

PRELIMINARY INVESTIGATIONS OF THE FLUORITE MINERALIZATION IN THE SEDIMENT- AND RHYOLITE-HOSTED AGS VEIN SYSTEM, ST. LAWRENCE, NEWFOUNDLAND

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ABSTRACT

Fluorite veins in the St. Lawrence area were traditionally thought to be mainly hosted in the St. Lawrence Granite. The lack of economic fluorite deposits in the country rocks was explained by the notion that the sedimentary rocks were hornfelsed by the intrusion of the granite, thereby becoming impermeable to the mineralizing fluids; and/or that the fluorite being deposited in fissures formed as a result of cooling and contraction in the granite and that these fissures narrowed and closed as they entered the country rocks. The AGS vein system is the first known example of economic quantities of fluorite mineralization being hosted in country rocks.

The AGS vein system is hosted in sedimentary rocks and rhyolite sills that intrude the sediments. The rhyolite sills are believed to be genetically associated with the St. Lawrence Granite, but the relative timing of the two rock types is not known. The two main controls on fluorite mineralization in the AGS area are the high-angle faults that contain most of the fluorite veins and the rhyolite sills that are spatially associated with the fluorite mineralization. The role of the rhyolite sills is not well understood, but they are likely responsible for fracturing the overlying sedimentary rocks; thereby preparing the groundwork for fluid influx. Repeated movements along the faults allowed for several phases of fluorite mineralization.

The paragenetic sequence for mineralization at the AGS vein system includes seven phases of hydrothermal activity: 1) brecciation of the host rocks, 2) purple fluorite stockwork and hydrothermal breccia, 3) banded, fine-grained, fluorite and coarse-grained yellow, red, clear and white fluorite, 4) chalcedony–fluorite, 5) grey, green, blue and clear, cubic fluorite, 6) blastonite, and 7) late quartz. The evolution of the mineralizing fluids shows similarities to that described in the fluorite deposits of the Nabburg–Wölsendorf area in Germany, where a low-viscosity fluid-type mineralization changed into a high-viscosity fluid type. The change in viscosity is interpreted to be related to increasing amounts of clay minerals in the fluid, resulting from extended fluid–rock interactions, eventually leading to the formation of argillaceous fault gouges. In the St. Lawrence area, the first type of mineralization is represented by the purple fluorite and the second type is represented by the coarse-grained yellow, green, blue-grey, white and clear fluorites. The banded, fine-grained and yellow fluorite may represent a transition between the two types.

INTRODUCTION

Fluorite mineralization on the Burin Peninsula has long been known to be associated with the St. Lawrence Granite (SLG), occurring as veins that are typically hosted in the granite. A few peripheral veins had been previously identified, but no significant mineralization was associated with these until the discovery of the sediment- and rhyolite-hosted AGS deposit by Canada Fluorspar Inc. (CFI) in 2013. This discovery expanded exploration efforts and shifted the focus to include the country rocks that were previously not considered to have potential to host significant mineralization.

This study investigates the AGS vein system to better understand the genesis of the fluorite mineralization, which will help in further exploration for similar-style deposits in the St. Lawrence area and elsewhere in Newfoundland.

EXPLORATION HISTORY

Fluorite in the St. Lawrence area was discovered in the 1800s by local residents, with the first mining possibly having been undertaken by French settlers before 1870 (Edwards, 1991). Exploration work in the early 1900s identified over 35 fluorite veins (Sparkes and Reeves, 2015). The St. Lawrence Corporation of Newfoundland started

mining from the Black Duck Vein in 1933, and since then mining had continued intermittently until the early 1990s.

Fluorite in the AGS area was first discovered by Newfoundland Fluorspar Ltd. (Newfluor) at the Open Cut Pit (west end of AGS vein system) in the late 1940s, and the occurrence was called the Grebes Nest (Smith, 1957; Sparkes and Reeves, 2015). Limited diamond drilling and trenching in 1940s by Newfluor only intersected a few narrow fluorite veins east of Grebes Nest, and trenching completed by Alcan in the 1960s produced mixed results (Smith, 1957; Sparkes and Reeves, 2015). Around 1990, Minworth mined out approximately 4000 tonnes of ore from the Open Cut Pit area, and in 1999 Burin Minerals removed some material from the Open Cut Pit for lapidary and ornamental use.

Since 2012, CFI has carried out extensive exploration in the St. Lawrence area, including in the AGS area (Sparkes and Reeves, 2015). The program included ground Horizontal Loop Electromagnetic (HLEM) Max-Min and magnetometer surveys, airborne Versatile Time Domain Electromagnetic System (VTEM) and magnetometer surveys, prospecting, mapping, trenching and drilling. In 2013, based on the results of the geophysical surveys, drilling and trenching were undertaken in the AGS area, which resulted in the discovery of the AGS deposit.

FLUORITE USES AND MARKET

The mineral fluorite (CaF_2) is the main source of fluorine that has a wide variety of industrial uses. Fluorite ore is divided into three main types based on the purity. ‘Acid grade’ fluorite (more than 97% fluorite) is used in oil refinery, production of organofluorine compounds (Teflon, refrigerants, Freon, *etc.*), and in etchant and cleaning agents (<https://www.earthmagazine.org/>, USGS webpage: <https://minerals.usgs.gov/minerals/>). ‘Ceramic grade’ fluorite (85–97% fluorite) is used in manufacturing of opalescent glass, enamels and cooking utensils. ‘Metallurgical grade’ fluorite (60–85% fluorite) is used as a flux in steel and aluminium production.

World production of fluorite gradually increased through most of the 20th century, but declined slightly in the early 1990s due to restrictions in chlorofluorocarbon (CFC) use in refrigerants (USGS: <https://minerals.usgs.gov/minerals/>). The leading producers of fluorite, in decreasing order, are China, Mexico, Mongolia, South Africa, Vietnam and Kazakhstan.

GEOLOGICAL SETTING

REGIONAL GEOLOGY

Rocks in the St. Lawrence area are part of the Avalon Zone, which is the most easterly tectonostratigraphic com-

ponent of the Appalachian orogeny in Newfoundland (Williams *et al.*, 1974; Williams, 1995; van Staal and Zagorevski, 2017; Figure 1). The Avalon Zone, as defined in North America, extends from eastern Newfoundland to North Georgia for approximately 3000 km (O’Brien *et al.*, 1998). Avalonian rocks are correlated with the Caledonides in the United Kingdom, as well as with the rocks of the Pan African orogenic system. In Newfoundland, the Avalon Zone is approximately 600 km wide, extending from the Dover Fault in the west to the eastern boundary of the Grand Banks in the east.

The Avalon Zone consists of Neoproterozoic arc-related volcanic and sedimentary rocks that are fault-bounded and were subjected to the Neoproterozoic Avalonian orogeny, resulting in folding, faulting, uplift and erosion (Williams *et al.*, 1974; Williams, 1995; Taylor, 1976; King, 1988; O’Brien *et al.*, 1996; van Staal and Zagorevski, 2017). The metamorphic grade is generally low, ranging up to lower greenschist facies (Papezik, 1974). This was followed by the deposition of Cambrian–Early Ordovician platformal shales. The Avalon Zone is intruded by late Precambrian and late Devonian granites (Van Alstine, 1948; King, 1988; Krogh *et al.*, 1988). The late Precambrian granites are calc-alkaline and intruded in arc and back-arc settings, followed by folding and thrust faulting and the intrusion of late Devonian granites, including the SLG (O’Brien *et al.*, 1996).

LOCAL GEOLOGY

The first detailed mapping in the St. Lawrence area was completed by Strong *et al.* (1976, 1978) to the north, and O’Brien *et al.* (1977) to the south (Figure 2). Additional work by Hiscott (1981), Strong and Dostal (1980), O’Brien and Taylor (1983), Krogh *et al.* (1988), O’Brien *et al.* (1996, 1998) and O’Driscoll *et al.* (2001) helped in further understanding the geology of the area. The following provides an overview of the geology and descriptions proceeding from the oldest rocks in the area to the youngest.

Proterozoic Rocks

Burin Group

The Burin Group represents the oldest rocks in the area, dated using U–Pb isotopes in zircon, yielding an age of 765 \pm 2.2–1.8 Ma (Krogh *et al.*, 1988; Figure 2). It is subdivided into eight formations composed of pillow lavas, mafic pyroclastic flows, tuffs and agglomerates, minor clastic sediments ranging from conglomerate to shale, limestone, gabbro sills and ultramafic rocks of the Burin Ultramafic Belt (Strong *et al.*, 1976, 1978; O’Driscoll *et al.*, 2001). The rocks are deformed and weakly metamorphosed.

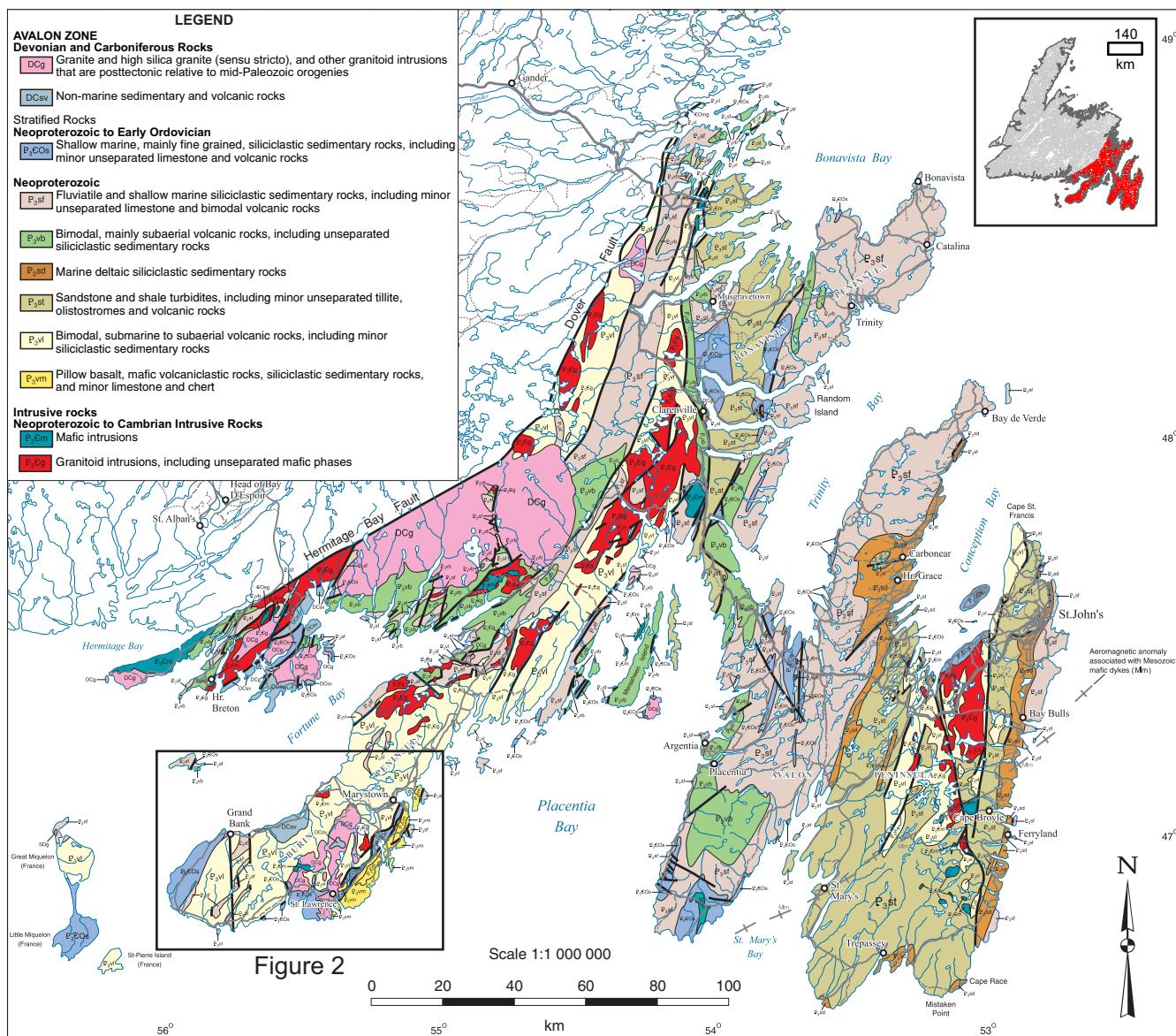


Figure 1. Simplified geological map of the Avalon Zone (after Colman-Sadd *et al.*, 1990).

The oldest rocks in the Burin Group are alkalic that changes abruptly to tholeiitic, suggesting an ophiolitic origin in an extensional environment (Strong *et al.*, 1978). The rare-earth element (REE) signatures suggest a progressive partial melting and depletion of a single mantle source (Strong and Dostal, 1980). The Burin Group is coeval with Neoproterozoic ophiolite sequences in the Pan African orogenic system and represents rifting of the same age (Buisson and LeBlanc, 1986; LeBlanc, 1986; Naidoo *et al.*, 1991; Hefferan *et al.*, 2000; O'Driscoll *et al.*, 2001). Deformation and low-grade metamorphism suggest that rifting was followed by a weak compressional environment, likely related to the accretion of Avalonia to the northern margin of

Gondwana (Strong *et al.*, 1978; Murphy *et al.*, 2000, 2008; Nance *et al.*, 2002). The group contains documented mesothermal gold occurrences (O'Driscoll *et al.*, 2001).

Marystown Group

The Marystown Group is subdivided into six formations and is characterized by bimodal, subaerial volcanic rocks, indicating a significant change in the tectonic environment relative to the Burin Group (Strong *et al.*, 1978; Figure 2). It formed in an arc to back-arc environment (Strong *et al.*, 1978; O'Brien *et al.*, 1996; Nance *et al.*, 2002; Hibbard *et al.*, 2007).

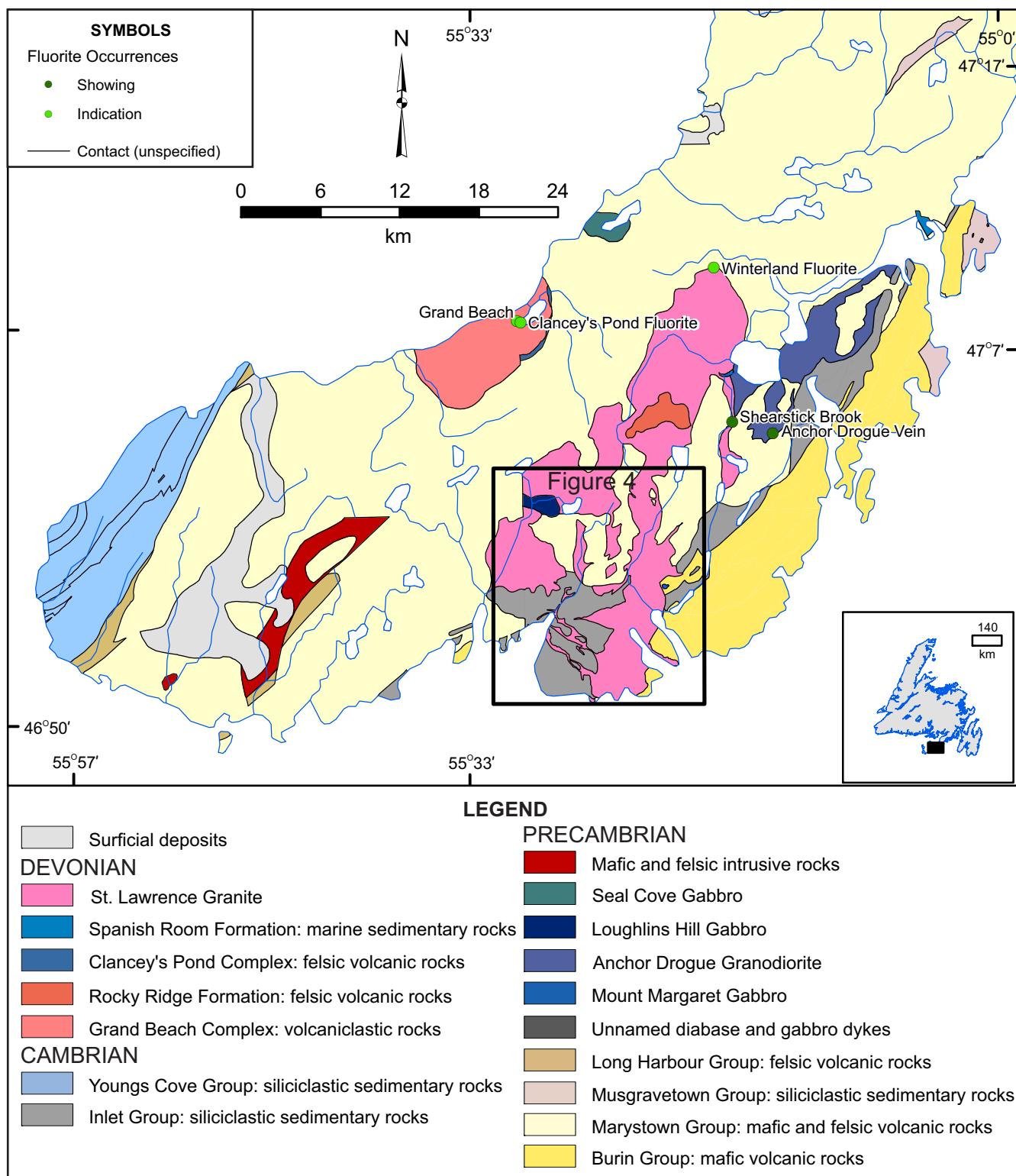


Figure 2. Geology of the St. Lawrence area (after O'Brien et al., 1977 and Strong et al., 1978).

The group is composed of felsic and mafic, dominantly pyroclastic rocks, volcanoclastic sedimentary and minor clastic sedimentary rocks. Early U–Pb zircon age dates from Marystown Group yielded an age of $608 \pm 20/-7$ Ma (Krogh *et al.*, 1988). However, more recent dating by Sparkes and Dunning (2014) yielded ages between 576.8 ± 2.8 Ma and 574.4 ± 2.5 Ma; indicative of a more complex geology than originally interpreted. The Marystown Group hosts several epithermal gold occurrences (O’Brien *et al.*, 1998, 1999; Sparkes, 2012; Sparkes and Dunning, 2014; Sparkes *et al.*, 2016).

Musgravetown Group

The Musgravetown Group is subdivided into three formations consisting of fining-upward clastic sedimentary rocks ranging from conglomerate to siltstone, and minor dolomitized limestone beds and clasts in conglomerate (Strong *et al.*, 1978; Hiscott, 1981; Figure 2). This is indicative of nearshore conditions with alluvial components, and the limestone likely represents a tidal-flat environment. The Musgravetown Group deposited synchronously with the last period of Avalonian magmatism (570–550 Ma, not represented on the Burin Peninsula) that is linked to transition to an extensional transform fault system (Nance *et al.*, 2002).

This group was initially described as the Rock Harbour Group (Strong *et al.*, 1978), and was therein interpreted as the oldest rocks in the area. However, based on detailed stratigraphic relationships, Hiscott (1981) placed it above the Burin Group. Further stratigraphic interpretations led O’Brien and Taylor (1983) to place Rock Harbour Group above Marystown Group, and they renamed it to Musgravetown Group. Krogh *et al.* (1988) dated a quartz–feldspar–porphyry clast from a conglomerate using U–Pb isotopes in zircon, which yielded an age of $623 \pm 1.9/-1.7$ Ma, suggesting that the clast likely originated from the Marystown Group. More recent dating of a rhyolite from the upper portion of the Musgravetown Formation yielded an age of $570 \pm 5/-3$ Ma (O’Brien *et al.*, 1989).

Cambrian Rocks

Inlet Group

The Inlet Group is subdivided into three formations and is composed of dark-green and grey siltstone, and shale with minor sandstone and locally abundant limestone nodules (Strong *et al.*, 1978; Figure 2). It formed in a shallow-marine, possibly intertidal environment. The Inlet Group was deposited in a Cambrian stable platform environment, which was followed by separation of the Avalon Zone from Gondwana (van Staal *et al.*, 1998; Fortey and Cocks, 2003; Hamilton and Murphy, 2004). Recently,

Evans and Vatcher (2009) suggested that these rocks are part of the Marystown Group based on the degree and style of deformation they exhibit.

Devonian Rocks

The Devonian rocks formed by the accretion of the Avalon rocks to Laurentia during the Acadian orogeny in Late Silurian–Early Ordovician (van Staal, 2007; van Staal *et al.*, 2009).

The Rocky Ridge Formation (RRF) occurs as a discontinuous sequence of riebeckite-bearing felsic volcanic rocks in the SLG (Strong *et al.*, 1978; Figure 2). It consists of rhyolite flows, ignimbrite, agglomerate and tuffs. The mineralogy of the RRF is similar to the mineralogy of the SLG, and it is a volcanic equivalent of the granite.

The Clancey’s Pond Complex is composed of ignimbrites and pyroclastic breccia (Strong *et al.*, 1978; Figure 2). It occurs in the vicinity of the Grand Beach porphyry and is the volcanic equivalent of the porphyry, which has a chemical affinity to the SLG.

Intrusive Rocks

Nine rock types have been described as occurring in dykes. In decreasing order of abundance, they are hornblende diorite, gabbro, coarse diabase, fine diabase, felsite, quartz–feldspar porphyry, trachybasalt, trachyandesite and granite (Wilton, 1976; Strong *et al.*, 1978). The dykes are most abundant in the Burin Group.

Other intrusive rocks include the Mount Margaret Gabbro, Loughlins Hill Gabbro, Seal Cove Gabbro, Anchor Drogue Granodiorite, Grand Beach Complex and SLG (Strong *et al.*, 1978; Figure 2). The age of most of the intrusions is uncertain. The Grand Beach Complex yielded an age of $394 \pm 6/-4$ Ma (Krogh *et al.*, 1988; Kerr *et al.*, 1993b). The SLG is genetically and spatially associated with fluorite mineralization and is described in more detail below.

St. Lawrence Granite

The SLG is a north-trending intrusion outcropping over an approximate area of 30 by 6 km (Teng, 1974; Figure 2). Four phases of the granite have been described by Teng (1974), which from oldest to youngest are coarse-grained granite, medium-grained granite, fine-grained granite and porphyritic granite. The contacts between the different phases are sharp. Tuffisites, consisting of fragments of granite in a fine-grained material of similar composition, are common. Quartz–feldspar porphyritic (rhyolite porphyry) sills occur to the west of the SLG, specifically in the AGS area, as noted

by both Van Alstine (1948) and Teng (1974). The sills generally dip gently to moderately to the north.

The granite is composed of quartz, orthoclase and albite and minor amounts of riebeckite, aegirine, biotite, fluorite, magnetite and hematite (Teng, 1974). Chlorite occurs as an alteration from biotite. The rhyolite porphyry consists of the same minerals and has a porphyritic texture, where the phenocrysts are composed of euhedral quartz and orthoclase.

The SLG intruded along pre-existing normal faults that influenced the northerly elongated shape of the granite in a direction of 10° (Teng, 1974). Tension fractures perpendicular to the normal fault ($\sim 100^\circ$), and associated shear structures (~ 60 and 140°) controlled the orientation of the fluorite veins (see below).

The SLG is interpreted to have been intruded at shallow depth based on the presence of extensive dyke swarms of rhyolite porphyries, preserved portions of a volcanic cover sequence (Rocky Ridge Formation), miarolitic cavities, gas breccias (tuffisites), and vuggy pegmatitic segregations indicative of volatile exsolution (Van Alstine, 1948; Strong *et al.*, 1978; Kerr *et al.*, 1993a, b).

A Rb–Sr age for the SLG of 334 ± 5 Ma (Bell *et al.*, 1977) was recalculated by Kerr *et al.* (1993b), to 315 Ma. However, the most recent and likely the more accurate dating of the intrusion yielded an age of 374 ± 2 Ma with U–Pb in zircon (Kerr *et al.*, 1993b).

Major-element chemistry suggests that the SLG is an alkali-feldspar granite, being slightly peralkaline (metaluminous to peralkaline), ferroan in composition and having a high SiO_2 content (Kerr *et al.*, 1993a). The trace-element compositions indicate that the SLG is highly fractionated (depleted in Sr, Ba, Eu) and plots as a ‘within-plate granite’ (A-type). It has a very high volatile content, including fluorine (average 1308 ppm, Teng, 1974). According to Kerr *et al.* (1993a), the SLG originated from the melting of a feldspar-rich source (or possibly a hornblende-bearing source material from the lower crust) with progressive melting of feldspars, represented first by plagioclase, and then K-feldspar (suggested by the Ba depletion). The high fluorine is postulated to have originated from fluorine being trapped in hornblende (Van Alstine, 1976).

The SLG is one of many Devonian postorogenic granites that intruded the Avalon and Gander zones (Kerr *et al.*, 1993a). The source of these intrusions is mantle-derived magmas of mafic or intermediate composition that interacted with various components of the continental crust. As suggested by Nd-isotope geochemistry, the continental crust in

the eastern Avalon region was more juvenile in character than elsewhere in eastern Newfoundland (Kerr *et al.*, 1993a).

FLUORITE

BACKGROUND

Fluorite (CaF_2) crystallizes in the cubic system, forming cubes, octahedra, dodecahedra or combinations of all, with cubes being the most common (Anthony *et al.*, 2011). It has four perfect octahedral cleavages and displays a wide variety of colours including yellow, red, white, purple, green, blue, pink, brown and bluish black. It fluoresces blue, violet, yellow or red under UV light.

The colour of fluorite has attracted the most attention over the years, because fluorite occurs in the largest variety of possible colours of potentially all natural minerals. The cause of colour variation is complex and is still not well understood. In some samples, colour centres consisting of REE impurities or calcium impurities and/or oxygen give the colour variation; however, the presence of REEs alone will not produce a colour (Allen, 1952; Bill and Calas, 1978; Nassau, 1980). Dill and Weber (2010) summarize the causes of different colours in fluorite from earlier studies (Table 1). The variations in the morphology of fluorite are a function of temperature and the rate of cooling (Zidarova *et al.*, 1978; Dill and Weber, 2010; Figure 3).

Strong *et al.* (1984) divided fluorite deposits into three main genetic types:

1. Sedimentary, dominantly carbonate hosted. This occurs in an environment similar to Mississippi Valley Type (MVT) deposits.

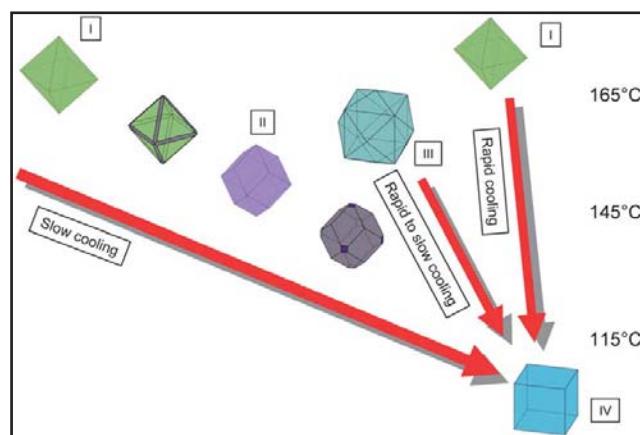


Figure 3. Crystal morphology of fluorite as a function of temperature and rate of cooling (after Zidarova *et al.*, 1978 and Dill and Weber, 2010).

Table 1. Compilation of causes of colour variations in fluorite (Dill and Weber, 2010)

Colour	Cause	References
Blue	Fe ³⁺ / Fe ²⁺ plus Cu	Przibaum (1953)
	Colloidal calcium	Allen (1952), Mackenzie and Green (1971), Braithwaite <i>et al.</i> (1973), Calas (1995)
	Y-associated chromophores/centers REE	Calas (1972), Bill and Calas (1978) Calas (1972)
Brown	Organic compounds Mn ²⁺ , Mn ³⁺ , thorium	Calas <i>et al.</i> (1976) Kempe <i>et al.</i> (1994)
Yellow	Eu ²⁺ Fe plus REE OF ₂ or OF O ₃ or O ₃ ⁻ centres	Przibaum (1953) Przibaum (1953) Neuhaus <i>et al.</i> (1967) Bill and Calas (1978), Trinkler <i>et al.</i> (2005)
Yellowish green	Y/Ce - associated chromophores/centers	Bill and Calas (1978)
Green	Colloidal calcium	Allen (1952)
	Fe ²⁺ , plus Mn, Cr, Ni or Cu	Przibaum (1953)
	Sm ²⁺	Bill and Calas (1978)
	Sm ³⁺	Bailey <i>et al.</i> (1974)
Orange	Mn ²⁺	Bailey <i>et al.</i> (1974)
Pink to red	Fe ³⁺	Przibaum (1953)
	Cr plus Mn ³⁺	Przibaum (1953)
	YO ₂	Bill (1978), Bill and Calas (1967)
	Organic compounds	Joubert <i>et al.</i> (1991)
Purple to black	Colloidal calcium	Allen (1952)

2. Magmatic-hydrothermal vein deposits associated with dominantly alkaline-peralkaline igneous rocks. The fluorite deposits in St. Lawrence are an example.
3. Intermediate type found at contacts between limestone and granitoid rocks.

Van Alstine (1976) noted that fluorite districts are commonly located along normal faults within 100 km from a graben or continental rift; also they are genetically related to rifting, which provides access to the volatile fluorine from depth. Possible sources of fluorine include volatiles from crystallizing alkali and silicic magma, re-melting of late F-rich alkali fractions of intrusive rocks, F-bearing minerals (fluorapatite, hornblende) in source ultramafic rocks, and/or F-bearing minerals in subducting crustal rocks.

St. Lawrence Fluorite Deposits

The fluorite deposits in St. Lawrence have been the focus of many studies including Van Alstine (1948, 1976),

Williamson (1956), Teng (1974), Teng and Strong (1976), Strong *et al.* (1978), Richardson and Holland (1979), Strong (1982), Strong *et al.* (1984), Collins (1984), Irving and Strong (1985), Gagnon *et al.* (2003), Kawasaki and Symons (2008), Kawasaki (2011), Sparkes and Reeves (2015) and Reeves *et al.* (2016). The following is a summary from these studies.

Fluorite mineralization associated with the SLG formed as open-space fillings in tension fractures that were created by regional stresses and contraction resulting from the cooling of the granite. Fluorine-rich volatiles separated from the cooling granite, and escaped along structures to be subsequently deposited in fractures in the upper part of the granite. Repeated movement along fractures resulted in the brecciation of host rocks and pre-existing vein material, thus creating space for several successive phases of fluorite mineralization. Volatiles generally did not escape into the host sedimentary rocks due to the impermeability of the hornfelsed sediments overlying the granite (Teng, 1974; Strong, 1982). As such, most of the fluorite veins are hosted in the granite. Further, the lack of fluorite veins in the country

rocks may be due to open fissures, formed as a result of cooling in the granite, narrowing and closing as they passed from the granite into the country rocks that were not subjected to cooling and contraction (Williamson, 1956). The AGS vein system is an exception, being hosted in sedimentary rocks and rhyolite sills intruding the sediments (see below). The fluorite veins are epithermal, suggested by low temperature and pressure assemblages, vuggy veins, abundance of breccia, and colloform and crustiform structures.

The main control on fluorite deposition is an increasing pH caused by the boiling of magmatic fluids (Strong *et al.*, 1984). Fluid-inclusion studies suggest that the fluorite formed between temperature ranges of 100 and 500°C, with both increasing and decreasing temperatures observed during crystal growth. Formation pressures were between 65 and 650 bars. Oxygen isotopes suggest mixing of magmatic fluids with cool meteoric fluid. Also, REE concentrations in the different ore zones and textural types of fluorite indicate a magmatic origin (Strong *et al.*, 1984).

There are more than 40 fluorite veins in the St. Lawrence area, ranging in size from a few cm to 30 m in width and up to 3 km in length (Figures 2 and 4). There are variations in thickness along strike and with depth. Four major types of fluorite veins have been described:

1. North-south-trending low-grade veins (Tarefare, Director, Hares Ears, Blue Beach North and South);
2. East-west-trending high-grade veins (Black Duck, Lord and Lady Gulch, Iron Springs, Canal);
3. Northwest-southeast-trending veins in sedimentary rocks containing high-grade mineralization (AGS); and
4. East-west-trending peripheral veins containing significant amounts of barite with fluorite (Meadow Woods, Lunch Pond, Clam Pond, Anchor Drogue).

Table 2. Paragenetic sequence of fluorite veins in the St. Lawrence area from Reeves *et al.* (2016)

Phase	Vein Description	Remarks
1	Purple fluorite	Thin veins in joints and filling small fractures
2	Red, yellow, clear, and blue-green fluorite	Massive and coarsely crystalline CaF_2
3	Sulphides – galena, sphalerite, minor chalcopyrite and pyrite	Disseminated and finely banded
4	Green and white fluorite	Thin veins (<2 m) crosscutting earlier fluorite mineralization
5	Clear fluorite	Observed in voids and fractures as a deposit over earlier phases of mineralization
6	Quartz–carbonate veining, blastonite	Quartz–carbonate infilling and blastonite
7	Carbonate–fluorite stockwork-massive veining	Carbonate–fluorite stockwork-massive veining in new fracture systems and pre-existing ore structures

Table 2 shows the paragenetic sequence in all fluorite veins including the AGS area described by Reeves *et al.* (2016). In addition to the differences in the orientation and grade between the major types of fluorite veins, Van Alstine (1948), Williamson (1956), Wilson (2000) and Reeves *et al.* (2016) also noted the abundance of green fluorite and increased amount of sulphides in the peripheral veins and veins not hosted in granite compared to the granite-hosted veins.

The Re–Os isotopes in molybdenite, from a quartz–fluorite veinlet within the SLG, yielded an age of 365.8 ± 2.8 Ma, which is significantly younger than the granite and likely represents a prolonged hydrothermal activity during cooling and/or unroofing of the granite (Lynch *et al.*, 2012). According to Lynch (personal communication, 2017), the age likely constrains the timing of a late-stage hydrothermal activity, therefore, it may postdate the main fluorite mineralization event.

AGS Deposit

Field Work

Although the main focus of the field work in 2017 was the AGS area, some of the fluorite occurrences hosted in granite were also examined for comparative purposes, including the Red Head Vein, Lord and Lady Gulch Vein, Chambers Cove and Salt Cove Valley Vein. Along the AGS vein system, samples were collected from the Grebes Nest Pit, Center Pit and Open Cut Pit (Figure 5) to assess the changes in fluorite mineralization across and along the vein.

Some of the samples from the Grebes Nest Pit were not technically ‘*in-situ*’, because the pit is an active mining area and most of the vein was covered by boulders from blasts (blast rock) happening on a regular basis. However, all blast rock originated from the Grebes Nest Pit and likely did not come from afar even within the pit. Due to this, the parage-

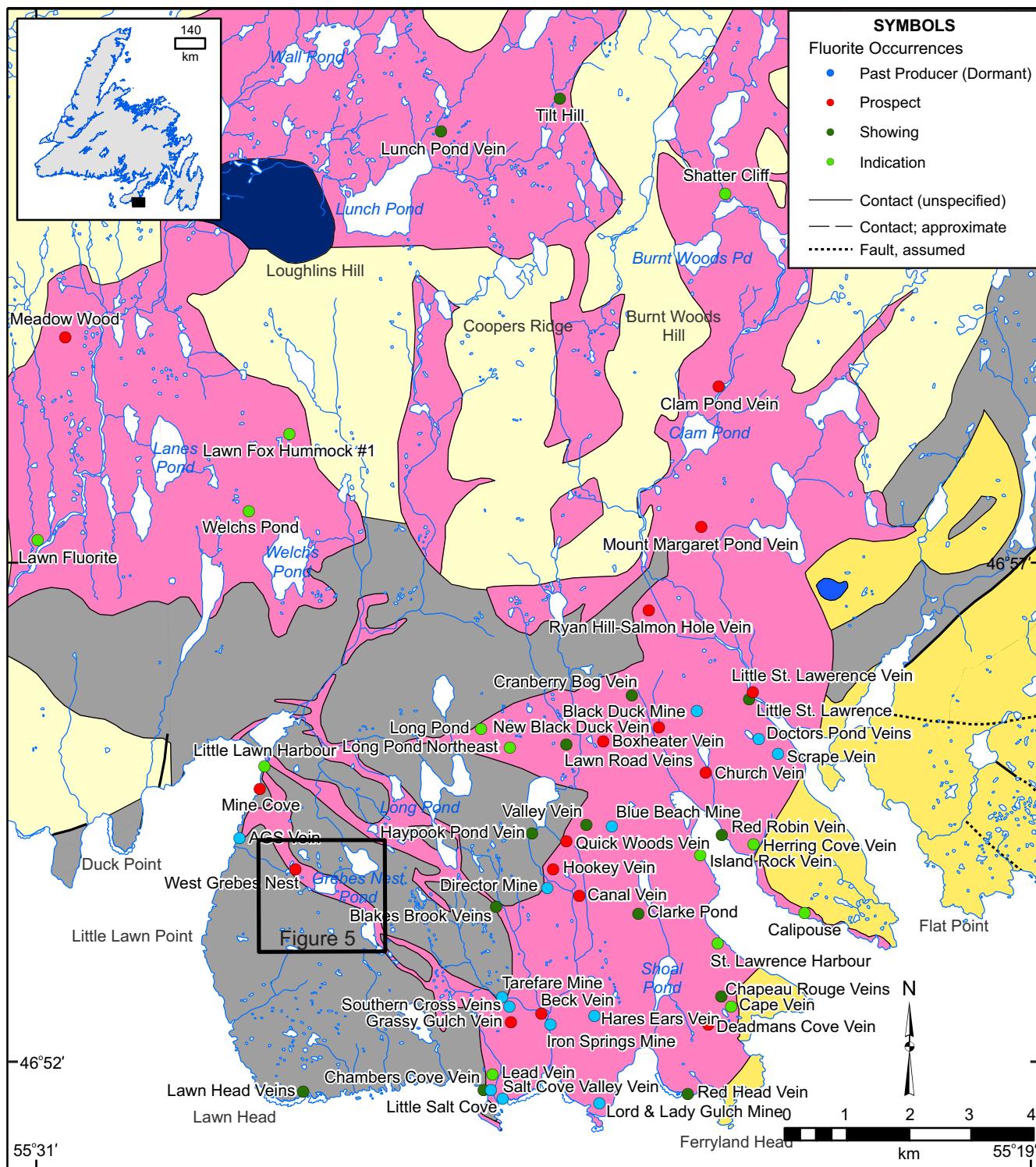


Figure 4. Fluorite occurrences in the St. Lawrence area (Mineral Occurrence Data System, Geological Survey of Newfoundland and Labrador).

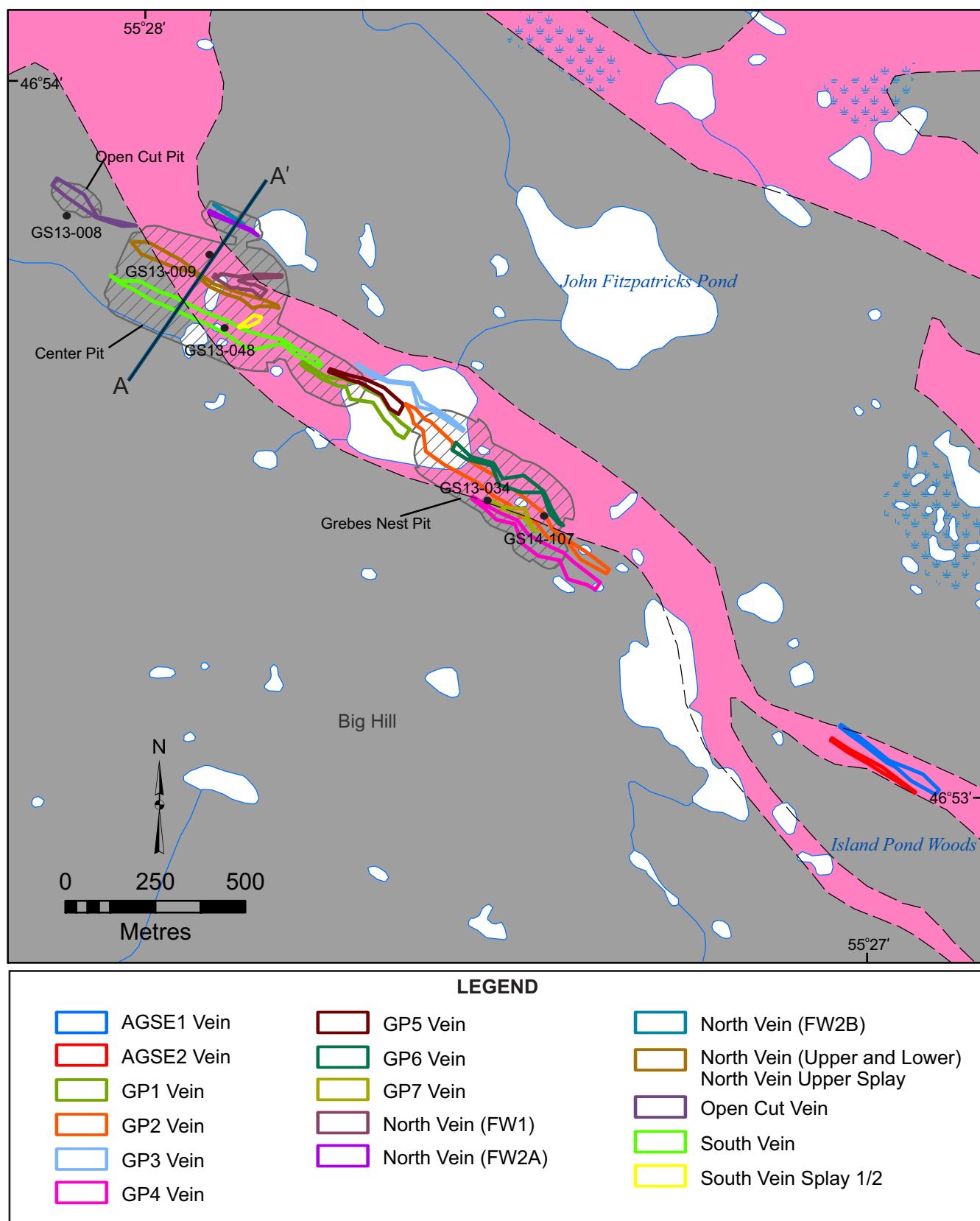


Figure 5. Plan map of the AGS area showing veins of the AGS vein system (modified after surface plan map prepared by Sparkes, CFI in 2016). Black dots are locations of drillhole collars. A-A' shows the location of cross-section in Figure 6.

netic sequence of the fluorite phases relied mostly on textual, rather than field relationships. Sampling difficulties were encountered in some areas (Open Cut Pit, Center Pit, granite-hosted veins) of high-grade fluorite ore. Therefore, five drillholes, drilled by CFI in 2013 and 2014, were also examined. Samples were not collected from the drillcores. Drillholes from the granite-hosted fluorite veins were not examined.

AGS Vein System

The AGS vein system, as currently defined, is approximately 1.85 km long and consists of several fluorite veins running almost parallel to each other, with local pinching and swelling observed (Sparkes and Reeves, 2015; Reeves *et al.*, 2016; Figures 5 and 6). The majority of the veins strike southeast ($\sim 110^\circ$ to 130°) and dip steeply ($\sim 80^\circ$ to 85°) to the southwest. There are also several smaller east-west-striking and steeply dipping veins in the AGS area (B. Sparkes, written communication, 2018). The veins are fault-controlled and range in width from less than 2 m to up to 30 m. The strike length of major veins is between 400 and 700 m. The three major veins include the North, South and GNP veins.

The veins are hosted in sedimentary rocks, as well as in rhyolite sills that intrude the sediments and dip gently to the north. The sedimentary rocks are dark-grey to green shales of the Inlet Group. The rhyolite has a porphyritic texture and is composed of quartz and feldspar (orthoclase and minor amounts of plagioclase) phenocrysts in a groundmass composed of the same minerals and minor amounts of chlorite alteration. Trace amounts of zircon, rutile and several REE minerals (monazite, xenotime, thorite) also occur in the rhyolite. The rhyolite is assumed to be genetically related to the SLG, but the relationship is not well understood. According to Teng (1974), the rhyolite sills represent the youngest phase of the granite and Cooper *et al.* (2014) state that the rhyolite dykes have been observed to cut the granite in the St. Lawrence area. No field relationships between the rhyolite sills and the SLG in the AGS area have been observed to date (B. Sparkes, written communication, 2018). The SLG underlies the AGS area and has been intersected by deeper drillholes between 250 and 350 m (Sparkes and Reeves, 2015).

Reeves *et al.* (2016) suggested that the rhyolite sills likely played a key role in fluorite mineralization in the AGS area by exerting pressure on the sedimentary rocks that resulted in fracturing the sediments along pre-existing structures. This

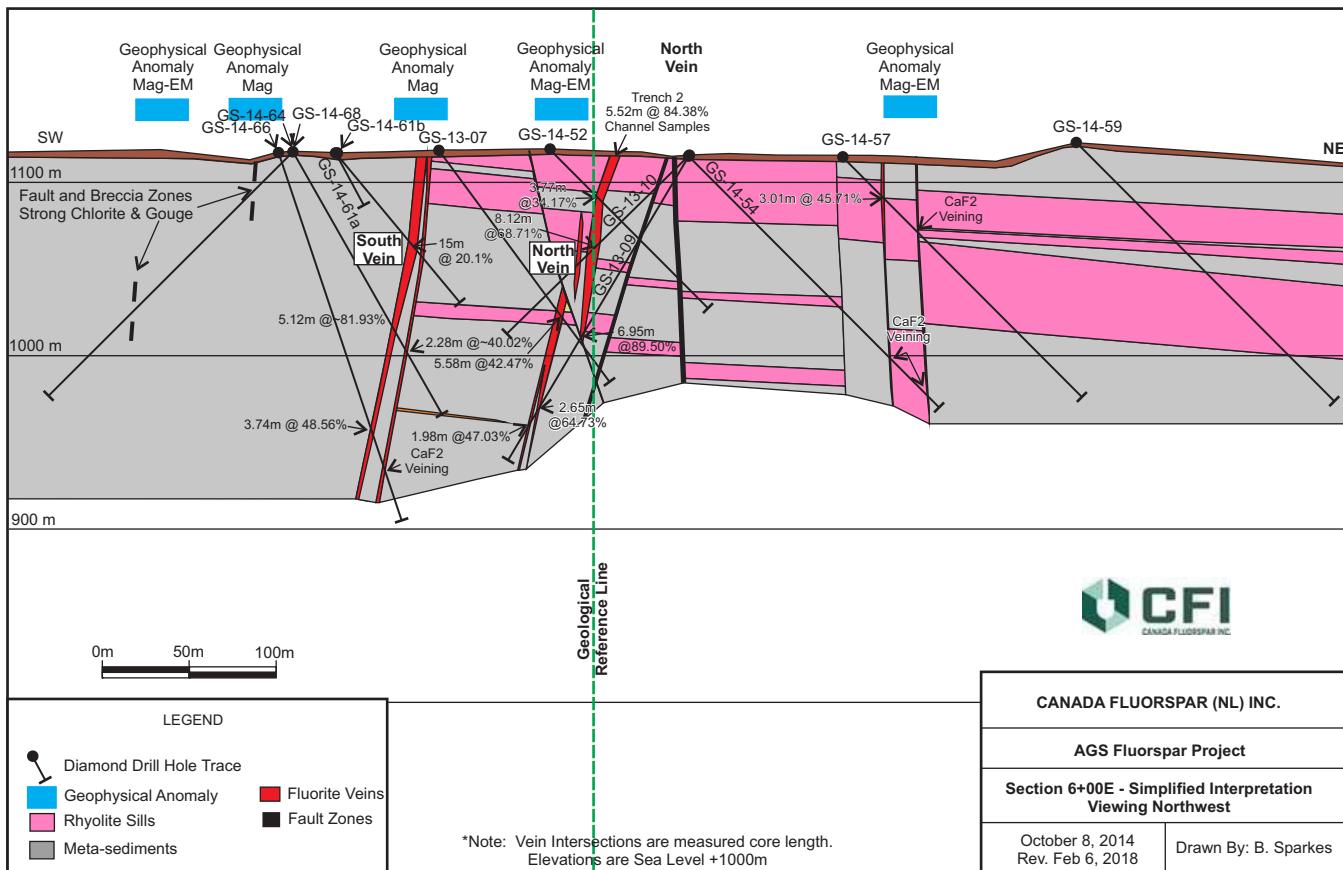


Figure 6. Cross-section of the Center Pit area of the AGS vein system looking northwest (after Sparkes and Reeves, 2015).

enabled the fluids to travel into the sediments and allowed the formation of fluorite veins. Alternatively, the AGS fault system may represent large-scale tear faults related to north-south structures controlling the emplacement of the SLG and other deposits in the area (Tarefare, Director and Blue Beach) (B. Sparkes, written communication, 2018).

The amount of fluorite in the AGS vein system has been calculated by CFI based on drilling (Sparkes and Reeves, 2015). In 2014, the resource was 9 389 049 tonnes at 32.88% fluorite (NI 43-101 compliant).

Fluorite Mineralization

In the AGS vein system, as in the other fluorite vein systems in the St. Lawrence area, repeated re-activation of fault structures induced brecciation of the host rocks and earlier vein material. This provided a mechanism for multiple pulses of mineralized fluids to circulate the rocks, resulting in the formation of several ore-forming events. The different hydrothermal phases are easily distinguished based on the various colours and textures of the fluorite.

Mineralogy

Fluorite is the main mineral in the veins and occurs in purple, yellow, green, blue, grey, white, red, pink and tan. The pink and tan occur in fine-grained, banded fluorite ore and the colour is likely due to the presence of fine-grained hematite. Purple fluorite varies from being fine or coarse grained, whereas the other coloured fluorites are typically coarse to very coarse grained. Two fluorite samples containing purple, green and grey fluorite were examined using a Scanning electron microscope (SEM), with no detectable compositional differences observed.

Quartz is a very common accessory mineral, especially in the earlier phases of hydrothermal activity (barren brec-

cia, purple fluorite) and in the late phases (blastonite, late quartz). Calcite is especially common in the High Carbonate Zone, in parts of the Grebes Nest Pit (Sparkes and Reeves, 2015), where the amount of calcite in the veins may locally reach 50% or more. Barite was observed, using the SEM, as small grains in some samples at the AGS vein system and as bigger grains in the Chambers Cove area. The possibility exists that there is barite present in other samples as well. Sulphide minerals identified include sphalerite, galena, pyrite and chalcopyrite. Sulphides are more common in samples from the Open Cut Pit. Increased amount of sulphides were also observed close to the contact of the SLG with the sedimentary rocks at Chambers Cove. Williamson (1956) also noted that sulphides are more common near the granite contacts, as well as in country-rock-hosted veins. Hematite is locally common and typically occurs intergrown with chalcedony or quartz and fluorite.

Paragenetic Sequence

Table 3 shows the paragenetic sequence of hydrothermal activity associated with fluorite mineralization as observed during the current study. The following is a detailed description of each stage.

1. Brecciation of Host Rocks

The breccia consists of clasts of country rocks in a matrix of hydrothermal quartz and minor fluorite (Plate 1A, B). The host sedimentary rock and rhyolite clasts are weakly to strongly altered to light green to tan, representing chlorite and sericite alteration. This early phase of brecciation served as a mechanism of ground preparation for the influx of later fluorine-bearing hydrothermal fluids that utilized the same fluid pathways.

In the study area, barren or weakly mineralized hydrothermal breccia associated with this initial brecciation

Table 3. Paragenetic sequence of hydrothermal events in the AGS area observed in this study

Phase	Vein Description	Remarks
1	Brecciation of host rocks	Brecciated, weakly to strongly altered sedimentary rocks and rhyolite in a quartz-rich matrix
2	Purple fluorite stockwork and/or hydrothermal breccia	Purple fluorite and quartz forming stockwork veins and hydrothermal breccia with clasts of host rocks
3	Banded, fine-grained fluorite and coarse-grained yellow, red, clear and white fluorite	Finely banded, fine-grained fluorite and local calcite and coarse-grained yellow, red, clear and white fluorite with thin hematite layers
4	Chalcedony–fluorite	Chalcedony surrounded by quartz and fluorite
5	Grey, green, blue, white and clear, cubic fluorite	Alternating layers of coarse-grained fluorite and later clear cubic fluorite
6	Blastonite	Breccia composed of fragments of previous phases in a matrix composed of quartz, calcite (in calcite-rich areas) and fine-grained fluorite
7	Late quartz	Quartz filling late vugs in previous phases

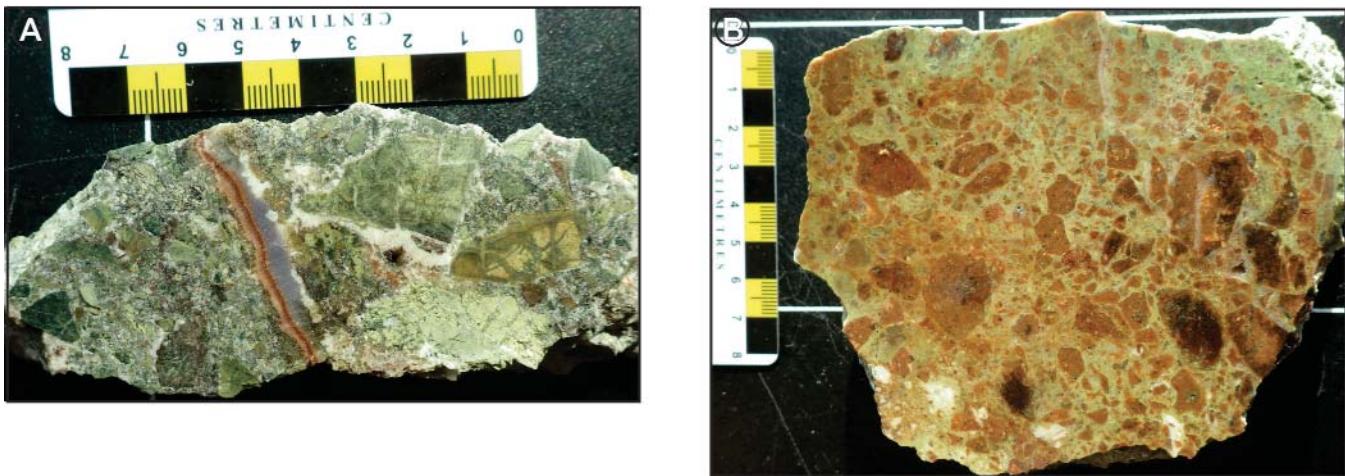


Plate 1. Brecciation of host rocks representing the first phase of hydrothermal activity. A) Strongly altered rhyolite breccia cut by a fluorite vein; B) Moderately altered rhyolite clasts in strongly altered matrix.

phase displays more intense alteration than that observed in later mineralized samples. This suggests that the nature (composition, temperature, *etc.*) of this early fluid was different from the later mineralizing fluids.

2. Purple Fluorite Stockwork and/or Hydrothermal Breccia

Purple fluorite represents the first phase of fluorite mineralization, although it may be locally absent in individual samples. It either forms as stockwork veins in the host rocks (Plate 2A–C), or as the matrix of hydrothermal breccias (Plate 2D). The veins and the matrix of the breccia are composed of purple fluorite, quartz and locally calcite. Calcite is common in samples from the Grebes Nest Pit, especially in the High Carbonate Zone (Sparkes and Reeves, 2015).

In several samples, there is further evidence to support two generations of purple fluorite, with the first one generally darker compared to the second generation (Plates 2D, F and 3C). The grain size ranges from fine to medium grained, with the first generation typically being the coarser grained, but the opposite has been observed as well (Plate 2F).

The purple fluorite is locally associated with variable amounts of sphalerite and/or galena (Plate 2B, E, G), where the quantity of sulphide mineralization is higher in the Open Cut area. Sphalerite and galena appear to have precipitated prior to the purple fluorite (Plate 2G), with sphalerite displaying growth zones in some samples.

The host rock, cut by the purple fluorite veins, is generally weakly to moderately altered with alteration extending generally less than 5 mm from the fluorite vein. Samples displaying strong alteration of the host rocks are interpreted to have been exposed to multiple hydrothermal fluid pulses;

as exemplified by the purple fluorite veins cutting earlier green alteration selvages in a rhyolite sample (Plate 2A).

Purple fluorite veins are cut by yellow and finely banded fluorite (Plates 2C and 3C, D), blue and green fluorite (Plates 2E and 5E), and green fluorite and the hematite–chalcedony–fluorite phase (Plate 4A). This textural evidence indicates that all these phases formed later than the purple fluorite. In some samples, there is evidence of a late purple fluorite phase crosscutting the yellow fluorite (Plate 3C) or forming alternating bands with the yellow fluorite (Plate 3E), but this relationship is rare.

3. Banded, Fine-grained Fluorite and Coarse-grained Yellow, Red, Clear and White Fluorite

The banded fluorite consists of alternating thin layers (<5 mm) of very fine-grained, tan, beige, pink and brick-red fluorite having cm-scale layers of coarse-grained yellow fluorite and black, clear or pink calcite (Plate 3A, B). The proportion of coarse-grained yellow fluorite and fine-grained fluorite is very variable, and some areas contain entirely one type and not the other. However, the textural relationship between the two styles of mineralization suggests that they are part of the same ore-forming phase (Plate 3A, C, D). The banded, fine-grained and yellow fluorite changes into massive clear and white fluorite, with fine-grained red layers, probably composed of hematite. The end of this phase is marked by the appearance of clear and grey fluorite with fine-grained sulphides suggesting a change from oxidizing to reducing conditions. The massive, coarse-grained clear, white and grey fluorite was only observed in drillcore and no samples were collected.

The fine-grained layers are composed of a mixture of fluorite, calcite and various amounts of hematite, resulting

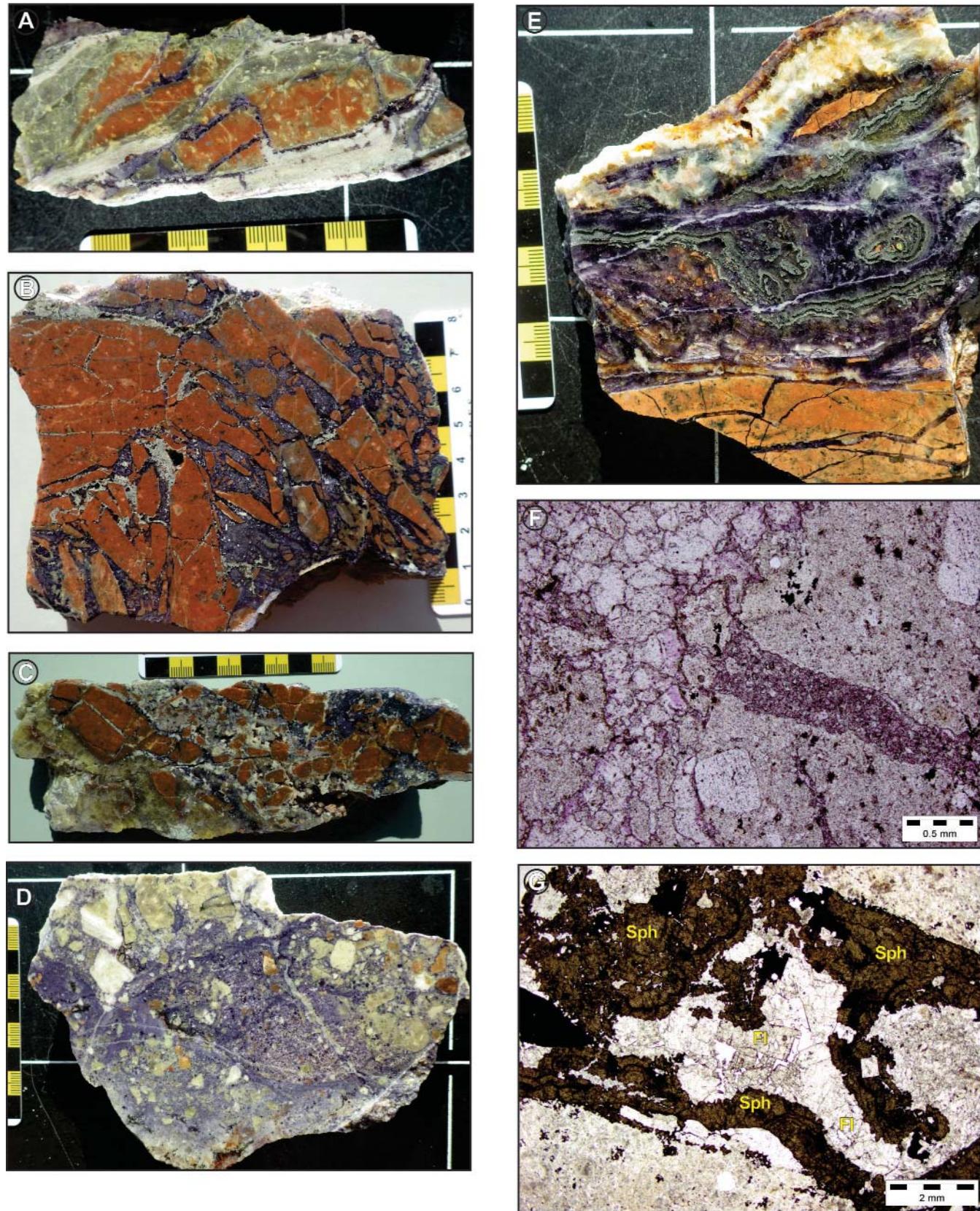


Plate 2. Caption on page 109.

in beige, pink and red colours (Plate 3A, B). Black calcite occurs as long blades crystallized with inclusions of a fine-grained, yet undetermined, opaque mineral. The yellow fluorite is coarse to very coarse grained (~1 cm), and in rare examples it is interlayered with coarse-grained purple fluorite (Plate 3E). Pyrite occurs in the yellow fluorite, and is commonly partially replaced by hematite. The abundance of hematite in this phase is indicative of oxidizing conditions.

Whereas this phase of mineralization is voluminous in some areas, forming the main ore-forming event in parts of the Grebes Nest Pit and at Little Salt Cove, it is less common in other areas such as at the Open Cut Pit. The relative timing of this mineralizing event with the later phases is not always clear, with various relationships observed. At the Open Cut Pit, this phase was only observed in drillcore (GS13-008), where it occurs with the chalcedony–hematite–fluorite phase; either forming before this phase or at the same time (Plate 3F). In a drillhole from the Center Pit (GS13-048), fine-grained banded fluorite is truncated by green fluorite, indicating that it formed earlier (Plate 3G). A sample from the Grebes Nest Pit displays fine-grained banded fluorite forming colloform banding that is followed by blue fluorite (Plate 5D). Another relationship observed in drillcore from the Grebes Nest Pit (drillhole GS13-034) displays layered fine-grained fluorite and medium-grained yellow fluorite in association with blue-green fluorite (Plate 3H); representing the only sample examined in this study that contains both yellow and blue-green fluorite.

The banded, fine-grained nature of the fluorite in this phase suggests fast nucleation and slow crystal growth. Fluorite veins at Nabburg-Wölsendorf in Germany having similar fine-grained fluorite, as observed in this phase, formed as a result of phreatomagmatic reaction at shallow depth, when hot aqueous solutions came into contact with cooler meteoric water (Dill and Weber, 2010).

4. Chalcedony–Fluorite

This phase is composed of fibrous chalcedony and fine-grained hematite surrounded by quartz and fluorite (Plate

4A–C). Pyrite and other sulphides (sphalerite, galena, chalcopyrite) have been partially replaced by hematite (Plate 4D). The amount of fluorite ranges from minor to approximately 50% (Plate 4E–G). Fine-grained barite, pyrite, chalcopyrite and sphalerite commonly occur together with quartz and chalcedony.

This phase is locally abundant in the Open Cut Pit, but also present in the Grebes Nest Pit. It is preceded by the purple fluorite phase and followed by green fluorite (Plate 4A). Textural relationships with banded fluorite in drill-hole GS13-008 suggest that they may be coeval (Plate 3F).

5. Grey, Green, Blue, White and Clear, Cubic Fluorite

The grey, green, blue and white fluorites are coarse to very coarse grained, typically ranging between 1- and 5-cm-size grains (Plate 5A–L). Clear, cubic fluorite is medium to coarse grained (up to 1 cm size cubes) and has been observed only at the Open Cut Pit, where it formed later in the paragenetic sequence than the green fluorite (Plate 5G). Precipitation of the green and blue fluorites was likely synchronous, as suggested by textural relationships. In some samples, blue fluorite veins cut green fluorite veins (Plate 5E), whereas in other samples blue fluorite occurs around rhyolite clasts and is, in turn, surrounded by green fluorite (Plate 5F). In the High Carbonate Zone in the Grebes Nest Pit, blue-grey and green fluorites are interlayered (Plate 5A). Fluorite in some samples is zoned, defined petrographically by fine silicate (quartz, orthoclase and/or plagioclase) inclusions (Plate 5I, J).

Most of the fluorite associated with the AGS vein system has been described as having a cubic habit. However, in the Open Cut Pit, at least some, possibly all, of the green fluorite is octahedral. In samples with octahedral fluorite, the purple fluorite phase is often missing and the green fluorite forms the stockwork/hydrothermal breccia phase; potentially indicative of differences in the conditions of formation compared to the cubic green fluorite elsewhere (Plate 5B). The typical paragenetic sequence in these samples is quartz, green octahedral fluorite stockwork/hydrothermal breccia, followed by clear, cubic or grey fluorite, which is followed by smoky quartz-

Plate 2 (page 108). Purple fluorite represents the second phase of hydrothermal activity. A) Purple fluorite stockwork showing purple fluorite cutting an alteration selvage from the first hydrothermal event; B) Purple fluorite, sphalerite and galena stockwork in rhyolite (Open Cut Pit); C) Purple fluorite and carbonate stockwork in rhyolite, truncated by yellow fluorite (Grebes Nest Pit); D) Purple fluorite hydrothermal breccia with strongly altered rhyolite clasts showing two generations of purple fluorite (Grebes Nest Pit). Darker purple fluorite is cut by light-purple, very fine-grained fluorite; E) Purple fluorite with thin sphalerite and galena layers and later blue fluorite (Grebes Nest Pit); F) Photomicrographs of two generations of purple fluorite veins crosscutting each other (Grebes Nest Pit). Fine-grained, dark-purple fluorite veins are cut by a coarser grained, lighter purple fluorite vein; G) Purple fluorite and zoned sphalerite vein. Relationship suggests that the sphalerite formed before the purple fluorite (Open Cut Pit).

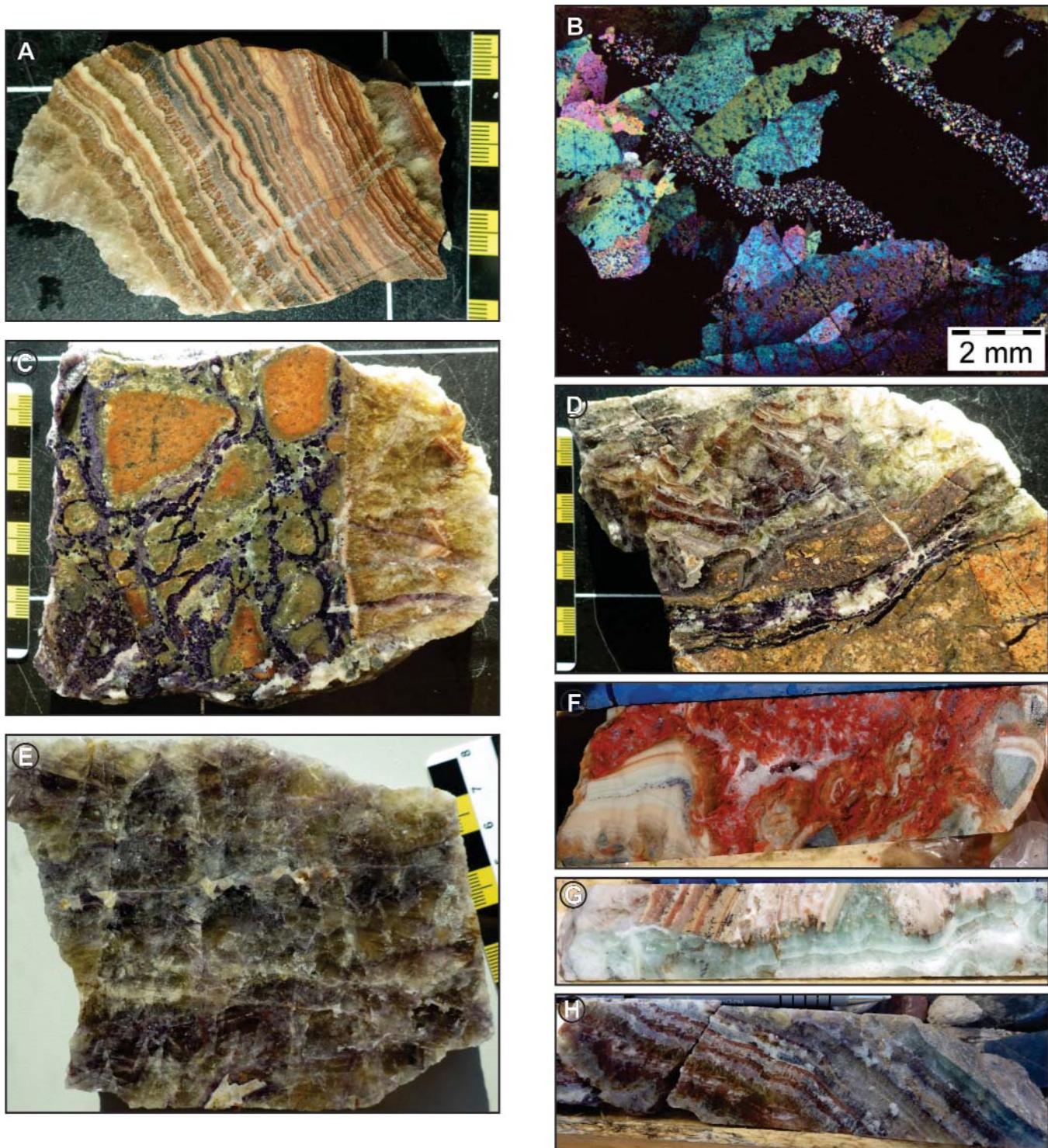


Plate 3. Banded and yellow-clear-red fluorite. A) Banded fluorite with layers of coarse-grained yellow fluorite (Grebes Nest Pit); B) Photomicrograph of calcite-rich banded fluorite under crossed polars from the High Carbonate Zone (Grebes Nest Pit). Fluorite is black and calcite displays high birefringence colours; C) Stockwork purple fluorite truncated by yellow fluorite with banded fluorite, cut by later purple fluorite (Grebes Nest Pit); D) Yellow coarse-grained fluorite with banded fluorite between growth zones (Salt Cove Valley Vein); E) Interlayered coarse-grained yellow and purple fluorite (Grebes Nest Pit); F) Banded fluorite with chalcedony-fluorite (drillhole GS13-008, Open Cut Pit, 11 cm in length); G) Banded fluorite truncated by green-white fluorite (drillhole GS13-048, Center Pit, 15 cm in length); H) Banded fluorite and yellow coarse-grained fluorite with blue fluorite (drillhole GS13-034, Grebes Nest Pit, 20 cm in length).

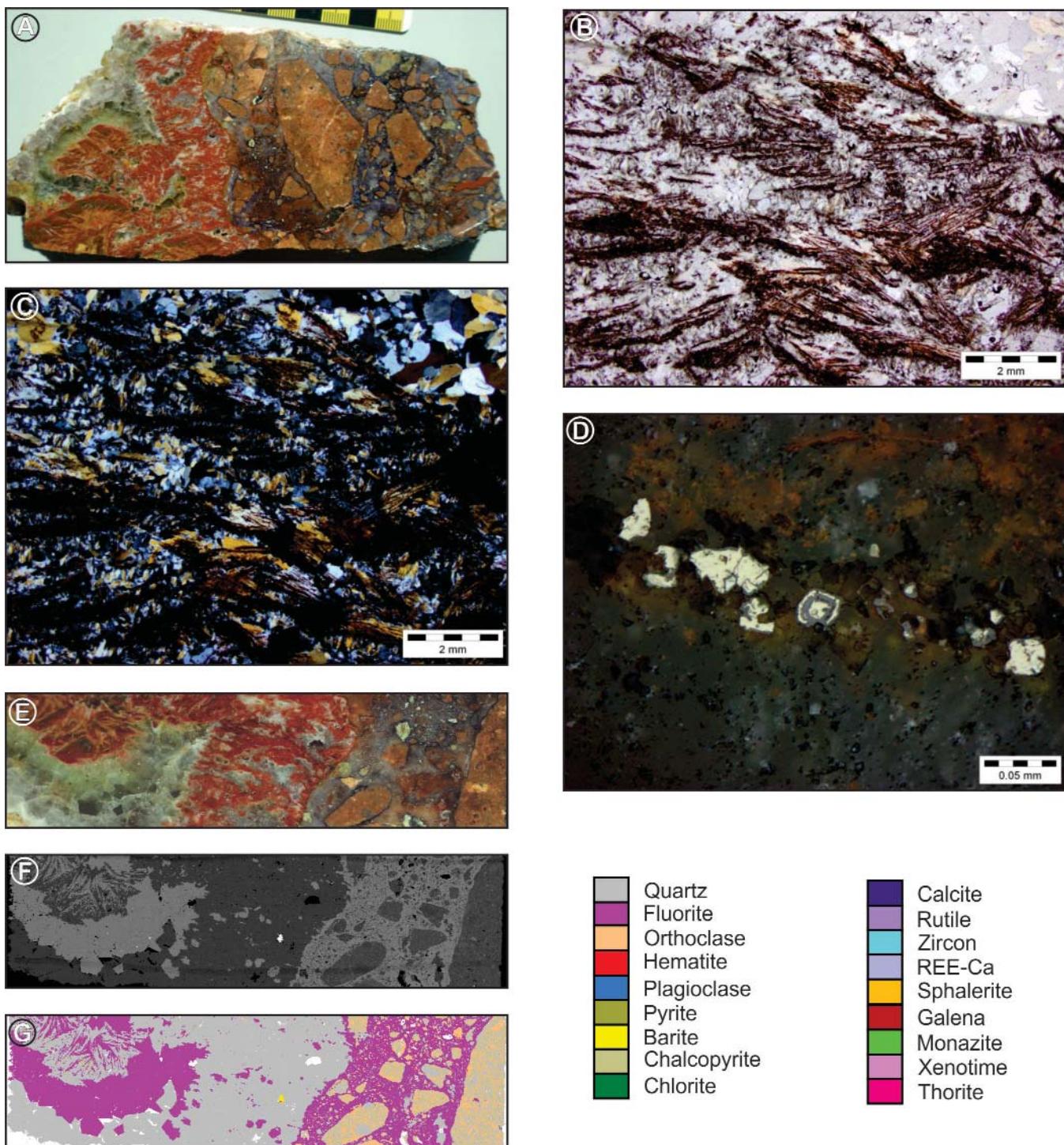


Plate 4. Chalcedony–fluorite phase. A) Purple fluorite breccia, truncated by chalcedony–fluorite, which is surrounded by green fluorite and quartz (grey) (Open Cut Pit). B) Photomicrograph of chalcedony, quartz, fluorite and hematite (Open Cut Pit); C) Same as A under crossed polars; D) Pyrite partially replaced by hematite (Open Cut Pit); E) Hand sample of the area scanned with SEM; F) Back-scattered electron (BSE) image; G) X-ray map.

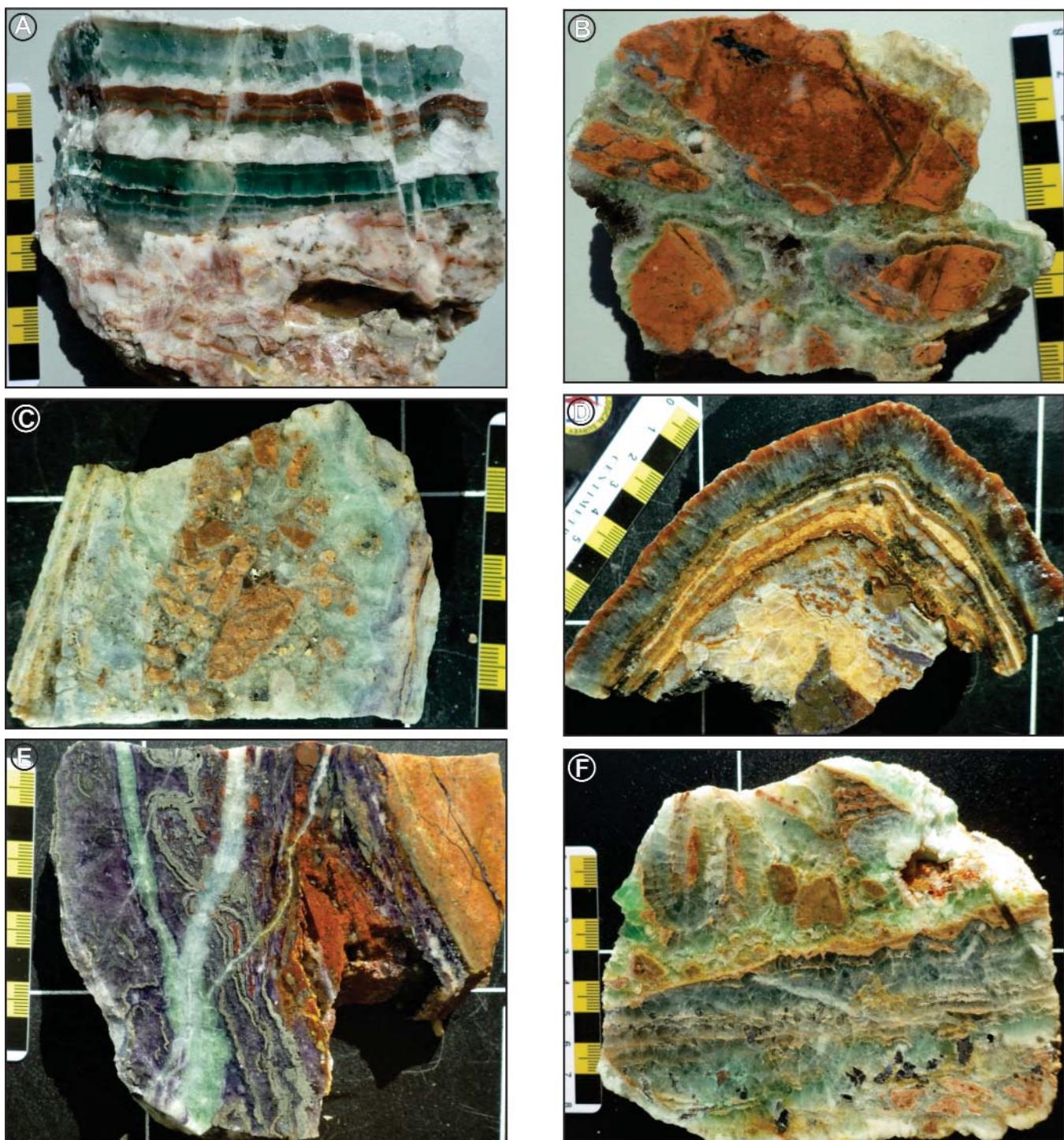


Plate 5. Green, blue-grey and clear; cubic fluorite. A) Interlayered green and red fluorite and white calcite with brecciated calcite-rich material (Grebes Nest Pit); B) Green and grey fluorite hydrothermal breccia with rhyolite clasts (Open Cut Pit). Later vugs in fluorite are filled with smoky quartz; C) Green and blue-purple fluorite, galena, sphalerite and chalcopyrite vein with granite clasts (Chambers Cove Vein); D) Colloform banding composed of, from core to rim, purple fluorite breccia, coarse-grained calcite, calcite-rich hydrothermal breccia, banded fluorite and coarse-grained blue fluorite (Grebes Nest Pit); E) Purple fluorite with layers of sphalerite and galena, cut by a green fluorite vein, which is cut by a blue fluorite vein. A first generation of sphalerite forms fine-grained, thin layers in purple fluorite and is cut by a blue fluorite vein containing a second generation of coarser grained, light-brown sphalerite; F) Blue and green fluorite with galena. Blue fluorite surrounding rhyolite clasts and being surrounded by green fluorite, suggesting that blue fluorite preceded green fluorite;

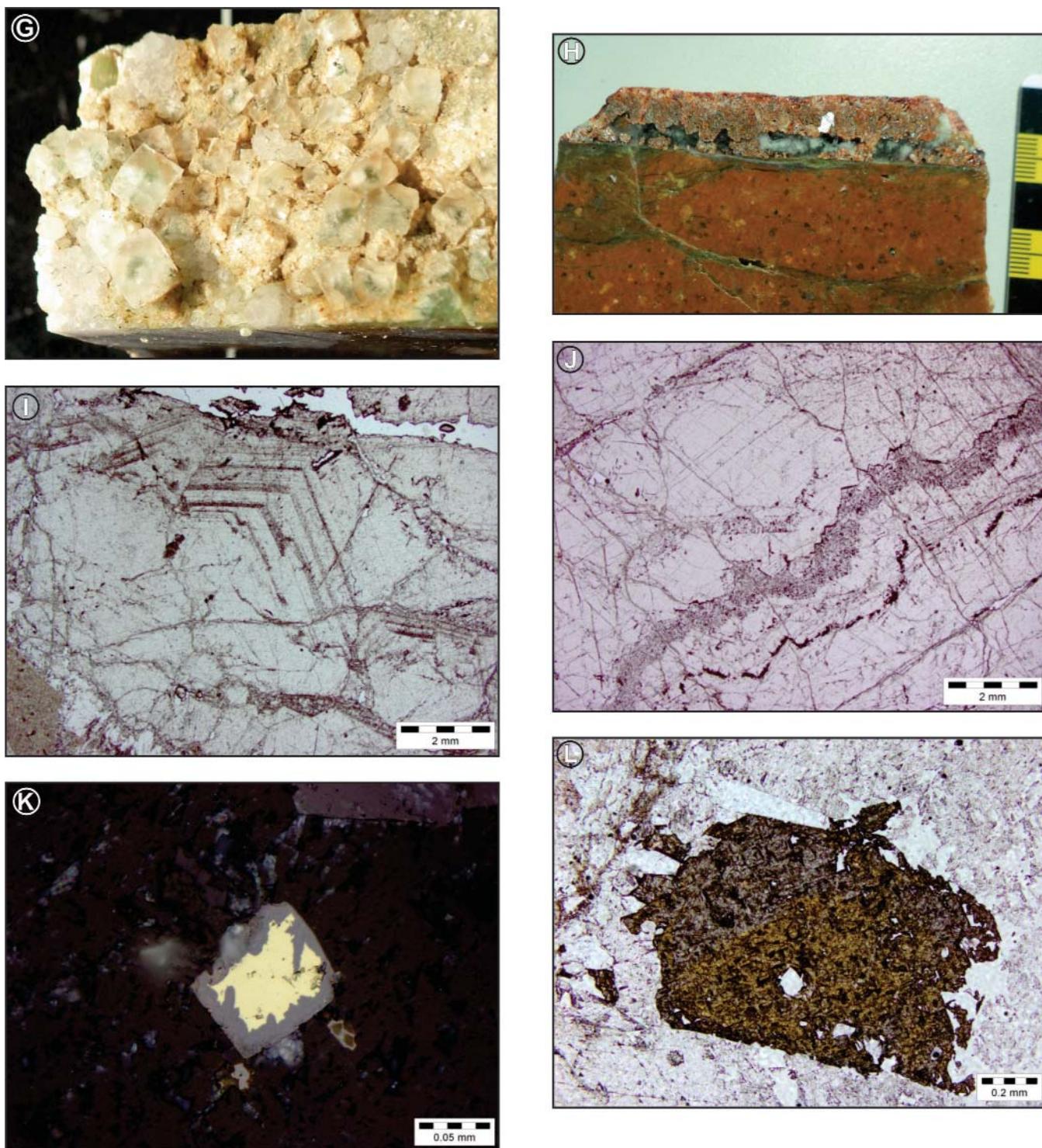


Plate 5 (continued). G) Clear cubic fluorite with green fluorite in the centre (Open Cut Pit). Largest fluorite cube is 1 cm in size. The green fluorite is likely octahedral; H) Green fluorite with coarse-grained, light-brown sphalerite; I) Photomicrograph of zoned green fluorite (Open Cut Pit). Zoning is defined by tiny silicate (quartz, orthoclase ± plagioclase) inclusions; J) Photomicrograph of purple and blue fluorite separated by a thin hematite-rich layer (Center Pit); K) Photomicrograph of pyrite, which has been partially replaced by hematite in green fluorite (Grebes Nest Pit); L) Photomicrograph of zoned sphalerite in green fluorite (Open Cut Pit).

filled vugs. In the Grebes Nest Pit, green, octahedral fluorite has been observed in the eastern end of the pit, in a calcite-rich vein that cuts the main AGS vein system obliquely. Whilst the morphology of fluorite crystals cannot be easily determined in many samples, it is possible that octahedral fluorite is more common than previously thought.

Green and blue fluorite in all areas is associated with minor amounts of coarse-grained (~0.5 cm) galena and/or sphalerite (Plate 5C, F, H). Galena appears to be more common at Grebes Nest Pit and sphalerite is more common at Open Cut Pit, but there are local variations. In some samples, two generations of sphalerite have been observed (Plate 5E). The first generation occurs within purple fluorite, is fine grained and a yellow, metallic colour. The second generation occurs within the blue fluorite vein, is coarser grained, zoned (Plate 5L), and light brown; possibly suggesting that it is richer in iron. Pyrite is also locally present, and is partially replaced by hematite (Plate 5K).

6. Blastonite

'Blastonite' is a local term describing a late hydrothermal event resulting in breccia composed of various sized fragments of previous mineralized phases in a matrix composed of quartz, calcite (in calcite-rich areas) and fine-grained fluorite (Plate 6). Quartz in the matrix commonly has a milky appearance. The blastonite results from fracturing and brecciation of previous veins and an influx of silica rich material. Blastonite was only observed at the Grebes Nest Pit.

7. Late Quartz

Late quartz associated with the AGS vein system is observed filling vugs in previous phases, including blastonite (Plate 7A, B). Other minerals associated with this phase include chalcopyrite and/or pyrite, and rarely galena (Plate 7B). Quartz forms terminated crystals ranging up to 0.5 cm in length, but typically occurring as 1-2 mm crystals.



Plate 6. Blastonite composed of purple, green, blue, white and grey fluorite in quartz-rich matrix (Grebes Nest Pit).

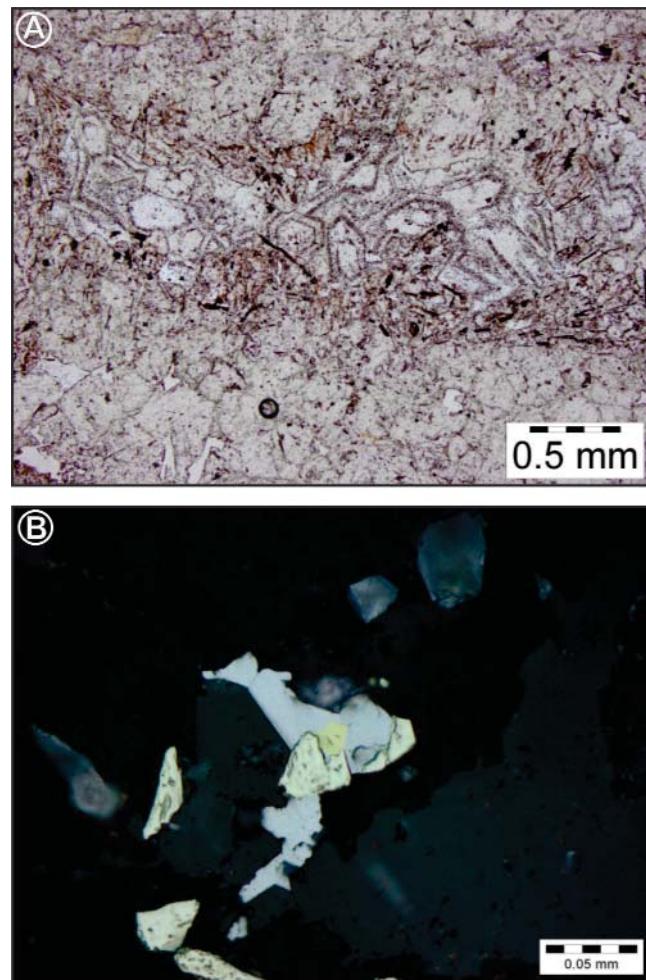


Plate 7. Late quartz phase. A) Photomicrograph of late, zoned quartz (Grebes Nest Pit). Zoning is defined by tiny unidentified inclusions; B) Photomicrograph of late quartz with pyrite, galena and chalcopyrite (Open Cut Pit).

The quartz is clear at the Grebes Nest Pit, but is often smoky at the Open Cut Pit. Thin sections of late quartz show zoning defined by tiny black impurities (Plate 7A).

Variations in Fluorite Mineralization

There are significant variations in the styles of fluorite mineralization, not only between granite and sediment-hosted fluorite veins, but also along the AGS vein system. There are variations among the different granite-hosted fluorite veins that were examined as well.

The major variations along the AGS vein system include:

- abundance of calcite in the Grebes Nest Pit (High Carbonate Zone),

- abundance of the chalcedony–fluorite–hematite phase in the Open Cut Pit, probably at the expense of banded and yellow fluorite, which are almost absent,
- higher sulphide content in the Open Cut Pit,
- abundance of green, octahedral fluorite in the Open Cut Pit,
- presence of clear, cubic fluorite in the Open Cut Pit, and
- lack of blastonite in the Open Cut Pit.

Most of the fluorite veins examined in the granite were either too small, or had been trenched and the high-grade fluorite zone removed, to allow for a proper detailed documentation. Phases observed in the granite-hosted veins include the barren breccia, purple fluorite, banded and yellow fluorite, blue-green fluorite and blastonite. The observations in the granite-hosted veins agree with the paragenetic sequence described in the AGS area. The Red Head Vein and an unnamed small fluorite vein along the shoreline in Salt Cove contained significant amounts of calcite. Sulphide content is higher in the Chambers Cove area, with the sulphide located close to the contact of the SLG with the sediments. Sulphides identified to date include galena, sphalerite, and chalcopyrite. Barite is also common.

DISCUSSION

COMPARISON TO OTHER STUDIES

St. Lawrence

The paragenetic sequence described here generally agrees with previous studies (Sparkes and Reeves, 2015; Reeves *et al.*, 2016; Tables 2 and 3). The paragenetic sequence described by Reeves *et al.* (2016) included both the AGS area and the granite-hosted fluorite veins, which may be one reason for the differences (Table 2). The sampling method in the current study compared to the other two studies may be another reason for some of the differences in the paragenetic sequence. Sampling could not systematically cover the entire AGS area due to lack of outcrop, fresh surface, precise sample locations, and time restrictions. The previous studies were based mostly on information gleaned from drillholes, whereas the current study focused more on field relationships and hand-sample description. Differences include the timing of some of the fine-grained sulphides, separation of the second phase of the paragenetic sequence of Sparkes and Reeves (2015) and Reeves *et al.* (2016) into two separate phases, the presence of a second green fluorite phase, and the timing of carbonate precipitation.

Fine-grained sulphides were observed with the purple fluorite phase, possibly forming prior to the fluorite, and with the grey fluorite at the end of Phase 3. Reeves *et al.*

(2016) describe fine-grained sulphides only with the grey fluorite in Phase 3.

Reeves *et al.* (2016) state, the second phase included coarse-grained, red, yellow, clear and blue-green fluorite, and the banded fine-grained fluorite. Several samples in this study suggest that the yellow fluorite was coeval with the banded, fine-grained fluorite and preceded the formation of blue and green fluorite.

The chalcedony–fluorite phase was not described by Sparkes and Reeves (2015) or Reeves *et al.* (2016). It is recognized that this phase may not be widespread and it is likely coeval with the banded fine-grained fluorite and yellow fluorite; hence, this may not represent a separate temporal phase.

Reeves *et al.* (2016) described a second green-white fluorite event; but this was not observed from the AGS vein system. In this study, all the green fluorite was interpreted to have formed in Phase 5, locally alternating with blue and grey fluorite and followed by clear, cubic fluorite.

Reeves *et al.* (2016) described a late carbonate–fluorite event, but in the High Carbonate Zone there is evidence for carbonate in the earlier phases. There, purple fluorite–white calcite veins are truncated by yellow fluorite (Plate 2C), calcite locally occurs with the banded, fine-grained fluorite phase (Plate 3A, B), and calcite is interlayered with green ± blue-grey fluorite (Plate 5A). Some samples may represent an additional late carbonate–fluorite event, but the relative timing could not be determined.

Nabburg–Wölsendorf, Germany

The paragenetic sequence of fluorite mineralization in the St. Lawrence area shows similarities to that in the Nabburg–Wölsendorf area in Germany, where Dill and Weber (2010) describe two main types of fluorite mineralization. The first type is related to a low-viscosity fluid and is characterized by dark-blue, purple and black, fine- to coarse-grained fluorite that forms thin veins or fine-grained groundmasses in hydrothermal breccia. These fluorites are typically poor in trace elements.

The second type is associated with a high-viscosity fluid and is characterized by coarse- and minor fine-grained, green, white and yellow fluorite. These are enriched in trace elements, particularly in yttrium. The high viscosity of the fluid is related to the presence of clay minerals in the fluid, eventually leading to argillaceous fault gouge precipitation. The clay minerals originate from ongoing, extended fluid–rock interaction (Dill and Weber, 2010).

These two colour groups of fluorite are also observed in the St. Lawrence area. The purple fluorite represents the first type, followed by the second type which is represented by green, white, light-blue and yellow fluorite. Early fluorite in St. Lawrence show a flat REE pattern similar to the SLG, compared to the late, coarse-grained fluorites that have a more evolved REE pattern, suggesting changing fluid composition (Strong *et al.*, 1984; Gagnon *et al.*, 2003). The banded fine-grained fluorite and the yellow fluorite may represent a transition between the two types. The AGS vein system is also characterized by locally excessive argillaceous fault gouge. At Nabburg-Wölsendorf, the two types of fluorite mineralization are sometimes also spatially separated, but in the AGS area, the two types are separated temporally.

GENETIC IMPLICATIONS

Fluorite mineralization is typically interpreted to result from fluorine-rich volatiles separating from a cooling granite (Van Alstine, 1948; Teng, 1974; Strong *et al.*, 1984), a model that is probably accurate in the AGS area, particularly since the AGS vein system is underlain by the SLG. It is possible that volatiles from the cooling rhyolite sills also contributed to the fluorite mineralization in the AGS area, although the significance of this is unknown. The two main controls on fluorite mineralization in the AGS area are the rhyolite sills and the high-angle faults. The sills are cut by the faults, but faulting may have started prior to the intrusion of the rhyolite sills. The fluorite veins follow the faults, and repeated movement along them allowed for deposition of several phases of fluorite mineralization.

The rhyolite sills are spatially associated with the fluorite, but their role in mineralization is less understood. They are likely responsible for fracturing of the overlying sedimentary rocks as suggested by Reeves *et al.* (2016). This process was caused by a buildup of pressure due to gas formation from boiling of pore fluids in the surrounding sedimentary rocks, degassing of the cooling magma and possible contact metamorphic reactions (Jamtveit *et al.*, 2004; Planke *et al.*, 2005). Since the rhyolite sills were close to the surface and rich in volatiles, the pressure became higher than the lithostatic pressure and the gases started to rise and expand due to decompression, causing fracturing of the overlying sedimentary rocks. Interactions between magmatic fluids and meteoric water may have also helped this process. This provided the groundwork for the influx of mineralizing fluids. The rhyolite sills may have also provided fluid pathways along the contact with the host sedimentary rocks for the circulation of mineralizing fluids from the granite. Contraction of rhyolite sills as a result of cooling may have provided additional space for fluorite mineralization (Jamtveit *et al.*, 2004; Svensen *et al.*, 2010).

The abundance of green fluorite in the AGS area is probably due to the influence of country rocks (Gagnon *et al.*, 2003) and/or formation fluids (Strong *et al.*, 1984; Collins and Strong, 1988), rather than a later, localized reactivation of faults resulting in late fluorite veins dominated by green fluorite (Reeves *et al.*, 2016). According to Gagnon *et al.* (2003), fluorite from veins not hosted in granite and peripheral veins are enriched in some elements (Sr, Ba, Y and REE) and have more fractionated REE signatures (LREE enriched) compared to fluorite in granite-hosted veins. Possible causes of the green colour in fluorite include the presence of colour centres associated with coexisting Y and Ce and the presence of Sm (Bill and Calas, 1978; Bailey *et al.*, 1974), which are all enriched in non-granite-hosted fluorite occurrences compared to granite-hosted fluorite occurrences (Gagnon *et al.*, 2003).

Future exploration should concentrate on locating additional rhyolite sills and high-angle fault structures, which are the two main controls on fluorite mineralization in the AGS area. Country rocks may contain structures that are older than, and hence not present in, the SLG. Additionally, it must be recognized that veins outside of the granite need not be continuations of existing veins within the granite, although they could follow the same structures. Also, further exploration should examine other rock units that may have acted as conduits for mineralizing fluids.

FURTHER RESEARCH

Understanding the role of the rhyolite sills in fluorite mineralization in the AGS area is crucial, because the rhyolite is spatially and most likely genetically associated with the fluorite veins. Therefore, further research will concentrate on the relative timing and relationship of the rhyolite sills and SLG using geochronology data, and geochemical analysis. The major- and trace-element geochemistry will be used to address the unknown relationship of the rhyolite sills and the SLG, whereas the geochronology will shed some information on the relative timing of the two.

The REE chemistry of fluorites will examine the relationship of the different fluorite phases within the granite, rhyolite and sedimentary rocks; and the nature and evolution of the mineralizing fluids. Fluid inclusion studies will be used to determine changes in the temperature, pressure and composition of fluids during the various phases of fluorite crystallization. The fluorite content of each mineralizing phase will help understand the conditions (pressure, temperature, fluid composition) during the formation of higher grade fluorite and will also be beneficial in visually distinguishing high-grade areas during exploration.

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