

Article

Controls on Barite Mineralization in a Major Intracontinental Shear Zone: Carboniferous of the Cobequid Highlands, Nova Scotia

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Abstract: Prominent veins of late Carboniferous barite, associated with fluorite and calcite, outcrop close to older granite plutons along an intracontinental shear zone that was active throughout the Carboniferous in southeastern Canada. Some barite is stratigraphically constrained to younger than 315 Ma and final mineralization is constrained by a published Rb–Sr isochron of 300 ± 6 Ma. Barite occurrences in the Carboniferous basins of central Nova Scotia, 50 km to the south, are synchronous with or post-date ankerite-siderite-magnetite-pyrolusite and Pb–Zn mineralization, which was facilitated by fluid interaction with thick evaporites. This study aims to determine controls on the distribution of barite in the shear zone, from field relationships, vein petrography and isotope geochemistry of minerals. The isotope chemistry of shear zone barite is similar to that occurring in Pb–Zn–Mn–Ba mineralization to the south, suggesting a common origin. Veins of barite, associated with fluorite, represent the youngest and regionally coolest phase of a 70 Ma history of Carboniferous mineralized veins along the Minas Fault Zone. Their prominence close to granite plutons reflects brittle deformation of the deeply-rooted granites in a complexly deforming fault zone, but the origin of abundant F remains uncertain.

Keywords: barite; veins; isotope chemistry; petrography

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1. Introduction

Barite commonly occurs in faults and fractures in Lower Carboniferous sedimentary rocks close to the continental-scale Cobequid Shear Zone and the later Minas Fault Zone along the southern margin of the Cobequid Highlands of northern Nova Scotia (Figure 1) [1–4]. In many cases, the barite occurs together with specularite, other iron minerals (e.g., goethite, ankerite, siderite, and pyrite), or fluorite and less commonly with chalcopyrite, sphalerite, galena or manganese minerals. This complex fault system was initiated in the Late Devonian following collision of the outboard peri-Gondwanan Appalachian terranes with Laurentia [5], with the local component of the fault system known as the Cobequid Shear Zone, with dextral slip on ENE-trending faults. The western part of this shear zone was reactivated with continuing dextral slip as part of the E–W Minas Fault Zone in the late Carboniferous, during the final Gondwana–Laurentia collision that resulted in the formation of Pangea [6]. These fault systems continued into the USA in the southwest and into Europe in the east. Deformation along these faults extended at least from 370 to 300 Ma and localised a complex succession of vein minerals [6], including important iron deposits interpreted as part of an iron-oxide–copper–gold (IOGC) mineralizing system [4]. The barite mineralization appears to be late in this succession of mineral types [6].

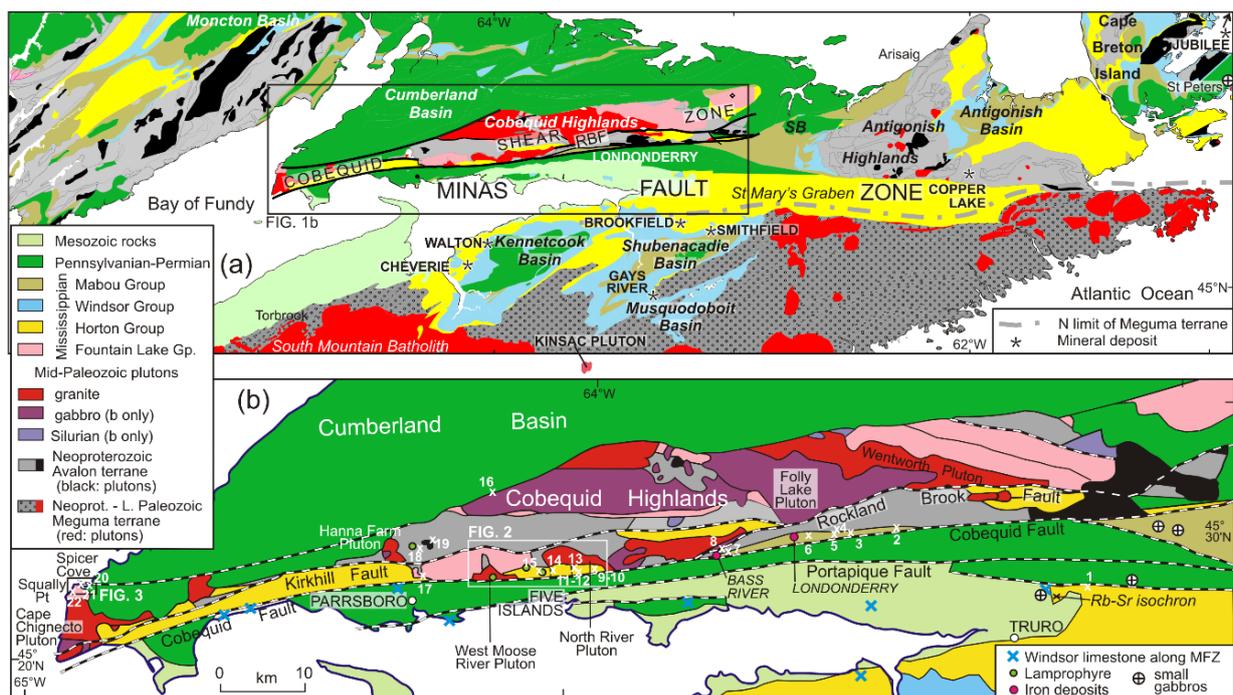


Figure 1. (a) Geological map of the Minas Fault Zone in northern Nova Scotia (modified from [4]) and (b) more detailed map of the Cobequid Highlands showing location of barite mineralization (numbers refer to Table 1; modified from [6]).

The general style of this mineralization is similar to the barite-lead-zinc mineralization of the Carboniferous basins of central Nova Scotia (Figure 1a), including the former Walton barite mine and the active Gays River lead-zinc mine [7]. These deposits are generally carbonate hosted sulfide deposits with minor liquid petroleum. The barite veins are clearly epigenetic and structurally controlled. On the other hand, the distribution of barite mapped by [2,3] in the Cobequid Highlands shows a close spatial association with granite and/or gabbro plutons close to the Cobequid Fault (Figure 1b). Barite deposits are notably absent, for example, east of the Wentworth pluton or between the Cape Chignecto and Hanna Farm plutons. This raises the question as to whether the mineralization and alteration of country rock is genetically associated with early Carboniferous igneous activity in the Cobequid Highlands [8] or whether it is part of the ca. 300 Ma metallogeny of the Carboniferous basins of central Nova Scotia [7,9].

We have studied this problem by detailed examination of barite in two general areas. (1) At Five Islands, barite veins in the Lower Carboniferous Horton Group sandstones and shales are found close to the North River granite pluton, and the Horton Group itself is cut by hypabyssal porphyritic rhyolite. (2) In the northern Chignecto Peninsula, barite veins are geographically remote from the mineralization of the Carboniferous basins of central Nova Scotia, and are close to the Cape Chignecto granite pluton emplaced in the latest Devonian to earliest Carboniferous [6].

2. Regional Geological Setting and Previous Studies of Barite Distribution

The Cobequid Highlands (Figure 1b) form a horst with Neoproterozoic crystalline basement of the Avalon terrane, as summarized by [6]. In the study area, the volcanogenic Jeffers Group is intruded by diorite-granodiorite plutons. The late Devonian to early Carboniferous Cobequid Shear Zone formed part of a NE–SW-trending, crustal-scale, orogen-parallel shear system, with some 300 km dextral displacement, extending from the southern Appalachians to the Caledonides of Scotland [5]. Granite and gabbro plutons, together with coeval flood basalts, were emplaced between 370 and 355 Ma and progressively deformed in this shear system. The plutons have a general A-type geochemical character with trace elements characteristic of within-plate granites. In the early Carbonif-

erous, the Kirkhill and Rockland Brook faults (Figure 1b) formed the abrupt northern edge of the Kennetcook Basin half-graben (Figure 1a). This basin, and the Shubenacadie and Musquodoboit basins to the south in central Nova Scotia, accumulated several kilometres of terrestrial, lacustrine and marine sandstone, shale, limestone, gypsum and salt, assigned to the Horton, Windsor and Mabou groups. In the late Carboniferous to Permian, the collision of Africa with Laurentia in the southern Appalachians resulted in the Alleghanian orogenic phase. In the northern Appalachians, much of this deformation was taken up along the E–W-trending Minas Fault Zone [4]. Parts of the Minas Fault Zone reactivated older faults within the Cobequid Shear Zone. Late Carboniferous mineralization along the Minas Fault Zone includes large iron ore deposits, base metal sulfides, barite and REE minerals [4]. Thick fluvial deposits of the Cumberland and Pictou groups accumulated to the north and south of the Cobequid Highland horst.

In Nova Scotia generally, six styles of barite mineralization were recognised in the classic review of Felderhof [1]. Type A occupies faults and fractures in unaltered country rock, and is commonly associated with fluorite and celestite. All the occurrences from the Cobequid Highlands considered in this paper (Table 1) are type-A deposits, except for the Bass River mine deposit (11 in Table 1), which is a stratigraphically controlled replacement mineral deposit designated as type B [1].

Table 1. Barite deposits in the Cobequid Highlands and location of samples analysed in this study.

| No | UTM North | UTM East | Location | Minerals | Analysed Samples | References |
|----|-----------|----------|------------------------------|---|------------------------|------------|
| 1 | 5,029,120 | 487,260 | East Mountain | pyrol, mang, psilom, brt | | [3] |
| 2 | 5,038,175 | 462,865 | Totten Brook | hem, lm, ank, brt | | [3] |
| 3 | 5,036,110 | 452,470 | Londonderry | brt, sd, ank | | [3] |
| 4 | 5,037,390 | 451,290 | Londonderry | hem, lm, gt, sd, ank, py, mrc, mag, brt | | [1–3] |
| 5 | 5,036,685 | 451,315 | Londonderry | ank, sd, gt, lm, spec, brt | | [2] |
| 6 | 5,036,320 | 448,535 | Londonderry | brt, ank, sd, gt, lm, spec | | [2] |
| 7 | 5,034,550 | 439,510 | Bass River (mine) | brt | | [1,2] |
| 8 | 5,034,750 | 439,255 | Bass River falls | mag, py, brt | | [3] |
| 9 | 5,032,235 | 420,765 | East River | brt, spec, ccp, fl, py, cal, chl, qtz | 8015, 8016, 8018 | [1,3] |
| 10 | 5,033,055 | 421,285 | East River | brt, spec, fl, py, cal, chl, qtz | 7791, 8023, 8025, 8026 | [1,3] |
| 11 | 5,032,375 | 418,530 | Bass River of Five Is (mine) | brt, spec, ccp, fl | 8069, 8071, 8079 | [1–3] |
| 12 | 5,032,125 | 418,320 | Bass River of Five Is | brt, fl | | [2] |
| 13 | 5,033,320 | 416,780 | Vault Brook | brt | | [3] |
| 14 | 5,032,090 | 414,515 | Lynn Road | ccp, gn, brt, fl | | [2] |
| 15 | 5,031,755 | 412,710 | Lynn Road | brt, fl, spec, ank, cal | 8032, 8054 | [2,3] |
| 16 | 5,031,570 | 398,510 | Gavin Brook | brt, gn, ccp, sp | | [1] |
| 17 | 5,045,940 | 407,470 | South Brook | brt | | [1] |
| 18 | 5,035,100 | 397,450 | Jeffers Brook | gn, ccp, sp, brt | | [3] |
| 19 | 5,036,485 | 398,965 | Jeffers Brook | gn, ccp, sp, brt | | [3] |
| 20 | 5,032,373 | 351,636 | Spicer Cove | brt | | [1] |
| 21 | 5,032,414 | 350,705 | Squally Point | brt, fl | 5003 | [1] |
| 22 | 5,032,075 | 350,262 | Andersons Cove | brt | | [10] |

Mineral abbreviations follow Whitney and Evans [11] and pyrol = pyrolusite, mang = manganite, and psilom = psilomelane; minerals given in approximate order of abundance.

Along the Cobequid Shear Zone and Minas Fault Zone in the study area, complex veins including albite, quartz, chlorite, siderite, ankerite and magnetite are widespread. Their paragenetic sequence and age have been determined, ranging from at least 355 to 320 Ma [6]. No discrete barite veins were investigated, but at least half of the samples examined in that study contained trace amounts of barite (Supplementary Table S1). Modes of occurrence of this minor barite included (1) as patches or filling voids in minerals such as quartz, albite, calcite, and a TiO₂ mineral (likely rutile) referred to subsequently as titania; (2) at the rims of open fractures; (3) in calcite veins; (4) associated with limonite and Mn–Mg siderite; (5) associated with galena, pyrite and limonite in open fractures. All these modes of occurrence suggest that barite mineralization was late.

In central Nova Scotia, commercially important barite deposits are found at Walton and Brookfield [7,9] (Figure 1a). The Walton Ba-Pb-Zn-Cu-Ag deposit includes barite and sulfide ore bodies in lower Windsor Group limestone, with barite synchronous with and post-dating sulfides. A similar paragenesis is found at the smaller Smithfield deposit. The Brookfield barite deposit occupies a fault zone in the Horton Group and was synchronous with and post-dates siderite. Additionally of note is the Gays River Zn-Pb sulfide deposit which contained 12 million metric tons of 7% combined lead and zinc hosted in a dolomitized carbonate bank of the basal Windsor Group. In the region, barite veins also occur in Windsor Group limestones and in granite of the Kinsac pluton [1,7]. In the Minas Fault Zone, Horton Group shales at Upper Brookside yielded a Rb-Sr isochron age of 300 ± 6 Ma, interpreted as the last time that there was flow of hydrothermal fluids with Sr [7]. In the literature, this age has been widely applied to the sulfide mineralization in central Nova Scotia.

3. Materials and Methods

Field mapping and sampling were carried out, principally in brooks and coastal cliffs. Bedrock in other areas is obscured by glacial till. Polished thin sections were examined by scanning electron microscope and minerals were analysed by energy dispersive spectroscopy (EDS) in the same manner as [12]. A set of 24 host rock samples (Supplementary Table S2) were analysed for 10 major and minor element oxides and 14 trace elements on a Philips PW 1400 sequential X-ray fluorescence spectrometer using a Rh-anode X-ray tube at Saint Mary's University. The major element analyses were made on fused beads prepared from ignited samples, whereas the trace element analyses were made on pressed powder pellets. Analytical precision, as determined from replicate analyses, is generally better than 2%, except for MgO, Na₂O and Nb which are better than 5% and Th which is better than 10%. Some barite samples were analysed in the same way. Strontium isotopes in barite, fluorite and calcite were analysed by Geospec Consultants Ltd., Edmonton, AB, Canada, in a Micromass (Manchester, UK) VG354 mass spectrometer using a five collector peak hopping technique. Oxygen and sulfur isotopes were determined on barite samples by Actlabs Ltd. (Ancaster, ON, Canada) [13]. Lead isotopes were determined by Geospec Consultants Ltd. using procedures summarized by [8].

4. Results

4.1. Field Observations

In the Five Islands area, the major barite occurrence in the East River section (10 in Table 1, Figure 2) occurs in fine-grained sandstones and dark gray and black siltstones of the basal Carboniferous Horton Group, and the mineralization is hosted within common lenticular barite veins that pinch and swell forming pods of barite. A typical vein is approximately 10 cm × 30 cm in size; however, there are rare pods ranging up to 100 cm in length. The mineralization infilling these veins consists predominantly (95%) of coarse, tabular, pinkish-white and white barite, with well-formed euhedral crystals of purplish-brown calcite along the margins. A 1 m in width breccia zone located in this area is also partially cemented with medium-grained, tabular, white barite. There is no wall-rock alteration apparent in hand samples associated with the mineralization.

Barite mineralization in the Bass River of Five Islands (Figure 2) is found at the site of the abandoned Eureka barite mine (11 in Table 1), worked between 1866 and 1876 [1], and 200 m farther downstream (12 in Table 1). The host rock is thinly-bedded, gray silty argillite and siltstone, with interbedded fine- to medium-grained gray sandstone. Several fault zones in the area are filled with fault gouge containing cataclastic country rock, locally cemented with calcite. Hand specimens show wall-rock alteration. The country rock in Bass River is less deformed than that of the East River; however, bedding orientations are similar, generally striking east-west and dipping between 40° and 70° S. Faults, vein, fractures, and breccia zones cross cut bedding, and most trend east-west dipping at 30° to 70°. They are cut by rare younger northwest- to southeast-trending shears and calcite

veins dipping 50–75°. Near the Eureka mine, the country rock is cut by several irregular barite veins of 1–2 cm in length with no visible calcite. Barite also cements breccia zones up to 30 cm in width and forms lenticular veins. The veins contain pinkish-white, coarse, tabular, barite, whereas the barite in the breccia zones is more massive (95%) and occurs with calcite (4%) and rare fluorite (1%) that is purple, colourless, or amber.

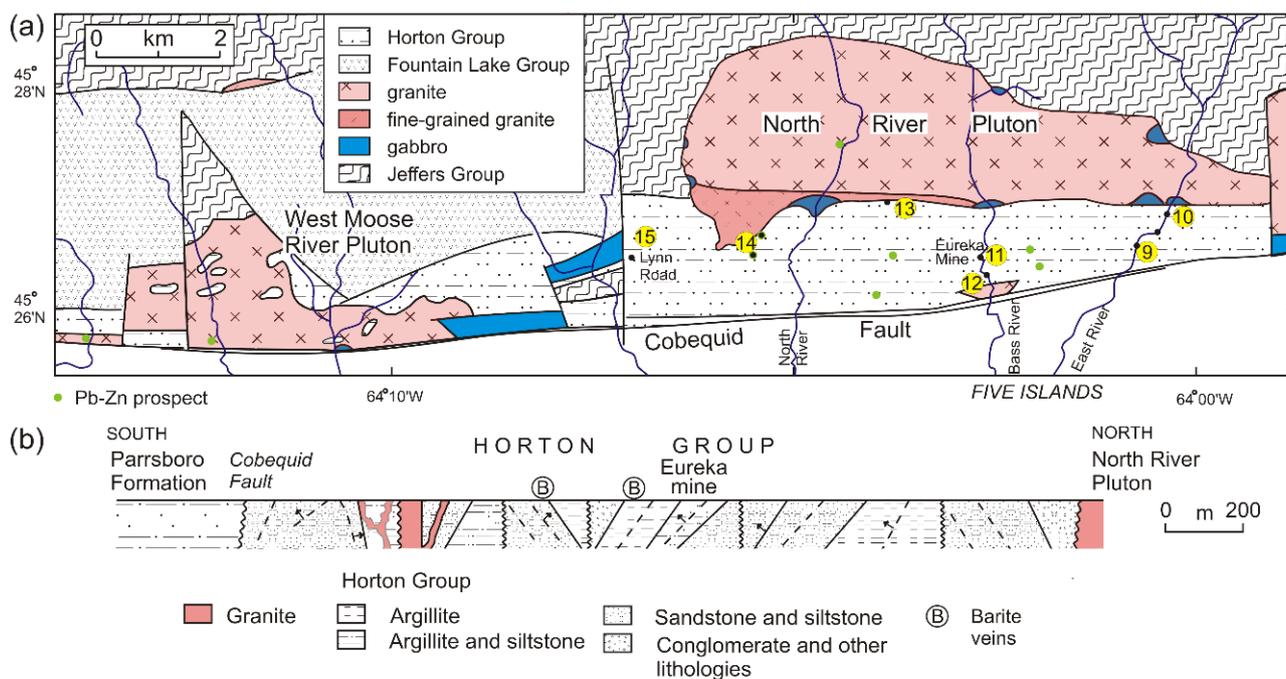


Figure 2. (a) Geological map of the area north of Five Islands and (b) cross section down the Bass River, showing location of barite mineralization (numbers refer to Table 1). Pb-Zn mineralization from [3] also shown. Base map modified from [14].

Barite was only found in one locality along the numerous road-cut exposures on the west side of Lynn Road (15 in Table 1, Figure 2), where it is hosted by grey siltstones and argillites. Barite is found filling small (1 cm or less) irregular and lenticular fractures, generally associated with calcite. The barite is generally more massive than that found further to the east, but is still occasionally found as medium- to coarse-grained, tabular, pinkish-white crystals. The veins consist primarily of massive orange-pink calcite (80%) with minor barite (20%), and the two minerals often appear to be intermixed.

North of the Cape Chignecto granite pluton (Figure 1b), three barite localities are known. In Andersons Cove (Figure 3), steeply dipping barite (70%) and calcite (30%) veins cut a highly sheared diabase dyke that cuts flow-banded rhyolite of the Fountain Lake Group. A little to the north, steeply-dipping barite veins cut hyaloclastites of the Fountain Lake Group. A series of subvertical barite (90%) and fluorite (10%) veins cut Fountain Lake Group rhyolite east of Squally Point (21 in Table 1) and may be a continuation of the veins in Andersons Cove. The fluorite occurs in the outer part of the veins and the barite in the centre. Wider barite veins (with some calcite, ~10%) outcrop on the foreshore of Spicer Cove along the fault contact between the Bashkirian (Duckmantian) Ragged Reef Formation [15,16], and Tournaisian Falls Formation conglomerate (Figure 3).

4.2. Alteration of Country Rock

Twelve samples from Horton Group argillite and sandstone forming the host rocks of the barite veins in the Five Islands area have been studied in detail using BSE images and EDS analyses of mineral chemistry (Figures 4 and 5; Supplementary Figure S1). Detrital minerals seen in these rocks include: quartz, K-feldspars, albite, muscovite, clays, and apatite. Bedding-parallel diagenetic pyrite and chlorite are common in argillite. Fine-

grained sandstones have laminae rich in detrital muscovite that is partially altered to chlorite (Figure 4A). In addition, one rhyolite from the Squally Point has been analysed (Figure 5A,B).

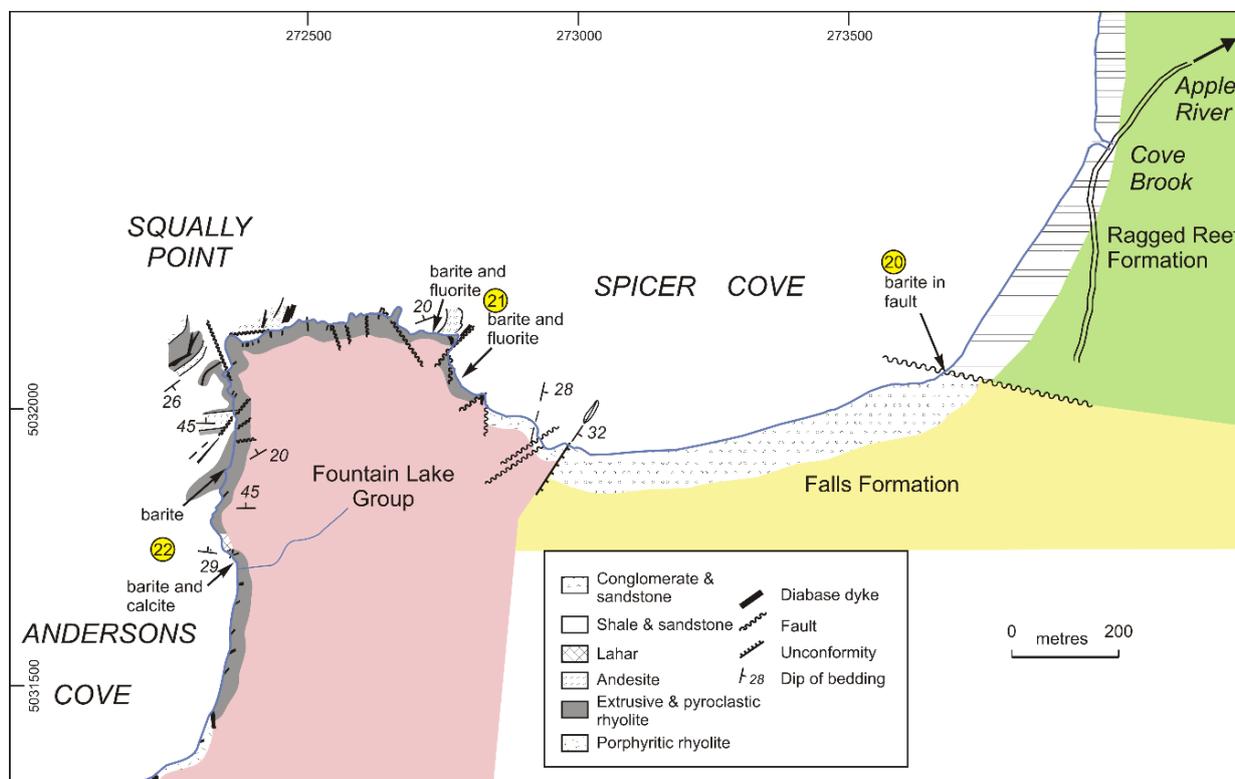


Figure 3. Geological map of the Squally Point area (UTM coordinates), showing location of barite mineralization (numbers refer to Table 1). Base map modified from [10]. Lithologies of coastal outcrops in legend; colours indicate stratigraphic units.

At first sight, the barite veins cut altered country rock. However, there is no direct evidence that any of the macroscopic alteration in the country rock is related to the barite veins. Argillite and sandstone are in places cut by composite veins that predate the barite, with later minerals filling the centre of a widening vein, or filling intergranular voids that opened up during renewed deformation. The most common veins (Figure 4B) have an outer rim of quartz + Mg-chlorite, passing towards the centre of the vein first to predominant Mg-chlorite, then calcite, and finally to a central zone with Fe-chlorite, ankerite, pyrite and quartz (Figure 4A,B; Supplementary Table S3). In places, internal deformation of veins (red circle in Figure 4B) created space for precipitation of minerals characteristic of the central zone such as Fe-chlorite and ankerite altered to limonite (Figure 4D). This deformation appears to post-date the precipitation of calcite.

Almost all of the thin sections of unaltered argillite host tiny 1–3 mm fracture infills or small tension gashes, generally filled with quartz and/or calcite. The altered argillites exhibit either partial calcite replacement of the clays and feldspars or an alteration halo of chlorite around veins and tension gashes. Two slides (7781B and 8053B) also contain scattered minor blebs of chalcopyrite within the host. Pyrite is common: some is clearly post-compaction but some is clearly early diagenetic.

Alteration in sandstones is visible as calcite replacement of plagioclase, interstitial chlorite growths, and muscovite and minor biotite growths in interstitial openings. Many samples host traces to approximately 2% small hematite crystals throughout the ground-mass. Sample 8015 contains common late biotite (Figure 5C) that fills porosity between quartz grains, but may have nucleated on original detrital biotite grains. The biotite is Mg rich with $\text{TiO}_2 < 1 \text{ wt.}\%$ (Supplementary Table S4) and is similar to secondary biotite in the

nearby West Moose River Pluton [17]. Similar biotite, but in much smaller quantity, is seen in other altered sandstone samples.

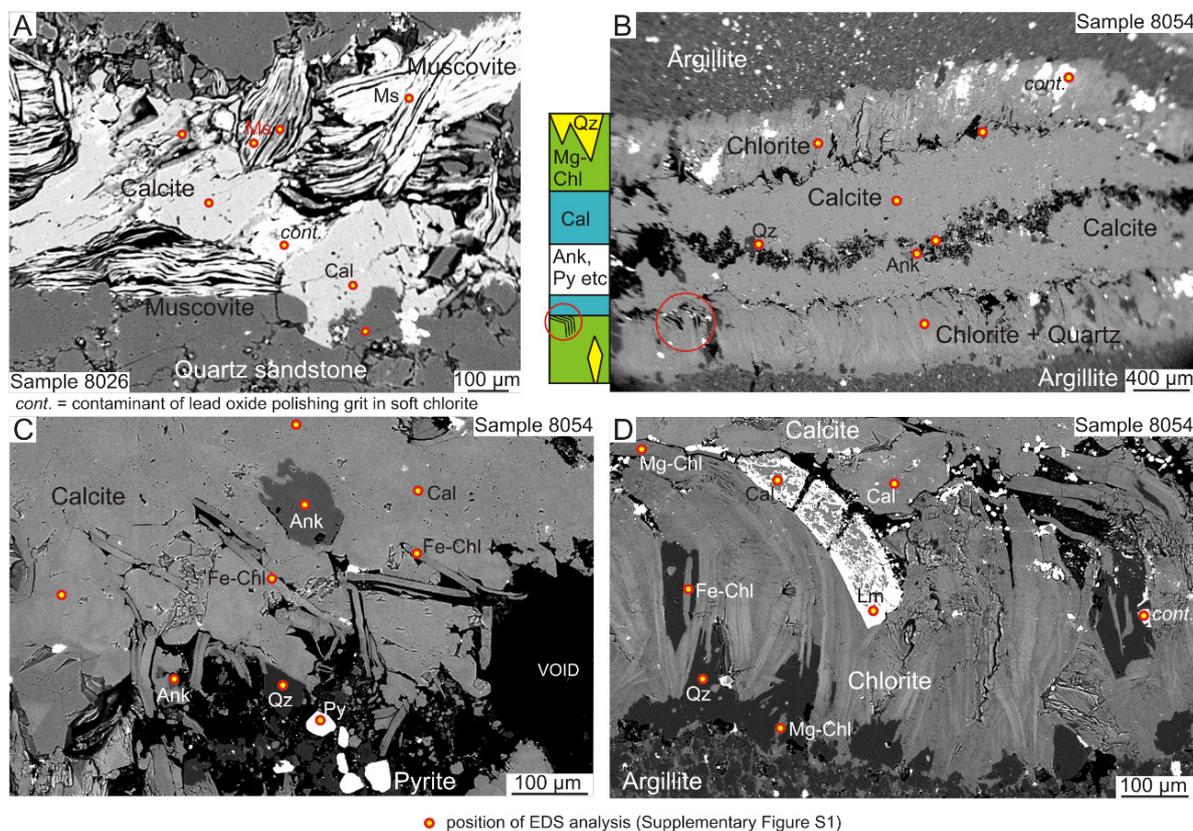


Figure 4. Backscattered electron images of veins in argillite and sandstone, Five Islands area. cont. = contaminant from polishing process. (A) Micaceous lamina in quartz sandstone cut by irregular calcite vein. (B) Composite quartz–chlorite–calcite vein with central zone of ankerite, pyrite, Fe-chlorite and quartz. Red circle shows deformed area. (C) Zoom of part of the central zone showing corrosion of calcite and precipitation of minerals. (D) Deformation of the outer Mg-chlorite zone and growth of Fe-chlorite and limonite after ankerite. Mineral abbreviations as in Table 1.

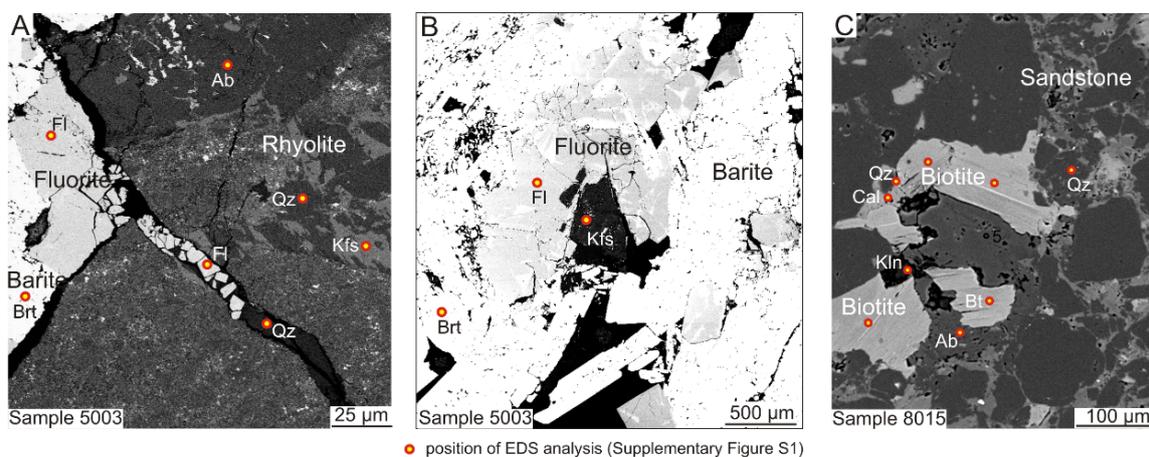


Figure 5. (A,B) Backscattered electron images of veins of fluorite and barite in rhyolite, Squally Point. (C) Secondary biotite in calcite-cemented sandstone, Five Islands. Mineral abbreviations as in Table 1.

4.3. Petrography of Barite Veins

Barite in veins is generally coarse grained with tabular white or pinkish barite crystals. Some veins have euhedral calcite crystals at their margin; a few veins from Lynn Road have abundant calcite (70%) with interstitial barite. Barite shows two orthogonal sets of cleavage in thin sections. Decrepitated fluid inclusions typically a few tens of micron in size yield EDS analyses with Na and Cl (Figure 6B). Some inclusions are strongly elongated parallel to cleavage (Figure 7C). Cataclastic barite with micron-size clasts occurs in irregular patches in and veinlets parallel to cleavage (Figure 7A,B).

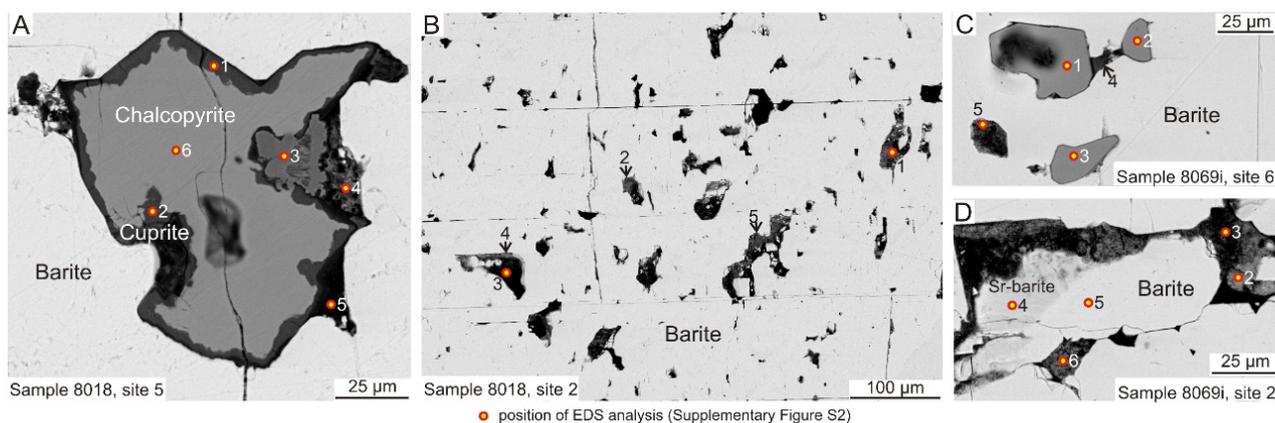


Figure 6. BSE images of mineral and fluid inclusions in barite veins. (A) Fractured chalcopyrite inclusion (analysis 6) with a cuprite and barite rim (1, 2) and engulfing pyrite (3). (B) Decrepitated fluid inclusions showing presence of trace amounts of Si, Al, Ca, Cl, Na (1, 2, 3, 4, 5) in various combinations. (C) Barite with anhedral chalcopyrite inclusions (1, 2, 3, 4) and decrepitated fluid inclusions (including traces of Si, Al, Fe, Na) (5). (D) Cluster of decrepitated fluid inclusions (2, 3, 6) following fractures, and patches of Sr-rich barite (4).

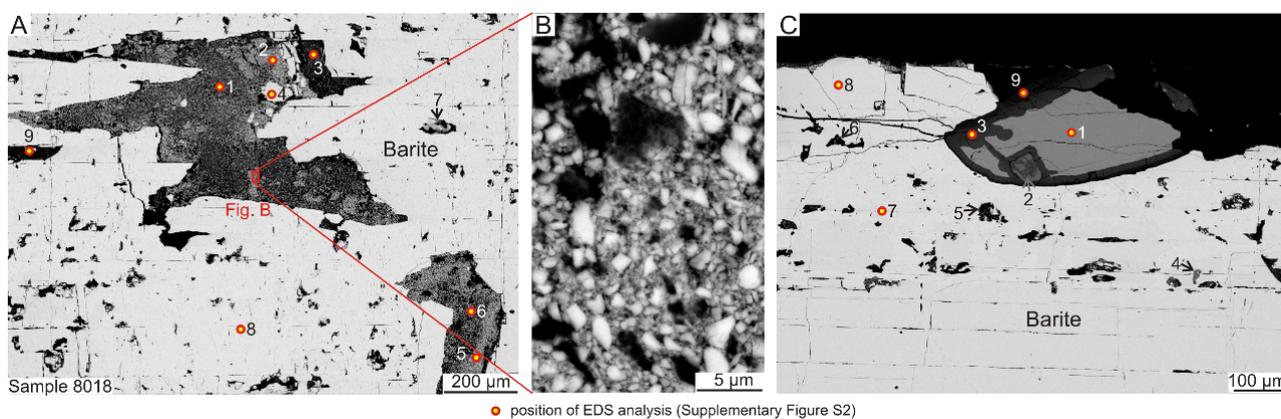


Figure 7. BSE images of cataclastic barite, chalcopyrite and pyrite in sample 8018. (A) Barite with fragmental (cataclastic) texture (1–4, 5–6) and cations in various combinations (Si, Al, Mg, Ca) plus Cl. (B) Zoom showing barite fragments with varying combinations of cations. (C) Barite engulfing chalcopyrite and pyrite (1, 2) with alteration halo made up of cuprite and limonite (3, 9). Fluid inclusions (5, 6) each show a strong alignment (horizontal in the image).

Two representative samples from barite veins, one from East River (8018) and the other from Bass River of Five Islands (8069i), were studied in detail using both BSE images and mineral analyses (Supplementary Figure S2). Barite in both samples contain chalcopyrite inclusions (Figure 6A,C), with an alteration halo at their rim enriched in Fe and Si with some Al and Ca (e.g., analysis 1 in Figure 6A). Such inclusions in a few cases engulf pyrite (Figure 6A). Chlorite inclusions (Figure 6 in Supplementary Figure S2) have FeO/MgO ~1.2. Cataclastic barite in sample 8018 (Figure 7A,B) has rare quartz grains (Figure 5a in Supplementary Figure S2). Both the cataclastic barite and many decrepitated fluid

inclusions yield EDS analyses with a few percent of the elements Si, Al, and Ca and in some cases K and Fe. Barite contains a few discrete patches tens of microns wide with high Sr (<2.5 wt.%) (Figure 6D; Supplementary Table S5), but otherwise Sr and Pb are below the detection limit.

4.4. Chemistry of Barite from Five Islands

Trace elements were determined by X-ray fluorescence (XRF) from six barite samples from the Five Islands area (Table 2). Strontium is relatively abundant in all samples (1.8% to 3.0%). As celestite was not observed in any of the field investigations, it is probable that most of the Sr is in the barite lattice, where it substitutes for barium. The Sr-rich patches analysed by EDS seem to be insufficient to account for the abundance of Sr by XRF. Barite (BaSO_4) and celestite (SrSO_4) are isostructural and form a complete solid solution series [18]. Some of the lead found in each of the samples may also substitute for Ba in the barite, since anglesite (PbSO_4) and barite are also isostructural. The site of rubidium and thorium within the barites is unknown and the amount of thorium found in the samples (40 to 50 ppm) is high. We could not locate any Th analyses from other Nova Scotian barites, but generally vein barite is reported in the literature to normally have <1 ppm Th [19,20].

Table 2. Trace element content of selected barite samples by XRF.

| Sample | 7791 | 8018 | 8023 | 8025 | 8069 | 8079 | Detection Limit |
|--------|------|------|------|------|------|------|-----------------|
| Sr | 2.8% | 1.8% | 2.6% | 3.0% | 2.5% | 2.7% | 0.01% |
| Pb | 9 | 8 | 9 | 10 | 9 | 10 | 1 ppm |
| Rb | 10 | 8 | 11 | 11 | 10 | 11 | 1 ppm |
| Th | 48 | 40 | 47 | 49 | 46 | 49 | 1 ppm |

Strontium can enter the lattice of minerals such as calcite, fluorite and barite, and can therefore be used to constrain the genesis of such low-Rb minerals [7,21]. Strontium isotope analyses (Table 3) were made on one fluorite, two calcite, and five barite samples from the Five Islands barite veins. Within the exception of the one fluorite sample (0.7127), the samples exhibit very uniform $^{87}\text{Sr}/^{86}\text{Sr}$ ratios between 0.71021 and 0.71054 (Figure 8). Other late Carboniferous analyses from the literature are also shown in isotope plots. These include analyses from barite deposits at the Brookfield [22], Walton [23,24] and Kinsac [25] deposits and Pb-Zn mineralization at those localities and at the Gays River and Jubilee deposits [7,26] (Figure 1a).

Sulfur and oxygen isotopes were determined on six barite samples from Five Islands. The $\delta^{34}\text{S}$ ranges from 14.0 to 16.2‰ (VCDT). These analyses fall within the range of barite at Walton and are a little higher than barite from Brookfield (Figure 9). The $\delta^{18}\text{O}$ ranges from 9.9 to 10.8‰ (VSMOW) (−19.5 to −20.3‰ PDB). We found no oxygen isotope data for barite elsewhere, but the value is lower than that found in calcite veins at Gays River [9].

Lead isotopes were determined on one galena sample (SFB87-2016) from the N-S fractures at Five Islands. The data compare well with other late Carboniferous galenas from the Kennetcook basin (Figure 10). These galenas have Pb isotopes that are similar to those of late mafic rocks, including dykes cutting Horton Group in the Kennetcook basin, late gabbro in the Wentworth pluton, and the youngest basalt in the Fountain Lake Group [8].

Table 3. Strontium, oxygen and sulfur isotope analyses of fluorite, calcite and barite.

| Sample | Locality No. | Mineral | Occurrence | $^{87}\text{Sr}/^{86}\text{Sr}$ | Uncertainty (2 Sigma) | $\delta^{18}\text{O}$ ‰ (VSMOW) | $\delta^{34}\text{S}$ ‰ (VCDT) |
|--------|--------------|----------|-----------------|---------------------------------|-----------------------|---------------------------------|--------------------------------|
| 8071 | 11 | Fluorite | breccia cement | 0.71271 | 0.00002 | | |
| 8071 | 11 | Calcite | breccia cement | 0.71054 | 0.00002 | | |
| 8025 | 10 | Calcite | vein | 0.71045 | 0.00003 | | |
| 7791 | 10 | Barite | lenticular vein | 0.71042 | 0.00002 | 10.40 | 14.60 |
| 8018 | 9 | Barite | vein | 0.71047 | 0.00002 | 10.50 | 16.23 |
| 8023 | 10 | Barite | lenticular vein | 0.71021 | 0.00002 | 10.80 | 14.50 |
| 8025 | 10 | Barite | lenticular vein | 0.71021 | 0.00003 | 10.70 | 13.98 |
| 8069 | 11 | Barite | lenticular vein | 0.71026 | 0.00002 | 9.90 | 14.28 |
| 8079 | 11 | Barite | lenticular vein | | | 10.50 | 14.98 |

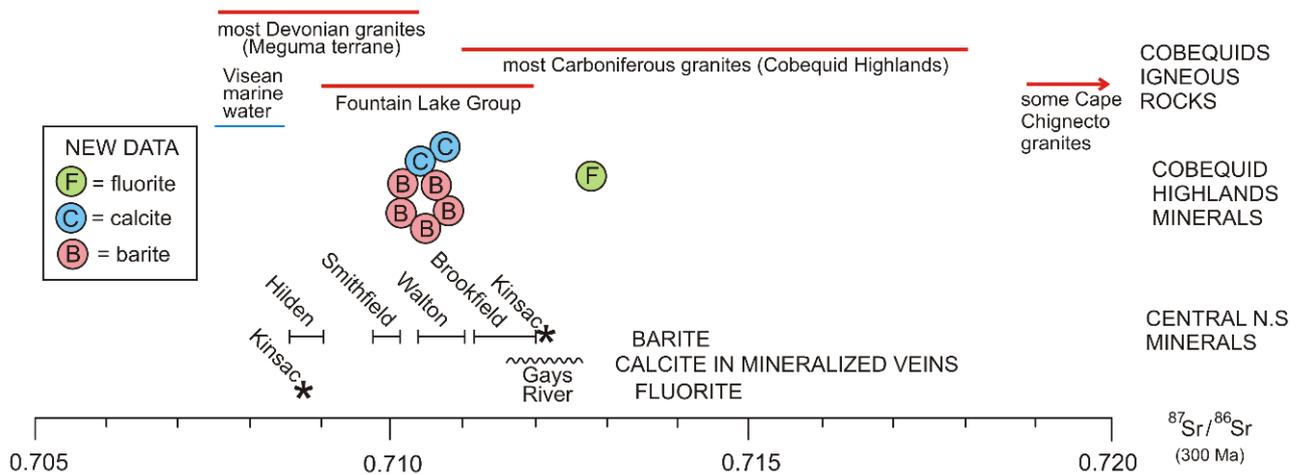


Figure 8. Initial Strontium isotope ratios. Data from Cobequid Highlands from this study; for central Nova Scotia from [7] (excluding outlier values), except [25] for Kinsac; for granites, etc., from [27,28].

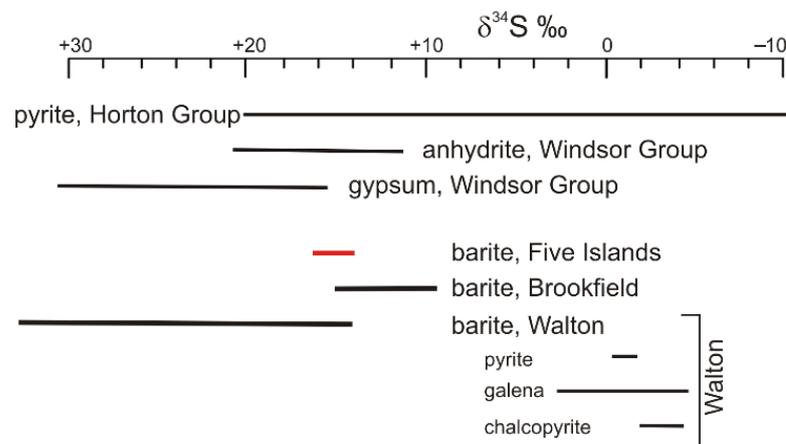


Figure 9. Sulfur isotope composition of barite and comparative rocks. Data from Cobequid Highlands from this study; for central Nova Scotia from [23,24].

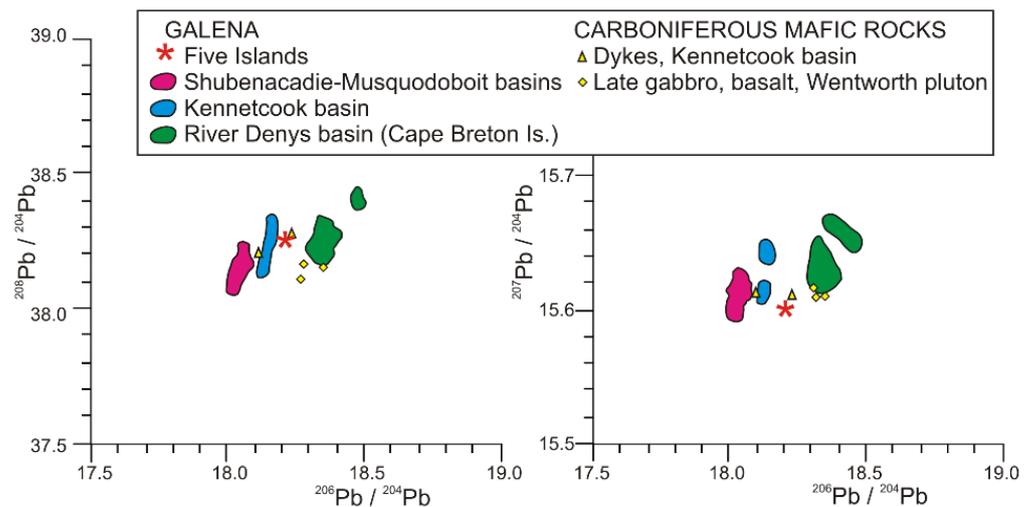


Figure 10. Lead isotope ratios from galena sample from Five Islands. Other data from galena in central Nova Scotia from [26]. Selected mafic rocks from [6].

4.5. Chemistry of Host Rocks from Five Islands

Petrographic studies of argillites and sandstones show that many have mm-scale tension gashes or small veins filled with quartz and/or calcite. Samples identified as altered also show calcite replacement of detrital plagioclase and an alteration halo of chlorite around tension gashes. Most argillites and many sandstones contain 1–2% hematite and argillites have 1–5% pyrite and in a few samples also minor chalcopryrite. Small veins in sandstones may have minor muscovite or chlorite.

Comparison of bulk chemical composition between altered and fresh host rock is evaluated according to distance from barite veins (Figure 11). There appears to be no relationship between Ba content and proximity to barite veins, consistent with the field observation that there is no systematic alteration halo adjacent to barite veins. The barite veins intruded country rock that had already been cut by different sets of mineralized veins. There is no systematic enrichment for any element except Ca in samples identified as altered, not even for Fe despite the observations of hematite and pyrite. Some altered samples show enrichment or depletion in K, Na and Mg, probably reflecting relative amounts of secondary muscovite, albite and chlorite, respectively.

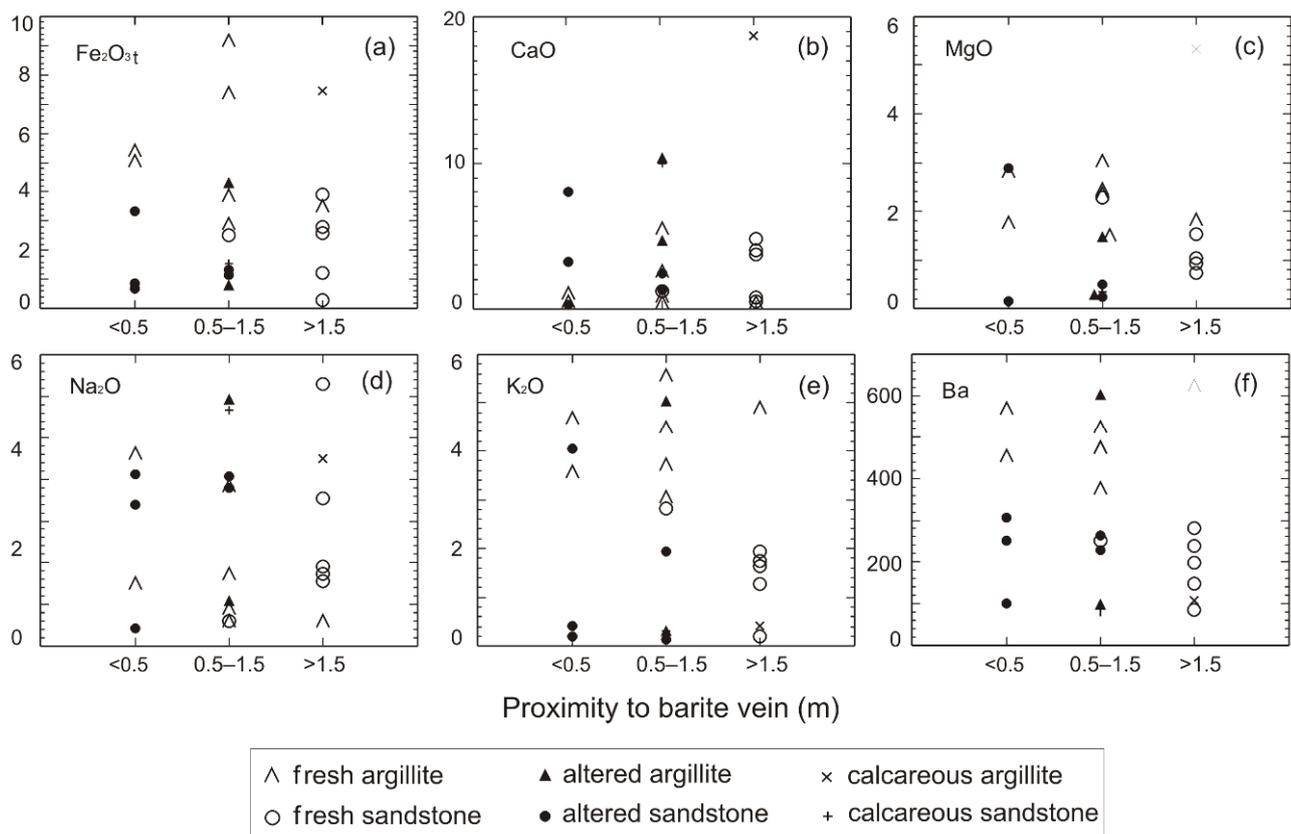


Figure 11. Geochemical composition of Horton Group host rocks compared with distance from barite veins, from the area north of Five Islands (localities 9–15). (a–f) show plots for different elements.

5. Discussion

5.1. Paragenesis of Veins Older Than the Barite Veins

We have used mineral textural relationships to establish the paragenetic sequence of the veins that cut the Horton Group sandstones and argillites (Figure 12). The relative ages of these mineral veins are consistent with the dated sequence of vein minerals mostly in Horton Group rocks along the Cobequid Fault from Lynn Road to West Advocate [6] (Figure 1b). In this sequence, albite veins seem to be the oldest, but overlap in age with quartz-chlorite veins and potassic alteration (producing secondary biotite) and are followed by calcite (\pm dolomite) veins, ranging in age from ca. 355 Ma to ca. 330 Ma during progressive deformation along the Cobequid Shear Zone (Figure 12). A very different mineral assemblage, in places occupying new fractures, is recognised following the onset of E–W deformation on the Minas Fault Zone at ca. 327 Ma. This assemblage includes pyrite, ankerite, hematite and magnetite, and younger titanite, zircon and REE minerals, which were not noted in the barite veins at Five Islands. In general, the Fe-rich mineralization is not well developed in the Five Islands country rock, but farther west trace amounts of barite post-date alteration of ankerite to limonite and partial dissolution of titanite in mineral vein fills (Supplementary Table S1). The fluorite-barite veins studied are located directly in country rock rather than being associated with older veins. This suggests a deformation phase with a different stress field from that earlier in the Carboniferous.

5.2. Geochronologic Constraints on Timing of the Barite Veins

The timing of emplacement of barite veins is poorly constrained (Figure 12). At Lynn Road, imprecise U–Pb ages were obtained from REE-rich allanite (313 ± 7 Ma) and monazite (320 ± 7 Ma), apparently older than the Five Islands barite [6]. The Pb–Zn–Mn–Ba mineralization at the Walton mine is younger than the emplacement of the Cheverie dyke,

which has similar mineralization, where fresh dyke rock was dated at 319 ± 4 Ma [29] (when corrected to modern standards as in [6]). The published Rb–Sr isochron age of 300 ± 6 Ma on altered Horton Group rocks [7] is interpreted as the last time that there was flow of hydrothermal fluids with Sr, and thus probably corresponds to the youngest barite precipitation event. The barite at Spicer Cove postdates deposition and deformation of the upper Ragged Reef Formation, dated as late Bashkirian (ca. 314 Ma) [16,30]. The possibility of a much younger age within the Carboniferous or even early Permian cannot be ruled out.

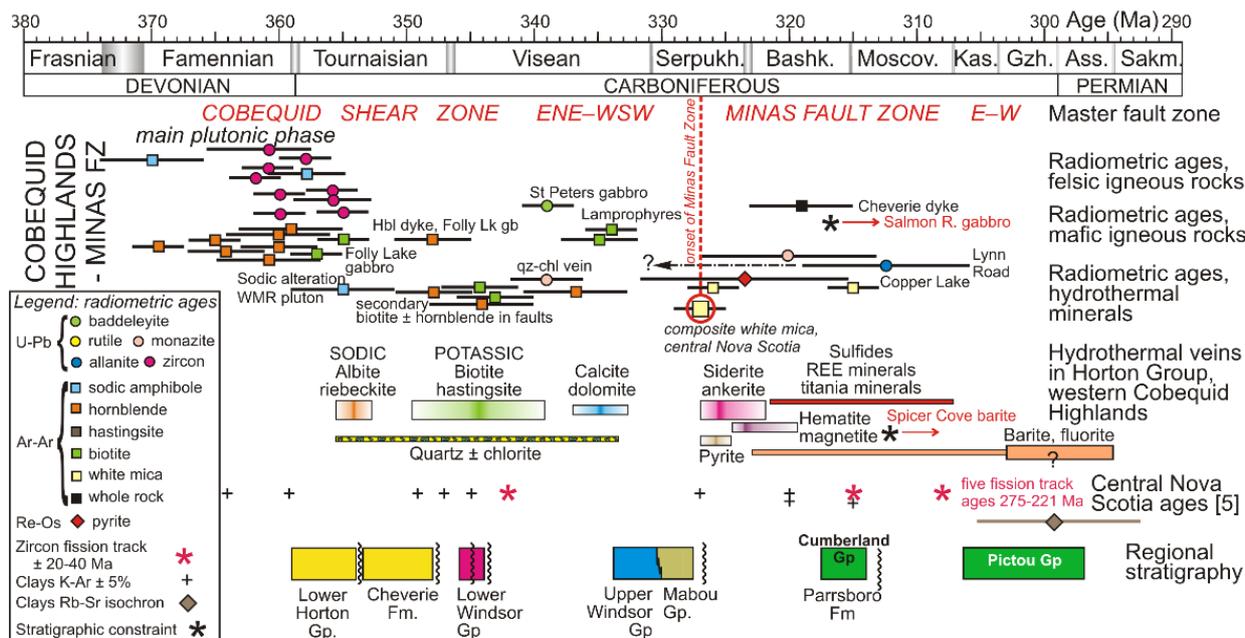


Figure 12. Timeline for mineral veins in Carboniferous rocks of the Cobequid Highlands.

5.3. Relationship of Barite to Pb-Zn Sulfide and Fe-Mn Oxide Mineralization

Barite is commonly associated with Mississippi Valley type Pb-Zn mineralization and in the Carboniferous basins of Nova Scotia barite has been regarded as co-genetic with Zn and Pb mineralization [22,24,31]. In the Walton deposit (Figure 1a), rare type 3 barite is described as intergrown with sulfides, perhaps by replacement of pre-existing siderite; types 1 and 2 barite show no distinctive relationship with sulfides, type 4 cross-cuts types 1–3, and type 5 lines vugs [24]. At Brookfield (Figure 1a), barite occurs in the centre of siderite veins and some barite veins cross-cut earlier deformed barite and siderite veins in which the two minerals appear intergrown [22].

Ankerite-siderite-magnetite mineralization is widespread along the Minas Fault Zone [6], including the large ankerite deposit at Londonderry (Figure 1a) with supergene enrichment to goethite and specularite. Nineteenth-century quarries, now overgrown, showed the iron ores cut by barite veins [32] and barite veinlets cut host sandstone [1]. At the East Mountain mine, barite fills vugs in the main pyrolusite-manganite deposit [3].

In the western Cobequid Highlands, studies of sequential vein fills [33] (p. 84, Figure 21D) show rare textural evidence for both galena and barite being late in the mineral paragenesis. Prospectors reports of localities 18 and 19 (Table 1) suggest mineral showings with galena, sphalerite and barite [34]. On the other hand, in the Five Islands area (occurrences 9–15, Table 1) barite is found in E–W brecciated fault zones lacking galena and sphalerite, and rare showings of galena and sphalerite are either stratabound or on N–S faults (localities 226, 227, 233, 234, 239 of [3]).

Thus the field occurrence of barite suggests that some barite veins are genetically related to Pb-Zn mineralization, but many barite occurrences post-date ankerite-siderite-magnetite mineralization and Pb-Zn mineralization. Analyses of decrepitated fluid inclu-

sions (Figure 6) and fluid inclusion studies at Brookfield [22] indicate an important role for Lower Carboniferous evaporites in the mineralizing process. The Sr isotope results suggest that the mineralizing fluids exchanged with a radiogenic source, with the arkosic Horton Group being generally interpreted as the most likely reservoir. The similarity of Sr isotopes (Figure 8) and S isotopes (Figure 9) in barite from Five Islands compared with data from Walton and Brookfield is also evidence for a common source.

5.4. Relationship of Barite Veins to Granites

There is a clear geographic relationship between the presence of late Devonian–earliest Carboniferous granite and the occurrence of barite veins (Figure 1b). Clusters of barite occurrences are found south of the Wentworth pluton, near the Pleasant Hills and North River plutons, close to the large granite dykes east of the Hanna Farm pluton [35] (p. 227), and north of the Cape Chignecto pluton. These plutons have experienced pervasive brittle deformation and fracturing through the Carboniferous [17,36] and have bulk rock contents of Ba averaging only a few hundred ppm. The uniformity of Sr and S isotopes, regardless of proximity to granite plutons, suggests that the granite was not a significant source of Ba. Furthermore, Pb isotopes suggest that substantial supply of Pb from the rather radiogenic granites [8] is unlikely. Rather, during regional deformation, sub-surface rooted granites deformed in a brittle manner providing pathways for mineralizing fluids. In contrast, in the intervening sedimentary rocks, commonly steeply dipping and cut by subvertical faults, deformation was more widely distributed.

5.5. The Significance of Fluorite

Globally, barite commonly co-occurs with fluorite [37] and these two minerals are characteristically found together in the Five Islands and Squally Point localities, but fluorite is absent farther east (localities 1–8, Table 1). Other evidence for abundant fluorine in late Carboniferous fluids is provided by the distribution of minor amounts of a TiO₂ mineral phase, zircon and some REE-fluorocarbonates in vein fills younger than ankerite and magnetite [6] (Figure 12). All these late minerals have mobility and precipitation favoured by abundant F [38–40] (respectively). The reason for evidence of high F in the late Carboniferous is unclear. In the early Carboniferous, alteration of amphibole and biotite in plutons has been proposed as a source of F [40]. In fluorite-barite deposits in the Rio Grande Rift (New Mexico, USA), the F has been shown to be derived from upwelling asthenosphere [41,42]. There, the F is associated with low pH magmatic fluids, which mixed with sedimentary brines and sulfide precipitation was inhibited by the low pH. Why F is more abundant in the later mineralization of the western Cobequid Highlands, compared to the east, remains unknown.

5.6. Events Younger Than the Barite Veins

The barite veins in the field are locally cut by NW–SE shears with calcite veins. Some barite veins also have euhedral calcite at their margin. At a microscopic level, the latest mineral phases to precipitate in almost open fractures include chlorite and kaolinite (Figure 5). Similar late open fractures with chlorite and kaolinite are found elsewhere in the Horton Group along the Minas Fault Zone (e.g., Lynn Road, [33]). The presence of trace amounts of Si, Al, and Fe in decrepitated fluid inclusions and cataclastic zones in barite veins suggest the percolation of late chlorite and kaolinite into barite veins along fractures and opened cleavage. The high Th content of barite veins may be of similar origin. The presence of cataclastic patches in barite veins, presumably the result of hydraulic fracturing based on its geometry, suggests a late overpressured fluid event. In the Bass River of Five Islands, some faults parallel to the barite veins contain a fault pug decimeters thick, comprising altered cataclastic country rock loosely cemented by quartz and calcite.

The timing of the late kaolinite and chlorite is unknown. Continuing fault movement along the Minas Fault Zone is assumed for the Permian and clearly demonstrable for the Triassic (particularly late Triassic) and early Cretaceous [43]. Kaolinite is unlikely under

arid conditions in the Permian, but has been recorded in both Triassic and particularly Cretaceous mudstones [44]. Fluids favouring precipitation of chlorite could be related to the North Mountain Basalt of late Triassic age [43].

5.7. Tectonosedimentary History of Carboniferous Mineralization

Two aspects of the Lower Carboniferous sedimentation south of the Cobequid Highlands played an important role in the history of mineralization in the region (Figure 13). First, the Horton Group includes arkosic sandstones and thick organic rich shale successions, which during mid-Carboniferous thrusting in the Kennetcook Basin [45] produced overpressured formation waters, presumably with considerable amounts of Ba from feldspars and HCO_3^- from breakdown of organic matter [9,26]. Second, the abundance of halite and gypsum in the lower Windsor Group provided abundant Cl^- and SO_4^{2-} anions that at elevated temperatures complexed with metallic cations.

Along the northern margin of the basin, igneous rocks provided an important heat source throughout the late Devonian and early Carboniferous (Figure 12). Even in the late Carboniferous, two mafic intrusions are known, one dating from ~319 Ma [29] and one 315 Ma or younger [46]. Thus, associated with this continental-scale shear zone there was a prolonged heat source to drive hydrothermal circulation. The sequence of sodic, potassic and carbonate vein minerals in the early Carboniferous (Figure 12) may represent relatively local circulation of fluids.

The major change in mineralization at the mid-Carboniferous unconformity can be related to overthrusting in the Kennetcook Basin [45] and the migration of overpressured fluids along the newly formed Minas Fault Zone. The occurrence of the large ankerite deposit at Londonderry and magnetite at Bass River (Figure 1b) close to the Folly Lake gabbro, the largest ferrogabbro intrusion in the Appalachians, is unlikely to be coincidental. Even the Pb isotope composition of galena in the Kennetcook Basin (Figure 10) is close to the composition of late mafic rocks in the region.

In central Nova Scotia, the availability of Windsor Group evaporites favoured the occurrence of Pb-Zn mineralization, with significant Fe and Mn mineralization at Walton and Brookfield, including some barite. As reviewed above, much of the barite in these two deposits appears to be late in the paragenetic sequence. As igneous activity waned and the geothermal gradient diminished, higher-temperature sulfides and carbonates were no longer transported in hydrothermally circulating fluids, but with the availability of SO_4^{2-} , barite became the dominant mineral even at relatively low temperatures. Solubility of barite diminishes rapidly at temperatures below 100 °C [47]. The source of Ba might have been from the breakdown of detrital feldspar in sandstone during burial to depths >2 km as Upper Carboniferous sediment continued to accumulate in the region immediately south of the Minas Fault Zone (Figure 1b), similar to the interpreted source for Pb in galena in central Nova Scotia [26].

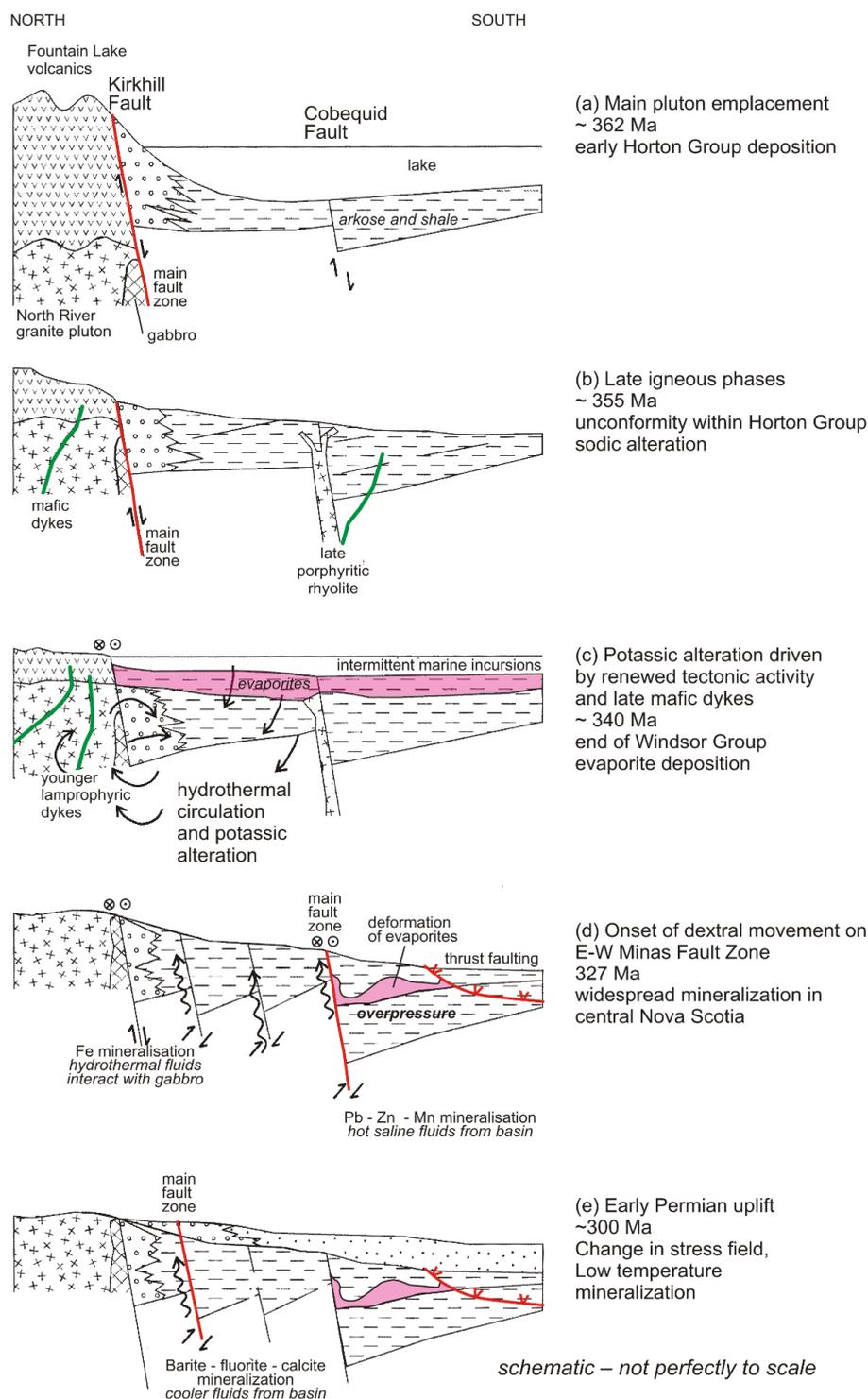


Figure 13. (a–e) Sequential evolution of the southern of the Cobequid Highlands through the Carboniferous.

6. Conclusions

1. Veins of barite, associated with fluorite and/or calcite, represent the youngest and probably coolest phase of a 70 Ma history of Carboniferous mineralized veins along the Minas Fault Zone. Their prominence close to granite plutons reflects brittle deformation of the deeply-rooted granites in a complexly deforming fault zone creating pathways for mineralizing fluids.

2. Many barite occurrences in the Carboniferous basins of central Nova Scotia post-date ankerite-siderite-magnetite-pyrolusite mineralization and Pb-Zn mineralization, some of which is younger than 319 Ma. Stratigraphic control shows that some barite is younger than 315 Ma. The published Rb–Sr isochron of 300 ± 6 Ma [7] marks the youngest significant Sr mobility event, likely related to barite emplacement.
3. The isotope chemistry of barite and associated fluorite and calcite is similar to that occurring in Pb-Zn-Mn-Ba mineralization, suggesting a role for fluids derived from evaporite deposits in the Lower Carboniferous basins of central Nova Scotia.
4. In the western part of the Minas Fault Zone, the availability of F played an important role in the fill of veins by a late titanite mineral, zircon, and REE fluorocarbonates. Comparison with Rio Grande Rift fluorite-barite deposits suggests the possibility of a mantle source for F. The precipitation of barite but no sulfides might reflect either relatively low temperatures (100–140 °C) or low pH.

Supplementary Materials: The following are available online at <https://www.mdpi.com/article/10.3390/min11121413/s1>, Figure S1: SEM data on host rocks, Figure S2: SEM data on barite veins, Table S1: Barite mode of occurrence, Table S2: Country rock XRF geochemistry, Table S3: Chlorite EDS geochemistry, Table S4: Biotite EDS geochemistry, Table S5: Barite EDS geochemistry.

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