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Halogen-rich scapolite and biotite: Implications for metamorphic fluid-rock interaction

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ABSTRACT

Abundant Cl-rich scapolite and biotite indicate high Cl activities during greenschist- through amphibolite-facies regional metamorphism of metasedimentary rocks northwest of the Idaho batholith. Biotite-zone granofels contain up to 40 modal percent Cl-rich scapolite. The strict stratigraphic control on the occurrence of scapolite and the fine-scale interlayering of Cl-rich and Cl-poor metasedimentary rocks suggest that scapolite was formed during regional metamorphism by reaction of plagioclase with calcite and halite. Mass-balance constraints on the formation of scapolite show that, prior to metamorphism, sedimentary units containing 10 modal percent halite along restricted sedimentary horizons, 0.5 to 20 cm thick, would have been sufficient to form the most scapolite-rich layers. The abundance of Cl-rich phases decreases abruptly with the appearance of zoisite-bearing assemblages in the metasedimentary rocks, suggesting infiltration of low-Cl H_2O at higher grades. Scapolite compositions range from 32 to 62 equivalent anorthite (EqAn) and 0.76 to 0.06 X_{Cl}. There is a general increase in EqAn and decrease in X_{Cl} with increasing metamorphic grade. However, local variations in scapolite composition suggest that metamorphic fluid compositions were heterogeneous and internally buffered. Biotites coexisting with scapolite contain up to 0.51 wt% Cl (biotite grade) and 2.58 wt% F (kyanite + sillimanite grade). Biotite compositions indicate significant differences in log (f_{HF}/f_{HCl}) values of fluids in equilibrium with low-grade, biotite- and carbonate-rich granofels. Differences in the inferred metamorphic fluid compositions are observed, in some cases, down to a scale of <1 cm.

Cl is strongly partitioned into an aqueous fluid relative to solid phases and is removed by metamorphic devolatilization and infiltration by dilute fluids. Therefore, the occurrence of buffered activity gradients in Cl, as indicated by scapolite and biotite compositions, suggests that metamorphic fluid flow was highly channelized and aqueous fluid–rock interaction was limited. High and variable Cl activities were not smoothed out by aqueous fluid–rock interaction through two regional metamorphic events.

INTRODUCTION

Several recent studies have emphasized the role of fluids as active agents of prograde regional metamorphism. Fluid flow during metamorphism may drive mineral reactions, enhance reaction rates and facilitate transport of elements and heat (Etheridge et al., 1983, 1984; Ferry, 1984; Walther and Wood, 1984, 1986). Metamorphic fluid–rock interaction can be monitored by mineral reaction progress or stable-isotope data (Rumble et al., 1982; Ferry, 1983, 1986; Graham et al., 1983; Tracy et al., 1983; Nabelek et al., 1984; Valley and O'Neil, 1984; Bebout and Carlson, 1986; Valley, 1986). Fluid-rock ratios thus calculated are time-averaged, minimum estimates of the amount of fluid that has passed through a rock.

Gradients in the activities of species—such as Na^+, K^+, F^-, or Cl^-—that are readily exchangeable with externally derived fluids may further constrain metamorphic fluid–rock ratios (Wood and Walther, 1986). Cl is strongly partitioned into aqueous fluids relative to solid phases (Munoz and Swenson, 1981; Volfinger et al., 1985). Therefore, minerals that concentrate Cl, such as scapolite, biotite, apatite, and amphibole, may be particularly sensitive indicators of fluid-rock interaction. In certain circumstances, gradients in Cl activity inferred from Cl-rich micas or scapolite require low metamorphic fluid–rock ratios and may thus constrain the maximum amount of aqueous fluid added to a rock by metamorphic devolatilization or infiltration. Water-rock ratios greater than 0.01–0.1 may smooth out Cl activity gradients in metamorphic rocks (Wood and Walther, 1986). Additionally, these measurements help to delineate metamorphic fluid pathways and to define the scale of pervasive fluid flow.

Few papers have examined Cl chemistry as an indicator of metamorphic fluid composition and fluid-rock interaction (Rich, 1979; Yardley, 1985; Oliver and Wall, 1987; Sisson, 1987), and no detailed study of Cl activity

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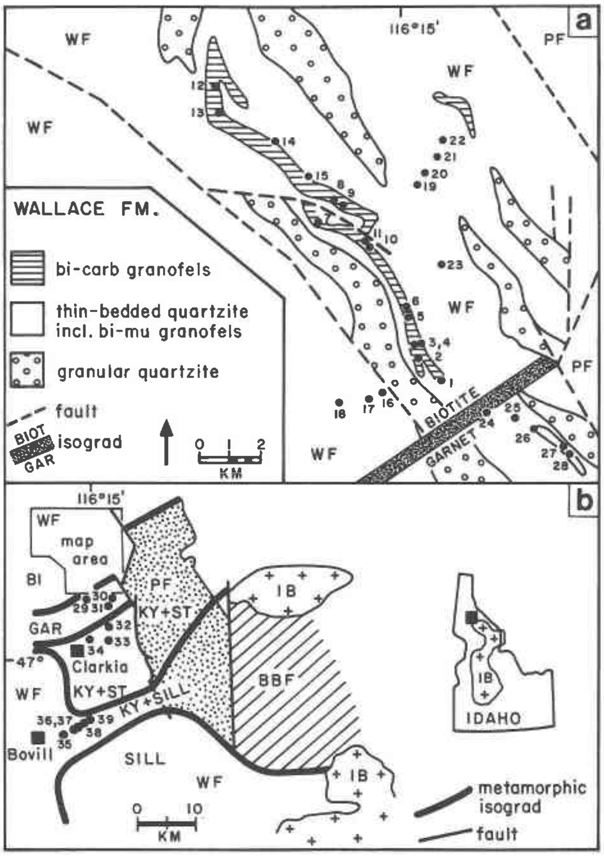

Fig. 1. (**a**) Generalized geologic map of biotite- and garnet-zone Wallace Formation metasedimentary rocks north of Clarkia, Idaho (after Hietanen, 1967). Sample locations are cross-referenced in Tables 3 and 4. (**b**) Locations of metamorphic isograds (Hietanen, 1984) and higher-grade samples. WF = Wallace Formation (upper Belt Group), PF = Prichard Formation (lower Belt Group), BBF = Boehls Butte Formation (pre-Belt), IB = Idaho batholith.

gradients over a range of regional metamorphic pressures and temperatures has been made. In this paper, we present compositional data for Cl-bearing scapolites and biotites from low-variance, greenschist- through amphibolite-facies metasedimentary rocks in the Proterozoic Belt Supergroup in northern Idaho. Moderate to high fluid-rock ratios coincident with regional metamorphism of these rocks have been inferred from whole-rock oxygen-isotope data (Criss et al., 1984; Fleck and Criss, 1985; Criss and Fleck, 1987). However, oxygen-isotope values for mineral separates indicate that isotopic depletions in these scapolite-bearing rocks are the result of fluid-rock interaction *after* the peak of regional metamorphism (Mora and Valley, 1988). In this study, we use experimentally determined mineral-fluid equilibria to estimate the activities of NaCl, HCl, and HF in the metamorphic fluids. In particular, we establish that high, locally controlled Cl activities existed in the fluid compositions, requiring low metamorphic fluid–rock ratios during greenschist-facies regional metamorphism.

GEOLOGIC SETTING

Scapolite-bearing rocks form part of a thick prograde metamorphic sequence exposed in the northwestern border zone of the Idaho batholith (Figs. 1a, 1b). This metasedimentary sequence has been correlated with the lowermost formations of the Proterozoic Belt Supergroup (Hietanen, 1963; Reid et al., 1981; Harrison et al., 1981). Two episodes of metamorphism have affected the rocks. The first episode, M1, was syntectonic and resulted in the formation of a primary penetrative fabric. Equilibrium mineral assemblages and the mapped isograds (Fig. 1b) are attributed to M2 (Hietanen, 1984; Lang and Rice, 1985). Some flattening of micas around M2 porphyroblasts is seen. M2 isograds increase in grade to the south, approximately concentric to the northern Idaho batholith (Fig. 1b). Local development of crenulated foliation and low-pressure, high-temperature mineral assemblages is tentatively correlated with post-M2 isothermal decompression associated with rapid uplift of the batholith (Grover et al., 1987; Ruendal and Rice, 1987). Peak M2 pressures and temperatures in the study area range from 480 °C and 4 kbar in the biotite zone to 590 °C and 5 kbar in the kyanite-sillimanite zone (Tomten and Bowman, 1984; Mora, 1988).

In Belt Supergroup metasedimentary rocks 50 km east of the study area, Lang and Rice (1985) have identified a relict M1 staurolite isograd defined by pseudomorphs of muscovite after M1 staurolite. Hietanen (1963) also reported pseudomorphs after an orthorhombic mineral, possibly andalusite, occurring west of Clarkia, Idaho (Fig. 1b). The lack of pseudomorphs north of the relict isograd suggests that M1 metamorphism also increased in grade to the south. The major focus of this study is rocks exposed in the biotite and garnet zones, north of Clarkia. These rocks consist predominantly of weakly foliated, thin-bedded quartzites and carbonate-bearing biotite granofels. Sedimentary features such as mudcracks, ripples, cross-bedding, and channels are well-preserved in biotite-zone rock types, and no muscovite pseudomorphs have been observed. These features suggest that the M2 metamorphism was the highest-grade episode to have affected these rocks.

The timing of metamorphism is poorly constrained. Lang and Rice (1985) demonstrated that isograds east of the study area postdate thrust faulting inferred to be >100 m.y. (Harrison et al., 1981). The distribution of the M2 isograds suggests that regional metamorphism may be temporally related to Cretaceous to early Tertiary emplacement of the Idaho batholith. Rb/Sr and K/Ar isotopic studies of the batholith suggest nearly continuous igneous activity between 80 and 40 Ma, with early Tertiary rapid uplift (Armstrong, 1975, 1976; Criss et al., 1982; Criss and Taylor, 1983; Fleck and Criss, 1985; Criss and Fleck, 1987). Abundant kyanite in the prograde metamorphic sequence and the inferred early Tertiary rapid uplift of the area are consistent with peak M2 metamorphism during the earliest phase of batholith formation.

ANALYTICAL PROCEDURES

Quantitative chemical analyses of scapolite and biotite (Table 1) were made on the ARL-SEMQ electron microprobe at the University of Wisconsin, Madison. Minerals were analyzed by wavelength-dispersive analysis using an accelerating potential of 15 kV and a sample current of 15 nA. F and Cl in biotite were analyzed at 10 kV, with the beam slightly defocused (10 μm). Volatilization checks were made for four times the counting time for Na, F, and Cl; no volatilization occurred. Natural, crystalline standards were used for all elements except F, for which synthetic fluorphlogopite was used. Matrix corrections were made using a modified Bence-Albee scheme (1968) or a ZAF correction program (EMPADR VII; Rucklidge and Gasparrini, 1969). For all elements except F and Cl, count times varied from 10 to 20 s per spot, with a total of 5 to 10 spots analyzed per grain. Analyzed minerals are compositionally homogeneous.

Because of their importance to this study, special care was taken to increase the reliability of the F and Cl analyses. For each sample, a minimum of 10000 total counts was collected. Count time per spot was 30 to 60 s and 10 to 60 spots were analyzed. Low concentrations of F and Cl in some biotites required extremely long total count times of from 360 to 3600 s in order to accumulate the necessary counts. Under these operating conditions, the minimum detection limit is 0.02 wt% for Cl and 0.06 wt% for F. For sample 84MC147, with 0.05 wt% Cl, the peak values were 6.9 standard deviations above background (1 s.d. = $\sqrt{N_{\text{bkg}}}$, where N = number of counts) with a peak/background ratio of 1.6. Sample 84FW70, with 0.44 wt% F, had a peak/background ratio of 3.2 with the peak value 21.7 standard deviations above background. As these values represent the minimum amount of F and Cl reported in this study, it is concluded that all the reported analyses are statistically significant.

Analyzed scapolites contain no detectable F and little or no SO_4 (Mora, 1988). Scapolite was normalized to 16 total cations. Normalization to 16 cations reduces the effect of reasonable analytical errors for Si and Al, which is especially important for low-grade scapolites that contain numerous inclusions of quartz. For the same reason, CO_3 in scapolite was calculated by difference ($CO_3 = 1 - Cl - SO_4$) rather than charge balance. The sum of Ca + Na + K in scapolite averages 3.93 ± 0.06 (2σ), differing by less than 2% from the ideal formula ($n = 4$). Scapolite compositions are reported as "equivalent anorthite" (EqAn, where EqAn = 100 × (Al − 3)/3 where Al is calculated on the basis of 16 cations; Orville, 1975) and the mole fraction of Cl [X_{Cl}, where $X_{Cl} = Cl/(Cl + CO_3)$]. The analytical error is ±3 EqAn.

SCAPOLITE IN THE WALLACE FORMATION

Mineral assemblages

Geologic maps and a detailed description of scapolite-bearing rocks of the Wallace Formation are given by Hietanen (1967). In the biotite and garnet zones north of Clarkia (Fig. 1a), scapolite occurs in layers 1 cm to several meters thick composed of biotite-rich granofels, interbedded with fine-grained, thin-bedded biotite quartzite. Two types of biotite granofels are distinguished: a biotite-carbonate granofels, containing 30–50% calcite + dolomite and no muscovite, and a biotite-muscovite granofels, containing 0–25% carbonate and up to 2% muscovite (Table 2). One 30-m-thick unit of interbedded biotite-carbonate granofels and quartzite crops out discontinuously along strike for approximately 15 km (Fig. 1a). In the kyanite-staurolite zone, scapolite occurs in well-foliated biotite-scapolite or actinolite-scapolite schists. Kyanite-sillimanite–zone scapolites occur in diopside-bearing layers up to 10 cm thick interbedded with massive biotite quartzite east of Bovill (Fig. 1b). Mineral assemblages and approximate modes for the major scapolite-bearing rock types are listed in Table 2. Complete mineral assemblages are given in Mora (1988).

In lower-grade samples, scapolite occurs as large, subhedral porphyroblasts within a much finer matrix. The porphyroblasts are up to 1 cm in diameter and 2.5 cm in length, although more typically less than 0.5 cm in maximum dimension. Coexisting phases are generally less than 0.2 mm in diameter. Scapolite crystals are elongate parallel to foliation (if present). Scapolites in low-grade rocks are poikiloblastic and optically unzoned; they contain numerous inclusions of quartz and other matrix minerals. Compositional core-to-rim zonation is also rare, with a maximum relative difference of 4.6 EqAn and 0.06 X_{Cl}; cores may be either relatively Cl rich or Cl poor. Higher-grade rocks have granoblastic-polygonal textures and rare inclusions of quartz in scapolite.

Origin of scapolite

The occurrence of Cl-rich scapolite is an indicator of high NaCl activity at the time of crystallization (Orville, 1975; Ellis, 1978; Vanko and Bishop, 1982). The NaCl may have been an original sedimentary constituent or may have been introduced from an outside source. Hietanen (1967) noted that strict stratigraphic control on the occurrence of scapolite in the Wallace Formation, with >90% of the scapolite distributed parallel to bedding, suggests that scapolite crystallized during regional metamorphism in rock layers that originally contained halite. Salt casts and large skeletal halite crystals have been described in unmetamorphosed, cyclic Wallace Formation sedimentary rocks and stratigraphic equivalents, suggesting evaporitic sedimentation (Fenton and Fenton, 1937; Grotzinger, 1986). In other studies, abundant Cl-rich scapolite and hypersaline fluid inclusions have been inferred to indicate the presence of metaevaporites (Hietanen, 1967; Ramsay and Davidson, 1970; Serdyuchenko, 1975; Rich, 1979; Behr and Horn, 1982; Vanko and Bishop, 1982; Roedder, 1984a). Additionally, the occurrence of abundant Mg- and Al-rich biotite with only minor chlorite, muscovite, and K-feldspar may indicate metamorphism of evaporitic argillites (Moine et al., 1981). The compositions of Cl-rich biotite coexisting with scap-

Table 1a. Representative electron-microprobe analyses of scapolite from the Wallace Formation

Sample:	3	4	5	6	9	14	15	22	23c	23b
Zone:*	biot	biot	biot	biot	biot	biot	biot	biot	biot	biot
SiO_2	54.22	54.72	54.43	55.12	55.27	53.21	53.58	53.60	54.24	53.05
Al_2O_3	23.83	23.27	23.34	23.00	23.06	23.66	23.79	24.80	23.78	24.47
CaO	8.66	8.33	9.20	8.20	7.69	10.43	9.77	8.76	8.17	9.42
Na_2O	8.52	8.53	8.08	8.02	9.20	7.25	7.88	8.27	9.00	8.33
K_2O	0.42	0.69	0.39	0.53	0.62	0.54	0.50	0.75	0.48	0.45
Cl	2.72	2.87	2.49	2.81	2.99	2.20	2.33	2.61	2.94	2.57
SO_3	0.42	0.25	0.48	0.29	b.d.	0.09	0.07	b.d.	b.d.	b.d.
CO_2**	1.37	1.27	1.60	1.26	1.31	2.13	2.00	1.76	1.34	1.79
Total†	99.55	99.25	99.45	98.60	99.46	99.01	99.39	99.96	99.29	99.50
				Formulae based on 16 cations						
Si	7.983	8.067	8.067	8.224	8.093	7.955	7.939	7.853	7.955	7.808
Al	4.141	4.046	4.078	4.045	3.976	4.171	4.155	4.282	4.111	4.244
Ca	1.363	1.319	1.460	1.311	1.205	1.672	1.548	1.375	1.284	1.486
Na	2.433	2.435	2.324	2.320	2.612	2.103	2.260	2.349	2.560	2.378
K	0.080	0.133	0.071	0.101	0.114	0.099	0.098	0.141	0.090	0.084
Cl	0.681	0.717	0.623	0.710	0.739	0.557	0.588	0.649	0.732	0.640
SO_4	0.044	0.027	0.053	0.032	0.000	0.009	0.009	0.000	0.000	0.000
CO_3††	0.275	0.256	0.324	0.258	0.261	0.434	0.403	0.351	0.268	0.360
EqAn‡	38.0	34.9	35.9	34.8	32.5	39.0	38.5	42.7	37.0	41.5
X_{Cl}§	0.712	0.737	0.658	0.733	0.739	0.562	0.593	0.649	0.732	0.640

Note: Additional analyses in Mora (1988). Sample numbers are cross-referenced in Tables 3 and 4 and Fig. 1. b.d. = below minimum detection.
* Metamorphic zones after Hietanen (1984) isograds: biot = biotite zone, gar = garnet zone, k + st = kyanite + staurolite zone, k + s = kyanite + sillimanite zone.
** Calculated from stoichiometry.

olite in the Wallace Formation are discussed in a later section. Apatite and tourmaline may also incorporate F or Cl. Apatite occurs in trace amounts in some samples. Tourmaline is relatively more abundant, but its occurrence is often restricted to scapolite-bearing horizons. The restriction of B-rich minerals, such as tourmaline, to certain sedimentary units may also indicate metaevaporite horizons (Abraham et al., 1972).

Table 1b. Representative electron-microprobe analyses of biotite from the Wallace Formation

Sample:	1	5	6	11	14	17	19	23c	23b	24	27	28
Zone:*	biot	biot	biot	biot	biot	biot	biot	biot	biot	gar	gar	gar
SiO_2	40.18	40.20	40.33	40.20	37.82	37.03	37.45	37.08	37.87	38.25	38.87	40.01
TiO_2	2.16	1.28	1.31	2.12	0.93	2.17	1.87	1.07	1.10	1.95	1.20	1.81
Al_2O_3	15.05	16.73	16.33	14.12	19.57	17.94	18.55	19.05	18.96	18.08	17.64	17.00
FeO	9.37	7.73	7.04	9.13	11.42	14.27	14.27	11.83	12.13	12.90	7.19	7.08
MnO	b.d.	b.d.	0.05	0.06	0.10	0.10	0.07	0.09	0.08	0.12	b.d.	b.d.
MgO	19.07	19.57	20.36	19.26	16.10	13.11	13.45	15.55	15.35	14.70	19.38	19.94
CaO	0.08	b.d.	0.05	b.d.	0.17	0.10	b.d.	0.13	0.08	0.07	0.11	0.07
Na_2O	b.d.	0.08	0.12	b.d.	0.18	0.11	0.18	0.07	0.09	0.09	0.10	0.13
K_2O	9.88	9.88	9.55	10.49	9.99	10.11	10.25	9.93	9.61	10.12	10.20	9.74
H_2O**	3.55	3.91	3.86	3.38	3.74	3.67	3.53	3.64	3.68	3.60	3.69	3.77
F	0.94	0.63	0.54	1.09	0.58	0.44	0.76	0.68	0.65	0.74	0.82	0.79
Cl	0.43	0.21	0.17	0.41	0.24	0.24	0.36	0.17	0.16	0.22	0.05	0.06
Total†	100.22	99.91	99.44	99.71	100.54	99.90	100.34	98.97	99.47	100.48	98.89	100.05
					Formulae based on 7 tetrahedral + octahedral cations							
Si	2.935	2.915	2.916	2.967	2.781	2.815	2.826	2.776	2.816	2.854	2.850	2.886
$^{[4]}Al$	1.065	1.085	1.084	1.033	1.219	1.185	1.174	1.224	1.184	1.146	1.150	1.114
$^{[6]}Al$	0.231	0.345	0.307	0.196	0.476	0.423	0.476	0.457	0.477	0.444	0.374	0.331
Ti	0.119	0.070	0.071	0.177	0.051	0.124	0.106	0.060	0.062	0.109	0.066	0.098
Fe^{2+}	0.572	0.469	0.425	0.564	0.702	0.961	0.901	0.741	0.754	0.805	0.441	0.427
Mn	0.000	0.000	0.003	0.003	0.006	0.007	0.004	0.006	0.006	0.007	0.000	0.000
Mg	2.078	2.116	2.194	2.120	1.765	1.485	1.513	1.736	1.701	1.635	2.119	2.144
Ca	0.006	0.000	0.004	0.000	0.013	0.008	0.000	0.010	0.006	0.006	0.009	0.005
Na	0.000	0.012	0.017	0.000	0.025	0.016	0.026	0.010	0.013	0.013	0.013	0.018
K	0.920	0.914	0.881	0.988	0.937	0.980	0.986	0.948	0.912	0.963	0.956	0.896
OH‡	1.729	1.835	1.856	1.690	1.835	1.863	1.773	1.817	1.827	1.797	1.804	1.812
F	0.217	0.140	0.123	0.258	0.135	0.106	0.181	0.161	0.153	0.175	0.190	0.180
Cl	0.054	0.025	0.021	0.052	0.030	0.031	0.046	0.022	0.020	0.028	0.006	0.008

Note: Additional analyses in Mora (1988). Sample numbers are cross-referenced in Tables 3 and 4 and Fig. 1. b.d. = below minimum detection.
* Metamorphic zones defined in Table 1a.
** Calculated.
† Adjusted for F and Cl.
‡ OH = 2.00 − F − Cl.

TABLE 1A—*Continued*

24	26	27	29	30	32	33	35	37	38
gar	gar	gar	gar	gar	k + st	k + st	k + s	k + s	k + s
54.04	52.46	51.14	47.01	49.55	52.67	48.48	48.51	52.41	47.27
23.73	24.76	24.25	27.00	25.68	24.34	25.62	25.95	24.29	26.88
8.46	10.87	12.87	16.45	14.08	9.84	16.03	16.58	12.28	17.42
8.69	7.25	5.80	4.07	5.48	7.88	4.45	4.20	6.46	3.54
0.69	0.48	0.47	0.28	0.44	0.97	0.33	0.47	0.68	0.20
2.94	2.12	1.42	0.40	1.08	2.38	0.65	0.51	1.70	0.24
0.17	0.14	0.59	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.
1.24	2.22	2.74	4.33	3.51	2.01	4.02	4.23	2.82	4.50
99.30	99.82	98.94	99.45	99.58	99.55	99.43	100.33	100.26	100.00
Formulae based on 16 cations									
7.943	7.773	7.766	7.184	7.475	7.773	7.395	7.344	7.794	7.225
4.117	4.327	4.340	4.863	4.565	4.233	4.610	4.633	4.263	4.837
1.334	1.728	2.094	2.694	2.275	1.556	2.621	2.694	1.958	2.855
2.473	2.083	1.708	1.206	1.601	2.255	1.320	1.238	1.860	1.046
0.133	0.089	0.092	0.053	0.084	0.183	0.064	0.091	0.125	0.037
0.733	0.534	0.365	0.104	0.276	0.594	0.165	0.127	0.429	0.064
0.018	0.018	0.067	0.000	0.000	0.000	0.000	0.000	0.000	0.000
0.249	0.448	0.568	0.896	0.724	0.406	0.835	0.873	0.571	0.936
37.2	44.2	44.7	62.1	52.2	41.1	53.7	54.4	42.1	61.2
0.746	0.544	0.391	0.104	0.276	0.594	0.165	0.127	0.429	0.064

† Adjusted for Cl.
†† $CO_3 = 1 - Cl - SO_4$.
‡ EqAn = 100(Al − 3)/3.
§ $Cl/(Cl + CO_3)$.

An alternative source of high salinity might be provided if the interbedded metasedimentary rocks had been infiltrated by Cl-rich brines of either an igneous or sedimentary origin. However, we consider that such brines are unlikely to have been the major source of saline pore fluids for several reasons. The distribution of Cl-rich scapolite is not spatially related to igneous intrusives in the area. In fact, the highest salinities are found in the biotite zone, farthest from the Idaho batholith. Furthermore, fine-scale interbedding of compositionally similar scapolite-bearing and scapolite-free layers, which differ only in their Cl contents, argues strongly for an in situ sedimentary origin of the salt and against brine infiltration (Hietanen, 1967). For example, scapolite in sample 84FW81A occurs along a single biotite-rich layer <2 mm thick within a cross-bedded biotite quartzite (Fig. 2). Other biotite-rich layers contain plagioclase and calcite, but no scapolite. Finally, scapolite-bearing layers are widespread in low-grade Wallace Formation rocks throughout a large area. Abundant Cl-rich scapolite is found in stratigraphically identical, low-grade rocks 50 km east of the study area (Hietanen, 1967; King and Rice, 1984), and scapolite is also reported in equivalent low-grade Wallace Formation argillites in Montana (Ackerman, 1959). These observations are consistent with a model of scapolite formation by reaction of plagioclase with calcite and halite present in the metasedimentary rocks rather than by infiltration of plagioclase-bearing metasedimentary rocks by an externally derived brine.

TABLE 1B—*Continued*

29	30	31	35	37	38
gar	gar	gar	k + s	k + s	k + s
38.70	38.02	38.39	37.70	39.51	39.21
1.53	1.23	1.17	0.81	0.87	0.26
17.25	17.48	16.62	16.46	14.31	15.36
11.75	14.27	11.31	11.64	12.47	10.52
b.d.	0.12	0.18	0.07	b.d.	0.09
16.34	14.52	17.05	17.85	17.92	19.39
b.d.	b.d.	0.05	b.d.	b.d.	0.17
b.d.	b.d.	0.13	0.11	0.05	0.07
10.35	10.00	10.16	10.63	10.50	9.38
3.72	3.57	3.44	3.27	2.95	3.20
0.61	0.83	1.17	1.55	2.24	1.86
0.07	0.14	0.11	0.07	0.09	b.d.
100.05	99.80	99.26	99.49	100.10	98.73
Formulae based on 7 tetrahedral + octahedral cations					
2.871	2.855	2.860	2.804	2.935	2.881
1.129	1.145	1.140	1.196	1.065	1.119
0.379	0.402	0.325	0.247	0.187	0.211
0.085	0.069	0.066	0.045	0.049	0.014
0.729	0.896	0.704	0.724	0.774	0.646
0.000	0.008	0.011	0.004	0.000	0.006
1.807	1.625	1.894	1.980	1.984	2.123
0.000	0.000	0.000	0.000	0.000	0.014
0.000	0.000	0.019	0.016	0.008	0.010
0.979	0.957	0.966	1.008	0.995	0.879
1.841	1.785	1.710	1.626	1.462	1.568
0.143	0.197	0.276	0.365	0.527	0.432
0.016	0.018	0.014	0.009	0.011	0.000

Scapolite chemistry

Scapolite in the Wallace Formation shows a range of compositions from Cl-rich to almost fully carbonated with little or no SO_4 solid solution (Table 3; complete analyses in Mora, 1988). In Figure 3, the equivalent anorthite content and the mole fraction of Cl in scapolite are plotted. The dashed lines show the stoichiometry of commonly proposed solid solutions (Shaw, 1960; Evans et al., 1969)

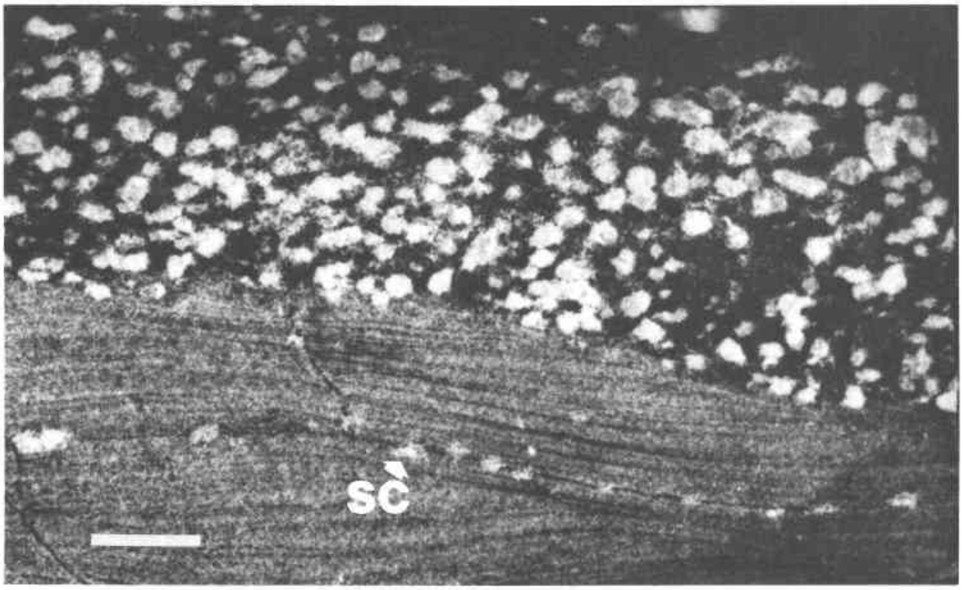

Fig. 2. Hand-sample 84FW81A showing interlayered scapolite-bearing biotite-carbonate granofels and cross-bedded biotite quartzite. Granofels contains white, porphyroblastic scapolite and fine-grained calcite, dolomite, plagioclase, and tourmaline. Quartzite also contains minor calcite and plagioclase. SC = porphyroblastic scapolite growing along a single biotite-rich bed in quartzite. This mode of occurrence suggests scapolite formation in sedimentary horizons that originally contained halite. Scale bar is 1 cm.

between marialite (Mar), mizzonite (Miz), and meionite (Mei). Many scapolites analyzed in this study are significantly more Cl-rich than scapolites on the Mar-Mei join, as the marialitic scapolites (12–37 EqAn, 0.72–0.96 X_{Cl}) reported by Vanko and Bishop (1982).

Scapolite compositions vary according to rock type and metamorphic grade. Compositions of biotite-zone scapolites fall in the range 32–43 EqAn and 0.59–0.76 X_{Cl}. These values are close to the Al-Si–ordered scapolite composition (33 EqAn) predicted by crystal chemistry to have the lowest temperature stability (Oterdoom and Wenk, 1983; Sheriff et al., 1987). Although there is some overlap, scapolite compositions in biotite-carbonate granofels are more NaCl-rich than those in biotite-muscovite granofels. Biotite-carbonate granofels average 34.8 ± 1.5 (2σ) EqAn and 0.71 ± 0.04 X_{Cl} (Table 2). Biotite-

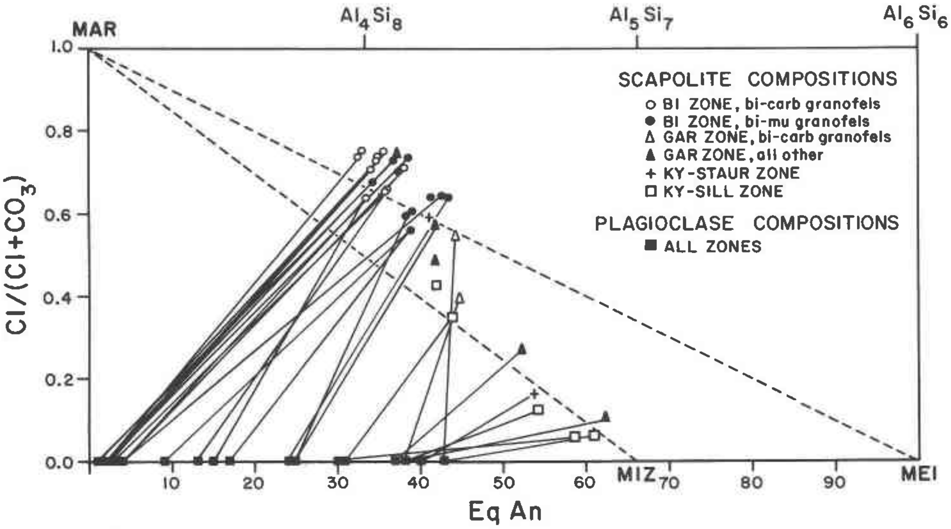

Fig. 3. Compositions of coexisting scapolite and plagioclase in the Wallace Formation. Plagioclase compositions are plotted along the horizontal axis. Dashed lines are solid solutions between marialite (Mar) and mizzonite (Miz) or meionite (Mei). In general, Cl in scapolite decreases with increasing metamorphic grade; however, compositional variations within each grade suggest local control of fluid and scapolite compositions.

TABLE 2. Approximate modes of scapolite-bearing rock types of the Wallace Formation

Rock type	Carb	Bt	Qtz	Scp	Pl	Kfs	Ms	Act	Di	Czo	Other
Bt-Carb granofels	30–50	10–30	10–25	20–40	0–5	0–2	0	0–5	0	0–1	0–2
Bt-Ms granofels	0–25	30–40	10–25	10–40	0–5	0–3	0–2	0	0	0–1	0–2
Bt schist	0–10	20–40	20–40	5–20	0–10	0–5	0–5	0–5	0	0–5	0–2
Act schist	0–5	0–10	10–15	5–20	0–5	0–5	0	10–40	0	3–5	0–2
Di gneiss	5–10	0–5	5–10	5–10	5–10	10–20	0	0	30–40	1–2	0–5

Note: Carb = calcite + dolomite, Bt = biotite, Qtz = quartz, Scp = scapolite, Pl = plagioclase, Kfs = K-feldspar, Ms = muscovite, Act = actinolite, Di = Diopside, Czo = clinozoisite. Other includes sphene, apatite, tourmaline, pyrite, zircon, allanite, and ilmenite.

TABLE 3. Compositions of coexisting scapolite and plagioclase and estimated metamorphic fluid salinities (Eq. 4)

Sample	EqAn	Cl/(Cl + CO_3)	X_{Ab}*	ln K_D**	$X_{\mathrm{NaCl}}^{\mathrm{fluid}}$†
		Biotite zone			
Biotite-carbonate granofels					
(2) 84MC73	32.9	0.751	‡		
(3) 84MC74	38.0	0.712	0.96	−1.0970	0.78
(4) 84MC75	34.9	0.737	0.98	−1.2417	0.77
(5) 84HUK77	35.9	0.658	0.97, 0.87	−1.2061	0.55
(6) 84MC150	34.8	0.733	0.97	−1.3351	0.68
(7) 84FW79	34.3	0.709	0.97	−1.2105	0.68
(8) 84FW80	34.5	0.679	0.99	−1.1878	0.62
(9) 84FW81A	32.5	0.739	0.98	−1.3408	0.70
(11) 84FW84B	35.6	0.747	0.98	−1.1938	0.85
(12) 84FW96	33.5	0.641	0.96, 0.85	−1.2990	0.46
(13) 84FW97	35.7	0.653	0.96, 0.87	−1.2163	0.52
Average	34.8(1.5)	0.71(0.04)			0.66(0.12)
Biotite-muscovite granofels					
(14) 84FW98	39.0	0.562	0.91, 0.83	−1.0548	0.43
(15) 84FW95	38.5	0.593	0.75	−1.0619	0.47
(19) 84HUK86	43.6	0.641	0.76	§	
(20) 84HUK88	39.3	0.606	‡		
(21) 84HUK90	38.7	0.739	0.98	§	
(22) 84HUK91	42.7	0.649	0.96	−0.9153	0.70
(23) 86HUK111c	37.0	0.732	n.a.	−1.1122	0.87
(23) 86HUK111b	41.5	0.640	n.a.	−0.9258	0.68
(23) 86HUK108c	32.4	0.755	n.a.	−1.3533	0.78
(23) 86HUK108b	33.5	0.709	n.a.	−1.2895	0.66
Average	39.6(3.6)	0.66(0.07)			0.67(0.15)
		Garnet zone			
Biotite-carbonate granofels					
(26) 84MC67	44.2	0.544	0.57	−0.8499	0.48
(27) 84MC147	44.7	0.391	0.62	−0.8381	0.26
Biotite-muscovite granofels					
(24) 84MC149	41.8	0.573	0.75	−0.9070	0.51
(25) 84MC66B	37.2	0.746	0.98	−1.1001	0.96
(29) 86MC99B	62.1	0.104	0.62	−0.4334	0.07
(30) 86MC120	52.2	0.276	0.63	−0.6139	0.20
Average	47.0(8.8)	0.44(0.23)			0.41(0.32)
		Kyanite-staurolite zone			
(31) 84MC59	42.0	0.502	‡		
(32) 84MC64	41.1	0.594	‡		
(33) 83MC95	53.7	0.165	0.60	−0.5720	0.11
Average	46.0(6.7)	0.42(0.23)			
		Kyanite-sillimanite zone			
(35) 84BO49	54.4	0.127	0.62	−0.5492	0.08
(36) 84BO51B	45.4	0.352	0.69	−0.7837	0.24
(37) 84BO52	42.1	0.429		−0.9052	0.30
(38) 84BO53B	61.2	0.064	0.57	−0.4496	0.04
(39) 84BO55	58.4	0.065	0.70	−0.4765	0.04
Average	52.7(7.9)	0.21(0.17)			0.14(0.12)

Note: Complete analyses in Mora (1988). Prefix to sample number (in parentheses) refers to sample location (Fig. 1); c and b following sample numbers refer to carbonate-rich and biotite-rich layers, respectively; n.a. = not analyzed. 2σ deviations given in parentheses after average values.

* Composition of plagioclase; two values indicate coexisting plagioclases.

** Calculated from Eq. 3.

† Calculated from Eq. 2.

‡ No plagioclase present.

§ No calcite present.

muscovite granofels average 39.6 ± 3.6 EqAn and 0.66 ± 0.07 X_{Cl}. Similar NaCl enrichment of scapolite in low-grade calcareous metapelites is observed at Notch Peak, Utah, and Mary Kathleen, Australia (Ramsay and Davidson, 1970; Hover Granath et al., 1983). At higher grade, Wallace Formation scapolites range from 37–62 EqAn and 0.75–0.06 X_{Cl}. There is a *general* decrease in the X_{Cl} and an increase in EqAn with increasing metamorphic grade (Fig. 3), as is found in metamorphic rocks in many regions (Oterdoom and Wenk, 1983). However, compositional variations within each metamorphic grade suggest that local rock and/or local metamorphic fluid compositions exert an important control on scapolite compositions.

Plagioclase coexists with scapolite in nearly all samples, and scapolite-plagioclase relations are also shown in Figure 3. Scapolite is always more calcic than coexisting plagioclase. Tie-line slopes in Figure 3 are similar over most of the compositional range but begin to rotate for scapolite compositions greater than 50 EqAn. In several biotite-zone samples ($T = 480$ °C), scapolite coexists with two plagioclases, the compositions of which roughly define the peristerite solvus. Similar scapolite-plagioclase $K_D^{Na\text{-}Ca}$ values are reported for other metamorphosed Wallace Formation samples (Hietanen, 1967; King and Rice, 1984). Scapolite-plagioclase relations are consistent with experimental (Orville, 1975; Ellis, 1978) and natural (Shaw, 1960) observations of plagioclase-scapolite relations in systems with relatively sodic plagioclase ($<An_{40}$), indicating that Wallace Formation mineral compositions are in chemical equilibrium.

SCAPOLITE STABILITY AND FLUID COMPOSITIONS

The stability of scapolite in the system Ab-An-$CaCO_3$-NaCl has been experimentally determined by several studies (Orville, 1975; Goldsmith and Newton, 1977; Ellis, 1978; Vanko and Bishop, 1982; Aitken, 1983). These studies indicate (1) that increasing the concentration of NaCl greatly expands the stability of scapolite and the range of stably coexisting scapolite + plagioclase compositions and (2) that concentrations of NaCl are high in fluids in equilibrium with Cl-rich scapolite. Ellis (1978) investigated the reaction

$$NaCl_{\text{in scapolite}} + (CaCO_3)_{\text{in calcite}} = (CaCO_3)_{\text{in scapolite}} + NaCl_{\text{in fluid}} \quad (1)$$

at 750 °C and 4 kbar. For this reaction,

$$K_D = \frac{(X^{Scap}_{CaCO_3})(X^{Fluid}_{NaCl})}{(X^{Scap}_{NaCl})(X^{Calcite}_{CaCO_3})} \quad (2)$$

where X^j_i is the mole fraction of NaCl or $CaCO_3$ (i) in the respective phases (j). From measured values of K_D for Reaction 1, run at different (fixed) values of EqAn, Ellis (1978) derived the expression

$$\ln K_D = -0.0028(X_{Al})^{-5.5580}, \quad (3)$$

where X_{Al} is the atomic ratio Al/(Al + Si) in scapolite. This expression can be used to estimate the NaCl content of fluid coexisting with scapolite of a given composition at 750 °C and 4 kbar.

It is important to evaluate the assumptions that must be made in order to apply Equation 3 to naturally occurring scapolites and the limitations these assumptions impose on estimates of the metamorphic fluid compositions. Fluid activities are strongly temperature dependent; therefore, the accuracy of data derived from Equation 3 is diminished for scapolites crystallized at other than the experimental conditions of 750 °C and 4 kbar. Equation 3 assumes that NaCl and $CaCO_3$ mix ideally in scapolite and NaCl and H_2O mix ideally in the fluid. Ideal mixing in scapolite cannot be evaluated, as the activity-composition relations for Cl-rich scapolite have not yet been determined. The assumption of ideal mixing in the fluid must be viewed with caution. Fluid compositions in experiments of Ellis (1978) are in the system H_2O-CO_2-NaCl; however, Equation 2 considers X^{Fluid}_{NaCl} = NaCl/(NaCl + H_2O). Significant nonideality exists in the ternary system (Bowers and Helgeson, 1983). High concentrations of NaCl may result in immiscibility and separation of the fluid into an aqueous brine and a relatively CO_2-rich vapor. However, the equation of state for H_2O-CO_2-NaCl fluids is not yet established over the pressure and temperature ranges of metamorphism for the Idaho rocks (480–590 °C, 4–6 kbar), and Ellis's expressions cannot be reformulated at present.

Calculated values of ln K_D and X^{Fluid}_{NaCl} for Wallace Formation metasedimentary rocks are given in Table 3. Values for X^{Fluid}_{NaCl} decrease with metamorphic grade and range from 0.46 to 0.85 in biotite-zone biotite-carbonate granofels, 0.47 to 0.87 in biotite-zone biotite-muscovite granofels, 0.07 to 0.96 in garnet-zone samples, and 0.04 to 0.30 in the kyanite-sillimanite zone. Equilibrium compositions of metamorphic fluids estimated from calc-silicate equilibria in these samples indicate the presence of CO_2 ($X_{CO_2} \leq 0.7$) as well as H_2O and NaCl (Mora, 1988); therefore, the reported values of X_{NaCl} are maximum values.

The higher values of X^{Fluid}_{NaCl} are clearly unrealistic. Values calculated for X^{Fluid}_{NaCl} in biotite-zone samples correspond to fluid salinities of 62 to >90 wt% NaCl equivalent. The maximum solubility of NaCl in water along the three-phase boundary vapor-liquid-NaCl is about 55 wt% at 500 °C (Keevil, 1942). Solubility of NaCl decreases as CO_2 is added to the system (Takenouchi and Kennedy, 1965). Hydrothermal experiments by Vanko and Bishop (1982) show that at 750 °C and 2.8 kbar and with excess calcite, scapolite with composition 28 EqAn and 0.63 X_{Cl} is stabilized by a fluid with X_{NaCl} = NaCl/(NaCl + H_2O) = 0.5–0.7. Fluid-inclusion studies indicate that metamorphic fluids may contain significant amounts of NaCl. These studies indicate that metamorphic fluid salinities range from 0 to 6 wt% NaCl equivalent in pelitic schists and gneisses (Poty et al., 1974; Hollister and Burruss, 1976) and from 20 to 25 wt% NaCl equivalent in calcareous rocks (Crawford et al., 1979a, 1979b; Kreulen, 1980;

Sisson et al., 1981). Higher salinities (up to 50 wt% NaCl equivalent) are noted where evaporites are suspected (Rich, 1979; Behr and Horn, 1982; Roedder, 1984a). Fluid inclusions associated with porphyry ore deposits may contain as much as 70 wt% NaCl equivalent (Roedder, 1984b).

Reconnaissance study of fluid inclusions in scapolite-bearing Wallace Formation metasedimentary rocks indicates that small (<10 μm), isolated saline inclusions occur in matrix quartz in all metamorphic zones. Daughter minerals were not observed in inclusions at any grade. Liquid + vapor inclusions in two kyanite-sillimanite–zone samples had melting temperatures (T_m) in the range -5 to -15 °C, indicating moderate salinities (10–20 wt% NaCl equivalent; Potter et al., 1978). Attempts to determine T_m for two-phase (liquid + vapor) inclusions in several low-grade samples were unsuccessful as no freezing and/or melting behavior was observed between 25 and -150 °C. Crawford et al. (1979a, 1979b) observed similar behavior in metamorphosed carbonate-rich metasedimentary rocks. Cl-rich fluids that are high in Ca and Mg may contain no daughter minerals and be very difficult to freeze because of the high viscosities of such brines at low temperature (Roedder, 1984a). Thus, preliminary examination of fluid inclusions suggests the presence of metamorphic brines.

Cl-rich scapolite compositions clearly indicate highly saline fluids during crystallization, although more accurate estimates of X_{NaCl} must await calibration of Reaction 1 at lower temperatures. Despite these limitations on the *accuracy* of quantitative estimation of fluid compositions coexisting with scapolite, the *precision* of these estimates is sufficiently high to be useful for qualitative comparisons of fluid-rock interaction among our metasedimentary samples, especially among samples of similar metamorphic grade and bulk composition.

Prograde metamorphic fluid compositions

Several lines of evidence suggest that scapolite is a sensitive indicator of metamorphic fluid composition. Scapolite modal abundance in the Wallace Formation decreases from up to 40% in scapolite-bearing layers of biotite-zone rocks to less than 10% at higher grade (Table 2). The abrupt decrease in the abundance of scapolite may in part reflect a facies change in the sedimentary protolith in which NaCl and/or plagioclase components decrease in the direction of increasing grade. Alternatively, prograde metamorphic fluid compositions affect the stability of scapolite. The percentage of scapolite decreases approximately coincident with the appearance of low-variance, zoisite-bearing assemblages in the calc-schists. These assemblages require water-rich metamorphic fluids even though volatilization products are CO_2 rich. This situation can only be satisfied by combined buffering and infiltration of an aqueous fluid ($X_{CO_2} \leq 0.15$) during metamorphism (Mora and Valley, 1986a). Infiltration of water-rich fluid would dilute highly saline pore fluids, reducing the stability of Cl-rich scapolite. For example, scapolite compositions in garnet-zone, zoisite-bearing samples 86MC99B and 86MC120 reflect equilibration with a relatively Cl-poor fluid ($X_{NaCl}^{Fluid} = 0.07$–0.20) by comparison with zoisite-free samples of similar grade (Table 3).

In general, X_{Cl} decreases with increasing grade (Fig. 3) indicating that scapolite composition, and thus the inferred X_{NaCl}^{Fluid}, changes with prograde metamorphic devolatilization and/or infiltration. For example, scapolite compositions show a decrease from 0.71 to 0.45 X_{Cl} between biotite- and garnet-zone samples in the same rock type (biotite-carbonate granofels; Table 3). The mineral assemblage dolomite + quartz + tremolite + calcite in garnet-zone sample 84MC147 (Table 3) suggests dilution of metamorphic salinity by the prograde reaction dolomite + quartz + H_2O = tremolite + calcite + CO_2. The composition of scapolite in this sample is 44.7 EqAn 0.39 X_{Cl}; the inferred $X_{NaCl}^{Fluid} = 0.26$ (Table 3). By comparison, scapolite in sample 84MC67 (Table 3), which contains dolomite + quartz + calcite unreacted to tremolite, indicates significantly less dilute metamorphic fluids (44.2 EqAn 0.54 X_{Cl}; $X_{NaCl}^{Fluid} = 0.48$).

Samples from the kyanite-sillimanite–zone in the Wallace Formation were collected from thin (<10 cm) diopside-rich layers in massive quartzite and contain nearly identical zoisite-bearing assemblages (phlogopite + calcite + quartz + diopside + K-feldspar + zoisite + plagioclase + scapolite; sample 84BO55 has no phlogopite; Table 2). These assemblages indicate combined buffering and infiltration of an aqueous fluid, with equilibrium $X_{H_2O} \geq 0.90$ (Mora and Valley, 1986a). Despite these similarities, X_{Cl} in scapolite varies from 0.06 to 0.43 ($X_{NaCl}^{Fluid} =$ 0.04 to 0.30; Table 3). Differences in the amount or composition of fluids infiltrated into these layers may account for the range of scapolite compositions observed. Alternatively, variable amounts of halite contained along these layers in the protolith may also have contributed to differences in scapolite compositions. It is important to note that aqueous infiltration did not overwhelm the buffering capacity of the scapolite-bearing layers, nor did aqueous fluid flow smooth compositional heterogeneities between rock layers.

Local gradients in metamorphic salinities

Local gradients in the Cl content of metamorphic fluids are inferred between thin (<2 mm), plagioclase + calcite, scapolite-free and scapolite-bearing layers, as seen in Figure 2. Gradients are also observed between adjacent scapolite-bearing layers in samples 86HUK111 and 86HUK108 (Table 3). These rocks consist of carbonate-rich and biotite-rich layers intimately mixed on a scale of ≤ 2 cm (Fig. 4). The carbonate-rich layers contain abundant blue-gray euhedral scapolite up to 7 mm in length and 2 mm in cross section. Scapolite in the fine-grained biotite-rich layers forms white, round crystals <4 mm in diameter. Differences in X_{NaCl}^{Fluid} of up to 0.19 are inferred from scapolite compositions (37.0 vs. 41.5 EqAn) in adjacent (within 1 cm) carbonate- and biotite-rich layers.

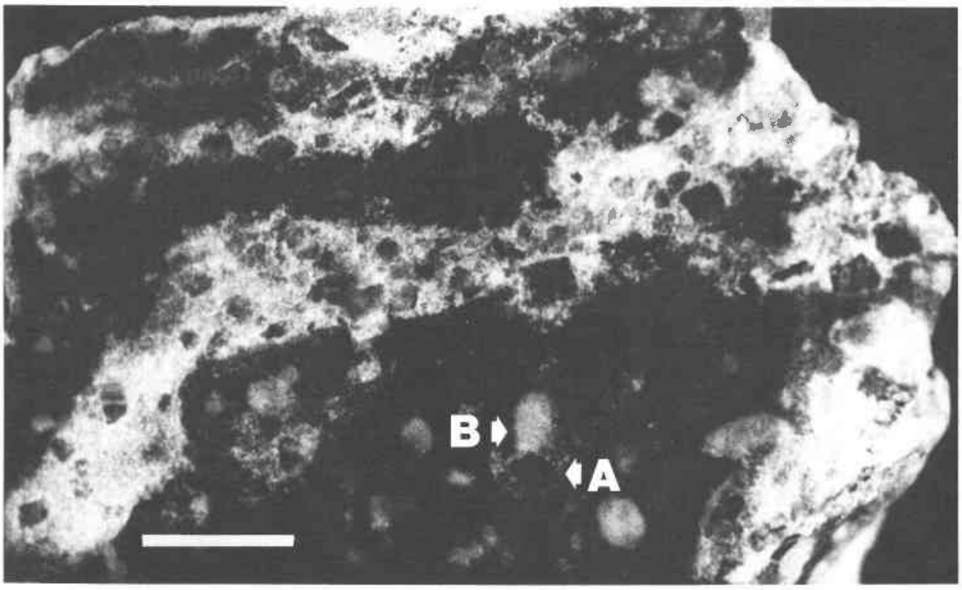

Fig. 4. Mixed carbonate-rich and biotite-rich layers (sample 86HUK108). Light gray, carbonate-rich layers contain dark gray, euhedral scapolites (A) whereas dark brown, biotite-rich layers have rounded, gray scapolites (B). Sharp gradients in $X_{\mathrm{NaCl}}^{\mathrm{Fluid}}$ of up to 0.19 per 1 cm are inferred from scapolite compositions in this sample and others from this outcrop (sample 86HUK111; Table 3). Scale bar is 1 cm.

The compositional differences between adjacent scapolites are much greater than the analytical error (allowing ±10% relative Cl) and indicate that significant differences in fluid compositions existed in these rocks on a scale of <1 cm. The finely interbedded nature of the Wallace Formation metasedimentary rocks suggests that other examples of fine-scale gradients in metamorphic salinities may be widespread in the study area.

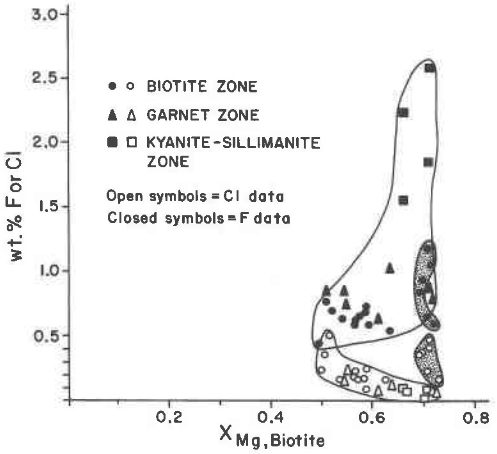

Fig. 5. Halogen chemistry, wt% Cl or F, plotted against the mole fraction of Mg in biotite. Open symbols are Cl data and closed symbols are F data. In general, Cl decreases and F increases with increasing metamorphic grade. The high and variable Cl content of biotites in low-grade biotite-carbonate granofels (stippled) indicates local differences in metamorphic fluid compositions and internal buffering of saline metamorphic fluids.

HALOGEN COMPOSITIONS OF BIOTITES

Biotite coexists with scapolite at all metamorphic grades, and biotite compositions yield independent information on the metamorphic fluid compositions. Experiments indicate that the F ⇌ OH and Cl ⇌ OH exchange in biotite is governed by several independent factors including temperature, the activities of halogen acids, and the compositions of biotite (Munoz and Ludington, 1974; Ludington and Munoz, 1975; Munoz and Swenson, 1981; Volfinger et al., 1985). Experimental studies indicate that F is preferentially incorporated into biotites with high Mg/Fe ratios. "Fe-F avoidance" (Ramberg, 1952) has also been extensively documented in natural systems (Ekstrom, 1972; Zaw and Clark, 1978; Jacobs and Parry, 1979; Valley and Essene, 1980; Valley et al., 1982). The compositional control of Cl in biotite is not as well understood. Experimental studies suggest "Mg-Cl avoidance," the preferential incorporation of Cl into Fe-rich biotites (Munoz and Swenson, 1981; Volfinger et al., 1985).

The relation of Mg/Fe and halogen content in biotite varies in metamorphic and hydrothermal environments as a function of temperature, pressure, and halogen activities (cf. Fig. 4 of Sisson, 1987). Compositions of biotites coexisting with scapolite in the Wallace Formation are summarized in Table 4. The wt% of Cl and F have been plotted versus X_{Mg} (X_{Mg} = Mg ÷ total octahedral cations) in Figure 5. The percentage of Cl decreases with increasing metamorphic grade, from 0.16–0.51 wt% in the biotite zone to 0.00–0.09 wt% in the kyanite-sillimanite zone, whereas F shows the opposite trend, increasing from 0.44–1.09 wt% to 1.55–2.58 wt%. Most samples reflect the pre-

TABLE 4. Biotite compositions and log fugacity ratios of halogen acids

Sample	X_{Mg}*	X_{Sid}**	X_{Ann}†	F (wt%)	Cl (wt%)	$\log \frac{f_{H_2O}}{f_{HCl}}$	$\log \frac{f_{H_2O}}{f_{HF}}$
Biotite zone: P = 4.5 kbar, T = 480 °C							
Biotite-carbonate granofels							
(1) 84MC69A	0.688	0.152	0.160	0.84	0.42	2.03	4.89
(1) 84MC69B	0.693	0.142	0.165	0.94	0.43	2.00	4.84
(5) 84HUK77	0.705	0.203	0.092	0.63	0.21	2.32	5.06
(6) 84MC150	0.731	0.165	0.104	0.54	0.17	2.35	5.15
(10) 84FW83	0.712	0.102	0.186	1.04	0.47	1.91	4.81
(11) 84FW84	0.707	0.115	0.178	1.09	0.41	1.98	4.78
Average	0.706(0.02)			0.85(0.22)	0.35(0.13)	2.10(0.19)	4.92(0.15)
Biotite-muscovite granofels							
(16) 84FW70	0.495	0.426	0.079	0.44	0.24	2.64	4.90
(17) 84FW71	0.535	0.381	0.084	0.63	0.25	2.55	4.80
(18) 84FW72	0.592	0.393	0.015	0.73	0.07	2.95	4.80
(19) 84HUK86	0.504	0.471	0.025	0.76	0.36	2.44	4.65
(20) 84HUK87	0.568	0.412	0.020	0.62	0.18	2.62	4.84
(21) 84HUK90	0.515	0.391	0.094	0.69	0.47	2.27	4.72
(14) 84FW98	0.588	0.391	0.021	0.58	0.24	2.48	4.90
(15) 84FW95	0.628	0.325	0.047	0.52	0.16	2.59	5.02
(23) 86HUK111c	0.579	0.384	0.037	0.68	0.17	2.63	4.81
(23) 86HUK111b	0.567	0.412	0.021	0.65	0.16	2.70	4.82
(23) 86HUK113A	0.565	0.427	0.008	0.58	0.23	2.53	4.86
Average	0.557(0.04)			0.63(0.09)	0.23(0.11)	2.58(0.17)	4.83(0.10)
Garnet zone: P = 5 kbar, T = 505 °C							
Biotite-carbonate granofels							
(27) 84MC147	0.706	0.184	0.110	0.82	0.05	2.73	4.83
(28) 84MC148	0.715	0.163	0.122	0.79	0.06	2.59	4.87
Average	0.711(0.01)			0.81(0.02)	0.05(0.00)	2.66(0.10)	4.85(0.03)
Biotite-muscovite granofels							
(24) 84MC149	0.545	0.313	0.142	0.74	0.22	2.37	4.64
(29) 86MC99B	0.602	0.249	0.149	0.61	0.07	2.51	4.82
(30) 86MC120	0.542	0.302	0.156	0.83	0.14	2.56	4.59
(31) 84MC146	0.632	0.219	0.149	1.17	0.11	2.48	4.55
Average	0.580(0.04)			0.84(0.24)	0.14(0.06)	2.48(0.08)	4.65(0.12)
Kyanite-sillimanite zone: P = 6 kbar, T = 590 °C							
(35) 84BO49	0.660	0.205	0.135	1.55	0.07	1.90	4.19
(36) 84BO51B	0.710	0.124	0.166	2.58	0.07	1.83	3.97
(37) 84BO52	0.661	0.127	0.212	2.24	0.09	1.77	3.99
(38) 84BO53B	0.708	0.139	0.153	1.86	‡	0.00	4.16
Average	0.685(0.03)			2.06(0.45)	0.06(0.04)		

Note: Complete analyses in Mora (1988). Prefix to sample number (in parentheses) refers to sample (Fig. 1); c and b following sample numbers refer to carbonate-rich and biotite-rich layers, respectively. 2σ deviations given in parentheses after average values. Metamorphic P and T from mineral thermobarometers (see text).

* X_{Mg} = Mg ÷ total octahedral cations.

** $X_{Sid} = (X_{[VI]Al}/0.167)(1 - X_{Mg})$ (J. Munoz, personal communication).

† $X_{Ann} = 1 - X_{Mg} - X_{Sid}$.

‡ Cl below minimum detection.

dicted compositional trends of Fe-F and Mg-Cl avoidance. Biotites shown in the stippled pattern in Figure 5 occur within a single rock type (biotite-carbonate granofels; Fig. 1a) and equilibrated at the same metamorphic pressure and temperature. The biotites have approximately the same Mg-rich compositions (Table 4). Their high and variable halogen contents must therefore reflect local variations in pore-fluid composition that have not been homogenized by metamorphic fluid flow.

F/Cl ratios and fluid compositions

Experimental studies have determined the temperature and compositional (Fe-Mg-Al) dependence of biotite F ⇌ OH and Cl ⇌ OH exchange reactions (Munoz and Ludington, 1974; Ludington and Munoz, 1975; Munoz and Swenson, 1981). On the basis of these data, Munoz (1984) derived the following expressions:

$$\log(f_{H_2O}/f_{HF}) = 2100/T + 1.52X_{mg} + 0.42X_{Ann} + 0.20X_{Sid} - \log(X_F/X_{OH}) \tag{4}$$

$$\log(f_{H_2O}/f_{HCl}) = 5151/T - 5.01 - 1.93X_{Mg} - \log(X_{Cl}/X_{OH}). \tag{5}$$

The variables X_{Mg}, X_{Ann}, and X_{Sid} are defined in Table 4. OH in biotite is usually determined from mineral stoichiometry and is thus subject to greater uncertainties than F or Cl, which are measured directly by electron microprobe. Equations 4 and 5 can be combined to eliminate the hydroxyl variable:

$$\log(f_{HF}/f_{HCl}) = 3051/T - 5.01 - 3.45X_{Mg} - 0.42X_{Ann} - 0.20X_{Sid} + \log(X_F/X_{Cl}). \tag{6}$$

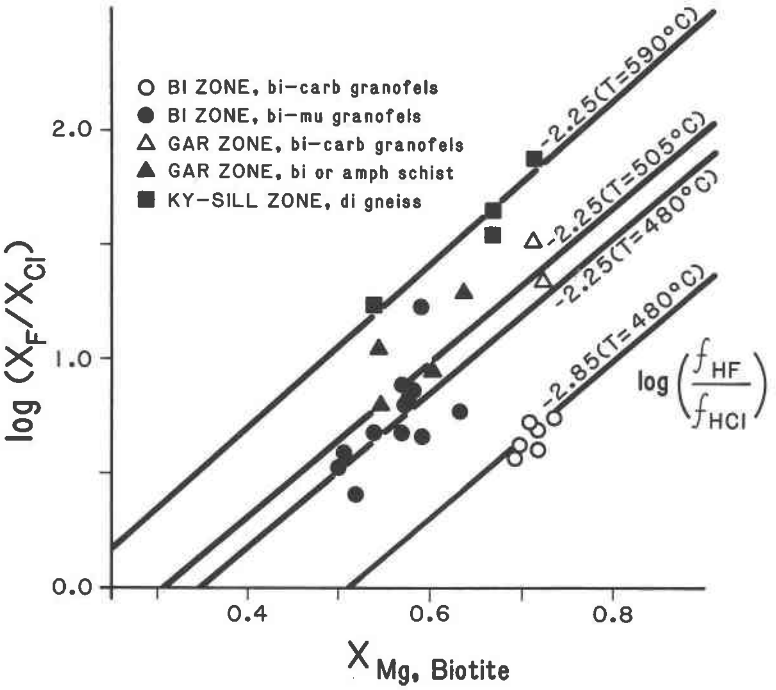

Fig. 6. Log(X_F/X_{Cl}) in biotites plotted against the mole fraction of Mg. Diagonal contours are log(f_{HF}/f_{HCl}) in fluid calculated from Eq. 6 for the estimated metamorphic temperatures of the biotite, garnet, and kyanite-sillimanite zones. The data indicate that the two biotite-zone rock types equilibrated with metamorphic fluids of significantly different composition.

Equation 6 permits evaluation of the halogen content of biotite as a function of biotite composition, equilibration temperature, and fluid compositions. In Figure 6, log (X_F/X_{Cl}) in Wallace Formation biotites is plotted against X_{Mg}. Biotites with varying X_{Mg}, which equilibrated at the same temperature and with the same fluid composition (f_{HF}/f_{HCl} = constant) form an approximately linear array on this type of diagram. The arrays lie along isopleths of the log(f_{HF}/f_{HCl})^{Fluid}. The slopes of the sample arrays depend, to a small degree, on the annite and siderophyllite content of the biotites. Values of X_{Ann} and X_{Sid} are very similar within each rock type and metamorphic zone in the Idaho samples (Table 4). The positions of the fluid isopleths in Figure 6 were calculated using average values of X_{Ann} and X_{Sid} for each group of samples and the appropriate metamorphic temperatures (Tomten and Bowman, 1984; Mora, 1988). Higher temperatures shift the isopleths upward.

Of particular interest are the biotite-zone samples, which form two distinct groups in Figure 6. Biotites with high X_{Mg} are from biotite-carbonate granofels (closed circles), and biotites in the other group are from biotite-muscovite granofels (open circles). These rock types are interbedded on the scale of 1 cm to 10 m. Calcite-dolomite thermometry in 12 samples indicates that all of the biotite-zone samples equilibrated at 480 ± 11 °C (2σ) (Mora and Valley, 1986b). Therefore, the bimodal distribution does not result from variable temperature between the two rock types. Instead, the data suggest that these rock types equilibrated with metamorphic fluids having substantially different relative halogen activities. Halogen activity gradients between the rock types were not smoothed out by fluid circulation.

It is important to recognize the opposing behavior of Cl and F in hydrous minerals during prograde metamorphism. F is increasingly concentrated in the residual hydrous phases as metamorphic devolatilization proceeds because it is so strongly partitioned into solid phases. For this reason, F is relatively insensitive to infiltration of externally derived aqueous fluids. Cl, on the other hand, is strongly partitioned into an aqueous fluid, and the Cl content of metamorphic minerals will be increasingly diluted by exchange with aqueous fluids produced internally or infiltrated into the rocks. Calculated log fugacity ratios (f_{H_2O}/f_{HF}) and (f_{H_2O}/f_{HCl}) are listed in Table 4 and plotted (as crosses) against the equilibration temperature in Figures 7a and 7b. Error bars are shown for a relative analytical uncertainty of ±10% for F and Cl and ±25 °C for temperature. Halogen enrichment increases to the left in both figures. Shown for comparison (dots) are values of the log ratios calculated from biotite compositions reported in other studies of regionally metamorphosed metasedimentary rocks (Tyler, 1979; Valley and Essene, 1980; Hoschek, 1980; Valley et al., 1982; Yardley, 1985; Sisson, 1987). Values of log(f_{H_2O}/f_{HF})$_{Fluid}$ in Wallace Formation samples are comparable to values reported for other amphibolite-facies metasedimentary rocks (Fig. 7a). In contrast, $\log(f_{H_2O}/f_{HCl})_{Fluid}$ values are much lower in the Idaho samples than in amphibolite-facies pelitic schists (Yardley, 1985), probably reflecting the evaporitic protolith of the Wallace Formation calc-silicates (Fig. 7b).

Values of $\log(f_{H_2O}/f_{HF})_{Fluid}$ in the Idaho samples decrease with increasing metamorphic grade, reflecting concentration of F in hydrous phases during prograde metamorphism (Fig. 7a). An increase in $\log(f_{H_2O}/f_{HCl})_{Fluid}$ with increasing grade would be the predicted result of metamorphic devolatilization or aqueous infiltration. Such an increase is not seen in Figure 7b, suggesting that the metamorphic fluids were not substantially diluted by prograde volatilization products or aqueous infiltration, or that biotites in these samples have interacted with an externally derived Cl-rich fluid. However, the predicted trend of Cl dilution strictly applies only in the case of rocks with the same initial degree of Cl enrichment. If high-grade samples were initially enriched in Cl relative to low-grade samples, prograde Cl dilution may not be recognized on a plot such as Figure 7b, although it may in fact have occurred.

Prograde changes in the buffered halogen contents of metamorphic fluids may be reflected in Cl partitioning between biotite and scapolite. Although scapolite compositions are a function of the a_{NaCl}^{Fluid} whereas biotite compositions are a function of the f_{HCl}^{Fluid}, both should reflect the same relative trends of Cl enrichment or depletion. Coexisting scapolite-biotite pairs are plotted in Figure 8 with X_{Cl}^{Scap} versus $IV(Cl)_{Biot}$, where $IV(Cl)_{Biot}$ is a measure of Cl enrichment in biotite [$IV(Cl)_{Biot} = -5.01 - 1.93X_{Mg} - \log(X_{Cl}/X_{OH})$; Munoz, 1984]. High and variable values of both X_{Cl}^{Scap} and $IV(Cl)_{Biot}$, especially in low-grade rocks, reflect the heterogeneous metamorphic fluid compositions. By comparison, zoisite-bearing samples from the garnet and kyanite-sillimanite zones have nearly constant values of $IV(Cl)_{Biot}$ and markedly lower values of X_{Cl}^{Scap} (Fig. 8). Prograde zoisite formation requires infiltration of an aqueous fluid (Hewitt, 1973; Ferry, 1976). Aqueous infiltration results in smoothing of values of $IV(Cl)_{Biot}$ and reducing X_{Cl}^{Scap} at higher grade. Thus, although infiltration and consequent Cl dilution are not identified in the general trend in Figure 7b, they are inferred from the compositional trends of coexisting scapolite and biotite in Figure 8.

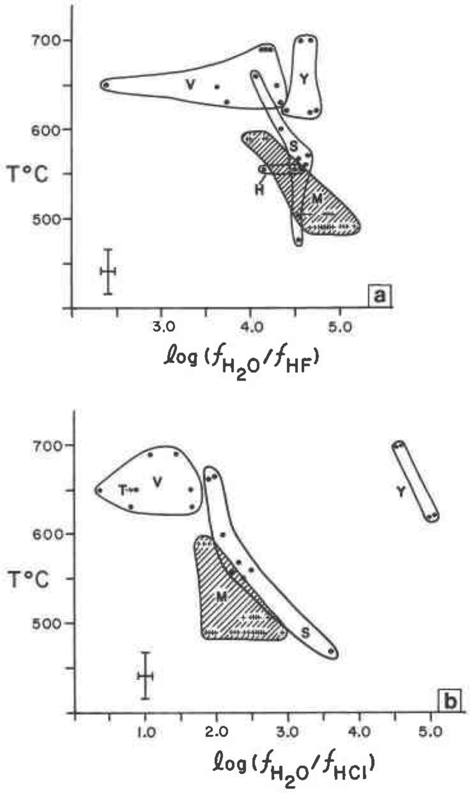

Fig. 7. (**a**) $\log(f_{H_2O}/f_{HF})$ determined from biotite composition (Eq. 4) plotted against metamorphic temperature for regionally metamorphosed samples. Data from this study are shown with an M and diagonal lines. Crosses indicate individual data points. Other data sets are (V) Valley and Essene (1980) and Valley et al. (1982), (H) Hoschek (1980), and (S) Sisson (1987; corrected values; Sisson, personal communication). Data for (Y) Yardley (1985) are estimates based on apatite compositions. Error bars are shown for ±25 °C and ±10% F (relative). Decreased log ratios with higher metamorphic grade reflect the relative immobility of F during devolatilization or infiltration. (**b**) $\log(f_{H_2O}/f_{HCl})$ determined from biotite composition (Eq. 5) plotted against metamorphic temperature. All labels for references are as in Fig. 7a, except (T) Tyler (1979). Decreased log ratios with higher metamorphic grade suggest that pore fluids were not substantially diluted by devolatilization or aqueous infiltration or have interacted with an externally derived Cl-rich fluid.

CONSTRAINTS ON METAMORPHIC FLUID-ROCK RATIOS AND FLUID FLOW

Metamorphic fluid–rock ratios can be estimated on the basis of the reaction progress of fluid-buffering mineral equilibria. Biotite-zone assemblages of calcite + dolomite + quartz + biotite ± K-feldspar ± tremolite (Table 2) restrict the equilibria to lie along or between the two reactions

$$3 \text{ Dolomite} + \text{K-feldspar} + H_2O = \text{Phlogopite} + 3 \text{ Calcite} + 7CO_2. \quad (7)$$

$$5 \text{ Dolomite} + 8 \text{ Quartz} + H_2O = \text{Tremolite} + 3 \text{ Calcite} + 7CO_2. \quad (8)$$

At 500 °C and 4.5 kbar, these reactions restrict $X_{CO_2} = CO_2/(CO_2 + H_2O)$ to ~0.40 (Mora, 1988). If solid solution and a ±20 °C error in temperature are taken into account, $0.20 \leq X_{CO_2} \leq 0.75$. Mineral assemblages in kyanite-sillimanite–zone samples are located at the intersection of the devolatilization reactions

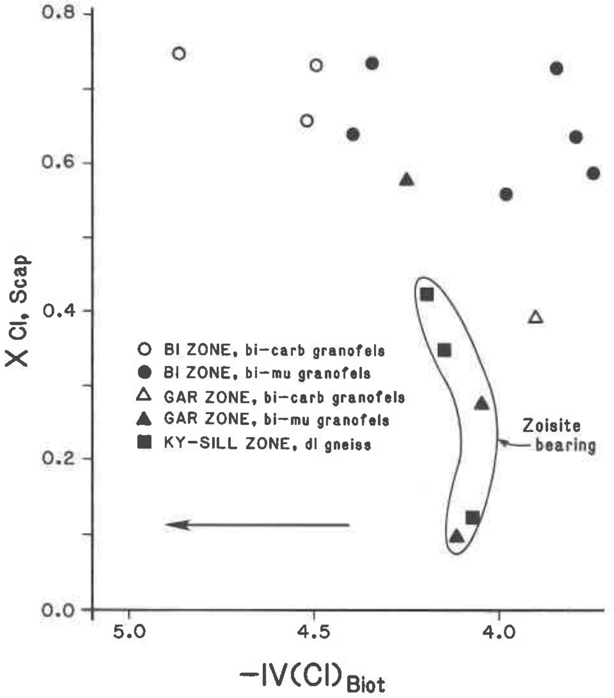

Fig. 8. Cl enrichment of biotite [IV(Cl)$_{\mathrm{Biot}}$; see text] and mole fraction of Cl in coexisting scapolite. High and variable values of both parameters in low-grade rocks reflect Cl-rich, heterogeneous metamorphic fluid compositions. Values are smoothed or reduced in higher-grade, zoisite-bearing samples. Arrow shows direction of Cl enrichment.

$$\text{Phlogopite} + 3\ \text{Calcite} + 6\ \text{Quartz} = 3\ \text{Diopside} + \text{K-feldspar} + H_2O + 3CO_2. \quad (9)$$

$$2\ \text{Zoisite} + CO_2 = 3\ \text{Anorthite} + \text{Calcite} + H_2O. \quad (10)$$

At 590 °C and 6 kbar, the equilibrium fluid composition for this intersection is $X_{CO_2} = 0.10$, if the effects of solid solution on the location of the invariant equilibria are modeled (Mora, 1988).

A typical mode for biotite-zone samples is 20% biotite, 20% quartz, 25% scapolite, 25% calcite, 5% dolomite, and 5% plagioclase + K-feldspar. If it is assumed that all of the biotite was formed by Reaction 7 and that the equilibrium $X_{CO_2} = 0.40$, the conditions would require metamorphic infiltration of the metasedimentary rocks by at least 0.734 mol of pure H_2O per 100 cm^3 of rock. This corresponds to a minimum fluid-rock ratio of 0.09, on an atomic oxygen basis (volumetric fluid-rock ratio = 0.15, assuming pure H_2O infiltration at 480 °C and 4.5 kbar, molar volume data of Burnham et al., 1969). For the minimum $X_{CO_2} = 0.20$, similar calculations indicate a fluid-rock ratio of ~0.35 for biotite-zone samples. Mineral assemblages in the kyanite-sillimanite samples indicate invariant equilibria at the intersection of Reactions 9 and 10 with equilibrium $X_{CO_2} = 0.10$. For a rock containing 39.7% diopside and 1.4% zoisite (sample 84BO49), the conditions require infiltration of 5.25 mol of pure H_2O per 100 cm^3 of rock, or a fluid-rock ratio of 0.64 (atomic oxygen basis; volumetric fluid-rock ratio = 1.10 at 590 °C and 6 kbar). It must be emphasized that fluid-rock ratios are minimum estimates that depend on the inferred mineral reaction, the rock mode, the temperature, and the composition of the infiltrating fluid. Fluid-rock ratios in the biotite-zone rocks are also sensitive to the choice of biotite-forming reaction. For example, biotite formation involving dehydration of clay minerals may require much less aqueous infiltration than biotite formation by Reaction 7.

These calculated fluid-rock ratios can be considered in light of mass-balance constraints on the formation of scapolite. Scapolite in low-grade Wallace Formation metasedimentary rocks may have formed during metamorphism of a halite-bearing protolith by the reaction 3 Albite + Anorthite + 0.667NaCl + 0.333 Calcite = Scapolite (EqAn 33). By this reaction, it requires only 1.5 modal percent halite to form a rock with 25 modal percent scapolite, assuming a closed system. In an open system, fluid escape during diagenesis, metamorphic dehydration, and infiltration will remove halite in solution and increase the necessary amount of halite in the sedimentary protolith. Halite will be dissolved into infiltrated aqueous fluid in order to maintain the highly saline fluid in equilibrium with Cl-rich scapolite. To maintain $X_{\mathrm{NaCl}}^{\mathrm{Fluid}} = \mathrm{NaCl}/(\mathrm{NaCl} + H_2O) = 0.5$ in biotite-zone metasedimentary rocks infiltrated by 0.734 mol of pure H_2O (assumes $X_{CO_2} = 0.40$; see above) requires dissolution of 0.734 mol NaCl (21 cm^3 per 100 cm^3 of rock) into the fluid. Infiltration of 5.25 mol of pure H_2O into kyanite-sillimanite–zone metasedimentary rocks (see above) requires dissolution of 23 cm^3 of NaCl per 100 cm^3 of rock to preserve a fluid composition with $X_{\mathrm{NaCl}}^{\mathrm{Fluid}} = 0.14$ (Table 2). Infiltration of substantially larger amounts of water (fluid-rock ratios > 0.4 in biotite-zone samples; atomic oxygen basis) would require amounts of halite (30–100%) for which there is no evidence in unmetamorphosed equivalent sedimentary rocks.

These mass-balance calculations consider only the mineral equilibria present in scapolite-bearing layers and do not apply to the metasedimentary sequence as a whole. The requirement that ~20% halite is necessary in the protolith to stabilize abundant, Cl-rich scapolite is limited to the relatively thin and volumetrically minor sedimentary horizons that contain scapolite. The abundance of halite required, if scapolite-free layers within the Wallace Formation are included in the mass balance, is many times less. If $X_{\mathrm{NaCl}}^{\mathrm{Fluid}}$ is reduced by one-half (to 0.25 for the biotite-zone example and 0.07 for the kyanite-sillimanite–zone example), only 10 modal percent halite is required. Immiscibility in the NaCl-rich metamorphic fluid may concentrate NaCl in an aqueous brine and reduce the necessary amount of halite. Finally, although the distribution of Cl-rich minerals suggests very limited fluid exchange between scapolite-bearing and scapolite-free layers, some bedding-parallel flow of saline fluid may have occurred. Such fluid flow may also reduce the amount of halite required to be present in the protolith.

DISCUSSION

In all Wallace Formation scapolite-bearing rock types and at all metamorphic grades, scapolite and biotite compositions indicate considerable variation in the Cl content of the metamorphic fluid with heterogeneous fluid compositions preserved on a scale of <1 cm. Metamorphic fluid flow is thus inferred to have been channelized, and/or fluid-rock interaction was limited. Cl present in the Wallace protolith would have been sensitive to dilution or removal by aqueous fluid–rock interaction during the entire metamorphic history of the rock. It is therefore very significant that high and variable Cl activities have not been smoothed out by fluid-rock interaction through *two* regional metamorphic events.

It is possible that metamorphic fluids were predominantly channelized into the adjacent impure and massive quartzites rather than into the scapolite-bearing layers. It is difficult to mineralogically document fluid-rock interaction in the quartzites because of the lack of reactive mineral assemblages. However, the fine-scale interlayering of low-grade, Cl-rich granofels with quartzite and the high and variable Cl activities recorded in the thin scapolite-bearing layers argue against extensive interaction of the adjacent quartzites with externally derived aqueous fluids.

Thus, Cl-rich, but heterogeneous fluid compositions reported here support low fluid-rock ratios throughout this portion of the metasedimentary pile. This conclusion differs from that in recent oxygen-isotope studies that have proposed large-scale, pervasive circulation of moderate to high fluid-rock ratios of aqueous fluid through the Wallace Formation in the study area, occurring approximately concurrently with regional metamorphism (Criss et al., 1984; Fleck and Criss, 1985). Furthermore, any fluid present at the peak of regional metamorphism would have been at lithostatic pressure (4–6 kbar), on the basis of geobarometry in the metapelites, and the viability of *lithostatically pressured* fluid convection is controversial at present (e.g., Valley, 1986). Oxygen-isotope analyses of mineral separates from the scapolite-bearing metasedimentary rocks examined in this study show isotopic depletions that are due to interaction with *hydrostatically pressured* meteoric-hydrothermal fluids *after* the peak of regional metamorphism (Mora and Valley, 1988). It is clear that the details of any large-scale fluid event in these rocks are yet to be elucidated.

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