

High-chlorine amphiboles from oceanic rocks: product of highly-saline hydrothermal fluids?

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Abstract

High-precision analyses of chlorine and fluorine in amphiboles were performed by electron microprobe for five selected samples of metagabbro, amphibolite and metadiabase from the Mathematician Ridge failed spreading center, East Pacific Ocean. Fluorine is consistently very low, less than or equal to 0.2 wt.% in all amphiboles. Chlorine concentration is variable and forms a trimodal distribution that correlates with amphibole type in the following way: greenschist-grade actinolites generally contain less than or equal to 0.05 wt.% Cl; amphibolite-grade hornblendes contain 0.1 to 0.6 wt.% Cl; small irregular zones within actinolite bear up to 4.0 wt.% Cl. The high-chlorine amphiboles (hastingsite) probably formed as a result of locally elevated chlorine activity in hydrothermal fluids at upper greenschist-grade temperatures. The amphibolite-grade hornblendes with a few tenths of a percent chlorine may have formed in the presence of a saline hydrothermal fluid or a fluid of near seawater salinity. The amount and distribution in the ocean crust of saline hydrothermal fluids and their associated chlorine-bearing alteration products may be an important factor in understanding ocean hydrothermal systems, particularly in terms of the amount and nature of variability in these systems.

Introduction

Present day hydrothermal activity within the oceanic crust has been the recent focus of numerous field, laboratory, and theoretical studies (e.g., Rona, 1984, and references therein). The best known examples of active ocean hydrothermal systems are found at actively spreading mid-ocean ridges, and less thoroughly studied hydrothermal activity also occurs associated with oceanic volcanoes (e.g., Lonsdale et al., 1982; Malahoff et al., 1982; Exon and Cronan, 1983; Vanko et al., 1984). As more examples of active hydrothermal activity are discovered the emerging view is that ocean hydrothermal systems are complex and highly variable, both spatially and temporally, in terms of size, longevity, temperatures, fluid compositions, and the mineral and amorphous solid precipitates that are formed. Despite our qualitative knowledge of variability among known ocean hydrothermal systems, general models of hydrothermal circulation are only beginning to account for changing parameters such as temporal variations in temperature and water: rock (W/R) ratio (Mottl, 1983) and spatial shifts of hydrothermal convection cells relative to a fixed point in the spreading ocean crust (Fehn, 1984).

Additional information on ocean hydrothermal activity can be obtained by studying metamorphic rocks from oceanic layer 2 (extrusive basalts and diabase) and layer 3 (gabbro and related plutonic rocks). Samples from layer

3 have been recovered directly in dredges, drillcore, and by submersible, and indirectly from on-land fragments of ocean crust, or ophiolites (Coleman, 1977). In a recent study of dredged samples from the Mathematician Ridge failed spreading center, East Pacific Ocean (Vanko and Batiza, 1982; Batiza and Vanko, 1985), plutonic rocks were described that had been hydrothermally metamorphosed at temperatures as high as $600 \pm 100^\circ\text{C}$, corresponding to amphibolite-facies conditions. One interesting feature of these rocks is that the amphiboles are characterized by highly variable chlorine concentrations. The purpose of the present paper is to describe this occurrence of Cl-bearing amphiboles (with up to 4.0 wt.% Cl and <0.2 wt.% F) in metagabbros, diabase, and amphibolites from the Mathematician Ridge, and to explore the question of variable chlorine fixation in the ocean crust as a result of variations in hydrothermal systems. A significant gap in our knowledge of amphibole mineralogy arises, to wit, how does the chlorine content of amphibole depend upon temperature, pressure, and compositional parameters of the coexisting fluid? At present, this question may be answered only in very general terms. A related general question is, are there significant variations in the chlorinity of hydrothermal fluids that are now evidenced by anomalous chlorine concentrations in altered ocean crust? Based on the assumption that high-chlorine fluids

give rise to Cl-rich amphiboles, the available chemical data on oceanic amphiboles suggest that there are significant variations.

Measured chlorine concentrations in the amphiboles of coarse-grained oceanic rocks have been reported in several previous studies. Examples are from St. Paul's Rocks, a fracture zone exposure in the Atlantic Ocean (Melson et al., 1972; Jacobson, 1975); the Romanche Fracture Zone (Honnorez and Kirst, 1975); a DSDP hole near the mid-Atlantic Ridge (Hodges and Papike, 1976); Gettysburg Bank, in the Atlantic Ocean (Pritchard and Cann, 1982); and the Mid-Cayman Rise, Caribbean Sea (Ito and Anderson, 1983). Representative microprobe analyses of some of those amphiboles are listed in Table 8 of Ito and Anderson (1983). In addition, there are some studies of coarse-grained, amphibole-bearing oceanic rocks that report chlorine as undetected in some amphiboles, and other studies that did not entail analyses for chlorine at all. The data presented in this paper show that aluminous amphiboles (hornblendes) in Mathematician Ridge rocks presumably altered by seawater-derived fluids generally contain a background level of several tenths of a weight percent chlorine. Anomalous chlorine concentrations, from about 1 to 4 wt.% Cl, probably represent the products of alteration by anomalously saline hydrothermal fluid.

Analytical methods

Amphiboles in Mathematician Ridge samples were analyzed with a JEOL 733 electron microprobe at Washington University in St. Louis. The eleven element analyses were performed under the following operating conditions: 15 kV accelerating voltage, 25 to 30 nA cup current, 1 to 2 μm spot diameter. Data reduction was accomplished by a Bence-Albee type method modified slightly from software supplied by Tracor Northern, Inc. Under the routine operating conditions, the detection limit for halogens was: Cl 0.015 wt.%, and F 0.24 wt.%. These limits are the concentration equivalent of three times the square root of background counts.

X-ray maps for chlorine were used to identify anomalously Cl-rich amphiboles, whereupon precise analyses of Cl and F were obtained by increasing the cup current (to 250 nA) and the counting times (to 60 sec. on peak; 30 sec. at each of two background positions). The resulting detection limits were typically 0.003 wt.% Cl, and 0.07 wt.% F. Data were accumulated on three spectrometers simultaneously: fluorine on one spectrometer using a TAP crystal, and chlorine on two spectrometers, each using a PET crystal. The two Cl spectrometers provided an immediate check, and in most cases the results overlapped at the ± 1 st. dev. level.

The standard used for fluorine was a tremolite containing nominally 1.90 wt.% F. The standard used for chlorine was a scapolite with nominal 1.43 wt.% Cl. A check on the scapolite standard was made using halite as a primary standard. Analyzed as an unknown, data from both Cl spectrometers indicated that the scapolite contains 1.45 ± 0.02 wt.% Cl.

Amphibole analyses ($n = 125$; available by request to the author) were recalculated using a procedure (summarized by Robinson et al., 1982) that assigns cations to crystallographic sites in a variety of ways. By assuming that the cation sum, minus Na and K, equals 15.0, the recalculation results in all Na and K being forced into the A site. This method yields acceptable formulas

for actinolite (Anl. 10 and 11, Table 1). For hornblendes, the sum of cations excluding Na, K, and Ca, is assumed to equal 13.0. This method results in a partitioning of Na, K and Ca between the A and B(M4) sites, and consistently yields acceptable hornblende formulas. Alternate recalculations that were attempted yielded unrealistic $\text{Fe}^{2+}/\text{Fe}^{\text{TOTAL}}$ ratios of nearly zero or nearly one. In some studies comparing recalculated analyses with chemical analyses, the "13eCNK" procedure used here was found to be the best for rocks saturated in epidote as well as hornblende (Robinson et al., 1982), as is true for most of the Mathematician Ridge metagabbros.

Sample location

Two dredges of the axial rift valley walls of the Mathematician Ridge recovered plutonic and metamorphic rocks, as well as basaltic rocks. Dredge locations and sample descriptions are given by Vanko and Batiza (1982), and more petrologic data and interpretations are being presented elsewhere (Batiza and Vanko, 1985). In the region of the two dredges (around 17°N), the Mathematician Ridge spreading center was abandoned about 6.5 Ma, and spreading has now been taken up by the East Pacific Rise.

Sample descriptions

Gabbroic rocks from the Mathematician Ridge range from fresh, nearly anhydrous types with igneous textures to variably foliated types that are lightly to heavily amphibolitized. Associated amphibolites containing no relict igneous phases are considered to have formed from a gabbroic protolith (Vanko and Batiza, 1982). Short descriptions of the five samples whose halogen contents were studied in detail are given below. Sample 8-24 is a meta-gabbro with greenschist-facies mineralogy, sample 7-37 is an amphibolite-facies metagabbro, samples 7-41 and 7-45 are retrograded amphibolites, and sample 8-9 is a greenschist-facies metadiabase.

Greenschist-facies metagabbro

This metagabbro (sample 8-24) has a clearly relict gabbroic texture of plagioclase tablets about 3-mm-long and similarly-sized crystals and clots of amphiboles. The plagioclase is mostly unzoned An_{60} , and is heavily veined by late stage (secondary) albite of composition An_{10} . The amphiboles are mostly actinolite with relict magnesiohornblende (Table 1, analyses 9 and 10), using the terminology of Leake (1978). They are pleochroic from light green to light brown, contain numerous dusty inclusions, and commonly contain a number of optically continuous islands of relict igneous clinopyroxene of composition $\text{Wo}_{44}\text{En}_{38-40}\text{Fs}_{16-18}$. As the amphibole commonly encloses plagioclase, one can assume that the original gabbro had a subophitic texture. Other secondary minerals in the sample, particularly concentrated in a secondary "patch" of bladed actinolite and interstitial albite, include epidote (Ps_{21-23}), apatite, analcime, titanite and ilmenite.

The halogen contents of several amphiboles from 8-24 range from undetectable to about 0.5 wt.% Cl and generally undetectable F (Table 2). The larger actinolic hornblendes that have replaced clinopyroxene are the chlorine-

Table 1. Representative electron microprobe analyses of amphiboles

Anl. # Sample #	1 7-41	2 7-41	3 7-41	4 7-45	5 7-45	6 7-45	7 7-37	8 7-37	9 8-24	10 8-24	11 8-9
SiO ₂	49.32	41.93	37.17	45.74	44.53	50.28	45.28	44.22	49.99	52.38	51.42
TiO ₂	0.06	1.21	0.18	1.65	1.65	0.83	0.36	2.22	0.69	0.18	0.47
Al ₂ O ₃	3.38	9.63	14.57	9.14	10.55	5.38	8.11	8.76	5.40	2.41	3.52
FeO ^I	24.52	23.42	27.63	14.70	14.17	13.39	24.51	18.27	14.98	18.60	15.69
MnO	0.49	0.20	0.21	0.24	0.26	0.29	0.18	0.26	0.08	0.19	0.28
MgO	7.74	7.64	3.14	13.41	13.63	15.94	7.01	10.73	13.79	11.91	14.81
CaO	12.04	10.96	11.08	11.13	11.08	10.76	11.85	10.51	12.58	12.11	11.13
Na ₂ O	0.15	2.08	2.94	2.13	2.10	1.29	0.96	2.55	0.74	0.24	0.64
K ₂ O	0.02	0.11	0.36	0.07	0.06	0.04	0.07	0.10	0.06	0.06	0.09
Cl	0.02	1.01	3.16	0.33	0.26	0.12	0.12	0.50	n.d.	n.d.	n.d.
F	<0.24	<0.24	<0.24	<0.22	<0.22	<0.22	<0.22	<0.22	n.d.	n.d.	n.d.
-O=Cl,F	0.00	0.23	0.71	0.07	0.06	0.03	0.03	0.11	--	--	--
Total	97.74	97.96	99.73	98.47	98.23	98.29	98.42	98.01	98.31	98.08	98.05
Atom Proportions*											
Si	7.472	6.387	5.860	6.589	6.390	7.070	6.828	6.554	7.219	7.718	7.468
Al ^{IV}	.528	1.613	2.140	1.411	1.610	.930	1.172	1.446	.781	.282	.532
Al ^{VI}	.076	.117	.570	.142	.175		.270	.085	.138	.137	.071
Fe ³⁺	.482	1.005	.813	.868	1.077	1.190	.697	.776	.382	.025	.162
Ti	.007	.139	.021	.179	.178	.088	.041	.247	.075	.020	.051
Mg	1.748	1.734	.738	2.879	2.915	3.340	1.575	2.370	2.968	2.615	3.206
Fe ²⁺	2.625	1.979	2.830	.903	.624	.384	2.393	1.488	1.427	2.202	1.511
Mn	.063	.026	.028	.029	.032	.035	.023	.033	.010		
Fe ²⁺										.064	.234
Mn										.024	.034
Ca	1.954	1.789	1.872	1.718	1.704	1.621	1.915	1.669	1.946	1.912	1.732
Na	.044	.211	.128	.282	.296	.352	.085	.331	.054		
Na		.403	.771	.313	.288		.195	.402	.154	.069	.180
K	.004	.021	.072	.013	.011	.007	.013	.019	.011	.011	.017
Cl	.005	.261	.844	.081	.063	.029	.031	.126	--	--	--

1. n.d. = not determined.

2. Analyses 1-3: mottled amphiboles (actinolite, hornblende, and hastingsite, respectively) with variable chlorine. Analyses 4-6: mottled hornblendes with similar chlorine contents. Analysis 7: from a thin zone of blue ferro-hornblende that flanks a microfracture through brown hornblende. Analysis 8: brown hornblende. Analyses 9-10: magnesio-hornblende and actinolite, respectively. Analysis 11: actinolite.

3. For the maximum of 4.02 wt. % Cl (see table 2), the number of Cl in the anion position is about 1.1, or more than 50% of the anion site.

*Distribution of atoms calculated assuming that their sum, minus Ca, Na and K, equals 13.00. Analyses 10 and 11 were calculated assuming that the cation sum, minus Na and K, equals 15.00, forcing all Na and K into the A site. See text for details and justification.

bearing ones, whereas smaller grains and irregular areas of actinolite within the larger actinolitic hornblende grains are chlorine-poor.

Amphibolite-facies metagabbro

This metagabbro (sample 7-37) is strongly foliated, typical of dozens of metagabbros from the Mathematician Ridge collection (Batiza and Vanko, 1985). Plagioclases are up to 6 mm long and are essentially unzoned An₃₂₋₃₇. They typically have wavy extinction, are partially surrounded by smaller anhedral plagioclase grains, and exhibit limited stress-induced twin lamellae. Relict igneous clinopyroxene grains, surrounded by and including horn-

blende alteration, are unzoned Wo₄₆₋₄₇En₃₇₋₃₆Fs₁₇. Most of the amphibole is pleochroic from deep brown to yellowish green, and ranges in composition from tschermakitic hornblende to magnesio-hornblende (Table 1, analysis 8). It forms elongate subhedral crystals preferentially oriented and segregated to define the foliation. Ilmenite forms grains interstitial to the amphibole. Late stage brittle deformation is indicated by numerous cracks in the amphiboles that cut across the foliation and are flanked on either side by an isopachous blue-green alteration zone of ferro-hornblende (Table 1, analysis 7). None of the common greenschist-grade alteration phases such as albite, epidote, or actinolite are present.

Table 2. Precise halogen content determinations

Sample No.	Wt. % F ¹	Wt. % Cl ²	Wt. % Cl ³	Avg. Wt. % Cl	Anl. #, Table 1	Remarks
7-41	<0.07	0.012	0.016	0.013	1	Cl-poor zone, fig. 2
	<0.07	2.86	2.84	2.85		Cl-rich zone, fig. 2
	0.12	3.42	3.58	3.50		do
	<0.07	4.02	4.02	4.02	2	do
	<0.07	1.13	1.12	1.13		do
	0.12	1.13	1.11	1.12	3	do
	<0.07	3.10	3.04	3.07		do
	<0.07	0.98	0.97	0.98		do
	n.d.	3.51	3.27	3.4		blue vein hastingsite, fig.1
	n.d.	0.96	0.94	0.95		do
	n.d.	3.17	3.17	3.17	do	
n.d.	3.44	3.36	3.40	do		
7-45	<0.07	0.353	0.340	0.348	4	brown hornblende
	0.07	0.287	0.277	0.284	5	do
	<0.07	0.324	0.332	0.326	6	do
	<0.07	0.144	0.142	0.143		do
	<0.07	0.361	0.348	0.357		do
<0.07	0.476	0.458	0.469	do		
7-37	0.15	0.152	0.164	0.156	7	blue ferro-hornblende
	0.21	0.137	0.142	0.139		do
	0.11	0.552	0.555	0.553	8	brown hornblende
	0.08	0.485	0.490	0.487		do
	0.10	0.569	0.575	0.572		do
8-24	<0.07	0.147	0.141	0.145	9,10	brown-green actinolitic hornblende
	<0.07	0.168	0.165	0.167		do
	0.12	0.323	0.314	0.319	do	uralite, in clinopyroxene
	0.12	0.335	0.322	0.329		do
	<0.07	0.007	0.006	0.007	do	smaller grain of actinolite
	<0.07	0.004	0.008	0.006		do
	<0.07	0.491	0.463	0.477	do	Cl-bearing area
	<0.07	0.499	0.478	0.489		do
<0.07	0.007	<0.006	<0.006	adjacent Cl-free area		
8-9	n.d.	0.013	0.008	0.011	11	actinolite
	n.d.	0.009	0.003	0.006		do
	n.d.	2.280	2.264	2.274	do	Cl-rich area, fig. 3
	n.d.	3.021	2.979	3.000		do
	n.d.	0.165	0.167	0.166	do	Cl-poor area, fig. 3
	n.d.	0.112	0.111	0.112		do
KAK Hb	0.13	0.025	0.023	0.024		see note 5

1. TAP crystal, gas flow detector.

2. PET crystal, sealed detector.

3. PET crystal, gas flow detector.

4. n.d. = not determined.

5. Kaersutite from Kakanui, New Zealand; this standard is available in many electron microprobe laboratories. Fluorine is ± 0.08 wt. %, chlorine is ± 0.01 wt. %.

Halogen contents for 7-37 hornblendes range from 0.1 to 0.6 wt.% Cl, with up to 0.2 wt.% F (Table 2). Neither Cl-free nor anomalously Cl-rich areas were apparent in Cl X-ray maps from this sample.

Amphibolite 7-41

This amphibolite has a relict gabbroic texture and contains a 10- to 20-mm-wide planar zone of amphibolite breccia in a quartz and epidote matrix. Clasts in the brecciated portion are sub-rounded and up to 5 mm in diameter, and are made predominantly of actinolite (Table 1, analysis 1), relict calcic plagioclase and hornblende (Ta-

ble 1, analysis 2), chlorite, opaques (Mn-ilmenite with rods and granules of magnetite), and epidote (Ps₂₅₋₂₈). The quartz-epidote matrix also contains minor actinolite and rare interstitial Cu-Fe-S sulfides. Fluid inclusions are abundant in the quartz grains, and many primary fluid inclusions contain daughter crystals of halite, indicating that a saline fluid was present at the time of quartz growth.

Preliminary fluid inclusion microthermometry (Vanko and Stakes, 1985; and manuscript in preparation) indicates that the quartz-epidote vein matrix grew initially in the presence of dense saline fluids (around 50 wt.% NaCl equivalent) in the temperature range 400–500°C. Subse-

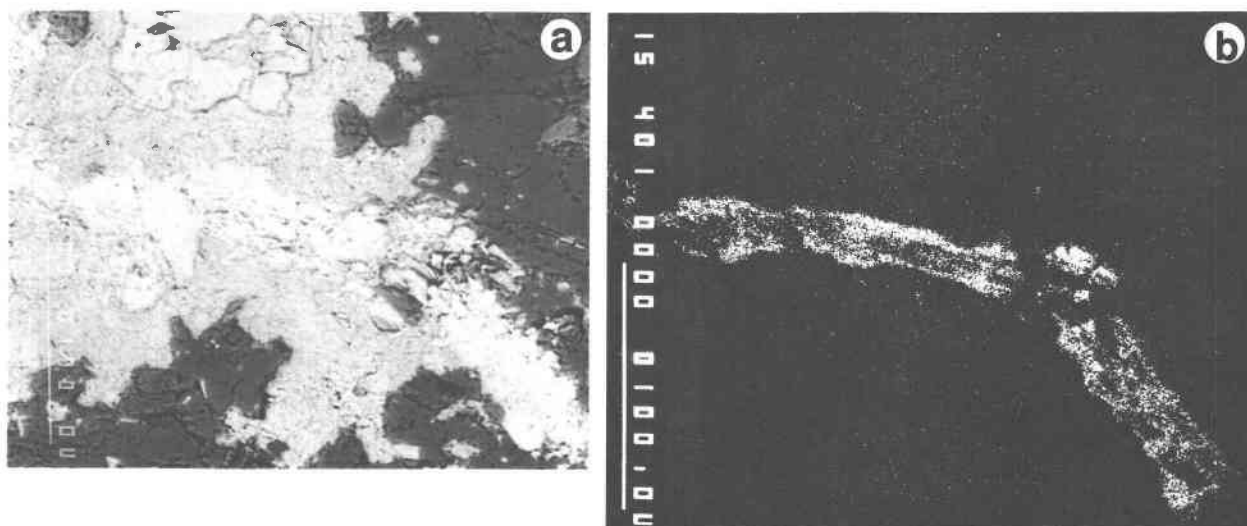


Fig. 1. Two images of the same area of sample 7-41, showing a thin vein of amphibole (hastingsite), blueish in transmitted light, set in a mat of chlorite. This area is part of a small clast in a quartz-epidote-hosted breccia. (A) Backscattered electron image: amphibole vein is bright, chlorite is slightly darker, grain of epidote is partially shown at top, and quartz is dark grey. Scale bar is 100 μm long. (B) X-ray map for Cl shows high Cl concentration within hastingsite vein (maximum 3.40 wt.% Cl, see analyses in Table 2).

quently, fluids of near-seawater salinity were trapped as secondary fluid inclusions along healed fractures in the quartz. The homogenization temperatures of these secondary inclusions cluster around 350°C, and range from 360 to 150°C.

The halogen contents of amphiboles in 7-41 range from 0.1 to 4.0 wt.% Cl, with uniformly low F (Table 2). As shown in Figures 1 and 2, chlorine-rich zones of amphibole are very small, extremely irregular and patchy

with respect to the chlorine-poor zones. In one instance, the amphibole with Cl-rich areas comprises a late-stage blueish colored (in plane light) vein, set in chlorite, that reaches into an amphibolite clast from the quartz-epidote matrix (Fig. 1). The amphibole here and in other examples is too small to determine detailed optical properties. By microprobe analysis, and assuming a large amount of ferric iron (consistent with the abundant epidote present), the amphibole is a hastingsite (Table 1, analysis 3). In a

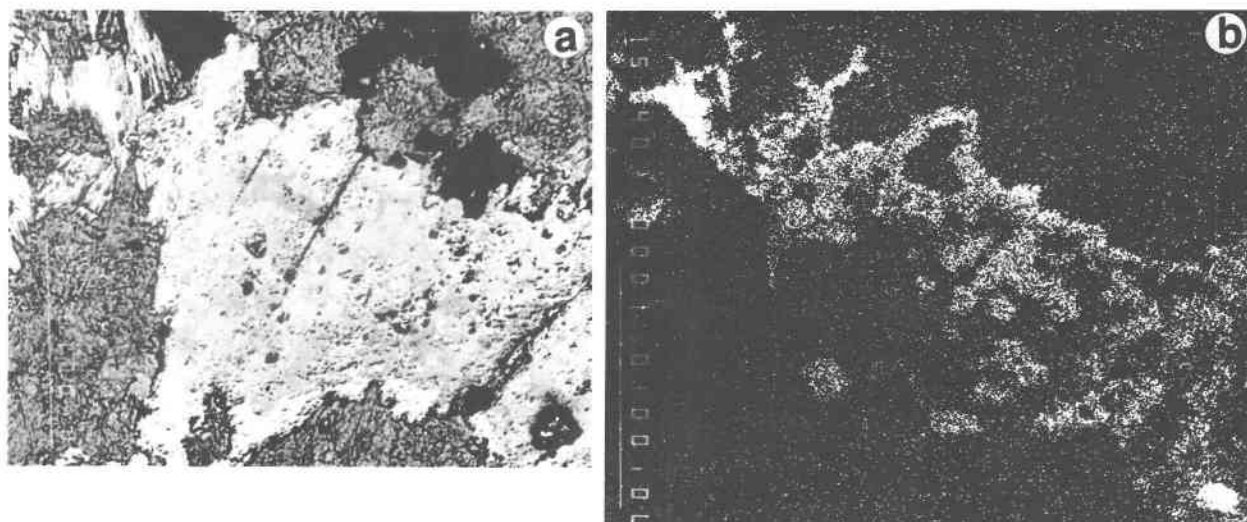


Fig. 2. Backscattered electron image and X-ray map for identical areas of sample 7-41. Scale bar is 100 μm long. (A) Bright grains are actinolite with mottled zoning; see analyses in Table 1. Grey areas are chlorite patches. Black areas are holes. A fragment of dust is present in the lower right hand corner of the image. (B) X-ray map reveals irregular zones of Cl-rich hastingsite (maximum 4.02 wt.% Cl, see analyses in Table 2) within the actinolite. The dust particle at lower right appears bright, probably due to fluorescence or an intense continuum (bremsstrahlung).

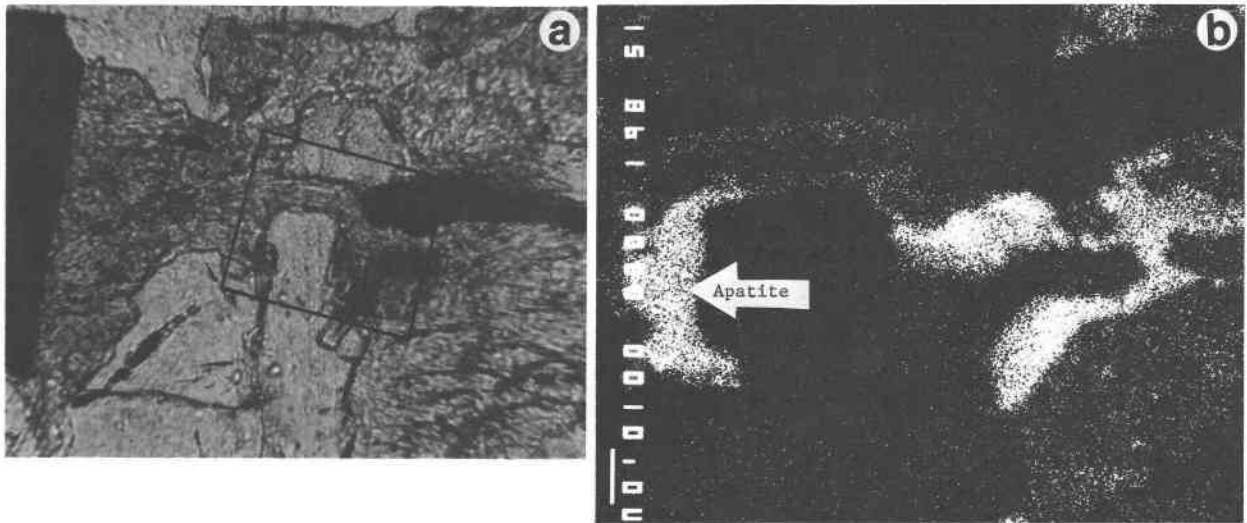


Fig. 3. Two images of the same area of sample 8-9. Scale bar is 100 μm long. Box in 3a outlines area of Fig. 3b. (A) Photomicrograph in plane-parallel light. The clear grains are plagioclase, the darker areas are amphibole, and the opaque grains are ilmenite. (B) X-ray map for Cl shows the distribution of Cl-rich (hastingsite) and Cl-poor (actinolite) amphibole (maximum 3.0 wt.% Cl, see analyses in Table 2), as well as Cl-rich apatite.

second case, Cl-rich amphibole occurs as irregular zones in a 0.1-mm-diameter anhedral flake of actinolite, which is surrounded by chlorite (Fig. 2). This example is from a polished rock chip, so no optical properties were determined.

Amphibolite 7-45

This amphibolite contains hornblende of variable composition, ranging from more aluminous tschermakitic hornblende to less aluminous actinolitic hornblende (Table 1). Plagioclase is absent, and scant opaques consist of intergrowths of ilmenite, titanite, and a pure TiO_2 phase. The sample is a breccia with a network of quartz veins that contain minor euhedral grains of titanite and subhedral amphibole. The quartz veins contain saline fluid inclusions, many of which appear primary and contain one, or rarely two, solid daughter crystals, most commonly halite. Despite this evidence for the presence at some time of very saline fluids, hornblendes in 7-45 seem to contain a fairly uniform content of a few tenths of a percent chlorine (Tables 1, 2).

Greenschist-facies metadiabase

This metadiabase (sample 8-9) contains abundant plagioclase tablets less than 0.5 mm in length in a subophitic texture with clinopyroxene. Several larger plagioclase crystals, from about 1.0 to 2.5 mm in length, are also present. Plagioclase compositions are normally zoned, ranging from An_{59} to An_{48} , and abundant albite (An_{07}) occurs in irregular mottled areas throughout the plagioclases. These areas have no apparent relation to visible intragrain fractures or cleavage. The larger plagioclases have rounded central core zones, and thick, strongly zoned mantles. Clinopyroxene is variable $\text{Wo}_{37-41}\text{En}_{42-49}\text{Fs}_{10-20}$,

and is extensively altered, particularly on the edges, to actinolite (Table 1). Other phases present are prehnite, chlorapatite, and magnetite.

Chlorine concentrations in the actinolite of 8-9 are generally very low—about 0.01 wt.% Cl. However, zones of Cl-rich hastingsite, with up to 3.0 wt.% Cl, occur along with chlorapatite in trace amounts (Table 2, Fig. 3).

Conditions of formation of Cl-bearing amphiboles

Dredged samples from the Mathematician Ridge contain mineral assemblages that represent a wide range of physical-chemical conditions, from fresh, nearly anhydrous gabbros to highly altered greenschists. We have interpreted these rocks as the products, at a failing spreading center, of the following processes (Vanko and Batiza, 1982; Batiza and Vanko, 1985):

Gabbros were emplaced, with some of them obtaining a cumulus texture, at magmatic temperatures probably around 1100–1200°C (typical MORB liquidus temperatures). Some of these gabbros experienced only slow anhydrous cooling, with little or no subsequent alteration. These gabbros were apparently unaffected by a mid-ocean ridge hydrothermal system; however, this is presently being tested using oxygen isotopic determinations because even optically fresh igneous minerals may be isotopically modified (e.g., Stakes et al., 1984). Certain of the gabbros were hydrated and deformed in a ductile fashion, at temperatures on the order of 600°C (Batiza and Vanko, 1985) resulting in foliated metagabbros and amphibolites having a typical amphibolite-facies assemblage of calcic plagioclase and hornblende. Sample 7-37, described above, is an example of this. However, almost all samples contain evidence of further retrograde reactions. For instance, 7-37 contains evidence of brittle deformation in the form of

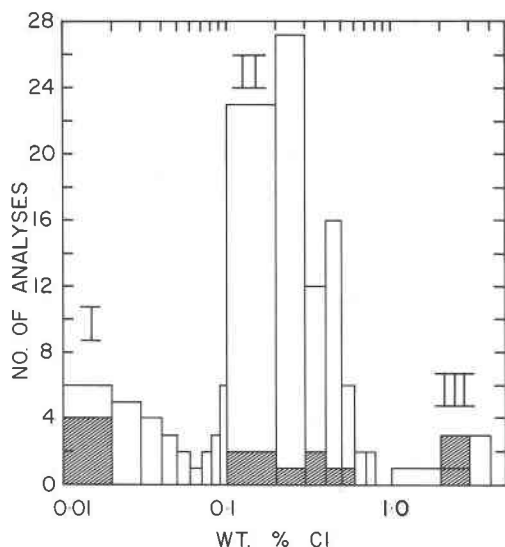


Fig. 4. Histograms of chlorine contents in amphiboles from Mathematician Ridge plutonic rocks. Note the logarithmic abscissa. The open bars are for all routine amphibole analyses performed ($n = 125$). The shaded bars are for the *average* chlorine concentration of different amphibole types in the five samples listed in Table 2 (data from Table 2, $n = 14$). In both cases, a trimodal distribution is indicated.

cracks with flanking alteration zones cutting across the foliation. Retrograde reactions, commonly incomplete, formed greenschist-facies minerals such as actinolitic hornblende and actinolite, albite, epidote and chlorite in many samples. Samples 8-24, 8-9, and 7-41 contain these phases, probably formed at a few hundred degrees centigrade. Brittle deformation is seen in the breccias, 7-41 and 7-45, as quartz and quartz-epidote veins were formed within brecciated zones.

Thus, the Mathematician Ridge samples record variations in the effect of hydrothermal activity ranging from no alteration (equals vanishingly small W/R ratio) to high temperature (600°C) hydration and lower temperature (greenschist) alteration. The problem at hand is to determine how the chlorine-bearing amphiboles fit into this general picture of varying hydrothermal system parameters. A histogram of analyzed concentrations (Fig. 4) shows clearly a trimodal distribution, whether one plots the Cl concentration from all routine microprobe analyses ($n = 125$, from Table 1 and unpublished data), or a less-weighted data set such as the average Cl concentration of different grain types from the five samples described above ($n = 14$, from Table 2, remarks). Invariably, the low chlorine amphiboles (mode I in Fig. 4) are actinolite, whereas the common, typical brown hornblendes and actinolitic hornblendes contain 0.1 to 0.6 wt.% Cl (mode II in Fig. 4). Data from the most common metamorphic (or hydrothermal) amphiboles thus suggest that higher temperatures promote the formation of hornblendes containing a few tenths of a percent chlorine, but that lower temperatures favor formation of low-Cl actinolite.

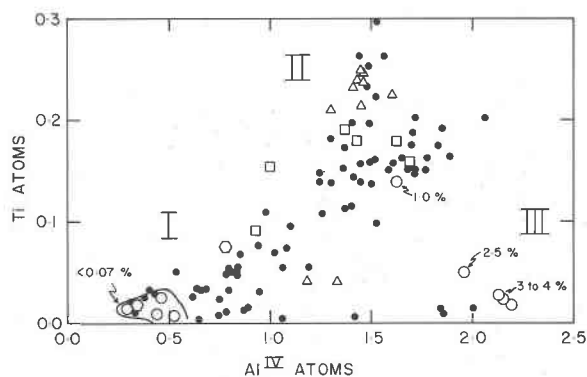


Fig. 5. Plot of atomic Ti vs. tetrahedral Al in analyzed Mathematician Ridge amphiboles. Analyses from the samples described in the text are shown by large open symbols: circles: 7-41; squares: 7-45; triangles: 7-37; hexagons: 8-24. Small solid dots represent all other samples (unpublished data). Numbers indicate the weight percent chlorine in the 7-41 amphiboles. Note that high-Cl amphiboles do not follow the general trend of Ti-Al-Cl concentrations established by most of the other amphiboles. See text for discussion.

A graph of Ti versus tetrahedral Al in amphiboles can, in many cases, be used to ascertain qualitatively the metamorphic grade of the host rock (e.g., Raase, 1974; Robinson et al., 1982). This applies to most Mathematician Ridge amphiboles (Fig. 5), as low-grade actinolites have lower Ti and Al^{IV} , and higher grade hornblendes have higher Ti and Al^{IV} . In general, plotting the amphibole analyses from a particular rock on this, or one of a number of related diagrams, allows one to determine the metamorphic grade, and the result is normally consistent with the other mineralogical and deformational features of the rock in question. However, the high chlorine amphiboles from sample 7-41 violate the simple trend established for lower Cl amphiboles, and one cannot simply "read off" the metamorphic grade of a high Cl amphibole (Fig. 5). Nonetheless, it is clear from the descriptions given above that the occurrence in samples 7-41 and 8-9 of high-chlorine hastingsite with actinolite and other greenschist-grade minerals suggests that the high Cl amphibole forms at relatively low temperature. This notion contradicts the earlier conclusion derived from the observation that amphibolite-grade hornblendes contain a few tenths of a percent chlorine, whereas greenschist-grade actinolite contains very little or undetectable chlorine. Therefore, the presence of high-chlorine greenschist-grade hastingsite requires not a different temperature but probably a different Cl (or NaCl) activity in the coexisting hydrothermal fluid.

Several authors have suggested that a structural control exists on the chlorine content of hornblende and actinolite (Ito and Anderson, 1983; Volfanger et al., 1985). Volfanger et al. (1985) suggest that significant increases in the degree of replacement of OH^- must be accompanied by either an increase in large octahedral cations (particularly Fe^{2+}), or in small tetrahedral cations (Si rather than Al). On the other hand, Ito and Anderson (1983) favor the notion that

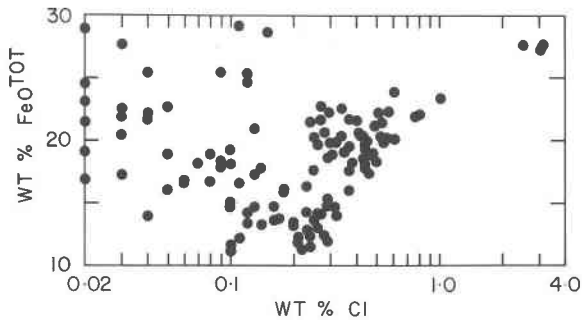


Fig. 6. Plot of $\text{FeO}^{\text{TOTAL}}$ vs. chlorine concentration in routinely analyzed Mathematichian Ridge amphiboles (unpublished data). Note the logarithmic abscissa.

a coupled substitution of Al^{3+} into tetrahedral sites and Fe^{3+} into octahedral sites allows increased replacement of OH^- by Cl^- . Both schemes have the same effect of increasing the size of the cavity normally occupied by OH^- , so that Cl^- can be accommodated. Several examples of good correlations between Cl and Fe concentrations in actinolites and hornblendes are presented by Volfinger et al. (1985) and Ito and Anderson (1983).

A plot of Cl concentration vs. weight percent Fe (calculated as FeO) for 125 amphibole analyses from the Mathematichian Ridge (Fig. 6) shows a correlation between FeO^{T} and Cl at high Cl concentrations, but not at low Cl concentrations. In particular, actinolites and actinolitic hornblendes contain low Cl (less than 0.2 wt.%) at any FeO^{T} content, unlike the linear correlation that Volfinger et al. (1985) found for actinolites in the French Pyrenees. Furthermore, many iron-rich amphiboles (ferro-hornblendes) from the Mathematichian Ridge contain very low Cl. I conclude that for the Mathematichian Ridge, the Cl content of amphibole varies as a function of the Cl activity of coexisting hydrothermal fluid. This is not to suggest that structural controls are not present. It means instead that Cl^- does not simply replace OH^- whenever Fe is available in the fluid phase.

The presence of high-Cl amphiboles, the third mode in the trimodal distribution of Figure 4, suggests the former presence of a fluid which is certainly more saline than seawater-derived fluids sampled thus far from ocean hydrothermal systems. Analyzed samples range from near-seawater chlorinity to a value about 30% greater than seawater chlorinity (Edmond et al., 1979; Michard et al., 1984). A perplexing question that remains, and that cannot be adequately answered here, is whether the "common" Mathematichian Ridge hornblende, with a few tenths of a percent chlorine, also grew in the presence of a very saline fluid. If the fluid was simply modified seawater of near seawater chlorinity, then a few tenths of a weight percent chlorine should be considered "typical" for oceanic amphibole. On the other hand, perhaps the "common" hornblende also grew from a saline hydrothermal fluid. If so, then rocks from the Cayman Trough (Ito and Anderson, 1983), Gettysburg Bank (Pritchard and Cann, 1982),

and St. Paul's Rocks (Melson et al., 1972) also represent products of saline hydrothermal systems. More work is needed, both analytical and perhaps experimental, to interpret these results further.

Implications of saline ocean hydrothermal systems

Although not yet observed in modern hydrothermal systems in the oceans, the considerations above suggest that saline hydrothermal fluids occur in some ocean hydrothermal systems on a scale that remains unknown. In the ocean crust, two possible mechanisms to generate saline hydrothermal fluid exist: (1) a residual Cl-enriched fluid forms as crustal rocks are hydrated under low W/R conditions, and (2) in situ phase separation (boiling or condensation) of hydrothermal fluid forms a water-rich vapor and a Cl-rich condensed fluid (e.g., Delaney et al., 1982; Vanko and Bishop, 1982; Gallinatti, 1984). Alternatively, some chlorine could be magmatic in origin, being enriched either in areas of advanced igneous differentiation such as in the vicinity of failed rifts (Vanko and Batiza, 1982), propagating rifts (Christie and Sinton, 1981), and ridge-transform intersections (e.g., Stroup and Fox, 1981), or in areas where the mantle source region is volatile enriched (Schilling et al., 1978, 1983). In the present case, however, oxygen isotopic analyses (Stakes and Vanko, 1984) point undeniably to seawater as the agent of hydration and metamorphism at the Mathematichian Ridge. The distribution of high-chlorine hydrothermal systems is important in determining the distribution and amount of chlorine fixed within the ocean crust (Ito et al., 1983). High-chlorine hydrothermal fluids may in some circumstances efficiently transport certain dissolved elements as chloride complexes (e.g., Chou and Eugster, 1977; Frantz et al., 1981; Susak and Crerar, 1985). Finally, variation in the rate of Cl fixation in the ocean crust could cause variation in ocean salinity with time.

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