

Sulfide and silicate anatexis in the Balmat zinc deposit (New York, USA) and its implications for ore remobilization

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ABSTRACT

The Cross-Cutting zone of the Fowler ore body is one of the many ore bodies of the Balmat, NY massive sulfide zinc deposit that underwent remobilization during upper amphibolite metamorphism and associated deformation. The kilometer-scale remobilization is difficult to reconcile with purely solid-state processes. Given that other polymetallic ores of similar metamorphic grade have been shown to have undergone varying degrees of anatexis, SEM-EDS micro-petrographic analysis of ores was undertaken to determine if melts were present in Balmat ores during metamorphism and deformation. Low melting temperature micro-inclusions of sulfosalt and sulfide assemblages 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 $\pm$ carbonate $\pm$ 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. These low-volume melts and residual fluids would have wetted grain boundaries, affecting the rheology of the bulk ore, and facilitating remobilization of the ores through a combination of solid- and liquid-state processes.

1. Introduction

The carbonate-hosted Balmat sedimentary exhalative Zn deposit of the Adirondack Lowlands of New York State (Fig. 1) underwent unusually extensive remobilization during upper amphibolite facies metamorphism. Some translocated (daughter) ore bodies moved at least 500 m across stratigraphy from their source (parent) beds and 1200 m down-plunge (deLorraine, 2001). Other translocated daughter ore bodies have undiscovered parents, suggesting that these distances are conservative for the deposit as a whole. Remobilization at Balmat has been interpreted to have resulted from solid state processes (deLorraine, 2001) given that: 1) the host rocks are generally anhydrous; 2) there are no hydrous alteration zones around individual ore bodies; and 3) peak metamorphic conditions were well below the melting point of the dominant ore minerals, sphalerite and pyrite (Barton and Toulmin, 1966). However, it is generally recognized that large-scale translocation of ore bodies (external remobilization) requires the involvement of a fluid, either in pure liquid-state or by mixed

liquid-solid mechanisms (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) (Frost et al., 2002, 2011; Hofmann, 1994; Mavrogenes et al., 2001; Pruseth et al., 2014; Sparks and Mavrogenes, 2005; Tomkins et al., 2004, 2006, 2007). 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).

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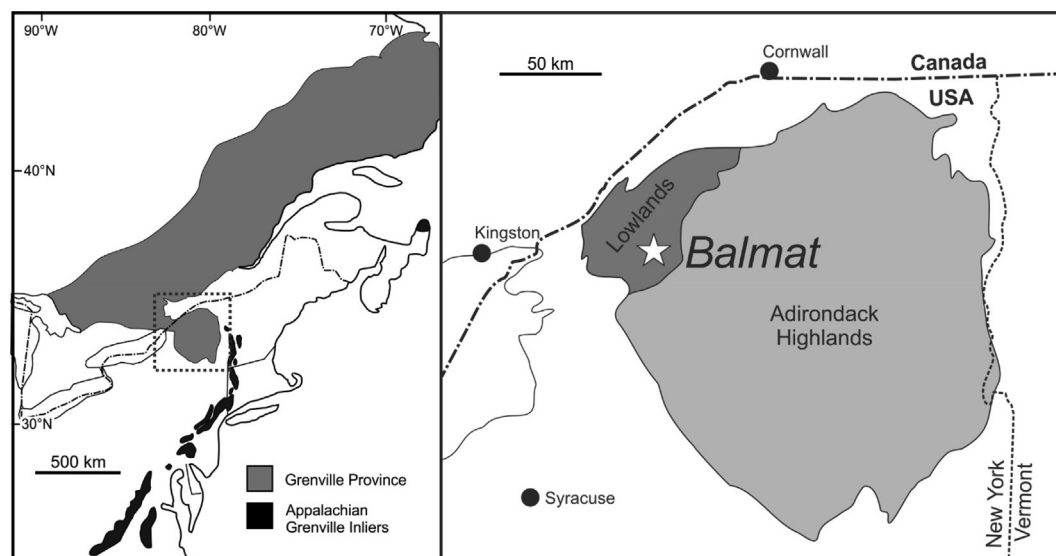


Fig. 1. Left, the Grenville Province in Canada and northwestern New York State with its inliers in the Appalachian region. Right, the Adirondack region with its subdivisions showing the location of Balmat in the Adirondack Lowlands.

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 et al. (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 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, jordanite, 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.

2. 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). 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 (Poppo 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 1100 m 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 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. 2). The ore follows the regional shallow NNE plunge for at least 1067 m. The Fowler thrust fault developed in the axial planar region of the fold. It separates the Fowler ore body from its sister Sylvia Lake ore body located 1219 m to the east in the lower limb.

Heumann et al. (2006) reported SHRIMP U-Pb dates from zircon and monazite grains in metapelitic migmatites, indicating partial anatexis in the Lowlands from ~1180 to 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 Shradly, 2011).

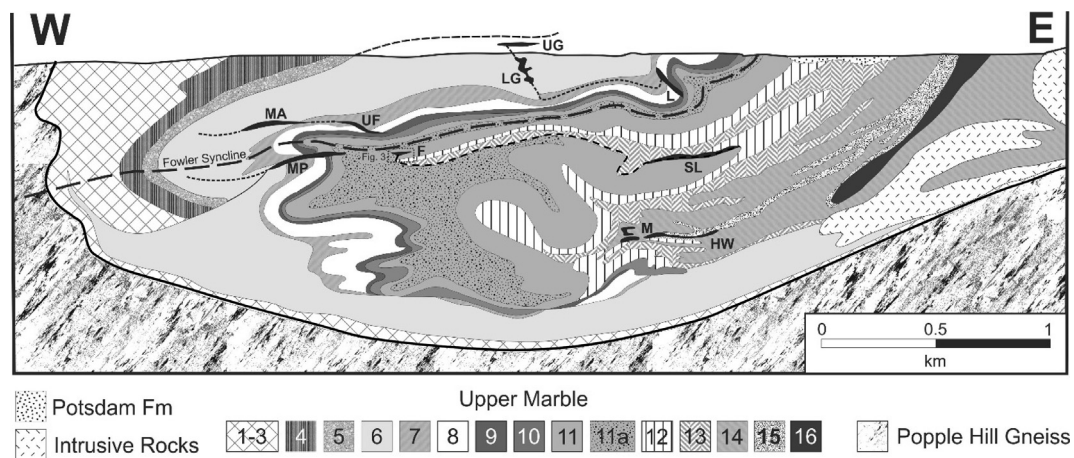


Fig. 2. Cross section of the Balmat mining district. Ore bodies in black are MA-Mahler; MP-Mud Pond; UF-Upper Fowler; F-Fowler; UG-Upper Gleason; LG-Lower Gleason; L-Loomis; SL-Sylvia Lake; M-Main; HW-Hanging Wall. Dashed box encloses Fowler ore body, enlarged in Fig. 3. Short dashed line between F and 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 and calcitic 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.

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 $640 \pm 30^\circ$, 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 X_{CO_2} of 0.7 (Petch, 1992). Brown et al. (1978) calculated peak pressure of ~6.5 kbar, assuming peak temperature of $625^\circ\text{C} \pm 25^\circ$. 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.

3. 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 deLorraine (1979). Expanding upon deLorraine's petrographic microscopic analysis, additional mineral assemblages and textural features were described at the sub-millimeter to micron scale using SEM-EDS (Hitachi TM 3030 Plus). EDS point analyses were used to characterize large grains ($> 100 \mu\text{m}$). 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 Fig. 4.

The 32 polished sections analyzed herein are from the Cross-Cutting zone of the Fowler ore body (Fig. 3), one of five subdivisions recognized within the hinge zone of the Fowler syncline (deLorraine, 1979, 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; Unit 11A, massive Anh; Unit 12, dolomitic marble; Unit 13, Tlc-Tr-Ath schist.

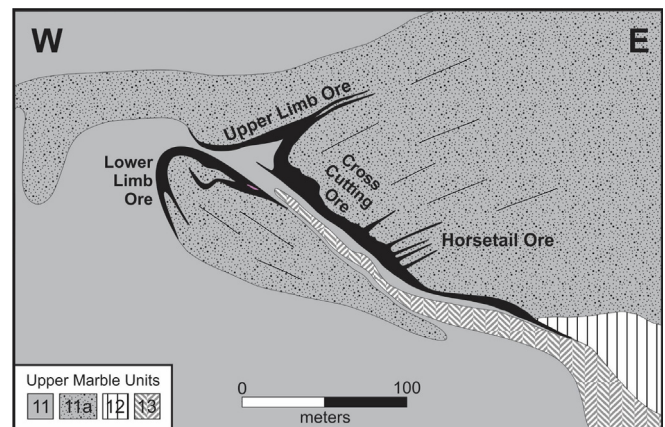


Fig. 3. Cross-sectional view of the Fowler orebody at N-9800. Most samples reported on herein were taken from the Cross-Cutting Ore zone at the 1900 + 140 level. Thin solid black lines show orientation of bedding in the host rock. Solid black areas are sulfide ore bodies. Upper Marble subunits 11–13 as in Fig. 2.

4. 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.

4.1. Granoblastic ore and gangue assemblages

Granoblastic assemblages (Fig. 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 $> 2 \text{ mm}$, 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.

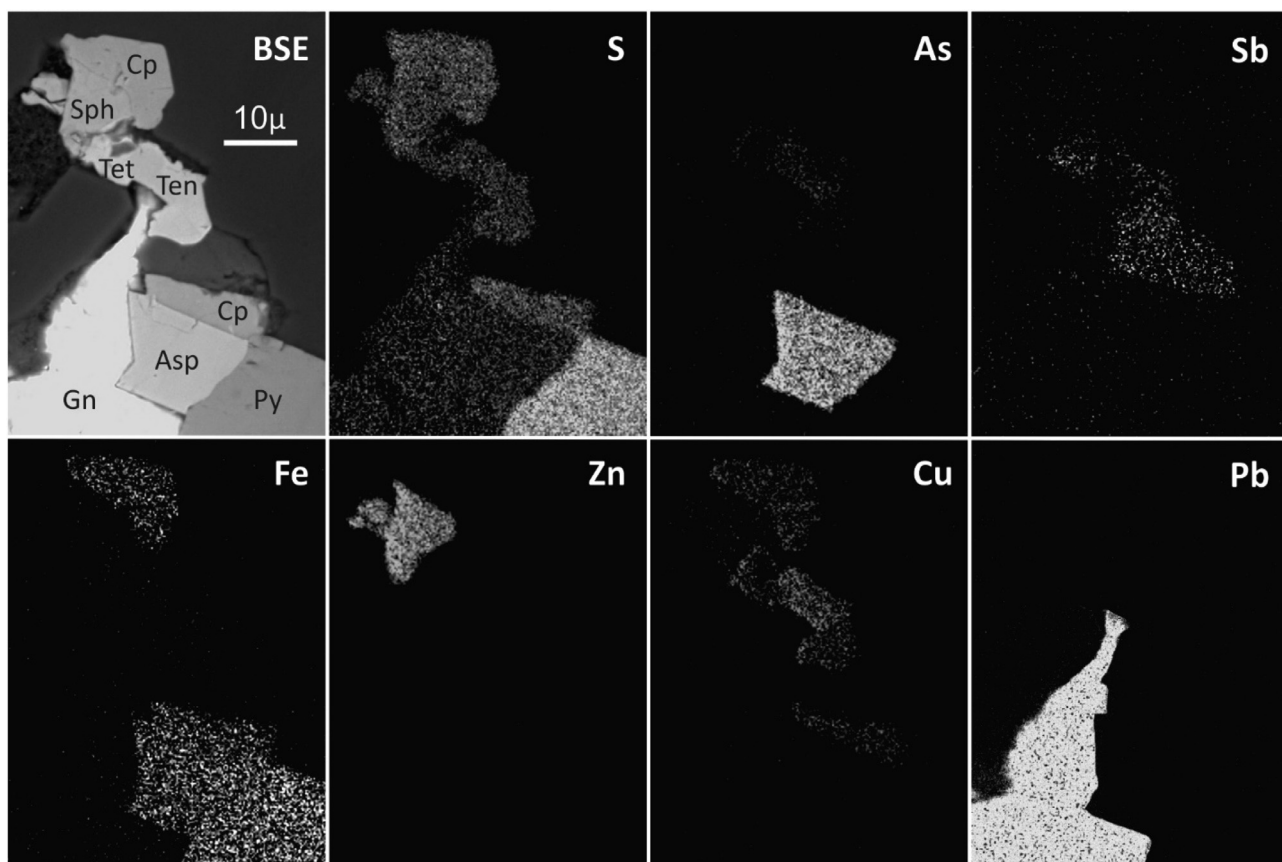


Fig. 4. Back-scattered image of a polysulfide microinclusion (also seen in Figs. 6C and 7A), upper left. Unlabeled, dark gray phases are gangue minerals. Directly right of and below the BSE image are EDS element X-ray maps of the same area, at the same scale. High Sb in a gangue phase (calcite) is produced by overlap of the emission spectra of Ca and Sb. Asp = arsenopyrite; Cp = chalcopyrite; Gn = galena; Py = pyrite; Sph = sphalerite; Ten = tennantite; Tet = tetrahedrite.

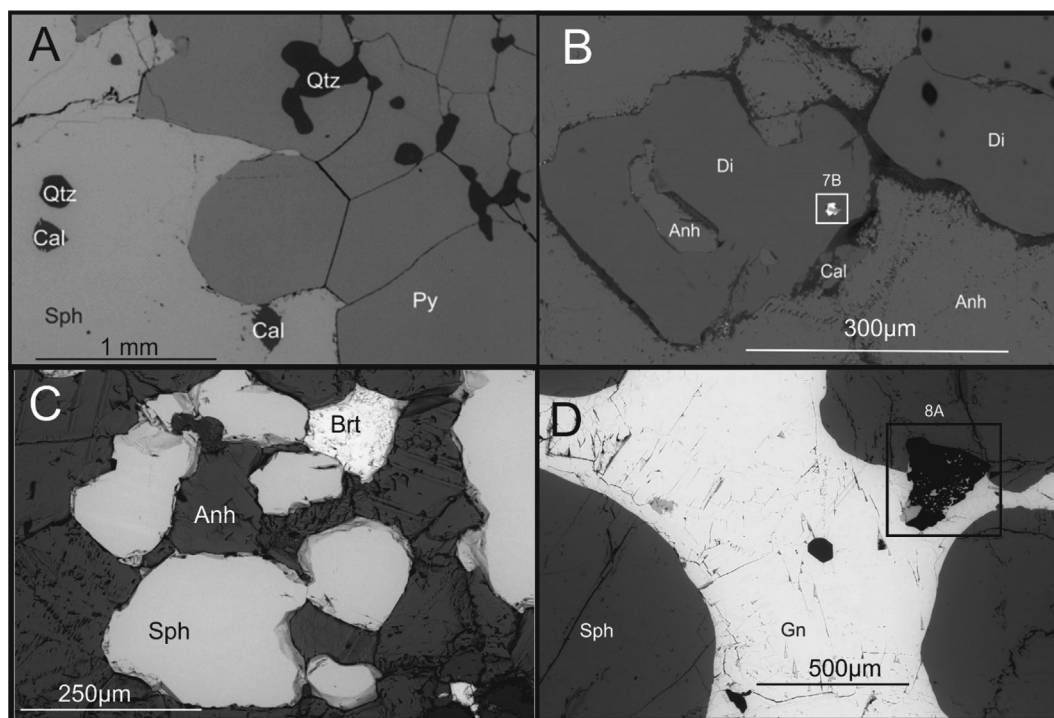


Fig. 5. Granoblastic domains. Anh = anhydrite, Brt = barite, Cal = calcite, Di = diopside, Gn = galena, Py = pyrite, Qtz = quartz, Sph = sphalerite. A-ore-rich domain; B-gangue-rich domain; bright microinclusion at center is enlarged in Fig. 7B; C-mixed ore and gangue domain; D-ore-rich domain, note control of galena habit by sphalerite, euhedral apatite at center, silicate assemblage (Qtz-Kfs) with small sulfosalt at lower left of silicate assemblage, enlarged in Fig. 8A.

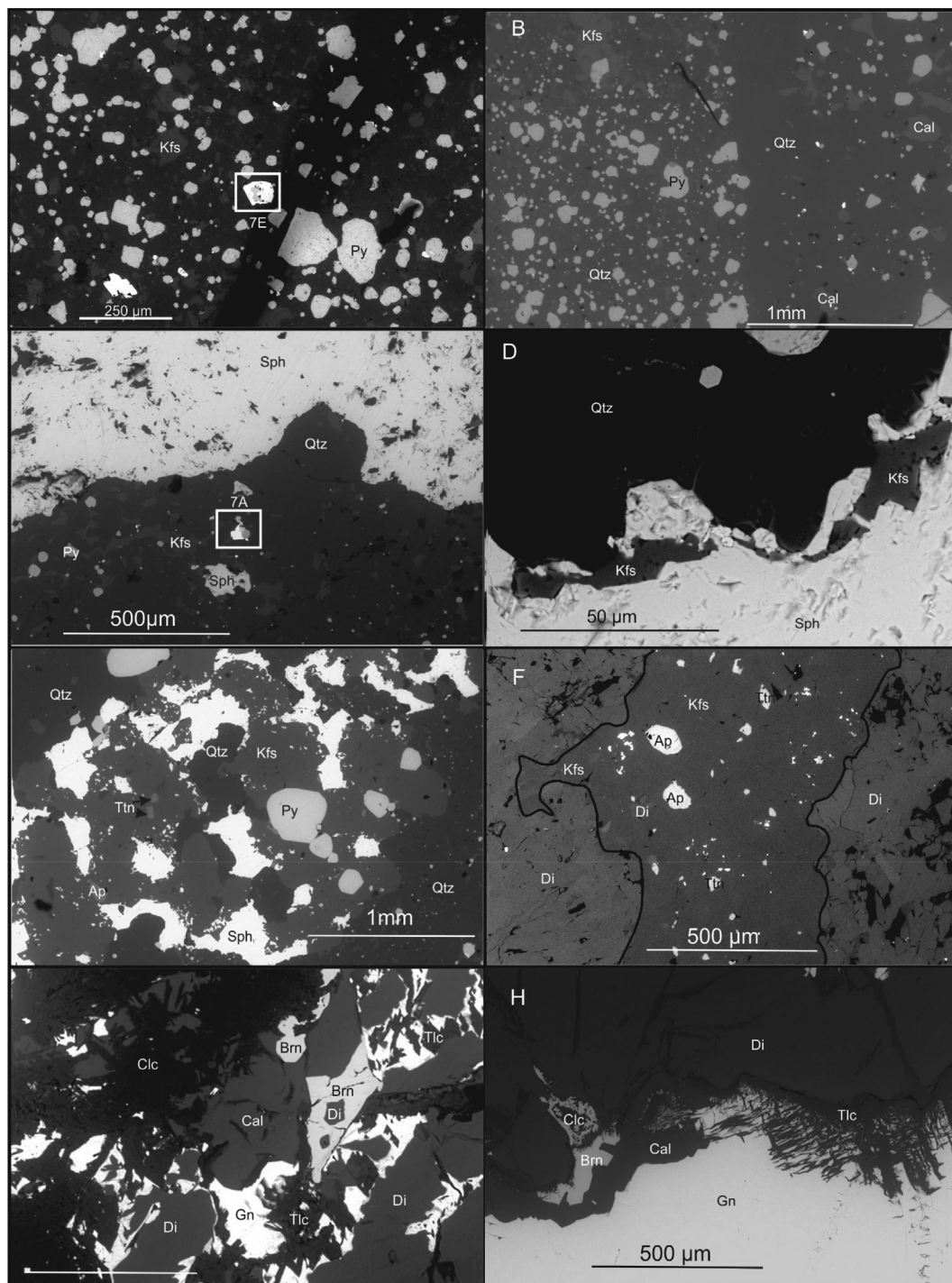


Fig. 6. Quartz-rich, K-feldspar-rich and talc-rich domains. Abbreviations as above, plus Ap = apatite, Asp = arsenopyrite; Brn = bournonite, Clc = clinocllore, Kfs = K-feldspar, Tlc = talc, Ttn = titanite. A-Qtz-Py domain with abundant K-feldspar. Outlined polysulfide grain of Asp + Py enlarged in Fig. 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. 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.

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. 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.

4.2. Quartz-Pyrite-Dominant domains

This domain type is characterized by modal abundances of quartz > 50%, and pyrite ~25% (Fig. 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 ~200 μ but average around 10 μ . Measurement of 100 pyrite grains on one slab showed a mode of 4 μ . 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 100–250 μ . 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. 6C), sometimes displaying fine, irregular intrusive forms (Fig. 6D).

4.3. Potassium Feldspar-Rich domains

K-feldspar is the predominant minerals 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 to 500 μ . Grain boundaries between K-feldspar and sphalerite are complex in form with interdigitations and embayments (Fig. 6E). Sphalerite inclusions in K-feldspar are abundant and complex in form, commonly exhibiting a graphic intergrowth texture (Fig. 8C). Pyrite is euhedral to subhedral with grains 50–200 μ . Quartz is anhedral with grains 40–500 μ . K-feldspar-rich and Qtz-Py dominant domains exhibit sharp contacts between each other (Fig. 6E). Kfs-rich material exhibits a cross-cutting relationship with granoblastic diopside rock (Fig. 6F).

4.4. Retrograde Talc-Rich domains

These zones within diopsidic marble are characterized by the replacement of diopside or calcite by talc $\pm$ clinocllore (Fig. 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 clinocllore. Diopside is euhedral to subhedral with grain sizes between 200 μ and 1 mm. Calcite is subhedral to anhedral with grains 40–400 μ . Talc is generally euhedral, with growth parallel to cleavage up to ~100 μ . 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. 6H). Clinocllore occurs as anhedral masses up to 500 μ but without visible crystal boundaries. However, euhedral clinocllore occurs as inclusions within bournonite (Fig. 6H), as does graphic K-feldspar.

4.5. 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. 7A), less frequently within granoblastic domains (Fig. 7B); 2) as fracture-filling material in gangue or ore phases commonly in association with retrograde talc and/or clinocllore (Fig. 7C); and 3) along grain boundaries in granoblastic domains (Fig. 7F).

Arsenic- and/or antimony-bearing polysulfide grains range in size from several microns to 1 mm, with most ranging from 25 to 60 μ . 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. 7E). The most common mineral assemblage in polysulfide grains is Asp-Py ($\pm$ Gn $\pm$ Ten $\pm$ Ccp $\pm$ Sph) (57%), followed by Ten-Gn ($\pm$ Py $\pm$ 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 (PbCuSbS₃) with galena occurs as fracture fill in granoblastic domains (Figs. 7C, 8B), both ore and gangue. Most frequently, it forms anhedral masses 100–200 μ in maximum dimension, although sub-to euhedral habits are also present (Fig. 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 $\pm$ Gn is spatially associated with mats of talc and/or clinocllore. Where fractures occur in granoblastic sphalerite, talc is absent but apatite, 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 ~10 μ in maximum dimension, although crystals up to 100 μ have been found (Fig. 7F). Arsenopyrite is also found intergrown with Py $\pm$ Gn, forming roughly equant, 25–50 μ aggregations of individual euhedral to subhedral crystals < 1 μ m to several microns in maximum dimension (Fig. 7G). Larger (~10 μ m) 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 sub-micron-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. 7H).

5. 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 $\pm$ 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.

5.1. Origin of Bournonite-Bearing assemblages

Granoblastic assemblages of Di-Cal $\pm$ Sph are cut and replaced by complex, fine grained assemblages of talc and/or clinocllore 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

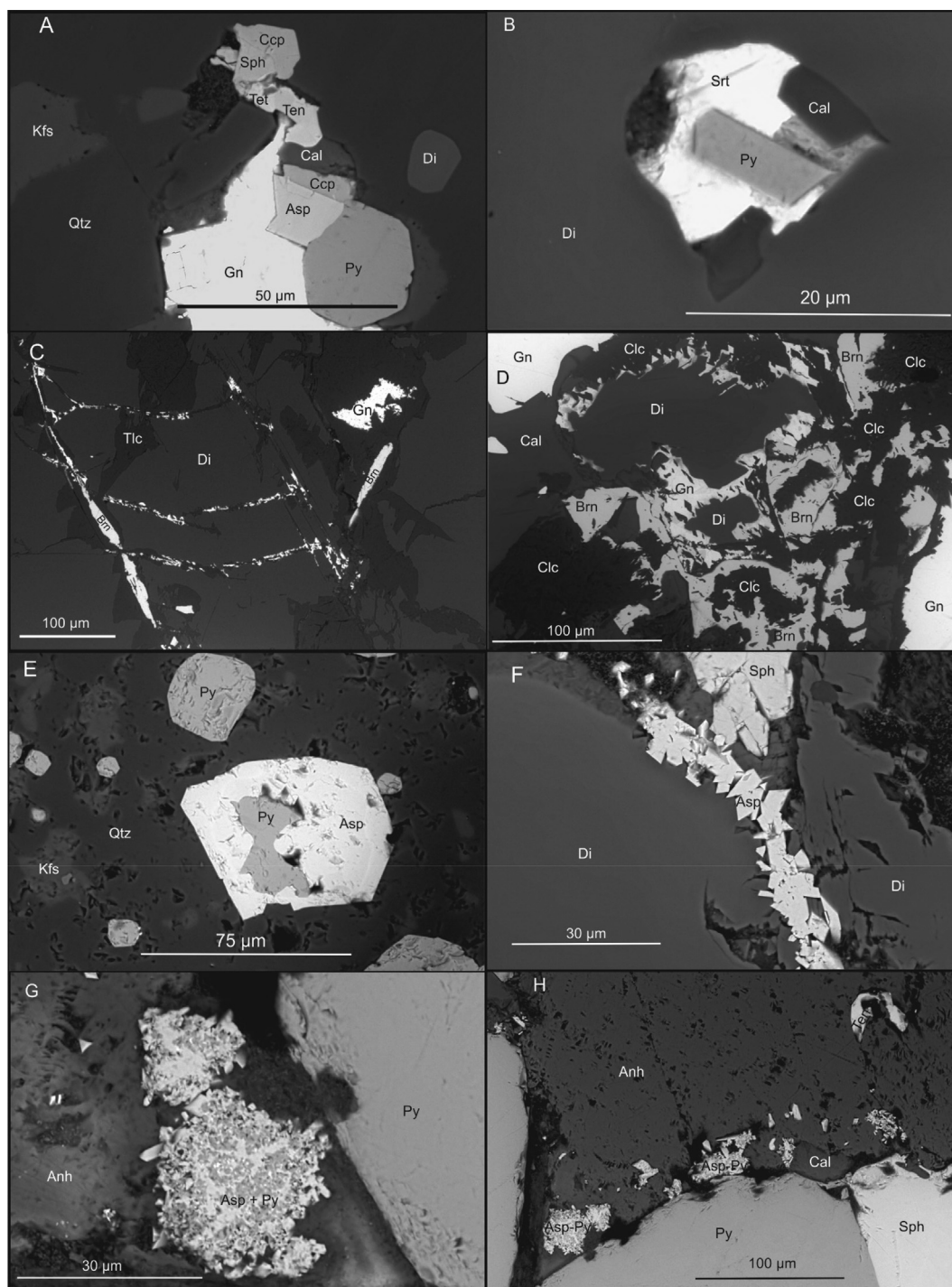


Fig. 7. LMCE-rich subdomains. Abbreviations as in Figs. 5 and 6, plus Ccp = chalcopyrite, Srt = sartorite, Ten = tennantite, Tet = tetrahedrite. A-Complex polysulfide grain in a Qtz-Py domain. B-Two-phase polysulfide grain in granoblastic diopside. Note perfectly euhedral pyrite at center of grain, surrounded by sartorite (PbAs_2S_4), T_{MELT} 305° C. C-Fractures in granoblastic diopside filled by bournonite, galena and talc. D-Hydrothermal domain showing anhedral to euhedral bournonite intergrown with clinocllore. 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° right. Shows additional Asp-Py intergrowths plus spatially associated tennantite, upper right.

effect of pressure suggests that melting temperature for Sb-bearing compounds is likely to decrease with increasing pressure (Frost et al., 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 CO_2 -rich (Petch, 1992; Petersen et al., 1993). Given the slow, post-Shawinigan cooling rate of $\sim 1.5^\circ \text{C}/\text{Ma}$ (Mezger et al., 1991; Dahl et al., 2004), talc-associated hydrothermal processes must have occurred $\geq 80\text{My}$ after peak metamorphism. Bournonite in these assemblages is

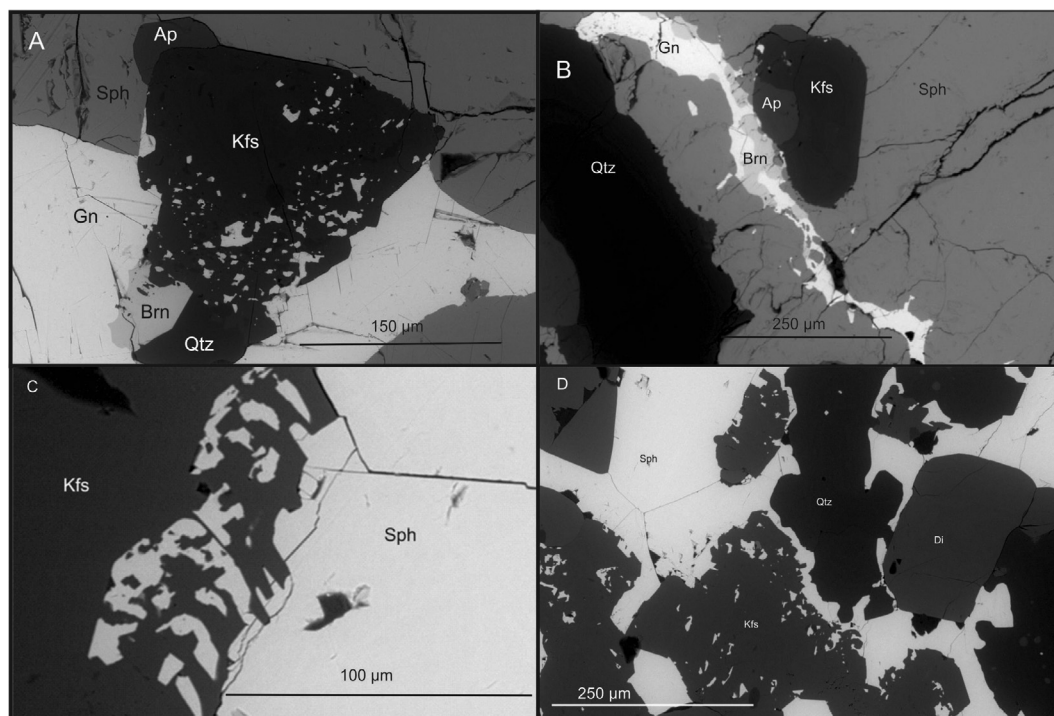


Fig. 8. A-Silicate assemblage in granoblastic Gn + Sph with bournonite at boundary. Note typical graphic inclusions of sulfide in Kfs. B-Galena-bournonite assemblage fills fracture in granoblastic Sph. C-Graphic intergrowth of Sph in Kfs at grain boundary. D- Quartz-rich and Kfs-rich domains cut granoblastic domain of Sph and Di. Note sharp, curvilinear boundaries with Qtz, numerous inclusions of Sph in Kfs.

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 (Fig. 8A, B). 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.

5.2. 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. 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 metawacks have been attributed to a sub-solidus 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. 8C) and complex, interdigitating crystal forms (Fig. 8D). 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 devolatilization reactions. Fluorapatite, fluorophlogopite, fluoro-tremolite, norbergite, h  uyne, 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.

Table 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 Figs. 5–8, plus Rlg = realgar; Jrd = jordanite. Cu Jrd? indicates unidentified phase bearing Cu, Pb, As and S.

Polysulfide Grains	Gangue Host Assemblage
Asp-Ccp	Cal-Kfs-Qtz
Asp-Ccp-Gn-Py	Qtz
Asp-Ccp-Gn-Py-Sph-Ten-Tet	Kfs-Qtz
Asp-Ccp-Py	Cal-Qtz
Asp-Gn	Di ± Kfs ± Cal
Asp-Gn-Py	Kfs-Qtz; Di
Asp-Gn-Py-Ten	Qtz ± Kfs
Asp-Py	Kfs-Qtz ± Ttn
Asp-Py	Anh-Cal-Di; Cal
Brn-Ccp-Gn-Sph-Tet	Cal-Dol
Ccp-Py-Sph ± Gn	Qtz
Ccp-Ten	Kfs
Cu Jrd?-Rlg	Qtz
Gn-Py-Ten ± Sph	Qtz ± Kfs ± Ap
Gn-Sph-Ten	Qtz
Gn-Ten	Qtz ± Cal
Jrd-Py	Qtz
Jrd-Ten	Qtz ± Cal
Py-Srt	Di
Py-Ten	Qtz

5.3. Origin of polysulfide micro-inclusions

Sulfosalt-bearing micro-inclusions 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, Fig. 7B, E). 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. 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 (PbAs₂S₄) (Fig. 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 sulfosalt-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.

5.4. 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 fS_2 (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. 7E). The aggregations of complex intergrowths between arsenopyrite and pyrite observed at Balmat have been documented elsewhere as evidence for reaction (1) (Tomkins et al., 2004).



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 et al., 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.

6. 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.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.oregeorev.2019.03.002>.

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