HCO_3^-) = 0.2$. This value of $X(HCO_3^-)$ matches the data but may overestimate the carbon content of the infiltrating fluid. The model cannot take into account organic carbon content of the protolith carbonate rock, which would lower calcite $\delta^{13}C$ upon equilibration with a possible lower $X(HCO_3^-)$ hydrothermal fluid. It is also difficult to assess dispersion of the isotope composition fronts of oxygen and carbon along the hydrothermal flow path, which can cause models of water-rock interaction to overestimate $X(HCO_3^-)$ (see Bowman, 1998)

Igneous fluids typically have $\delta^{13}C$ of –5 to –8 per mil and $\delta^{18}O$ of 5 to 10 per mil, but igneous-derived fluids involved in hydrothermal alteration of carbonate rocks typically have lower $\delta^{18}O$ due to interaction with oxygen evolved from wall rocks and/or externally derived surface fluids (e.g., Bowman, 1998). Modeling of hydrothermal alteration matches the protolith values of most marble-hosted magnetite deposits for values of water/rock ranging from 0.5 to 10 using both open- and closed-system interaction. Allowing $\delta^{18}O$ (fluid) to vary between 2 and 5 per mil at 150°C encompasses most of the
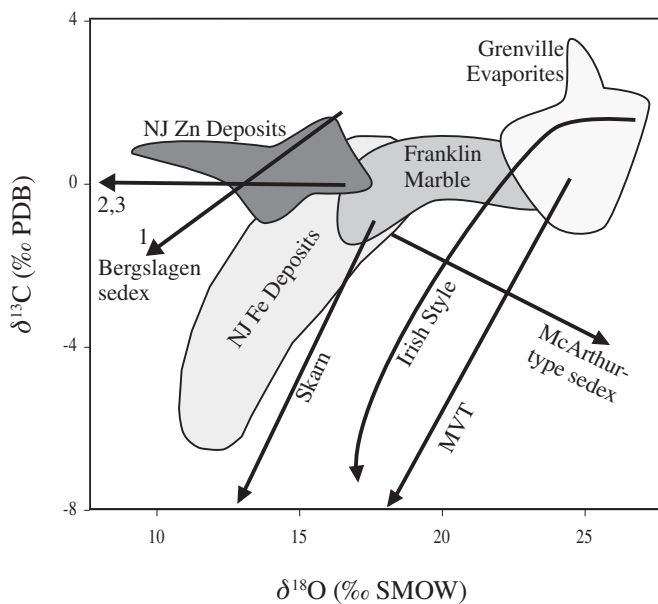

FIG. 10. Fields of Franklin-Sterling Zn-Fe-Mn ores (this study; Johnson, 1990; Johnson et al., 1990) marble-hosted Fe deposits (this study; Johnson and Skinner, 2003), Franklin Marble (Peck et al., 2006), and Grenville evaporites at the Balmat Zn deposit and Kilmar magnesite deposit (Whelan et al., 1990; Eppich and Peck, 2006). Isotope trajectories of other carbonate-hosted ore deposits are from Large et al. (2001a) and references therein. Sedimentary-exhalative (sedex) deposits from the Bergslagen district are the following: 1 = the Långbad deposit (Jonsson, 2004); 2 = the Sjögruvan Långbadtype deposit (Holtstam and Mansfeld, 2001); and 3= other stratiform Fe oxide deposits analyzed by De Groot and Sheppard (1988).
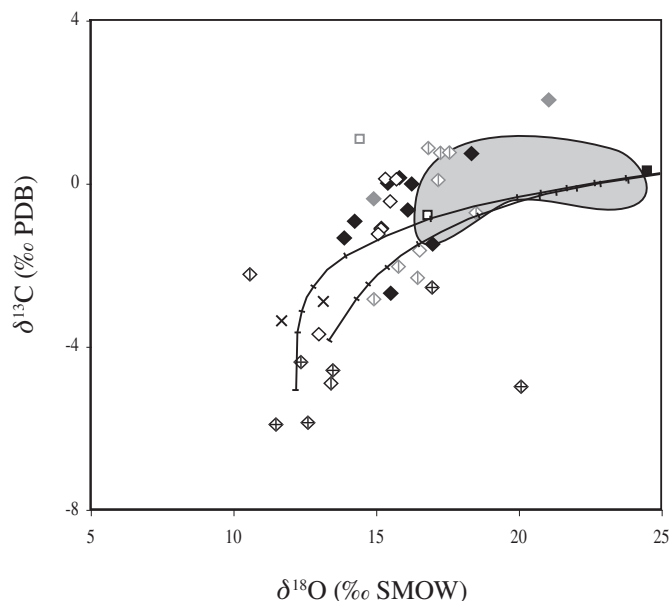

FIG. 11. Water-rock interaction model of Franklin Marble protoliths to form marble-hosted Fe ore deposits. Symbols as in Figure 7—black symbols are measured values, gray symbols are calculated protoliths corrected for decarbonation. Infiltrating fluids ($\delta^{18}O = 2‰$ and $\delta^{13}C = -7‰$), water/rock ranging from 0.5 to 10, and $X(HCO_3^-) = 0.2$ at 150°C matches the protolith values of most marble-hosted magnetite deposits, using both open- and closed-system interaction (upper and lower curves, respectively).

data in Figure 11. Similarly, the models closely match measured data using a temperature variability of 125° to 175°C. This calculation cannot uniquely fingerprint the fluid source but is consistent with mixtures of igneous fluids, seawater, and/or formation water in a submarine setting. Using the same temperatures and fluid isotope ratios but a very water rich fluid ($X(HCO_3^-) = 0.01$) the isotope ratios of the Franklin and Sterling Hill deposits can be modeled at similar W/R ratios to the magnetite deposits.

The lowest carbon and oxygen isotope ratios are found in the Tar Hill and Sulphur Hill deposits and the Furnace bed. These deposits are in the northern half of the western Highlands where the Franklin and Sterling Hill Zn-Fe-Mn orebodies are located, and this is where isotope ratios of magnetite ores and ore host rocks differ most from magnetite-free Franklin Marble values. Deposits located farther away, including much of the Jenny Jump group (Fig. 3) and marble-hosted magnetite deposits in the eastern Highlands and southern New York Hudson Highlands, generally possess higher carbon and oxygen isotope ratios compared to those from unaltered Franklin Marble. This is compatible with the diminished effect of hydrothermal fluids away from the western New Jersey Highlands and/or fluids buffered to carbonate $\delta^{13}C$, either of which may reflect the area around the Zn-Fe-Mn orebodies as being more proximal to the hydrothermal system.

Constraints on the formation of the magnetite and Zn-Fe-Mn ores

Sources of Fe in marble-hosted magnetite deposits: Several different theories have been advanced for the source of the Fe in the marble-hosted magnetite deposits in the New Jersey Highlands. Collins (1969) and Kastelic (1980) proposed that the deposits formed through metamorphism of an Fe carbonate-rich protolith. The results of this study, however, demonstrate that Fe carbonate is an unlikely source for the Fe for reasons discussed earlier in the paper. We agree with Johnson and Skinner (2003) that iron oxides or hydroxides are a more likely protolith than siderite or ankerite for the magnetite ores.

Because amphibolites are commonly intercalated with marble host rocks, we evaluated whether the Fe in the deposits may have been derived from mafic metavolcanic wall rocks through the breakdown of mafic minerals during metamorphism. Amphibolites from mines in the Andover group have total Fe of 12.86 wt percent Fe_2O_3, very similar to amphibolites a few kilometers to the north that have total Fe of 12.73 wt percent Fe_2O_3 (W. Peck and R. Volkert, unpub. data) and are distal to the mines. Thus, based on a comparison of amphibolite geochemistry there appears to be little evidence for mobilization of Fe from mafic wall rocks.

Some workers proposed that magmatic fluids from the 1.18 Ga granite intrusions are the source of Fe in marble-hosted deposits (e.g., Bayley, 1910; Sims and Leonard, 1952). This interpretation is not supported by the field relationships because plutonic rocks are not found near any of the deposits (Kastelic, 1979; Puffer, 1997). Furthermore, magmatic fluids would need to pass through amphibolites intercalated with host marble in order to react with the carbonate rocks and no development of skarn is seen in amphibolites at the marble-hosted

deposits. In addition, Sulphur Hill garnets have low Ti (~0.25 wt %) which is not compatible with skarn formed from Fe-rich magmatic fluids (e.g., Meinert, 1984).

We propose that the Fe in the marble-hosted deposits was precipitated as low-temperature oxides and hydroxides via hydrothermal fluids derived through sea-floor vents in the back arc. The current distribution of the deposits, mainly confined to linear belts in the western Highlands, may indicate a structural control by premetamorphic tectonic lineaments related to extensional faulting in the back arc. Gauthier and Brown (1986) pointed out the role of regional fracture zones in focusing metalliferous hydrothermal brines into carbonate host rocks in Fe and Zn deposits in southeast Canada. We envision a similar process for the New Jersey Fe and Zn deposits in which metals migrated upward and were discharged along basinal fracture zones, subsequently precipitating in carbonate rocks. Precipitation of Fe occurred on mixing with seawater, but the variable abundance of Mn in the Fe deposits is likely related to redox conditions in the depositional environment that were only locally sufficiently oxidizing to precipitate Mn (e.g., Pichler and Veizer, 1999). The uniformly low Fe and Zn contents of unmineralized marble requires introduction of the metals into the carbonate protolith from an external source prior to high-grade metamorphism. We interpret metal input to have been synchronous with bimodal volcanism in the back arc at 1.29 to 1.25 Ga. This is supported by the close spatial association of amphibolites and marble at the Highlands Fe and Zn deposits, implying that volcanism and carbonate sedimentation were coeval. Mafic magma beneath the sea floor in the back arc was the source for the amphibolites and also likely supplied the heat to drive the hydrothermal system.

Problems with a banded iron formation model: Some workers have emphasized the similarity of the marble-hosted Fe deposits in the New Jersey Highlands (Puffer, 1997) and New York Hudson Highlands (Gunderson, 2004) to Proterozoic banded iron formation (BIF) and suggested an exhalative origin in a marine setting for the deposits. Magnetite deposits in the Highlands differ from banded iron formation in lacking banding of the ore and in the absence of intercalated quartzite layers. The trends in the carbon and oxygen isotope data for unmineralized Franklin marble and the Fe ore deposits are consistent with hydrothermal alteration and replacement of preexisting marine carbonates but not with an exhalative genesis involving precipitation at the sea floor.
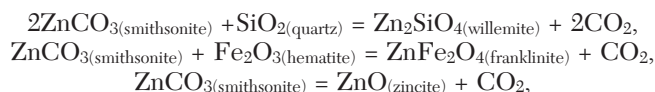
Johnson and Skinner (2003) also highlighted a possible similarity between the depositional environments of banded iron formation and the New Jersey Fe deposits. Their comparison was based in part on low carbon isotope values (i.e., –5 ± 1‰) from the Furnace Bed and the marine carbon isotope signature of the Franklin Marble, which was taken as suggestive as a stratified marine basin with low ^{13}C values below a chemocline. A stratified basin model for Proterozoic banded iron formations does explain the bimodal values of $\delta^{13}C$ of carbonates in these deposits. For example, the Kuruman iron formation (Transvaal Supergroup, South Africa) has BIF carbonate with $\delta^{13}C$ = –5.3 per mil while limestone is –1.3 per mil (Beukes et al., 1990). Similar bimodal values are seen in the Hamersley basin, with values lower than –5 per mil in BIF carbonates, reflecting the effects of diagenesis (Kaufman

et al., 1990). In contrast, our data show that the distinctly low $\delta^{18}O$ values of the New Jersey Fe deposits are coupled with a smooth variation between marine $\delta^{13}C$ values and low $\delta^{13}C$ of the most extreme Fe deposits (Fig. 7), making a stratified basin unlikely. In summary, although similarities to banded iron formation were suggested by previous data, results of this study favor more direct hydrothermal replacement processes for the Highlands Fe deposits.

Protoliths and fluid chemistry of the Franklin and Sterling Hill Zn-Fe-Mn orebodies

In terms of the New Jersey Zn deposits, calculations based on rock major element and stable isotope chemistry led Johnson et al. (1990) to propose that smithsonite was the major Zn-bearing phase in the protoliths of the Zn-Fe-Mn orebodies at Franklin and Sterling Hill. Normative calculations of Johnson et al. (1990) yield carbonate/silicate ratios that average ~7/1 for protoliths of Zn ores where this ratio is now ~2/1.

As with calc-silicate and skarn, metamorphic devolatilization is expected to cause a measurable change in $\delta^{13}C$ and $\delta^{18}O$ between carbonate-rich protolith rocks and ores. Published modal mineralogy of the Franklin and Sterling deposits was used to calculate the effect of Raleigh fractionation on hypothetical ore protoliths where smithsonite is the primary Zn mineral and rhodochrosite is the primary Mn mineral. These devolatilization reactions were modeled as follows:

$$2ZnCO_{3(smithsonite)} + SiO_{2(quartz)} = Zn_2SiO_{4(willemite)} + 2CO_2,$$
$$ZnCO_{3(smithsonite)} + Fe_2O_{3(hematite)} = ZnFe_2O_{4(franklinite)} + CO_2,$$
$$ZnCO_{3(smithsonite)} = ZnO_{(zincite)} + CO_2,$$

and

$$2MnCO_{3(rhodochrosite)} + SiO_{2(quartz)} = Mn_2SiO_{4(tephroite)} + 2CO_2.$$

Calculations were made using isotope fractionation factors appropriate for amphibolite- and granulite-facies rocks from Valley (1986). These fractionation factors use common calc-silicates and carbonates, but in the absence of isotope exchange experiments for Zn-bearing minerals the fractionations of Valley (1986) represent a good approximation for this system and are in agreement with estimates and empirical data (Zheng, 1999; Boni et al., 2003).

Franklin Zn ores average ~80 percent ore minerals (Spencer et al., 1908; Pinger 1950), which would represent a loss of 85 percent protolith C from smithsonite to form willemite, franklinite, and zincite. The average isotope shifts of $\delta^{13}C$ and $\delta^{18}O$ are calculated to be 4.3 and 2.8 per mil, respectively, for these reactions. Similarly, ores from Sterling Hill would indicate average shifts in $\delta^{13}C$ of 2.4 per mil and $\delta^{18}O$ of 2.2 per mil, and protoliths would range in $\delta^{13}C$ from 0.9 to 7.4 per mil and $\delta^{18}O$ from 12.6 to 20.6 per mil, basing calculations on modal mineralogy (Johnson, 1990). The carbon and oxygen isotope compositions of hypothetical smithsonite-rich protoliths are shown in Figure 12.

In light of the identical isotope ratios of the ores and unmineralized Franklin Marble, it is unlikely that smithsonite or hydrozincite were dominant components of the ore protoliths. Away from ore deposits, Franklin Marble has an average $\delta^{13}C$ = 0.25 ± 0.73 per mil (n = 46), which is a very limited range compared to marbles in other Grenville terranes (Peck et al., 2006) and is typical for Mesoproterozoic carbonates (Shields
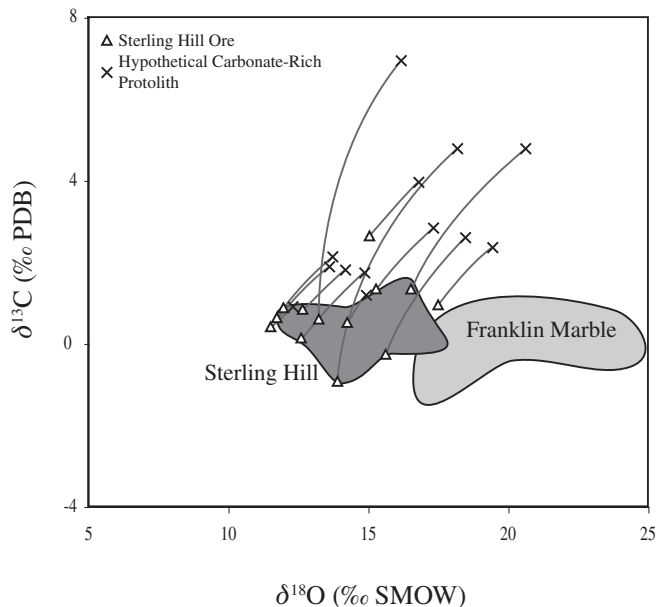

FIG. 12. Hypothetical carbonate-rich protoliths of Zn-Fe-Mn ores at Franklin and Sterling Hill. Using whole-rock $\delta^{18}O$ values for this calculation results in protolith values ~3 per mil lower but does not change calculations for $\delta^{13}C$. Note that the effect of decarbonation on carbon isotope ratios indicates that these protoliths would have distinct isotope ratios from barren Franklin Marble. Measured values are shown as open triangles and calculated protoliths as an "X." Franklin Marble field is from Peck et al. (2006), Sterling Hill ore field and data are from Johnson (1990) and Johnson et al. (1990).

and Veizer, 2002). Ores from Franklin and Sterling Hill have an average $\delta^{13}C$ = 0.50 ± 0.64 per mil (n = 41; Johnson, 1990; Johnson et al., 1990; this study), which is indistinguishable from the Franklin Marble. A Zn carbonate protolith for the ores would require original $\delta^{13}C$ values that were 0.5 to 6.8 per mil higher and would predict a larger range in $\delta^{13}C$. For example, 13 Sterling Hill samples reported by Johnson (1990) have a 3.8 per mil range in $\delta^{13}C$, but calculated smithsonite protoliths have a 5.8 per mil range. Even if the protolith Zn had 50 percent carbonate host minerals, the shift in average $\delta^{13}C$ of ores by decarbonation would be ca. 1.2 per mil at Franklin and 0.7 per mil at Sterling Hill. It is much more likely that ores and unmineralized marbles have identical average $\delta^{13}C$ values and comparable ranges because $\delta^{13}C$ of the ore protolith has been largely unchanged during metamorphism and reflects its marine protolith. Therefore, Zn silicates and oxides in the Franklin and Sterling Hill orebodies probably formed from other Zn oxides, hydroxides, or silicates.

We propose that willemite represents an important protolith mineral for the Franklin and Sterling Hill deposits, possibly in addition to other Zn silicates and to Zn oxides and (or) hydroxides required by metal/silicon ratios in the ores (Johnson et al., 1990). Willemite is stable over a wide range of temperatures and is found in hydrothermal to granulite-facies environments (see Hitzman et al., 2003). Geochemical modeling by Brugger et al. (2003) indicates that willemite could form in a sea-floor hydrothermal environment at ca. ≥150°C, intermediate pH, and high f_{O_2}/f_{S_2} and is compatible with magnetite formation. Hydrothermal willemite would be consistent

with magnetite mineralization in the New Jersey Highlands by the same or a related hydrothermal system.

Comparison to McArthur- and Långban-type sedex deposits: Similarities and differences

Johnson and Skinner (2003) and Gauthier and Chartrand (2005) proposed that the Franklin and Sterling Hill deposits might have similarities to McArthur-type stratiform sediment-hosted Pb-Zn sedex deposits. These deposits are formed from oxidized brines deposited in basins that are dominated by chemical and hematite-bearing siliciclastic sediments (Cooke et al., 2000). Johnson and Skinner (2003) proposed that similar fluids could explain the sulfide-poor mineralogies and low tin, gold, and barium contents of Franklin and Sterling Hill ores. Gauthier and Chartrand (2005) emphasized the association of ankerite and siderite halos around McArthur-type deposits, linking this to the marble-hosted magnetite deposits associated with the Franklin and Sterling Hill deposits in the Franklin Marble. Although some of these characteristics are similar to Franklin and Sterling Hill, the stable isotope systematics of Zn and Fe mineralization in New Jersey are distinct from McArthur-type deposits.

As discussed above, ankerite- and siderite-rich sediments as protoliths are not consistent with the isotope ratio and mineralogy of marble-hosted magnetite deposits in the Franklin Marble (Johnson and Skinner, 2003). Moreover, the stable isotope systematics of McArthur-type sedex deposits and their isotope halos are distinctly different than marble-hosted deposits in the New Jersey Highlands. Ankerite- and siderite-rich halos around the McArthur river deposit (Fig. 10) have $\delta^{18}O$ higher than sedimentary protoliths (23–26‰; Large et al., 2001a). In contrast, New Jersey marble-hosted magnetite has lower $\delta^{18}O$ than protoliths (11–24‰, Fig. 10).

Modeling of McArthur-type sedex deposits points toward low-temperature (50°–120°C) deposition in sedimentary brine pools (Large et al., 2001a). Marble-hosted magnetite deposits in New Jersey have isotope signatures more consistent with higher temperatures (~150°C) and hydrothermal replacement of preexisting sediments. Although less restrictive, isotope signatures of ores at the Franklin and Sterling Zn-Fe-Mn deposits yield similar constraints (Johnson et al., 1990).

The stable isotope compositions of the Highlands marble-hosted deposits have similarities to the metamorphosed Långban Fe-Mn stratiform oxide deposit and related ores in the Bergslagen district, Sweden (Fig. 12). Långban-type ore deposits are carbonate hosted and have some mineralogical characteristics of Franklin and Sterling Hill but lack abundant franklinite and are distinct in detail (Dunn, 1995). Most models for ore deposition in the Bergslagen district favor a sedex origin in a continental back-arc rifting environment (e.g., Allen et al., 1996). Sedex deposits from the Bergslagen district have $\delta^{18}O$ values that are generally in the range of 6 to12 per mil, lower than unmineralized marbles. Like New Jersey Zn deposits, carbon isotope ratios in Bergslagen stratiform ores are similar to, or slightly lower than, unmineralized marbles, which are thought to be inherited from marine protolith values (De Groot and Sheppard, 1988; Holstam and Mansfeld, 2001; Jonsson, 2004). Carbon isotopes in the studies in the Bergslagen district are thought to reflect premetamorphic values and are consistent with hydrothermal alteration by

seawater (perhaps with a magmatic component), similar to that shown for the New Jersey ore deposits discussed here.

Conclusions

Mesoproterozoic marble in the New Jersey Highlands hosts low Ti magnetite deposits that are locally closely associated with marble-hosted Zn-Fe-Mn deposits at Franklin and Sterling Hill. Marble host rocks and intercalated bimodal volcanic rocks (amphibolites and rhyolitic gneisses) were deposited synchronously in a back-arc basin along the Laurentian continental margin. Moderate to severe alteration of volcanic rocks proximal to the Fe deposits, and the carbon and oxygen isotope data of host marble provide evidence for a widespread and extensive 1.3 to 1.25 Ga sea-floor hydrothermal system in the back arc that is presently centered in the western Highlands. Mafic magma beneath the back arc that was the source for the amphibolites probably supplied the heat to drive the hydrothermal system.

We propose that related hydrothermal systems were responsible for Fe in the marble-hosted magnetite deposits and the Zn-Fe-Mn in the deposits at Franklin and Sterling Hill. Iron and Zn were derived via hydrothermal fluids and discharged along basinal fracture zones in the back arc, subsequently precipitating in the carbonate protolith of the marble. Uniformly low Fe and Zn and other metal contents of unmineralized marble require introduction of the metals into the carbonate protolith from an external source prior to high-grade metamorphism.

Carbon and oxygen isotope ratios from the magnetite deposits trend to lower values from unmineralized marbles, consistent with water-rock interaction with a mixture of igneous fluids and seawater and replacement of carbonate host rocks at moderate temperatures (ca. 150°C). The Franklin and Sterling Hill deposits have lower oxygen isotope ratios than host marbles but identical carbon isotope ratios, which is evidence for alteration of marble host rocks by water-rich fluid and preservation of protolith carbon isotope ratios. Stable isotope data from these deposits do not support Fe or Zn carbonate protoliths but are more compatible with premetamorphic metal oxides and hydroxides, and, in the case of Zn ores, possibly Zn silicates.

Acknowledgments

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