The Role of Fluids in Ore Remobilization at the Balmat Zinc Deposit, NY

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THE ROLE OF FLUIDS IN ORE REMOBILIZATION AT THE BALMAT ZINC DEPOSIT, NY

by

PETER MATT

A dissertation submitted to the Graduate Faculty in Earth and Environmental Sciences in partial fulfillment of the requirements for the degree of Doctor of Philosophy,

The City University of New York.

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by

PETER MATT

This manuscript has been read and accepted for the Graduate Faculty in Earth and Environmental Sciences in satisfaction of the dissertation requirement for the degree of Doctor of Philosophy.

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THE CITY UNIVERSITY OF NEW YORK
ABSTRACT

THE ROLE OF FLUIDS IN ORE REMOBILIZATION AT THE BALMAT, NY, ZINC DEPOSIT

By

PETER MATT

Advisor: Wayne Powell

Shear zone-hosted orebodies at the Balmat, NY, zinc deposit were remobilized at the kilometer scale during amphibolite facies regional metamorphism ca. 1180 Ma. Despite there being little evidence for interaction of hydrous fluids and ores during deformation, such translocation distances are considered unlikely without the assistance of fluids. Two independent research methods, SEM-EDS micro-petrography and zinc isotope geochemical analysis, demonstrate that anatectic sulfide and silicate melts were generated during metamorphism. Micro-petrography of the Fowler ore body reveals low melting-temperature micro-inclusions of sulfosalt and sulfide assemblages which occur predominantly in Qtz-Py and Kfs-Py domains that cross-cut peak metamorphic assemblages. These results indicate that localized anatexis occurred on the prograde path, producing low volumes of melts of varying composition. Polymetallic sulfide melts were initiated by the prograde breakdown of minor phases containing low melting temperature chalcophile elements including As, Sb, Pb, and Cu. Alkaline silicate±carbonate±sulfide melts were fluxed by halogens, sulfur and other volatile components released during metamorphism of evaporitic and organic-rich horizons in the marble-dominated host sequence.
Measurements of Zn isotopic composition of sphalerite from six Balmat orebodies that originated from the same stratigraphic level (Upper Marble Unit 6) reveal variation between ore bodies, as well as intra-orebody trends of down-plunge decrease in δ⁶⁶Zn. In general, increasing distance of remobilization correlates with decreasing δ⁶⁶Zn. The syn-tectonic isotopic fractionation recorded in Balmat sphalerite is interpreted to have resulted from the interaction between the ore and low-volume sulfide magmas that were fluxed by H₂S localized in Upper Marble Unit 7 (fetid dolomite). Lighter isotopes of Zn were enriched in the melt, leaving the residual ore enriched in heavier Zn isotopes. Down-plunge and along-fault migration of fluids resulted in lower δ⁶⁶Zn at the down-plunge end of orebodies that occur in cross-stratigraphic fault zones. These observations support petrographic evidence for the presence of anatectic melts at Balmat and help to explain the unusual scale of translocation at Balmat by means of fluid-assisted remobilization during which rock competency was decreased due to the presence of intergrain fluid films.
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Chapter 1: Sulfide and Silicate Anatexis and its Implications for Ore Remobilization

Introduction

The carbonate- and evaporite-hosted Balmat zinc deposit, with past production in excess of 40M metric tons, is located near Gouverneur in the Adirondack Lowlands of New York, a part of the global Grenville Orogen (Fig. 1.1). The deposit formed in the Trans-Adirondack back-arc basin ca. 1250-1225 Ma through seafloor exhalative processes (DeLorraine 2001, Chiarenzelli et al. 2010), and subsequently underwent upper amphibolite-facies regional metamorphism (~640°C at 6.5 kbar) (Kitchen and Valley 1995) during the Shawinigan Orogeny (1180-1140 Ma) (Chiarenzelli et al. 2010, Baird and Shrady 2011). Deformation during this time resulted in unusually large distances of ore remobilization. Some individual, shear-zone hosted ore bodies are known to have moved over 500m laterally across stratigraphy, and others have moved over 2000m down plunge (DeLorraine 2001). These distances are considered conservative given that the original position of some ore bodies remains unknown.

The mechanisms associated with the large-scale remobilization are poorly understood. Historically, solid-state ductile flow was thought to be the predominant means of ore translocation, based in part on a lack of evidence of fluid involvement: 1) the anhydrous nature of the host mineral assemblages; 2) the lack of hydrous alteration selvages around ore bodies (DeLorraine 2001); and 3) peak metamorphic conditions were well below the melting point of the predominant sphalerite-pyrite assemblage (Barton and Toulmin 1966). However, external remobilization at the scale observed at Balmat is considered unlikely, if not impossible, without

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1 This chapter is adapted from a version published under the title “Sulfide and silicate anatexis in the Balmat zinc deposit (New York, USA) and its implications for ore remobilization,” Matt et al. 2019, Ore Geology Reviews, V. 107, pp. 392-401, https://doi.org/10.1016/j.oregeorev.2019.03.002
the involvement of fluids, either operating alone (e.g., dissolution and reprecipitation) or together with solid-state processes (e.g., decreased competency due to intergrain fluid films) (Marshall et al. 2000).

Field observations of numerous polymetallic ore deposits, along with related laboratory melting experiments, have demonstrated that partial melting of sulfides may occur under metamorphic conditions as low as upper greenschist to lower amphibolite facies for sulfosalt-bearing ores (e.g., Lengenbach, Rajpura-Darida), and most certainly in the upper amphibolite to granulite facies where galena is present (e.g., Broken Hill, Hemlo, Montauban, Geco) (Hofmann 1994, Mavrogenes et al. 2001, Frost et al. 2002, Tomkins et al. 2004, Sparks and Mavrogenes 2005, Tomkins et al. 2006, Tomkins et al. 2007, Frost et al. 2011, Pruseth et al. 2014). Although the base metal sulfide assemblages vary between these deposits, they have the shared compositional characteristic of being enriched in precious metals, metalloids, and heavy metals such as Cu, Pb, Cd, Hg, Sn and Tl. The low eutectic temperature associated with mineral assemblages consisting of these low melting temperature chalcophile elements (LMCE) allows for the production of sulfide melts, and the subsequent scavenging of metals from solid sulfide assemblages (Frost et al. 2002, Tomkins et al. 2007).

Based on the published descriptions of mineral assemblages and micro- and mesoscale textures in a variety of metamorphosed ore deposits worldwide, Frost et al. (2002) identified 26 that were likely to have undergone partial melting, one of which is the Ag-rich Edwards deposit in the Balmat-Edwards camp. Subsequent work has confirmed several of the predictions of Frost et al. (2002). Tomkins (2004) showed that partial melting contributed to the concentration of Au at Hemlo in Ontario. Other work by Tomkins (2007) confirmed that small amounts of sulfide melt
were generated during metamorphism at the volcanogenic massive sulfide deposits of Montauban, Calumet and Geco.

Most base metal deposits contain trace to minor amounts of low melting temperature chalcophile elements (LMCE) and, therefore, would be expected to generate trace to minor volumes of syn-metamorphic sulfide melts. Balmat is a compositionally typical massive sulfide ore (i.e., low amounts of LMCE), composed predominantly of sphalerite and pyrite with minor galena, but trace sulfosalts have been documented, including tetrahedrite, tennantite, jordanelite, orpiment, realgar, and boulangerite (DeLorraine 2001, Chamberlain et al. 2018). It is the presence of a low-T eutectic assemblage, not its abundance, that determines whether anatexis will occur (Mavrogenes et al. 2001). For this reason, any metamorphosed sulfide deposit which contains LMCE phases and/or major mineral assemblages whose eutectic point is the same or lower than the peak metamorphic temperature may be assumed to have undergone some degree of partial melting, even though the total volume of melt may have been very small. Accordingly, the ore assemblages and textures of the Balmat deposit were documented to determine if sulfide anatexis occurred in this deposit, potentially facilitating ore remobilization.

Geologic Background

The Balmat mine is located in the Adirondack Lowlands region of New York State, part of the southern extremity of the contiguous Grenville Province, part of a Mesoproterozoic global orogenic system (Fig. 1.1). The Adirondack Lowlands was a depocenter of the Trans-Adirondack Back-Arc Basin, ca. 1300-1250 Ma (Chiarenzelli et al. 2015). Basin fill includes deep-water (pelitic gneiss), shallow water (marble) and transitional facies (quartzites) (Chiarenzelli et al. 2015). Later accumulation of clastic material (Popple Hill Gneiss) is attributed to the initiation of basin closure
and uplift to the south. Further compression cut off the basin from general oceanic circulation, leading to repeated episodes of evaporation, represented by evaporites in the youngest stratigraphic component of basin fill (Upper Marble). Compression also drove hydrothermal circulation within the basin, resulting in the formation of sedimentary exhalative horizons in second- or third-order basins. Subduction-influenced magmatism of the Antwerp-Rossie suite marked the closure of the basin, with subsequent metamorphism of its sediments during the Shawinigan Orogeny, 1200-1160 Ma (Chiarenzelli et al. 2010).

The 1100m thick Upper Marble that hosts the Balmat deposit (DeLorraine 2001) is generally dolomitic, locally siliceous and graphite-poor. Extensive drilling during eight decades of exploration at the Balmat zinc mine has allowed the definition of 16 sub-units in the formation. Of these, four contain >40% quartz or diopside, with dolomite making up most of the balance (Whelan et al. 1990). On the basis of structural and stratigraphic relationships, fifteen distinct ore bodies have been recognized as the disaggregated products of stratiform massive sulfides located at three original stratigraphic horizons in the Balmat section. Differing abundances of major and trace elements in sphalerite is consistent with these structural-stratigraphic interpretations. From lowest to highest stratigraphic position, these horizons are characterized by decreasing Zn and Hg, and increasing Fe, Pb, Ba. The trace element assemblage Sr, Co, Ge and Ag also increases in abundance stratigraphically upwards. This assemblage, along with the other elements listed, was determined by factor analysis to be most indicative of geochemical variation with location (Swanson 1979). Each of the three primary ore horizons is associated with an underlying layer of anhydrite. The Fowler ore body, on which the petrographic part of this study focused, is a member of the middle horizon.
The Fowler orebody occupies the upper limb of the dismembered and thrust faulted axial region of the Fowler syncline, a major D2 isocline (Fig. 1.2). The ore follows the regional shallow NNE plunge for at least 1067m. The Fowler thrust fault developed in the core region of the fold and separates the Fowler ore body from its sister Sylvia Lake ore body located 1219m to the east in the lower limb.

Heumann et al. (2006) reports SHRIMP U-Pb dates from zircon and monazite grains in metapelitic migmatites, indicating partial anatexis in the Lowlands from ~1180-1160 Ma. Ptygmatic folding of leucosomes from which the dated minerals were taken shows that deformation occurred concurrent with or subsequent to crystallization. SHRIMP-RG U-Pb dates from zircon grains in granites with a well-defined relationship to deformation show that major events (D1 and D2) occurred between 1185 and 1145 Ma, and that melting was persistent throughout (Baird and Shrady 2011).

Traditional geothermometry using a variety of mineral pairs shows that metamorphic isograds in the Adirondack Lowlands are roughly aligned with NE-SW structural trends and record a west to east temperature gradient from ~650°C W-NW of Gouverneur to 700-750°C near Colton (Bohlen et al. 1985). In contrast, C and O isotope geothermometry shows a temperature valley in the central Lowlands (Balmat’s location) of 640 ± 30⁰, bordered by highs of 680 to the east and 670 to the west (Kitchen and Valley 1995). Phase equilibria calculations for mineral assemblages in the Lower Marble produced a peak temperature at 725° C, assuming XCO₂ of 0.7 (Petch 1992). Brown et al. (1978) calculated peak pressure of ~6.5 kbar, assuming peak temperature of 625°C ± 25°. Thus, peak metamorphic conditions reached upper amphibolite to lower granulite facies.
at moderate pressure, conditions under which it would be expected that melts associated with LMCE-bearing and/or Pb-Cu-Fe-bearing assemblages would form.

**Method and Samples**

Although the Balmat mine was closed in 2001, and throughout the interval that research was conducted for this study, it reopened for production in January of 2017. Accordingly, this study was based upon the re-examination of existing drill core and historic research materials and collections. This study utilized the archived research specimens associated with the graduate research of W. deLorraine (1979). Expanding upon deLorraine’s petrographic microscopic analysis, additional mineral assemblages and textural features were described at the submillimeter to micron scale using SEM-EDS (Hitachi TM 3030 Plus). EDS point analyses were used to characterize large grains (>100μm). The composition of micron-scale minerals and mineral assemblages were characterized qualitatively using EDS X-ray mapping and correlated with mineral species that have been documented previously at the Balmat deposit, as is illustrated in figure 1.4.

The 32 polished sections analyzed herein are from the Cross-Cutting zone of the Fowler ore body (Fig. 1.3), one of five subdivisions recognized within the hinge zone of the Fowler syncline (deLorraine 1979, deLorraine 2001). This remobilized orebody is in contact with four stratigraphic units of the Upper Marble along its down-plunge length: Unit 11, Qtz-Di-Dol rock; Unit11A, massive Anh; Unit 12, dolomitic marble; Unit 13, Tlc-Tr-Ath schist.

**Results**

Based on modal mineral assemblages, the Cross-Cutting zone of the Fowler orebody may be subdivided into four distinct compositional domains observable at the scale of a polished
section: 1) granoblastic ore and host rock; 2) quartz-pyrite-dominant domains; 3) potassium feldspar-rich domains; and 4) retrograde talc-rich domains. All samples are from a zone of deformation in which ore and gangue minerals have been tectonically mixed to some extent.

Granoblastic Ore and Gangue Assemblages

Granoblastic assemblages (Fig. 1.5) are defined by the geometric grain boundaries of the main ore and gangue phases, with a tendency towards 120° triple junctions and grain sizes from 0.1 to >2 mm, suggesting equilibration and annealing recrystallization accompanying peak metamorphism and subsequent cooling. Granoblastic texture is more uniformly displayed by the most competent phases, pyrite and diopside, and in monomineralic rock. The form of less competent phases (e.g. sphalerite and galena) is controlled by the more competent phases in the assemblage. When in contact with more competent phases, sphalerite exhibits irregular forms between grains and smaller angles at triple junctions. In galena-rich samples, the habit of galena is controlled by that of other phases, including sphalerite. K-feldspar is a minor phase in granoblastic domains where it is subhedral, frequently occurs in association with apatite and/or titanite and often has numerous small inclusions of major sulfides near grain boundaries with those phases (Fig. 1.5D). Calcite is anhedral to subhedral, forms mutual curvilinear embayments with quartz, and may occur as inclusions in sphalerite with intricate geometric intergrowths at their boundaries.

Quartz-Pyrite-Dominant Domains

This domain type is characterized by modal abundances of quartz >50%, and pyrite ~25% (Fig. 1.6A, B). Pyrite is subhedral to euhedral, with individual grains often displaying square, rectangular or six-sided cross sections. Pyrite ranges in size from a few microns to ~200μ but
average around 10μ. Measurement of 100 pyrite grains on one slab showed a mode of 4μ. Quartz-pyrite domains may have either K-feldspar or calcite as the secondary non-sulfide phase. K-feldspar is subhedral to anhedral with wispy extensions, with a size range similar to that of pyrite. Calcite is anhedral to subhedral with a size range of 100-250μ. In contrast to K-feldspar, calcite is generally inclusion-free at boundaries with major sulfides. Although calcite does display some tendency to elongation, it does not routinely exhibit the extreme, wispy attenuation more common to K-feldspar. The relative abundance and identity of the secondary phase (Kfs or Cal) commonly define sharp boundaries within Qtz-Py domains (Fig.6B). When in contact, granoblastic and Qtz-Py domains are typically separated by sharp but scalloped boundaries (Fig. 1.6C), sometimes displaying fine, irregular intrusive forms (Fig. 1.6D).

**Potassium Feldspar-Rich Domains**

K-feldspar is the predominant mineral in these domains, in contrast to Kfs-bearing Qtz-Py dominant domains, where K-feldspar is subordinate. K-feldspar is subhedral to anhedral with grains from ~200-500μ. Grain boundaries between K-feldspar and sphalerite are complex in form with interdigitations and embayments (Fig. 1.6E). Sphalerite inclusions in K-feldspar are abundant and complex in form, commonly exhibiting a graphic intergrowth texture (Fig. 1.8C). Pyrite is euhedral to subhedral with grains 50-200μ. Quartz is anhedral with grains 40-500μ. K-feldspar-rich and Qtz-Py dominant domains exhibit sharp contacts between each other (Fig. 1.6E). Kfs-rich material exhibits a cross-cutting relationship with granoblastic diopside rock (Fig. 1.6F).

**Retrograde Talc-Rich Domains**

These zones within diopsidic marble are characterized by the replacement of diopside or calcite by talc ± clinochlore (Fig. 1.6G). Galena, the dominant ore phase in these domains, is
anhedral and occurs in a wide range of sizes, from a few microns to a few hundred microns, in areas where it is disrupted by or intergrown with talc and/or clinochlore. Diopside is euhedral to subhedral with grain sizes between 200μ and 1 mm. Calcite is subhedral to anhedral with grains 40-400μ. Talc is generally euhedral, with growth parallel to cleavage up to ~100μ. Calcite is often replaced by talc in a network-like pattern of veinlets. Talc also fills brecciated fractures in diopside. Talc replaces diopside, extending away from fractures towards the cores of diopside grains. Talc and galena are frequently intergrown at a microscopic scale (Fig. 1.6H). Clinochlore occurs as anhedral masses up to 500μ but without visible crystal boundaries. However, euhedral clinochlore occurs as inclusions within bournonite (Fig. 1.6H), as does graphic K-feldspar.

**LMCE-Rich Mineral Assemblages**

Arsenic- and/or antimony-bearing minerals occur in three texturally distinct contexts: 1) as small, isolated polysulfide grains, mainly within Qtz-Py domains (Fig. 1.7A), less frequently within granoblastic domains (Fig. 1.7B); 2) as fracture-filling material in gangue or ore phases commonly in association with retrograde talc and/or clinochlore (Fig. 1.7C); and 3) along grain boundaries in granoblastic domains (Fig. 1.7F).

Arsenic- and/or antimony-bearing polysulfide grains range in size from several microns to 1 mm, with most ranging from 25-60μ. Individual phases within such grains are subhedral to euhedral, commonly exhibiting planar grain boundaries. An exception is often found where arsenopyrite and pyrite are in contact. These contacts frequently show arsenopyrite replacing pyrite (Fig. 1.7E). The most common mineral assemblage in polysulfide grains is Asp-Py(±Gn±Ten±Ccp±Sph) (57%), followed by Ten-Gn(±Py±Sph) (25%). Other mineral combinations were documented, but each with only one or two occurrences. Of 28 documented polysulfide
grains, 23 (82%) occur in Qtz-Py domains, 4 in granoblastic gangue domains. Although only one grain was documented within Kfs-rich domains, additional grains were observed but not documented. All polysulfide grains are in textural equilibrium with their host gangue phases.

Bournonite (PbCuSbS$_3$) with galena occurs as fracture fill in granoblastic domains (Figs. 7C, 8B), both ore and gangue. Most frequently, it forms anhedral masses 100-200μ in maximum dimension, although sub-to euhedral habits are also present (Fig. 1.7D). Tetrahedrite is also present in talc-bearing domains, but is rarer than bournonite. Galena is generally in close spatial association with both bournonite and tetrahedrite. Where the fractures occur in diopside or calcite, Brn±Gn is spatially associated with mats of talc and/or clinochlore. Where fractures occur in granoblastic sphalerite, talc is absent butapatite, rutile and quartz have been observed in association with bournonite.

Arsenopyrite is the most common LMCE-bearing phase found along or near grain boundaries between neighboring gangue phases, or between gangue and ore phases. In these settings, arsenopyrite occurs most frequently in clusters of small, randomly oriented, euhedral crystals averaging ~10μ in maximum dimension, although crystals up to 100μ have been found (Fig.7F). Arsenopyrite is also found intergrown with Py±Gn, forming roughly equant, 25-50μ aggregations of individual euhedral to subhedral crystals <1 μm to several microns in maximum dimension (Fig. 1.7G). Larger (~10 μm) individual euhedral crystals of arsenopyrite occur at the borders of some aggregations. Distribution of pyrite and arsenopyrite within aggregations may be uniform, however some aggregations are Py-rich near their centers and Asp-rich at their boundaries with host gangue minerals. Some other aggregations display the opposite distribution, with Asp-rich centers and Py-rich boundaries. Galena, where present, occurs either
as submicron-scale grains of uncertain shape, or as subhedral, roughly equant grains several microns in maximum dimension. Tennantite is spatially associated with some of the intergrowths (Fig. 1.7H).

Discussion

Balmat is a syn-sedimentary, seafloor exhalative massive sulfide deposit that formed within the Trans-Adirondack Back-Arc Basin, ~1300-1250 Ma (Chiarenzelli et al. 2010). Subsequent upper amphibolite facies metamorphism (640 ± 30°C) and annealing recrystallization during the Shawinigan orogeny (~1200-1140 Ma) resulted in the development of equilibrium granoblastic textures in both ore and the associated calc-silicate host rocks. However, micro-petrographic analysis has documented common occurrences of sulfide and gangue minerals with complex forms that are inconsistent with having experienced high-grade metamorphism. These textures are often associated with lower-temperature mineral assemblages, both sulfides and silicates, that must have formed after the peak of metamorphism. In addition, there are numerous examples of fine-grained rocks that exhibit complex crystal boundary forms that are inconsistent with equilibrium at upper amphibolite facies.

Origin of Bournonite-Bearing Assemblages

Granoblastic assemblages of Di-Cal±Sph are cut and replaced by complex, fine grained assemblages of talc and/or clinochlore that commonly contain bournonite. The presence of this sulfosalt provides an upper limit on the temperature of its formation given that the experimentally determined melting temperature of bournonite is 522°C at 1 atm (Barton and Skinner 1979). Limited experimental work on the effect of pressure suggests that melting temperature for Sb-bearing compounds is likely to decrease with increasing pressure (Frost,
2002), so 522°C is a reasonable estimate for the maximum stability limit of bournonite at Balmat. This estimate is consistent with the associated phyllosilicate assemblages; the assemblage Tlc+Cal has an upper stability limit of 550°C e.g., (Winkler 1979).

The hydrous nature of the assemblages, the absence of new calcite precipitation, and their association with fractures suggests that they formed through retrograde hydrothermal processes associated with water-rich fluids. In contrast, peak metamorphic fluids were CO₂-rich (Petch 1992, Petersen et al. 1993). Given the slow, post-Shawinigan cooling rate of ~1.5° C/Ma (Mezger et al. 1991, Dahl et al. 2004), talc-associated hydrothermal processes must have occurred ≥80My after peak metamorphism. Bournonite in these assemblages is consistent with precipitation from late-stage hydrothermal fluids, or alternatively from crystallization of a water-rich, highly differentiated remnant of a polymetallic melt, as has been argued for late-stage sulfosalt assemblages at Broken Hill (Frost et al. 2011).

Bournonite also occurs in anhydrous assemblages in association with coarser masses of galena. In such assemblages bournonite occurs both along grain boundaries between Kfs-Qtz assemblages and granoblastic ore, and as fracture filling in sphalerite. These assemblages and their textures are consistent with their derivation through exsolution of bournonite from galena during post-metamorphic cooling (Figs. 8A, 8B). Given the slow cooling rates in the Adirondack Lowlands, the exsolved bournonite could have migrated from the ductile galena and collected on grain boundaries and in dilational features.

**Origin of Qtz-Py and Kfs-Rich Domains**

The timing of Qtz-Py and Kfs-rich domains must be post-metamorphic based on textural relationships: 1) they cross-cut granoblastic ores and gangue along curvilinear boundaries (Figs.
6C, 8D); 2) crystals that comprise these domains are very fine grained and non-granoblastic; and 3) crystals within these domains commonly exhibit complex, interdigitating, and mutually embayed boundaries, or graphic intergrowths (i.e., high surface energy boundaries) (Fig. 1.8C, D). Given that they cross-cut ores, they must be “intrusive” in nature, either magmatic or hydrothermal.

Quartz-feldspar veins of both hydrothermal and magmatic origin are relatively common in high-temperature environments. Syntectonic quartz-plagioclase veins in metawackes have been attributed to a subsolidus closed-system segregation (Sawyer and Robin 1986). But given the lack of Si-Al-rich mineral assemblages in the Balmat deposit, this mechanism is not applicable. Albite-quartz veins within granitoids have been attributed to late-stage migration of residual melts into dilational zones e.g. (Kretz 1966), but the absence of syn- or late-tectonic intrusives in the Balmat mine precludes such an origin. Quartz-K-feldspar veins of hydrothermal origin are also associated with Cu-Mo porphyry deposits e.g. (Zeng et al. 2014), but in these cases the feldspar is the product of potassic alteration of existing aluminous assemblages and display distinct alteration selvages, aspects inconsistent with Balmat.

Arguments against a simple hydrothermal vein origin for the Qtz-Py and Kfs-rich domains include a lack of hydration or alteration selvages against anhydrous peak-metamorphic mineral assemblages, and mineral assemblages contain an abundance of elements such as aluminum and titanium that are insoluble in aqueous fluids. Furthermore, these post-metamorphic domains exhibit textures common to felsic igneous rocks, including graphic growth surfaces on K-feldspar crystals (Fig. 1.8C) and complex, interdigitating crystal forms (Fig. 1.6D). Although the predominant binary assemblage of K-feldspar and quartz has a eutectic temperature of
approximately 990°C, the addition of network modifying fluxes such as H, F, and P reduce the melting temperature significantly. In fact, experimental studies indicate that volatile-rich silicate melts may persist to temperatures well below 500°C (Simmons and Webber 2008). The non-sulfide mineral assemblage comprising the Qtz-Py and Kfs-rich domains (Qtz-Kfs-Cal-Ap-Ttn) is consistent with that of pegmatites and aplites, and such melts would be expected to persist into post-metamorphic cooling, given that feldspar solvus thermometry indicates that the crystallization temperature of pegmatites is approximately 425-450°C (London and Morgan 2012).

Metamorphic reactions involving the ores and host rocks of Balmat would have released a variety of elements and compounds that would act as fluxing agents and network modifiers in a silica-rich melt. The strata contain evaporitic units, predominantly anhydrite, that would have released S, Cl, and F during devolatization reactions. Fluorapatite, fluorophlogopite, fluoro-tremolite, norbergite, häuyne, and lazurite have all been documented at Balmat, attesting to the activity of these elements during metamorphism. Given the full assemblage Qtz-Kfs-Cal-Ap-Ttn-Py-Sph, the network modifiers K, Ca, P, Cl, F, S, Fe, and Zn were abundant. Accordingly, the composition and textures of the Qtz-Py and Kfs-rich domains are most consistent with emplacement as a low-volume, high-volatile siliceous melt that was produced during metamorphism and crystallized during uplift and cooling.

Origin of Polysulfide Micro-Inclusions

Sulfosalt-bearing micro-inclusions (Table 1.1) occur predominantly in Qtz-Py and Kfs-Py domains, where the micro-inclusions are in textural equilibrium with the host gangue (i.e., smooth, non-embayed contacts with approximately circular cross-sections, Figs. 7B, 7E). Tomkins
and Mavrogenes (2002) documented similar relationships in the Challenger gold deposit in South Australia where rounded gold-bearing polymetallic inclusions occur within the quartz-feldspar leucosome of migmatitic gneisses.

The majority of polysulfide grains contain the assemblage Asp-Py along with a variety of other phases, most frequently galena. Textural relationships indicate that arsenopyrite was growing as pyrite was being consumed (Fig. 1.7E). (Sharp et al. 1985) documented that the assemblage Asp-Py melts at ~560°C at 5 kbar, and so the reactions associated with the growth of arsenopyrite must have occurred at less than 560°C. The Pb sulfosalts jordanite (Pb₁₄(As,Sb)₆S₂₃) and sartorite (Pb₃As₂S₄) (Fig. 1.7B) with melting temperatures of 525°C and 305°C, respectively (Tomkins et al., 2006) also have been found as components of micro-inclusions (Table 1). Such sulfosalts-bearing polysulfide grains must have remained molten well after the peak of metamorphism, and migrated to the same dilational zones in the host rock as Kfs- and Qtz-rich domains. The polysulfide droplets were fixed in place as either solid (higher-T assemblages) or liquid (lower-T assemblages) when the silicates crystallized.

**Origin of Arsenopyrite**

The genesis of As-S melts is considered an important process in the initiation of sulfide anatexis, broadly applicable to massive sulfide deposits because of the prevalence of pyrite and/or pyrrhotite as major phases, and arsenopyrite as a minor phase. Pyrite and arsenopyrite react to form an As-S melt plus pyrrhotite at 491°C and 1 atm, with a temperature increase of 15°C/kb (Sharp et al. 1985, Tomkins et al. 2006). Arsenopyrite may also react with S in fluids to produce an As-S melt plus pyrite over a broad range of temperature beginning at ~350°C, dependent on fS₂ (Tomkins et al. 2006) (his Fig.2).
At Balmat, arsenopyrite occurs in three textural contexts: in polysulfide micro-inclusions, as complex intergrowths with pyrite along grain boundaries, and as clusters of randomly oriented euhedra along grain boundaries. The most frequent occurrence of arsenopyrite is as clusters of crystals along grain boundaries. These crystals are clearly post-deformation and metamorphism, given their euhedral habits, fine-grained nature, and random orientation (Lentz 2002).

In some polysulfide micro-inclusions, arsenopyrite has clearly grown at the expense of pyrite (Fig. 1.7E). The aggregations of complex intergrowths between arsenopyrite and pyrite observed at Balmat have been documented elsewhere as evidence for reaction 1 (Tomkins, 2004).

\[ \text{As-S}_{\text{melt}} + \text{FeS}_2 = \text{FeAsS} + \text{S}_2 \]

Accordingly, it is likely that the post-metamorphic arsenopyrite at Balmat had a similar origin. During prograde reactions, sulfur would have been liberated from reactions involving sulfates, and is consistent with the presence of lazurite in Balmat ores. Sulfur liberated in reaction 1 may partially buffer decreasing \( fS_2 \) during decompression, but total \( fS_2 \) must remain low enough to stabilize solid arsenopyrite (Tomkins 2006). Thus, the presence of post-metamorphic arsenopyrite-bearing assemblages provides evidence of the existence of an As-S melt within the Balmat ores during cooling and uplift.

**Conclusion**

Granoblastic domains in ore and host rocks of the Fowler ore body represent equilibrium textures achieved under peak metamorphic conditions at Balmat. Evaporitic and organic-rich units in the host rock released volatiles along the prograde metamorphic path, providing fluxes to complex silicic±carbonate±sulfidic, alkaline anatectic melts. Low melting-temperature
chalcophile elements produced low-volume polymetallic melts during prograde heating, which increased in volume and complexity as they scavenged metals along grain boundaries. Fluids moved along grain boundaries and into extension features throughout the deformation and uplift cycle. Undercooled silicic melts ultimately crystallized during uplift, trapping LMCE-bearing sulfide assemblages. As sulfur fugacity dropped in response to the cessation of S-liberating metamorphic reactions and the influx of water-rich fluids, As-S liquid reacted with pyrite to form euhedral arsenopyrite, now mostly found in grain boundaries and as complex intergrowths with pyrite. Water was released during late-stage melt crystallization, remobilizing metals into the Tlc-Clc-Brn-Gn-bearing domains, perhaps 80 Ma after metamorphic peak conditions. The fact that these domains do not include Kfs- or Qtz-rich assemblages shows that silicic domains had already crystallized at the time the hydrous domains were mobile. Thus low-volume melts were present at the Balmat deposit over an extended period during the metamorphic cycle. These fluids would likely have affected the rheology of the ores, reducing their competency, and facilitating remobilization of ores.
<table>
<thead>
<tr>
<th>Polysulfide Grains</th>
<th>Gangue Host Assemblage</th>
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<tbody>
<tr>
<td>Asp-Ccp</td>
<td>Cal-Kfs-Qtz</td>
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<tr>
<td>Asp-Ccp-Gn-Py</td>
<td>Qtz</td>
</tr>
<tr>
<td>Asp-Ccp-Gn-Py-Sph-Ten-Tet</td>
<td>Kfs-Qtz</td>
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<tr>
<td>Asp-Ccp-Py</td>
<td>Cal-Qtz</td>
</tr>
<tr>
<td>Asp-Gn</td>
<td>Di±Kfs±Cal</td>
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<tr>
<td>Asp-Gn-Py</td>
<td>Kfs-Qtz; Di</td>
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<tr>
<td>Asp-Gn-Py-Ten</td>
<td>Qtz±Kfs</td>
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<tr>
<td>Asp-Py</td>
<td>Kfs-Qtz±Ttn</td>
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<tr>
<td>Asp-Py</td>
<td>Anh-Cal-Di; Cal</td>
</tr>
<tr>
<td>Brn-Ccp-Gn-Sph-Tet</td>
<td>Cal-Dol</td>
</tr>
<tr>
<td>Ccp-Py-Sph±Gn</td>
<td>Qtz</td>
</tr>
<tr>
<td>Ccp-Ten</td>
<td>Kfs</td>
</tr>
<tr>
<td>Cu Jrd?-Rlg</td>
<td>Qtz</td>
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<tr>
<td>Gn-Py-Ten±Sph</td>
<td>Qtz±Kfs±Ap</td>
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<tr>
<td>Gn-Sph-Ten</td>
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<td>Gn-Ten</td>
<td>Qtz±Cal</td>
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<td>Jrd-Py</td>
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<td>Py-Srt</td>
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<td>Py-Ten</td>
<td>Qtz</td>
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Table 1.1—Mineral components of polysulfide grains and host gangue assemblages identified on polished slabs. Multiple grains with the same assemblage are not indicated. Abbreviations as in Fig. 1.5-1.8, plus Rlg=realgar; Jrd=jordanite. Cu Jrd? indicates unidentified phase bearing Cu, Pb, As and S.
Figures

Figure 1.1-Left, the Grenville Province in Canada and northwestern New York State with its inliers in the Appalachian region. Right, the Adirondack region with its subdivisions showing the location of Balmat in the Adirondack Lowlands.

Figure 1.2-Cross section of the Balmat mining district. Ore bodies in black are MA-Mahler; MP-Mud Pond; UF-Upper Fowler; F-Fowler; UG-Upper Gleason; LG-Lower Gleason; L-Loomis; SL-
Sylvia Lake; M-Main; HW-Hanging Wall. Dashed box encloses Fowler ore body, enlarged in Fig. 1.3. Short dashed line between F and SL is the Sylvia Lake slide, a ductile fault. Recognized sub-units of the Upper Marble: 1-3, two units of dolomitic marble separated by pyritic schist; 4, laminated quartz-diopside rock; 5, dolomitic marble; 6, quartz-diopside rock, dolomitic marble and anhydrite; 7, fetid dolomitic marble; 8, quartz-diopside rock with interlayered dolomitic marble; 9, white dolomitic marble; 10, serpentine-talc rock; 11, quartz-diopside rock with interlayered dolomitic and calcitic marble; 11a, anhydrite; 12, dolomitic marble; 13, talc-tremolite-anthophyllite schist; 14, laminated quartz-diopside rock, calcitic marble, serpentinous dolomitic marble; 15, phlogopitic calcitic marble; 16, quartz-biotite-diopside-scapolite gneiss.
Figure 1.3-Cross-sectional view of the Fowler orebody at N-9800. Most samples reported on herein were taken from the Cross-Cutting Ore zone at the 1900+140 level. Thin solid black lines show orientation of bedding in the host rock. Solid black areas are sulfide ore bodies. Upper Marble subunits 11-13 as in Fig. 1.2.
Figure 1.4-Back-scattered image of a polysulfide microinclusion (also seen in Fig. 1.6C and 1.7A), upper left. Unlabeled, dark gray phases are gangue minerals. Directly right of and below the BSE image are EDS element X-ray maps of the same area, at the same scale. High Sb in a gangue phase (calcite) is produced by overlap of the emission spectra of Ca and Sb.
Figure 1.5-Granoblastic domains. Anh=anhydrite, Brt=barite, Cal=calcite, Di=diopside, Gn=galena, Py=pyrite, Qtz=quartz, Sph=sphalerite. A-ore-rich domain; B-gangue-rich domain; bright microinclusion at center is enlarged in Fig. 1.7B; C-mixed ore and gangue domain; D-ore-rich domain, note control of galena habit by sphalerite, euhedral apatite at center, silicate assemblage (Qtz-Kfs, outlined in black) with small sulfosalt at lower left of silicate assemblage, enlarged in Fig. 1.8A
Figure 1.6-Quartz-rich, K-feldspar-rich and talc-rich domains. Abbreviations as above, plus Ap=apatite, Asp=arsenopyrite; Brn=bournonite, Clc=clinochlore, Kfs=K-feldspar, Tlc=talc, Ttn=titanite. A-Qtz-Py domain with abundant K-feldspar. Outlined polysulfide grain of Asp+Py enlarged in Fig. 1.7E; B-Two Qtz-Py domains, one with abundant Kfs, left, the other with abundant Cal, right. Note sharp division between these. C-Sharp, mutually embayed boundary between granoblastic Sph and a Qtz-Py domain. Outlined polysulfide grain enlarged in Fig. 1.7A. D-complex contact of Kfs and Sph at boundary between Qtz-Py domain with granoblastic Sph. E-Kfs-rich domain, showing sharp, mutually embayed boundaries with Qtz-Py domains above and below. Note abundant inclusions of Sph in Kfs and apparent disruption of Sph by growth of Kfs. Note association of Ap and Ttn with Kfs. F-K-feldspar dike in granoblastic diopside, contacts drawn in black. Note bright inclusions of galena and sulfosalts, Ttn and Ap and fragments of Di in dike. G-Hydrous domain with Tlc, Clc and Brn. H-Hydrous domain occupying grain boundary between granoblastic Di and Gn. Note fabric-like intergrowth between Tlc and Gn, inclusion of Clc in Brn.
Figure 1.7-LMCE-rich subdomains. Abbreviations as in Figs. 1.5 and 1.6, plus Ccp=chalcopyrite, Srt=sartorite, Ten=tennantite, Tet=tetrahedrite. A-Complex polysulfide grain in a Qtz-Py domain. B-Two-phase polysulfide grain in granoblastic diopside. Note perfectly euhedral pyrite at center of grain, surrounded by sartorite (PbAs2S4), T\text{MELT} 305\degree C. C-Fractures in granoblastic diopside filled by bournonite, galena and talc. D-Hydrothermal domain showing anhedral to euhedral bournonite intergrown with clinochlore. E-Asp replaces pyrite. F-Randomly oriented arsenopyrite euhedra fill grain boundary in granoblastic diopside. G-Microcrystalline intergrowth of Arsenopyrite and pyrite at grain boundary between pyrite and anhydrite. H- Smaller scale view of G, rotated 90\degree right. Shows additional Asp-Py intergrowths plus spatially associated tennantite, upper right.
Figure 1.8-A-Silicate assemblage in granoblastic Gn+Sph with bournonite at boundary. Note typical graphic inclusions of sulfide in Kfs. B-Galena-bournonite assemblage fills fracture in granoblastic Sph. C-Graphic intergrowth of Sph in Kfs at grain boundary. D- Quartz-rich and Kfs-rich domains cut granoblastic domain of Sph and Di. Note sharp, curvilinear boundaries with Qtz, numerous inclusions of Sph in Kfs.
Chapter 2: Zn-Isotopic Evidence for Fluid-Assisted Ore Remobilization

Introduction

At the Balmat, NY, zinc deposit, three original sedimentary ore horizons were deformed and remobilized during regional metamorphism to form 15 different ore bodies. The Upper Gleason, Lower Gleason, Loomis, Mahler, Upper Fowler, and Mud Pond orebodies (Fig. 1.2), on which the zinc isotopic geochemistry part of this study focused, are all members of the lowest syngenetic ore horizon in Upper Marble Unit 6. The Upper Gleason, Lower Gleason and Loomis orebodies are recognized respectively as parent and cogenetic daughters, based on structural and textural relationships (deLorraine 2001). The terms parent and daughter are used to describe the source beds and final positions, respectively, of externally remobilized orebodies (Marshall et al., 2000). The shear zone-hosted Mahler, Upper Fowler and Mud Pond orebodies are daughters with undiscovered parents (deLorraine 2001).

Recently, mineral assemblages were documented in the Cross-Cutting zone of the Fowler orebody which indicate that small volumes of low-melting-temperature sulfosalt and undercooled silicate melts were present at Balmat up to 80 Ma after peak metamorphism (Matt et al. 2019). Although it is unlikely that the volume of melt now preserved in the Fowler would have significantly affected the rheological character of the ore, the actual volume of melt that was present during the peak of metamorphism is unknown. Given its mobile nature, it is possible much of the polymetallic melt migrated from the main orebodies to distal or external positions. This hypothesis is supported by the observations of Matt et al. (2019) who noted that the melt-related sulfosalt assemblages were preserved in the gangue assemblages and not the massive
sphalerite ore itself. (Pruseth et al. 2016) documented that sphalerite and pyrite is the first assemblage to crystallize from sulfosalt-bearing Zn-Fe-Cu-Pb melts, with metal-rich and sulfosalt-rich immiscible melts persisting to lower temperatures, thereby having more time to migrate from the ore.

Patterns in Zn isotope composition may assist in characterizing the relative role of fluid involvement in the deformation and translocation of Balmat ores. Isotopic fractionation of zinc would not be expected to occur unless two states of matter (e.g. fluid and solid, vapor and solid) are present. With its single valence state (Zn$^{2+}$), the system would be unaffected by redox-related reactions, unlike many other metals including Cu (Mathur et al. 2005), Fe (Lee et al. 2010), Ag (Mathur et al. 2018), and Sn (Wang, D. et al. 2019). Furthermore, equilibrium partitioning of Zn isotopes between phases can be excluded at Balmat because sphalerite is the only major Zn-bearing phase. Sphalerite has been shown to deform by translation glide and twinning over a wide range of experimental temperature and pressure (Clark and Kelly 1973), and it has been demonstrated that this deformation mechanism does not result in isotopic fractionation (Krohe and Wawrzenitz 2000).

Diffusion, although a cause of fractionation in numerous isotopic systems (Hoefs 2015) (and references therein), in all cases relies on the existence of a temperature or concentration gradient. However, even where such gradients exist, diffusion is not expected to cause fractionation within a solid crystal lattice without the involvement of a fluid phase. For example, there is no diffusion of isotopes of oxygen in some high-grade metamorphic terranes, even where sharp differences in the isotopic character exist between different rock types in contact (Johnson and Skinner 2003, Peck 2009). This observation allowed these authors to deduce that no
pervasive fluids were present during metamorphism. Lithium is the exception to the requirement of a fluid to promote isotopic fractionation within a solid due to its high diffusion rates and large weight percent difference between isotopes (Parkinson et al. 2007). Therefore, in the case of purely solid-state deformation of sphalerite ore in the absence of fluids, little or no fractionation of Zn would be expected to be induced.

No studies directly address isotopic fractionation associated with the simple melting of sphalerite or diffusion of Zn from sphalerite into sulfosalt melts. However, significant isotopic fractionation has been documented to occur between co-existing solids and liquids for a wide range of elements, including Zn. Fractional crystallization enriches basaltic magma in heavier Zn isotopes due to the preferential incorporation of lighter isotopes of Zn in early crystallizing olivine and Fe-Ti oxides (Chen et al. 2013). Although primarily focused on Fe, (Telus et al. 2012) found that the δ^{66}Zn of pegmatites was about 0.4 ‰ higher than δ^{66}Zn of granitoids and migmatites, an effect they attributed to the incorporation of lighter isotopes of zinc (and iron) into fluids exsolved from highly evolved magmas. Furthermore, isotopic fractionation may be induced through dissolution, as has been demonstrated for Zn where experiments on acid dissolution of biotite granite resulted in rapid enrichment of light isotopes in the fluid and corresponding increase in δ^{66}Zn in the undissolved residue (Weiss et al. 2014). Thus, if significant fluid-ore interaction occurred at Balmat, it would likely have induced some degree of isotopic fractionation of Zn.

Methods

Samples of drill core from the Balmat mine core library were selected on the basis of location along the trend of each of six orebodies that originated from Unit 6 of the Upper Marble.
Samples were spaced as evenly as possible between end points. Individual sphalerite grains (1-2 mm) were hand-picked from crushed drill core, and further crushed to -100 mesh in an alumina mortar. Approximately 30-50mg of powdered sphalerite were dissolved in 4 ml of heated ultra-pure aquaregia (3:1 HCl to HNO₃), and complete dissolution was confirmed visually. These solutions were dried and the salts were purified with ion exchange chromatography using MP-1 BioRad resin following the technique described by (Marechal et al. 1999).

The solutions were measured in two locations, on the Isoprobe MC-ICPMS at the University of Arizona and the Neptune at Rutgers University. Solutions and standards were diluted to 150 ppb Zn, and sphalerite samples were doped with 976 NIST Cu isotope standard. Standards and ore samples were measured within 0.5V. Mass bias was corrected using the exponential correction using Cu and sample bracketing. Thirty ratios were measured for each sample, and each sample was measured in duplicate. Values were measured relative to the IRMM 3702 Zn standard (equivalent composition to AA-ETH standard, (Archer et al. 2017), which can be correlated with the JMC-Lyon standard using the equation \( \delta^{66}\text{Zn}_{\text{JMC-Lyon}} = \delta^{66}\text{Zn}_{\text{IRMM 3702}} + 0.28\%\) (Archer et al. 2017). \( \delta^{66}\text{Zn} \) values are reported relative to the JMC-Lyon standard to facilitate comparisons with prior studies. Experimental error (2 sigma) was 0.04\%.

Results

Zinc isotopic compositions were determined for 47 samples of sphalerite from six orebodies that are geochemically related (Swanson 1979, deLorraine 2001) and constitute a set of translocated mobilizates that originated from a single stratigraphic horizon (Upper Marble Unit 6) in the pre-metamorphic deposit (Table 1).
The mean $\delta^{66}$Zn value for Balmat orebodies is 0.18‰, within the range of $\delta^{66}$Zn obtained from most other zinc ores globally (Fig. 2.3). Balmat ores display distinct variations in Zn isotopic composition, both between orebodies and along the length of single orebodies (Fig. 2.4). For the related Gleason-Loomis ore bodies, there is an apparent pattern of decreasing $\delta^{66}$Zn from the parent Upper Gleason, to the daughter Lower Gleason, to the cogenetic daughter Loomis, although within the range of experimental error (Table 2.2). The Upper Gleason, the parent orebody that remained within its original stratigraphic unit (Upper Marble Unit 6), does not exhibit systematic isotopic variation along plunge. Nor does the daughter Lower Gleason which, despite crossing several subunits, remains hosted within the strata of Unit 6. In contrast, four other ore bodies that occur in cross-stratigraphic shear zones (Upper Fowler, Mahler, Mud Pond, and Loomis), and which were structurally emplaced in stratigraphically higher units (Units 7 through 9), display decreasing $\delta^{66}$Zn along the current down-plunge trend (Fig. 2.4). In all orebodies, the lowest $\delta^{66}$Zn values occur toward the down-plunge end. The sample with the highest $\delta^{66}$Zn value (0.56‰) occurs at the up-plunge end of the Mahler orebody, and the lowest value (-0.02‰) occurs at the down-plunge ends of the Loomis and Mud Pond orebodies.

Discussion

Structure of the Orebodies -The orebodies analyzed occur in the upper overturned limb of the Sylvia Lake syncline (Fig. 1.2) and are thus inverted, as are the host rock units 6-10. Structural inversion occurred late in the deformational history of the region, and after the large-scale translocation of orebodies, as is indicated by the refolding of the orebodies and their connecting durchbewegung sheets by minor folds related to the Sylvia Lake syncline (e.g., Fig. 2.5 and 2.7).
Thus, the isotopic patterns reported herein are reported with respect to their current geometries, not their orientation during remobilization.

**Epigenetic versus Metamorphic Isotopic Patterns** - Undeformed massive sulfide deposits exhibit a spatial pattern of increasing δ^{66}Zn in sphalerite with distance from the hydrothermal vent. This is attributed to rapid kinetic fractionation of light zinc during precipitation and resulting progressive increase in δ^{66}Zn of the fluid as it moves away from its source (Mason et al. 2005, Wilkinson et al. 2005, Kelley et al. 2009). Thus, it would be expected that prior to metamorphism, disaggregation, and remobilization, the more distal ores at Balmat would have exhibited the highest δ^{66}Zn values. The present pattern of decreasing δ^{66}Zn from parent to daughter (i.e., further from the center) is counter to the expected syngenetic signature, and so must be post-depositional in its origin.

**Parent and Daughter Orebodies** - At the No. 3 mine, the Upper Gleason, Lower Gleason and Loomis orebodies are recognized as parent, and cogenetic daughters, respectively, because the daughter orebodies are directly linked to each other and parent along the Gleason-Loomis Slide (Fig. 2.5). They have been described by deLorraine (2001) as follows. The North-trending Upper Gleason is massive and relatively compact, measuring some 470 m long by 200 m with a maximum thickness of 26 m. It is composed of sphalerite and variable amounts of coarse-grained pyrite and gray quartz. The NE-SW trending Lower Gleason is recognized at its intersection with the Upper Gleason by a ~37° change in trend, from which it extends 900 m both up and down-plunge along the Gleason-Loomis “slide” (a brittle-ductile fault), cutting the upper subunits of unit 6 up to the contact with Unit 7. The Loomis ore body is parallel to, and approximately the
same size as, the Lower Gleason but is localized further east along the Gleason Loomis slide where it slices through Upper Marble units 7, 8 and 9, ending at the contact with Unit 10. Much of the ore exhibits durchbewegung texture, although it is coarse-grained in some places and is described as banded marble-sphalerite tectonite where it occurs in unit 9 (deLorraine 2001).

The known relationship between these three orebodies allows for correlation of isotopic trends with relative translocation and degree of deformation. The relatively uniform, slightly positive $\delta^{66}\text{Zn}$ of both the Upper Gleason and Lower Gleason suggest that little or no isotopic fractionation of Zn occurred during metamorphism and deformation of these ores (Fig. 2.4). In contrast the Loomis displays a trend of decreasing $\delta^{66}\text{Zn}$ down-plunge, from 0.23 to $-0.02\%_o$. The lower mean $\delta^{66}\text{Zn}$ of the Loomis (0.12$\%_o$) relative to the Upper and Lower Gleason (0.19$\%_o$ and 0.16$\%_o$, respectively) suggests that the fractionating mechanism enriches the daughter orebodies in lighter Zn isotopes.

In general, parent and daughter ore bodies at Balmat can be distinguished on the basis of textural characteristics. Parent orebodies are massive, coarse-grained and conformable with bedding in the host rocks. Daughter orebodies are finer-grained, generally displaying durchbewegung texture, and occur within shear zones that cut bedding in host rocks (deLorraine 2001). On this basis, the Mahler, Upper Fowler and Mud Pond orebodies have been recognized as daughters with undiscovered parents.

The Mahler-Upper Fowler trend (Fig. 2.6) has a mineable length of $\sim$4600 m within a cross-stratigraphic shear zone, displays the fine-grained durchbewegung texture characteristic of daughter ore bodies, and is composed of nearly monomineralic sphalerite. Since no parent ore body for the Mahler-Upper Fowler has been discovered, its translocation distance is unknown.
The Upper Fowler is connected to the Mahler by a folded durchbewegt sheet which indicates a cogenetic daughter relationship between the Mahler and Upper Fowler (Fig. 2.6). The Mahler is distinct from all other orebodies studied in terms of its high δ⁶⁶Zn values (mean 0.33‰), and the down-plunge range of δ⁶⁶Zn (0.43‰) over 2000m, and so recorded the greatest degree of remobilization-associated fractionation. Both the Mahler and Upper Fowler exhibit the same fractionation trend as the Loomis, with δ⁶⁶Zn decreasing down-plunge.

Mud Pond (Fig. 2.7) is compositionally similar to other daughter orebodies in that it is composed predominantly of fine-grained sphalerite with minor pyrite. It also crosses the same stratigraphic units, 6 through 10, and extends more than 2100 m along plunge. Its parent remains undiscovered and it has a single cogenetic daughter orebody, the Davis (not sampled in this study.) Of all the orebodies examined, Mud Pond displays the lowest mean value of δ⁶⁶Zn (0.07‰), and so is likely to have experienced the greatest displacement during deformation. Although it lacks a consistent down-plunge trend in δ⁶⁶Zn, the lowest δ⁶⁶Zn values occur at the down-plunge end.

Fractionation of Fe and Zn in Magmatic Systems—Melting of silicate assemblages induces isotopic fractionation of zinc, with the heavy isotopes being enriched in the melt. This has been documented in peridotites and basalts (Chen et al. 2013, Doucet et al. 2016, Wang et al. 2017, McCoy-West et al. 2018) as well as granitoids (Telus et al. 2012, Xu et al. 2019). In each case, the fractionation results from Zn having a lower coordination number (tetrahedral) in silicate melts than residual silicate minerals (olivine, pyroxene, biotite) where Zn is octahedrally coordinated (Sossi et al. 2018, Williams et al. 2018). Given that heavier isotopes are favored by stronger bonding environments, δ⁶⁶Zn is greater in the melt fraction. For the same reason,
spinels, in which Zn is tetrahedrally coordinated, exhibit higher $\delta^{66}$Zn than coexisting olivine and pyroxene (Wang et al. 2017).

Given their similar chemical behavior, Zn$^{2+}$ and Fe$^{2+}$ exhibit similar fractionation patterns with respect to partial melting and equilibrium partitioning between silicate phases (Wang et al. 2017, Sossi et al. 2018). Accordingly, the more extensively studied behavior of Fe$^{2+}$ may provide insight into the behavior of Zn in sulfide systems. Within silicate melts, immiscible sulfide melts have been shown to be enriched in light isotopes of iron due to the Fe-S bond being weaker than the Fe-O bond (Williams et al. 2018). Iron in molten FeS is held in 6-fold coordination in sulfide melts (Urakawa et al. 1998), whereas it is tetrahedrally coordinated in silicate magmas. Given the geochemical similarity of ferrous iron and Zn$^{2+}$, it is expected that the melting or incorporation of Zn from tetrahedrally coordinated sphalerite into a sulfide melt would result in enrichment of the melt in light isotopes of Zn, leaving the residual sphalerite with higher $\delta^{66}$Zn.

The pattern in Zn isotopic data (decreasing $\delta^{66}$Zn along the current trend of shear zone-hosted ore bodies and between parent-daughter) is consistent with syn-deformational interaction between sphalerite ores and migrating fluids. Lighter isotopes of Zn were scavenged from the ore during flow along grain boundaries and enriched in the fluid, leaving the residual solid sphalerite enriched in heavier Zn isotopes. Subsequent precipitation/crystallization of sphalerite from the light isotope-enriched fluid resulted in a decrease in $\delta^{66}$Zn along the path of fluid flow, and from parent to daughter.

Fluids and Remobilization-The important role of fluids in the remobilization of metals in ore deposits is well established. (Marshall et al. 2000) suggested that liquids may be involved even in cases where solid-state transfer is considered the primary mechanism, such as the healing of
fractures in high competence sulfides by minerals with low competence. Fluid pressure is invoked as causing fractures in wall rock, and dissolution and precipitation are at least partly involved in sulfide infilling of those fractures at the Black Angel mine (Greenland), based on the metal content of fluid inclusions (Pedersen 1980).

Dissolution and reprecipitation has been shown experimentally to favor remobilization of chalcopyrite over pyrrhotite at high temperature, notwithstanding the greater competence of chalcopyrite at high temperature (Zheng et al. 2012). Dissolution and reprecipitation have been invoked to explain the remobilization of ore minerals into shear zones which become favored conduits for hydrothermal fluids, e.g. in southwest France (Bellot 2004), at Pau Branco, Brazil (Rosière et al. 2013) and in the New York Hudson Highlands (Kalczynski and Gates 2014).

Sulfide magmas have been credited with extensive remobilization of ore minerals at the Broken Hill Pb-Zn-Ag deposit (New South Wales, AU) (Mavrogenes et al. 2001, Frost et al. 2011), and for the redistribution of Au and sulfosalts into low-stress domains at the Hemlo gold deposit, (Ontario, CA) (Tomkins et al. 2004). Sulfide anatexis and associated metal remobilization is also known to have occurred at Geco and Calumet (Ontario, CA), Montauban (Quebec, Ca) (Tomkins 2007, Tomkins et al. 2007), Challenger (South Australia) (Tomkins and Mavrogenes 2002) and Lengenbach (Switzerland) (Hofmann 1994).

Deposits where extensive sulfide anatexis has been documented (e.g., Broken Hill, Challenger, Hemlo) are highly enriched in Pb, Cu, and other low melting temperature chalcophile elements relative to Balmat, and so such extensive melt generation would not be expected at this deposit. However, other elements may act as powerful fluxes in sulfide systems. For example, excess sulfur may generate As-S rich melts and pyrite by reaction with arsenopyrite at
temperatures as low as ~375°C (Tomkins et al. 2006). At Rajpura-Dariba (India), free sulfur from dissolution of barite lowered the eutectic in the system Zns-PbS-FeS-Cu₂S to below 600°C (Pruseth et al. 2016).

Unit 7 of the Upper Marble is a medium-grained, dark gray, graphitic, dolomitic marble which emits a distinct odor of H₂S when crushed, and accordingly is referred to as fetid dolomite or “stinkstone.” As described by (Brown and Engel 1956), Unit 7, “…because of its odor and color which are confined almost wholly to this dolomite, is one of the best marker units in the entire sequence.” Thus, at Balmat, abundant volatile sulfur within Unit 7 would have acted as a flux for the sulfide ores.

Given the documented fluxing effect of sulfur, increased melting would have occurred when ores were tectonically emplaced in contact with Unit 7. Migration of the relatively low-volume melt would have resulted in the redistribution of lighter isotopes of zinc and facilitated the remobilization of the solid sphalerite ore. This is consistent with the fact that only those orebodies that are in contact Unit 7 exhibit along trend Zn isotope fractionation, and that the Unit 7-associated Loomis and Mud Pond orebodies yield the lowest δ⁶⁶Zn values.

The data presented here, in conjunction with the petrographic analysis of (Matt et al. 2019) indicate that magmatic fluids were involved in the remobilization of massive sulfide ores at Balmat. Intergranular sulfide and silicate melts would have decreased the competency of the ores and thereby enhanced predominantly solid-state deformational processes.

Conclusions

Systematic variations in Zn isotopic composition of sphalerite occur both between and within cogenetic ore bodies associated with Unit 6 of the Upper Marble at the Balmat mine: 1)
parent-cogenetic daughter ore bodies display decreasing average δ⁶⁶⁶⁶\text{Zn}; 2) orebodies that lie in cross-stratigraphic fault positions in contact with Unit 7 (fetid dolomite) tend to display decreasing δ⁶⁶Zn along their current down-plunge trend; 3) ore bodies that remained hosted within Unit 6 do not display down-plunge Zn isotope fractionation or trends toward low δ⁶⁶Zn compositions. The observed differences and trends are interpreted to have resulted from involvement of low-volume sulfide melts during the predominantly solid-state remobilization of ore during upper amphibolite facies metamorphism. Sulfide melt generation was augmented when units were emplaced in the sulfur-rich dolomite of Unit 7. The presence of small volumes of magmatic fluid affected the overall rheological character of the ores by wetting grain boundaries, thereby facilitating long-distance remobilization. Given that lower values of δ⁶⁶Zn correlate with greater remobilization distances, Zn isotopic analysis could provide an exploration tool for tracing undiscovered parent ore bodies.
<table>
<thead>
<tr>
<th>Sample</th>
<th>$\delta^{66}$Zn</th>
<th>Sample</th>
<th>$\delta^{66}$Zn</th>
</tr>
</thead>
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<tr>
<td>UG 1</td>
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<td>F-HT1</td>
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<tr>
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<td>0.31</td>
<td>MA 1</td>
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<tr>
<td>UG 3</td>
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<td>MA 5</td>
<td>0.44</td>
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<td>MA 6</td>
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</tr>
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<td>MA 7</td>
<td>0.13</td>
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<td>0.19</td>
</tr>
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<tr>
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<tr>
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<td>UF 3</td>
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<td>UF 4</td>
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<tr>
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<td>MP 2</td>
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</tr>
<tr>
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<td>MP 3</td>
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</tr>
<tr>
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<td>MP 4</td>
<td>0.12</td>
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<tr>
<td>LO 5</td>
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<td></td>
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</tbody>
</table>

Table 2.1 - Analytical results for Balmat samples. UG = Upper Gleason; LG = Lower Gleason; LO = Loomis; F-HT = Horsetail; MA = Mahler; UF = Upper Fowler; MP = Mud Pond. Sample numbers denote order in analytical runs and have no relationship to sample position along plunge. Values of $\delta^{66}$Zn have been normalized to the Lyon JMC 3702 standard.
<table>
<thead>
<tr>
<th>Ore Body</th>
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<th>Min</th>
<th>Max</th>
<th>Range</th>
<th>No.</th>
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</thead>
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<td>0.56</td>
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<td>0.34</td>
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<tr>
<td>Upper Gleason</td>
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<td>0.06</td>
<td>0.31</td>
<td>0.24</td>
<td>6</td>
</tr>
<tr>
<td>Lower Gleason</td>
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<td>0.02</td>
<td>0.25</td>
<td>0.23</td>
<td>9</td>
</tr>
<tr>
<td>Loomis</td>
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<td>-0.02</td>
<td>0.23</td>
<td>0.25</td>
<td>8</td>
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<td>Mud Pond</td>
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<td>-0.02</td>
<td>0.13</td>
<td>0.15</td>
<td>10</td>
</tr>
<tr>
<td>All</td>
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<td>-0.02</td>
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<td>0.58</td>
<td>48</td>
</tr>
</tbody>
</table>

Table 2.2-Analytical results for Balmat ore bodies. Ore bodies are listed from heaviest to lightest mean values of $\delta^{66}$Zn relative to the Lyon JMC 3702 standard.
Figures

Figure 2.3-World ore bodies whose zinc isotopic character has been analyzed. Circles show mean δ66Zn for each locality. Short horizontal lines show upper and lower limits of range. Data sources are: Irish Midlands, sphalerite (239 Wilkinson, J.J. 2005); Red Dog, sphalerite (Kelley et al. 2009); Hydrothermal vent fluids and sulfide minerals from chimneys, (John et al. 2008); Dongshengmiao, sphalerite (Gao et al. 2018); Navan, sphalerite (Gagnevin et al. 2014); Cantabrian, Zn-bearing minerals (predominantly sphalerite) (Pašava et al. 2014); Alexandrinka, whole rock (predominantly sulfides) (Mason et al. 2005); Balmat, this study; Franklin/Sterling Hill, two mineral separates, one of zincite and one of franklinite from the Sterling Hill mine; Tianquiao and Babanquiao, sphalerite (Zhou et al. 2014). All values normalized to the Lyon JMC 3702 standard.
Figure 2.4—Graphs of δ⁶⁶Zn vs. down plunge distance. Circles show analytical result, lines above and below show analytical error. On the x axis, zero is fixed at the position of the sample located farthest up plunge. Note lack of spatial trends in Upper and Lower Gleason ore bodies. Loomis, Mahler, and Upper Fowler show clear trends of isotopic lightening down plunge. Mud Pond lacks a clear trend but has the lowest mean isotopic values of all ore bodies and lowest internal values at the down plunge end.
Figure 2.5-Cross section of the Gleason-Loomis family, No. 3 mine. Upper Gleason is the parent, Lower Gleason the daughter, and Loomis the granddaughter. The three ore bodies are structurally connected by faults. Rock unit symbols as in Fig. 1.2.
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