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# Anomalous SedEx mineralization at the Walton Ag-Pb-Zn-Cu carbonate-hosted sulphide deposit (Nova Scotia, Canada): result of hydrocarbons?

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**Abstract:** Walton is a past-producing Ag-Pb-Zn-Cu sulphide carbonate-hosted deposit (0.41 Mt; head grade of 350 g/t Ag, 4.28% Pb, 1.29% Zn, and 0.52% Cu) hosted primarily by sideritized Viséan Macumber Formation limestone and juxtaposed to and replacing a barite ore body (4.5 Mt of >90% barite). Previous work demonstrated that mineralization came from heated (~300°C), saline (20–28 wt. % equiv. NaCl) fluids. The present study uses optical microscopy, SEM-EDS, and major- and *in situ* LA-ICP-MS trace-element signatures of the host, gangue, and ore phases to refine our understanding of the mineralizing fluid system. Sideritization of the Macumber Formation occurred after dolomitization. Dolomite and siderite are generally LREE-depleted, with mostly negative Ce anomalies and prominent negative Y anomalies. Pyrite has As levels ranging from <1 ppm to 7.7 wt. % that correlate positively with Ag (values up to 2,400 ppm); the latter likely accounts for most of the Ag in the deposit. The LREE-depleted patterns of various carbonate phases indicate that the ore fluids did not equilibrate with a LREE-rich reservoir, whereas negative Ce anomalies suggest precipitation from an oxidised fluid. The positive correlation between Ag and As implies their coupling and thus a similar source and/or transport mechanism. The proposed source of metals is from hydrocarbons, now preserved as abundant petroleum inclusions, sourced in the underlying Horton Group that may have been enriched in Ag, As, and Cu. The derivation of metals from hydrocarbons could explain differences between mineralization at Walton and other carbonate-hosted sulphide deposits in Nova Scotia that do not contain significant petroleum or Ag, As, and Cu.

**Keywords:** Walton deposit, Nova Scotia, sideritization, dolomitization, Macumber Formation, LREE patterns, trace element geochemistry, hydrocarbons.

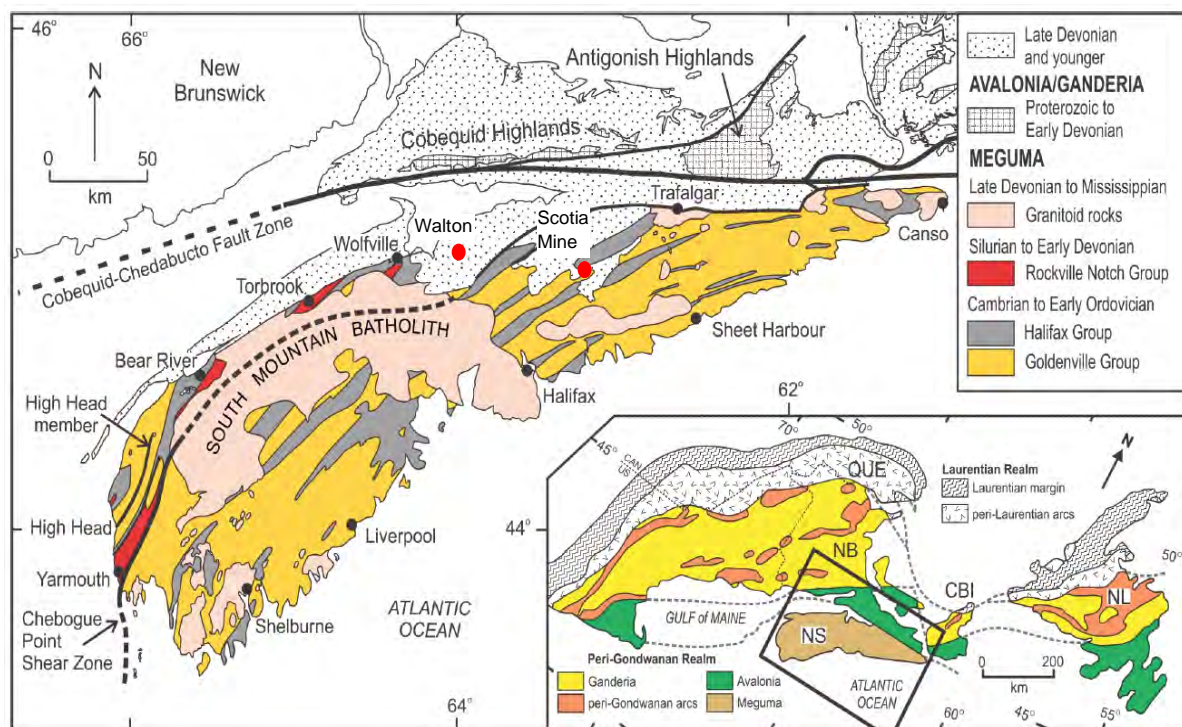
## Introduction

The past-producing Walton deposit located in Nova Scotia (Canada) consists of a composite sulphide ore body (0.41Mt; head grade values of 0.52% Cu, 4.28% Pb, 1.29% Zn, and 350 g/t Ag) that is overlain by a barite ore body (4.5Mt of >90% barite) (Cranstone, 1982). Walton has recently been referred to as a sedimentary exhalative (SedEx) deposit (Sangster, 2020), although previous studies have not assigned the deposit as such (e.g., Burt, 1995; Kontak & Sangster, 1998). The presence of a barite body overlying the sulphide Zn-Pb ore body is more comparable to a number of SedEx deposits (e.g., Anarraaq, Kelley *et al.*, 2004) and the extensive siderite alteration associated with the sulphide ore body (e.g., Savard *et al.*, 1998) is also a feature more common to SedEx deposits than Mississippi Valley-type (MVT) or Irish-type deposits (Leach *et al.*, 2005; Wilkinson, 2014). However, the anomalous Ag grades (>150 g/t) are not typical of SedEx, MVT, or Irish-type deposits. This study uses petrography and LA-ICP-MS analysis of host rock, gangue, and sulphide minerals to provide insights into the origin of the pre-ore siderite alteration and the anomalous metal content.

## Geological Setting

The Walton deposit is located in the Kennetcook sub-basin of southern Nova Scotia which overlies siliciclastic basement rocks of the Meguma terrane, the most outboard terrane of the northern Appalachian orogen (Fig. 1). This terrane is dominated by metaturbiditic rocks of the Neoproterozoic-Ordovician Meguma Supergroup (Waldron *et al.*, 2009; White, 2010) and Late Devonian meta- to peraluminous granites (*ca.* 380Ma; Bickerton *et al.*, 2022), with lesser amounts of Silurian to Triassic strata.

The Meguma Supergroup is dominated by a lower sandstone unit that is overlain by a shale-rich unit (White, 2010). Overlying this are metavolcanic and metasedimentary rocks of the Silurian-Devonian Rockville Notch Group (White & Barr, 2012). Regional Neocadian deformation and lower greenschist facies metamorphism of these rocks was followed by deposition of the Late Devonian-Early Carboniferous (Tournaisian) Horton Group, which predominantly consists of terrestrial sandstone, shale, and conglomerate (Giles *et al.*, 1979; Utting *et al.*, 1989). This succession thickens

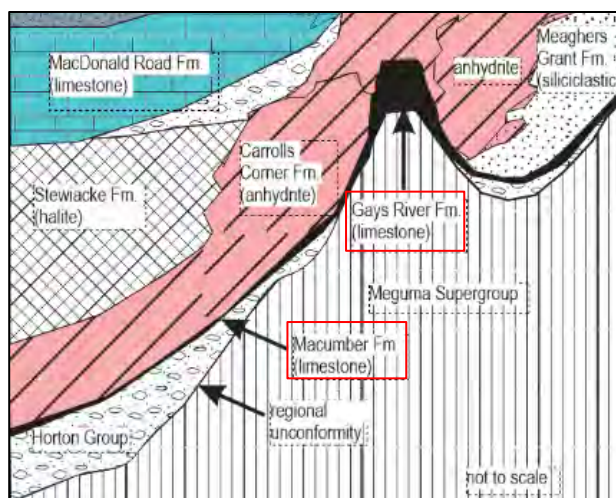


**Figure 1.** Simplified geological map of Nova Scotia with the locations of Walton and Scotia Mine in red. Modified from White & Barr (2012) and references therein.

considerably offshore in the large Maritimes Basin depocentre (Howie & Barss, 1975) and importantly includes widespread bimodal volcanic rocks at its base (see Dunning *et al.*, 2002 for discussion). This clastic sequence has been suggested as a potential source of MVT-mineralizing fluids (Ravenhurst *et al.*, 1989; Sangster *et al.*, 1998b, c).

The Mississippian (Viséan) Windsor Group, which overlies the Horton Group, consists of several carbonate and evaporitic units that commence with a basal marine transgression referred

to as the Macumber Formation (Boehner *et al.* 1989; Fig. 2). This formation is a laminated, bituminous limestone that locally passes laterally to biohermal carbonate mud mounds on basement palaeotopographic highs (Gays River Formation; Giles *et al.*, 1979; Lavoie & Sami, 1998). Both facies host mineralization – the Scotia Mine (formerly known as Gays River) deposit in dolomitized mound facies (Akande & Zentilli, 1984) and the Walton deposit in sideritized laminated facies (Sangster *et al.*, 1998a). The overlying formations are the Carrolls Corner (anhydrite), Meaghers Grant (sandstone and sandy shale), or Stewiacke (halite) formations.



**Figure 2:** Simplified stratigraphy at Scotia Mine and Walton. Note that the Gays River and Macumber formations represent different facies of time stratigraphic equivalent units. Modified from Giles & Boehner (1982).

## Methods

Petrography was carried out on approximately 50 polished thin sections to document alteration and mineralization styles. From these, a suite of carbonate (calcite, dolomite, ankerite, and siderite) and pyrite phases were characterised using BSE-EDS-CL imaging at Laurentian University (Sudbury, ON, Canada). The latter provided the basis for *in situ* trace element analysis using laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) analysis at Laurentian University. Details of the analytical protocol used can be found in Mathieu *et al.* (2022). Spot size for carbonates was either 15µm or 50µm depending on the size of the mineral, whereas all sulphide spots were 15µm.

## Results

### Petrography

The three general stages of the paragenesis (pre-ore, ore-stage, and post-ore; Fig. 3) were established by using transmitted and reflected light microscopy and BSE-EDS-CL imaging and



	Pre-ore	Ore-stage	Post-ore
Limestone	—		
Calcite	—		—
Pyrite	—	— — —	
Marcasite	—	—	
Dolostone	—		
Siderostone	—		
Baryte ore body	—		
Sulphate	—		
Siderite		—	—
Galena		— —	
Baryte		—	—
Tennantite		— —	
Chalcopyrite		— — —	
Sphalerite		— —	
Bornite			—
Arsenopyrite			—

**Figure 3:** Simplified mineral paragenesis at Walton based on earlier studies by Boyle (1972), Burt (1995), and this study.

analysis of mineralized and unmineralized samples. Representative photomicrographs of the mineralogy of the deposit are depicted in Figure 4.

Unmineralized and unaltered Macumber Formation limestone from an area well outside of the Walton deposit has primary porosity that was occluded by a blocky calcite cement (Fig. 4A). At Walton, the Macumber Formation is sideritized, but this study indicates evidence for a prior dolomitization event (with some ankerite) (Fig. 4B, C). Pseudomorphs of siderite-galena-barite after an earlier mineral (identity uncertain; likely a sulphate such as anhydrite) are abundant (Fig. 4G). The siderite is grouped into multiple types: siderostone (sideritized limestone), siderite pseudomorphs after sulphate, and various types of siderite cement. The base-metal ore-stage is dominated by massive pyrite with varying amounts of chalcopyrite, tennantite, galena, and sphalerite (Fig. 4D-L). The pyrite can be grouped into pyrite framboids, fine-grained pyrite in the Horton Group, and hydrothermal pyrite (includes replacement and colloform textures). Abundant hydrocarbon inclusions (i.e., petroleum) are present in the barite and seen as light blue under ultraviolet light (Fig. 5).

#### **Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) analyses of carbonates and sulphides.**

Post-Archaeon Australian Shale (PAAS)-normalised spider diagram for the Macumber Formation limestone (Fig. 6A) is convex-like with slightly positive Ce and Y anomalies, whereas the blocky calcite cement in it has a light rare-earth element (LREE)-depleted pattern with a large negative Ce anomaly and

slightly positive Y anomaly (Fig. 6A). The dolostone, dolomite, ankerite, and siderite spider diagrams are mostly LREE-depleted with positive Eu and negative Ce and Y anomalies (Fig. 6B, C). The  $\Sigma$ REEY (sum of rare-earth elements and yttrium) in carbonates ranges from 1 to 290 ppm and is generally lowest in dolomite and ankerite and highest in siderite.

Several different pyrite types occur, and their trace metal contents are summarised in Figure 7. Whereas the Ni and Co contents vary greatly from <10 to 10,000 ppm and overlap (Fig. 7A), the hydrothermal pyrite shows higher As (up to 7.8 wt. %) and Ag (<2,400 ppm) with an overall positive correlation (Fig. 7B). Hydrothermal pyrite also contains significant Pb (up to 7,700 ppm) and Tl (up to 1,300 ppm) and is more enriched than other pyrite types (Fig. 7C); these elements show a weakly positive correlation. Additional elements such as Cu and Zn are also enriched in hydrothermal pyrite.

Pyrite framboids have more Mo and Se on average than hydrothermal pyrite (Fig. 7D), which typically has Se below the limit of detection (LOD) and Mo <100 ppm. Arsenic (average = 1,800 ppm) and Ag (average = 170 ppm) are also enriched in the pyrite framboids but not as much as in the hydrothermal pyrite (Fig. 7B). Horton Group pyrites are very similar in their element concentration to the pyrite framboids. Positive correlations are noted between As and Ag for these pyrites, but less so for Pb and Tl (Fig. 7B, C).

## **Discussion**

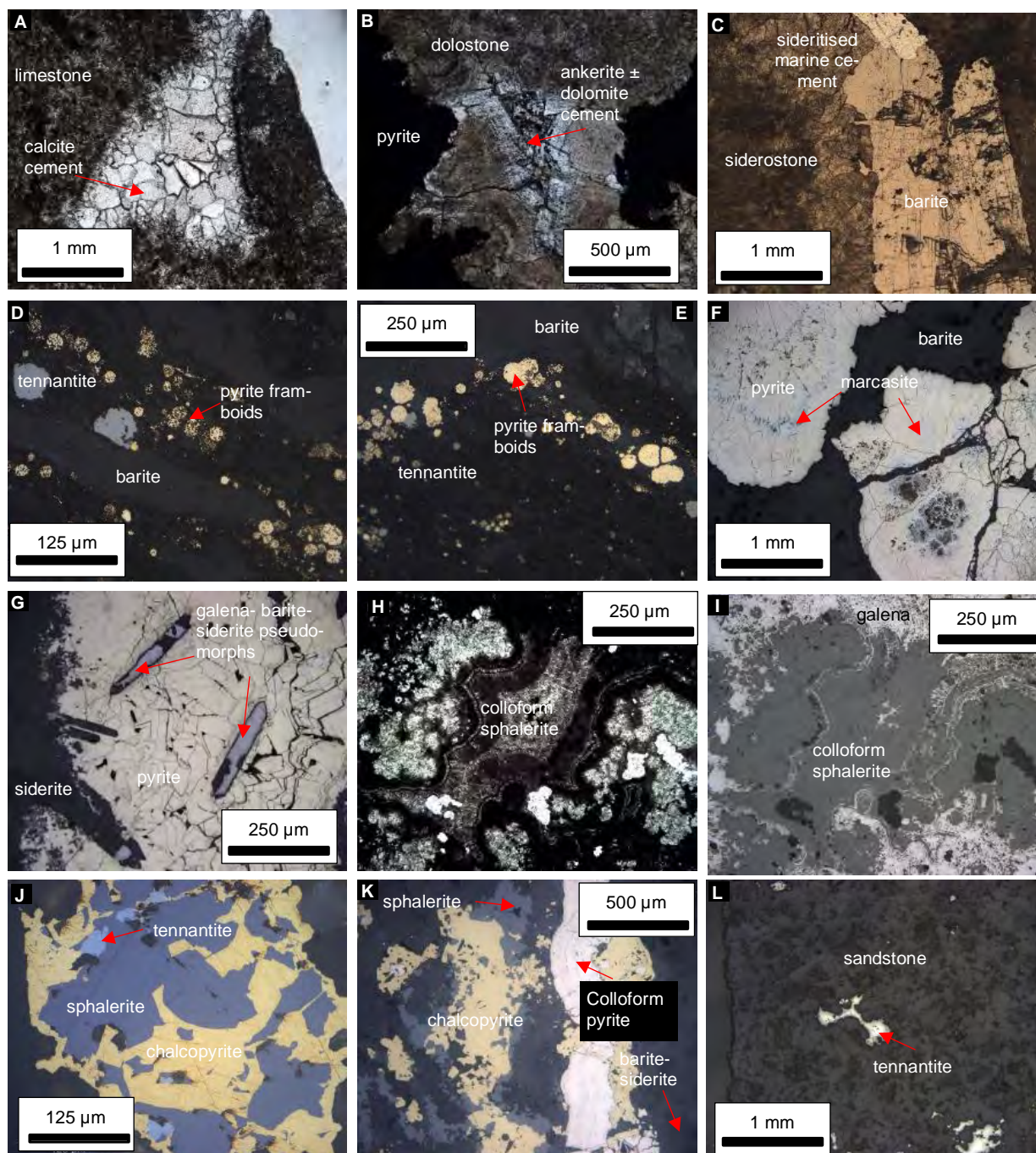
### **Sulphates**

The origin of the overlying barite ore body is unclear with previous studies suggesting replacement of the Macumber Formation or the overlying evaporites (Boyle, 1972). Sulphide ore bodies at numerous SedEx deposits are interpreted to represent replacement of earlier overlying barite bodies (e.g., Kelley *et al.*, 2004; Magnall *et al.*, 2016b; Reynolds *et al.*, 2021). Observations at Walton are no different with abundant sulphide pseudomorphs after sulphates and also cutting and replacing the barite ore body (Burt, 1995; this study).

### **Nature of Sideritization**

The unaltered Macumber Formation limestone has a shale-normalised REEY pattern that is slightly convex-like and unlike that of seawater with elevated LREEs and absence of negative Ce anomalies (e.g., Bau *et al.*, 1997). The reason for this is unclear, but it could be due to the adsorption of REEs onto fine-grained material (e.g., organic matter and/or clays) affecting the pattern, as has been widely suggested in many studies (e.g., Bau *et al.*, 1996). In contrast, calcite cement in the Macumber Formation limestone is clearer than the host limestone and has a REEY pattern similar to seawater, i.e., a large negative Ce anomaly, a slight positive Y anomaly, and LREE < middle rare-earth element (MREE) < heavy rare-earth element (HREE) (e.g., Bau *et al.*, 1997).

Whole-rock REEY data for unaltered and sideritized Macumber Formation limestone, the former from outside the mineralized area, have flat PAAS-normalised REEY patterns (Sangster *et al.*, 1998a; Fig. 6D) that are shale-like but relatively depleted in  $\Sigma$ REEY.



**Figure 4:** Walton mineralogy in plane polarised light (PPL: A, B, C, H) and reflected light (RL: D, E, F, G, I, J, K, L) (A) Macumber Formation limestone with primary porosity occluded by blocky calcite cement. (B) Dolomitized Macumber Formation limestone with ankerite-dolomite cement. (C) Sideritized Macumber Formation limestone, sideritized marine calcite cement, and barite occluding primary porosity. (D-E) Pyrite framboids. (F) Concentric pyrite with marcasite bands. (G) Galena-barite-siderite pseudomorphs after sulphate (likely anhydrite). Host rock replaced by colloform pyrite. (H-I) Photomicrographs of colloform sphalerite partially replaced by galena. (J) Early tennantite replaced by chalcopyrite. Sphalerite precipitated after this earlier chalcopyrite and is then replaced by a second generation of chalcopyrite. (K) Colloform pyrite and sphalerite replaced by chalcopyrite. (L) Tennantite in the Horton Group sandstone.



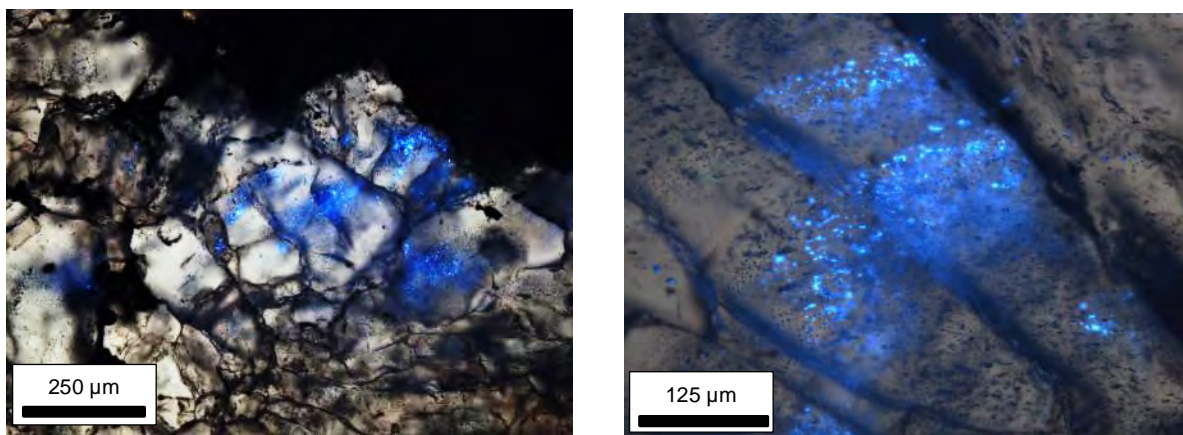


Figure 5: Photomicrographs of hydrocarbon inclusions (i.e., petroleum) in the barite under ultraviolet light showing light blue fluorescence.

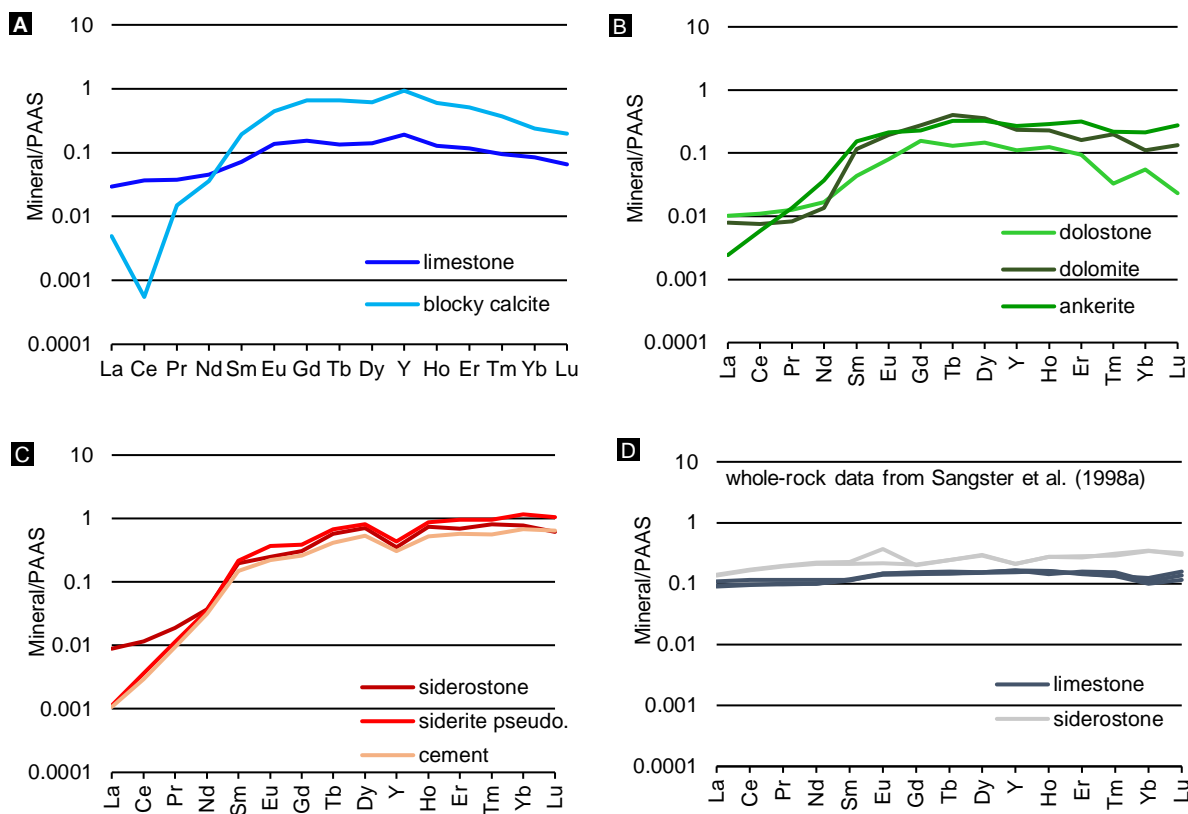
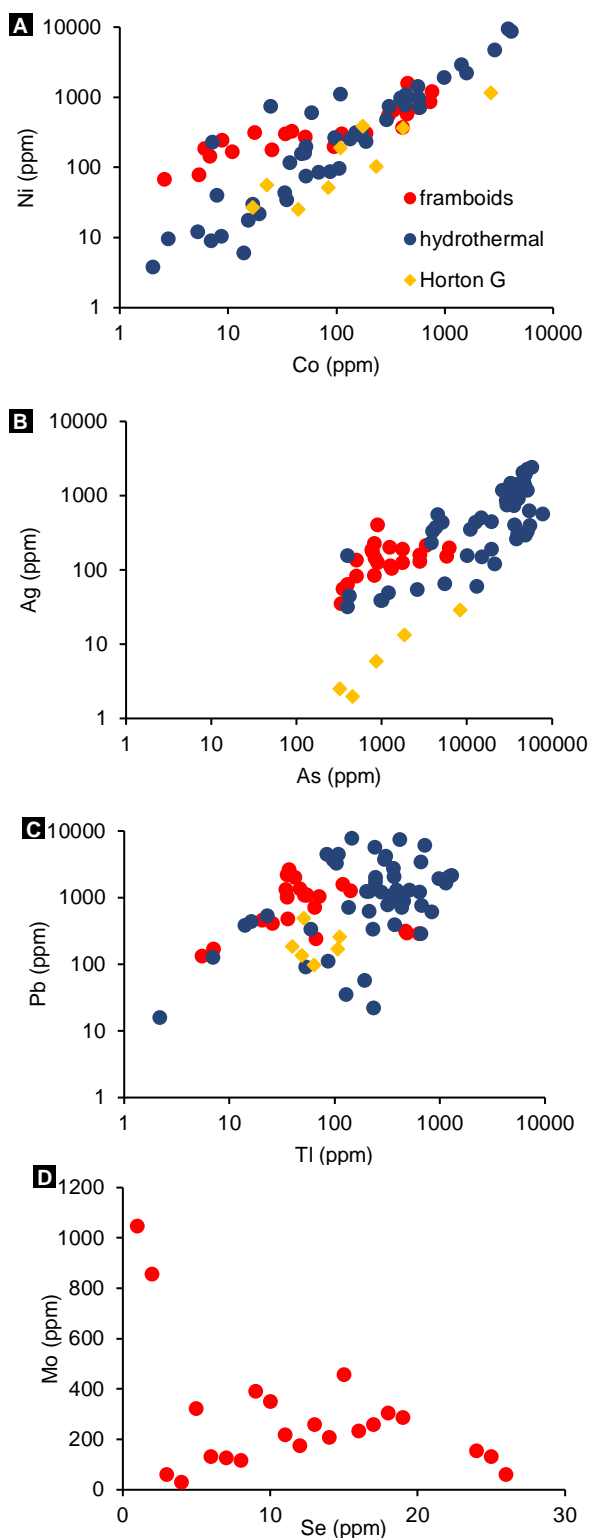


Figure 6: Representative PAAS-normalised (Pourmand et al., 2012) plots of LA-ICP-MS analyses of different carbonate stages from Walton: (A) calcite, (B) dolomite and ankerite), (C) various siderites. (D) PAAS-normalised plot of whole-rock data of Macumber Formation limestone and siderostone from Sangster et al. (1998a).



**Figure 7:** Bivariate plots of trace element data in pyrite types at Walton as determined from LA-ICP-MS spot analyses.

This is in contrast with the LA-ICP-MS data of the limestone and siderostone and support the contribution of organic matter and clays to the REEY pattern. Additionally, it is noted that the sideritized samples have a larger  $\Sigma$ REEY than the unaltered limestone samples which Sangster *et al.* (1998a) attributed to

a net loss of mobile elements relative to the immobile REEY or uniform enrichment of REEY in the siderite by the sideritising fluids. A description of the samples used was lacking, but the whole-rock data shows 7.85 wt. % Ba (suggesting the presence of barite). Therefore, incorporation of REEY in barite must also be considered a possibility.

The REEY patterns for all types of siderite (Fig. 6C) are consistently LREE-depleted and contrast to the patterns for the blocky calcite (i.e., lack negative Ce and positive Eu anomalies; Fig. 6A) and the whole-rock data from Sangster *et al.* (1998a). Their LREE depletion and negative Y anomalies likely reflect the input of diagenetic or hydrothermal fluid(s) that were oxidized based on the slight negative Ce anomalies (<0.90) and positive Eu anomalies (up to 1.40) (anomalies quantified using equations in Bau & Dulski, 1996). The patterns for the various types of Ca-Mg carbonates (Fig. 6B) are generally like the siderites except their relative enrichment in LREE, which is likely contamination related. It is noted that ankerite and siderite from the MacMillan Pass SedEx district (NWT, Canada) also exhibit LREE-depleted patterns (Magnall *et al.*, 2016a). The LREE-depleted signals of the Walton carbonates suggest fluids did not equilibrate with a reservoir enriched in LREEs, such as the underlying Horton Group, which has previously been the suggested fluid aquifer and/or proposed source of the metals in the fluids for Walton (Kontak & Sangster, 1998), or possibly even the much deeper Meguma Supergroup rocks. The actual timing and duration of of sideritization post limestone deposition remains unclear, although we note that Savard *et al.* (1998) suggested that the siderostone is probably not related to mineralization.

Savard *et al.* (1998) interpreted the siderostone to be a product of diagenesis that formed under shallow burial conditions based on petrography and an interpretation of the  $\delta^{18}\text{O}$  ( $\delta^{18}\text{O}_{\text{VSMOW}} = 25.0$  to  $27.6\%$ ), and  $\delta^{13}\text{C}$  ( $\delta^{13}\text{C}_{\text{VPDB}} = -5.1$  to  $-2.8\%$ ) isotopic data. Such negative C isotopic values are observed in the Windsor Group carbonates (Savard & Kontak, 1998; Savard *et al.* 1998) and indicate an unknown amount of involvement of organic matter (the absolute amounts depend on the  $\delta^{13}\text{C}$  signature of the organic component). Negative  $\delta^{13}\text{C}$  signatures can be generated during or immediately after bacterial sulphate reduction (BSR) or thermochemical sulphate reduction (TSR) (e.g., Mozley & Carothers, 1992; Machel, 2001). At Walton, the reduction of evaporites is likely TSR-related and utilised organic matter and/or petroleum (Boyle *et al.*, 1976; Kontak & Sangster, 1998) which could have generated C with negative  $\delta^{13}\text{C}$  values, thus TSR reactions and siderostone formation may be coupled. Alternatively, and as was alluded to above, there is significant organic matter in the Macumber Formation limestone and obtaining C isotopes using a technique, such as bulk sampling, that is not *in situ* could have resulted in the C isotopes having a mixed signature of siderite and organic matter.

### Pyrite Chemistry

High As in pyrite is consistent with previous studies showing late pyrite rims have > 4 wt. % As (Burt, 1995; Sangster *et al.*, 1998a). Arsenic and Ag in pyrite are variable but are positively correlated which suggests a similar paragenesis and thus were

likely transported together. Pyrite is abundant in the studied samples and when combined with their high Ag values (to 2,400 ppm) it can account for much of the Ag at the deposit. The hydrothermal pyrite is chemically distinguished from pyrite framboids by higher Pb, Tl, and As contents, which were likely inherited from the hydrothermal fluid(s). Sedimentary-diagenetic pyrite typically fall within the range of  $0.5 < \text{Ni}/\text{Co} < 100$  (Gregory *et al.*, 2015); however, at Walton even the hydrothermal pyrite falls within this range. The average Palaeozoic sedimentary pyrite has 35.4 ppm Co and 243 ppm Ni ( $n = 626$ ; Gregory *et al.*, 2015), which are both lower than for the averaged pyrite framboid data at Walton ( $n = 19$ ; Co = 236 ppm, Ni = 463 ppm). Partitioning of trace elements into pyrite is likely influenced by sedimentary clays and organic matter (e.g., Large *et al.*, 2014) and could explain the enrichment observed in the pyrite framboids at Walton.

### Metal content of hydrocarbons

Both the Macumber Formation and the Horton Group at Walton contain organic matter. Boyle (1972) reports that the Horton Bluff Formation of the Horton Group contains up to 4.75 wt. % carbon. Bitumen has been demonstrated to be enriched in As (to 400 ppm), Cu (to 80 ppm), Ag (to 300 ppm), and Fe (to 4.4 wt. %) (Saintilan *et al.*, 2019; Herazo *et al.*, 2020). Therefore, it is possible that the organic matter in the Macumber and Horton Bluff formations was enriched in these metals, which would explain anomalous base-metal concentrations, if these rocks were in fact the source of the metals, as has been suggested (Boyle, 1972; Kontak & Sangster, 1998).

### Conclusions

Evaporites overlying the Macumber Formation were important as a sulphur source that complemented the ingress of mineralizing fluids to form the Walton deposit. Reduction of sulphate to sulphide was likely coupled to oxidation of organic carbon which contributed to the subsequent sideritization of the Macumber Formation limestone and its light  $\delta^{13}\text{C}$  signal. The siderostone was not of marine origin but instead likely part of the ingress of a preceding Fe-rich hydrothermal event prior to mineralization. Hydrocarbons (i.e., petroleum) seen in barite was likely sourced from the reduced, organic-rich sulphidic units in the Horton Group and may have been a source of the metals at Walton. Future work will involve *in situ* analysis of isotopes (O, S) using secondary ion mass spectrometry (SIMS) to further refine these data from previous studies. Additionally, the metal concentration of petroleum inclusions will be measured via LA-ICP-MS to determine if in fact they are metalliferous.

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