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Nitrogen-isotope record of fluid-rock interactions in the Skiddaw Aureole and granite, English Lake District

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ABSTRACT

The Skiddaw Granite and its contact metamorphic aureole in the English Lake District provide an excellent opportunity to test the capability of the N-isotope system to trace devolatilization and large-scale transfer of crustal fluids. In the aureole, Skiddaw Group metasedimentary rocks with relatively uniform lithology and major-element compositions show a dramatic decrease in N content toward the granite contact (from ≥800 ppm at distances >2.5 km from the contact, to <410 ppm ≤0.55 km from the contact). Far from the intrusive body (>1.5 km), these rocks have extremely uniform $\delta^{15}N_{air}$ near +3.7‰, whereas closer to the contact (≤1 km) $\delta^{15}N$ is shifted to higher values (up to +8.7‰). The coupled decreases in N content and increases in $\delta^{15}N$ are compatible with the removal of N having low $\delta^{15}N$ in fluids during continuous, prograde devolatilization reactions involving the breakdown of white mica and the stabilization of biotite-, cordierite-, and andalusite-bearing assemblages. In the same metasedimentary rocks, the lack of obvious trends in major-element concentrations (including SiO_2/TiO_2, SiO_2/Al_2O_3, and the ratios of other major oxides to TiO_2 and Al_2O_3) with distance from the granitic contact is consistent with minimal change in major element composition during the contact metamorphism. Ratios of whole-rock N, B, Rb, and Ba concentrations to whole-rock K_2O content are believed to reflect the differing fluid-mica partitioning (and involving varying relative proportions of white mica and biotite) of these trace elements during devolatilization reactions.

Greisenized Skiddaw Granite from a borehole is enriched in N (range of 17–225 ppm for whole rocks and white mica separates) relative to the unaltered granite (whole-rock <30 ppm), and has $\delta^{15}N$ of +1.0 to +4.8‰. The N concentrations and $\delta^{15}N$ of the wall-rocks and greisenized granites, combined with C isotopic data (carbonate and carbonaceous matter) for the same rocks, are consistent with the mobilization of fluids having low $\delta^{15}N$ and $\delta^{13}C_{PDB}$ values from the devolatilized aureole into the cooling intrusive body. Such transport is consistent with the predictions of recent theoretical models of late-stage hydrothermal evolution in cooling intrusive systems.

INTRODUCTION

Many igneous and metamorphic rocks contain appreciable amounts of nitrogen (N), primarily as structurally bound NH_4^+; however, the N-isotope system has not yet been extensively exploited as a tracer of high-temperature fluid-rock interactions and other crust-mantle mixing processes. Because of the affinity of NH_4^+ for potassic mineral phases such as the micas and potassium feldspar (see Honma and Itihara 1981), N isotopes are likely to be particularly effective at tracing K-rich metasomatism in many different geological settings (Bebout 1997). Nitrogen owes its presence in crustal rocks largely to its fixation in sedimentary environments by biological processes. Thus, N concentrations and isotopic compositions are potentially useful tracers of the transfer of sediment-sourced C-O-H-S-N fluids or silicate melts in the crust and mantle (Bebout and Fogel 1992; Boyd et al. 1993; Bebout 1997; Boyd and Philippot 1998; Bebout et al. 1999).

Previously presented NH_4^+ concentration and O- and S-isotopic data for the Skiddaw Granite and its contact metamorphic aureole, exposed in the English Lake District, are consistent with a mixed, aureole-derived, magmatic, and meteoric source for the fluids that hydrothermally altered the granite during its cooling (Shepherd et al. 1976; Cooper and Bradley 1990; Lowry et al. 1991). In this study, the Skiddaw Granite and aureole were exploited in an N-isotope investigation of: (1) the mechanisms of devolatilization in contact metamorphosed pelitic rocks; and (2) the late-stage hydrothermal alteration occurring at/near the top of a relatively shallowly emplaced granitic intrusion. These well-studied rocks provide an excellent test of the capability of the N-isotope system to constrain crustal fluid sources and pathways and the metasomatic processes by which economically significant, K-rich ore deposits are produced.

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GEOLOGIC SETTING

The Skiddaw Granite (O'Brien et al. 1985) is an early Devonian (398±8 Ma; Rundle 1992), peraluminous biotite granite pluton that intrudes folded Ordovician sedimentary rocks of the Skiddaw Group in the northern part of the English Lake District (Fig. 1a). The Skiddaw Group in this region is dominated by silty mudstones of turbidite origin that show relatively little compositional variation (Fortey 1989; Cooper and Bradley 1990; Cooper et al. 1995; see whole-rock major-element compositions in Table 1). The roof of the granite is close to the present land surface and exposed in only three small areas (Grainsgill, Caldew River, Sinen Gill; Fig. 1b); however, a borehole into the granite at the Caldew River exposure samples to a depth of 280 m (Webb and Brown 1984). The granite is variably greisenized, with W mineralization occurring as wolframite- and scheelite-bearing quartz veins in the Grainsgill exposure (Shepherd et al. 1976; Roberts 1983; whole-rock major element analyses of three greisenized granite samples are given in Table 1).

The granite is surrounded by a concentrically zoned contact metamorphic aureole nearly 10 km in diameter (Fig. 1b). The rocks of the Skiddaw Group experienced a regional low-grade metamorphism associated with the Caledonian orogeny (dominantly anchizone in the Skiddaw area; see detailed white mica crystallinity study of the region by Fortey 1989). Toward the granite, these rocks show a classic progression (Harker 1939; Pattison and Tracy 1991) into silty mudstones with small andalusite porphyroblasts and/or spots of chlorite/cordierite (andalusite ± cordierite + biotite + chlorite + white mica), to more recrystallized andalusite- and cordierite-bearing rocks (cordierite + andalusite + biotite + chlorite + white mica), into crystalline hornfels that locally contains sillimanite closest to the granite (andalusite + cordierite + biotite + white mica ± garnet ± sillimanite). In the contact aureole, NH$_4^+$ concentration decreases towards the contact with the pluton; NH$_4^+$ in greisenized granite was attributed to additions from the aureole (Cooper and Bradley 1990). Samples of the contact aureole analyzed in this study were collected from surface exposures along a traverse across the southeastern section of the aureole (X-Y in Fig. 1b; Cooper and Bradley 1990), and samples of the granite are from the borehole drilled into the Caldew River granite exposure (Fig. 1b).

Approximately 15 km southwest of the Skiddaw Granite, a large area of Skiddaw Group rocks, the Crummock Water aureole, shows bleaching and geochemical modification (substantial net gain of As, B, Ca, F, K, Si, and Rb; net loss of C, Cl, Ni, S, Zn, Mn, Fe, and H_2O) attributed to throughput of fluids above an igneous hydrothermal system (Cooper et al. 1988; see location of Crummock Water Aureole on Fig. 1a). The timing of this alteration (~400 Ma; Rb-Sr isochron dating by Cooper et al. 1988) was contemporaneous with the emplacement of the Skiddaw Granite, which forms part of the second and last magmatic phase responsible for the Lake District batholith underlying most of the region (Lee 1986; Hughes et al. 1996). Mobilization of the elements removed by this process, and mobilization of materials derived from the intrusions themselves and materials scavenged from the host rocks by circulating fluids driven by heat from the intrusions, are believed to have led

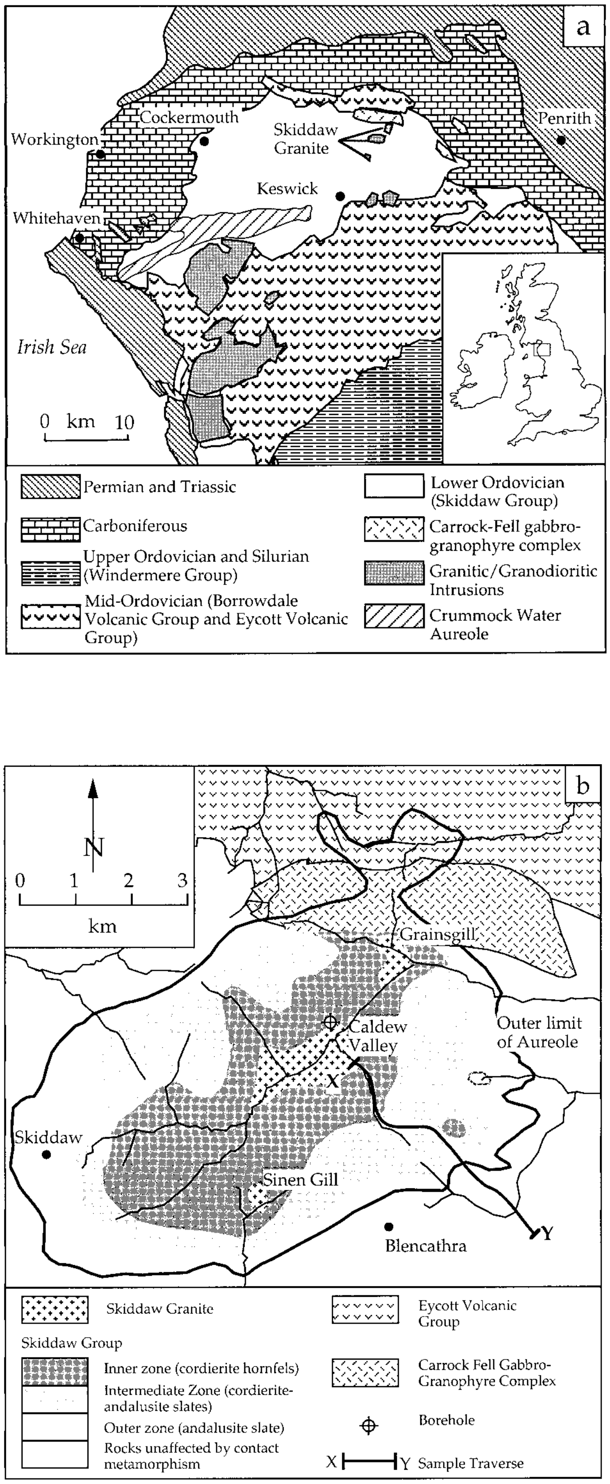


FIGURE 1. Simplified geological maps of (**a**) the English Lake District, showing the location of the Skiddaw aureole and granite and the Crummock Water aureole, and (**b**) the contact aureole adjacent to the Skiddaw granite, divided into three zones (after Eastwood et al. 1968), showing the aureole traverse (X-Y) along which the sampling was conducted.

TABLE 1. Whole-rock chemical compositions of variably metamorphosed sedimentary rocks in the Skiddaw Aureole and variably greisenized Skiddaw Granite (in weight percent)

Sample	Distance* (km)	SiO_2†	Al_2O_3	TiO_2	Fe_2O_3	MgO	CaO	Na_2O	K_2O	MnO	P_2O_5
				Outer Mudstones and Siltstones							
KDC-50	3.85	54.31	23.83	1.04	9.16	1.72	0.33	0.80	3.07	0.63	0.10
KDC-45	3.55	54.34	23.54	0.98	9.79	1.99	0.33	0.74	2.89	0.44	0.18
KDC-30	2.85	55.33	23.71	1.17	7.79	1.70	0.34	0.96	3.50	0.05	0.18
KDC-26	2.55	55.97	22.84	1.18	8.97	1.76	0.33	0.81	3.11	0.09	0.17
				Andalusite + Biotite ± Cordierite Slates‡							
KDC-23	2.45	54.69	23.46	1.21	9.35	1.91	0.36	0.94	3.31	0.08	0.23
KDC-19	2.40	56.11	22.91	1.16	9.16	1.74	0.09	0.69	3.34	0.15	0.11
KDC-13	2.00	56.71	21.94	1.11	9.62	1.23	0.05	0.55	3.07	0.07	0.15
KDC-12	1.95	55.31	23.22	1.16	8.35	1.25	0.08	1.21	3.04	0.07	0.21
KDC-8	1.85	56.01	22.68	1.17	9.52	1.26	0.05	0.73	3.25	0.09	0.15
KDC-7	1.75	55.36	22.86	1.16	9.69	1.50	0.20	0.79	3.35	0.14	0.17
KDC-5	1.65	53.30	24.41	1.25	8.94	1.24	0.04	0.43	4.43	0.04	0.15
				Outer Hornfels Zone§							
KDC-61	1.00	56.41	23.01	1.18	9.61	1.83	0.38	0.42	2.74	0.11	0.20
KDC-62	0.93	55.35	23.22	1.17	9.37	1.95	0.50	0.76	3.25	0.11	0.21
KDC-65	0.85	56.28	23.18	1.15	9.72	1.78	0.70	0.61	3.27	0.11	0.25
KDC-66	0.84	55.88	22.94	1.13	9.85	1.82	0.73	0.65	3.26	0.07	0.28
KDC-70	0.68	53.61	24.98	1.15	10.13	1.85	0.45	0.64	2.90	0.46	0.17
KDC-72	0.63	54.37	25.45	1.11	8.30	1.34	0.21	0.17	3.36	0.12	0.18
KDC-73	0.61	54.13	23.68	1.17	9.29	1.86	0.34	0.73	3.76	0.16	0.19
				Inner Hornfels Zone§							
KDC-75	0.55	55.73	23.55	1.22	9.52	1.71	0.34	0.85	3.65	0.32	0.13
KDC-76	0.53	56.98	20.20	1.08	10.28	2.05	0.69	0.87	3.39	0.25	0.22
KDC-77	0.48	62.38	18.37	1.00	8.22	1.93	0.58	0.64	3.18	0.19	0.25
KDC-80	0.38	57.63	21.32	1.16	7.07	1.86	0.55	1.03	4.46	0.11	0.20
KDC-81	0.25	55.77	23.58	1.19	7.15	1.80	0.33	0.93	4.64	0.09	0.22
KDC-82	0.13	61.04	20.90	1.05	7.11	1.59	0.64	1.17	3.60	0.17	0.15
	core depth‖			**Variably Greisenized Granite Samples**							
1715	95.4	72.36	12.86	0.22	0.85	0.86	1.83	0.37	6.17	0.09	0.09
1717	181	68.40	14.19	0.41	2.31	0.93	2.47	2.86	4.47	0.11	0.12
1718	280.3	68.10	13.79	0.39	1.77	1.02	3.01	2.45	4.62	0.14	0.14

* Distance (in kilometers) along the X-Y traverse shown on Figure 1b.
† Whole-rock major element data were obtained by X-ray fluorescence techniques.
‡ Equivalent to Eastwood et al.'s (1968) Intermediate and Outer Zones (see Fig. 2).
§ The Outer and Inner Hornfels Zones of Cooper and Bradley (1990) are equivalent to the Inner Zone of Eastwood et al. (1968; Fig. 2).
‖ Depth in core (in meters), the location for which is indicated on Figure 1b.

to the metal-rich, vein-style mineral deposits in the Lake District (Cooper et al. 1988; cf., Lowry et al. 1991; Plant 1986; Plant et al. 1990).

ANALYTICAL TECHNIQUES

The analytical techniques employed in this study involved sealed-tube combustions and conventional, dual-inlet, viscous-flow mass spectrometry (modified only slightly after Bebout and Fogel 1992; Bebout 1997). Some of the samples were analyzed on a modified double-focusing, double-collector, double-inlet DuPont 491 mass spectrometer at the Geophysical Laboratory (Carnegie Institution of Washington); the majority of the samples were analyzed on the Finnigan MAT 252 at Lehigh University. Analytical precision (1σ) for silicate samples is typically ~0.1‰ (generally ≤ 0.1‰ for n ≥ 3). For 35 analyses of a whole-rock metasedimentary sample (WS-1), including 20 analyses at Lehigh University, mean $\delta^{15}N = +3.0$, $1\sigma = 0.09$‰ (value of +2.9, with a 1σ of 0.1‰, obtained by K. Brauer and D. K. Haendel for the same sample, using dissolution and distillation techniques; see Haendel et al. 1986 for description of the techniques employed by this other laboratory); for 25 analyses of a buddingtonite sample (NH_4^+-rich feldspar; sample ID no. 117751-6 from the Smithsonian Institution) in the two laboratories, mean $\delta^{15}N = -1.2$, $1\sigma = 0.08$‰. Fifteen analyses of a fuchsite mineral separate sample (WE-2) at Lehigh University yielded a mean $\delta^{15}N$ value of +2.0 ($1\sigma = 0.07$‰; see other data for phengitic (some Cr-rich) white micas from low-grade metamorphic rocks in Bebout 1997). Nitrogen concentrations were estimated from the ion beam intensity of N_2 observed for a calibrated volume of the mass spectrometer inlet. Concentrations and isotopic compositions of the reduced C in the whole-rock metasedimentary samples were analyzed by standard sealed-tube heating techniques and CO_2 from the minor calcite in the greisen samples was extracted using the conventional phosphoric acid dissolution techniques of McCrea (1950).

Variations in the isotopic composition of N in samples (spl) relative to the standard (std) are reported as:

$$\delta^{15}N = \left[\frac{\left({}^{15}N/{}^{14}N\right)_{spl} - \left({}^{15}N/{}^{14}N\right)_{std}}{\left({}^{15}N/{}^{14}N\right)_{std}}\right] \times 10^3$$

where the standard is atmospheric N_2.

Two studies (Richet et al. 1977; Hanschmann 1981) have published calculated N-isotope fractionation factors based on spectroscopic data; experimental data of mineral-fluid fractionations are conspicuously absent. Of the two theoretical studies, only Hanschmann (1981) calculated fractionations involving NH_4^+ in solid phases.

For the metasedimentary rocks in the aureole, major elements and trace elements other than B were obtained by X-ray fluorescence (XRF) spectrometry using the Phillips PW 1400 instrument at the Nottingham University Geology Department (analysts, P.K. Harvey and B.P. Atkin). Major element analyses in that laboratory were conducted on glass beads, whereas the trace elements other than B were obtained on pressed powder pellets with elvacite binder. Boron data for the aureole rocks were obtained using the inductively coupled plasma emission spectrometer (ICP) at the British Geological Survey Grays Inn Road Laboratory (analysts, L. Ault and D. Bradley). Major element analyses of the variably altered granites were obtained by XRF spectrometry on glass beads, using the Phillips PW 2400 at the British Geological Survey Keyworth Laboratory (analysts, A. Robertson and M. Ingham).

RESULTS

Extractions of N from the aureole rocks using the sealed-tube heating techniques yield concentrations similar to slightly higher than those obtained using the distillation-specific ion

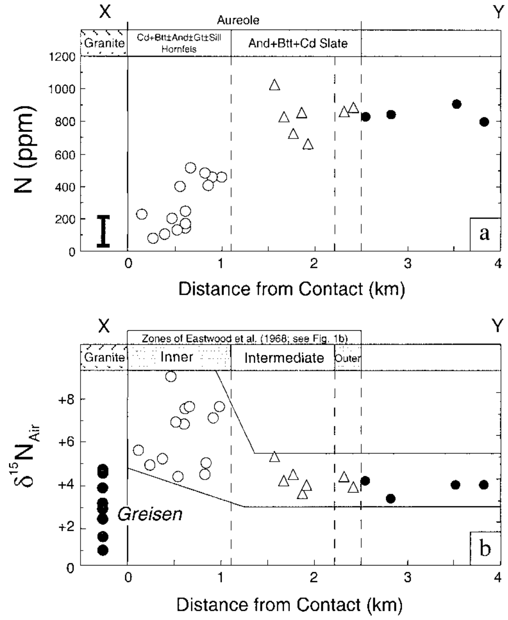


FIGURE 2. Variation in N concentration (**a**) and $\delta^{15}N$ (**b**) in the Skiddaw contact metamorphic aureole as a function of distance across the aureole (traverse on Fig. 1b). Also shown are the range in N concentration and the $\delta^{15}N$ values of samples of greisenized granite.

TABLE 2. Nitrogen and C and other trace element data for Skiddaw aureole (using the zones of Cooper and Bradley, 1990)

Sample	Distance* (km)	N† (ppm)	$\delta^{15}N_{air}$	$C_{reduced}$‡ (wt.%)	$\delta^{13}C_{PDB}$‡ (cm)	B§ (ppm)	Rb (ppm)	Ba (ppm)	Sr (ppm)
				Outer Mudstones and Siltstones					
KDC-50	3.85	803	3.7	0.40	-29.7	76	151	650	113
KDC-45	3.55	908	3.7	0.39	-28.1	85	147	607	100
KDC-30	2.85	848	3.1	0.38	-28.5	119	160	925	152
KDC-26	2.55	837	3.9	0.36	-29.4	89	146	673	124
				Andalusite + Biotite ± Cordierite Slates‖					
KDC-23	2.45	893	3.6	0.41	-29.7	94	157	691	135
KDC-19	2.40	863	4.1	0.40	-29.7	94	155	642	83
KDC-13	2.00	667	3.7	0.44	-29.1	76	150	695	70
KDC-12	1.95	859	3.3	0.37	-30.3	163	151	643	131
KDC-8	1.85	730	4.2	0.42	-29.0	104	155	750	77
KDC-7	1.75	831	3.9	0.23	-28.5	110	165	737	108
KDC-5	1.65	1039	5.0	0.56	-30.2	133	201	810	70
				Outer Hornfels Zone#					
KDC-61	1.00	466	7.3	0.25	-29.7	68	146	809	89
KDC-62	0.93	462	6.8	0.33	-28.3	88	150	784	136
KDC-65	0.85	425	4.7	0.23	-28.0	59	158	734	139
KDC-66	0.84	493	4.2	0.21	-27.0	62	161	712	152
KDC-70	0.68	528	7.3	0.42	-28.7	68	159	707	134
KDC-72	0.63	147	7.2	0.36	-26.8	62	192		61
KDC-73	0.61	150	6.5	0.08	-26.7	186	218	705	90
				Inner Hornfels Zone#					
KDC-75	0.55	409	4.1	0.09	-26.4	107	155	707	152
KDC-76	0.53	141	6.6	0.12	-25.1	103	186	641	173
KDC-77	0.48	206	8.7	0.11	-25.4	76	170	594	127
KDC-80	0.38	113	4.9	0.12	-25.2	54	185	814	135
KDC-81	0.25	85	4.6	0.23	-24.9	70	196	837	128
KDC-82	0.13	237	5.3	0.31	-27.1	128	149	768	156

* Distance along the X-Y traverse shown on Fig. 1b.

† Whole-rock N concentrations with ≤ 5% uncertainty.

‡ Concentration and C-isotope data for carbonaceous matter.

§ B data obtained using ICP methods (see Cooper et al. 1988).

‖ Equivalent to Eastwood et al.'s (1968) Intermediate and Outer Zones (see Fig. 2).

The Outer and Inner Hornfels Zones of Cooper and Bradley (1990) are equivalent to the Inner Zone of Eastwood et al. (1968; see Fig. 2).

electrode technique of Cooper and Bradley (1990)—the new concentration data are, on the average, ~6% higher than those of the earlier study. The whole-rock N concentration data demonstrate dramatic reductions in N content nearer to the granitic body (Fig. 2a; Table 2). The rocks far from the contact (>1.5 km) have relatively uniform $\delta^{15}N_{air}$ (mean $\delta^{15}N = +3.72$; $1\sigma = 0.34$; $n = 10$) and N concentrations (mean $N = 824$ ppm; $1\sigma = 74$; $n = 10$) similar to those of many seafloor sediments (cf., Rau et al. 1987; Williams et al. 1995). Figures 2b and 3 demonstrate increases in the $\delta^{15}N$ of the wall rocks toward the contact, which accompany the decreases in N content. The $\delta^{13}C$ of the reduced C (metamorphosed organic matter) in the wall rocks also shows a shift toward higher values (from ~–29‰ to values of ~–26‰ near the contact; see Table 2), with most of this shift occurring in the inner hornfels zone (see data indicated on Fig. 4). This C-isotopic shift is accompanied by a decrease in the concentration of reduced C in the metasedimentary aureole samples, from ~0.4 wt% far from the contact to as low as 0.09 wt% adjacent to the contact with the granite (Table 2, Fig. 4).

Assessment of whether or not whole-rock metasedimentary samples are changed in their major element compositions during prograde metamorphism and devolatilization (cf., Ague 1994, 1997) is in many metamorphic suites complicated by the large degree of variability in composition related to protolith lithology (see discussion by Bebout et al. 1999; cf., Ague 1994, 1997; Moss et al. 1995, 1996; Roser and Nathan 1997). However, in contrast with the Catalina Schist (cf., Bebout and Fogel 1992; Bebout et al. 1999) and other metamorphic suites showing large degrees of chemical variability related to protoliths, the Skiddaw aureole metasedimentary rocks are relatively uniform in their major-element chemistry across the aureole (see major-element concentration data in Table 1, Fig. 5a, and statistical data in Table 3). Lacking in the metasedimentary rocks in the aureole are convincing trends, with decreasing distance from the igneous contact, of decreasing SiO_2/TiO_2 or SiO_2/Al_2O_3 (or ratios of other major oxides to TiO_2 and Al_2O_3; see Fig. 5a; Table 3) reported for other metasedimentary suites and interpreted as evidence for significant loss of mass during prograde metamorphism (cf., Ague 1994, 1997). Some of the variability in major element compositions (sample KDC-77, with somewhat higher SiO_2/Al_2O_3) within 0.5 km of the contact with the granite is related to the occurrence of a sandy sedimentary horizon (see Fig. 5a). There is some indication that SiO_2, Na_2O, and K_2O concentrations are somewhat higher in the innermost parts of the aureole (see SiO_2/Al_2O_3, Na_2O/Al_2O_3, and K_2O/Al_2O_3 data in Fig. 5a; statistical data in Table 3). Ratios of N, Rb, Ba, and

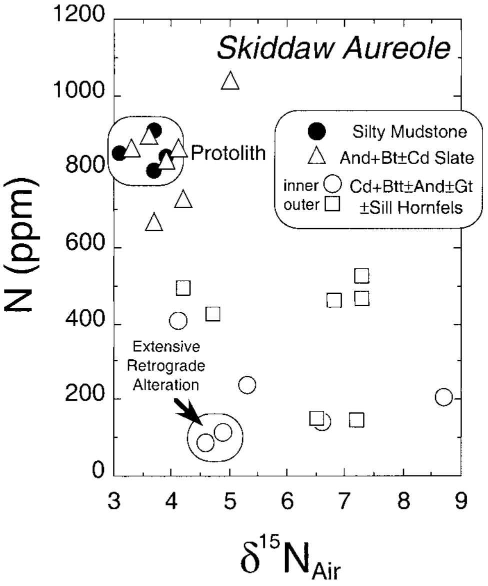


FIGURE 3. Plot of N concentration vs. $\delta^{15}N$ for wall-rocks in the Skiddaw contact metamorphic aureole (data in Table 2). In this figure, samples of the hornfels zone within ~1 km of the contact with the intrusive body are subdivided into the "outer hornfels zone" (squares; cordierite + biotite + andalusite) and the "inner hornfels zone" (circles; cordierite + biotite ± andalusite ± garnet ± sillimanite; cf., Cooper and Bradley 1990). Some of the high-grade wall rock samples with lower $\delta^{15}N$ similar to greisen (e.g., KDC-80, 81; circled) show extensive retrograde replacement of cordierite, andalusite, and biotite by fine-grained white mica, which led Eastwood et al. (1968) to suggest that these rocks experienced white mica alteration similar to that experienced by the cooling granite (i.e., greisenization).

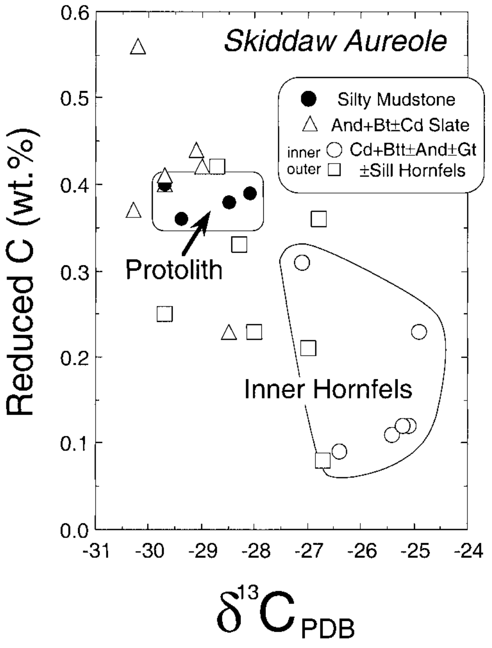
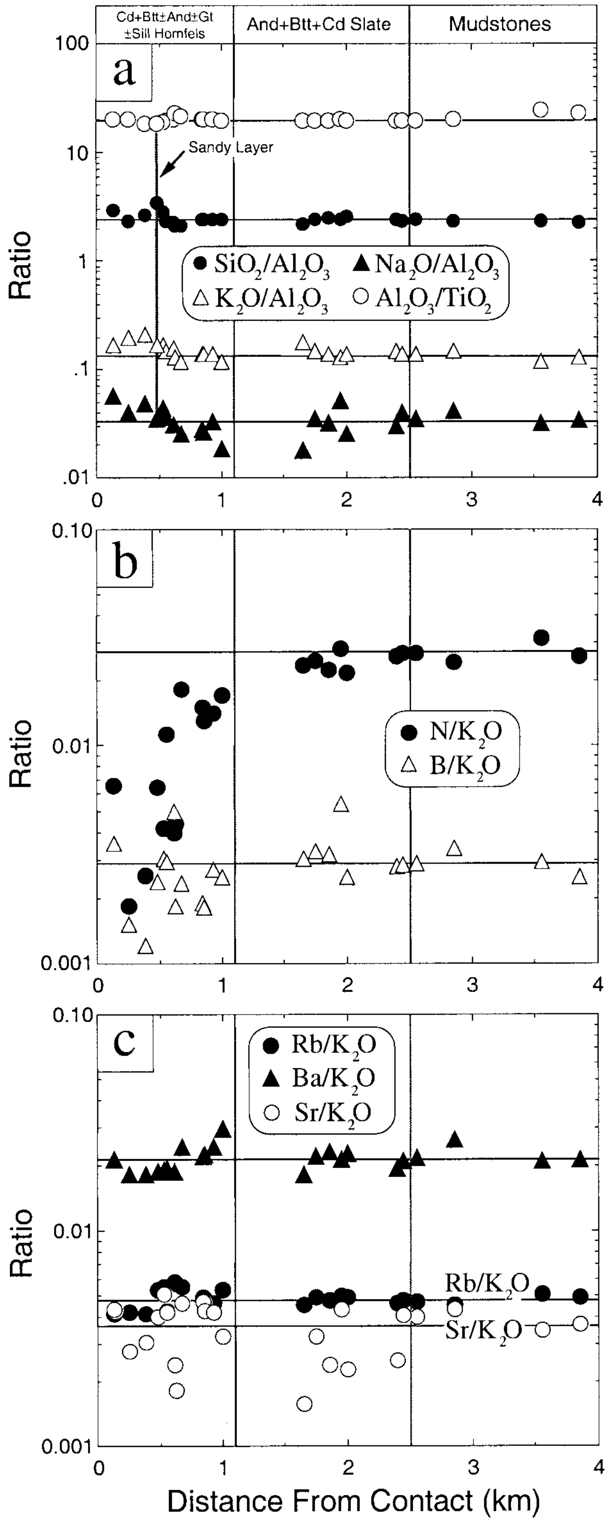


FIGURE 4. Plot of reduced C concentration vs. $\delta^{13}C_{PDB}$ for wall-rocks in the Skiddaw contact metamorphic aureole (data in Table 2). As in Figure 3, samples of the hornfels zone within ~1 km of the contact with the intrusive body are subdivided into the "outer hornfels zone" (cordierite + biotite + andalusite) and the "inner hornfels zone" (cordierite + biotite ± andalusite ± garnet ± sillimanite; cf., Cooper and Bradley 1990).

B (all trace elements that are likely to be concentrated strongly in the micas in these rocks; cf., Bebout et al. 1999) to K_2O (Figs. 5b and c) reflect the concentrations of these trace elements in the micas, the only K_2O-rich phases present in these rocks. The ratio N/K_2O (possibly also B/K_2O) decreases in the higher-grade metamorphosed rocks nearer the igneous contact (whole-rock N losses demonstrated in Fig. 2a), reflecting the lower N (and B) contents of the micas (varying modal proportions of white mica and biotite) near the granite. In contrast, Rb/K_2O, Ba/K_2O, and Sr/K_2O remain relatively constant across the aureole (Fig. 5c), presumably reflecting the relatively constant Rb, Ba, and Sr concentrations of the bulk mica component of these rocks across the aureole. Strontium may be more widely distributed among multiple mineral phases, likely occurring in the minor carbonate in the lower grade rocks and in other calcic phases across the aureole (e.g., apatite, minor clinozoisite, garnet).

In the Skiddaw Granite, the white mica is secondary (as judged petrographically), replacing biotite/chlorite and the feldspars (Cooper and Bradley 1990). Webb and Brown (1984) reported that hydrothermal alteration of the granites also resulted in additions of K, Rb, Ca, Mg, S, As, and carbonate, and losses of Na, Sr, Ba, Fe, Zn, and Pb. Nitrogen concentration in these rocks is correlated with petrographically observed degrees of replacement of feldspars by fine-grained white mica (Cooper and Bradley 1990), with whole-rock samples and separates of variably altered feldspar (showing replacement by fine-grained white mica) together showing a range in N concentration of 17-225 ppm. Greisen samples from the borehole have $\delta^{15}N$ values of +1.0 to +4.8‰ which vary independently of N concentration and depth in the core (Table 4). The $\delta^{13}C_{PDB}$ value of the minor calcite (<2 wt%) in greisenized samples (finely disseminated and in microveinlets) ranges from –11.7 to –6.4‰ (see Table 4).



◀ **FIGURE 5.** Major- and trace-element compositions (all on weight basis) across the traverse of the Skiddaw aureole. (**a**) Ratios of SiO_2, K_2O, and Na_2O to Al_2O_3 and TiO_2, demonstrating lack of obvious change as a function of metamorphic grade (proximity to granitic intrusion). CaO, MnO, and P_2O_5 contents similarly show no obvious evidence of change near the intrusive body. (**b**) Demonstration of decrease in N/K_2O (and possibly also B/K_2O) nearer the granitic intrusion. (**c**) Ratios of Rb, Ba, and Sr to K_2O, demonstrating lack of depletion of these trace elements in the higher-grade metasedimentary rocks adjacent to the contact with the granite. Rubidium and Ba are expected to reside predominantly in the micas, whereas Sr may be somewhat more distributed and also present in other calcic phases in these rocks (e.g., minor carbonate, apatite, clinozoisite, and garnet). In (**a**) and (**c**), horizontal lines are calculated median values (for all samples in the traverse) included to demonstrate the lack of (or only minimal) chemical change across the aureole. Horizontal lines on (**b**) indicate mean values for the data for low-grade rocks far from the contact (see Table 3), and emphasize the change in concentrations of N (and possibly also B) nearer the contact. The N, B, Rb, and Ba behavior in the metasedimentary rocks in the contact aureole are believed to reflect the differing fluid-mica partitioning for these elements during metamorphic devolatilization (see ion microprobe trace-element data and discussions in Bebout et al. 1999). Note that the lower sampling density in the distal part of the traverse (i.e., in the mudstones > 2.5 km from the contact with the granite) complicates these comparisons of chemical compositions across the aureole.

TABLE 3. Statistical data: major and trace element compositions of the Skiddaw aureole*

Ratio (by weight)	Outer Mudstones (n = 4)	Andalusite + Biotite ± Cordierite Slates (n = 7)	Outer Hornfels Zone (n = 7)	Inner Hornfels Zone (n = 5 or 6)†
SiO_2/Al_2O_3	2.34 (0.08) mean (1σ)	2.40 (0.13)	2.33 (0.13)	2.76 (0.39) 2.64 (0.26)†
Al_2O_3/TiO_2	21.64 (2.19)	19.65 (0.23)	20.67 (1.21)	19.08 (0.69) 19.22 (0.67)
K_2O/Al_2O_3	0.134 (.011)	0.147 (0.016)	0.136 (0.015)	0.179 (0.020) 0.180 (0.022)
Na_2O/Al_2O_3	0.035 (0.004)	0.033 (0.011)	0.024 (0.009)	0.043 (0.008) 0.044 (0.008)
N/K_2O	0.027 (0.003)	0.025 (0.002)	0.012 (0.006)	0.005 (0.003) 0.005 (0.004)
B/K_2O	0.0029 (0.0004)	0.0033 (0.0010)	0.0026 (0.0011)	0.0024 (0.0010) 0.0024 (0.0010)
Rb/K_2O	0.0048 (0.0002)	0.0048 (0.0002)	0.0052 (0.0005)	0.0046 (0.0006) 0.0044 (0.0006)
Ba/K_2O	0.023 (0.003)	0.021 (0.002)	0.024 (0.004)	0.019 (0.001) 0.017 (0.005)
Sr/K_2O	0.0039 (0.0004)	0.0029 (0.0010)	0.0034 (0.0011)	0.0039 (0.0009) 0.0039 (0.0010)

* Data are mean and, in parentheses, one standard deviation.
† Lower numbers in this column, for each ratio, are for data excluding those for the metasandstone, sample KDC-77.

DISCUSSION

The relative uniformity in lithology and whole-rock major element compositions of the aureole rocks (e.g., K_2O = 3.34 ± 0.3 wt%; Tables 1 and 3; Fig. 5a), and the uniformity in N content and $\delta^{15}N$ of the rocks outside the aureole (the protoliths; Table 2; Fig. 2), simplify the identification and interpretation of the effects of contact metamorphism. Loss of N in the Skiddaw aureole is believed to reflect the speciation of N initially bound in low-grade white micas as N_2 in H_2O-rich metamorphic fluids during continuous metamorphic reactions of the following general types (cf. Pattison and Tracy 1991):

muscovite + chlorite + quartz = cordierite + biotite + H_2O

muscovite + chlorite = andalusite + biotite + quartz + H_2O

muscovite + chlorite + quartz = andalusite + cordierite + biotite + H_2O.

Because phases capable of hosting significant NH_4^+ other than the micas (e.g., potassium feldspar), are absent in these rocks (cf., Honma and Itihara 1981), and because the wall rocks are relatively constant in their K_2O contents and the combined modal abundance of the two micas (white mica and biotite) remains relatively constant, it is inferred that the whole-rock N losses and reductions in N/K_2O (at relatively constant whole-rock K_2O content) reflect a decrease in the concentrations of N in the micas toward the contact with the pluton (Fig. 5b). However, varying modal abundances of the two micas, which differentially partition NH_4^+ (white mica generally contains ~0.4× the NH_4^+ of coexisting biotite; Honma and Itihara 1981; Sadofsky and Bebout 1997; Boyd and Philippot 1998) also impact the bulk-rock N distribution. Recent N isotope analyses by S.J. Sadofsky and G.E. Bebout (manuscript in preparation) of coexisting white mica and biotite in coarse-grained metapelitic rocks in south-central Vermont and western Maine (U.S.A.) demonstrate the absence of significant systematic variations in $\delta^{15}N$ between the two phases (also see Zhang 1988; Boyd and Philippot 1998). Changes in the relative modal abundances of these minerals during prograde devolatilization reactions (cf., Chamberlain et al. 1990) are thus unlikely to impact N-isotope fractionation between the bulk rocks and the fluids ($\Delta^{15}N_{rock-fluid}$) during prograde metamorphism and related N loss. The coupled losses of N and shifts in $\delta^{15}N$ are interpreted to reflect the release of N with relatively low $\delta^{15}N$ during contact metamorphism. The overall inferred degrees of N loss and shift in $\delta^{15}N$ (Fig. 3) are similar in magnitude to those for the Catalina Schist subduction-zone metasedimentary rocks (for the Skiddaw Slates, ~3.5‰ shift in $\delta^{15}N$; up to ~75% loss of N; cf., Bebout and Fogel 1992), and potentially reflect a similar Rayleigh distillation-like devolatilization process involving NH_4^+ in the micas and N_2 as the dominant N fluid species (Fig. 6a). Ratios of N, B, Rb, and Ba (all trace elements that are strongly concentrated in the micas in these rocks) to K_2O in whole-rocks (Figs. 5b and 5c) demonstrate the preferential loss of N (and possibly B) relative to the other trace elements (Rb and Ba) during the prograde continuous metamorphic reactions (above) that resulted in changing mica major-element chemistry and modal relative proportions of white mica and biotite.

TABLE 4. Nitrogen and C isotope data for altered granite (core depths in meters)

Sample†	$\delta^{15}N_{air}$	N* (ppm)	$\delta^{13}C_{PDB}$ calcite‡
1718 (280.3)	1.0	225	–7.8
SAG 278.6	4.7	46	–7.1
SAG 196.73	3.3	17	–11.7
1717 (181)	1.6	58	—
SAG 178.7	4.8	73	–6.7
SAG 96.25	3.1	24	–11.1
SAG 96.8	4.0	36	–11.6
1715 (95.4)	2.8	95	–6.4

* N concentrations with ≤5% uncertainty.
† Whole-rock samples in bold type; all others are feldspar/mica aggregate separates.
‡ Finely disseminated calcite in whole-rock samples.

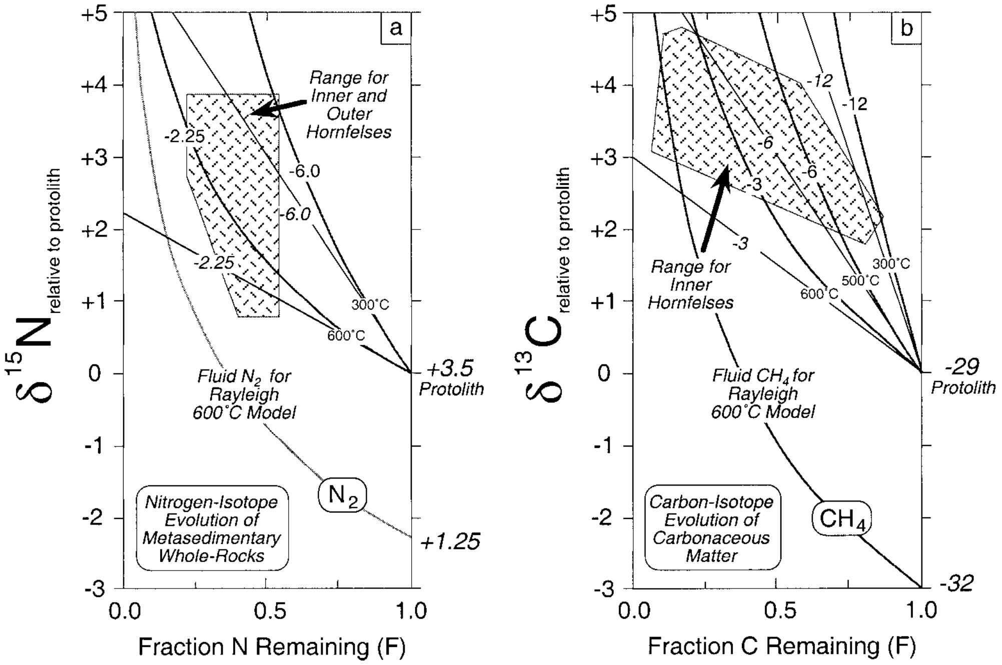


FIGURE 6. Demonstration of the Rayleigh distillation and batch devolatilization models as applied to the N and $\delta^{15}N$ shifts (**a**) and C and $\delta^{13}C$ shifts (**b**) in the Skiddaw aureole (shaded regions are ranges for hornfelses relative to low-grade protoliths). Rayleigh distillation is calculated as δ_{final}-$\delta_{initial}$ = $1000(F^{(\alpha-1)}-1)$ and batch volatilization is calculated as $\delta_{final} = \delta_{initial} - (1-F)1000\ln\alpha$, where α is the fractionation factor for the fluid-mineral combination being considered, F is the fraction of the initial amount of the element under consideration remaining in the rock, and δ_{final} and $\delta_{initial}$ refer to the final and initial isotopic compositions of the rock (see discussions by Valley 1986; Nabelek 1991). The lines (labelled with the appropriate $\Delta^{15}N$ or $\Delta^{13}C$ for fluid-mineral equilibration) indicate calculations for 600 and 300 °C, respectively, and the regions between these lines represent rock shifts due to Rayleigh distillation (curves with italicized labels) and batch volatilization (straight lines with non-italicized labels) at intermediate temperatures. On (**b**), lines labeled with "-6" indicate rock evolution corresponding to devolatilization at 500 °C. On (**a**), the line labeled, "N_2", indicates the evolution in fluid N_2 $\delta^{15}N$ during Rayleigh distillation at 600 °C (similarly done for CH_4 in b); a similar process at the other temperatures would produce differing ranges in fluid $\delta^{15}N$ related to differing fluid-mica fractionation factors (fractionation data from Hanschmann 1981, and Bottinga 1969).

Rayleigh distillation calculations such as those demonstrated in Figure 6 assume that stable isotopic equilibrium is maintained between the fluid phase and the remaining mineral phases during incremental loss of fluid—the mechanisms affording this continual reequilibration presumably involve diffusive exchange and dissolution-reprecipitation during grain coarsening (see detailed discussion of the applications of Rayleigh and batch-loss models by Bebout and Fogel 1992; also see Valley 1986; Nabelek 1991). In the Skiddaw Aureole, continuous metamorphic reactions like those that stabilized cordierite and andalusite and that resulted in changed compositions and modal proportions of white mica and biotite, could have afforded continual reequilibration of fluid and rock stable isotope composition during progressive devolatilization. Interestingly, the evidence for B loss in the Skiddaw Aureole contact metamorphosed sedimentary rocks is not as convincing as the evidence for N loss in the same rocks (see Fig. 5b). In the Catalina Schist, reductions in B concentration with increasing metamorphic grade correlate closely with N losses in the same rocks (see Fig. 7 in Bebout and Fogel 1992) and Moran et al. (1992) demonstrated losses of B with increasing metamorphic grade in metamorphic suites that experienced a wide range of prograde *P-T* histories (i.e., resulting from subduction-zone-related, contact-related, and Barrovian-style metamorphism).

Regarding B and N behavior in the inner aureole, it is noteworthy that some samples collected from within ~0.6 km of the contact with the intrusive body show significant replacement of prograde phases (particularly cordierite, andalusite, and biotite) by fine-grained white mica and chlorite. This tendency led Roberts (1983) and Eastwood et al. (1968) to infer additions of fluids from the granite to the immediately surrounding hornfels during greisenization of the intrusive body. The several hornfels samples nearest the intrusive contact have SiO_2/Al_2O_3, K_2O/Al_2O_3, and Na_2O/Al_2O_3 somewhat higher than the median ratios in the aureole (see Fig. 5a), perhaps consistent with some Si-Na-K enrichment during late-stage hydrothermal processes. We suggest that the reductions in $\delta^{15}N$ (approaching or overlapping with values for the greisens themselves) and some localized enrichments in B in the hornfels directly adjacent to the granite body (Figs. 2b, 3, 5b), could have resulted from this fluid addition during part of the late-stage cooling of the granite-aureole system. Outer hornfels zone samples (collected at 0.63–1.00 km from the contact with the granite) are, on the average, lower in B concentration (with mean B ≅ 67

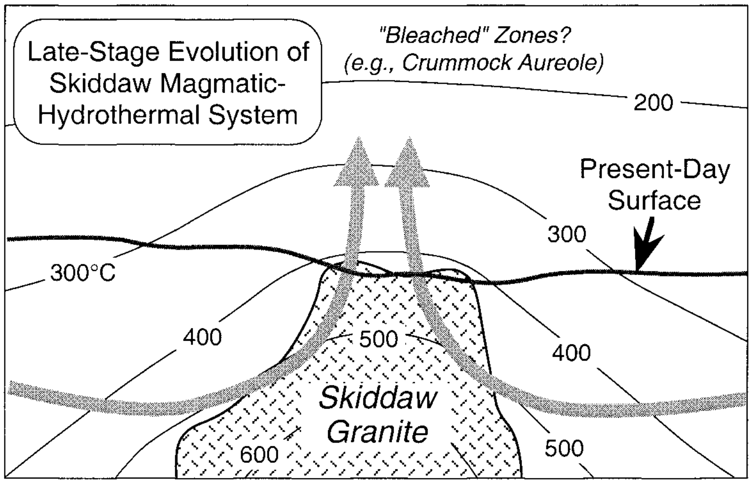


FIGURE 7. Possible model of the thermal and fluid regimes during late-stage cooling of the Skiddaw granite and aureole. Isotherms are schematic and patterned loosely after the calculations of Hanson (1995). Large arrows indicate convective transport of aureole-derived fluid toward the cooling granite. Also shown is the location, above the Skiddaw Granite, of a bleached zone analogous to the Crummock Water aureole (see line indicating present erosional surface). Moseley (1979; cf., Pattison and Tracy 1991) estimated that the present level of exposure of the Skiddaw aureole reflects a depth range at the time of magma emplacement corresponding to 2–3 kilobars. The shape and size of the intrusion are those of Lee (1986) based on a gravity survey of the region (also see Furlong et al. 1991). Because the shapes of the contact metamorphic zones (see Fig. 1b) agree with the relatively narrow zones predicted by a 3-dimensional heat conduction model, Furlong et al. (1991) concluded that the hydrothermal flow in the aureole did not significantly influence the formation of isograds in the Skiddaw Aureole.

ppm) than the lower-grade equivalents farther from the intrusive body (away from the effects of the B addition during greisenization; mean B ~104 ppm, combining the data in Table 2 for the "Outer Mudstones and Siltstones" and "Andalusite + Biotite ± Cordierite Slates"), conceivably reflecting some loss of B to metamorphic fluids during the devolatilization (see Fig. 5b). Detailed study of B contents in individual mineral phases will be necessary to understand better the behavior of B in the Skiddaw Aureole. Likewise, the potential isotopic impact of N_2 in the channels of cordierite (cf., Scalan 1958; Winslow et al. 1991) in the Skiddaw aureole warrants examination.

For the batch loss and Rayleigh distillation N-isotope models in Fig 6a, the combined range in N_2 $\delta^{15}N$ released over the temperature range of 300–600 °C is ~–2.9 to +5.1‰, using the calculated NH_4+–N_2 fractionation factors of Hanschmann (1981). Equilibration of the N_2 released from the aureole (i.e., N_2 with $\delta^{15}N$ of ~–2.9 to +5.1‰) with greisen white micas at temperatures of 350–450 °C would have yielded a range in greisen white mica $\delta^{15}N$ of ~–0.6 to +8.5‰, a range that includes the observed range for the greisen samples (+1.0 to +4.8‰; Table 4; Fig. 2b; cf., temperatures of 250–450 °C for all mineralization at Carrock Fell inferred by Shepherd et al. 1976). The shift in $\delta^{13}C$ of carbonaceous matter toward higher values with progressive devolatilization in the aureole is consistent with the release of C having low $\delta^{13}C$ into fluids (as CH_4, plausibly the dominant C fluid species during devolatilization of these graphite-bearing rocks; cf., Ohmoto and Kerrick 1977; Connolly and Cesare 1993), by a process approximating Rayleigh distillation during devolatilization reactions (Fig. 6b; Table 2). The $\delta^{13}C$ of the greisen calcite (~–12 to –6‰; Table 4) is compatible with equilibration with CH_4 previously equilibrated with the wall-rock carbonaceous matter (calculated CH_4 $\delta^{13}C$ range of ~–42 to –28‰, based on fractionation factors of Bottinga 1969), using the same temperature range for devolatilization in the aureole (300–600 °C) but assuming a temperature range of 250–300 °C for the calcite-CH_4 equilibration (yielding calcite $\delta^{13}C$ of ~–19 to –0.4‰). Interestingly, the inferred somewhat lower-T equilibration of the fluids with the calcite (relative to N-isotope fluid-mica equilibration at ≥350 °C) is consistent with textural evidence for calcite alteration at stages later than that which precipitated white mica during cooling of the intrusion (Ball et al. 1985).

We suggest that, during cooling of the intrusion and surrounding aureole, convective flow of fluid, perhaps in part up-temperature, could have resulted in significant transfer of N (and C) from the aureole into the cooling, altering granite (Fig. 7; see the recent modeling by Hanson 1995). This fluid-flow scenario would require that, although mixed to varying degrees with surficial waters (and possibly also magmatic fluids), the N_2-bearing fluids released in the aureole during an earlier stage dominated by fluid production (with fluid pressures closer to lithostatic) were mobilized into the cooling intrusive body during the later-stage fluid regime in which fluid pressures were closer to hydrostatic and fluid flow was dominantly fracture-controlled (see Hanson 1995). Shepherd et al. (1976), using fluid inclusion and O isotopic compositions of granite, greisen, and veins, concluded that the Carrock Fell W deposits (Fig. 1b) resulted from interaction of the granite and relatively low-$\delta^{18}O$ ($\delta^{18}O_{SMOW}$ near +3.85‰), aureole-derived "formation waters" possibly with a significant meteoric component. Based on S-isotope analyses of sulfide in altered granite and wall-rocks, Lowry et al. (1991) suggested that the altered granites incorporated both magmatic S and S in fluids that had circulated through and exchanged with the surrounding Skiddaw Group. In a study of N-isotope behavior during formation of the Eastern Erzgebirge Sn ore deposits (Germany), Junge et al. (1989) similarly invoked increasing components of low-δ^{15}N, aureole-derived metamorphic fluid during late-stage hydrothermal alteration of granitoids leading to the formation of extensive greisen with low δ^{15}N (average δ^{15}N for 17 greisen samples is –2‰). Beyond implying the addition to the granite, at relatively low temperatures, of a N_2-bearing fluid with δ^{15}N similar to that calculated for the aureole-derived fluids, the N isotopic data presented here are not alone a sufficient constraint on the likely complex hydrodynamics of the Skiddaw intrusive episode (see Fig. 13 in Hanson 1995 for depiction of transient heat flow, mechanical, and fluid flow dynamics in a contact metamorphic system). We believe that, based on the N, O, and S isotope data for this system (Shepherd et al. 1976; Lowry et al. 1991; this study) and the previously published models of the hydrodynamics of such systems (e.g., Hanson 1995), it is likely that the fluids that interacted with the Skiddaw Granite during its late-stage cooling (250–450 °C) contained components of fluid generated in the aureole by devolatilization, but also surficial waters modified chemically and isotopically by exchange over a range of temperatures with the extensive mudrock-dominated sequence surrounding the intrusion.

As illustrated in Figure 7, the Crummock Water aureole conceivably could represent the effect of the upward flow of fluid at the top of the hydrothermal system resulting from the emplacement of another, contemporaneous granitic body in the region (also see conceptual model in Fig. 17 in Cooper et al. 1988). A N-isotope study of the Crummock Water Aureole has not yet been conducted. However, it is likely that the process producing this regional-scale “bleached zone” (see Fig. 1a) was similar to that invoked by Krohn et al. (1993) to produce ammonium-rich alteration haloes above buried geothermal sources in the western U.S.

CONCLUDING REMARKS

Several recent studies have proposed the transfer of N from country rocks into evolving, hydrothermally altering granitic intrusives, based on analyses of N concentrations or N-isotopic composition in variably altered granitic rocks (e.g., Junge et al. 1989; Hall et al. 1991), or based on trends of decreasing N content in wall rocks near contacts with granites (e.g., Wilkinson 1991). Nitrogen isotope data for the Skiddaw aureole and altered granite, together with C-isotope data for the same rocks, strongly support a previously proposed model of aureole-to-intrusive transfer of volatiles proposed by Shepherd et al. (1976), Plant (1986), Cooper and Bradley (1990), and Lowry et al. (1991). The results of this study complement previous work indicating the utility of N concentrations and isotopic compositions for tracing hydrothermal alteration producing economically significant Sn-W deposits (Junge et al. 1989; Wilkinson 1991), and Hg and disseminated Au deposits (Krohn et al. 1993).

The direction and magnitude of the N-isotope shift accompanying N losses in the Skiddaw aureole are consistent with the speciation of N as N_2 in the metamorphic fluids, as predicted by recent theoretical considerations of N speciation in metamorphosing, graphite-bearing metasedimentary rocks (cf., Moine et al. 1994). The N loss accompanied metamorphic devolatilization reactions largely involving the destabilization of chlorite and changes in the relative abundances and compositions of white mica and biotite, and resulting in the production of H_2O-rich C-O-H-S-N fluids. Metamorphic devolatilization should be regarded as a significant geochemical pathway affecting the overall abundance and isotopic composition of N in the deep crust and mantle (Boyd et al. 1993; Bebout 1995; Bebout et al. 1999). This and other recent studies (Haendel et al. 1986; Zhang 1988; Junge et al. 1989; Bebout and Fogel 1992; Krohn et al. 1993; Boyd et al. 1993; Mattey et al. 1994; Bebout 1997; Boyd and Philippot 1998) have demonstrated that the relatively underused N isotope system may yield valuable, unique constraints on the nature of fluid-rock interactions and large-scale crustal volatile transfer.

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