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## Regional-scale fluid flow and element mobility in Barrow's metamorphic zones, Stonehaven, Scotland

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**Abstract** The geochemistry of metamorphic quartz vein formation in Barrow's index mineral zones north of Stonehaven, Scotland, was investigated in order to assess regional fluid flow and mass transfer. Metamorphic grade in the Dalradian metasediments increases to the north–northwest away from the Highland Boundary Fault (HBF) and associated ophiolitic rocks of the Highland Border Complex (HBC), passing through the Chlorite (Chl), Biotite (Bt), Garnet (Grt), Chloritoid (Cld), and Staurolite (St) zones. Syn-metamorphic fluid infiltration at  $462 \pm 8.8$  Ma (Breeding et al. in *Am Mineral* 89:1067, 2004) produced considerable quartz veining. Vein abundance varies from about 5 to 15 volume percent of the outcrops; veins tend to be more abundant in metapelitic layers than in metapsammitic ones. Metamorphic veins are surrounded by centimeter- to decimeter-wide zones of chemical and mineralogical alteration (selvages). Porphyroblasts, particularly Bt, Grt, Cld, and St, are typically larger in selvages than in wallrocks distal to veins. The altered selvages underwent fluid-driven addition of Na, Ca, and Sr, and loss of K, Rb, and Ba. Alteration is most intense within  $\sim 750$  m of the HBF, but is still very significant at the northern end of the field area some 2 km away.  $\text{Mg}/\text{Fe}^{\text{T}}$  ( $\text{Fe}^{\text{T}}$  = total iron) was either unchanged or increased due to alteration. Silica was added at some Chl and Bt zone localities near the HBF. Pb mass transfer was variable

although Pb was added at a number of locations. Rare Earth elements (REE) were generally immobile, but light REE and possibly heavy REE were lost at one field site. The gain of Na and Ca and loss of K promoted the growth of plagioclase at the expense of micas (particularly muscovite) in selvages and wallrock inclusions throughout the field area and, probably, some calcite and/or dolomite growth directly adjacent to the HBF. The Ca gains were also critical for epidote production in the Bt zone. Gains of Ca and increases in  $\text{Mg}/\text{Fe}^{\text{T}}$  helped to stabilize Grt at the expense of Cld and St in some selvages. Hornblende and cummingtonite were discovered in strongly altered metapelitic rocks at one Cld zone locality. The metasomatism puts important constraints on the processes of mass transfer and suggests two models for regional fluid flow. In the first model, fluid flow in a direction of increasing temperature downward along the HBF added Na and Ca, and removed K from the Dalradian. In the second model, fluid flow upward from the HBC transported Na and Ca into the overlying Dalradian and, at the same time, stripped out K. The latter model is favored because it can most readily account for silica addition near the HBF, but neither model can be ruled out at present. In either case, the veins represent fractures that transmitted very large time-integrated fluid fluxes of at least  $\sim 10^4$  m<sup>3</sup> (fluid)/m<sup>2</sup> (rock). Consequently, the veins were conduits for regional fluid flow that caused considerable open-system chemical and mineralogical alteration during metamorphism.

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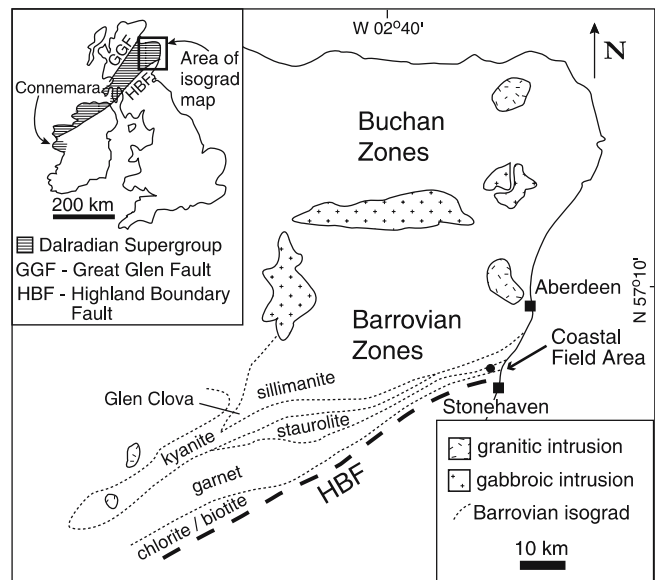
### Introduction

Study of the effects of fluids and fluid flow on metamorphic rocks is currently one of the foremost topics in metamorphic petrology and has been gaining momentum in the past few decades (cf. Rye et al. 1976; Bebout and Barton 1989; Ferry 1992, 1994; Dipple and Ferry 1992; Ague 1994, 2003a; Person and Baumgartner 1995;

Oliver 1996; Skelton et al. 2000; Wing and Ferry 2002). Despite evidence for considerable fluid flow, many models treat the regional metamorphism of marine siliclastic rocks as an “isochemical” process in which aqueous fluids have little effect on chemical and mineralogical evolution beyond dehydration/ decarbonation during prograde metamorphism (Wood and Walther 1986). However, research in the past decade indicates that rock chemical composition may not remain constant during metamorphism of metaclastic (metapelitic and metapsammitic) rocks (Ague 1994, 1997a). Metaclastic rocks make up a significant portion of nearly all orogenic zones around the world and, thus, determining how fluid flow influences their metamorphic evolution is essential for understanding the chemical and physical development of mountain belts. The Barrovian model, in which progressive changes in mineralogy are thought to result mainly from changes in the pressure and temperature of metamorphism, has been widely used to interpret mountain belts around the world for nearly a century. If typical regional metamorphism includes extensive fluid-driven redistribution of chemical species as well, then the concept of isochemical Barrovian metamorphism will need to be revisited.

In order to test the hypothesis of open-system mass transfer during metamorphism, a petrographic and bulk chemical study was conducted in one of the most extensively studied metasedimentary terranes in the world, the Dalradian Supergroup metasediments (Barrow 1893, 1898, 1912; Chinner 1960, 1967; Graham et al. 1983; Yardley and Baltatzis 1985; Harte 1988; Droop and Harte 1995; Skelton et al. 1995; Dempster et al. 2000; Oliver et al. 2000; Baxter et al. 2002). We investigated the history of crustal fluid flow during metamorphism in Barrow’s index mineral zones in the Dalradian north of Stonehaven, Scotland by constraining the source(s) and timing of fluid flow event(s) and determining the effects of metamorphic fluid flow on the chemical and mineralogical systematics of these rocks.

The area just north of Stonehaven, Scotland, is ideal for studying the effects of fluid–rock interaction (Figs. 1, 2). Here, there is nearly 100% exposure of key structures and rock packages involved in the crustal development of Scotland including the ophiolitic Highland Border Complex (HBC) of the Highland Boundary Fault (HBF), the intensely folded and boudinaged-metaclastic rocks of the Southern Highland Group of the Dalradian, and vein arrays in both the HBF and the Dalradian metasediments (syn- and post-metamorphic). A number of studies have now shown that fluid flow was integral to regional metamorphic and post-metamorphic processes in the Dalradian (cf. Graham et al. 1983, 1997; Craw 1990; Jenkin et al. 1992; Cole and Graham 1994; Fein et al. 1994; Skelton et al. 1995; Ague 1997a; Dempster et al. 2000; Masters et al. 2000). This study focuses on chemical and mineralogical alteration in envelopes or “selvages” adjacent to syn-metamorphic quartz veins and is based on detailed meter- to centimeter-scale mapping and sampling of vein, selvage, and little-altered



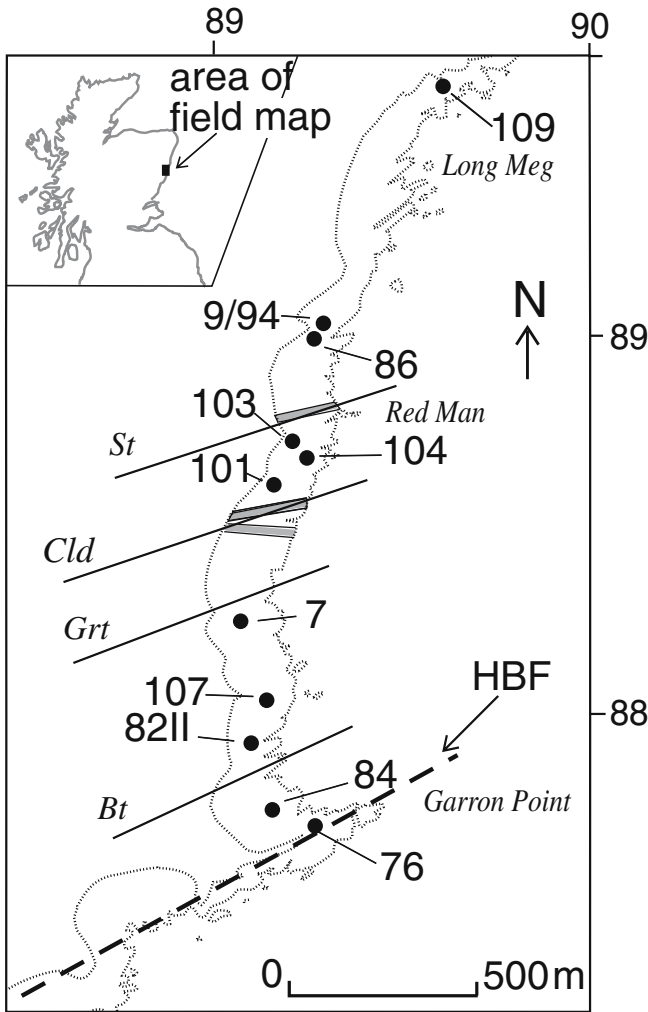
**Fig. 1** Map of Barrow’s zones in northeast Scotland (modified after Baxter et al. 2002). Isograds denoted by thin dashed lines. Main field area lies along the coast north of Stonehaven, extending from the Chlorite zone adjacent to the Highland Boundary Fault (HBF) to the Staurolite zone approximately 2 km to the north–northwest. Sample locality JAB 1 lies inland (filled circle) along the Cowie Water 200 m southeast of Ury House

wallrock at sites along a ~1.8 km-long traverse sub-perpendicular to the HBF. Understanding the role of vein formation in the petrologic and structural evolution of the Dalradian turns out to be critical for assessing the metamorphic fluid flow.

## Regional geology

The study area lies within the stratigraphically highest metasediments of the Dalradian Supergroup, the Southern Highland Group (SHG), whose protoliths were a succession of turbidites composed mainly of psammitic and pelitic sediments that included rare sedimentary carbonate layers and intermittent mafic volcanic rocks and volcanoclastic sediments called “green beds” (Harris et al. 1994). The Dalradian metasediments in Scotland and Ireland were metamorphosed and deformed during the Paleozoic Grampian Orogeny (480–465 Ma) (Soper et al. 1999; Oliver et al. 2000; Baxter et al. 2002). The orogeny was likely caused by accretion of an island arc and forearc with a passive continental margin (Friedrich et al. 1999; Soper et al. 1999; Oliver et al. 2000; Rose and Harris 2000). In Scotland, the Midland Valley and Grampian Terranes represent the fore-arc and passive margin, respectively (Oliver 2001).

Barrow’s classic index mineral zones, first defined in the vicinity of Glen Clova in the southeastern Highlands (Barrow 1893), extend from Scotland’s east to west coasts. Near the Highland Boundary Fault (HBF), metamorphic grade is greenschist facies, increasing to



**Fig. 2** Map of main field area showing field sites and isograds: Biotite (Bt), Garnet (Grt), Chloritoid (Cld), and Staurolite (St). Isograd locations based on Barrow (1912), Droop and Harte (1995), and this study. Highland Boundary Fault (HBF) denoted by thick dashed line, and post-metamorphic quartz-porphry dikes shown in gray. Coordinates correspond to the National Grid System; 1 km between divisions. Mineral symbols after Kretz (1983)

amphibolite facies northwest of the fault. Recorded pressures range from 3–5 kbar in northeastern Scotland (Droop and Harte 1995; Ague 1997a) to 8–10 kbar in the central and southwest Highlands (Harte 1988; Skelton et al. 1995). Barrovian metamorphism occurred during the mid-Ordovician (472–465 Ma), and exhumation was rapid (Oliver et al. 2000; Baxter et al. 2002). Textural evidence and geochronology indicate that fluid infiltration accompanied regional metamorphism (see below).

Four Grampian deformation events (D1–D4) affected the Dalradian, forming and refolding major nappe structures (Shackleton 1958; Harris et al. 1976). The first three (D1–D3) occurred during regional Barrovian metamorphism of the Dalradian metasediments; peak temperatures were reached during D3 (Harte et al.

1984). Regional planar fabrics dip steeply in the “Highland Border Steep Belt” (HBSB) adjacent to the HBF, whereas they are more flat-lying in the “Flat Belt” which begins ~5–15 km north of the HBF (Harte et al. 1984).

The HBF is a major tectonic boundary that has been traced east to west across Scotland and Ireland (cf. Anderson 1947; Henderson and Robertson 1982; Curry et al. 1984; Harte et al. 1984; Robertson and Henderson 1984; Hutton 1987; Ryan et al. 1995). In Scotland, the HBF divides the Devonian sediments of the Midland Valley Terrane from the Pre-Cambrian to Cambrian metasediments of the Grampian Terrane to the north. Embedded within the HBF are slivers of a dismembered ophiolite and associated sediments, the Highland Border Complex (HBC) (Henderson and Robertson 1982). Early fault motion was dominated by thrusting; strike-slip motion began after the Grampian Orogeny (Ramsay 1962; Dentith et al. 1992; Ryan et al. 1995). The assemblage of igneous rocks is consistent with early-stage oceanic crust development within a marginal basin (Ikin 1983; Robertson and Henderson 1984). Tanner (1995) concluded that the metasediments of the HBC and the upper Dalradian form a continuous sedimentary sequence that underwent the same deformation history. The stable isotope systematics of HBC rocks suggest hydrothermal alteration on the sea floor, greenschist facies metamorphism accompanied by exchange with Dalradian metamorphic fluids, as well as near-surface exchange with meteoric fluids (Ikin and Harmon 1983; Masters et al. 2000). In summary, the HBC was emplaced by thrust motion during the Grampian Orogeny, and the HBC and Dalradian have shared a complex tectonic history including metamorphism and deformation during the Ordovician.

### Field area and methods

The main field area lies north of the town of Stonehaven and is a ~2 km segment of continuous coastal exposure; it includes the HBF and HBC and continues north into the Dalradian metasediments within the Highland Border Steep Belt (HBSB) (Fig. 2). One site, located ~4 km inland is also within the HBSB (Fig. 1). The rock sequence is composed primarily of metamorphosed psammitic greywackes interbedded with pelitic layers, but also includes rare sedimentary carbonate layers and lenses. Metavolcanic “green beds”, if present, are exceedingly rare. Within ~40 m of the HBF, the sequence is dominated by what appear to be heavily-veined, strongly-deformed, albite-rich quartzites and meta-conglomerates that contain variable amounts of calcite and/or dolomite. Some of these carbonate minerals are undoubtedly prograde, but they are also found in retrograde veins that cross-cut the dominant foliation (Masters et al. 2000).

Metamorphic grade increases rapidly northward from the HBF through Barrow’s Chlorite, Biotite,

Chloritoid, Garnet, and Staurolite zones (Fig. 2; Barrow 1912; Atherton 1977; Yardley and Baltatzis 1985; Droop and Harte 1995). The chloritoid zone is restricted to a narrow band extending from the east coast to ~40 km inland (Barrow 1898). Metamorphic temperatures increase markedly from ~350°C near the HBF to ~600°C in the staurolite zone approximately 1 km north, and pressures were  $4 \pm 1$  kbar (Droop and Harte 1995; Ague 1997a; Masters et al. 2000). The close isograd spacing has been interpreted to be a primary metamorphic feature (Dempster et al. 2000), or the result of strong ductile deformation that compressed the original isograd sequence (Phillips and Auton 1997).

Tight to isoclinal folds are widespread in the field area. Primary sedimentary layering (where preserved) and axial planar foliations are sub-parallel and dip steeply (strike *c.* 70°, dip *c.* 60° N). Extension on fold

limbs resulted in extensive boudinage, masking or destroying fold hinges. A second set of folds with sub-horizontal axial planes is superimposed upon the steeply dipping tight-to-isoclinal folds. This second set becomes progressively more pronounced proceeding northward from the HBF, and is well developed in the Staurolite zone.

Petrographic observations and field structural data were used to classify vein generations and determine the relative timing of vein formation. Wavelength-dispersive chemical analyses of minerals were done using the JEOL-8600 electron microprobe at Yale University (see Ague 2002, for analytical protocols). Table 1 lists prograde mineral assemblages and vein thicknesses, and rock chemical data is given in eTables 1–3. Measurement of vein abundances is described by Ague (1994).

**Table 1** Prograde silicate and carbonate mineral assemblages for Dalradian samples

Sample	Type	Zone	Max. vein width (cm)	Vein type	Potassium feldspar	Muscovite	Epidote	Biotite	Chlorite	Garnet	Chloritoid	Staurolite	Calcite	Dolomite
76C	A	Chl	-	S	X	X	-	-	X	-	-	-	X	X
76E	A	Chl	10	A	-	-	-	-	X	-	-	-	X	X
76F	A	Chl	-	S	X	-	-	-	X	-	-	-	-	X
84A	P	Chl	-	A	X	X	-	-	X	-	-	-	X	-
82 II 1D	A	Bt	60	A	X	X	X	-	X	-	-	-	-	-
82 II 1E	A	Bt	60	A	-	X	-	-	X	-	-	-	-	-
82 II 1F	P	Bt	60	A	X	X	-	X	X	-	-	-	-	-
107A	P	Bt	40	A	-	X	-	X	X	-	-	-	-	-
107B	P	Bt	40	A	-	X	-	X	X	-	-	-	-	-
107D	A	Bt	40	A	-	X	-	X	-	-	-	-	-	-
7A	P	Bt	150	A	-	X	-	-	X	-	-	-	-	-
7C	A	Bt	150	A	-	X	-	-	X	-	-	-	-	-
7F	A	Bt	150	A	-	X	-	-	X	-	-	-	-	-
7H	P	Bt	150	A	-	X	-	-	X	-	-	-	-	-
7 I	A	Bt	150	A	-	X	-	-	X	-	-	-	-	-
7 Mi	A	Bt	150	A	-	X	X	-	X	-	-	-	-	-
7 Mii	A	Bt	150	A	-	X	X	-	X	-	-	-	-	-
1 DB-A	A	Cld	15	A	-	X	-	-	X	X	-	-	X	-
1 DB-B	A	Cld	15	A	-	X	-	-	X	X	-	-	X	-
1 DB-C	A	Cld	15	A	-	X	-	-	X	X	-	-	X	-
1F	P	Cld	15	A	-	X	-	-	X	-	-	-	-	-
101 L	A	Cld	1 <sup>a</sup>	A	-	X	-	X	X	X	-	-	-	-
101 L	P	Cld	1 <sup>a</sup>	A	-	X	-	X	X	-	X	-	-	-
103A	A	Cld	13	A	-	X	-	-	X	X	X	-	-	-
104 J	P	Cld	-	A	-	X	-	-	X	X	X	-	-	-
9D	A	St	30	B	-	X	-	X	-	X	-	X	-	-
94A	P	St	30	B	-	X	-	X	-	-	-	X	-	-
94B	A	St	30	B	-	X	-	X	-	-	-	X	-	-
94Ci	A	St	30	B	-	X	-	X	-	-	-	X	-	-
94Cii	A	St	30	B	-	X	-	X	-	X	-	X	-	-
94D	A	St	30	B	-	X	-	X	-	-	-	X	-	-
94E	P	St	30	B	-	X	-	X	-	-	X	X	-	-
109B	A	St	40	A	-	X	-	X	-	-	-	-	-	-
109C	P	St	40	A	-	X	-	X	-	X	-	X	-	-
109D	P	St	40	A	-	X	-	X	-	X	-	X	-	-

Sample site prefix JAB omitted for clarity. Sample Type: *A* alteration selvage, *P* precursor. Data for altered samples also distinguished by bold type. Vein types described in text: *A*, *B*, and *S* denote boudin-neck, flat-lying, and potentially pervasively silicified zones, respectively. *Max. vein width* maximum vein width adjacent to selvage. All samples contain quartz and plagioclase. K-spar is sedimentary in origin. Metamorphic zones: *Chl* Chlorite, *Bt* Biotite,

*Grt* Garnet, *Cld* Chloritoid, *St* Staurolite. Hornblende and cumingtonite found in wallrock inclusions in vein at site 1. Distances from Highland Boundary Fault: 76C=20 m; 76E=27 m; 76F=30 m; 84=100 m; 82=290 m; 107=370 m; 7=570 m; 101=900 m; 104=940 m; 103=980 m; 1=1000 m; 9/94=1260 m; 109=1730 m

<sup>a</sup>1 cm wide offshoot from 15 cm wide vein mass



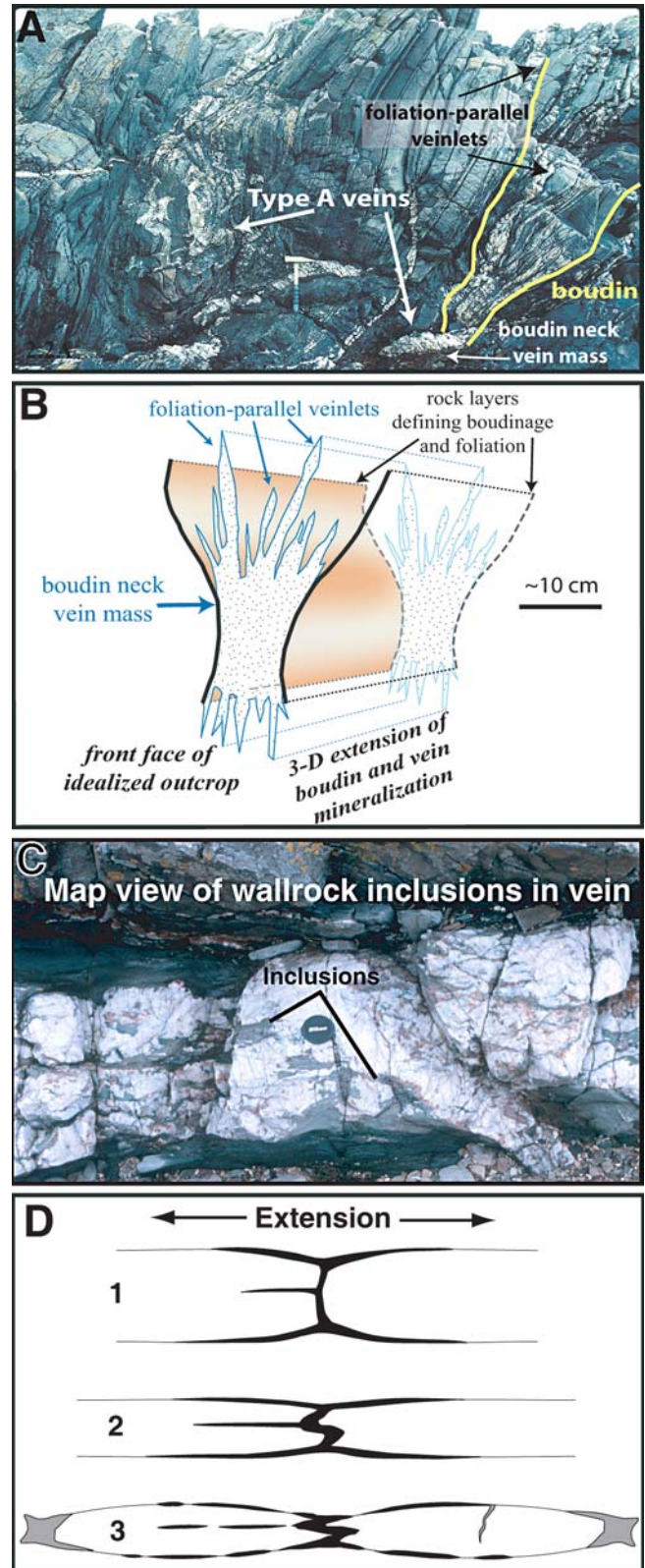
## Dalradian veins and alteration selvages

### Field relations

The Dalradian metasediments in Scotland and Ireland contain abundant vein arrays. Some veins were formed by silica diffusion from local wallrock into fractures during metamorphism and probably transmitted little fluid (e.g., Yardley and Bottrell 1992). Other veins, however, almost certainly represent conduits for regional-scale fluid flow. Where veins form primarily by the diffusion of solutes through a static fluid, the wallrock will be depleted in vein-forming components such as silica. In contrast, the mass present in veins representing ancient conduits for fluid flow will have, at least in part, been derived from outside the local wallrock depending on the length scale of fluid flow and the magnitude of the fluid flux (Ague 2003a).

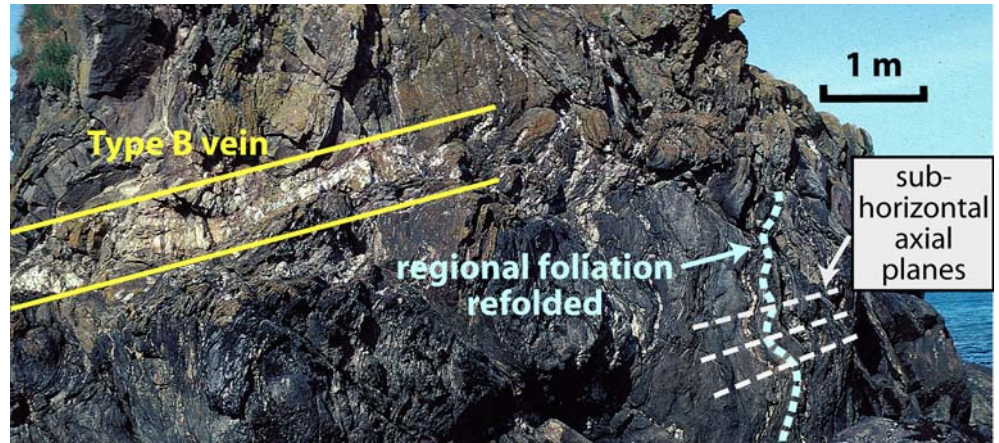
We concentrate on the petrologic features of the two sets of metamorphic veins, referred to herein as “Type A” and “Type B”. Syn-metamorphic alteration selvages ranging from several centimeters to about a decimeter in half-width surround both vein types (cf. Fig. 12 in Ague 2003a). Other vein types identified within the field area are discussed in Masters et al. (2000). Vein Type A is the most abundant and comprises tube-like veins and their planar offshoots (Fig. 3). These veins are often tens of centimeters wide, meters to tens of meters long, and are found: (1) mostly in the necks of the meter-scale boudins that dominate the structure of the metasediments adjacent to the HBF and (2) more rarely in fold hinges. Planar veins that extend from the Type-A veins into the surrounding wallrocks along cleavage planes defined by the steeply dipping regional foliation are included in Type A (Fig. 3). Major vein minerals include quartz, chlorite, biotite, and cream-to-orange plagioclase feldspar. Minor minerals are variably present and include Fe-Ti oxides and post-metamorphic cross-cutting dolomite and pyrite (Masters et al. 2000). Inclusions that are inferred to be pieces of wallrock that were incorporated into the veins during fracturing are common (Fig. 3c). Type A veins are generally layer- or foliation-parallel, but locally crosscut lithological layering.

Vein Type B includes sub-horizontally oriented, tens of centimeters wide, planar veins found north of the staurolite isograd (Fig. 4). These veins are axial planar to the flat-lying folds that become progressively more



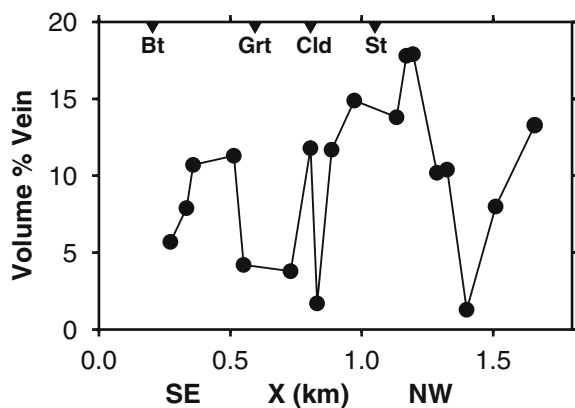
**Fig. 3 a–d** Type A veins. **a** Coastal exposure in the Biotite zone illustrating field relations of Type A veins. Hammer is 35.6 cm long. **b** Sketch illustrating Type A vein in boudin neck, and planar offshoots that extend parallel to foliation (bedding and/or rock cleavage) planes. **c** Map view looking down on exposure illustrating wallrock inclusions in a Biotite zone vein. These inclusions are interpreted to be pieces of rock that were ripped from the vein margin during fracturing and vein formation. Lens cap is 6 cm in diameter. **d** Cartoon of Type A vein formation in boudin neck during extension of competent layer (drawing 1; veins shown in black). As extension continues (drawings 2, 3) the veins become folded and boudinaged themselves. Further extension leads to new boudinage and vein formation (drawing 3; new veins shown in gray)

**Fig. 4** Type B vein, Staurolite zone



pronounced farther from the HBF. The mineralogy and vein-selvage relationships of Type B veins (also referred to as flat-lying veins) are similar to those of Type A and, therefore, we infer that the two vein types formed pencontemporaneously.

Vein abundances in the Biotite through Staurolite zones vary between  $\sim 1.0$  and  $\sim 18$  percent of the total rock volume; most sites contain between  $\sim 5$  and  $\sim 15$  percent vein (Fig. 5). Vein abundance is variable and is to some extent controlled by lithology. Metapelitic layers have vein abundances greater than nearby metapsammitic layers. Outcrops containing  $< 3$  percent vein are typically massive metapsammitic layers. Metapelitic rocks may have greater vein abundances because elevated fluid pressures generated by dehydration in these chlorite and mica-rich rocks promotes hydrofracturing (e.g., Yardley 1986; Ague et al. 1998). They are also relatively weak and thus could have undergone more extensive tectonic fracturing than competent metapsammitic layers. The largest vein abundances ( $\sim 15$ – $20\%$ ) are reached in the Chloritoid and Staurolite zones.



**Fig. 5** Volume percent vein as function of distance from the Highland Boundary Fault (HBF) in the Biotite (Bt), Garnet (Grt), Chloritoid (Cld), and Staurolite (St) zones; isograd positions denoted by inverted triangles. Areas of smallest vein abundance correspond to massive metapsammitic layers. Note that veins are generally quite abundant and commonly constitute a significant portion of the rock mass—10 to 20% at many sites

In addition, the metasediments  $\sim 40$  m from the HBF also appear highly veined (or silicified), but vein abundances are difficult to quantify in these strongly deformed rocks.

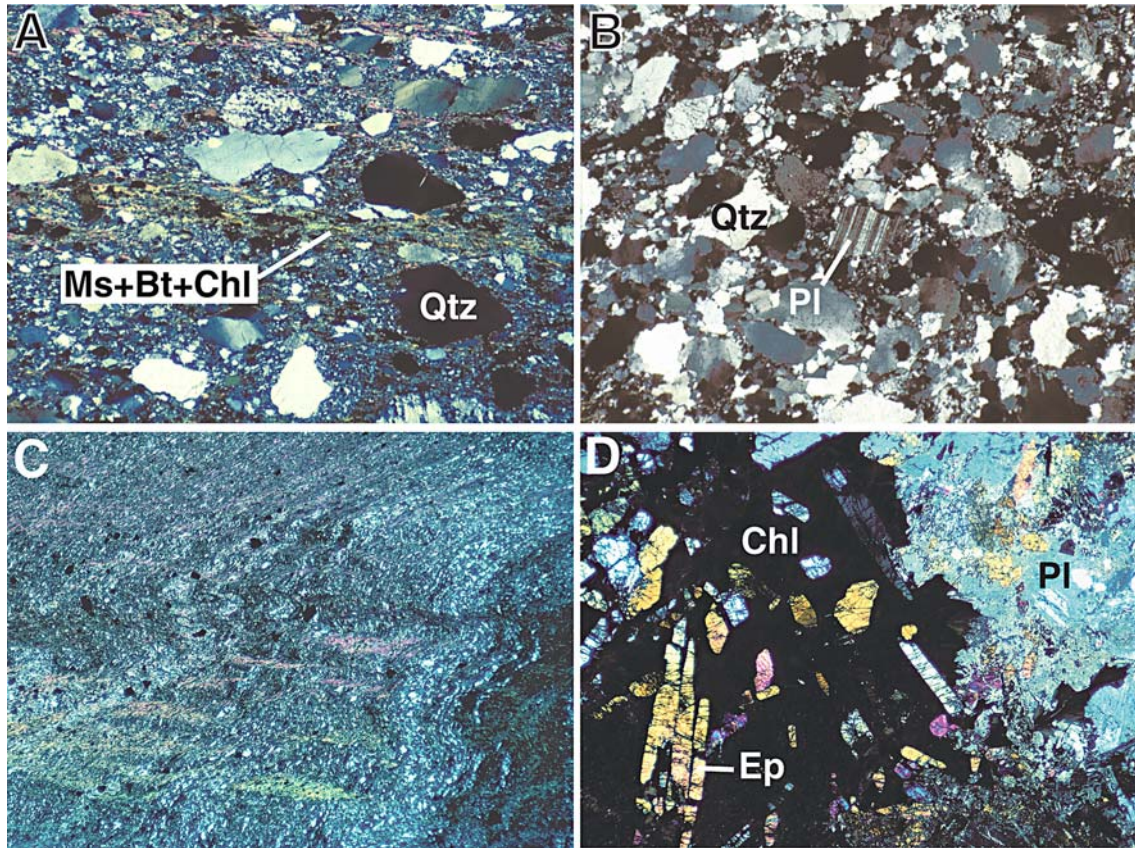
#### Sampling and precursor determination

Assessing mineralogical, textural, and quantitative compositional changes in vein selvages require a careful determination of the nature of the precursor at each vein site. Precursor rocks are inferred to have escaped most or all of the chemical and mineralogical alteration associated with vein formation and are found outside the selvages surrounding the Type A and Type B veins; they may, however, have undergone other forms of metasomatism during sedimentation, diagenesis, and metamorphism. Though the “precursor” is likely much closer to the original sedimentary composition than the selvage, this study does not assume that precursor samples are entirely unaltered.

Primary sedimentary bedding comprising metapelitic and metapsammitic layers can commonly be traced into cross-cutting veins (cf. Ague 1997a). At most sites, samples were taken from the same lithologic layer in precursor areas away from each vein and in altered selvages adjacent to each vein. Under the reasonable assumption that there was no significant difference in original composition on the outcrop scale within a primary sedimentary layer, the nature of the precursor can be defined for each sample site and compared directly to alteration selvage material. Sites 76 and 103 are exceptions to the above sampling protocol. Precursors are difficult to identify close to the HBF due to strong deformation and metasomatism, so samples from site 76 were compared geochemically to the closest Chlorite and Biotite zone precursors available (84A and 82II1F). Sample 103Aii was compared to sample 104J collected from a nearby, unveined layer taken as a proxy for the 103Aii precursor.

Considerable retrograde metamorphism and/or hydrothermal alteration occurred in the field area (cf. Munro 1986; Masters et al. 2000). Some sericite growth





**Fig. 6 a-d** Thin section photomicrographs of precursor-vein selvage relations in the Biotite zone. Fields of view 13.4 mm wide, crossed polarizers. **a** Typical precursor schist containing muscovite (Ms), biotite (Bt), chlorite (Chl), quartz (Qtz) grains, and albite plagioclase, site JAB 82II. **b** Altered selvage adjacent to quartz vein for layer depicted in **a**. Note destruction of foliation and growth of metasomatic quartz and albite plagioclase (Pl). **c** Schist derived from “oxidized” sedimentary protolith, site JAB 7. Schist composed mostly of Ms, Chl, Qtz, Fe-Ti oxides, and Pl. **d** Altered selvage for layer depicted in **c**. Note destruction of foliation and growth of coarse epidote (Ep), Chl, and Pl

is expected when detrital igneous sodic-potassic feldspars break down to form albite during prograde heating (Chlorite and Biotite zones), but the retrograde/hydrothermal effects are much more severe. They are evident from the Biotite through the Staurolite zones and include chloritization of biotite and garnet, sericitization of plagioclase and staurolite, replacement of plagioclase by carbonate minerals, and replacement of epidote by clay-rich pseudomorphs (Ague 1997a; Masters et al. 2000). This work is based on several hundred kilograms of samples; the large number and volume of samples ensured that fresh rocks with little or no low-temperature alteration could be studied.

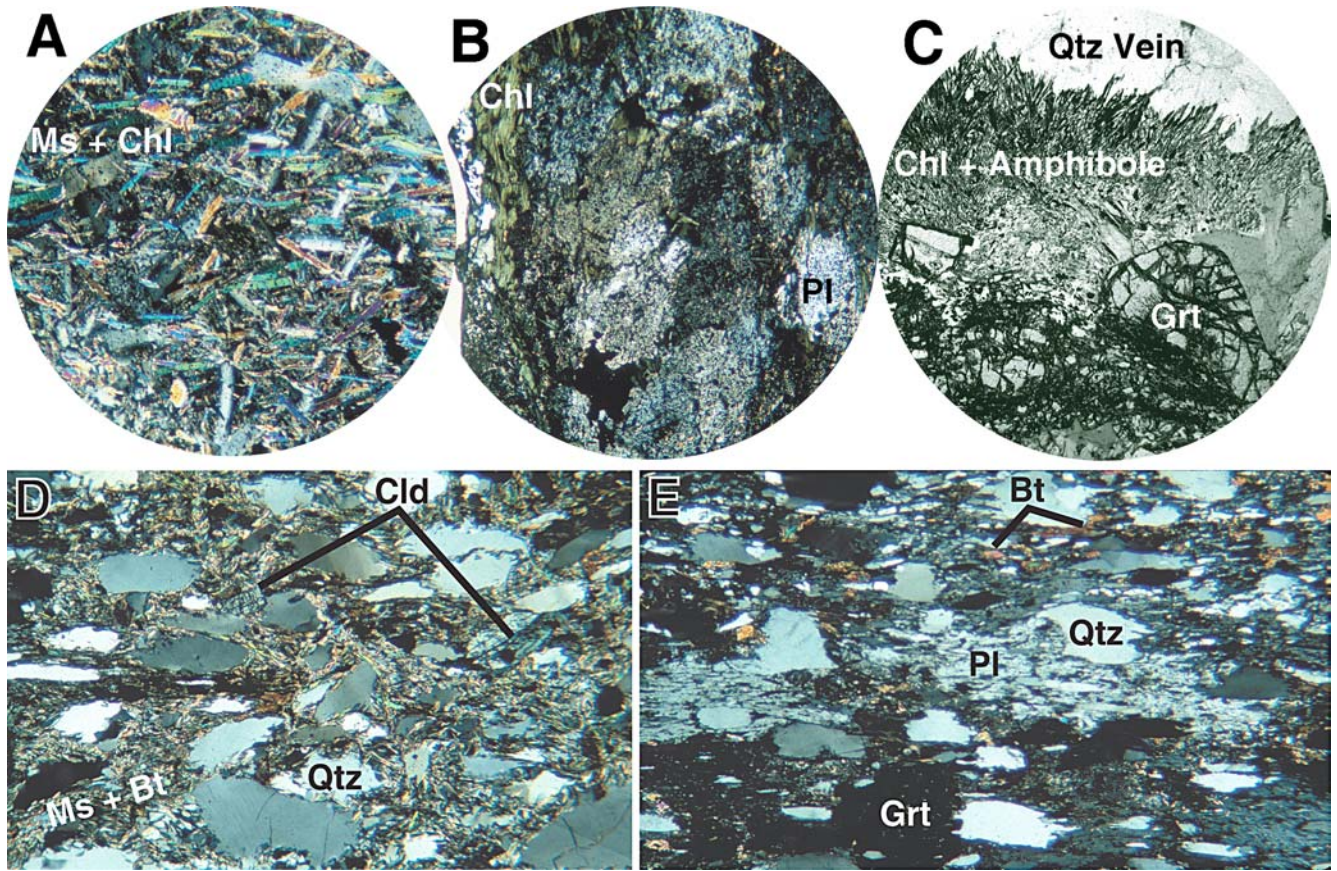
#### **Mineralogical and textural changes associated with vein formation**

This section examines petrographic evidence for mineralogical and chemical alteration in the vicinity of

syn-metamorphic veins. The schists developed from both “oxidized” (hematite-bearing) and more “reduced” sedimentary protolith layers (Chinner 1960; Ague et al. 2001). In the Biotite zone, biotite grew in the more “reduced” rocks but chlorite persisted without biotite in the “oxidized” rocks due to a lack of sufficient ferrous iron to form biotite. Porphyroblasts in the Biotite zone and higher metamorphic grades are commonly coarse grained in selvages adjacent to veins. Biotite porphyroblasts can be as much as 2 to 3 times longer in selvages than in wallrock distal to veins (eFig. 1A, B). Wallrock inclusions in veins as well as selvages in intensely fractured areas have greatly reduced mica content and larger modal abundances of quartz and plagioclase (albite-oligoclase) (Fig. 6). Pervasive deformational fabrics are generally obliterated by veining-related crystal growth (Fig. 6). Plagioclase is abundant in the selvages and wallrock inclusions found in more “oxidized” protoliths, as are large plates of chlorite. At several localities, fresh crystals of epidote were found in veins and selvages; this is the first report of epidote in metapelitic rocks near Stonehaven that we are aware of (Fig. 6d). Retrograde metamorphism produced whitish, clay-rich pseudomorphs after epidote.

In “oxidized” rocks of the Garnet and Chloritoid zones, mineral assemblages rich in muscovite and chlorite give way to plagioclase (mostly oligoclase-andesine) and chlorite-rich assemblages in vein selvages (Fig. 7a, b). Garnet can be found in intensely altered wallrock inclusions within veins, but is generally absent from the matrix





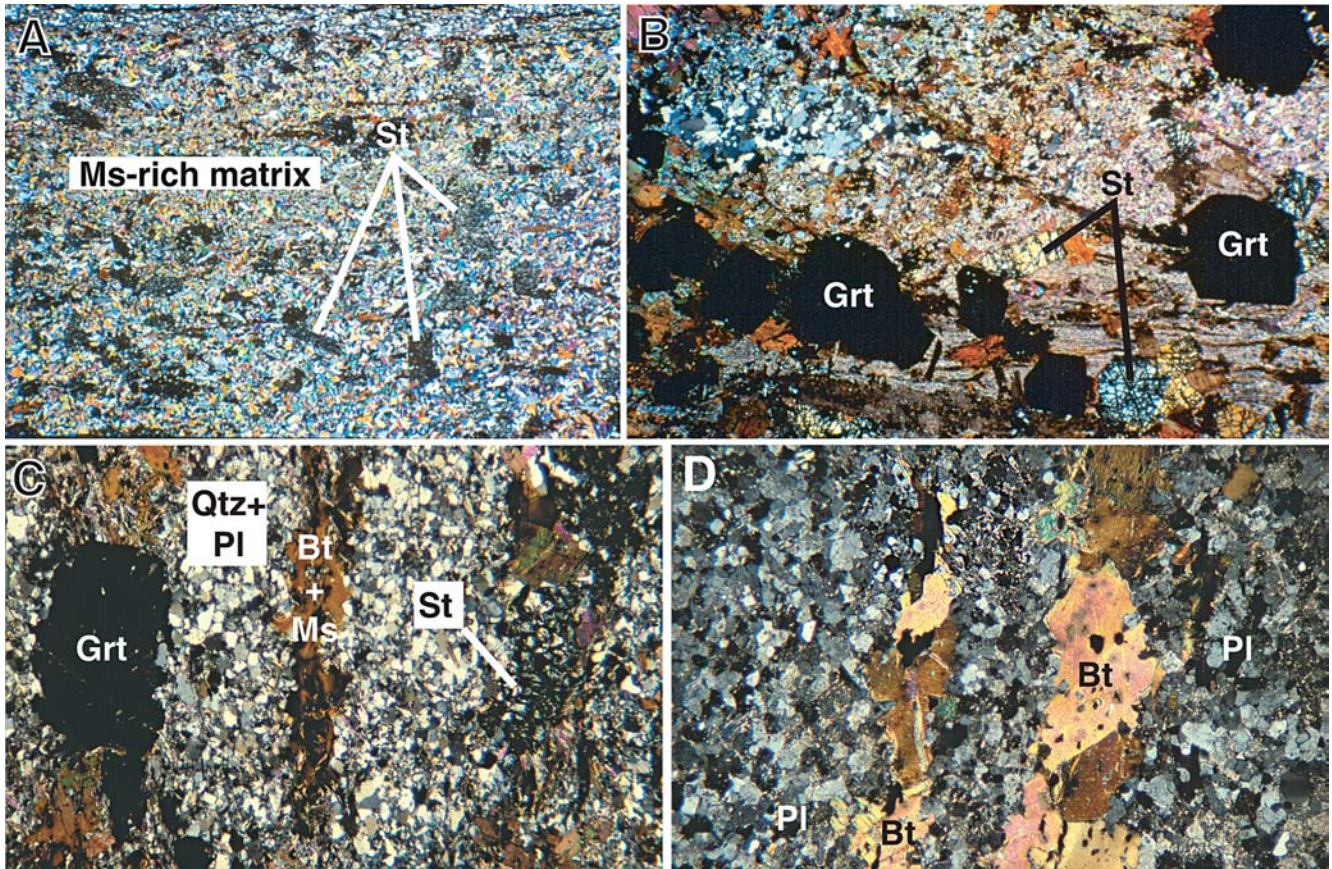
**Fig. 7 a–e** Thin section photomicrographs of precursor-vein selvage relations in the Chloritoid zone. Fields of view 2.1 mm (**a**, **b**), 2.3 mm (**c**), 2.8 mm (**d**), and 3.1 mm (**e**). Plane-polarized light for **c**, crossed-polarizers for others. **a** Muscovite-rich schist derived from “oxidized” sedimentary protolith, site JAB 1. **b** Altered selvage derived from layer depicted in **a**. Note near complete elimination of muscovite and growth of chlorite (Chl) and plagioclase (Pl) adjacent to quartz vein. Pl appears dark because it is crowded with inclusions of magnetite, rutile, and Ti-bearing hematite. **c** Wallrock inclusions in vein adjacent to selvage depicted in part **b**. Note growth of Garnet (Grt), absent from the wallrock. Hornblende and cummingtonite are found as needle-like inclusions in Grt, quartz (Qtz), and in the “spike-like” region of Chl growth. **d** Precursor chloritoid (Cld) schist, site JAB 101L. **e** Altered selvage adjacent to vein derived from layer depicted in **d**. Ms was almost completely destroyed, Cld was eliminated, and Pl and Grt grew during alteration. Pronounced planar fabric is the result of extension associated with boudinage. Sample is described in further detail by Ague (1997a) and Breeding et al. (2004)

(Fig. 7c; eFig. 1C, D). Moreover, at one locality, we discovered coexisting calcium-rich and calcium-poor amphiboles, partly replaced by chlorite, coexisting with garnet and chlorite in wallrock inclusions (Fig. 7c). Our preliminary electron microprobe analyses indicate the formulas  $(K_{0.017} Na_{0.311})(Na_{0.023} Ca_{1.664} Fe_{1.410} Mg_{3.054} Mn_{0.164} Ti_{0.009} Al_{0.676})(Al_{0.997} Si_{7.003})O_{22}(OH_{1.781} F_{0.217} Cl_{0.003})$  for hornblende and  $(K_{0.002} Na_{0.114} Ca_{0.243} Fe_{1.906} Mg_{3.734} Mn_{0.571} Ti_{0.010} Al_{0.358})(Al_{0.137} Si_{7.863})O_{22}(OH_{1.964} F_{0.036})$  for cummingtonite (all Fe as  $Fe^{2+}$ ). To our knowledge, this is the first reported occurrence of amphiboles in the metapelitic rocks near Stonehaven.

Cummingtonite is rare throughout the Dalradian, even in metamorphosed volcanic rocks (Smith and Phillips 2002). In general, garnet is much more abundant in the more “reduced” rocks, due to the ready availability of ferrous iron. Field observations indicate, however, that garnet first appears in selvages adjacent to veins, before it becomes widespread in the rocks distal to veins. Sample JAB-101L, described in detail by Ague (1997a), is characterized by muscovite, biotite, and chloritoid distal to a boudin-neck vein (Fig. 7d, e). In the selvage, chloritoid is eliminated, muscovite is rare or absent, and garnet is present. Extension in the boudin-neck selvage strengthened the planar schistosity defined by biotite and flattened quartz and plagioclase grains. For metasedimentary layers in which chloritoid is present in precursors and selvages, the crystals tend to be largest in the selvage areas.

The localization of garnet near veins continues to some degree in Staurolite zone rocks, although garnet is generally widespread. Garnets are commonly larger and much more abundant in selvages; selvage staurolites also tend to be larger than their counterparts distal to veins (Fig. 8a, b). In some instances, typical peraluminous schists dominated by quartz, muscovite, biotite, plagioclase, garnet, and staurolite grade into selvage rocks rich in plagioclase, quartz, and biotite which contain no garnet or staurolite (Fig. 8c, d). The planar fabric defined by mica-rich and quartzofelspathic domains in the garnet- and staurolite-bearing schists can be traced into the selvages (Fig. 8c, d).





**Fig. 8 a-d** Thin section photomicrographs of precursor-vein selvage relations in the Staurolite zone. Fields of view 15 mm (a), 17 mm (b), and 3.1 mm (c, d). Crossed polarizers. **a** Staurolite (St) schist precursor, site JAB 86. Composed mostly of muscovite (Ms), biotite (Bt), St, quartz (Qtz), and plagioclase (Pl). **b** Altered vein selvage derived from layer depicted in a. Note coarse-grained garnet (Grt) and St. **c** Precursor schist composed mainly of Qtz, Pl, Ms, Bt, St, Grt, and Pl, site JAB 109. **d** Altered vein selvage rich in Pl and Bt derived from layer depicted in c. St, Ms, and Grt were destroyed and Pl produced during alteration

The mineralogical effects of vein and selvage formation are clear from the petrographic relations, but the timing of veining must also be established. One key characteristic of the vein selvages is the widespread occurrence of plagioclase porphyroblasts, often in the form of ovoid “spots” which increase in size progressively toward veins (Ague 1997a). These porphyroblasts overgrow pre-existing metamorphic minerals, planar schistose fabrics, and folds, thus demonstrating that the vein-related “spot” growth was neither pre-metamorphic nor pre-deformational (eFig. 2). This conclusion is reinforced by the observation that many of the veins are found in deformation-related structures such as boudin necks; the folding and boudinage of the veins themselves is a natural result of their formation during bulk deformation of the rock mass (Fig. 3d; see also Fig. 12 in Ague 1994). The veins are not retrograde, post-metamorphic features either because: (1) peak metamorphic porphyroblasts grow in the vein selvages and (2) the porphyroblasts were not retrograded by vein- and

selvage-forming processes. Furthermore, the ion-microprobe depth-profiling study of Breeding et al. (2004) establishes that the age of fluid-driven alteration in a vein selvage ( $462 \pm 8.8$  Ma) is indistinguishable from the “peak” metamorphic age of  $464.8 \pm 2.7$  Ma obtained by Baxter et al. (2002).

### Metasomatism

Petrographic and geochronological relationships establish that vein-related mineralogical and chemical alteration occurred during deformation and “peak” metamorphism. The corresponding metasomatic changes in rock chemistry resulting from vein formation can be assessed using mass balance relations based on an appropriate geochemical reference frame. Ti and Zr can have low solubilities under regional metamorphic conditions and are often considered to be relatively immobile on the hand sample and larger scales compared to more soluble elements such as Si, Ca, Na, and K (Ayers and Watson 1991; Ague 1994). Al is also often considered to be “immobile” but field studies (Ague 2003b) and experimental results (Manning 2004) demonstrate substantial Al mobility is possible during regional metamorphism. Al clearly cannot be used as a reference frame in this study because it has been mobile, at least on the hand sample scale; feldspar and other Al-bearing phases are found in vein selvages and in vein inclusions.

Titanium, was avoided because rutile has been found in some veins (JAB 7, 107), suggesting Ti mobility at least on a centimeter scale (cf. Ague 2003b). Zr was chosen as the geochemical reference frame as there is no mineralogical evidence that suggests significant Zr mobility. For example, metamorphic chemical and isotopic alteration of zircons from site JAB 101 was limited to mineral surfaces at micron to sub-micron depths and no new zircons have been found growing in veins or vein selvages (Breeding et al. 2004).

The standard equation for calculating the fractional mass change ( $\tau$ ) for a mobile constituent  $j$  in an open system (e.g., Ague and van Haren 1996), written here for a Zr reference frame, is:

$$\tau_j = \frac{\text{final mass}_j - \text{initial mass}_j}{\text{initial mass}_j} = \left[ \left( \frac{C_{Zr}^o}{C_{Zr}'} \right) \left( \frac{C_j'}{C_j^o} \right) - 1 \right] \quad (1)$$

in which  $C$  is concentration (e.g., moles, wt.%, or ppm),  $^o$  indicates precursor, and  $'$  indicates alteration selvage rock. Multiplication of  $\tau_j$  by 100 yields percentage mass changes (note that  $-100$  percent is the maximum possible mass loss). It follows that  $\tau_j + 1$  is the ratio of the mass of a given element in the altered rock divided by its mass in the precursor. Note that  $\tau + 1$  takes into account the overall rock mass change via the  $C_{Zr}^o/C_{Zr}'$  term and is thus not equivalent to the simple altered/precursor concentration ratio ( $C_j'/C_j^o$ ). This latter ratio proves highly useful, however, for graphically demonstrating compositional differences between altered and precursor rocks.

### Evidence for Metasomatism

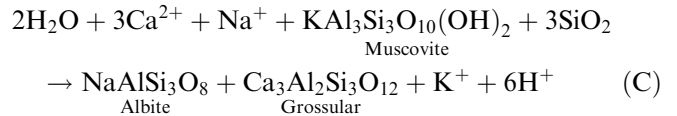
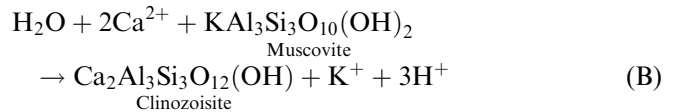
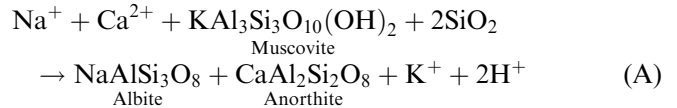
Changes in selected elemental ratios as a function of distance from the Highland Boundary Fault (HBF) are shown in Fig. 9. Ratios among the alkali and alkaline earth elements are immediately striking. At most sites, Na/K, Ca/K, and Sr/Rb are strongly elevated in altered rocks relative to rocks distal to veins. One notable exception is site 107 for which the sense of metasomatism is reversed (see below). In general, the degree of alteration is greatest near the HBF and decreases but is still significant at higher metamorphic grades. Note that these ratio systematics demonstrate unequivocally metasomatic compositional changes and are independent of any geochemical reference frame (e.g., Zr). Ba/Zr is in general much smaller in altered rocks than in rocks distal to veins. Mg/Fe<sup>T</sup> values for altered rocks either overlap those of their inferred precursors, or exceed precursor values (eFig. 3A; Fe<sup>T</sup> is total moles of Fe<sup>2+</sup> and Fe<sup>3+</sup>). The Si/Zr in altered rocks near the HBF can exceed inferred precursor values, but is more variable farther away (eFig. 3B). Pb/Zr tends to be larger in altered rocks than in precursors, particularly near the HBF, although there are exceptions at some sites

(eFig. 3C; cf. Breeding et al. 2004). Precursor rocks are difficult to identify at site 76. However, because most elemental ratios for samples at this site fall within the range of ratios determined for selvage rocks, they are classified as “altered” rocks herein (see below).

### Quantification of mass changes

Mass changes estimated using Eq. 1 clearly indicate that the increases in Na/K, Ca/K, and Sr/Rb in altered rocks relative to their inferred precursors resulted from strong gains in Na, Ca, and Sr, and losses of K, Rb, and Ba (Fig. 10). Variations in mass changes at a given site reflect variations in fluid flow and reaction along the length of veins. Mg/Fe<sup>T</sup> remained unchanged or increased during the alteration (Fig. 10e). Most mass changes appear largest nearest the HBF, but the mass changes 1 to 2 km from the fault are still very large for many elements, and were able to strongly influence the mineralogy of the selvage areas.

The gains of Na, Ca, and Sr and losses of K, Rb, and Ba in and around veins are directly related to syn-metamorphic changes in modal mineralogy and reflect primarily the growth of plagioclase at the expense of mica (particularly muscovite). The Pb added at some sites (eFig. 3C; Breeding et al. 2004) is inferred to be sequestered into the metasomatic plagioclase. Furthermore, the addition of Ca is manifested by epidote in some Biotite zone selvages, and the grossular component of garnet in some Garnet, Chloritoid, and Staurolite zone selvages (Ague 1997a). Schematic model reactions consistent with the mineralogical evidence (Figs. 6, 7, 8) include:

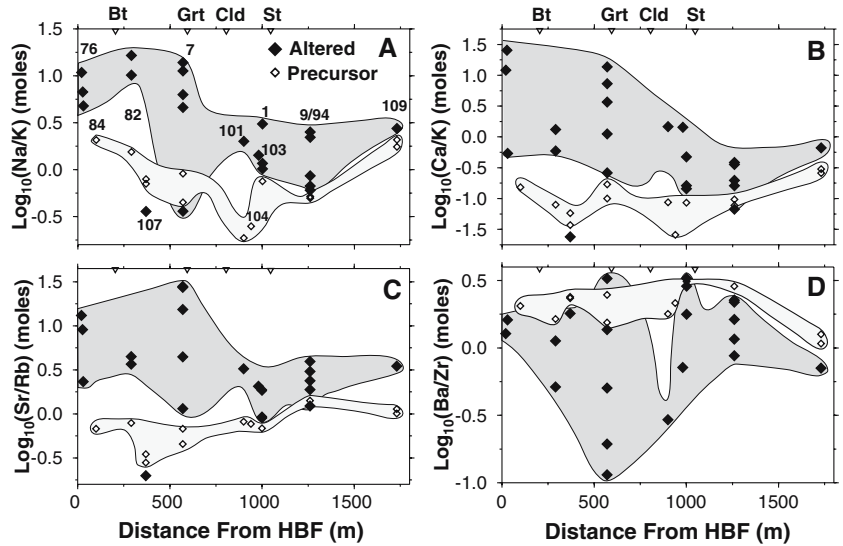


Samples at site 76 adjacent to the HBF can contain calcite and/or dolomite (particularly 76E). We suggest that these minerals were sinks for added Ca mass but admit that, because of uncertainties in precursor geochemistry at this site, a non-metamorphic origin (e.g., sedimentary or diagenetic) for some of the carbonate minerals cannot be ruled out at this time.

The most extreme examples of Mg/Fe<sup>T</sup> increase during alteration are found adjacent to the HBF and at two sites that had “oxidized” precursors (JAB 7 in the Biotite zone and JAB 1 in the Chloritoid zone; Fig. 10e).



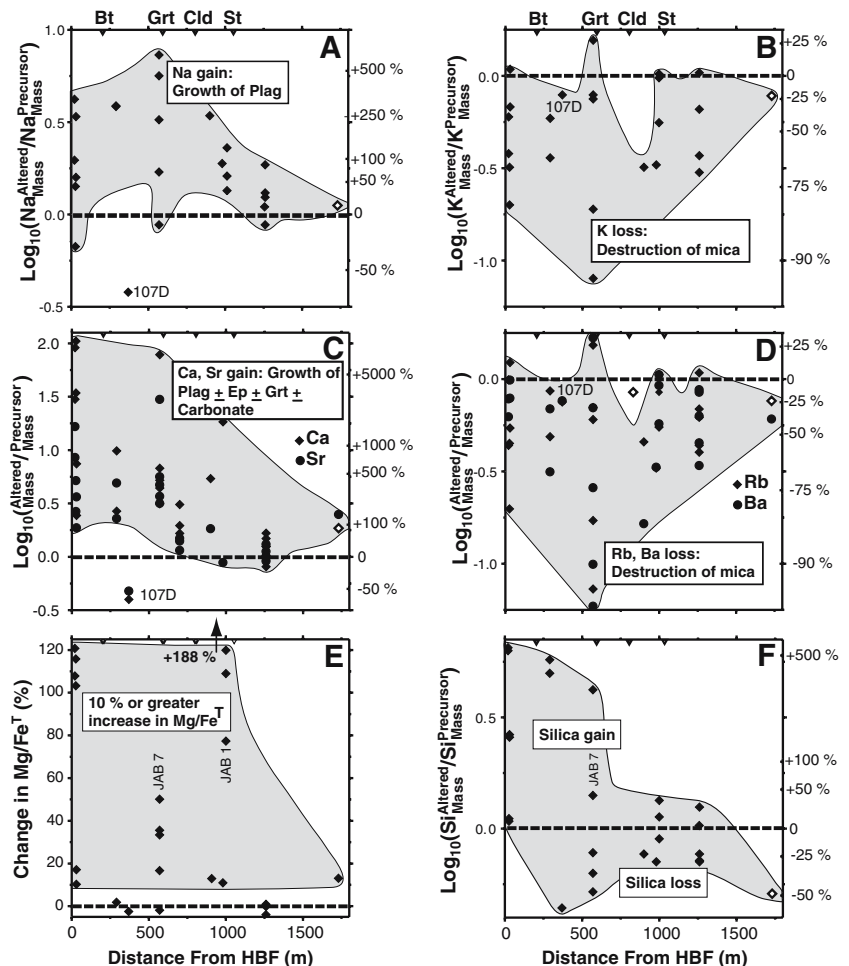
**Fig. 9 a–d** Base 10 log element ratios for altered vein selvages and their corresponding precursors. Fields for altered and precursor rocks denoted by dark and light gray shading, respectively. See text for additional discussion. **a**  $\text{Log}_{10}(\text{Na}/\text{K})$ . Note that at nearly all sites Na/K for altered rocks exceeds that for precursors, indicating an increase in Na/K during vein formation. The opposite sense of metasomatism is observed at site 107; this site is discussed further in the text. **b**  $\text{Log}_{10}(\text{Ca}/\text{K})$ . **c**  $\text{Log}_{10}(\text{Sr}/\text{Rb})$ . **d**  $\text{Log}_{10}(\text{Ba}/\text{Zr})$ . One sample (76E) containing traces of barite inferred to be of sedimentary origin plots off-scale



As discussed above, mass change estimates directly adjacent to the HBF are subject to large uncertainties due to uncertainties in precursor chemistry. At the other two sites, the increases in  $\text{Mg}/\text{Fe}^{\text{T}}$  are due mostly to Mg gains (not illustrated). In the Chloritoid zone example,

the mass transfer involved growth of rutile and near complete removal of magnetite and Ti-bearing hematite from strongly altered vein margins and wallrock inclusions. We infer that the removal of hematite corresponded to a syn-metamorphic decrease in oxygen

**Fig. 10 a–f** Estimated mass changes. For all graphs except part e, left vertical axes denote the mass change ratio and are given by  $\tau + 1$  computed from Eq. 1; right vertical axes are the corresponding percentage mass changes due to alteration. Zero mass change denoted by thick dashed horizontal lines. **a** Na mass changes. Na was gained at most sites. **b** K mass changes. K was lost at most sites. **c** Ca and Sr mass changes. Ca and Sr were gained at most sites. Note that garnet (Grt) is a major host for Ca, but not Sr. **d** Ba and Rb mass changes. Ba and Rb were lost at most sites. One sample (76E) containing traces of barite inferred to be of sedimentary origin plots off-scale. **e** Change in  $\text{Mg}/\text{Fe}$  during alteration ( $\text{Fe}^{\text{T}}$  is total iron). Zero ratio change denoted by thick dashed horizontal line. Increases in  $\text{Mg}/\text{Fe}^{\text{T}}$  of 10 percent or more were common. **f** Si mass changes



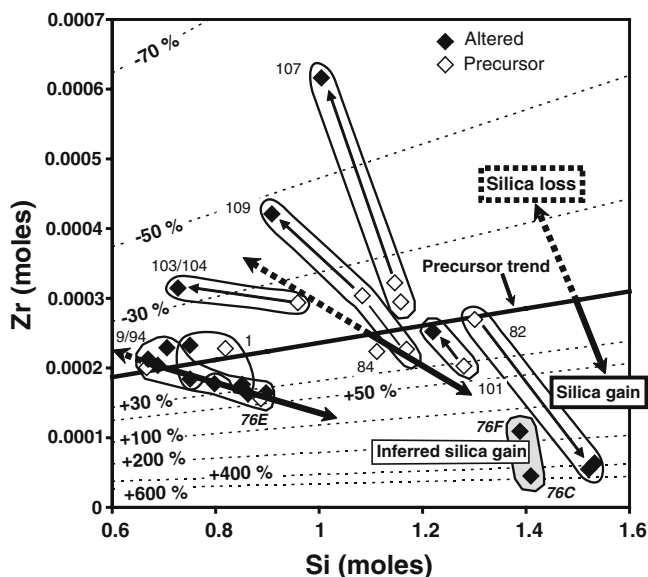
fugacity that produced enough  $\text{Fe}^{2+}$  to stabilize garnet in the most highly altered rocks (Fig. 7a–c; cf. Ague 1998; Ague et al. 2001; Baxter et al. 2002). At higher metamorphic grades, increases in  $\text{Mg}/\text{Fe}^{\text{T}}$  were less extreme but could still be significant in terms of mineral mode. Chloritoid and, to a somewhat lesser degree, staurolite require iron-rich bulk compositions in order to crystallize (cf. Chinner 1967; Droop and Harte 1995). Increases in  $\text{Mg}/\text{Fe}^{\text{T}}$  at several localities are inferred to have contributed to the growth of garnet in selvages in lieu of chloritoid and staurolite (Figs. 7e, 8b; cf. Ague 1997a).

Silica mass transfer was variable across the field area (Fig. 10f). Strong evidence for silica addition is found at the two sites nearest the HBF (76 and 82). The remaining sites show either: (1) mass gains and losses, suggesting at least some local redistribution of silica among altered zones in and around veins or (2) mass losses, suggesting silica removal from selvages and probable deposition in adjacent veins (e.g., Ague 2003a). The amounts of silica precipitated or dissolved by external fluids were not quantified.

Zr-Si relationships shed further light on silica mass transfer (Fig. 11). Quartz and zircon tend to be sorted together in sedimentary environments because of their similar resistance to weathering and the high degree of hydraulic equivalence between large quartz grains and smaller, higher density zircons (Sawyer 1986; Moss et al. 1996; Ague 1997b; Bauluz et al. 2000; Breeding and

Ague 2002). Consequently, Si and Zr should be positively correlated for precursor rocks far-removed from veins and selvages. Si may be mobilized on local scales or on regional scales if a sufficient flux of reactive fluid passes through the rocks. On the other hand, because little or no mass transfer of Zr occurs, it remains in the rock and its concentration increases if rock mass is lost overall (“residual enrichment”) or decreases if rock mass is gained (“residual dilution”) (cf. Grant 1986; Ague 1994; Ague and van Haren 1996). Thus, trends of silica gain or loss will have negative slopes on a Zr-Si plot if silica is the only mobile constituent (Moss et al. 1996; Breeding and Ague 2002). The theoretical trajectories of these Zr-Si trends can be calculated for any bulk composition using Eq. 1; however, in real rocks, the observed trends will diverge from the theoretical ones if other constituents, in addition to silica, were mobile.

Zr-Si systematics for a number of sites follow the theoretical trajectories reasonably well, indicating that silica loss or gain was a large part of the overall mass change at these sites (Fig. 11). There is a general positive correlation between Zr and Si for the precursor rocks, consistent with the relationship expected for sedimentary sorting. The Zr-Si systematics at site 76 directly adjacent to the HBF are particularly useful in view of the precursor uncertainties for this locality. Samples 76C and 76F clearly plot in the region of altered rocks that have undergone silica gain (Fig. 11). As a consequence, we conclude that the silica-rich nature of these rocks is primarily a metamorphic, as opposed to sedimentary, feature (the Zr-Si values of sample 76E are less diagnostic). This conclusion is consistent with our earlier inference that the site 76 rocks have probably undergone extensive geochemical alteration because their geochemical ratios are in general similar to those of altered selvages nearby. We note that data for one site in the Biotite zone scatters widely, indicating that changes in the masses of other constituents were important in controlling the Zr-Si systematics (JAB 7, not shown on Fig. 11). Samples from this site span a range of Si gains and losses (Fig. 10f), suggesting local redistribution of Si mass.



**Fig. 11** Zr-Si systematics. General Zr-Si trend for precursors denoted by *solid line* and is based on a least-squares fit to the precursor data (*open diamonds*). Contours of mass change percent based on this trend shown by *thin dotted lines*. Theoretical Zr-Si trajectories denoted by *heavy arrows* (*solid* in field of Si gain, *dashed* in field of Si loss). These trajectories are for mass transfer of silica only; the samples in this study also underwent other mass transfer so their trajectories differ from the theoretical ones. Note that samples JAB 76C and 76F (*gray-shaded field*) plot well within the region of mass addition, indicating substantial Si gain

#### Rare earth elements

Rare earth elements (REEs) are typically considered to be relatively immobile during fluid–rock interaction although there is increasing evidence for REE mobility, particularly in igneous hydrothermal environments (Gieré 1990) and during regional metamorphism (Ague 2003b). REE patterns for precursors and most selvages are consistent with those expected for typical metaclastic schists (Bauluz et al. 2000); light rare earths (LREE) are enriched relative to heavy rare earths and there is a negative europium anomaly. The concentrations of REEs in selvages increase where silica was lost, and decrease where silica was gained, suggesting that REE mobility was relatively limited during alteration.



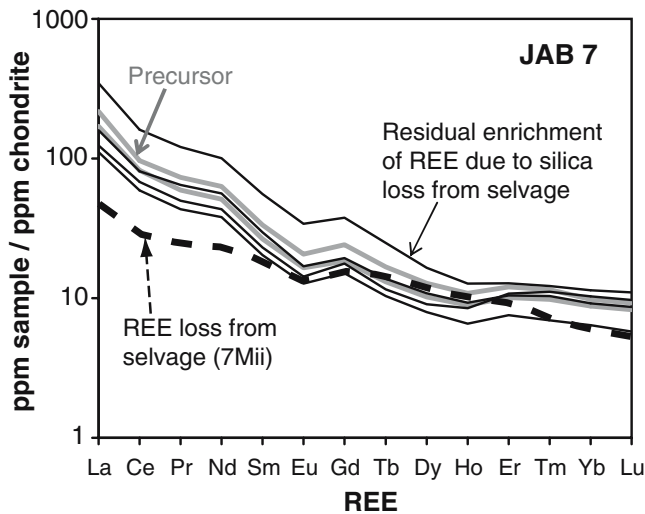
The REE pattern of one selvage sample, however, appears to reflect depletion of LREEs relative to protolith abundances and perhaps depletion of Yb and Lu as well (7Mii; Fig. 12; eTable 3). Transport of REEs in aqueous fluids can be enhanced by the formation of complexes with anions such as  $F^-$ ,  $Cl^-$ ,  $OH^-$ ,  $CO_3^{2-}$ ,  $SO_4^{2-}$ , and  $PO_4^{3-}$  (Gieré 1990). Notably, the  $P_2O_5$  contents of altered rocks at this site reach the highest values observed and correlate with apatite abundance ( $P_2O_5$  as great as 0.72 wt. %; eTable 1). The P addition to these altered rocks would indicate a high concentration of  $PO_4^{3-}$  in the metamorphic fluids that facilitated transport of REE (cf. Ague, 2003b).

## Discussion

Models for metamorphic fluid flow in the Dalradian must account for a broad spectrum of chemical and mineralogical evidence, including the following. Chemical alteration associated with syn-metamorphic fluid flow through fractures caused mass gains of Ca, Na, and Sr, and losses of K, Rb, and Ba. The major mineralogical result of these chemical shifts was the growth of plagioclase and destruction of mica (particularly muscovite). In addition, Ca gains are manifested in some rocks by the growth of epidote (Biotite zone), garnet

and, probably, calcite and/or dolomite adjacent to the HBF (Chlorite zone). Alteration increased  $Mg/Fe^T$  at a number of sites, helping to stabilize garnet at the expense of chloritoid or staurolite. Silica mass transfer resulted in Si gains near the Highland Boundary Fault (HBF). Further from the fault, silica redistribution involving at least local gains and losses occurred, but the magnitude of regional transport is unclear. In general, the degree of chemical alteration appears greatest in greenschist facies rocks within 750 m of the HBF, but significant alteration persists to the most distal part of the field area nearly 1800 m from the fault. In addition to these general systematics, altered rocks at one Biotite zone site underwent LREE loss, and Ca-rich and Ca-poor amphiboles grew in heavily altered wallrock inclusions in veins at a site in the Chloritoid zone.

The mass transfer of alkali and alkaline earth elements is perhaps the most striking aspect of the metasomatism (Figs. 9, 10). The gains of Na, Ca, and related elements cannot be due to a local “segregation” process that concentrated plagioclase in and around veins, for such a process would be unable to produce the observed strong losses of K, Rb, and Ba. Instead, the metasomatism operated at a larger scale and produced coupled elemental gains and losses. There are several scenarios of fluid–rock interaction that could explain the metasomatism, but two of them in particular are most consistent with the available data.



**Fig. 12** Rare Earth Element (REE) systematics at site JAB 7, Biotite zone. REE patterns for most samples have the same general shape. Those that plot above the precursors indicate overall mass loss of other constituents that lead to an increase in the concentrations of the nearly immobile REE (“residual enrichment”). On the other hand, overall mass gains of other constituents decreased the REE concentrations. A large fraction of these overall gains and losses resulted from redistribution of silica mass. However, the REE pattern for sample 7Mii diverges from the precursor pattern, indicating loss of the light REE (LREE) and, probably, the heaviest REE. Analytical errors for LREE in sample 7Mii are comparable to the thickness of the dashed line and cannot account for the difference in LREE between this sample and the precursor

## Fluid flow in a direction of increasing temperature

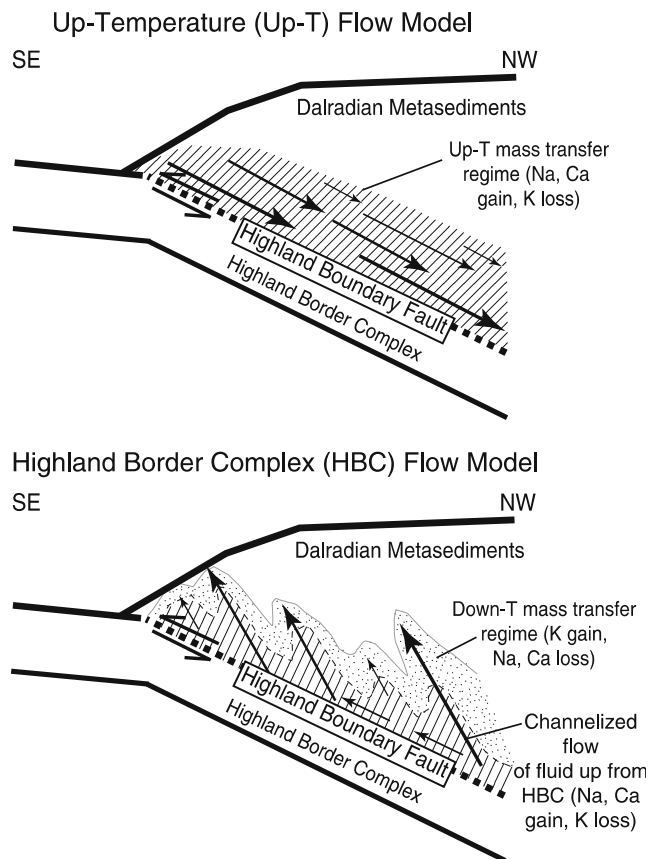
The first scenario requires fluid flow in a direction of increasing temperature (“up- $T$ ” flow), where the fluid is at or near local chemical equilibrium with the wallrocks. For example, reactive up- $T$  flow tends to deplete rocks in K and add Na and Ca, whereas flow in a down- $T$  direction tends to enrich K and remove Na and Ca (Orville 1962; Dipple and Ferry 1992; Ague 1994, 2003a). The sense of metasomatism around most veins in the field area—addition of Na and Ca, depletion of K, and increase in  $Mg/Fe^T$ —is consistent with an up- $T$  flow model as discussed by Ague (1997a) based on chemical data from site JAB 101.

It is highly probable that some degree of subduction of the Highland Border Complex beneath the southern margin of the Dalradian along the HBF occurred during metamorphism (cf. Dempster et al. 2000). Inverted geothermal gradients are unlikely for the hanging wall in the shallower parts of subduction zones (~15 km; Barr and Dahlen 1989). Thus, up- $T$  flow would have to be horizontal (e.g., Ferry 1992) or have a downward component. Downward flow is generally considered unlikely below the brittle-ductile transition during regional metamorphism (e.g., Hanson 1997). However, the ~15 km metamorphic depths suggest that the section could have, at least in part, resided in the brittle regime. Brittle behavior and fracturing may have been episodic, triggered by rapid seismic energy release associated with

movement along the HBF and/or hydrofracturing driven by dehydration reactions (e.g., Yardley 1986; Ague et al. 1998). Fracturing will tend to increase rock permeability and, therefore, the deformed, highly-veined Dalradian rocks along the HBF may have acted as a high-permeability zone in which fluids could flow into the Dalradian in an up- $T$  direction (“up- $T$  model”; Fig. 13). This model predicts that the degree of chemical alteration would be largest nearest the HBF, consistent with the available data.

Silica mass transfer provides additional constraints on flow models. Up- $T$  flow of aqueous fluids at or near local chemical equilibrium with quartz is expected to dissolve silica from rocks (e.g., Ferry and Dipple 1991; Manning 1994). The time-integrated fluid flux

( $q_{Ti}$ ) needed to produce the observed Na-Ca-K metasomatism as a result of up- $T$  flow is  $\sim 3 \times 10^4$  m<sup>3</sup> (fluid) per m<sup>2</sup> (rock) (Ague, 1997a). These fluxes, although very large, are still insufficient to result in large-scale silica removal for simple up- $T$  flow. In the up- $T$  model, therefore, most of the silica mass transfer must be due to local redistribution of mass. For example, fracturing due to elevated fluid pressures and/or tectonism could open up high-permeability conduits. Fluid would then flow through these fractures, leading to the observed alkali and alkaline earth metasomatism. Finally, aqueous silica could diffuse down chemical potential gradients due to, for example, lower fluid pressure in the cracks than in the rock, and precipitate as quartz to seal the cracks. This crack-flow-seal process (Ague 2003a) could easily deplete selvages in silica adjacent to veins, and add silica to veins and wallrock inclusions within veins. The one major problem for the up- $T$  model is that silica precipitation occurred near the HBF (Figs. 10f, 11), but near-equilibrium, up- $T$  flow will not precipitate silica. Consequently, if the up- $T$  model is correct, then silica precipitation must have occurred as a result of changes in fluid composition along the flow path (e.g., gradients in the activity of water due to the presence of other fluid species such as CO<sub>2</sub>; cf. Ague 2003a) and/or kinetic controls on silica dissolution/precipitation reactions (Bolton et al. 1999).



**Fig. 13** Two candidate models for regional metamorphic fluid flow. Flow directions indicated by *arrows* are highly schematic. Flow directions for the HBC model could have been directed to some degree to the southeast (SE; present-day coordinates) by steep foliations/layering in the Dalradian (cf. Wing and Ferry 2002); some component of flow could have been sub-parallel to the HBF as well. The directions shown on the cartoon are highly speculative, but we emphasize that flow in this model must have had a strong vertical component upward from the HBC. Areas of Na, Ca gain and K loss denoted by *diagonal rule pattern*; areas of K gain and Na, Ca loss denoted by *stipple pattern*. Note that the entire rock mass was not chemically altered in the patterned areas; alteration occurred mainly in selvages adjacent to veins. A possible exception is rocks directly adjacent to the HBF where alteration may have been nearly pervasive

#### Fluid flow from the HBC upward into the Dalradian

Na/K and Ca/K ratios would have also increased if the fractures hosted external, Na-rich, Ca-rich, and K-poor fluids derived from a rock mass having a bulk chemical composition that differed greatly from the Dalradian metasediments. In this type of scenario, the external fluid composition is strongly out of chemical equilibrium with the wallrocks and thus has a greater effect on the nature of the metasomatism than flow along a temperature gradient (cf. Ague 2003a). Consequently, flow could be in a down- $T$  direction and still result in Na and Ca gains and K losses in and around fractures if the infiltrating fluid was sufficiently out of local equilibrium with the wallrocks.

Possible sources for Na- and Ca-rich, K-poor fluids include evaporite deposits or dehydration fluids from spilitized metabasalt. Evaporites are unlikely as there are no evaporite deposits within the Dalradian metasediments (Ague 1997a). Spilitized metabasalt has been documented as a source of Na-, Ca-rich, K-poor, silica-saturated fluids. For example, fluids derived from subducting oceanic crust added Na, Ca, and Si and removed K in the overlying greenschist facies metapelitic rocks of the Otago accretionary prism, New Zealand (Breeding and Ague 2002).

The Highland Border Complex (HBC), which lies within the HBF, comprises a dismembered ophiolite, including metamorphosed mafic and ultramafic rocks,



and associated metasediments. The igneous rocks of the HBC have undergone extensive Na, Ca, Si, H<sub>2</sub>O, and CO<sub>2</sub> addition during spilitization on the seafloor (Seyfried et al. 1978; Robertson and Henderson 1984; Masters et al. 2000). Dehydration of these rocks would generate fluids enriched in Na and Ca and depleted in K, relative to Dalradian metasediments, capable of driving the dominant K losses and Na and Ca gains observed in and around syn-metamorphic veins (“HBC model”; Fig. 13). Fluid flow in a down-*T* direction, up from the HBC into the overlying Dalradian metasediments, could precipitate silica in fractures, as observed in close proximity to the HBF. Such fluids would probably be depleted in light REE and could account for the light REE losses observed at site JAB 7 (Fig. 12). The metamorphosed mafic rocks of the HBC descending beneath the Dalradian would likely have been in the greenschist, epidote-amphibolite, and/or amphibolite facies. Consequently, growth of epidote or amphiboles in some vein zones within the Dalradian is consistent with infiltration by fluids equilibrated with metamorphosed mafic rocks. Given that peak metamorphism and metasomatism coincided temporally, the HBC and up-*T* models predict that dehydration fluids from the Dalradian were also part of the regional flow system. In the HBC model, this metasedimentary fluid component would have been dominated by that from the subducted slab (cf. Breeding and Ague 2002).

Fluids ascending into the Dalradian would, at sufficient distances above the HBF, approach local equilibrium with the Dalradian after they had reacted to add Na and Ca and strip out K (Fig. 13). Then, down-*T* flow metasomatism characterized by K addition and Na and Ca loss would prevail (e.g., Dipple and Ferry 1992; Ague 2003a). Such metasomatism would be an important test of the HBC model, but we have not observed it to any significant degree in our study. One possible exception is site 107, where selvage rocks lost large amounts of Na and Ca, and small amounts of K (Fig. 10). This site may represent the transition to the down-*T* metasomatic regime; however, further research is needed at distances in excess of 2 km from the fault to test conclusively for the down-*T* metasomatism predicted by the HBC model. It is important to note that the metasomatism upward from the HBC would not be characterized by a single “front”. For example, the regional length scale of alteration for K would differ from that for Sr; fronts would vary in position depending on the reactions that operated, fluid composition, bulk fluid–rock partition coefficients, and other geologic factors (cf. Bickle 1992). Furthermore, the length scales would increase with time together with time-integrated fluid fluxes.

The time-integrated fluid flux ( $q_{TI}$ ) needed to achieve the chemical alteration observed adjacent to veins for the HBC model can be estimated. Chemical reactions in many selvages resulted in partial to complete destruction of muscovite coupled with the growth of plagioclase feldspar. A typical value for the modal abundance of muscovite in precursor rocks is 30 volume percent. Thus

$2.13 \times 10^{-3}$  mol K/cm<sup>3</sup> rock was removed if all muscovite was destroyed in the selvage (molar volume data of Berman 1991; rock density of 2.8 g cm<sup>-3</sup>). For an activity of H<sub>2</sub>O of 0.9 and a Cl<sup>-</sup> molality of 0.65 *m* (Ague 1997a), fluid speciation calculations indicate that a fluid in equilibrium with the model protolith composition would have had a mole fraction of K =  $1 \times 10^{-3}$  (calculations done using the methods and software of Ague 1997a). The equation for time-integrated fluid flux appropriate for the propagation of a geochemical “front” along cracks upward from the HBF into the Dalradian is (Ague 1998):

$$q_{TI} = L \frac{\bar{V}_f M_i}{\Delta X_i} + L\phi, \quad (2)$$

in which  $M_i$  is the moles of potassium removed from the rock per unit volume of rock,  $\Delta X_i$  is the difference in the total mole fraction of K between the input fluid and the equilibrium fluid,  $\phi$  is porosity (taken as 0.001; cf. Ague 1998),  $\bar{V}_f$  is the molar volume of H<sub>2</sub>O (21.5 cm<sup>3</sup>/mol H<sub>2</sub>O, 500 °C and 4 kbar; Kerrick and Jacobs 1981),  $\dot{V}_j$  and  $L$  is the regional-length scale of alteration for element *i*. Given the steep dip of the HBC beneath the Dalradian, a minimum value for  $L$  is  $\sim 1$  km; we use the representative range of 1 km to 10 km for the calculations below. The second term on the right-hand side of Eq. 2 has a minor effect on the  $q_{TI}$  estimates.

Assuming that the input fluid contained no potassium (based on the lack of potassic phases in the HBC spilites), Eq. 2 yields  $q_{TI} = 5 \times 10^4$  m<sup>3</sup>/m<sup>2</sup> for  $L = 1$  km and  $5 \times 10^5$  m<sup>3</sup>/m<sup>2</sup> for  $L = 10$  km. Potassium in the initial fluid would make the  $q_{TI}$  estimate a minimum whereas incomplete destruction of muscovite would require a proportionately lower  $q_{TI}$ . The calculated  $q_{TI}$  would also be a minimum if kinetic effects slowed the rates of fluid–rock interaction (Bolton *et al.* 1999). Time-integrated fluid fluxes of this magnitude have been calculated in other subduction zone settings. Breeding and Ague (2002) propose that  $q_{TI}$  of  $10^4$ – $10^5$  m<sup>3</sup>/m<sup>2</sup>, derived from subducted oceanic crust, produced similar major element metasomatism in the Otago Schist, New Zealand. Silicification of selvages and wallrock probably records even larger  $q_{TI}$ , approaching  $10^6$  m<sup>3</sup>/m<sup>2</sup> (Ferry and Dipple 1991). Better estimates of such fluxes, however, require quantification of the amounts of locally and externally derived silica in veins (Ague 1994). What is clear, however, is that metasomatic  $q_{TI}$  values for veins must have been at least  $10^4$  m<sup>3</sup>/m<sup>2</sup> for both the up-*T* and HBC models. Oxygen isotope systematics of vein quartz also indicate substantial fluid–rock interaction (Masters 2004) and will be the subject of a separate paper.

On balance, the HBC model appears most appropriate for the Dalradian because it can account in a straightforward way for all of the observed metasomatic effects, including silica addition to veins and selvages at greenschist facies sites close to the HBF. The up-*T* flow model cannot be ruled out, however, so further research is needed to differentiate between the possibilities. The

overall picture of fluid flow in the Dalradian may be even more complex, as Dempster et al. (2000) argue for a period of K addition and Na and Ca loss in Biotite zone metapsammities that pre-dated the peak metamorphic effects we document.

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### Concluding remarks

Historically, the metamorphic evolution of Barrovian-type metamorphic terranes has received a degree of attention commensurate with their place as a near-ubiquitous feature of mountain belts around the world. The evolution of these rock packages has extensive implications for the chemical and mineralogical make-up of the continental crust. Our results document that metamorphism in the Barrovian zones was a highly non-isochemical process. Syn-metamorphic fractures (veins) were conduits for regional fluid flow that drove chemical and mineralogical alteration and supported time-integrated fluid fluxes of at least  $\sim 10^4 \text{ m}^3(\text{fluid})/\text{m}^2$  (rock). The regional flow regime was strongly influenced by the Highland Boundary Fault; we conclude that fault movement deformed the Dalradian, opening fractures that served as high-permeability fluid conduits. If significant flow from the subducted slab into the Dalradian occurred, then the broad implication is that the geochemical evolution of continental and oceanic crust are more intimately linked than previously recognized (cf. Breeding and Ague 2002). Dehydration of subducting oceanic crust, long known to be a fluid source for hydration and partial melting in the mantle above subduction zones (e.g., Peacock 1993), may also be a fundamental source of enrichment for major rock-forming elements such as sodium, calcium, and silicon during greenschist and amphibolite facies metamorphism of the continental crust.

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