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**The fractured latest Devonian granites of the West Moose
River Pluton along the Cobequid Shear Zone, Nova Scotia:
implications for regional mineralisation**

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Abstract: Latest Devonian (~365–358 Ma) A-type granites in the Cobequid Highlands host complex sequences of rare earth element (REE) and other hydrothermal minerals. The West Moose River pluton is the only pluton truncated and brittly deformed by the mid Carboniferous (~327 Ma) strike-slip Minas Fault Zone during the Alleghanian orogeny. Fractures in the granite provide a record of several deformational and hydrothermal events with distinct mineral assemblages. Early sodic alteration produced albitisation of feldspar, and riebeckite and tourmaline veins. The $\delta^{18}\text{O}$ of albite and albitised granite (5–6 ‰) is similar to other regional granites, suggesting a mantle source of albitising fluids. Nearby halite deposits are younger and thus not a source of Na. Early chlorite veins were followed by potassic alteration and hydrothermal biotite, and by diabase and lamprophyre dyke emplacement. Euhedral magnetite occupies new cross-cutting fractures and vugs, correlated with regional iron oxide- carbonate- sulphide mineralisation following initiation of the Minas Fault Zone. This change in stress field resulted in widespread fracturing of the granite, greatly increasing its permeability. Magnetite is post-dated by titania minerals with hydrothermal REE-minerals in dissolution voids. The spatial variation in REE mineral types indicates variable availability of F, Cl and CO_2 in mineralising fluids derived from groundwater. REE mineralisation is rare in veins in country rock, demonstrating local plutonic sources of REE. The emplacement of REE minerals was complex in time and space and was a consequence of pervasive microfracturing of the granite.

240 words

Introduction

Plutons emplaced during the later stages of orogeny in orogen-parallel fault zones may provide a record of hydrothermal alteration during late orogenesis. The Cobequid Shear Zone of the northern Appalachians (Fig. 1) is the site of such plutons. In the late Devonian and early Carboniferous, the shear zone formed part of a NE–SW-trending crustal-scale, orogen-parallel system, with some 300 km of right-lateral offset, extending from the southern Appalachians to the Caledonides of Scotland (Hibbard and Waldron 2009). Granite and gabbro plutons, together with coeval flood basalts and felsic pyroclastic rocks up to 4 km thick, were emplaced and progressively deformed in this shear system, which included the Cobequid (*sensu stricto*), Kirkhill and Rockland Brook faults (Koukouvelas et al. 1996, 2002). This igneous activity took place during the Neo-Acadian tectonic phase of van Staal and Barr (2012) in the latest Devonian and earliest Carboniferous (ca. 365–355 Ma). The plutons and their master faults have been uplifted and exposed in the Cobequid Highlands (Koukouvelas et al. 2006; Papoutsas et al. 2016). These plutons have A-type geochemistry and are enriched in rare-earth element (REE) minerals (Papoutsas and Pe-Piper 2013, 2015).

In late Carboniferous to Permian, the collision of Africa with Laurentia in the southern Appalachians resulted in the Alleghanian orogenic phase. In the northwestern Appalachians, much of this deformation was taken up along the E–W trending Minas Fault Zone (Murphy et al. 2011), with 100 km of right-lateral offset (Waldron et al. 2015). Parts of the Minas Fault Zone reactivated some older faults, including the Cobequid Fault (*sensu stricto*). The onset of this E–W faulting is stratigraphically constrained to the mid Serpukhovian (~ 327 Ma) and was accompanied by iron-oxide mineralisation (Murphy et al. 2011). Base metal sulphides, barite and locally REE minerals also characterise the post-Serpukhovian mineralising systems along the

Cobequid Shear Zone and adjacent parts of the Minas Fault Zone (McHattie and O'Reilly 2008; Kontak et al. 2008) and in Carboniferous basins to the south (Sangster et al. 1998).

The West Moose River pluton is one of several granite plutons emplaced just north of the Cobequid Fault in the latest Devonian. Its southern margin appears truncated by late Carboniferous motion on the Cobequid Fault, as part of the Minas Fault Zone (Fig.1). The pluton consists principally of granite with lesser amounts of gabbro and diabase (Pe-Piper et al. 1991). Mafic dykes and sills intrude the granite: a few are lamprophyre, most are diabase. Pervasive fractures in the granite, related to Carboniferous deformation along the Cobequid Fault, host REE-bearing minerals, together with Fe-oxides, biotite, chlorite, ilmenite, TiO₂ mineral(s), and carbonates that have precipitated from hydrothermal fluids. The intensity of microfracturing in the West Moose River pluton is greater than in any of the other plutons along the Cobequid Shear Zone.

The objectives of this study are as follows:

1. To compare the REE mineral assemblages in the West Moose River pluton with those in less fractured plutons elsewhere in the Cobequid Highlands.

2. To establish the relative ages of the minerals in different types of fractures and to evaluate the role of fracturing in the development of the REE mineral assemblage.

3. To relate the regional distribution of REE minerals to REE abundance in host granites and to the varying sources of hydrothermal fluids.

4. Hence to determine the principal factors that resulted in large scale REE mineralisation along parts of the Cobequid Shear Zone.

Geological setting

The West Moose River pluton (Fig. 2) consists principally of granite, but along the southern margin of the pluton is minor diorite-gabbro that appears to pre-date the granite, suggesting that the pluton may have exploited a pre-existing fault. The present southern margin of the pluton is generally the Cobequid Fault. The northern margin comprises northward thinning, southward dipping granitic and mafic sheets, 0.5 m to 30 m thick, which thin rapidly northward, have mylonitic margins, less deformed interiors, and intruded Neoproterozoic country rock (Koukouvelas et al. 1996). Solid-state deformation is observed in the southern part of the pluton, with flattening of porphyroblasts of plagioclase and quartz grains, and growth of secondary riebeckite crystals. The pluton is cut by a penetrative system of planes that indicates southward movement on subhorizontal shear surfaces (Koukouvelas et al. 1996).

Several sets of mafic sheets (sills, dykes) cut the main pluton, and Piper et al. (1993) attempted to use structural evidence to define relative age of the sets. The oldest diabase sheets are sub-horizontal sills with associated minor dykes (2 - 20 mm wide) occupying fractures in the granite striking E-W and NE-SW. These early diabase sheets are commonly deformed (particularly near the Cobequid Fault) to give a flat lying foliation and a N-S trending mineral lineation, also visible in the granite. The NE-SW dykes show sinistral shear deformation. The pluton is cut by apparently later steep dykes striking 145° that also show sinistral shear deformation. The least deformed steep dykes strike 180° . All the rocks are cut by brittle fractures striking 075° to 110° (Piper et al. 1993). In previous studies "ferromagnesian stringers" were shown to occupy many of these fractures, consisting of green biotite, chlorite, ilmenite, titaniferous magnetite, and pyrite (Pe-Piper et al. 1991, 2004). In this study we demonstrate that

REE-bearing minerals are also hosted in fractures, in some cases together with “ferromagnesian stringers”.

Previous geochronological studies allow the identification and dating of several fracturing and hydrothermal events during and since the intrusion of the West Moose River pluton granites and associated mafic rocks in the Early Carboniferous (Table 1). A main phase of the West Moose River pluton, dated at 361 ± 5 Ma, cross-cuts clastic rocks of the late Devonian–early Carboniferous Horton Group that are hornfelsed but otherwise unmetamorphosed (Dunning et al. 2002). Regionally, the main plutons along the Cobequid Shear Zone are dated between 365 ± 4 Ma and 358 ± 4 Ma (Dunning et al. 2002; Pe-Piper et al. 2004). Sodic alteration with growth of albite and riebeckite in the West Moose River pluton is dated at about 355 ± 4 Ma by $^{40}\text{Ar}/^{39}\text{Ar}$ from riebeckite (Pe-Piper et al. 2004). The last evidence of major ductile deformation along the Cobequid Shear Zone, with growth of new datable mineral phases, took place ca. 344 Ma (Pe-Piper et al. 2004). This deformation was accompanied by potassic alteration resulting in alteration of hornblende to biotite in gabbro and diorite. A lamprophyre dyke in the West Moose River pluton and a similar dyke 10 km to the northwest cutting Neoproterozoic volcanic rocks both gave ages of ~ 334 Ma (Pe-Piper et al. 2004).

Methods

Field observations involved identifying mafic sheets (dykes and sills) and mineralised fractures (veins), and measurements of their attitudes and mineral lineations. Samples were collected with known relationship to fractures (Supplementary data Table S1).

Polished thin sections were prepared from selected samples of fractured granite (Fig. 2) and examined by petrographic microscope. Carbon-coated polished thin sections were analyzed

using a scanning electron microscope (SEM), acquiring back-scattered electron (BSE) images and energy dispersive spectroscopy (EDS) chemical analyses of minerals. Hydrrous phases or those containing ferric iron (Fe^{3+}) were identified by low totals in un-normalised EDS data. Minerals were identified on the basis of their elemental composition compared with mineral compositions reported in the literature (Supplementary data table S2). The term “ TiO_2 mineral(s)” is used for minerals with $>90\%$ TiO_2 , which are probably rutile, but also could be brookite or anatase: for simplicity they are identified as Rt in figures. The term “Fe-oxyhydroxides” is used for fine-grained Fe-rich minerals that may include mixtures of magnetite, hematite and goethite. Selected REE mineral grains were further analysed by electron microprobe by wavelength dispersive spectroscopy (WDS), using an analysis time of ~ 15 minutes. Analytical procedures are similar to those of Papoutsas and Pe-Piper (2013). Data from all these analyses are available in an Open File report (Pe-Piper et al. 2015). Geothermometry of chlorite uses the method of Kranidiotis and MacLean (1987).

Modal abundance of minerals in veins (Supplementary data table S3) was determined by image analysis of BSE images, supported by spot EDS analyses, measuring backscattered electron intensity using Image J software for Windows. Details of the procedure are given in Zhang et al. (2015) and Pe-Piper et al. (2015). Total percentage of rock samples occupied by veins was determined by point counting. Whole-rock powders from all samples were analysed for major and trace elements by Activation Laboratories according to their Code 4Lithoresearch and Code 4B1 packages, which combine lithium metaborate/tetraborate fusion ICP rock analyses with a trace element ICP-MS package (Supplementary data table 3). The magnetic susceptibility of selected samples was measured at five positions on 1 cm thick slabs using a Bartington MS2E point sensor. Oxygen isotopes (Supplementary data table S4) were determined on bulk rocks and

albite separates at the Laboratory for Stable Isotope Science, Western University, using methods summarised by Potter et al. (2012).

Results

Field setting and thin section observations of mafic sheets and hydrothermal veins

A variety of mafic sheets (dykes and sills) occur in the West Moose River pluton. (1) At the northern margin, northward-thinning wedges of both granite and diabase have intruded Neoproterozoic Jeffers Group country rock and both may show mylonitic deformation (Koukouvelas et al. 1996). All other mafic sheets cross-cut ductile deformation in the pluton, where present, and commonly invade cataclastic granite and contain small granite xenoliths (e.g., Figs. 3c, 4b). (2) Sills and related minor dykes mostly near the southern margin of the pluton show flat-lying fabrics (Fig. 3a) and the development of SW-plunging mineral lineations (Fig. 3b). (3) Steeply dipping sheets are of three orientations, of uncertain relative age. Dykes striking NE–SW are probably the oldest, as brittle fractures with a similar orientation that bound quartz-filled tension gashes indicating sinistral shear are cut and invaded by dykes striking NW–SE (Fig. 3c). Dykes striking N–S appear to be the least deformed. Some of the dykes show subhorizontal slickensides on N–S planes; one NE–SW dyke shows dip-slip slickensides, but similar planes in granite also show subhorizontal slickensides.

In the field, the most prominent vein sets are the dark fractures 0.5–3 mm wide occupied principally by either Fe-oxides (Fig. 3d) or chlorite (Fig. 3e) or both (Fig. 3g), forming both planar and irregular continuous veins, and in places invading cataclastic granite (Fig. 4b). Such veins are common within a metre of the mafic sheets. The planar veins are commonly developed on subparallel joint sets (Fig. 3d, g) that generally strike E–W. Less commonly, veins principally

of quartz or tourmaline cut granite (Fig. 3f, 4j), and carbonate veins cut the lamprophyre dykes (Fig. 4f).

In many granites, thin sections show a variety of fracture types. Some granites are highly cataclastic, with apparently dilational fractures separating brecciated granite fragments (Fig. 4b, c, j). Other granites are cut by more or less linear fractures (Fig. 4a, d, f, h) commonly filled by chlorite or Fe-oxide. The fractures have been locally enlarged to millimetre-scale patches of hydrothermal minerals as a result of dissolution or replacement of primary minerals (df in Fig. b dark patches in Fig. 4g), together with individual dissolution voids typically 5–50 mm in diameter (Fig. 5h, i, o). Chlorite-filled veins appear to have deformed in a somewhat ductile manner during later deformation (Fig. 5c, d), whereas the magnetite veins show more brittle deformation (Fig. 5j).

Mineral identification

Most REE-bearing minerals are small, have a patchy brown colour in transmitted light, and show no diagnostic optical properties, except for synchysite-(Ce), which resembles calcite. Identification of the REE minerals required study by SEM and confirmation by electron microprobe (Table 2). Most grains are typically composed of more than one mineral, likely representing some sort of solid solution or grain co-precipitation or incomplete alteration or replacement of pre-existing minerals. Sample 9835 contains a Y-rich silicate phase that resembles hingganite-(Y), except that it has higher FeO (> 8 wt.%; Table 2) than most reported hingganite-(Y) analyses in the literature (Uher et al. 2009). Both SEM-EDS and electron microprobe WDS analyses yield almost identical results of this mineral for the two analysed grains, and in both instances it occurs along with xenotime and Fe-oxyhydroxide filling a fracture. Analytical totals range from 90-91% by WDS (Table 2), indicating the presence of

volatiles. With the exception of FeO, all measured oxides match the chemistry of hingganite-(Y) more than any other known Y-silicate, and therefore it is tentatively identified as hingganite-(Y) in this work.

Iron oxides and hydroxides are abundant in many veins. Magnetite, hematite and goethite have all been identified, but distinguishing between these minerals in fine grained aggregates is difficult. Where unspecified Fe-oxyhydroxide is reported, it is too fine grained to discriminate magnetite or hematite either by reflected light microscope, or SEM and EDS, or WDS.

Comparison of measured magnetic susceptibility in samples 9835 and 9837 ($13, 14 \times 10^{-3}$ SI respectively) with the amount of fine-grained Fe-oxyhydroxide in fractures in the rock (2.3, 3.3 % of the total rock, respectively) suggests that magnetite makes up 10% and 7% of the Fe-oxyhydroxides in the two samples. The dominant Fe-oxyhydroxide in these samples is probably hematite.

Two chemically distinct types of chlorite are distinguished. Most chlorite has FeO_T about 30 wt. %, but a Fe-rich chlorite has FeO_T > 40 wt. %. Tourmaline is of the schorl-dravite series.

Alteration of magmatic minerals

Primary (magmatic) minerals in the granites are principally perthitic K-feldspar and quartz. Other magmatic minerals, present in some samples, include brown biotite and magmatic albite. Rare relicts of the magmatic REE-bearing silicate mineral chevkinite-(Ce) are partially replaced by ilmenite and several REE-bearing minerals including the carbonate bastnäsite-(Ce), the Nb-oxide samarskite-(Y) and the silicate thorite (Fig. 5a). Partial or complete alteration of K-feldspar to albite is widespread in the granites, principally along mineral cleavage planes and fractures (Fig. 5e). Magmatic biotite shows exsolution of rutile and is commonly altered to

217 chlorite ($\text{FeO}_T \sim 30$ wt. %), with later precipitation of iron oxide along the cleavage planes of the
218 altered magmatic biotite (Fig. 5b).

219 **Fracture-filling minerals**

220 *Mineralised veins and vugs*

221 Discrete veins sampled in the field have widths of 1–10 mm. They include veins
222 predominantly of: (1) Quartz, in some cases with biotite along the rim (Fig. 3c), both as
223 continuous veins and filling tension gashes. (2) Tourmaline (Figs. 3f, 4j). (3) Chlorite (Fig. 3g).
224 (4) Predominantly Fe-oxyhydroxide, with some zircon (Fig. 3e). (5) Pyrite, with some
225 chalcopyrite, is found only within centimetres of the Horton Group contact (Fig. 4a).

226 Image analysis of intergranular discontinuous fractures and dissolution patches in four
227 samples (Fig. 6) shows that several distinct mineral assemblages are present, confirmed by
228 petrographic observation of other samples. The most common types are:

229 1. Chlorite, generally with lesser rutile and zircon, in some cases with apatite. These minerals
230 predominate in 9838 and are common in 9840 (Figs. 5b–d; 6c, d). A chlorite and ilmenite patch
231 is present in 9837.

232 2. Chlorite and Fe-oxides, with common calcite in 9837 and common rutile in 9840 (Figs. 4h, i;
233 5k, l; 6b, d).

234 3. Fe-oxides either dominant or with lesser rutile or ilmenite (9835, Figs. 4d; 5f, g, j; 6a)

235 There is no apparent relationship between REE minerals and overall mineral assemblage,
236 except that synchysite is generally associated with calcite.

Relationship to mafic intrusions

At a thin section scale, some mafic intrusions show secondary biotite within fractures of cataclastic granite adjacent to the diabase (Fig. 4b, c) but there is no biotite in the diabase. Associated with the biotite are some chlorite and opaque minerals (ilmenite, titaniferous magnetite and pyrite). Green secondary biotite is of very variable composition but contains up to several percent of C1 and F (average 0.7% of each) and has low Ti compared with the apparently magmatic brown variety (Pe-Piper et al. 1991).

Sequence of minerals in veins and dissolution patches

Textural relationships between minerals in hydrothermal veins can be used to infer a relative chronology. A few veins have a symmetrical sequence of minerals from margin to centre, which is evidence of relative age. So too is where a younger vein clearly cross-cuts an older vein, or an older vein may be brecciated or fractured subparallel to its length and filled with a later mineral. Regional strain was largely taken up within the pluton on microfractures and cleavage planes, which then became sites for later mineral precipitation. Hydrothermal fluids corroded earlier vein minerals or host granite, particularly quartz and calcite, and younger minerals may precipitate in the resulting secondary porosity.

The sequence of minerals in dissolution patches can also be interpreted, although some textural information is ambiguous. For example, in the dissolution patch in quartz in sample 9837 (Fig. 5k), the earliest mineral appears to be rutile, which has been corroded along its cleavage planes. The rutile is invaded by sparry ferroan calcite that is itself partly dissolved along cleavage planes. Euhedral sheaves of chlorite cross-cut the corroded calcite (e.g. at the red circle in Fig. 5k). Subhedral manganoan ilmenite cross-cuts both rutile and calcite and is thus younger.

259 Chlorite appears to have largely altered to ferroan chlorite, but some remnants of earlier chlorite
260 can be recognised from their lower backscatter.

261 *Chlorite, riebeckite and tourmaline*

262 In cases where there are veins with multiple minerals present, chlorite commonly seems
263 to be the oldest hydrothermal mineral. In the large outcrop of samples 9873-77 (Figs. 3e, f; 7),
264 the earliest veins appear to be chlorite (Fig. 3e) or tourmaline (Figs. 3f; 4j). Geothermometry of
265 chlorite (method of Kranidiotis and MacLean 1987) in 9873–77 gives a mean temperature of
266 181°C (n=10). Elsewhere, the sodic amphibole riebeckite occupies small veins that cross-cut
267 foliated granite and has also partially replaced magmatic K-feldspars along fractures and
268 cleavage planes (Fig. 5d).

269 *Calcite, green biotite and chlorite*

270 The next oldest fracture-filling hydrothermal mineral appears to be calcite, for example in
271 sample 9837, with textures suggesting that it predates some chlorite (Fig. 4 h, i; 5k). Textures
272 suggest that calcite may surround, and thus post-date, a hydrothermal green biotite (Fig. 5l), but
273 this relationship is not certain. Hydrothermal biotite is patchily replaced by chlorite, Fe-chlorite,
274 Fe-oxyhydroxides and zircon (Fig. 5b).

275 *Fe-oxide rich veins, titania minerals, Fe-chlorite and REE minerals*

276 In general, Fe-oxides (magnetite, hematite, in places showing supergene alteration or
277 weathering to goethite) appear to be late in the mineral paragenesis and are in many cases
278 associated with REE minerals. Fe-oxides occupy dissolution voids in earlier minerals,
279 particularly quartz (Fig. 5f, h) but also feldspar (Figs. 5o; 7e), tourmaline, calcite (Fig. 5k) and
280 riebeckite (Fig. 5e). Magmatic zircon has also experienced dissolution, for example in sample

9839 where a zircon grain contains abundant dissolution voids, some of which are filled with an unidentified mineral with high backscatter. EDS analyses of such bright spots are imprecise due to the beam size being about an order of magnitude larger than the diameter of the mineral. Nevertheless values of UO_3 up to 7 wt. % and of Ag_2O up to 13 wt. % were recorded.

In places microfractures contain abundant euhedral magnetite grains (red ellipse in Fig. 5f). Fe-chlorite appears to post-date magnetite since in many cases the alteration of chlorite to Fe-chlorite took place preferentially along the contacts with euhedral magnetite (magenta lines in Fig. 5l); in contrast, the magnetite appears to have surrounded chlorite (red ellipse in Fig. 5l). Magnetite in places is corroded and altered along cleavage planes to TiO_2 minerals (Fig. 5i, j), with fractures and dissolution pores further filled by zircon and xenotime (Fig. 5i, o). Small veins of magnetite and TiO_2 minerals in sample 9835 (Fig. 6a) predate zircon, which predates xenotime that surrounds subhedral magnetite (Fig. 5g). Hingganite-(Y) (Fig. 5f), samarskite-(Y), niobaeschynite-(Y), cerianite, pyrochlore and thorite also appear to be late, as does a Nb-rich mineral with 40–50% Nb_2O_5 and ~10% each of SiO_2 and FeO. Synchysite is found only in samples with calcite and texturally appears to be late (Fig. 5l). Thorite appears to postdate synchysite, filling voids between synchysite crystals (Fig. 5m). In a few places, magmatic albite is overgrown by allanite-Ce, and fractures in this allanite-Ce are filled with thorite or samarskite-(Y).

The Ce-rich mineral cerianite, along with the clay mineral beidellite and small grains of Fe-oxyhydroxide, occupy voids created by expansion and deformation of biotite along its cleavage (Fig. 5n). Cerianite also occurs in the outer rim of a large cavity as the dominant phase in a grain that is 300 μm long (Fig. 8) and has inclusions of TiO_2 mineral(s), ilmenite, thorite and xenotime, the latter two in a solid solution series. Elemental X-ray maps show that the cerianite

grain contains most of the Ce, Nd, and F, whereas ilmenite, indicated by high amounts of Fe and Ti, also contains some La (Fig. 8). Chlorine, although present in minor amounts, is concentrated mostly in the cerianite (Fig. 8b). This sample also contains bastnäsite-(Ce) that seems to predate thorite-xenotime, and rare samarskite-(Y).

Black veins occupy fractures that cut the granite-hornfels contact (Fig. 4a) and consist mainly of fine grained Fe-oxyhydroxide, with minor chalcopyrite, chlorite, an aluminophosphate mineral and quartz. Such black veins cut earlier chlorite veins (Fig. 7g). Similar minerals fill dissolution voids, coat cataclastic breccia clasts and magmatic minerals (Fig. 7h) and occupy cleavage planes in feldspar and muscovite (Fig. 7c). In the fractures, this mineral assemblage has precipitated in successive zones inwards from the rims in a crustiform texture (Fig. 7b, c). The fractures also contain larger grains of euhedral to subhedral xenotime (Fig. 7d). Some fractures are filled principally by pyrite veins, rimmed by chalcopyrite and apparently hydrothermal K-feldspar (Fig. 7a), with later xenotime in enlarged fractures in the pyrite (Fig. 7d). The pyrite is partially replaced by or pseudomorphed by Fe-oxyhydroxides. The presence of zircon in contact with hornfels at the margin of Fe-oxyhydroxide veins, suggests the zircon is earlier (Fig. 7b). Dissolution voids contain samarskite-Y, aeschynite-euxenite and pyrochlore (Fig. 7e, f). Late largely barren fractures contain small amounts of barite, zircon, ilmenite, monazite and molybdenite (Fig. 7i).

Lamprophyre dykes and sills cut the West Moose River pluton within 200 m of the Cobequid Fault. Deformed dyke 2226 (Fig. 3a) is cut by calcite veins (Fig. 4f) that host synchysite-Ce. Sill 7106 is cut by an older set of veins principally of chlorite, with lesser amounts of Fe and Ti oxides, and a younger set of calcite with fluorite, synchysite-Ce and minor

barite. Minor pyrite is found at the margin of the younger veins. Geothermometry of chlorite in the older veins gives a mean temperature of 255°C (n=14).

Whole-rock geochemistry of granites

Distribution of REE

The West Moose River pluton granites have typical A-type granite geochemistry (Piper et al. 1991). Here, we focus on the geochemical consequences of granite alteration, particularly for bulk rock REE. Most granites have ~4% each of Na₂O and K₂O, but altered granites have <5% K₂O and <10% Na₂O (Fig. 9a). High ΣREE is found in samples with Na or K enrichment, and low values of magnetic susceptibility (Fig. 9d). The lowest values of ΣREE correlate with lowest Th content, but Th is almost constant at ~22 ppm for samples with ΣREE > 150 ppm (Fig. 9e) that also show LREE enrichment (Fig. 10b) and higher TiO₂. Th shows no systematic variation with either U or Nb, but may increase with decreasing Zr (with much scatter, Fig. 9b).

Chondrite-normalised REE abundance plots show similarities within geographic groups of samples. Granites from the northwestern part of the pluton (Fig. 10a) have almost flat MREE–HREE patterns, relatively low LREE normalised abundances except for a strong positive Ce anomaly, and a strong negative Eu anomaly. Farther east in the pluton (Fig. 10b), MREE–HREE patterns are flat and there is a strong negative Eu anomaly, but the LREE show a gradual increase in normalised abundance from Sm to La with no significant Ce anomaly. This geographic geochemical variation implies variation in the types of REE-bearing minerals. Bastnäsite -(Ce), cerianite and synchysite-(Ce) contain 50–75 wt. % ΣREE and therefore most influence bulk rock geochemistry, whereas allanite-(Ce), hingganite-(Y) and xenotime contain

only 15–20 wt. %. Most of these minerals fractionate the LREE (Fig. 11), but hingganite-(Y) fractionates the HREE and cerianite is enriched in Ce.

Oxygen isotopes

Oxygen isotopes have been determined on bulk rocks from the West Moose River pluton: five samples (plus one duplicate) of the main granites, two granites with riebeckite, and two highly albitised granites, as well as on albite separates from those two samples. In addition, 10 granites and two gabbros from other latest Devonian plutons in the Cobequid Highlands were also analysed (Fig. 12a; Supplementary data table S4).

Of 20 analysed granite samples, four show outlying values of $\delta^{18}\text{O}$. The remainder have a mean of 6.0 ‰ (sd = 0.4) (Fig. 12a). These values are lower than “normal” granites (e.g., Taylor 1968) and a little lower than most Paleozoic granites elsewhere in the Avalon terrane (Fig. 13) summarised by Potter et al. (2008). They are distinctly lower than Paleozoic granites in the Gander terrane (Potter et al. 2008) and Devonian granites in the Meguma terrane (Longstaffe et al. 1980). The mean $\delta^{18}\text{O}$ value of 6.0 ‰ is the value normally cited for mantle-derived mafic and ultramafic rocks (Bindeman 2008). An early gabbro sample from the Wentworth pluton also falls within one standard deviation of this mean value.

Three granite samples have $\delta^{18}\text{O} < 5$ ‰. Two are from late intrusive phases within the Pleasant Hills pluton (1.6, 3.8 ‰). The other sample is from an unusual granite from the Wentworth pluton (4.6 ‰) that has both sodic and calcic amphiboles present: this is characteristic of some late granites (sample 7710 of Papoutsas and Pe-Piper 2013), although the field relationships of the analysed sample are indeterminate. Late gabbro from the Wentworth pluton also has low $\delta^{18}\text{O}$ (4.5 ‰). The one high outlier (Cape Chignecto granite, 7.6 ‰) is close to the mean value (7.4 ‰) for Paleozoic Avalon terrane granites compiled by Potter et al. (2008).

The four granite samples with sodic alteration from the West Moose River pluton (albite $\pm$ riebeckite) have a mean $\delta^{18}\text{O}$ of 5.75 ‰, only slightly below the overall mean. These values may in part be because albite fractionates ^{18}O to 1–2 ‰ less than quartz. The possibility of some contribution of meteoric water cannot be excluded, but is not required by the data.

Discussion

Style of deformation and mafic intrusions in the West Moose River pluton

The early phases of the West Moose River pluton were emplaced into a deforming NE–SW trending shear zone that juxtaposed Neoproterozoic Jeffers Group with syn-plutonic lower Horton Group sedimentary rocks (Koukouvelas et al. 1996). The northern contact with the Jeffers Group shows syn-magmatic thrust deformation (Koukouvelas et al. 1996). Slivers of lower Horton Group are preserved as hornfels with NE-striking steep contacts with the granite (Fig. 2). The later phases of the pluton, dated at ~361 Ma (Table 1), are undeformed against Horton Group country rock. Subsequent deformation of the pluton during uplift took place under ductile conditions, resulting in southward extension marked by south-dipping foliation (Koukouvelas et al. 2006). Mafic sills were emplaced parallel to this foliation. Mafic dykes occupy three sets of fractures that are locally cataclastic: NE–SW parallel to the master shear zone, a set striking NW–SE, and a least deformed set of dykes striking N–S that may occupy wrench faults associated with southward extension (Fig. 3b).

A quite different type of strain, pervasively distributed throughout much of the granite, is represented by the microfractures and voids filled with Fe-oxyhydroxides, TiO_2 minerals and REE minerals. They appear to be related to small E–W striking joints and faults with little cataclasis (Figs. 3d, 4g). The microfractures and voids appear to have formed by a mix of

deformation and corrosion, to produce the geometry illustrated in Figure 4d, g and h. This change in style of strain is related to the onset of the E–W Minas Fault Zone at 327 Ma (Murphy and Collins 2008; Murphy et al. 2011). The late Devonian–early Carboniferous Fountain Lake Group volcanic rocks have flat-lying tectonic contacts with underlying Neoproterozoic Jeffers Group, Horton Group and West Moose River pluton north of the Cobequid Fault. This appears to be analogous to mid-Carboniferous thrusting in the Windsor-Kennetcook basin (Waldron et al. 2010). This thrust contact of the Fountain Lake Group is offset normally along two groups of faults: a NW–SE fault trend, which also defines the NE margin of the pluton, and in the western part of the pluton, there are N–S faults (Fig. 2). As older dykes parallel both of these fault trends, they are likely older lineaments that were reactivated during or after thrusting.

Two of the mafic sheets analysed by Pe-Piper et al. (1991), samples 1876 (Fig. 4c) and 1879 (Fig. 4b), have geochemical features that resemble lamprophyre, notably high K, Rb, and Ti, although in their mineralogical composition, they classify as diabase. Their degree of deformation also resembles that of the lamprophyre (Fig. 3a).

Paragenetic sequence of minerals

The textural evidence at both field and thin section scale indicates that the earliest brittle fractures and veins post-date some ductile deformation of the granites. Some early veins comprise quartz or chlorite, but most have sodic minerals: riebeckite, tourmaline or albite (Fig. 14). Biotite fills cataclastic granite adjacent to mafic sheets and appears to predate both calcite (Fig. 5l) and the emplacement of diabase that is likely related to the lamprophyres (Fig. 4b). A phase of corrosion, enlarging discontinuous fractures in the granite, took place before the precipitation of magnetite in porosity in the granite (Fig. 4b, d, h; 5f, h). In some cases, microfractures are filled exclusively with magnetite and REE minerals and lack common earlier

minerals such as chlorite (Fig. 5g, h). Some magnetite shows corrosion and alteration with growth of rutile along magnetite cleavage or fractures and in pores (Fig. 5j). Late zircon and xenotime cross-cut fractures (Fig. 5i, j). The growth of rutile is in places associated with Nb-rich magnetite (Fig. 5o) and the precipitation of Nb-Ti-Y-HREE-minerals (samarskite-Y, aeschynite-euxenite, and pyrochlore), and probably Fe-hingganite-Y, which form principally in dissolution voids and do not offer much textural evidence for determining paragenesis. Thorite is clearly a late mineral, post-dating synchysite (Fig. 5m) and it has a negative Eu anomaly (Fig. 11b) in contrast to that in the Wentworth pluton, where there is a positive Eu anomaly (Papoutsas and Pe-Piper 2013).

Granite within centimetres of the Horton Group contact has veins of massive pyrite (Fig. 7a) with minor chalcopyrite. Similar fractures are occupied by Fe-oxyhydroxide veins (Fig. 7b,c), interpreted as originally pyrite that experienced oxidation under supergene or weathering conditions. There are no rhombic pseudomorphs of the type found where ankerite and rhodochrosite veins have been oxidised in the western Cobequid Highlands (Pe-Piper et al. 2017). Rather, some pyrite is incompletely oxidised and cubic pseudomorphs are seen. The Fe-oxyhydroxide veins cut chlorite (Fig. 7g), surround secondary biotite, and appear younger than some zircon (Fig. 7b). Xenotime and other HREE minerals appear to post-date pyrite (Fig. 7d, f). Younger still are the minerals in largely barren veins, including barite, monazite and molybdenite. The unusual occurrence of pyrite in these veins may reflect the abundance of organic carbon in the Horton Group mudstone.

The LREE-mineral cerianite rims chlorite that has developed at the margins of fractures, and also occupies cleavage in feldspar, chlorite, biotite and muscovite (Fig. 5n). In general, it is not associated with magnetite, Fe-oxyhydroxides, and the HREE-minerals. These textural

relationships suggest that most cerianite predates the main magnetite event, but there is no definitive evidence for relative age. In the case of the vug illustrated in Figure 8, cerianite appears to be younger than ilmenite, rutile, and xenotime–thorite that it includes. The HREE minerals are absent in the lamprophyres and thus HREE mineralisation may predate lamprophyre intrusion at 334 ± 3 Ma, or the lamprophyres may not have provided a suitably porous host for their precipitation. In veins in the Horton Group along the Cobequid Fault, some monazite predates the Fe-oxide event based on both structural and geochronological evidence (Pe-Piper et al. 2017). The late cerianite contains chlorine (Fig. 8b), potentially available from dissolution of halite from the lower Carboniferous (Visean) Windsor Group in the Windsor-Kennetcook basin (Fig. 1b). On the other hand, the calcite veins in lamprophyre 7106 contain fluorite. Experimental data (Migdisov et al. 2009) show that F^- and Cl^- are almost equally capable of complexing with REE, and LREE complexes are more stable than HREE complexes up to 300 °C. Thus, Ce remained in solution until it precipitated under more oxidising conditions.

In summary, the likely paragenesis is (Fig. 14): (1) chlorite; (2) biotite, early calcite, perhaps cerianite and monazite; (3) a phase of corrosion; (4) magnetite; (5) further corrosion; (6) Fe-chlorite, Nb enrichment of magnetite, secondary TiO_2 minerals, zircon, Nb-Ti-Y-HREE-minerals (samarskite-Y, aeschynite-euxenite, pyrochlore and possibly Fe-hingganite-Y). Of uncertain relative age are (4a) pyrite and chalcopyrite, which may be temporally equivalent to magnetite, but pyrite is also known from the lamprophyres; (6a) late calcite, xenotime, LREE-minerals (monazite-Ce, synchysite-Ce, and cerianite) which seem to be associated with late TiO_2 minerals; and (7) late patchy mineralisation with minor barite and lesser thorite, zircon, ilmenite, monazite and molybdenite.

Controls on REE abundance

Relationship of REE minerals to chemistry and deformation of the granite

Primary (magmatic) REE minerals are very rare in the granite (Fig. 5a), although some REE minerals are held in magmatic zircon (which is commonly corroded) and even in feldspar and biotite. Where bulk rocks have high Σ REE, their REE patterns compare well with the identified REE mineral assemblages. The presence of widespread synchysite-(Ce) in sample 9837, and of cerianite and bastnäsité-(Ce) in sample 9840 is consistent with these two samples also having high abundance of REE in whole-rock analyses and abundant fractures and vugs (Fig. 6). Synchysite-(Ce) is abundant only where calcite veins are common (Fig. 6). The presence of hingganite-(Y) in 50% of the fractures of sample 9835 is consistent with the high HREE content of sample. On the other hand, a strong positive Ce anomaly is found in cerianite and chernovite (Fig. 11), neither of which was found in the western part of the pluton where the rocks show a positive Ce anomaly (Fig. 10a). In sample 9841, the only REE-bearing mineral found in thin section is zircon, yet Σ REE is high at 273 ppm. When REE minerals are sparse, a single thin section does not appear to be representative of the REE content of the bulk rock.

Almost all REE minerals occur in veins and vugs which appear to result from strain and corrosive fluids related to the 327 Ma onset of major brittle movement on the Minas Fault Zone. They are commonly associated with magnetite mineralisation. Scavenging of REE, predominantly Ce, on Fe-oxides is highest at the earliest stages of Fe precipitation, with active surface sites to bind trivalent cations (Bau 1999). The positive Ce anomalies (Fig. 10a) in the samples with the highest magnetic susceptibility (Fig. 9d) are consistent with such a scavenging mechanism, although they have relatively low Σ REE. Further evidence for this process is that hydrothermal magnetite from the North River pluton granite, 8 km to the east of the West Moose

484 River pluton (Fig. 1a), has high Ce, expressed as Ce_2O_3 , in the range of 2.4-2.7 wt. % apparently
485 dispersed within the magnetite structure.

486 *Controls on regional variation in ΣREE abundance and REE-bearing minerals*

487 The latest Devonian A-type granite plutons of the Cobequid Highlands show many
488 geochemical similarities that suggest a common origin. Based in part on Nd-Sm isotopes,
489 Papoutsas et al. (2016) concluded that extreme fractionation of enriched mantle yielded the
490 granites with sodic amphibole in the Wentworth pluton, and this magma mixed with 20-40% of
491 melts from intracrustal feldspathic rocks to yield granites with calcic amphibole or biotite in all
492 the plutons including the Wentworth pluton. The mantle source is illustrated by similar ϵNd
493 values for the granites and coeval gabbros and continental tholeiitic basalts (Fig. 12b). This
494 interpretation of a predominantly mantle source for magma in all analysed granites except the
495 Cape Chignecto pluton and some late phases is confirmed by our new oxygen isotope data (Fig.
496 12), which shows no detectable difference in crustal components between the Wentworth pluton
497 and the West Moose River pluton. Late granites and gabbros have lower $\delta^{18}\text{O}$, perhaps due to
498 some ingress of meteoric water. The lack of correlation with LOI or mineralogical indicators of
499 alteration indicates that the low $\delta^{18}\text{O}$ is not just the result of post-solidus alteration of feldspars
500 by meteoric water (Morrison 1994). The higher $\delta^{18}\text{O}$ for the one Cape Chignecto pluton granite
501 suggests a higher level of assimilation of crustal rocks.

502 In the Wentworth pluton, primary (magmatic) REE-bearing minerals comprise allanite-
503 (Ce), chevkinite-(Ce), zircon and hingganite-(Y) (Papoutsas and Pe-Piper 2013), with likely
504 significant sources of REE in feldspar and amphibole (Bea 1996). Minor allanite-(Ce) is the only
505 REE-bearing mineral found in the Pleasant Hills and Cape Chignecto plutons, and no primary
506 REE-bearing minerals are known from the North River pluton (Papoutsas and Pe-Piper 2015).

Nevertheless, these plutons have similar bulk rock Σ REE as the Wentworth pluton (Fig. 15). The West Moose River pluton has only trace presence of chevkinite (Fig. 5a).

In the Wentworth pluton, most of the postmagmatic REE-bearing minerals are found dispersed in the body of the rock, although Broughm et al. (2013) have reported concentration of REE in dykes. The granites of the Wentworth pluton are located at least 5 km north of the Cobequid Fault (Fig. 1a). Other plutons studied by Papoutsas and Pe-Piper (2015), the Pleasant Hills, North River and Cape Chignecto plutons, are all within a few km of the Cobequid Fault. In these plutons REE-bearing minerals occur mostly in fractures, which would have promoted a more efficient circulation and transport of these elements through hydrothermal fluids.

In general, the highest bulk rock Σ REE is found in Wentworth pluton granites with sodic amphiboles (Papoutsas and Pe-Piper 2013), with lesser amounts in granites with calcic amphibole and least in granites in the western plutons with biotite (Fig. 15). This distribution of REE is consistent with the concept that REE are originally derived from fractionation of mafic magmas derived from enriched subcontinental lithospheric mantle (Papoutsas et al. 2016) and the abundance of REE decreases as the component of assimilated crustal material increases westward. The abundance of bulk rock Σ REE in the West Moose River pluton is on average lower than in the other plutons, but the spread of values is larger. There thus appears to have been a net loss of REE from the pluton, but locally REE have been enriched. In veins in the Horton Group along the Cobequid Fault, REE-minerals are uncommon (Pe-Piper et al. 2017), but locally monazite, xenotime and synchysite are sinks for REE that might have been derived by hydrothermal leaching of the plutons.

Comparison can also be made with the hydrothermal minerals in plutons east of the West Moose River pluton (Figs. 1, 16). In the Wentworth pluton, > 5 km north of the Minas Fault

Zone, fracturing is less intense and magmatic REE minerals are common (Papoutsas and Pe-Piper 2013). Early REE-bearing hydrothermal fluids were low temperature and reducing, precipitating epidote and hydroxylbastnäsite-(Ce). Minor aeschynite-(Y) and titanite minerals correspond to the post-magnetite mineralisation in the West Moose River pluton. In the Pleasant Hills pluton, minor hydroxylbastnäsite-(Ce) is associated with biotite veins (Papoutsas and Pe-Piper 2015). Cerianite is also associated with biotite veins in the Pleasant Hills and Cape Chignecto plutons. Papoutsas and Pe-Piper (2015, their fig. 8) argued that the post-magnetite REE-minerals represented the most oxidising conditions based on relative abundance of magnetite in samples, with formation of hingganite-(Y), hydroxylbastnäsite-(Ce), parisite-(Ce), synchysite-(Ce), cerianite, and chernovite-(Y).

There are two groups of REE-bearing minerals based on Eu abundance in the West Moose River pluton: 1) chevkinite-(Ce) and bastnäsite-(Ce) with positive Eu anomalies suggesting lower hydrothermal temperature (for bastnäsite <250 °C) and 2) all other hydrothermal REE-bearing minerals (Fig. 14) that have negative Eu anomalies indicating higher hydrothermal temperatures (>250 °C) (Sverjensky 1984). In the eastern plutons, thorite texturally belongs to the early REE-bearing mineral assemblage associated with hydroxylbastnäsite-(Ce), and shows weak positive Eu anomaly, whereas in the West Moose River pluton and the Cape Chignecto pluton, thorite shows textural evidence that it precipitated later and at higher temperature, and it shows negative Eu anomaly and higher M-HREE concentrations (cf. Papoutsas and Pe-Piper 2015, their fig. 4c for Cape Chignecto pluton thorite).

Regional hydrothermal fluids and mineral paragenesis

The new observations in this study can be correlated with the dated tectonic, magmatic and hydrothermal events in the region (Fig. 16). The sodic metasomatic phase is recognised from

secondary riebeckite, sodic tourmaline and albitisation, and riebeckite has been dated at 355 ± 4 Ma (Table 1). The source of the Na is likely magmatic, based on the similarity of oxygen isotopes between bulk granites compared with highly albitised granite and albite separates (Fig.12). Residual heat in plutons and late minor magmatism were the likely driver of hydrothermal systems (Fig. 16a). The absence of hydrothermal REE-minerals in riebeckite-and tourmaline-filled fractures suggests that the circulation of REE-rich fluids and consequently the formation of hydrothermal REE-rich minerals was initiated later than the sodic alteration phase.

Along strike, in the Cape Chignecto pluton to the west and along the Rockland Brook Fault to the east, potassic alteration has been dated from hydrothermal biotite at ~ 344 Ma and is associated with the last phase of ductile deformation in the Kirkhill and Rockland Brook faults (Pe-Piper et al. 2004), approximately synchronous with the unconformable base of the Viséan Windsor Group, representing a basin inversion episode. Abundant green biotite is also found in the lamprophyric intrusions, which are dated at ~ 334 Ma (Pe-Piper et al. 2004). Biotite fills cataclastic fractures (Fig. 4B, C), indicating a higher structural level than at the localities where hydrothermal biotite was dated in ductile deformation zones. The age of any biotitisation event is thus not tightly constrained. The rare calcite that predates the magnetite mineralisation (Fig. 5k) is also of uncertain age, and it is unclear whether it correlates with the calcite veins in the lamprophyres.

Several features suggest correlation of the magnetite mineralisation with the regional mineralising event that started in the mid-Serpukhovian (Murphy and Collins 2008), related to the first establishment of some E–W components of the Minas Fault Zone (Murphy et al. 2011), allowing overpressured basinal fluids to migrate through the new permeable pathways. A magnetite deposit (with minor pyrite and chalcopyrite) at Bass River (Fig. 1a; Bond 1999;

O'Reilly 2002) post-dates mid-Serpukhovian deformation, and is hosted by the Londonderry Formation. In a similar structural setting 10 km farther east is the large Londonderry iron deposit, consisting principally of iron carbonate with supergene enrichment to hematite. Farther east (Fig. 1b), iron carbonate and oxides are found at the Brookfield deposit (Kontak et al. 2006b) and sulphide mineralisation with REE minerals at Copper Lake (Kontak et al. 2006a). Some magnetite (and pyrite) in the West Moose River pluton occupies new fractures that lack older minerals (Fig. 5G, 7) suggesting a change in stress field. The presence of chalcopyrite (Fig. 7) also suggests correlation with this event. The pervasive reddening of feldspar, presumably by nanoscale hematite (Putnis et al. 2007) may also be related to this event.

The predominance of Fe-oxides in the western Cobequid Highlands compared with Fe-carbonates in the east can be related to the source of hydrothermal fluids. We suggest that the Windsor-Kennetcook basin (a source of Cl^- and HCO_3^- from limestones and evaporites) lay adjacent to the eastern Cobequid Highlands, whereas the western Cobequid Highlands were adjacent to first cycle detritus from the South Mountain Batholith in the Horton Group, a source of F^- (Fig. 1b). Fluorite is also known from some of the A-type granite plutons of the Cobequid Highlands, so that F^- supply may also be local. The distribution of Fe-carbonates implies some 30 km of additional net dextral strike slip on the Cobequid Fault after the 327 Ma event, consistent with the offset of the Fountain Lake Group from West Moose River to Brookfield Rock (Fig. 1a; MacInnes and White 2004).

After the magnetite ($\pm$ pyrite) event in the West Moose River pluton, there is evidence for dissolution, alteration of magnetite and precipitation of a wide range of REE minerals together with common TiO_2 minerals ("rutile"). Mostly, these minerals do not occupy new veins; rather,

they appear to form in dissolution voids and earlier fractures incompletely filled by magnetite. A few late fractures contain barite among other minerals (Fig. 7i).

Regionally, barite mineralisation occurs in several generations. Barite cutting the Cumberland Group east of Squally Point (Fig. 1a) is younger than 305 Ma (Piper et al. 1996). Barite is most abundant where associated with base metal (Pb, Zn) mineralisation in Visean Windsor Group carbonates of the basins of central Nova Scotia (Sangster et al. 1998). The age of these deposits is poorly constrained, but cited as 320–300 Ma. They were precipitated from hot saline mineralising fluids, with a maximum 300°C temperature at Walton (Fig. 1b) (Sangster et al. 1998). The Pb and Sr isotopes of ore minerals suggest that the fluids leached basement rocks or Horton sedimentary rocks derived therefrom. Oxygen isotope compositions at Brookfield (Kontak et al. 2006b) were interpreted as basinal fluids derived from meteoric water influenced by limestones and evaporites.

By 325 Ma, Alleghenian collision and metamorphism were taking place on the present Scotian Shelf (Fig. 15c), presumably associated with uplift (Reynolds et al. 2012), and strike-slip deformation likely continued along the Minas Fault Zone (Murphy et al., 2011). The karstic Pembroke breccia (Lavoie et al. 1995) provides evidence of widespread meteoric water infiltration, which we suggest resulted in groundwater flow to the north. The Boss Point and Parrsboro formations around the Cobequid Highlands provide evidence of lowland depositional areas around a Cobequid horst. So there may have been prolonged supply of hydrothermal water after the 327 Ma mineralisation by magnetite.

Whether REE were leached by hydrothermal groundwater from the Lower Carboniferous sedimentary basins, or were sourced in the A-type granites of the Cobequid Highlands, is not known. The bulk abundance of Σ REE in the West Moose River pluton (Fig. 15) and the sparse

REE mineralisation in the Horton Group suggests a local granite source. The juxtaposition of the large Londonderry iron deposit with the large Folly Lake ferrogabbro in the Wentworth pluton (Fig. 1a) also suggests an important role for the Cobequid Highlands as a source of elements to mineralising fluids.

Thus both the textural style and composition of mineralisation in the West Moose River pluton evolved through time. The early phases of the pluton (older than 361 Ma) were emplaced into a deforming shear zone that preserves slivers of lower Horton Group as hornfels within the pluton. The later phases of the pluton at ~360 Ma are undeformed against country rock. Early deformation of the pluton during uplift and cooling of the pluton took place under ductile conditions, resulting in southward-dipping foliation (Koukouvelas et al. 2006) that may have facilitated albitisation by magmatic fluids rich in Na. With further uplift and cooling, granites began to deform brittly: small veins filled with quartz, chlorite, tourmaline or riebeckite. Continued release of K from K-feldspar in granite and alteration of amphibole in diorite resulted in local development of hydrothermal biotite. These potassic fluids exploited cataclastic fault zones within the pluton, that were subsequently intruded by diabase and lamprophyre. Strike-slip activity in the Cobequid Shear Zone continued to at least 344 Ma (Pe-Piper et al. 2004), correlated with basin inversion between the Horton and Windsor groups. Hydrothermal minerals from this time include chlorite, monazite, cerianite and calcite, probably reflecting the availability of mafic magmatic intrusions. The onset of the E–W Minas Fault Zone at 327 Ma (Murphy and Collins 2008) created large-scale cataclasis along the Cobequid Fault (O'Reilly 2002; MacInnes and White 2004). Deformation in the West Moose River pluton involved development of E–W striking faults and joints, the opening of new microfractures of variable width, and the enlargement of those interconnected microfractures by corrosive percolating

fluids. The granites developed an overall porosity of 3–8 %, with more ductile mafic intrusions and some chlorite veins acting as permeability barriers. Initially, the microfractures were the site of growth of magnetite crystals, except near Horton Group contacts where some pyrite and chalcopyrite precipitated. The source of Fe was probably from ferrogabbro and diorite components of the plutons along the Cobequid Shear Zone. After magnetite precipitation, few new fractures opened, suggesting that rather than being taken up throughout the pluton, strain was concentrated along the fault zone to the south. The pluton was still highly permeable, as the magnetite had not completely filled the microfractures and dissolution vugs. Minerals in the granite were thus susceptible to dissolution by permeating water, among them biotite, zircon and primary REE minerals. Elements such as Ti, Fe, Zr and the REE were redistributed and precipitated in the remnant pores as TiO_2 minerals, Fe-chlorite, zircon and REE-minerals. The fluids were similar to those at Brookfield (Kontak et al. 2006b): meteoric water driven by the hydraulic head in the Alleghenian uplift to the south and modified by its passage through Lower Carboniferous strata. Most of the water was likely F rich, derived from fluorite in the Cobequid Highland granites and fluorite-rich detritus from both the Cobequids and the South Mountain Batholith in the Horton Group. Water that significantly interacted with the Windsor Group limestones and evaporites would have been richer in Cl and CO_2 . These elements, together with the oxidation state of the fluids, influenced the details of the REE-mineral assemblages.

Conclusions

1. The sequence of hydrothermal mineralisation in the West Moose River granites is, from oldest to youngest: a) sodic alteration manifested by hydrothermal riebeckite, tourmaline and albite together with quartz (ca. 355 Ma); b) potassic alteration expressed by hydrothermal

biotite (ca. 344 Ma); c) quartz and chlorite, accompanied in places by calcite, and perhaps monazite, cerianite and pyrite (ca. 334 Ma); c) Fe-rich alteration, principally magnetite (ca. 327 Ma); e) titania minerals, Fe-rich chlorite, zircon, and a range of Nb-Ti-Y-HREE-minerals (samarskite-Y, aeschynite-euxenite, pyrochlore, and Fe-hingganite-Y); f) late calcite, xenotime, LREE-minerals (monazite-Ce, synchysite-Ce, and cerianite), thorite and barite (the last two phases poorly dated, likely 325–305 Ma).

2. Several phases of deformation of the pluton created permeability for the flow of hydrothermal fluids. The granite was emplaced within a deforming NE–SW trending shear zone, which produced fracturing along grain boundaries, and larger scale faulting and cataclasis that was exploited by hydrothermal fluids and mafic hypabyssal intrusions. The initiation of E–W brittle strike slip faulting at 327 Ma along the Minas Fault Zone led to widespread intergranular microfracturing, and permeability was enhanced by corrosive hydrothermal fluids resulting in 3–8 % porosity. Similar changes in stress field in other brittle geological settings would likely produce similarly permeable rocks.

3. The hydrothermal REE-rich minerals in the West Moose River pluton were predominantly derived from leaching of REE from the local granites. The abundance of hydrothermal REE-rich minerals correlates with the volume of fractures and voids in the samples. The highest amounts of REE-minerals are found in calcite-rich fractures. These observations may be of value as exploration guidelines. In contrast, in the Wentworth pluton, > 5 km north of the Cobequid Fault, magmatic REE minerals are common and the sequence of hydrothermal REE minerals is quite different. Thus both permeability and physico-chemical conditions influence the development of hydrothermal REE minerals.

4. Bulk rock and albite $\delta^{18}\text{O}$ values from the West Moose River pluton confirm its predominant mantle source and demonstrate a magmatic source for Na-rich fluids. The abundant Viséan halite of central Nova Scotia is younger and thus not a source of Na. K-rich fluids resulted from alteration of K-feldspar, amphibole and biotite in diorite and granite. The abundant Fe and Ti along the Minas Fault Zone were derived from the ferrogabbro and diorite components of the plutons. Local sources of elements including REE influenced the composition of mineral deposits.
5. The post-magnetite hydrothermal minerals were precipitated from meteoric water driven by the hydraulic head in the Alleghenian uplift to the south. Most of the water was F rich, but water that passed through the Windsor Group was richer in Cl and CO_2 . These elements, together with the oxidation state of the fluids, influenced the details of the main late REE-mineral assemblages.

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Figure captions

Figure 1. (a) Geological map of the Cobequid Highlands (modified from Pe-Piper and Piper 2003) showing the location of the West Moose River pluton and other localities discussed in the text. (b) Inset map shows regional setting relative to the Avalon and Meguma terranes of the northern Appalachians.

Figure 2. Geological map of the West Moose River pluton showing location of the principal studied samples and field photographs of Figure 3. Base map modified from Pe-Piper and Piper (2005). UTM zone 20.

Figure 3. Outcrop scale structures in the West Moose River pluton. (a) Deformed mafic sheet (lamprophyre dyke), West Moose River at southern margin of pluton. (b) Stereonet projection of poles to planar structures and mafic sheets in the West Moose River pluton. (c) Field cartoon of map view of mafic dyke striking NW–SE, and relationship to fractures. (d) Foliated granite sheet within Horton Group hornfels, cut by black Fe-oxide veins (magenta arrows). (e) Fractured granite with Fe-oxide veins. (f) Fractured granite with tourmaline and Fe-oxide veins. (g) Granite with E–W joint with black Fe-oxide vein, cutting earlier irregular chlorite vein.

Figure 4. Thin section photographs of veins. (a) Contact of granite with Horton Group hornfels, cut by irregular pyrite veins that have in places oxidised to Fe-oxyhydroxides. (b) Margin of small dyke in cataclastic granite showing granitic xenolith, zone of biotite veins (green) adjacent to dyke, and farther from the dyke a zone of dispersed irregular fractures with black Fe-oxide (df) and more pervasive fine fractures with red hematite. (c) Detail of cataclastic granite in B with biotite veins (ppl). (d) Granite 9835 showing linear veins of calcite (pink arrows) and cross-cutting linear veins of magnetite (red arrows) (Fig. 5f–g,

6a). Magnetite also occurs in larger vugs with later TiO_2 minerals, xenotime and zircon. (e) Same image as in (d), in crossed polars, showing fractures in granite. (f) Calcite vein cutting lamprophyre dyke, offset by fractures (ppl). (g) Granite 9837 showing vugs connected by fractures filled principally with chlorite, calcite and iron oxides (Figs. 5k–m, 6b). (h) Detail of granite 9837 showing linear veinlets of calcite and vugs with chlorite and magnetite. (i) Backscattered electron image of (h) showing identification of minerals. (j) Cataclastic granite with tourmaline vein (A) cut by small barren fracture (B) (ppl).

Figure 5. Backscattered electron (BSE) images showing relationships between minerals. (a) Chevkinite-(Ce) partly altered to ilmenite, thorite, samarskite-(Y) and bastnäsité-(Ce). (b) Biotite partly altered to chlorite and dissected by Fe-oxyhydroxide veinlets and spherulites. (c) Albite altering to allanite-(Ce), with late thorite. (d) Plastically deformed chlorite vein. (e) Vein of riebeckite cutting foliated granite, with later zircon and ilmenite. (f) Fracture with magnetite, euhedral against voids, with hingganite and xenotime. (g) Euhedral to subhedral grains of magnetite, zircon and rutile fill fractures in granite. Xenotime surrounds magnetite. (h) Bastnäsité-(Ce) and magnetite fill pores in quartz. (i) Corroded and fractured magnetite, with exsolution of rutile; fractures and margins of voids cut by younger zircon and xenotime. (j) Corroded magnetite with growth of rutile in pores and along cleavage, also late xenotime. (k) Vug in quartz with early rutile, corroded along cleavage planes and invaded by sparry ferroan calcite, itself partly dissolved. Euhedral sheaves of chlorite cross-cut the corroded calcite (e.g. at the red circle). Subhedral manganoan ilmenite cross-cuts both rutile and calcite. Chlorite has largely altered to ferroan chlorite, but some remnants can be recognised from their lower

backscatter. (l) Biotite surrounded by sparry calcite, overgrown by chlorite and euhedral magnetite. Alteration of chlorite to Fe-chlorite took place preferentially along contacts with euhedral magnetite (magenta lines) but magnetite surrounds chlorite (red ellipse). Synchysite appears late. (m) Synchysite-(Ce) forms acicular crystals in earlier chlorite and is replaced by thorite, which fills voids. (n) Magmatic biotite crystal with cerianite precipitated along cleavage, where there is also late beidellite. (o) Nb-rich Fe-oxide and later xenotime precipitated along feldspar cleavage. *Mineral abbreviations* in this and subsequent figures: Ab = albite, Ap = apatite, Bei = beidellite, Bsn = bastnäsite, Bt = biotite, Cal = calcite, Cer = cerianite, Che = chevkinite, Chl = chlorite, Fsp = feldspar, Hing = hingganite, Ilm = ilmenite, Kfs = K-feldspar, Mag = magnetite, Mo = molybdenite, Ms = muscovite, Nb-aes = niobaeschynite, Plag = plagioclase, Qz = quartz, Rbk = riebeckite, Rt = rutile, Sam = samarskite, Syn = synchysite, Thr = thorite, Tnt = titanite, Xtm = xenotime, Zrn = zircon.

Figure 6. Relative abundance of different microfracture and vug fills from four samples. Veins and vugs were classified according to minerals present in abundances of >10%. Relative abundance of each vein/vug type is shown on the x-axis; total abundance of all secondary minerals by each vein/vug type on the y-axis.

Figure 7. Veins cutting granite in contact with hornfels (cf. Fig. 4a). (a) Vein of pyrite with chalcopyrite and K-feldspar at the rim. (b) Fine-grained Fe-oxyhydroxide lines the wall of a fracture and shows zoning and volume reduction cracks. (c) Fe-oxyhydroxide fills cleavage planes of primary minerals. (d) Xenotime occupies cleavage and dissolution pores in pyrite vein. (e) Ilmenite surrounds TiO₂ mineral, and samarskite partially replaces pyrochlore along a dissolution void. (f) Fe-oxyhydroxide veins with later

aeschynite-euxinite. (g) Chlorite vein cut by younger Fe-oxyhydroxide vein. (h) Fe-oxyhydroxide rims breccia in fracture zone. (i) Fracture filled with Fe-oxyhydroxide is cut by later barren fracture with minor molybdenite and barite.

Figure 8. Microcrystalline cerianite, ilmenite and Fe-oxide along the outer rim of a cavity in sample 9840. (a) Backscattered electron image. EDS X-ray maps for Cl (b), F (c), Ti (d) La (e), Ce (f), Y (g), and Fe (h). Colour bar in ppm.

Figure 9. Various element biplots illustrating the whole rock geochemistry of the studied samples.

Figure 10: Chondrite-normalised whole-rock REE patterns of (a) granite samples from the northwestern part, and (b) from the eastern part of the West Moose River pluton.

Figure 11: Chondrite-normalised REE-patterns of various minerals found in the West Moose River pluton. (a) chevkinite-(Ce), (b) thorite, (c) zircon, (d) hingganite-(Y), (e) bastnäsite-(Ce), (f) tantaeuxenite, (g) xenotime, (h) niobo-aeschynite-(Y), (i) samarskite-(Y), and (j) cerianite. Normalising values for chondrite from Sun and McDonough (1989). Mineral analyses are given in Table 2. Theoretical compositions shown in Supplementary data table S2.

Figure 12. $\delta^{18}\text{O}$ values from the Devonian–Carboniferous plutonic rocks of the Cobequid Highlands. (a) Plotted by petrographic type and pluton. (b) Plotted against ϵ_{Nd} .

Figure 13. Histograms of $\delta^{18}\text{O}$ analyses from granites of the peri-Gondwanan Appalachians. (a) Meguma terrane Devonian (Longstaffe et al. 1980). (b) Devonian–Carboniferous, Cobequid Highlands (Avalon terrane) from this study. (c) Other Avalon terrane Paleozoic granites (Potter et al. 2008). (d) Gander terrane Paleozoic granites (Potter et al. 2008).

Figure 14. Cartoon summary of paragenetic sequence of minerals in veins.

Figure 15. Histograms of Σ REE abundance in the West Moose River pluton compared with other plutons along the Cobequid Shear Zone.

Figure 16: Schematic cross sections of the West Moose River pluton and Cobequid Shear Zone showing the geological evolution of the area from plutonic emplacement (a) to the development and evolution of the regional hydrothermal system (b and c). Available radiometric ages and studied hydrothermal mineral assemblages are plotted and correlated with the illustrated evolutionary stages. For further explanation, see text.

Tables

Table 1. Summary of published radiometric ages relevant to the West Moose River pluton

Table 2. Representative electron microprobe analyses of hydrothermal REE minerals in the West Moose River pluton.

Supplementary data

Table S1. Summary of key samples studied.

Table S2. Mineral compositions of REE minerals and their distributions

Table S3. Whole rock geochemical analyses of granites.

Table S4. Oxygen isotope determinations.

Figure 1

Figure 2

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Table 1. Summary of published radiometric ages relevant to the West Moose River Pluton

Event	Rock unit and location	Method	Mineral	Quoted age (Ma)	recali-brated age (Ma)	Reference	Original sample
Lamprophyre emplacement	Lamprophyre dyke, north of Parrsboro	⁴⁰ Ar/ ³⁹ Ar	Bt*	331±3	335	Pe-Piper et al. (2004)	L
	Lamprophyre dyke, West Moose River pluton		Bt	323±2	327		M
			Bt†*	330±2	334		
last ductile movement, biotization	NPz granodiorite, deformed by RBF		Bt	340±4	344		E
	NPz granodiorite, deformed by RBF		Bt	333±4	337		F
	Cape Chignecto pluton, mylonite		Hbl	344±3	348		G
	Cape Chignecto pluton, diorite and granite		Bt	340±3	344		H
	Cape Chignecto pluton, diorite, rutilated biotite		Bt	339±3	343		I
Sodic alteration	Foliated granite, West Moose River pluton		Rieb	350±4	355		N
emplacement	Granite at margin of West Moose R pluton	U-Pb	Zrn*	361±1.5	n.a.	Dunning et al. (2002)	M

* interpreted as emplacement age
† plateau age (otherwise Ar-Ar is total gas age)
RBF Rockland Brook Fault

Ar-Ar dates are corrected to modern standards (Kuiper et al., 2008). Rather than recalculate Ar-Ar ages from scratch, which requires laboratory data not accessible to us, we have used a correction factor of 1.3% based on the work of Pointon et al. (2012) on the Late Carboniferous, which is similar to the factor determined in the Jurassic by Trujillo and Kowallis (2015). We have made no attempt to estimate errors, using the originally calculated errors as indicative.

Table 2. Representative electron microprobe analyses of hydrothermal REE minerals from the West Moose River pluton

Sample	9834	9834	9834	9835	9835	9835	9835	9835	9835	9837	9837	9837	9837	9837	9837	9840	9840
Mineral	Ta-eux	Nb-aes	Thr-Zrn	Che	Sam	Bsn	Bsn	Hing	Hing	Syn	Syn	Thr	Thr	Aln	Xtm	Xtm	Cer
SiO ₂	5.21	8.95	19.69	19.09	0.48	0.23	0.15	26.48	27.21	0.09	b.d.	19.11	14.28	32.66	0.60	0.39	8.53
Al ₂ O ₃	b.d.	0.55	0.06	0.03	b.d.	b.d.	b.d.	0.07	0.27	b.d.	b.d.	0.23	0.79	15.58	b.d.	b.d.	2.64
FeO	1.42	7.46	0.52	12.45	0.88	0.29	0.26	10.79	9.29	2.10	0.15	1.25	5.02	14.59	0.37	0.81	10.84
MnO	0.03	0.14	0.06	0.52	0.04	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	0.03	0.19	b.d.	b.d.	3.83
MgO	b.d.	b.d.	0.03	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	0.11	0.00	0.53	b.d.	b.d.	0.22
CaO	0.88	1.26	1.35	0.25	0.11	0.13	0.09	1.85	1.88	14.38	18.53	1.13	2.76	10.59	0.08	0.13	0.54
Na ₂ O	b.d.	b.d.	0.01	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	0.04	b.d.	b.d.	b.d.	b.d.
K ₂ O	0.02	0.04	b.d.	0.05	0.05	0.04	0.05	0.03	0.04	0.01	0.05	0.03	0.04	0.02	0.04	0.03	0.14
P ₂ O ₅	b.d.	0.05	0.17	0.01	b.d.	0.01	0.01	0.02	0.02	0.05	0.04	0.46	0.79	b.d.	35.98	35.07	1.53
Nb ₂ O ₅	14.88	20.81	0.27	0.41	40.08	0.08	b.d.	b.d.	0.20	b.d.	0.03	0.27	0.21	b.d.	b.d.	b.d.	b.d.
Ta ₂ O ₅	27.32	9.30	b.d.	0.29	3.09	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.
TiO ₂	16.55	16.26	0.03	15.10	1.83	0.26	b.d.	b.d.	0.06	b.d.	b.d.	0.03	0.05	0.13	b.d.	0.09	b.d.
ZrO ₂	5.78	3.43	15.82	0.02	b.d.	0.05	b.d.	0.05	b.d.	b.d.	b.d.	b.d.	0.05	b.d.	b.d.	b.d.	0.08
HfO ₂	0.66	0.31	0.41	b.d.	0.07	b.d.	0.01	b.d.	b.d.	0.02	b.d.	b.d.	0.59	b.d.	b.d.	b.d.	b.d.
Y ₂ O ₃	16.70	10.45	2.18	0.72	23.73	0.28	0.21	28.61	28.28	2.45	3.62	8.13	4.47	0.08	48.45	47.83	0.86
La ₂ O ₃	b.d.	0.01	0.03	9.95	0.01	18.83	20.20	0.16	0.16	10.72	9.18	0.08	0.19	5.23	b.d.	0.03	0.74
Ce ₂ O ₃	b.d.	0.63	0.03	24.75	0.63	35.19	34.73	1.03	0.96	25.32	22.94	0.46	0.38	12.49	0.09	b.d.	56.64
Pr ₂ O ₃	0.04	0.10	b.d.	2.74	0.20	3.23	3.07	0.32	0.45	2.45	2.39	b.d.	0.19	1.28	b.d.	0.04	0.44
Nd ₂ O ₃	0.19	0.68	b.d.	9.02	1.74	10.37	9.38	2.90	2.76	12.00	10.33	0.14	0.36	4.43	0.05	0.04	1.51
Sm ₂ O ₃	0.46	0.69	b.d.	1.45	2.08	1.05	0.98	2.52	2.53	2.53	2.00	0.26	0.09	0.65	b.d.	b.d.	0.48
Eu ₂ O ₃	0.07	0.10	b.d.	0.72	0.05	0.83	0.80	0.13	0.16	0.87	0.68	0.03	0.06	0.33	b.d.	b.d.	0.01
Gd ₂ O ₃	2.35	2.94	0.16	0.68	6.17	0.41	0.39	5.72	5.70	2.07	1.64	1.69	0.55	0.23	2.72	2.42	0.52
Dy ₂ O ₃	2.93	4.42	0.24	0.28	6.86	0.04	b.d.	4.89	4.76	0.76	0.81	2.13	0.76	0.32	4.22	3.39	1.70
Ho ₂ O ₃	1.23	1.37	0.11	b.d.	2.70	b.d.	b.d.	2.41	2.41	0.12	0.07	0.89	0.35	b.d.	1.65	1.36	0.08

Er₂O₃	0.59	0.85	0.39	b.d.	b.d.	b.d.	b.d.	1.72	1.69	0.03	0.11	0.69	0.70	0.22	4.29	5.08	0.22
Yb₂O₃	2.16	1.31	0.42	b.d.	1.80	b.d.	b.d.	1.00	1.02	b.d.	b.d.	0.36	0.57	b.d.	3.92	4.80	0.01
ThO₂	0.46	3.22	44.74	0.11	2.94	0.14	b.d.	0.39	0.63	0.55	0.24	53.75	61.71	0.24	0.17	0.04	0.03
UO₂	0.20	0.78	7.35	0.04	0.52	b.d.	b.d.	0.00	0.09	b.d.	0.08	3.15	1.12	0.05	0.04	0.04	0.04
F	0.08	0.08	0.71	b.d.	0.28	5.43	5.58	0.19	0.19	2.21	2.10	0.65	0.59	b.d.	0.50	0.53	0.21
Total	100.18	96.15	94.45	98.68	96.22	74.59	73.54	91.17	90.64	77.79	74.09	94.76	96.47	99.85	102.94	101.88	91.71

Notes: Abbreviations: Ta-eux: tantaeuxenite, Nb-Aes: nioboaeshynite, Thr: thorite, Zrn: zircon, Che: chevkinite-(Ce), Sam: samarskite-(Y), Bsn: bastnäsite-(Ce), Hing: hingganite-(Y), Syn: synchysite-(Ce), Aln: allanite-(Ce), Cer: cerianite, Xtm: xenotime, b.d.: below detection limit. Low analysis totals are generally attributed to volatiles.

Draft

Table S1: Samples investigated in detail.

Sample	Lithology	UTM Northing Easting zone 20	Whole-rock geochemistry					Magnetic susceptibility (10^{-3} SI units) *	Fractures		alteration and vein types	Identified REE-bearing minerals
			SiO ₂	Na ₂ O	K ₂ O	LREE (ppm)	HREE (ppm)		% fractures in rock	% of fractures with Fe- oxide		
2009	diabase dyke intruding cataclastic granite	5031524 406155									(1) albitised feldspars; (2) biotite in cataclastic fractures adjacent to dyke; (3) diabase dyke, granite xenoliths with biotite; (4) Fe-oxides in fractures throughout granite	
4927	contact of diabase dykelet with granite										in steep E-W fault, small fragments of granite in dykelet	
4931	contact of diabase dyke with granite										(1) albitised feldspars; (2) biotite cataclastic fractures adjacent to dyke; (3) diabase dyke, granite xenoliths; (4) Fe-oxides in fractures throughout granite / foliation in diabase	
4842		5031498 405528									(1) mylonitic granite; (2) quartz veins; (3) black fractures	
9833	Rbk-bearing granite (white), foliated	5031883 404562	77.9	3.92	4.23	87	43	0.16	3.5	100	(1) K-feldspar → albite, riebeckite along fractures; (2) veins with zircon, Ti-magnetite, ilmenite	Zircon
9834	Granite (white), foliated	5031940 404639	79.1	4.03	4.12	40	34	7.43	n.a.	n.a.	(1) quartz; (2) magnetite, zircon; (3) xenotime, zircon → thorite	Niobo-aeschnite-(Y), Tantaloxenite, Thorite, Zircon, Xenotime
9835	Granite (pink)	5031940 404639	77.3	3.92	4.18	43	42	12.97	3	95	relicts of magmatic chevkinite; (1) veins of magnetite, minor titanite; → zircon; → xenotime, REE minerals	Chevkinite-(Ce), Bastnäsit-(Ce), Hingganite-(Y), Samarskite-(Y), Thorite, Zircon, Xenotime
9836A	Granite (pink), brittle deformation	5032083 404727	75.7	3.98	4.29	128	19				alteration to chlorite; albite → allanite	Samarskite-(Y), Nb-rich Ce-Pb-bearing phase. Thorite, Allanite-(Ce)
9836B								1.61	n.a.	n.a.		
9837	Albitized granodiorite (pink), ~50 m from Horton Gp	5032162 405963	62.0	9.51	0.09	454	93	13.90	7.7	100	(1) albitised feldspars; (2) chlorite veins; (3) calcite; (4) biotite; (5) magnetite; (6) Fe-chlorite; (7) REE minerals; (8) thorite	Synchysite-(Ce), Hingganite-(Y), Samarskite-(Y), Thorite, Xenotime, Zircon, Allanite-(Ce)
9838	Albitized granite (white), ~50 m from Horton Gp.	5032095 405975	71.1	9.33	0.14	60	18	0.15	3	8	(1) biotite → chlorite, later magnetite; (2a) chlorite; (2b) biotite; (3) → Fe-chlorite, titanite, zircon, Fe-oxides, REE minerals	Samarskite-(Y), Nb-mineral, Chernovite-(Y)?, Thorite, Xenotime, Zircon
9839	Granite (white), ~50 m from Horton Gp	5032095 405975	78.3	4.00	3.73	176	49	0.09	n.a.	n.a.	(1) biotite altered to chlorite, later REE minerals; (2) Fe-oxides, chlorite, REE minerals	Niobo-aeschnite-(Y), Samarskite-(Y), Hingganite-(Y), Thorite, Zircon
9840	Granite (pink) with Horton Gp. xenoliths	5032850 406899	75.7	3.43	5.00	427	62	0.43	4.7	49		Cerianite, Bastnäsit-(Ce), Samarskite-(Y), Thorite, Xenotime, Zircon
9841	Rapakivi granite (pink) cutting Horton Gp.	5032952 406837	76.99	3.74	3.91	232.8	40.7	0.11	n.a.	n.a.		Zircon
9873	Granite (pink), brittly deformed, within 10 m of Horton Gp.										(1) tourmaline veins cut by (2) Fe-oxide, thorite, xenotime veins	
9874											(1) chlorite, minor muscovite veins (seem equivalent to tourmaline in 9873; (2) → titanite, zircon, cerianite; (3) dissolution voids with REE minerals;	
9876												
9877	Granite at Horton Gp contact										(1) pyrite, rimmed by chalcopyrite and K-feldspar, later xenotime in fractures; (2) zoned veins with fine grained Fe-oxhydroxide, minor chalcopyrite, chlorite, Al-phosphate mineral, quartz. (3) mostly barren fractures, minor barite, zircon, ilmenite, monazite, molybdenite.	
											→ indicates that pre-existing magmatic or vein minerals have later minerals precipitated in dissolution voids, along cleavage, or as overgrowths.	

Table S2. Summary of REE-bearing minerals in granites of the Cobequid Highlands

Mineral	Ideal chemical formula	Plutons				
		West Moose River	Cape Chignecto	North River	Pleasant Hills	Wentworth
MAGMATIC						
Chevkinite-(Ce)		(x)				x
Allanite-(Ce)	{CaCe}{Al2Fe2+}{Si2O7}(SiO4)O(OH)		(x)			x
Zircon	ZrSiO4					
LATE MAGMATIC						
Hingganite-(Y)	(Y,REE,Ca)2(□,Fe2+)Be2[SiO4]2(OH)2					x
Samarskite-(Y)						X
VEIN MINERALS						
Zircon		X				
Allanite-(Ce)		x				
Chernovite-(Y)	YAsO4	x				
Hingganite-(Y)		x				
Niobo-aeschynite-(Y)		x				
Samarskite-(Y)	(Y,Fe3+,Fe2+,U,Th,Ca)2(Nb,Ta)2O8	x				X
Parasite-(Ce)	Ca(Ce,La)2(CO3)3F2					
Cerianite	(Ce4+,Th)O2	x				
Tantaeuxenite		x				
Fersmite						x
Xenotime		X				
Thorite	(Th,U)SiO4	x				
Ce-magnetite				x		
VEINS ASSOCIATED WITH CARBONATE						
Aeschynite-(Y)						x
Bastnäsite-(Ce)		x				
Hydroxylbastnäsite-(Ce)	(Ce,La)(CO3)(OH,F)					x
Synchysite-(Ce)	Ca(Ce,La)(CO3)2F	x				

Table S3 New geochemical analyses of granites									
Sample	9833	9834	9835	9836A	9837	9838	9839	9840	9841
Major oxides (wt. %)									
SiO ₂	77.87	79.13	77.33	75.66	61.97	71.10	78.27	75.66	76.99
TiO ₂	0.07	0.08	0.08	0.17	0.33	0.09	0.06	0.19	0.16
Al ₂ O ₃	11.25	11.40	11.48	12.18	16.98	17.04	11.61	12.24	12.05
Fe ₂ O _{3(T)}	1.54	1.46	1.77	1.66	3.74	0.81	1.02	1.48	1.51
MnO	0.03	0.01	0.01	0.02	0.05	0.01	0.01	0.02	0.02
MgO	0.02	0.02	b.d.	0.11	0.15	0.12	0.08	0.17	0.23
CaO	0.04	0.02	0.02	0.24	2.96	0.18	0.11	0.22	0.36
Na ₂ O	3.92	4.03	3.92	3.98	9.51	9.33	4.00	3.43	3.74
K ₂ O	4.23	4.12	4.18	4.29	0.09	0.14	3.73	5.00	3.91
P ₂ O ₅	0.02	b.d.	b.d.	0.02	0.02	0.06	0.02	0.03	0.03
F	b.d.	b.d.	0.01	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.
LOI	0.40	0.36	0.30	0.55	2.80	0.44	0.50	0.57	0.58
Total	99.39	100.60	99.10	98.89	98.62	99.32	99.40	99.01	99.58
Trace elements (ppm)									
Ba	11	30	25	305	23	61	56	285	263
Rb	236	138	161	114	1	3	127	133	124
Sr	b.d.	4	3	34	42	38	12	30	22
Y	66.6	61.3	78.7	27	175	26.7	78.1	106	52.5
Zr	322	356	325	290	750	251	200	346	247
Nb	45.3	44.2	30.5	27.4	47.9	24.9	57.8	36.9	48.6
V	b.d.	b.d.	b.d.	7	38	b.d.	5	7	b.d.
Cr	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.
Co	b.d.	1	1	3	12	b.d.	1	3	3
Ni	3	3	4	5	7	5	5	5	5
Cu	2	2	2	10	6	12	4	17	11
Zn	98	4	5	10	15	11	17	15	18
S	b.d.	b.d.	b.d.	b.d.	0.16	b.d.	b.d.	0.01	b.d.
Ga	25	24	24	19	38	36	27	25	26
Ge	2.8	2	2.2	2.1	1.6	0.9	2.8	2.7	2.4
Ag	0.5	0.3	0.4	b.d.	0.3	b.d.	b.d.	b.d.	b.d.
Sn	11	3	4	2	2	4	4	2	4
Sb	0.7	0.2	0.2	0.3	b.d.	b.d.	0.3	0.5	0.4
Sc	b.d.	b.d.	b.d.	2	3	1	b.d.	3	2
Cs	1.9	0.5	0.6	1	b.d.	0.1	0.4	1.3	1.7
La	13.2	2.9	4.8	20.3	96.6	13.2	38.3	109.0	53.0
Ce	44.9	28.6	24.8	81.4	218.0	29.2	71.9	177.0	102.0
Pr	4.2	1.1	1.7	5.1	25.3	3.0	11.2	26.2	14.0
Nd	18.1	4.7	7.8	17.6	93.9	11.3	43.1	94.7	51.7
Sm	6.7	2.4	3.6	3.5	19.7	2.6	10.8	19.2	11.2
Eu	0.2	0.1	0.2	0.4	0.7	0.3	0.3	1.3	0.9
Gd	8.2	4.4	6.5	3.0	20.1	3.2	9.7	17.5	9.4
Tb	1.7	1.2	1.5	0.6	3.9	0.7	1.9	2.9	1.7
Dy	11.7	9.1	11.2	4.6	26.1	5.2	12.8	16.6	10.8
Ho	2.6	2.2	2.6	1.1	5.6	1.1	2.8	3.4	2.3
Er	7.9	7.1	8.4	3.8	16.8	3.6	9.1	9.9	7.0
Tm	1.3	1.2	1.4	0.7	2.5	0.6	1.5	1.5	1.1
Yb	8.6	7.9	9.0	4.8	15.2	3.5	9.7	9.3	7.3
Lu	1.3	1.2	1.4	0.8	2.3	0.5	1.5	1.4	1.2
Hf	12	13	12	9	21	8	10	10	10
Ta	3.6	3.4	2.6	2.5	3.5	2.2	5.1	2.6	4.2
W	1.1	1.7	1.8	1.1	1.8	0.7	2.1	1.8	1.6
Tl	0.84	0.34	0.43	0.23	b.d.	b.d.	0.22	0.32	0.5
Pb	b.d.	b.d.	b.d.	16	b.d.	b.d.	b.d.	13	16
Bi	0.7	0.1	0.1	b.d.	b.d.	b.d.	0.1	0.1	b.d.
Be	6	4	5	4	7	6	6	5	6
Th	16.8	17.7	18.4	22.1	22.4	8.45	22.9	21	20.8
U	4.57	5.49	5.75	4.47	4.24	3.01	5.68	2.52	5.1

Notes: All major and trace elements were determined by fusion ICP-MS except for selected trace elements (Ni, Cu, S, Ag and Pb) that were determined by total digestion ICP-MS, b.d. : below detection limit. Analyses of these samples are reported in Piper et al. (1991).

Table S4: O-isotope determinations

Pluton	Sample number	UTM position		Granite type	Rock type	rock		Mineral	mineral		Field notes
		UTM easting	UTM northing			$\delta^{18}\text{O} \text{ ‰ VSMOW}$	yield $\mu\text{moles/mg}$		$\delta^{18}\text{O} \text{ ‰ VSMOW}$	yield $\mu\text{moles/mg}$	
WMRP	9834	404639	5031940	Whitish	Granite	5.9	14.07				Foliated granite, cut by quartz-filled tension gashes.
WMRP	9835	404639	5031940	Pinkish	Granite	5.3	16.4				Outcrop of riebeckite granite = 7054
WMRP	9836A	404727	5032083	Pinkish	Granite	6.5	14.08				Brittly deformed granite.
WMRP	9839	405975	5032095	Whitish	Granite	6.7	14				Local outcrop of granite
WMRP	9840	406899	5032850	Pinkish	Granite	6.7	14.19				
WMRP	9840 - dup					6.4	14.33				Small outcrop of white granite with Horton Group xenoliths.
WMRP	9841	406837	5032952	Pink	Rapakivi Grani	6.1	15.93				Coarse grained granite cutting Horton Group sediments.
WMRP	9837	405963	5032162	Pinkish	Albitized grd	5.7	13.21	albite	5.9	13.61	Granite in middle of Horton Group roof pendant.
WMRP	9838	405975	5032095	Whitish	Albitized granit	6.0	13.93	albite	5.3	15.19	Granite float in contact with Horton Group.
WMRP	9833	404562	5031883	White-brown	Rbk-granite	6.0	14.25				Outcrop with foliation of 025/50 SE.
CCP	3927	349388	5028949	biotitic	granite	7.6	15.43				highly fractured vuggy granite
NRP	1779	416224	5035107	biotitic	granite	6.1	14.87				na
PHP	4681	437475	5036547	calcic	granite unit 7	5.5	14.75				coarse grained granite with small digested mafic inclusions
PHP	4689	437371	5037132	calcic	granite unit 11	3.8	14.77				fractured hybrid rapakivi granite
PHP	42-1-2	427494	5035184	calcic	granite unit 10	1.6	14.53				coarse grained granit
WP	4636	455400	5048118	sodic	granite	5.5	15.28				medium-grained granite
WP	6419	451203	5049916	sodic	granite	6.0	14.73				coarse grained pink granite
WP	35-7-1	449984	5048870	sodic-calcic	granite	4.6	15.25				na
WP	4641	452932	5046282	calcic	granite	5.7	14.37				granitic outcrop
WP	7814	463361	5044863	calcic	granite	5.8	14.20				main granite against chilled gabbro
WP	9825	444475	5046408	early	gabbro	6.2	13.05				main coarse gabbro
WP	9826	444475	5046408	late	gabbro	4.5	13.85				late fine gabbro with lobate contacts

CCP = Cape Chignecto pluton; NRP = North River pluton; PHP = Pleasant Hills pluton; WMRP = West Moose River pluton; WP = Wentworth pluton