

Cl-BEARING AMPHIBOLE IN THE SALTON SEA GEOTHERMAL SYSTEM, CALIFORNIA

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ABSTRACT

Calcic amphiboles with up to 2.7 wt.% Cl occur in metasandstones, metabasites and veins at depths between 3,100 to 3,180 m and temperatures in excess of 350°C in the State 2-14 well of the Salton Sea geothermal system (California). These amphiboles were formed by reactions involving high-salinity geothermal fluids, with 15.4 to 19.7 wt.% total dissolved Cl. Coexisting phases include quartz, plagioclase, K-feldspar, epidote, clinopyroxene, apatite, and titanite. The Cl-bearing amphiboles range in composition from hastingsitic (Cl > 1 wt.%) to actinolitic (Cl < 0.5 wt.%). Texturally complex intergrowths of actinolitic and hastingsitic amphiboles occur at depths greater than 3,140 m, suggesting a miscibility gap between the two amphiboles. Measured compositional variations suggest a crystal-chemical control on the Cl content in the calcic amphiboles: (1) the chlorine content of amphiboles increases with increasing edenite substitution $\{^{[4]}(\text{Na,K})^{[4]}\text{Al}_{\square-1}\text{Si}_{-1}\}$; (2) the maximum observed Cl content of an amphibole increases with increasing $X(\text{Fe}^{2+})$ value. Comparison of Cl content in amphiboles from the Salton Sea geothermal system, submarine metabasites, skarns, high-grade metamorphic rocks and igneous rocks implies that a main factor in controlling Cl-for-OH substitution in amphibole is different in low- and high-chlorinity environments. In low-chlorinity environments, the Cl content of an amphibole increases with increasing chlorinity of the coexisting fluid, and is defined by partitioning of Cl between the two phases, as well as the crystal-chemical constraints imposed by (Na+K), Fe, and Al substitution. On the other hand, amphiboles coexisting with the Salton Sea and more saline fluids are enriched in Cl; Cl content strongly depends on $X(\text{Fe}^{2+})$ and the edenite content of the amphiboles. They may achieve a maximum Cl content, and the extent of Cl-for-OH substitution is crystal-chemically controlled.

Keywords: Cl-bearing amphibole, crystal chemistry, salinity, geothermal system, Salton Sea, California.

SOMMAIRE

Nous trouvons des amphiboles calciques ayant des teneurs en Cl jusqu'à 2.7% (poids) dans des grès métamorphisés, des metabasites, et des veines à profondeur, entre 3100 et 3180 m, et à des températures au dessus de 350°C dans le puits State 2-14 du système géothermique de la mer de Salton (Californie). Ces amphiboles ont été formées par réaction impliquant des saumures géothermiques, à salinité entre 15.4 et 19.7% en Cl dissout. Sont aussi présents quartz, plagioclase, feldspath potassique, épidote, clinopyroxène, apatite et titanite. Les amphiboles chlorifères ont une composition hastingsitique (>1% en poids de Cl) à actinolitique (< 0.5% de Cl). Une intercroissance complexe des deux amphiboles, rencontrées à une profondeur au delà de 3,140 m, témoignerait de l'importance d'une lacune de miscibilité entre les deux amphiboles. Les variations mesurées en teneur en Cl seraient régies par des contraintes cristalochimiques: (1) la teneur des amphiboles en chlore augmente avec l'importance d'une substitution vers le pôle édenite $\{^{[4]}(\text{Na,K})^{[4]}\text{Al}_{\square-1}\text{Si}_{-1}\}$, et (2) la teneur maximum observée en Cl augmente avec $X(\text{Fe}^{2+})$. Une comparaison de la teneur en Cl des amphiboles provenant du système géothermique de la mer Salton, des metabasites, des skarns, des roches métamorphisées à un facies élevé, et des roches magmatiques indique qu'un facteur différent régit la substitution du Cl dans des milieux à chlorinité faible et élevée. Dans un milieu à faible chlorinité, la teneur d'une amphibole en Cl augmente avec la chlorinité de la phase fluide coexistante, et dépend de la répartition du Cl entre les deux phases, et des contraintes cristalochimiques dues à l'incorporation de (Na+K), Fe *et al.* D'autre part, les amphiboles qui coexistent avec les saumures de la mer Salton et des saumures encore plus salines sont enrichies en Cl; leur teneur en Cl dépend de $X(\text{Fe}^{2+})$ et de la teneur en édenite. Elles peuvent atteindre la saturation en Cl, et la portée de la substitution du Cl au OH est ici régie par des contraintes cristalochimiques.

(Traduit par la Rédaction)

Mots-clés: amphibole chlorifère, chimie cristalline, salinité, système géothermique, mer de Salton, Californie.

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INTRODUCTION

High concentrations of Cl in calcic amphiboles have been reported from various rock-types: submarine metabasite, skarn, amphibolite, granulite, granitic and gabbroic rocks, but the conditions necessary for the formation of Cl-rich amphiboles are not well understood (see review by Suwa *et al.* 1987). Determination of Cl partitioning between calcic amphibole and a coexisting fluid is important for evaluating the geological cycling, amount and distribution Cl in the Earth's crust.

Relationships between Cl content and the major-element chemistry of amphiboles on one hand, and Cl content of the coexisting fluid have been discussed by many authors. Volfinger *et al.* (1985) and Kamineni (1986) emphasized that Cl content of a calcic amphibole increases with increasing of Fe²⁺. Ito & Anderson (1983) studied calcic amphibole in metamorphosed gabbros from the Mid-Cayman Rise and considered that Al substitution at tetrahedral sites allows increasing substitution of Cl for OH. These authors emphasized a crystal-chemical control of Cl content in amphibole. On the other hand, Vanko (1986) concluded that the Cl content of amphibole from the Mathematician Ridge varies as a function of the Cl activity of coexisting hydrothermal fluid, and pointed out that Cl does not simply replace OH wherever Fe is available in the fluid phase. Vanko (1986) also showed that some amphiboles in greenschists from the Mathematician Ridge are more Cl-rich than those in amphibolites. These observations and occurrences of Cl-rich amphibole in igneous rocks (*e.g.*, Kamineni 1986) and high-grade metamorphic rocks (*e.g.*, Sharma 1981) suggest that Cl substitution for OH in calcic amphiboles can occur over wide range of pressure, temperature, and fluid composition.

The Salton Sea Scientific Drilling Project successfully drilled Colorado River sediments within the Salton Sea geothermal system to a depth of 3,220 m, where temperatures exceed 350°C. Hydrothermal solutions of the Salton Sea geothermal system are NaCl-rich brines with Cl contents of approximately 15 wt.% (White 1968). Fluid inclusions within anhydrite contain up to 50% crystals of halite, sylvite and carbonates in a Na-Ca-K-Cl brine (*e.g.*, White 1968, McKibben *et al.* 1987). During the course of our study of amphibolite-facies mineral assemblages within core and chip samples of the State 2-14 well, we identified and analyzed grains of Cl-rich (up to 2.7 wt.%) calcic amphibole in hydrothermally altered metasandstones, metabasites and veins at depths greater than 3,140 m. To our knowledge, this is the first description of Cl-rich amphibole from an active geothermal system. In this paper, we report the chemical characteristics of the Cl-bearing amphibole from the State 2-14 well, and discuss the crystallographic constraints of Cl substitution in calcic amphibole in geothermal, metamorphic, and igneous environments.

GEOLOGICAL SETTING
AND PETROGRAPHIC DESCRIPTION

The Salton Sea geothermal system lies near the southeastern end of the Salton Sea, within the Salton Trough of southern California, which is the landward extension of the Gulf of California Rift system (White *et al.* 1963, Helgeson 1968). The high-temperature (>350°C) and high-salinity brine (> 15 wt.% total dissolved solids) is responsible for crystallization of silicate, sulfide, and oxide minerals throughout the geothermal system. Muffler & White (1969) and McDowell & Elders (1980) described greenschist-facies metamorphism occurring at temperature above 300°C at 2-3 km depth. On the basis of mineral parageneses in metasandstones from the Elmore 1 well (*cf.* Fig. 1), three mineral zones were identified with increasing temperature, and are referred to as the chlorite, biotite, and garnet zones (McDowell & Elders 1980). These studies have shown dramatic mineralogical modifications of Colorado River delta sediments within and near the numerous thermal anomalies at the Salton Trough. In particular, systematic changes in mineralogy of authigenic layer silicates (McDowell & Elders 1980) and alkali feldspar (McDowell 1986) with increasing temperature suggest an approach to chemical equilibration between the authigenic minerals and the coexisting fluid phase in the geothermal system.

The State 2-14 well is located near the northeastern flank of the Salton Sea geothermal system (Fig. 1). Greenschist- and amphibolite-facies metamorphism accompanying hydrothermal metasomatism observed in metasandstone and metashale core samples have been reported by Cho *et al.* (1988) and Shearer *et al.* (1988). Parageneses of secondary minerals along veins and fractures have been extensively investigated (*e.g.*, Caruso *et al.* 1988, McKibben & Elders 1985, McKibben & Eldridge 1989).

On the basis of degree of hydrothermal alteration of metasandstone, three zones have been described with increasing depth and metamorphic temperature: chlorite-calcite (610-2,480 m), biotite (2,480-3,000 m) and clinopyroxene (3,000-3,220 m) zones. Characteristic assemblages of minerals of metasandstone, in addition to epidote, quartz, albite, apatite and titanite, are: chlorite + K-feldspar + phengitic mica + calcite for the chlorite-calcite zone, biotite + chlorite + K-feldspar for the biotite zone, and diopside + actinolite (or actinolitic hornblende) + K-feldspar + oligoclase for the clinopyroxene zone (Cho *et al.* 1988, Enami *et al.*, in prep.). Low-grade amphibolite-facies assemblages of minerals, including hastingsitic amphibole and andesine or more calcic plagioclase, occur in metasandstone, metabasite and veins at depths greater than 3,140 m in the clinopyroxene zone. A chain silicate with composition intermediate between actinolite and diopside (Ca-bearing pyribole) was reported in a sample from the lowest-grade part of the clinopyroxene zone (Cho *et al.* 1988). A garnet-bearing

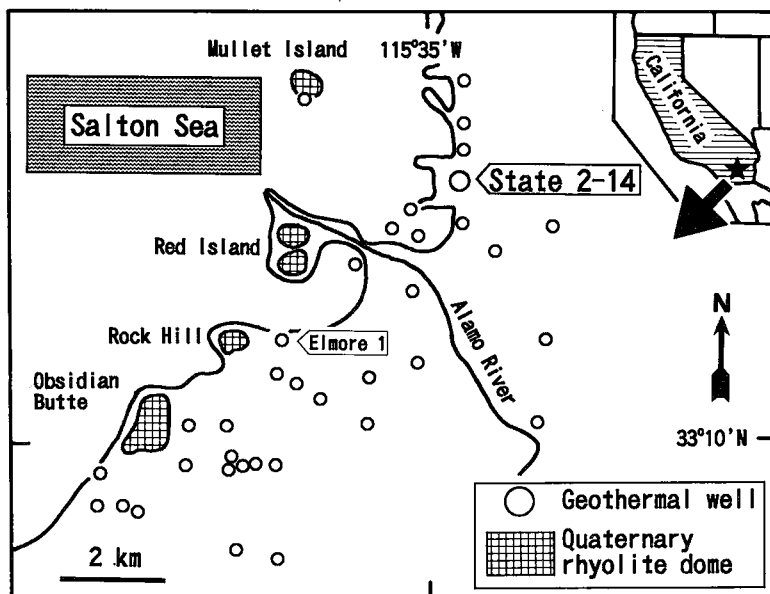


FIG. 1. Location map of the State 2-14 well, together with sites of previous drilling in the Salton Sea geothermal field.

ing assemblage reported from the Elmore 1 well (McDowell & Elders 1980) was not found in the samples studied.

SAMPLE DESCRIPTION AND ANALYTICAL PROCEDURES

The work reported here was done on ten samples from depths of 3,100 to 3,180 m in the State 2-14 well (Fig. 2), where the measured temperature exceeds 350°C (Sass *et al.* 1988). Excluding core sample 9907b, all the samples were drilling chips less than 0.5 cm in maximum dimension. The chips include mixtures of metashale and metasandstone with subordinate metabasite and aggregates of vein minerals. These samples were pulverized to 0.1–0.35 mm with a disk crusher. Amphibole-bearing fractions were concentrated with an isodynamic separator, impregnated with epoxy resin and polished for petrographic observation and electron-probe microanalysis.

Chlorine-bearing amphibole was identified using a KEVEX energy-dispersion spectrometer. Quantitative chemical analyses were done on automated JEOL electron-probe microanalyzers JXA-733 at Stanford University and Nagoya University. Accelerating voltage, specimen current and beam diameter were 15 kV, 12 nA and 3 μ m, respectively. Well-characterized minerals and synthetic phases, including sodalite and Cl-rich hastingsite (for Cl), were used as standards.

Precision (1σ level) of Cl microanalysis is 0.1 wt.% in count statistics on Cl-rich amphibole. Fluorine content for all analyzed grains is below the detection limit of 0.1 wt.%. Fe³⁺ contents were estimated using the methods of Papike *et al.* (1974).

AMPHIBOLES AND COEXISTING MINERALS

Mineral assemblages associated with Cl-bearing amphibole are given in Table 1. Owing to the small size of the chips, it was not always possible to determine whether the protolith is sandstone, basaltic material, or vein material. In such cases, quartz-bearing chips are considered to be metasandstone. Among undifferentiated quartz-free chips, monomineralic or K-feldspar-bearing chips are considered to be vein material, and where amphibole and plagioclase are dominant phases, the chip is considered to be metabasite.

The amphibole-bearing metasandstone chips analyzed are composed mainly of quartz, plagioclase, amphibole, epidote and K-feldspar; clinopyroxene, apatite, biotite, titanite, pyrite and zircon also occur as minor phases. The metabasite chips consist of amphibole, plagioclase and epidote, with minor amounts of clinopyroxene, quartz, apatite, and pyrite. The major phases of the veins are amphibole, epidote, and plagioclase; clinopyroxene, K-feldspar, quartz, apatite, titanite, and pyrite occur in some vein chips. Most grains of plagioclase in the metasandstone have An contents less than

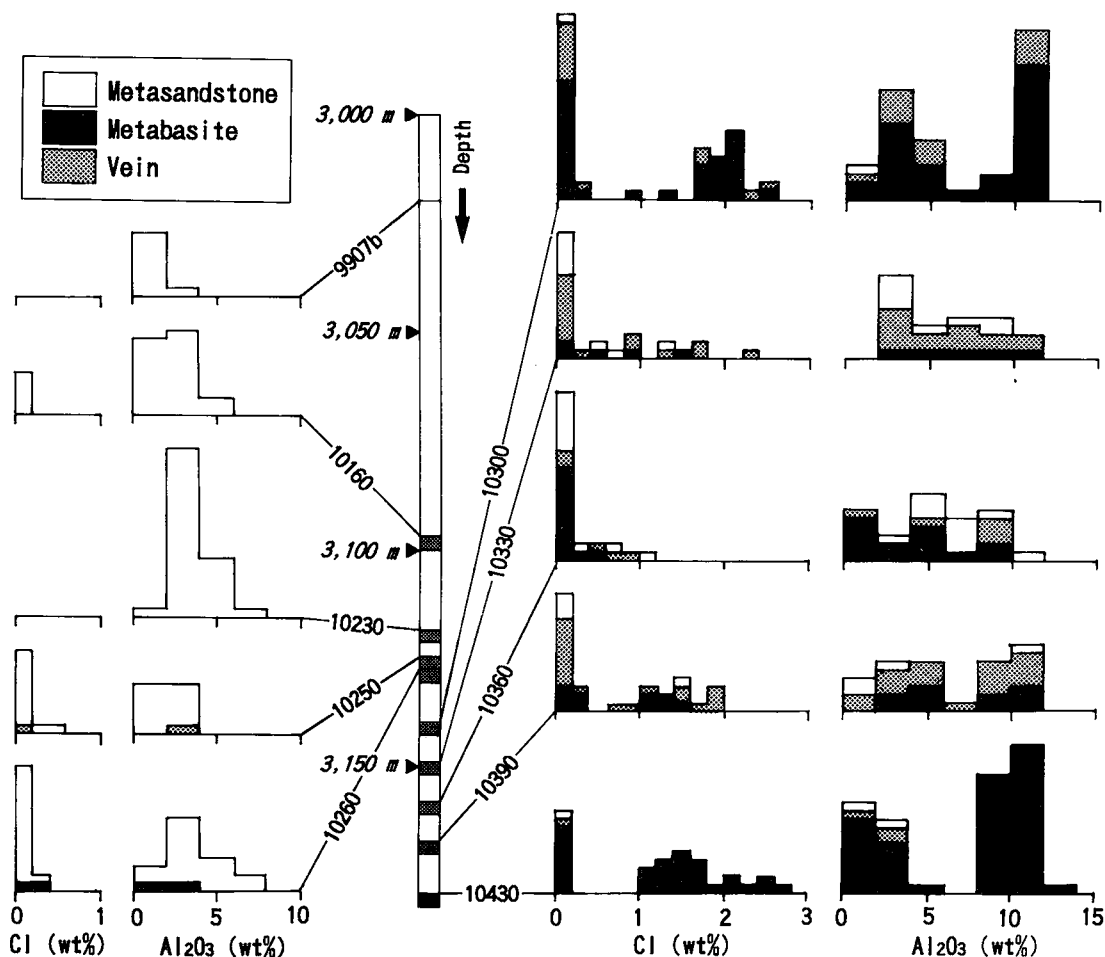


FIG. 2. Variations of the Cl and Al_2O_3 contents (wt.%) of calcic amphiboles in metasandstone, metabasite and vein chips from the Salton Sea State 2-14 well, with depths of chip samples. Some of the data on Al_2O_3 for samples 10160 and 10230 are from Cho *et al.* (1988).

50 mol%; some plagioclase in metabasite and vein chips are as calcic as An_{90} . The albite content of the K-feldspar coexisting with plagioclase is about 7-8 mol%, suggesting equilibrium temperatures of 350-400°C using the two-feldspar geothermometer proposed by Green & Usdansky (1986) and Fuhrman & Lindsley (1988). The Al_2O_3 , CaO contents, and $X(\text{Fe}^{2+})$ [= $\text{Fe}^{2+}/(\text{Fe}^{2+} + \text{Mg})$] value of clinopyroxene are < 0.5 wt.%, 23.5-24 wt.%, and 0.3-0.5, respectively. Phase relations, parageneses and chemical compositions of other minerals in the clinopyroxene zone of the State 2-14 well will be presented in a subsequent communication.

Major-element chemistry of amphiboles

More than 200 chemical analyses of calcic amphiboles were carried out; representative compositions are given in Table 2. Al-poor actinolitic amphibole occurs in all the samples studied (Fig. 2). Only five samples (10300, 10330, 10360, 10390, and 10430) from depths between 3,140 and 3,180 m contain coexisting Al-rich hastingsitic and Al-poor actinolitic amphiboles (Fig. 3a). There is a dramatic increase in the Cl and Al contents of amphibole between 3,130 m (sample 10260) and 3,140 m (sample 10300). This also corresponds to an increase in the abundance of metabasite sills and dykes in the

TABLE 1. MINERAL ASSEMBLAGES OF ANALYZED CHIPS

	Cam	Pl	Ep	Qtz	Kfs	Cpx	Others	Samples
Metasandstone	+	+	+	+	+		± Ap, Tit	6, 7
	+	+	+	+			± Tit	1, 6
	+	+	+					3
	+	+		+	+	+		4, 8
	+	+		+	+		± Ap, Tit, Zrn	2, 3, 7
	+	+		+			± Tit, Py	1, 5
	+	+			+		± Ap, Tit	2
	+		+	+	+		± Ap, Tit, Zrn, Py, Bt	5, 6
	+		+	+				5, 7
	+		+					2
Metabasite	+	+	+			+	± Py	4, 8
	+	+					± Ap	3, 4, 6, 7
	+	+				+		4
	+	+						4, 6
	+		+	+				5
	+		+				± Py	4, 5
	+					+	± Py	4
Vein	+	+	+					4
	+	+				+	± Ap, Tit	4
	+	+						4, 7
	+		+	+				5, 7
	+		+		+			5
	+		+			+		4, 6
	+		+				± Py	5
	+						± Py	2, 4, 5, 6, 7, 8

Note: Abbreviations are: Cam, calcic amphibole; Pl, plagioclase; Ep, epidote; Qtz, quartz; Kfs, K-feldspar; Cpx, clinopyroxene; Ap, apatite; Tit, titanite; Zrn, zircon; Py, pyrite; Bt, biotite; 1, 10160; 2, 10250; 3, 10260; 4, 10300, 5, 10330; 6, 10360; 7, 10390; 8, 10430.

chips recovered. The maximum Cl and Al contents of amphibole at 3,140 m are essentially the same as those observed at the bottom of the drill hole (3,180 m).

Most of the compositions correspond to actinolitic and hastingsitic amphiboles (Fig. 4). Some of the intermediate compositions may refer to mixtures of two or more amphiboles that could not be resolved with the analytical techniques used. Hastingsitic amphibole is dark bluish green and occurs as prismatic subhedral crystals 0.02–0.1 mm in size. Chemical variations from ferro-hornblende, through ferro-pargasitic hornblende and hastingsitic hornblende, to hastingsite (Fig. 4) reflect both chemical variations among different drill chips and zonation within single grains. Some grains show complex zoning represented by patchy intergrowths of hastingsite with either hastingsitic hornblende or ferro-pargasitic hornblende (Fig. 3b). The hastingsitic amphibole in metabasites and veins has a value of X(Fe²⁺) between 0.5 and 0.85; in metasandstone chips, values are between 0.45 and 0.65. The analyzed hastingsitic amphibole contains 0.3–0.7 wt.% TiO₂, similar to Cl-rich amphibole from submarine metabasites and skarns (e.g., 0.30–1.14 wt.%, Jacobson 1975). The total alkali content (Na+K) is between 0.5 and 0.8 pfu (per formula unit for O=23), and K content increases from 0.3 to 0.6 pfu with increasing total alkali content. Sodium is fairly constant at 0.27 ± 0.03 pfu. The actinolitic amphibole is colorless or pale green and occurs mostly as acicular subhedral crystals (less than

0.1 mm long). Some grains of actinolitic amphibole are intergrown with hastingsitic amphibole (Fig. 3a).

Two lines of evidence suggest that both hastingsitic and actinolitic amphiboles are formed in the present-day geothermal system: (1) they show a prismatic and subhedral habit, and occur as pore fillings in some metasandstones, and (2) Al, Na and K contents of amphibole increase with increasing depth and temperature (Fig. 2).

The coexisting actinolitic and hastingsitic amphiboles suggest a miscibility gap in the calcic amphibole series (Cooper & Lovering 1970, Tagiri 1977, Maruyama *et al.* 1983, Ishizuka 1985). In coexisting amphiboles, average contents of tetrahedrally coordinated aluminum, ^[4]Al, and A-site alkali contents, ^[A](Na+K), are 0.22–0.54 and 0.02–0.13 pfu, respectively, for actinolitic amphibole, and 1.42–1.79 and 0.47–0.73 pfu for hastingsitic amphibole (Fig. 5). The compositional range of the miscibility gap in terms of Tschermak substitution {= ^[4]Al - ^[A](Na+K)} is from 0.22 to 1.06 for a Mg-poor pair (Mg is 2.3 pfu in actinolitic amphibole and 0.9 pfu in hastingsitic amphibole), and from 0.41 to 0.98 pfu for a Mg-rich pair (3.1 pfu in actinolitic amphibole and 2.0 pfu in hastingsitic amphibole). The miscibility gap becomes narrower with increasing Mg content.

Cl content of amphibole

Relationships between Cl content of calcic amphi-

TABLE 2. REPRESENTATIVE ANALYSES OF CL-BEARING CALCIC AMPHIBOLES

Sample	10430			10390				10360		10330			10300			10260	10250	10160
Chip	01b	01b	01b	05v	05v	05v	14s	01s	04s	09v	06b	08s	12v	11b	16v	06s	10s	01s
SiO ₂	38.3	39.7	41.4	39.0	42.1	51.8	52.2	42.8	52.9	38.1	39.7	51.3	38.1	37.2	51.4	53.6	52.6	52.9
TiO ₂	0.44	0.46	0.53	0.32	0.33	0.16	0.03	0.51	0.03	0.14	0.48	0.19	0.33	0.55	0.09	0.07	0.15	0.11
Al ₂ O ₃	10.7	11.1	10.7	10.9	9.86	4.08	1.69	9.89	3.38	10.1	10.6	3.77	11.0	10.8	3.90	3.80	3.20	2.89
Cr ₂ O ₃	0.07	0.11	0.12	n.d.	n.d.	n.d.	n.d.	0.00	0.10	n.d.	n.d.	n.d.	0.00	0.10	0.03	n.d.	n.d.	n.d.
FeO*	28.8	26.8	25.3	26.4	23.5	13.7	25.1	18.2	10.6	28.1	23.7	14.2	29.4	29.8	19.1	16.0	18.0	13.0
MnO	0.51	0.33	0.34	0.28	0.29	0.32	0.69	0.34	0.22	0.29	0.24	0.23	0.34	0.48	0.18	0.23	0.37	0.17
MgO	2.59	3.59	4.58	5.37	7.44	14.4	6.88	9.62	16.9	4.73	7.08	14.8	2.78	2.75	10.2	12.2	11.8	15.6
CaO	10.9	11.4	11.8	11.7	12.0	12.4	11.9	12.1	12.6	11.6	11.9	12.5	11.5	11.2	12.3	12.5	12.3	12.6
Na ₂ O	0.87	1.01	0.97	0.75	0.87	0.31	0.18	1.07	0.28	0.72	0.85	0.40	0.82	0.79	0.30	0.37	0.31	0.23
K ₂ O	2.48	1.92	1.53	2.39	1.41	0.14	0.04	1.52	0.08	2.15	1.70	0.10	2.36	2.68	0.01	0.07	0.16	0.18
Cl	2.65	1.63	1.17	1.82	0.93	<0.02	1.09	0.05	2.27	1.54	0.05	2.42	2.40	0.04	0.04	0.13	0.13	0.04
O=Cl	0.60	0.37	0.26	0.41	0.21	0.02	0.00	0.25	0.01	0.51	0.35	0.01	0.55	0.54	0.01	0.01	0.03	0.01
Total	97.7	97.7	98.2	98.5	98.5	97.4	98.7	96.9	97.1	97.7	97.4	97.5	98.5	98.2	97.5	98.9	99.0	97.7

Formulae (O=23)																			
Si	6.271	6.361	6.505	6.159	6.451	7.511	7.888	6.572	7.559	6.125	6.210	7.425	6.169	6.067	7.644	7.725	7.662	7.602	
Ti	0.054	0.055	0.063	0.038	0.038	0.017	0.004	0.059	0.003	0.017	0.056	0.021	0.040	0.068	0.010	0.008	0.017	0.012	
Al	2.064	2.096	1.981	2.028	1.781	0.697	0.301	1.790	0.569	1.913	1.954	0.643	2.099	2.075	0.684	0.645	0.549	0.490	
Cr	0.009	0.014	0.015	n.d.	n.d.	n.d.	0.000	0.011	n.d.	n.d.	n.d.	0.000	0.013	0.004	n.d.	n.d.	n.d.	n.d.	
Fe ³⁺	0.579	0.394	0.278	0.891	0.742	0.215	0.003	0.339	0.281	1.143	0.921	0.399	0.746	0.882	0.000	0.000	0.090	0.249	
Fe ²⁺	3.363	3.195	3.045	2.594	2.268	1.445	3.168	1.997	0.985	2.633	2.179	1.319	3.234	3.182	2.374	1.928	2.101	1.314	
Mn	0.071	0.045	0.045	0.037	0.038	0.039	0.088	0.044	0.027	0.040	0.032	0.028	0.047	0.067	0.022	0.028	0.045	0.021	
Mg	0.632	0.857	1.073	1.263	1.699	3.111	1.549	2.201	3.598	1.133	1.650	3.192	0.671	0.668	2.260	2.620	2.561	3.340	
Ca	1.912	1.956	1.986	1.978	1.970	1.926	1.926	1.990	1.928	1.997	1.994	1.938	1.995	1.956	1.959	1.930	1.919	1.939	
Na	0.275	0.314	0.296	0.230	0.258	0.087	0.053	0.319	0.077	0.224	0.257	0.113	0.257	0.249	0.086	0.104	0.087	0.064	
K	0.517	0.393	0.306	0.480	0.276	0.026	0.007	0.297	0.014	0.440	0.338	0.019	0.486	0.556	0.002	0.012	0.030	0.033	
X _{Fe²⁺}	0.84	0.79	0.74	0.67	0.57	0.32	0.67	0.48	0.22	0.70	0.57	0.29	0.83	0.83	0.51	0.42	0.45	0.28	

Note: Abbreviations are: b, metabasite; v, vein; s, metasandstone; n.d., not determined. * Total Fe as FeO. X_{Fe²⁺} = Fe²⁺/(Fe²⁺ + Mg).

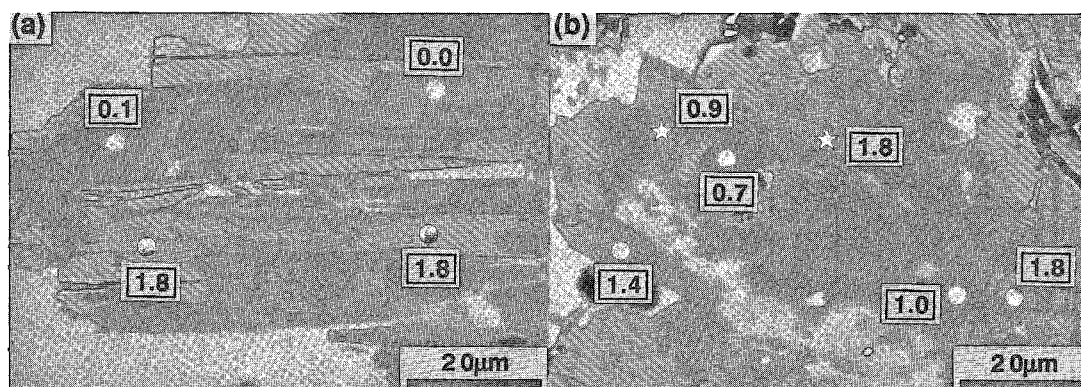


FIG. 3. Back-scattered-electron images of amphiboles in the Salton Sea samples. (a) Coexisting actinolitic (dark part) and hastingsitic (light part) amphiboles in sample 10330 (3,150 m depth). (b) Chemical heterogeneity in a hastingsitic amphibole in sample 10390 (3,170 m depth). Numbers illustrate Cl contents of amphiboles in weight %. Chemical compositions at points marked with stars in Figure 3b are given in Table 2.

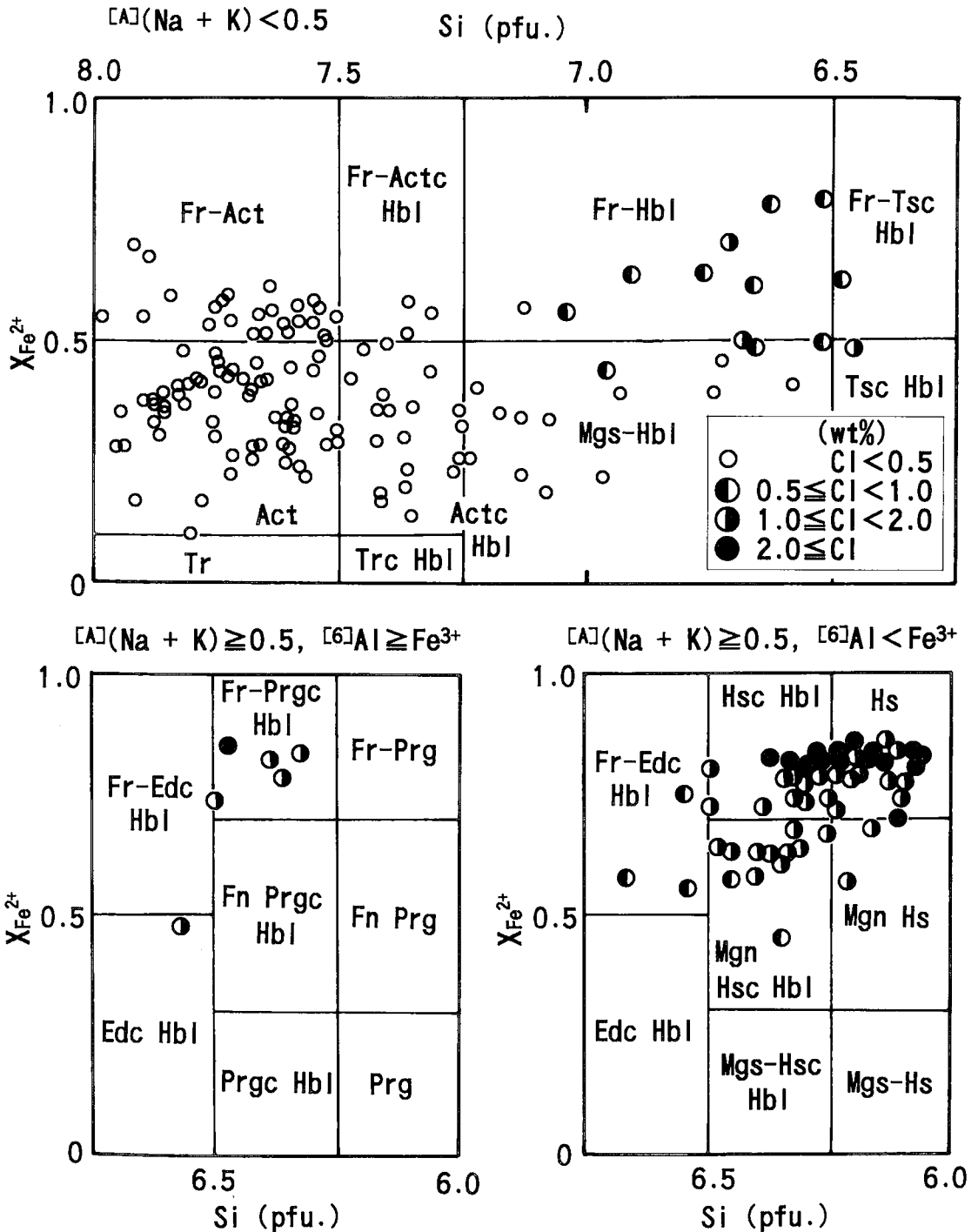


FIG. 4. Chemical characteristics of calcic amphiboles from the Salton Sea State 2-14 well as a function of $X_{Fe^{2+}}$ [= $Fe^{2+}/(Fe^{2+} + Mg)$], numbers of atoms of Si and (Na+K) in the A-site $\{[A](Na+K)\}$ per formula unit (pfu). The nomenclature of amphiboles follows Leake (1978). Abbreviations are: Act actinolite, Actc actonolitic, Edc edenitic, Fr ferro, Fn ferroan, Hs hastingsite, Hsc hastingsitic, Hbl hornblende, Mgn magnesian, Mgs magnesio, Prg pargasite, Prgc pargasitic, Tr tremolite, Trc tremolitic, Tsc tschermakitic.

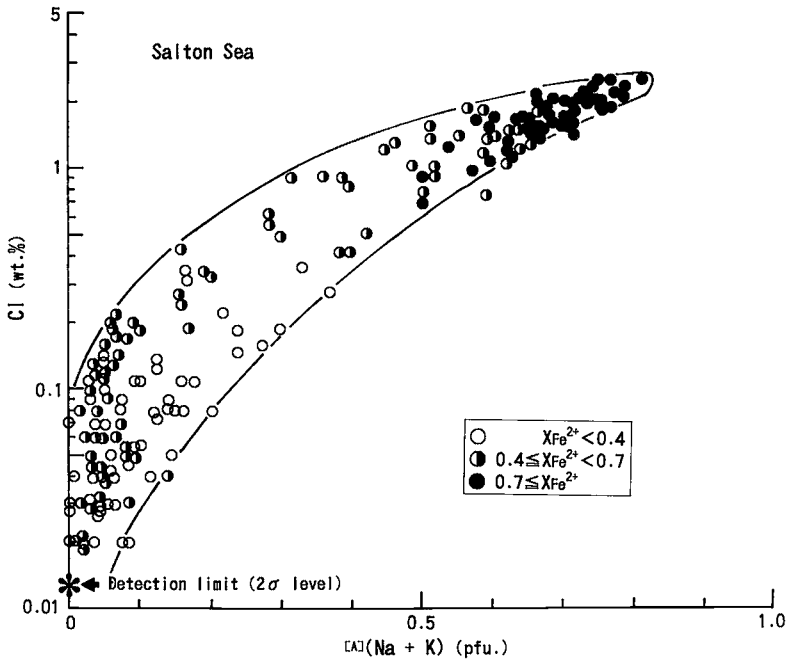


Fig. 6. Variations in proportion of Cl (wt.%) as a function of $^{[Al]}(\text{Na}+\text{K})$ and $X(\text{Fe}^{2+})$ in amphiboles from the Salton Sea State 2-14 well.

ous, and the Cl-rich domains are rich in Fe^{2+} , $^{[4]}\text{Al}$ and $^{[Al]}(\text{Na}+\text{K})$ (Fig. 3b, Table 2). Variations of Cl content in amphibole (Fig. 6) as functions of $^{[Al]}(\text{Na}+\text{K})$ and $X(\text{Fe}^{2+})$ suggest a crystal-chemical control on Cl content. Two characteristic features are apparent: (1) Cl content of amphibole increases with increasing $^{[Al]}(\text{Na}+\text{K})$, and (2) the maximum Cl content of amphibole increases with increasing $X(\text{Fe}^{2+})$. Amphibole compositions with Cl in excess of 0.5 wt.% plot along an edenite $\{^{[Al]}(\text{Na}+\text{K})^{[4]}\text{Al}_{\square-1}\text{Si}_{1-1}\}$ substitution vector (Fig. 5). This fact indicates that the extent of tschermakite substitution $\{^{[4]}\text{Al}^{[6]}\text{AlSi}_{1-1}(\text{Mg}, \text{Fe}^{2+})_{-1}\}$ in Cl-rich amphibole is relatively constant $\{0.9 < ^{[4]}\text{Al} - ^{[Al]}(\text{Na}+\text{K}) < 1.0\}$. The chemical characteristics shown in Figure 6 thus indicate that (1) Cl variation of the Salton Sea amphibole is controlled primarily by variations in the edenite component; (2) $X(\text{Fe}^{2+})$ value of the amphibole shows little correlation with Cl and edenite contents, but is correlated with the maximum Cl content of amphibole. Increasing $^{[Al]}(\text{Na}+\text{K})^{[4]}\text{Al}_{\square-1}\text{Si}_{1-1}$ and FeMg_{-1} substitutions favor incorporation of Cl in the amphibole structure. Both $^{[Al]}(\text{Na}+\text{K})^{[4]}\text{Al}_{\square-1}\text{Si}_{1-1}$ (Ito & Anderson 1983) and FeMg_{-1} (e.g., Volfinger *et al.* 1985) substitutions seem essential but not sufficient for Cl enrichment. Where coupled, the two substitutions seem to increase the content of Cl incorporation in amphibole. This scheme is consistent with the fact that examples of Cl-rich calcic amphibole (> 3 wt.% Cl) reported in

literature are mostly ferro-hastingsite with $X(\text{Fe}^{2+}) > 0.75$, $(\text{Na}+\text{K}) > 0.9$ pfu, and $^{[4]}\text{Al}$ between 1.8 and 2.3 pfu (total Fe as FeO and O = 23; Suwa *et al.* 1987).

Figure 7 shows the relationships among Cl, $^{[Al]}(\text{Na}+\text{K})$, $X(\text{Fe}^{2+})$, and $^{[4]}\text{Al}$ contents of the Salton Sea amphiboles. The data indicate that (1) on Figure 7a,

$$\begin{aligned} \frac{\partial n_{\text{Cl}}}{\partial n^{[Al]}(\text{Na}+\text{K})} &\approx 0.6 \text{ for } ^{[4]}\text{Al} < 1.6 \text{ and} \\ \frac{\partial n_{\text{Cl}}}{\partial n^{[Al]}(\text{Na}+\text{K})} &\approx 1.4 \text{ for } ^{[4]}\text{Al} \geq 1.6, \end{aligned}$$

and (2) on Figure 7b,

$$\begin{aligned} \frac{\partial n_{\text{Cl}}}{\partial X(\text{Fe}^{2+})} &\approx 0.3 \text{ for } ^{[Al]}(\text{Na}+\text{K}) < 0.55 \text{ and} \\ \frac{\partial n_{\text{Cl}}}{\partial X(\text{Fe}^{2+})} &\approx 0.8 \text{ for } ^{[Al]}(\text{Na}+\text{K}) \geq 0.55, \end{aligned}$$

where n is the number of atoms of the subscripted elements.

Volfinger *et al.* (1985) demonstrated the fundamental role of the local structure of the anion site in exchange of anions in silicate minerals. In the case of amphibole, the closer the symmetry of the ring of six tetrahedra in the double chain to ideal hexagonal symmetry, the larger the sizes of anionic and alkali sites. The adaptation of the tetrahedral chains to the octahedral strips is controlled particularly by their iron content. This scheme explains the positive correlation between Cl and $^{[Al]}(\text{Na}+\text{K})$ and that between Cl and $X(\text{Fe}^{2+})$ in calcic amphiboles. Figure 7, however, shows that (1) the extent of Cl substitution for OH as a function of edenite substitution at $^{[Al]}(\text{Na}+\text{K}) \geq 0.55$ is twice that for an amphibole with $^{[Al]}(\text{Na}+\text{K}) < 0.55$, and (2) the Cl content

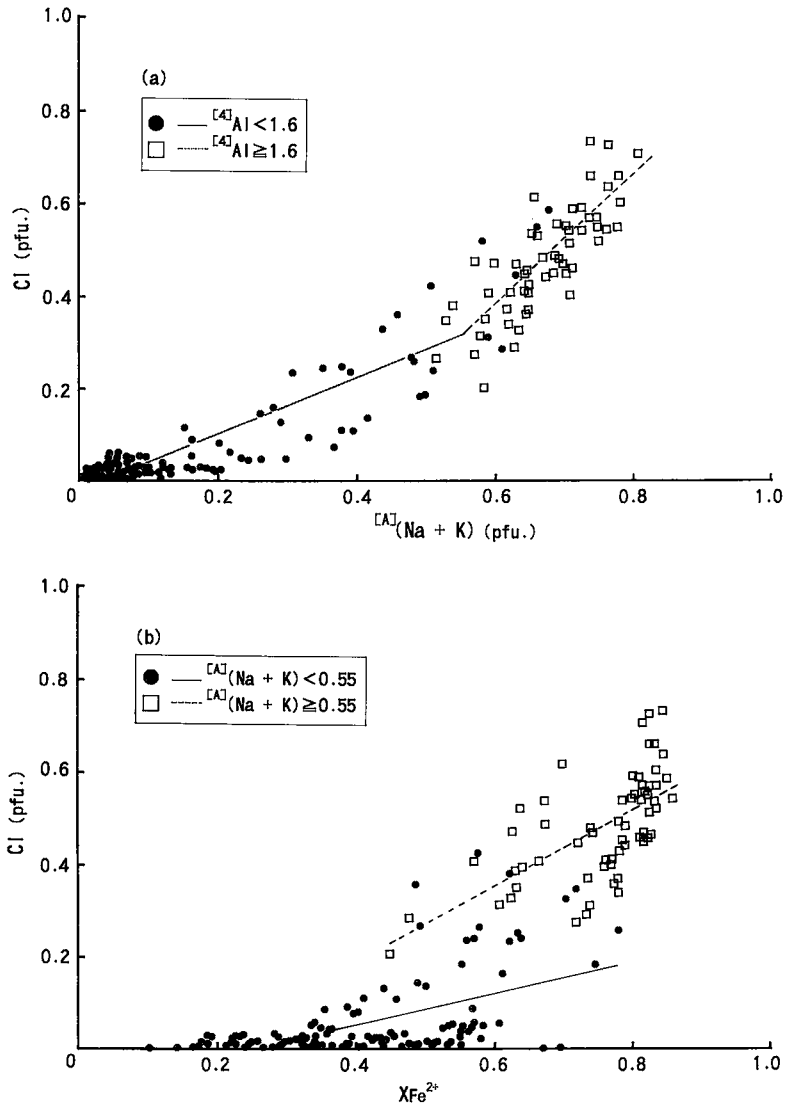


FIG. 7. Variations in the proportion of Cl (wt.%) as a function of (a) $[A](Na+K)$ and $[4]Al$, and (b) $X(Fe^{2+})$ and $[A](Na+K)$, in amphiboles from the Salton Sea State 2-14 well. Solid and broken lines indicate the regression lines for amphiboles with $[4]Al < 1.6$ and ≥ 1.6 in (a), and those with $[A](Na+K) < 0.55$ and ≥ 0.55 in (b), respectively.

of $[A](Na+K)$ -rich amphibole is higher than that of $[A](Na+K)$ -poor amphibole for a fixed $X(Fe^{2+})$. Total expansion of unit-cell volume with increasing edenite component may also make the increased substitution of Cl-for-OH possible.

Cl partitioning between amphibole and fluid

Figure 8 summarizes the relationships among Cl, $X(Fe^{2+})$, and $[A](Na+K)$ in calcic amphibole composi-

tions reported in the literature. The data pertain to amphibole formed under various geological environments: submarine metabasites (Fig. 8a), skarns (Fig. 8b), high-grade metamorphic rocks (Fig. 8c), and igneous rocks (Fig. 8d). Available data on fluid composition and P-T conditions of the representative examples are summarized in Table 3. Although the Cl-bearing amphiboles shown in Figure 8 were mostly formed under higher P-T conditions (0.4–10 kbar, 450–850°C) than those in the Salton Sea samples (0.3 kbar, 350°C), most

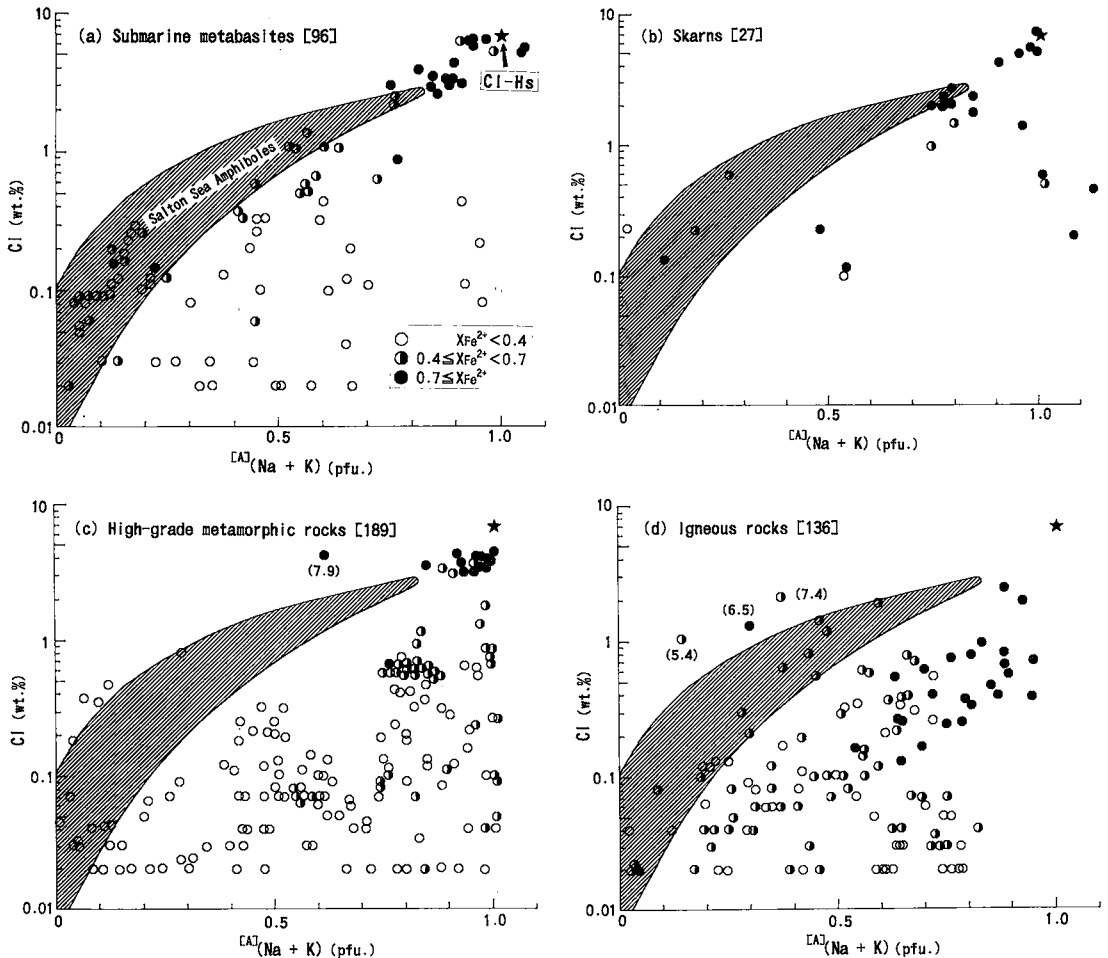


FIG. 8. Variations in proportion of Cl (wt.%) in calcic amphibole as a function of $[Al](Na+K)$ and $X(Fe^{2+})$ from various geological environments. The chemical data are based on the following literature. Submarine metabasite: Batiza & Vanko (1985), Enami & Suwa (unpubl. data), Honnorez & Kirst (1975), Honnorez *et al.* (1984), Ishizuka (1989), Ito & Anderson (1983), Jacobson (1975), Roden *et al.* (1984), Stakes & Vanko (1986), Vanko (1986). Skarn: Damman (1989), Dick & Robinson (1979), Gulyaeva *et al.* (1986), Jacobson (1975), Krutov (1936), Krutov & Vinogradova (1966), Matsumoto (1968, 1969), Matsumoto & Miyahisa (1960). High-grade metamorphic rocks: Compton (1958), Enami (unpubl. data), Enami *et al.* (1993), Goto & Banno (1990), Kamineni *et al.* (1982), Leelanandam (1970), Matsubara & Motoyoshi (1985), Sharma (1981), Suwa *et al.* (1987), Vielzeuf (1982). Igneous rocks: Beard & Day (1986), Bird *et al.* (1986), Bloomfield & Arculus (1989), Borley (1962), Buddington & Leonard (1953), Chivas (1981), Czamanske *et al.* (1977, 1981), Druitt & Bacon (1989), Kamineni (1986), Kolker & Lindsley (1989), Nabelek (1989), Nash (1976), Speer (1987), Whalen & Chappell (1988), Yamaguchi (1989). Stars indicate a composition of idealized chlorian hastingsite $[NaCa_2(Fe^{2+}_4Fe^{3+})(Si_6Al_2)O_{22}Cl_2]$. Numbers in parentheses and brackets show calculated Fe_2O_3 content (wt.%) of amphibole and numbers of data-sets cited, respectively.

of the measured compositions do not exceed the maximum Cl content of the Salton Sea amphiboles given in Figure 6. This finding suggests that (1) Cl substitution at O(3) apparently has a maximum value that is crystal-chemically controlled, (2) the maximum extent of Cl-for-OH substitution in calcic amphibole does not seem to be a sensitive function of pressure or temperature in metamorphic and hydrothermal environments. Indeed, Vanko (1986) has noted that Cl-rich (up to 4.0

wt.%) amphibole can form at lower temperatures than coexisting Cl-poor (less than 1.0 wt.%) amphibole.

Some amphiboles in granodioritic charnockite (Kamineni *et al.* 1982) and anorthosite-gabbro complex (Kamineni 1986) have Cl-rich compositions exceeding the maximum Cl-for-OH substitution of the Salton Sea amphiboles (Figs. 8c, d). This material has a higher calculated Fe_2O_3 content (5.4–7.9 wt.%) than the other samples ($Fe_2O_3 = 3.8 \pm 2.2$ wt.%). Increasing $Fe^{3+}Al_1$

TABLE 3. MODE OF OCCURRENCE OF SOME Cl-BEARING CALCIC AMPHIBOLES

	Cl-content of amphibole	Cl-content of fluid	Equilibrium condition	References
Submarine metabasite	* 6.03-6.51 wt.%	≥ sw(?)	amphibolite	Jacobson (1975)
	* 0.02-0.66 wt.%	≥ sw(?)	550-750°C	Ito and Anderson (1983)
	* 0.01-4.02 wt.%	≥ sw(?)	amphibolite f.	Vanko (1986)
	* 0.01-3.00 wt.%	≥ sw(?)	greenschist f.	Vanko (1986)
Skarn	* 7.24 wt.%	n.d.	pyroxene hf(?)	Krutov (1936)
	* 0.13-2.68 wt.%	n.d.	pyroxene hf(?)	Gulyaeva et al. (1986)
High-grade metamorphic rock	* 4.18 wt%	n.d.	granulite	Kamineni et al. (1982)
	* 0.0-0.65 wt.%	n.d.	800-850°C 8-10 kbar	Matsubara and Motoyoshi (1985)
Igneous rock	* 0.07-2.44 wt.%	n.d.	?	Czarnanske et al. (1977)
	* 0.00-2.08 wt.%	n.d.	400-600°C 1-2 kbar	Kamineni (1986)
	* 0.02-0.78 wt.%	4-6 wt.% in maximum(?)	500-750°C 0.4-0.7 kbar	Bird et al. (1986)
Geothermal metamorphic rock	* 0.0-2.7 wt.%	15-19.7 wt.%	350-400°C 0.3 kbar	This study

Note: Abbreviations are: n.d., not determined; sw, seawater; amphibolite f., amphibolite facies; greenschist f., greenschist facies; pyroxene hf, pyroxene hornfels facies.

substitution expands the entire chain of the amphibole (Ito & Anderson 1983) and thus may facilitate substitution of Cl for OH.

Variable Cl contents in amphibole have been correlated with water-rock interaction and Cl fixation during metamorphism and hydrothermal alteration of oceanic crust. In submarine metabasite and skarn, chlorine contents of some amphiboles attain 7.2 wt.% (Figs. 8a, b), which is distinctly higher than that of the Salton Sea amphiboles (up to 2.7 wt.%). Many authors have considered that Cl-rich amphibole grew from extremely chlorine-rich fluid (e.g., Ito & Anderson 1983, Vanko 1986). Such fluids may exist in oceanic hydrothermal systems and during skarn formation (e.g., Tan & Kwak 1979, Vanko 1988). However, cases of Cl-rich amphibole with more than 3 wt.% Cl have greater $^{[Al]}(Na+K)$ than the Salton Sea amphiboles. Therefore, the high Cl content of amphiboles is considered also to be due to increasing volume-expansion. The similarity in the maximum extent of Cl-for-OH substitution with fixed $^{[Al]}(Na+K)$ among the Salton Sea, submarine metabasite, and skarn amphiboles implies that the extent of Cl-for-OH substitution in these amphiboles is not sensitive to variations in fluid chlorinity.

Amphiboles in high-grade metamorphic rocks and igneous rocks contain less Cl than the maximum extent of Cl-for-OH substitution found in the Salton Sea samples. These amphiboles were formed under conditions of lower chlorinity than those in the Salton Sea geothermal system. Nabelek (1989) showed that the Cl content of calcic amphibole in mafic hornfelses around the Laramie anorthosite complex, Wyoming,

increases systematically from 0.03 to 0.37 wt.% with decreasing proportion (vol.%) of amphibole; he interpreted this finding in terms of progressive loss of water and preferential concentration of Cl in amphibole during contact metamorphism. These observations imply that the Cl content of amphiboles coexisting with a low-chlorinity fluid is sensitive to variations in fluid chlorinity and is controlled by Cl partitioning between the two phases as well as the crystal-chemical constraints imposed by (Na+K), Fe and Al substitutions.

Figure 9 illustrates Cl partitioning between coexisting amphibole and fluid, inferred from the chemical data of the Salton Sea geothermal system (this study) and Mathematician Ridge (Stakes & Vanko 1986, Vanko 1986, 1988, Suwa & Enami, unpubl. data). In low-chlorinity environments, the Cl content of amphibole is defined by partitioning of Cl between amphibole and fluid, and increases with increasing Cl content in fluid, $^{[Al]}(Na+K)$, and $X(Fe^{2+})$ of the amphibole. The estimated ratio of $\partial(X_{Cl})^{amp}$ to $\partial(X_{Cl})^{fluid}$ is approximately 3 at $0.4 \leq ^{[Al]}(Na+K) < 0.6$ and $0.4 \leq X(Fe^{2+}) < 0.7$, and approximately 4 or 5 at $0.6 \leq ^{[Al]}(Na+K) < 0.8$ and $0.4 \leq X(Fe^{2+}) < 0.7$. An amphibole with $^{[Al]}(Na+K) \geq 0.4$ and $X(Fe^{2+}) \geq 0.4$ seems to preferentially concentrate Cl relative to the coexisting fluid in low-chlorinity environments. On the other hand, amphiboles coexisting with the Salton Sea brine or with more saline fluids have nearly constant Cl content for fixed $X(Fe^{2+})$ and $^{[Al]}(Na+K)$ contents, and seem independent of variation of chlorinity in the coexisting fluid.

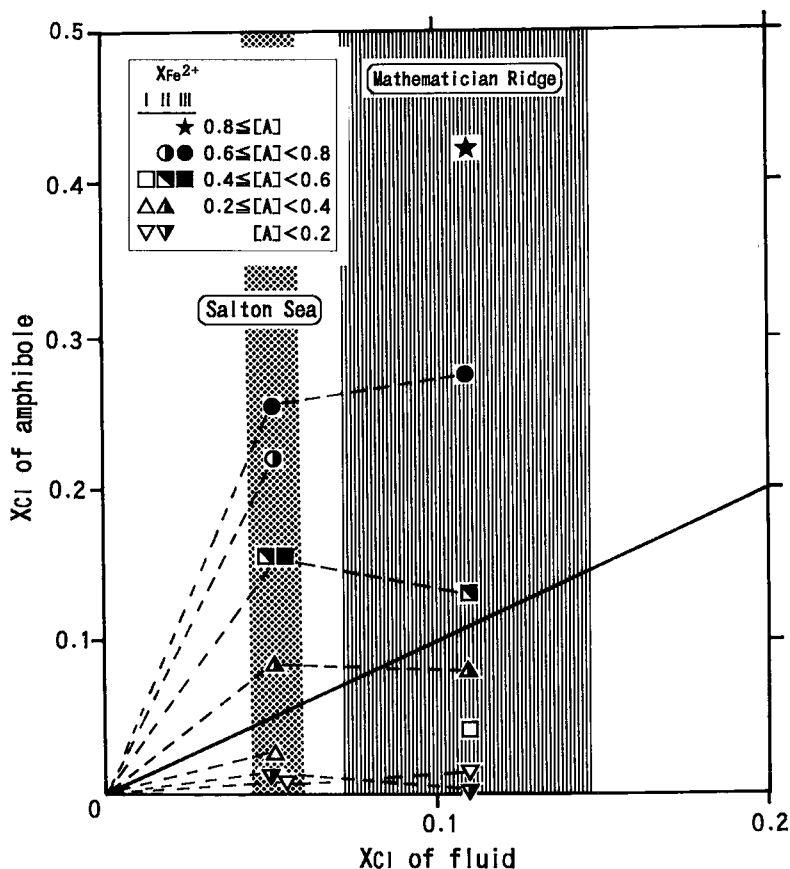


FIG. 9. Relationship between average X_{Cl} [= Cl/(Cl + OH)] of coexisting calcic amphibole and fluid in the Salton Sea geothermal system (this study) and Mathematician Ridge (Stakes & Vanko 1986, Vanko 1986, 1988, Enami & Suwa, unpubl. data). Abbreviations: I $X(Fe^{2+}) < 0.4$, II $0.4 \leq X(Fe^{2+}) < 0.7$, III $0.7 \leq X(Fe^{2+})$.

CONCLUSIONS

Chlorine-bearing actinolitic and hastingsitic amphiboles (< 2.7 wt.% Cl) occur in metasandstone, metabasite and vein chip samples recovered from a depth of 3,100–3,180 m of the State 2–14 well, Salton Sea. The actinolitic amphibole includes (ferro) actinolite and (ferro) actinolitic hornblende, and is observed throughout the samples studied. The hastingsitic amphibole shows wide chemical variations from ferro-hornblende, through ferro-pargasitic hornblende and hastingsitic hornblende, to hastingsite, and occurs in samples recovered at depths greater than 3,140 m.

The Salton Sea amphiboles have wide variations of Cl content, from less than 0.2 wt.% in actinolite to greater than 2 wt.% in hastingsite, and show some significant chemical correlation: (1) chlorine content increases with increasing $^{[A]}(Na+K)$ content; (2) the

maximum Cl content of amphibole increases with increasing $X(Fe^{2+})$.

In low-chlorinity environments, the Cl content of an amphibole increases with increasing chlorinity of the coexisting fluid and is defined by Cl-partitioning between the two phases. On the other hand, an amphibole coexisting with the Salton Sea and more saline fluids may be saturated with Cl. The extent of the Cl-for-OH substitution in amphibole is strongly controlled by $X(Fe^{2+})$ and the proportion of the edenite component.

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