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CHLORINE-BEARING AMPHIBOLES FROM THE FRASER MINE, SUDBURY, ONTARIO, CANADA: DESCRIPTION AND CRYSTAL CHEMISTRY

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ABSTRACT

Three chemically distinct populations of Cl-bearing amphibole have been recognized in association with contact Ni–Cu ore deposits in Footwall Breccia at the Fraser mine, Sudbury, Ontario. The first population, defined as halogen-poor (<0.5 wt.% Cl) actinolite and magnesiohornblende, occurs predominantly as pale green grains and cores. These are generally overgrown by amphibole of the other two populations: a) Fe-rich, halogen-poor deep green rim of ferro-actinolite to ferrohornblende, and b) Fe-rich, Cl-rich (up to 4 wt.% Cl) ferrotschermakite to hastingsite to potassic-chlorohastingsite, which exhibits a characteristic deep blue-green pleochroism. Rare F-rich (up to 1.1 wt.% F) magnesiohornblende also is observed in the same environment. Major-element data for the Cl-rich amphiboles indicate linear, positive relationships for both Mg# and K *versus* Cl, and a logarithmic, positive one for $^{[4]}$Al *versus* Cl. These data, along with selected X-ray maps, indicate that Cl is homogeneously distributed and likely structurally bound. Calculated Fe^{3+}/Fe^{2+} values suggest crystallization under conditions of relatively low $f(O_2)$. At least two chemically distinct fluids seem to have been responsible for crystallization of the amphiboles. The first, which resulted in the crystallization of halogen-poor, pale green actinolite and magnesiohornblende, was likely relatively hot (≥650°C) and contemporaneous with sulfide emplacement. This was followed by a lower-*T* (≥350°C), Cl-rich fluid from which the Cl-rich amphiboles crystallized. This latter fluid may have been a modified product of the initial fluid or possibly a second discrete fluid. A subsequent F-rich fluid led to development of F-rich magnesiohornblende. The source of both Cl and F is not clear; whole-rock analyses of Footwall rocks of the Levack Gneiss Complex, however, reveal anomalous enrichments in both Cl (>700 ppm) and F (2500 ppm). These rocks thus may have been a significant contributor to the fluids.

Keywords: amphibole, chemical composition, chlorine, halogens, fluids, contact sulfide deposits, Ni–Cu ore, Footwall Breccia, Sudbury, Ontario, Canada.

SOMMAIRE

Nous reconnaissons trois populations distinctes d'amphibole chlorée en assocation avec les gisements de Ni–Cu de type contact dans la brèche à la base du complexe igné de Sudbury, à la mine Fraser, à Sudbury, en Ontario. Le premier groupe, composé d'actinolite et de magnésiohornblende à faible teneur en halogénures (<0.5% Cl, poids), se présente surtout sous forme de grains ou de coeurs de grains vert pâle. Ceux-ci sont généralement recouverts d'une gaine d'amphibole d'un des deux autres groupes: a) liseré de ferro-actinolite ou ferrohornblende vert foncé, riche en Fe et à faible teneur en halogénures, et b) liseré de ferrotschermakite à hastingsite à potassic-chlorohastingsite, riche en Fe et en Cl (jusqu'à 4%, en poids), dont le pléochroïsme atteint un bleu-vert foncé. Il y a aussi dans le même milieu une magnésiohornblende enrichie en fluor (jusqu'à 1.1% F, en poids), beaucoup moins répandue. Les éléments majeurs décrivant la composition des amphiboles chlorées montrent une relation linéaire entre Mg# et K d'une part, et la teneur en Cl, et une relation positive et logarithmique entre $^{[4]}$Al et Cl. Ces données, ainsi que les schémas de distribution de certains éléments obtenus par rayons X, montrent que le Cl est réparti de façon homogène, et il est vraisemblablement impliqué dans la structure. Les valeurs calculées du rapport Fe^{3+}/Fe^{2+} indiquent une cristallisation à fugacité d'oxygène relativement faible. Au moins deux sortes de fluides semblent avoir été responsables de la cristallisation des amphiboles. La première vague, de laquelle s'est formée l'actinolite et la magnésiohornblende vert pâle, avait une température relativement élevée (≥650°C) et était contemporaine de la mise en place des sulfures. Ce fluide a soit évolué pour devenir plus riche en Cl, ou bien a donné lieu à une deuxième vague de fluide, à plus faible température (≥350°C), duquel les amphiboles riches en Cl se sont formées. Un fluide encore plus tardif a provoqué la formation de l'amphibole fluorée. L'origine des halogénures n'est pas établie. La présence, dans le socle composé du complexe gneissique de Levack, d'enrichissements anomales de Cl (>700 ppm) et de F (2500 ppm), fait penser que ces roches auraient pu être à l'origine de l'enrichissement.

Mots-clés: amphibole, composition chimique, chlore, halogénures, fluides, gisements de sulfures de type contact, minerai Ni–Cu, brèche footwall, Sudbury, Ontario.

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INTRODUCTION

Fluorine and chlorine are important components of orthomagmatic and metamorphic fluids owing to the control they exert on the crystallization, stability and alteration behavior of minerals. These halogens are typically accommodated in the structures of rock-forming minerals such as amphiboles and micas, as well as in accessory phases such as apatite. As such, determination of the halogen contents of these minerals can provide important data regarding the nature and evolution of magmatic and metamorphic fluids (Munoz & Ludington 1977, Zhu & Sverjensky 1991, Markl & Piazolo 1998).

Chlorine is of particular significance with regard to ore-forming processes in view of its ability to both enhance the solubility of many metals (*e.g.*, Cu, Pt, Pd; Mountain & Wood 1988) and to act as an important mechanism for metal transport (*via* complexation; Candela & Holland 1984, Boudreau *et al.* 1986, Fleet & Wu 1993, 1995). It has been recognized as an important component of the fluid phase in a number of magmatic ore deposits, including those found at Stillwater, Bushveld (Schiffries 1982, Boudreau 1995) and Sudbury (Li & Naldrett 1993a, Farrow & Watkinson 1996).

At Sudbury, amphiboles have been recognized as widespread components of assemblages in the Cu–Ni–PGE Footwall deposits (*e.g.*, Thompson *et al.* 1985, Li & Naldrett 1993a, Jago *et al.* 1994, Farrow & Watkinson 1997), contact Ni–Cu deposits (Fleet & Barnett 1978, McCormick *et al.* 1998) and locally developed, heavily altered Footwall Breccia (the so-called Ni-rich Epidote Zone; Farrow & Watkinson 1996). A limited number of authors have investigated the crystal chemistry of these minerals (Fleet & Barnett 1978, Thompson *et al.* 1985, Fleet *et al.* 1987), but they a) focused on environments along the South Range, b) did not analyze amphiboles from Footwall Breccia, c) did not determine the halogen contents of these amphiboles, and d) did not investigate potential relationships to sulfides or ore-forming processes. As part of an on-going project directed at understanding the formation and evolution of Ni–Cu ore deposits occurring in Footwall Breccia at the Fraser

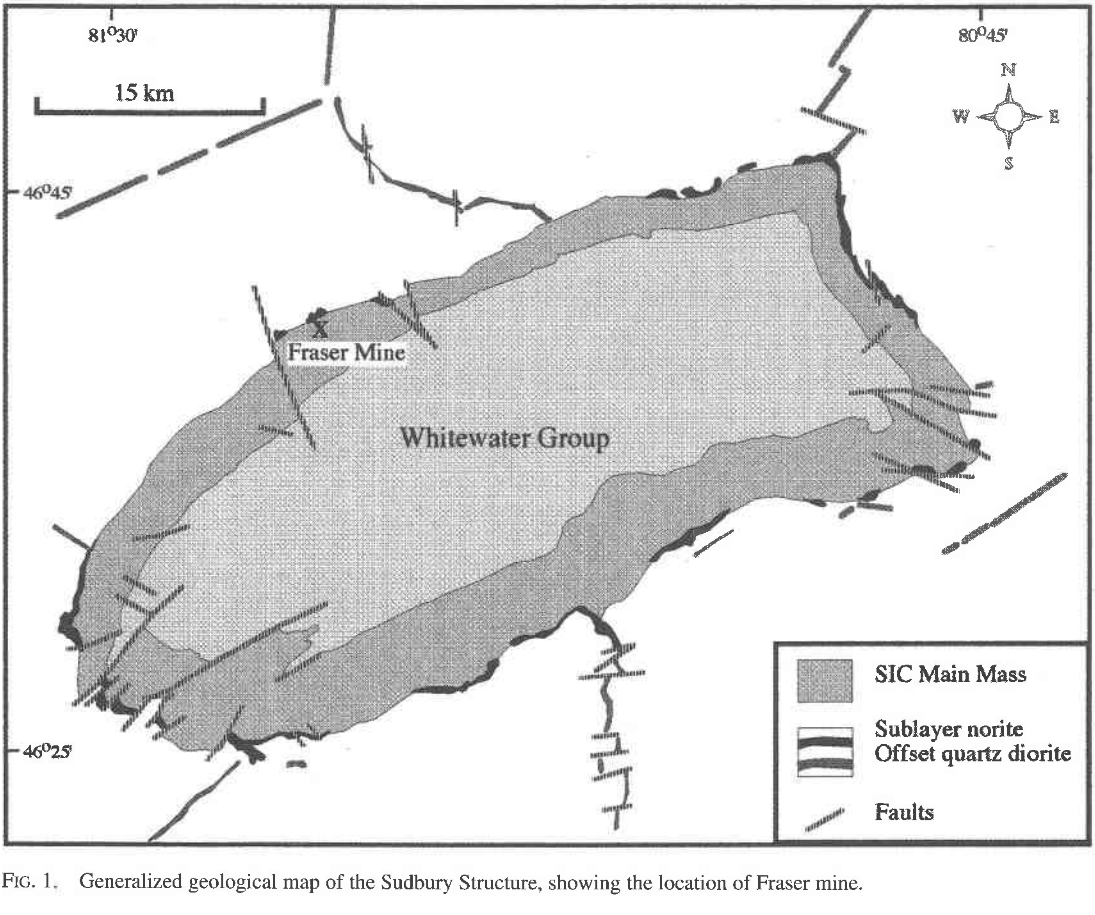

FIG. 1. Generalized geological map of the Sudbury Structure, showing the location of Fraser mine.

FIG. 2. Outcrop of Footwall Breccia near the Fraser mine (pen in center of photograph for scale). Note the variability in clast shape, size, and rock type. Photo courtesy of D. Rousell.

mine, in the Sudbury area, an intimate relationship between sulfides and Cl-rich amphiboles has been observed. The purpose of this report is to provide a description of the amphiboles found here (most notably those that are Cl-rich), an analysis of their crystal chemistry, and a mechanism for their paragenesis, and to outline ideas relating to their genetic relationship to sulfide emplacement.

GEOLOGICAL SETTING AND OCCURRENCE

The Fraser mine (Falconbridge Ltd.) is located in the North Range of the Sudbury Structure (Fig. 1). The geological setting of this area has been described by numerous investigators (a compilation of such work is presented in Pye *et al.* 1984) and will only be briefly discussed here. In short, the Sudbury Structure is located near the junction of the Superior, Southern, and Grenville Provinces of the Canadian Shield, and is believed to have formed at 1850 Ma by a meteorite impact (Dietz 1964, French 1967, Grieve *et al.* 1991, Golightly 1994, Grieve 1994, Stöffler *et al.* 1994). The Sudbury Structure consists of reworked breccias, melt bodies, sedimentary rocks (Whitewater Group), the Sudbury Igneous Complex (SIC) main mass, the Sublayer, Footwall Breccia, Sudbury Breccia and both concentric and radial dikes within the Footwall (Fig. 1). The SIC main mass varies downward in composition from granophyre and quartz gabbro to norite. At the base of main mass is the Sublayer, a discontinuous layer of xenolith-bearing, fine- to medium-grained noritic to gabbroic rock. The amphiboles analyzed in this study occur in Footwall Breccia (Fig. 2), which lies between lithologies belonging to the SIC and the Levack Gneiss Complex (LGC) in the West, North, and East Ranges. This breccia is composed predominantly of fragments derived from local Footwall rocks, although ultramafic fragments of unknown source also are observed. The breccia is quite heterolithic, with individual fragments ranging from several millimeters to tens of meters in size. It occurs as irregularly shaped, discontinuous units that are up to 150 m thick and is of economic significance, as it hosts many of the contact Ni–Cu deposits in the North Range. Compositionally, Footwall Breccia varies from a tonalitic–dioritic composition near the contact with the SIC, to a more granitic one in areas adjacent to the Footwall (Lakomy 1990, McCormick *et al.* 1998). In terms of mineralogy, it is dominated by feldspar [plagioclase (An_{51}–An_1) >> alkali feldspar (Or_{87}–Or_{97})] and quartz, with amphibole and pyroxene also abundant (up to 29 vol. %) in zones adjacent to the SIC. Associated phases include biotite, chlorite, epidote,

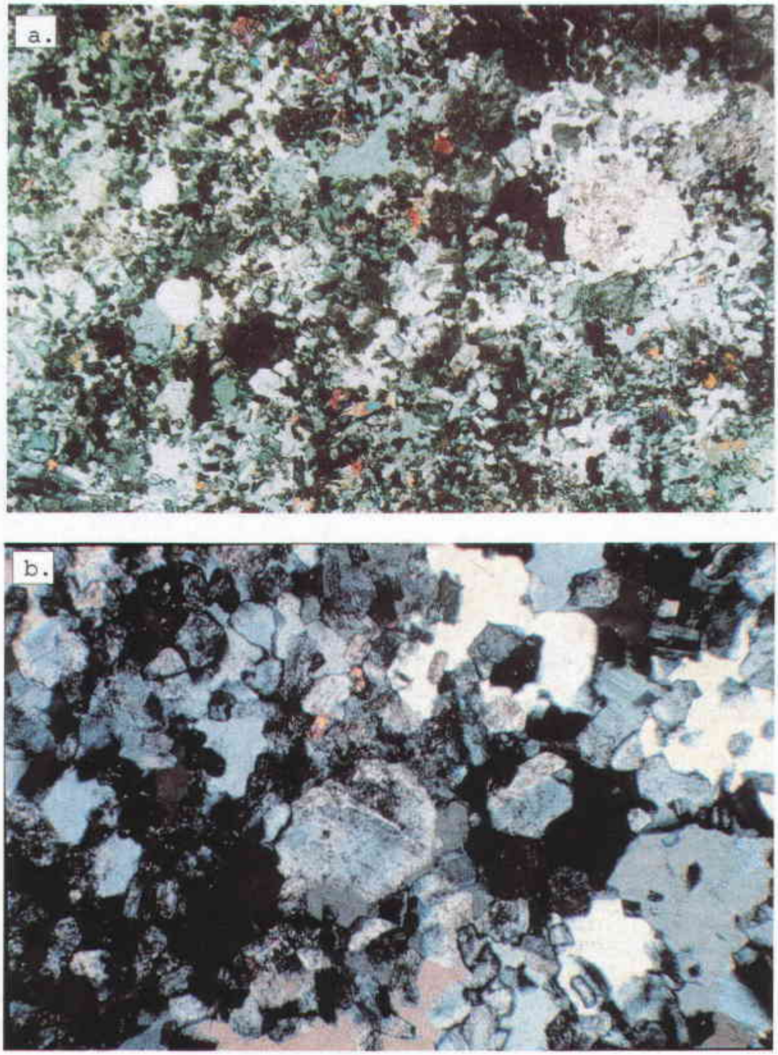

FIG. 3. Photomicrographs (crossed-polarized light) of Footwall Breccia textures. a. Polygonal to oikocrystic quartz, tablet-shaped plagioclase and epidote (high birefringence). Field of view is 5.7 mm in long dimension. b. Oikocrystic quartz enclosing tablet-shaped plagioclase. Field of view is 1.8 mm in long dimension.

titanite and apatite (Lakomy 1990, Farrow & Watkinson 1997, McCormick *et al.* 1998). The Footwall Breccia has a matrix dominated by textures that may be attributed to metamorphism (both thermal and regional processes; Fig. 3), although the textures become igneous in zones proximal to the SIC.

Detailed analyses of both halogen-poor (<0.5 wt.%) and Cl-rich (up to 4 wt.%) amphiboles were made in this study. In general, the two can be distinguished using optical microscopy; under plane-polarized light, the halogen-poor amphibole is pale to olive green, yellow-green to pale green, and more rarely, pale green to light brown in color, whereas the Cl-rich variety exhibits a deep blue-green to deep green color. Rims of blue-green tschermakite to ferrohastingsite around cores of green-brown actinolite have been described previously in norite and metamorphosed Footwall rocks of the South Range (*e.g.*, Thompson *et al.* 1985), but no information was provided on their halogen content. Chlorine-rich calcic amphiboles with a bluish green color similar to those noted in this study have been observed in granulite-facies metamorphosed iron formation (up to

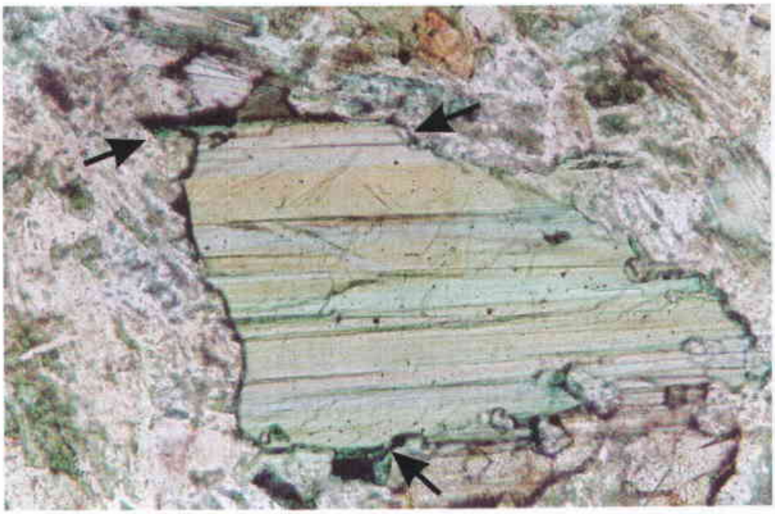

FIG. 4. Photomicrograph (plane-polarized light) of a thin, blue-green Cl-rich hastingsite rim (arrows) around a core of actinolite. Sample taken from a mineralized sample of Footwall Breccia. Field of view is 0.72 mm in long dimension.

2.8 wt.% Cl at Quad Creek in the Beartooth Mountains, Montana; Zhu *et al.* 1994), noritic granulites (up to 3.8 wt.% Cl in the Flakstadøy Basic Complex, Lofoten, Norway; Kullerud 1996) and anorthosite–gabbro complexes (up to 2.1 wt.% Cl in the East Bull Lake complex, northeastern Ontario; Kamineni 1986). The two types of amphibole observed in this study are commonly intimately associated. A halogen-poor, green amphibole generally occurs as a core, and Cl-rich blue-green amphibole develops as a thin overgrowth (up to 40 μm in thickness; Fig. 4). Infrequently, the latter occur as individual crystals up to 100 μm in length (Fig. 5a). Optical microscopy and single-crystal X-ray-diffraction techniques have confirmed that the Cl-rich blue-green overgrowth is monoclinic. Green amphibole is most common, developing as: (i) single, idiomorphic crystals up to 0.1 mm in length, (ii) small granular masses up to 0.15 mm in diameter, and (iii) large masses of intergrown crystals up to 0.5 mm in diameter. In addition, very rare F-rich (up to 1.1 wt.% F) green amphibole also was observed. It should be noted that such F-rich amphibole was never observed in direct association with blue-green Cl-rich amphibole during the course of this study. Modal concentrations of the Cl-rich amphibole are generally <0.5 vol.%. Our results indicate that a Cl-rich blue-green amphibole in the Footwall breccia is almost exclusively restricted to samples taken from mineralized Ni–Cu zones and is typically found in an intimate association with sulfides (Fig. 5b). In unmineralized zones, amphibole grains of a deeper green color are observed, but those with a blue-green hue are virtually absent.

The two types of Cl-bearing amphibole which serve as the focus of this study (*i.e.*, halogen-poor and Cl-rich) are commonly associated with biotite and chlorite, both latter minerals typically occurring as a rim on primary halogen-poor green amphibole or as an intergrowth (possible replacement) with Cl-rich blue-green amphibole. Less common associations include clino- and orthopyroxene, epidote (which is commonly found replacing amphibole) and F-bearing apatite-group minerals (occurring as both inclusions in amphibole and as grains nucleating on amphibole grain boundaries). In mineralized samples, the most commonly associated sulfide is pyrrhotite (which is the most abundant sulfide phase overall), with lesser amounts of chalcopyrite and pentlandite. Associated oxides include magnetite and, very rarely, ilmenite. No statistically significant correlations between the observed mineral associations and the presence of Cl-rich blue-green amphibole were discerned (based on both optical microscopy and image analysis), possibly because of the scarcity or heterogeneous distribution of this amphibole, even in massive sulfide zones.

ANALYTICAL TECHNIQUES

Major-element data were obtained using both a JEOL 6400 digital scanning electron microscope (operated with an accelerating voltage of 20 kV, beam current 2.5 nA) equipped with a Link analytical energy-dispersion spectrometry (EDS) detector, and a Cameca SX–50 electron microprobe (operated with an accelerating voltage of 20 kV, beam current of 15 nA) located

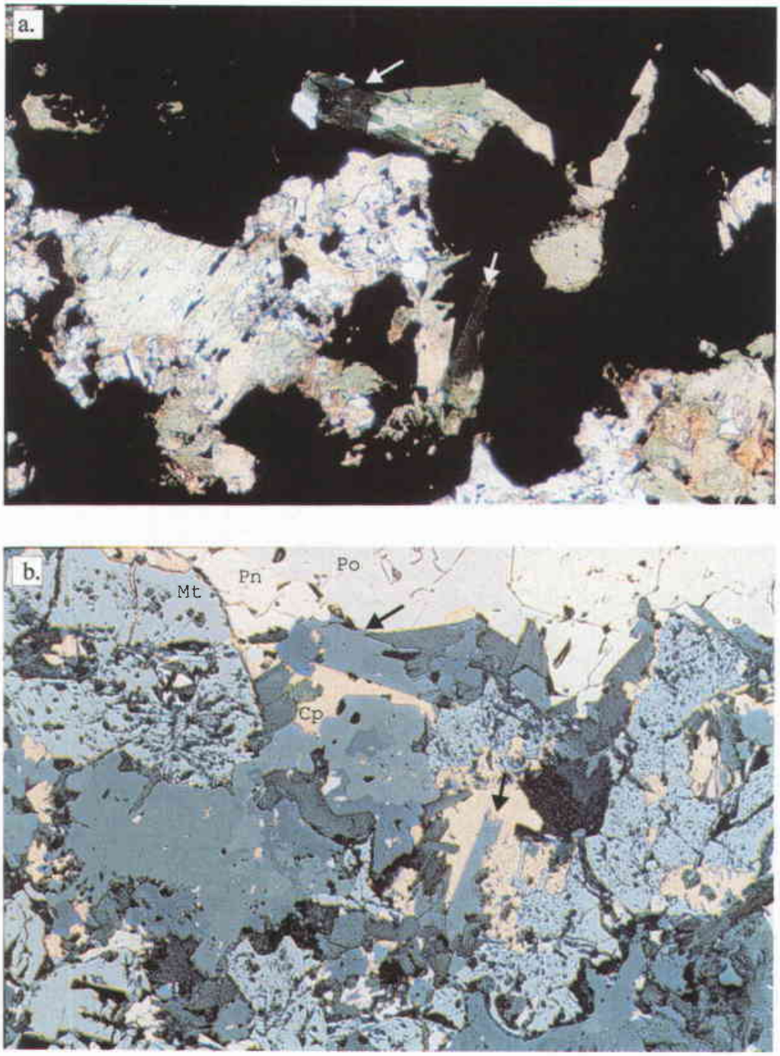

FIG. 5. Photomicrographs of two blue-green Cl-rich hastingsite grains associated with sulfides (pyrrhotite >> chalcopyrite > pentlandite). Field of view in both images is 1.43 mm in long dimension. a. Plane-polarized light. Arrows point to two such grains. b. Reflected light. Arrows point to the same grains as in (a). The two amphibole grains are enclosed in chalcopyrite and pentlandite. Po: pyrrhotite, Pn: pentlandite, Cp: chalcopyrite, Mt: magnetite.

at the Ontario Geosciences Laboratory. Data obtained on the JEOL 6400 scanning electron microscope (SEM) were collected using EDS and counting times of 100 seconds, with data reduction performed using Link Analytical software and a ZAF4 correction. Fit standards used were AMPKNZ and diopside. Data obtained with the Cameca SX–50 electron microprobe were collected using a combination of EDS (Si, Al, Mg, Ca, Fe) and WDS (Mn, Na, K, F, Cl). Data collected by wavelength-dispersion spectrometry (WDS) employed counting times of 20 seconds, and the primary standards included $MnTiO_3$ (Ti$K\alpha$), beryllonite (Na$K\alpha$), orthoclase (K$K\alpha$), BaF_2 (F$K\alpha$) and tugtupite (Cl$K\alpha$). Ba, Cr, V, Zn, and S were also sought, but not detected. The accuracy of results for all the major elements is estimated to be approximately 5%, with detection limits in the range of 0.1–0.2 wt.%.

Structural formulae (Table 1) were calculated on the basis of 13eCNK (13 cations excluding Ca, Na, and K), thus providing a maximum constraint for their Fe^{3+}

TABLE 1. REPRESENTATIVE COMPOSITIONS OF AMPHIBOLE IN THE FOOTWALL BRECCIA

Source	1 MC1	2 BC	3 MC1	4 MC1	5 BC	6 MC1	7 MC2
SiO_2 wt.%	52.9	54.6	50.8	48.5	49.6	41.6	37.9
TiO_2	0.11	*n.d.*	*n.d.*	0.88	0.38	0.07	*n.d.*
Al_2O_3	2.10	1.21	0.20	6.60	5.80	10.0	11.5
Cr_2O_3	*n.d.*	*n.d.*	*n.d.*	0.06	*n.d.*	*n.d.*	0.05
FeO_T	13.9	14.8	31.4	13.9	14.1	27.2	28.7
MnO	0.43	0.68	0.35	0.24	0.32	0.33	1.24
MgO	14.6	14.3	3.60	14.1	14.9	4.90	2.35
CaO	11.8	12.2	11.9	11.8	11.1	11.5	11.4
Na_2O	0.18	*n.d.*	0.05	0.95	1.08	1.08	0.39
K_2O	0.14	*n.d.*	0.02	0.53	0.52	0.90	2.55
Cl	0.08	*n.d.*	*n.d.*	0.50	0.13	0.90	2.45
F	*n.d.*	*n.a.*	*n.d.*	0.30	*n.a.*	*n.d.*	*n.a.*
O=F,Cl	–0.02	…	…	–0.24	–0.03	–0.20	–0.55
Total	96.2	97.8	98.3	98.1	97.9	98.3	98.0
Structural formula on the basis of 13eCNK							
Si *apfu*	7.72	7.86	7.96	7.02	7.08	6.46	6.15
$^{[4]}Al$	0.28	0.14	0.04	0.98	0.92	1.54	1.85
Sum*T*	8	8	8	8	8	8	8
$^{[6]}Al$	0.08	0.06	0.00	0.14	0.06	0.28	0.36
Fe^{3+}	0.41	0.32	0.03	0.61	0.99	0.92	0.86
Cr	0.00	0.00	0.00	0.01	0.00	0.00	0.01
Ti	0.01	0.00	0.00	0.10	0.04	0.01	0.00
Fe^{2+}	1.28	1.46	4.09	1.07	0.69	2.61	3.03
Mn	0.05	0.08	0.04	0.03	0.04	0.04	0.17
Mg	3.17	3.08	0.84	3.04	3.17	1.13	0.57
Sum *C*	5	5	5	5	5	5	5
Fe^{2+}	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Mn	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ca	1.85	1.88	2.00	1.83	1.69	1.91	1.99
Na	0.05	0.00	0.00	0.17	0.30	0.09	0.01
Sum *B*	1.95	1.88	2	2	1.99	2	2
Ca	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Na	0.00	0.00	0.02	0.10	0.00	0.24	0.11
K	0.03	0.00	0.00	0.10	0.09	0.18	0.53
Sum *A*	0.03	0	0.02	0.20	0.09	0.42	0.64
Cl	0.02	0.00	0.00	0.12	0.032	0.24	0.67
F	0.00	…	0.00	0.14	…	0	…

Samples: 1 actinolite core, 2 actinolite near core, 3 ferro-actinolite margin, 4 magnesiohornblende core, 5 magnesiohornblende core, 6 ferrotschermakite wedge in hastingsite, 7 hastingsite rim. MC: mineralized cores (either core 1 or 2 as in Figures), BC: barren core. n.a.: not analyzed, n.d.: not detected, *apfu*: atoms per formula unit.

TABLE 2. THE RANGE IN COMPOSITION OF THE AMPHIBOLE IN THE FOOTWALL BRECCIA

Source	1 MC1	2 MC2	3 BC	4 MC1	5 MC1	6 MC1	7 BC	8* BC
SiO_2	54.6	49.8	53.3	45.6	47.7	36.8	39.3	52.1
TiO_2	0.34	*n.d.*	*n.d.*	*n.d.*	1.40	*n.d.*	*n.d.*	0.42
Al_2O_3	1.20	0.52	0.69	6.42	7.30	10.9	13.9	0.69
Cr_2O_3	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	0.05	*n.d.*	*n.d.*
FeO_T	9.40	33.9	24.1	26.2	10.7	31.9	27.3	28.6
MnO	0.20	0.70	0.70	0.28	0.19	0.40	0.49	2.77
MgO	18.9	1.50	7.97	5.25	16.5	1.90	3.65	10.2
CaO	10.9	11.6	11.8	11.8	11.7	11.2	10.7	2.42
Na_2O	0.54	*n.d.*	*n.d.*	0.37	1.68	0.89	0.91	0.61
K_2O	0.07	*n.d.*	*n.d.*	0.74	0.68	2.69	1.45	0.00
Cl	0.08	*n.d.*	*n.d.*	0.42	n.d.	4.00	0.55	0.12
F	n.d.	*n.a.*	*n.a.*	*n.a.*	1.08	*n.d.*	*n.a.*	*n.a.*
O=F,Cl	–0.02	…	…	–0.09	–0.45	–0.90	–0.12	–0.03
Total	96.2	98.0	98.6	97.0	98.5	99.8	98.1	97.9
Structural formula on the basis of 13eCNK								
Si *apfu*	7.68	7.94	7.98	7.13	6.81	6.02	6.06	7.15
$^{[4]}Al$	0.20	0.06	0.02	0.87	1.19	1.98	1.94	0.11
Sum*T*	7.88	8	8	8	8	8	8	7.26
$^{[6]}Al$	0.00	0.03	0.11	0.32	0.04	0.11	0.58	0.00
Fe^{3+}	0.93	0.08	0.12	0.34	0.69	1.10	1.27	3.28
Cr	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00
Ti	0.04	0.00	0.00	0.00	0.15	0.00	0.00	0.04
Fe^{2+}	0.07	4.44	2.90	3.08	0.58	3.26	2.25	0.00
Mn	0.00	0.09	0.09	0.04	0.02	0.06	0.06	0.00
Mg	3.96	0.36	1.78	1.22	3.52	0.46	0.84	2.09
Sum *C*	5	5	5	5	5	5	5	5.41
Fe^{2+}	0.10	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Mn	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.32
Ca	1.64	1.98	1.89	1.97	1.79	1.96	1.77	0.36
Na	0.15	0.00	0.00	0.03	0.21	0.04	0.23	0.16
Sum *B*	1.91	1.98	1.89	2	2	2	2	0.84
Ca	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Na	0.00	0.00	0.00	0.09	0.25	0.24	0.04	0.00
K	0.01	0.00	0.00	0.15	0.12	0.56	0.29	0.00
Sum *A*	0.01	0	0	0.24	0.37	0.80	0.33	0
Cl	0.02	0.00	0.00	0.11	0.00	1.11	0.14	0.03
F	0.00	…	…	…	0.49	0.00	…	…

Samples: 1 tremolite core, 2 ferro-actinolite rim, 3 ferro-actinolite rim, 4 ferrohornblende rim, 5 magnesiohornblende core, 6 hastingsite within single hastingsite grain, 7 ferrotschermakite rim (the only Cl-rich amphibole found in the barren breccia to date), 8* anthophyllite remnant (the only non-calcic amphibole found); the sum of the *T* and *B* sites are low because Fe^{3+} was not assigned to fill the *T* site. MC: mineralized cores (either core 1 or 2 as in Figures), BC: barren core. n.a.: not analyzed, n.d.: not detected. Concentrations of oxides and halogens are in wt.%.

content (Schumacher 1991). The classification of amphibole species conforms to that proposed by Leake *et al.* (1997).

RESULTS

Representative compositions of amphibole are presented in Table 1, with ranges over the entire dataset shown in Table 2. Species classification of amphiboles from the entire dataset is shown in Figures 6a, b. The data demonstrate that all the amphiboles analyzed in this study, regardless of their halogen content, belong to the calcic amphibole subgroup. In general, the core zone of most of these amphiboles is actinolite or magnesiohornblende, although tremolite and, more rarely, ferro-actinolite also are encountered. These amphiboles may contain low concentrations of halogens (up to 0.5 wt.% Cl + F). Rare grains of F-rich (up to 1.1 wt.% F), Cl-poor amphibole are classified as magnesiohornblende.

The amphibole that overgrows many of the actinolite and magnesiohornblende cores falls into one of two categories: (a) Fe-rich, halogen-poor amphibole (Fig. 6a) and (b) Fe-rich, Cl-rich amphibole (Fig. 6b). The former ranges in composition from ferro-actinolite to ferrohornblende, and the latter, from hastingsite to potassic-chlorohastingsite. In most cases, the hastingsite

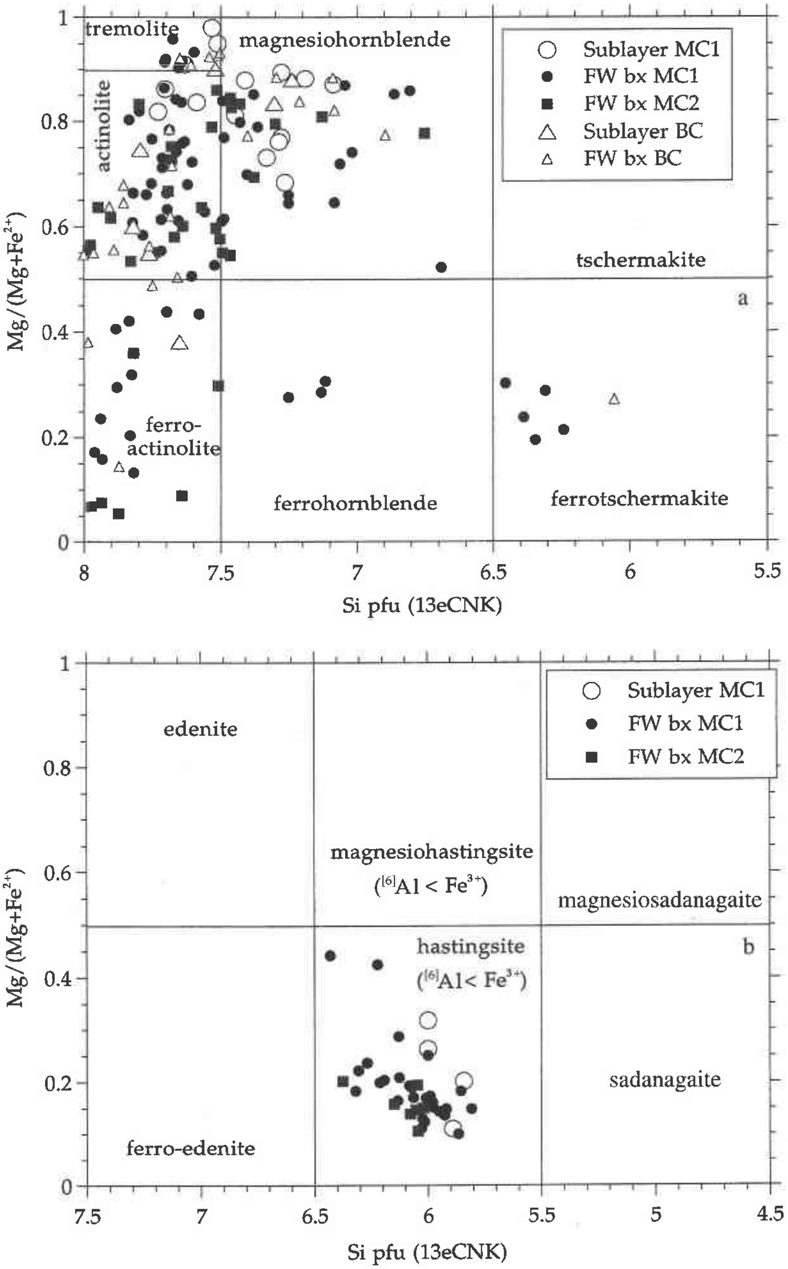

FIG. 6. Amphibole classification diagrams for calcic amphiboles (Leake *et al.* 1997). Data are from EPMA and SEM and recalculated on the basis of 13eCNK. a. For amphiboles with diagram parameters $Ca_B \geq 1.50$; $(Na+K)_A < 0.50$. b. For amphiboles with diagram parameters $Ca_B \geq 1.50$; $(Na+K)_A \geq 0.50$. The iron-rich calcic amphiboles typically occurs as a rim around actinolite and magnesiohornblende. Some grains of magnesiohornblende have up to 1.1 wt.% F. The ferrotschermakite ranges in Cl from 0.55 to 1.0 wt.%. The hastingsite samples in b are all Cl-rich (up to 4.0 wt.%).

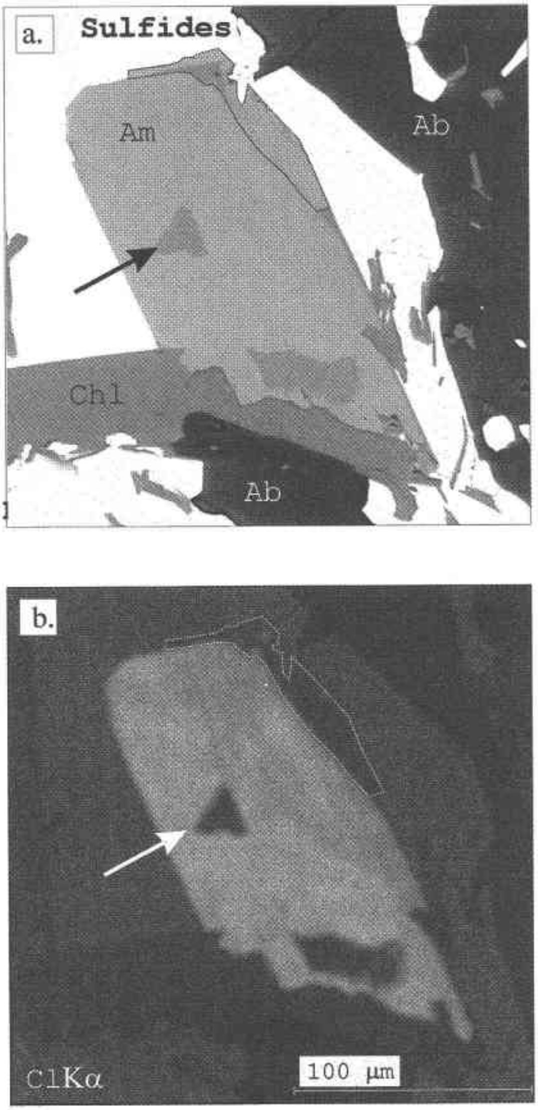

FIG. 7. A single grain of Cl-rich amphibole. a. Back-scattered electron image. b. Cl$K\alpha$ X-ray map of this grain. The Cl concentration varies across the grain, from 2.7 to 3.3 wt.%. The outlined region in a and b is an Fe-rich, halogen-poor amphibole rim (ferro-actinolite; Mg# = 0.13). The darker patches within the bright hastingsite grain in a (shown by arrow) are remnants of a halogen-poor ferro-actinolite core (Mg# = 0.41). Am: amphibole, Chl: chlorite, Ab: albite.

shows a marked enrichment in K, an observation consistent with data for other Cl-rich amphiboles (Krutov 1936, Kamineni *et al.* 1982). Single grains of Cl-rich hastingsite do show a variation in Cl content (2.5 to 4 wt.% Cl), but are always significantly enriched in Cl. A Cl$K\alpha$ X-ray map for a Cl-rich hastingsite (2.7 to 3.3 wt.% Cl) analyzed in this study is presented in Figure 7. It demonstrates that Cl is homogeneously distributed throughout the grain, and that the ferro-actinolite rim and remnant core do not contain Cl above its detection limits. The ferrotschermakite (Fig. 6a) also is Cl-rich (ranging in Cl content from 0.8 to 1.0 wt.%). As with the hastingsite, such amphibole almost always occurs as a rim around halogen-poor amphiboles, and only rarely as single grains.

The blue-green pleochroism observed in Cl-rich amphiboles in this study has been previously observed in compositionally comparable amphiboles. Such pleochroism is commonly encountered in alkali-subgroup amphiboles, where a variety of intervalence charge-transfer mechanisms (IVCT; *e.g.*, Fe^{2+}–Fe^{3+}, Fe^{2+}–Ti^{4+} and Fe^{2+}–Mn$^{2+,3+}$) have been invoked to explain this optical property (Bancroft & Burns 1969, Faye & Nickel 1970). Whereas the Cl-rich amphiboles in this study are relatively enriched in alkalis, these concentrations are below the levels required to classify them as alkali amphiboles. If the cause of the blue-green pleochroism is indeed due to an IVCT mechanism, it is unlikely that the transitions Fe^{2+}–Ti^{4+} and Fe^{2+}–Mn$^{2+,3+}$ can be invoked, owing to the very low to negligible concentrations of Ti and Mn in these minerals. The presence of significant concentrations of both Fe^{2+} and Fe^{3+} is indicated from charge-balance calculations. As such, the Fe^{2+}–Fe^{3+} IVCT mechanism would seem to be the most likely explanation for the observed pleochroism. However, without a direct analysis for both Fe^{2+} and Fe^{3+} in these Cl-rich amphiboles, this proposal can only be considered a working hypothesis.

Examination of major-element relationships among the Cl-rich amphiboles (*i.e.*, >0.5 wt.% Cl) reveals strong positive trends on plots of K and $^{[4]}$Al *versus* Cl (Figs. 8, 9) and a negative one for Mg# [Mg/(Mg +

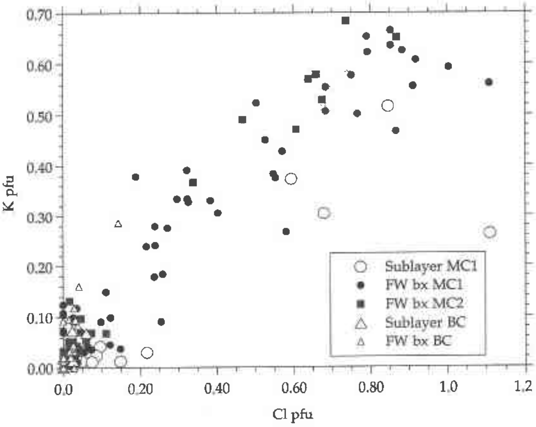

FIG. 8. A plot of K *versus* Cl (all data) showing a generally positive trend.

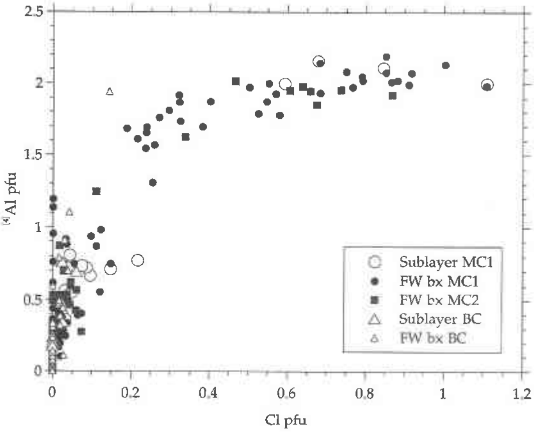

FIG. 9. A plot of $^{[4]}$Al *versus* Cl (all data) showing a well-defined, logarithmic trend.

Fe^{2+})] *versus* Cl (Fig. 10). These complex relationships are also clearly evident on X-ray maps for these elements obtained from Cl-rich blue-green amphibole (Fig. 11).

The relationship between Mg# and Cl is commonly observed in both Cl-rich amphiboles and micas, the explanation for which has been termed the Cl–OH (or Mg–Cl) Avoidance Rule (Volfinger *et al.* 1985). In simple terms, this rule states that owing to crystal chemical restrictions, Cl-rich amphiboles and micas must necessarily also be Fe^{2+}-rich. This requirement was originally ascribed to differences in the ionic radius of Cl (r = 1.85 Å) and OH (r = 1.36 Å), such that significant concentrations of Cl could only be accommodated with the concomitant substitution of $^{[6]}Fe^{2+}$ (r = 0.78 Å) for $^{[6]}Mg^{2+}$ (r = 0.72 Å) in the octahedral sites. Incorporation of $^{[6]}Fe^{2+}$ would result in an enlargement of the crystal structure, thus facilitating incorporation of the much larger Cl ion. The geometrical aspects of this substitution have been challenged by Oberti *et al.* (1993), who contend, on the basis of data from single-crystal XRD studies, that the incorporation of Cl into the amphibole structure results in an expansion of *both* the strips of octahedra and the chains of tetrahedra (the latter due to chain straightening resulting from increased substitution of $^{[4]}$Al for Si). They also argue that accommodation of Cl likely involves incorporation of $^{[6]}Fe^{2+}$, K as well as $^{[4]}$Al, substitutional relationships consistent with observations in natural Cl-rich amphiboles (*e.g.*, Vanko 1986, Morrison 1991, Enami *et al.* 1992, Kullerud 1996). These findings are consistent with results from our study, and clearly indicate that there are concomitant increases of these elements with increasing Cl. Oberti *et al.* (1993) argued further that the preference of Fe^{2+} over Mg^{2+} in the octahedral sites is likely due to short-range order, such that local chemical effects favor Fe–Cl bonds over Mg–Cl bonds. Figure 12 illustrates the direct relationship between Cl and Fe^{2+} in amphiboles from this study. Furthermore, data from this figure reflect low Fe^{3+}/Fe^{2+} values for the Cl-rich amphiboles, suggesting that they likely crystallized under relatively reducing conditions, which in turn may have been influenced by variations in Eh and pH of the fluids. Curiously, whereas the relationship between K and Cl is linear (Fig. 8), that between $^{[4]}$Al and Cl is best described as logarithmic (Fig. 9). This may indicate that the latter mechanism of substitution is most critical to the stabilization of the Cl-rich amphibole structure, and would lend support to the view of Oberti *et al.* (1993).

FIG. 10. Mg# *versus* Cl (*apfu*) for all data. The data define a diffuse, negative trend, illustrating the correlation of proportion of Fe^{2+} with that of Cl, as predicted by the Mg–OH avoidance rule.

Amphiboles containing both F and Cl were rarely encountered in this study. In cases where they were observed, their total halogen contents were found to be relatively low (<0.4 wt.% F, ~0.5 wt.% Cl), and typically with (F + Cl) less than 0.5 wt.% (Fig. 13). Whereas a direct relationship between these two halogens does not seem to exist, amphiboles containing the two halogens define two mutually distinct populations. This may be a feature related to the compositional attributes of their respective environments of formation, although crystal-chemical effects cannot be ruled out.

DISCUSSION

There has been discussion in the literature as to whether the Cl present in so-called Cl-rich amphiboles and micas is structurally bound or whether it is an artifact arising from submicroscopic solid or fluid inclusions (Zhu *et al.* 1994). This debate arises from the fact that many amphiboles exhibit large variations in Cl content between grains as well as within grains, in some cases ranging from quantities below detection to con-

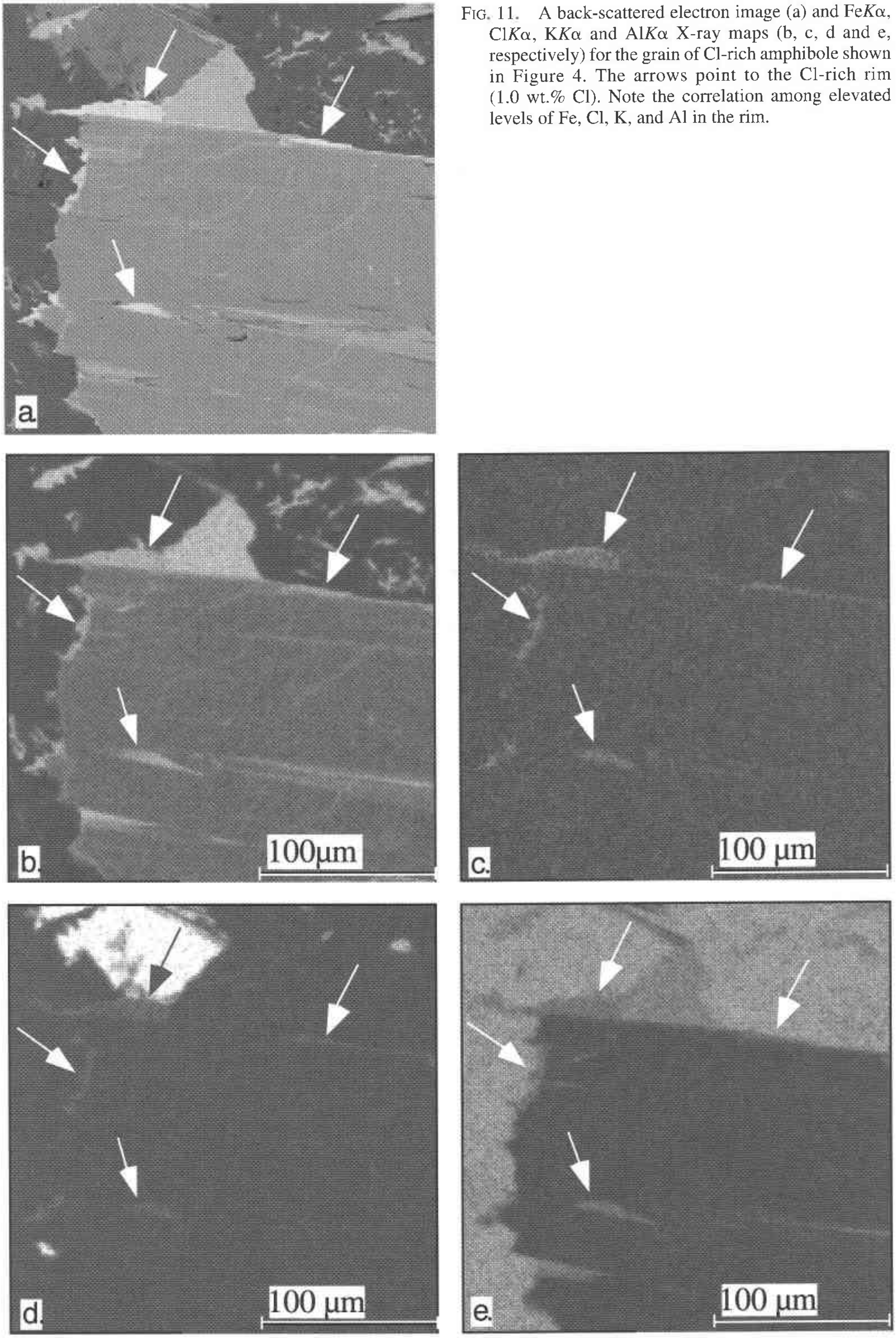

FIG. 11. A back-scattered electron image (a) and Fe$K\alpha$, Cl$K\alpha$, K$K\alpha$ and Al$K\alpha$ X-ray maps (b, c, d and e, respectively) for the grain of Cl-rich amphibole shown in Figure 4. The arrows point to the Cl-rich rim (1.0 wt.% Cl). Note the correlation among elevated levels of Fe, Cl, K, and Al in the rim.

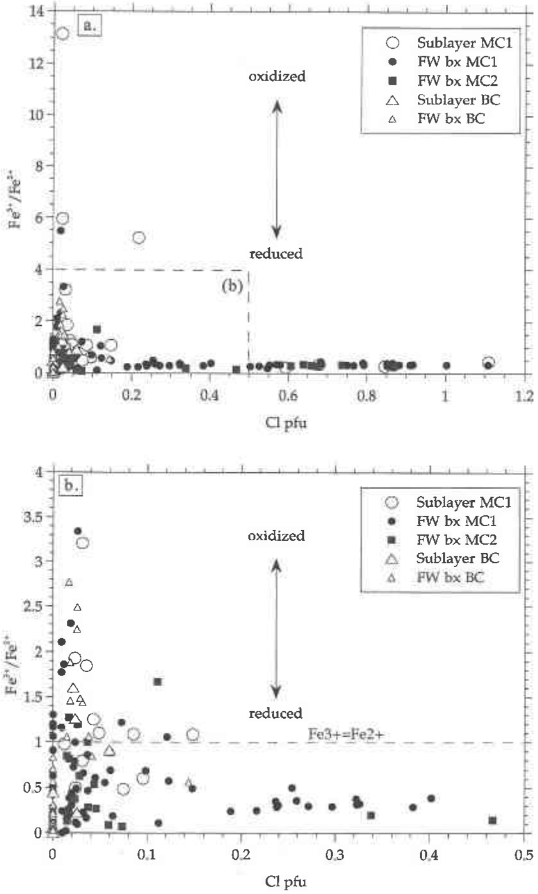

FIG. 12. a. Scatter plot of Fe^{3+}/Fe^{2+} *versus* Cl for all data. b. Expanded view of the dashed area given in a.

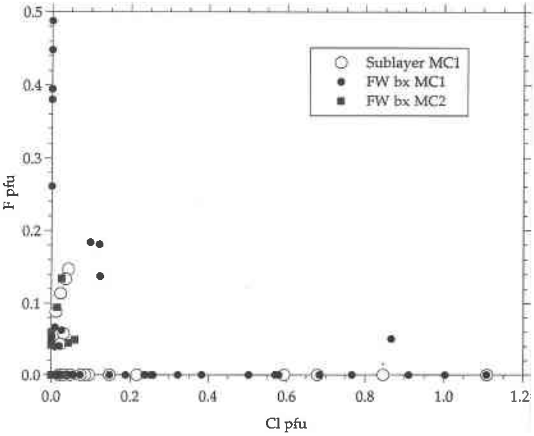

FIG. 13. Plot of proportion of F *versus* Cl for data collected by EPMA. For most amphiboles, F and Cl are mutually exclusive. Where both F and Cl are present, they never exceed 0.5 wt.% each for a given grain.

centrations exceeding 4 wt.% (Morrison 1991, Stakes *et al.* 1991, Zhu *et al.* 1994). Ascribing these variations simply to a crystal-chemical control is not sufficient, given the large range over which these variations occur. In their combined TEM–AEM study relating to this question and in their comparison of primary and retrograde amphibole from a metamorphosed (granulite-facies) iron formation, Zhu *et al.* (1994) demonstrated that two types of calcic amphiboles are present (hastingsite and grunerite, respectively), each characterized by a high Cl content (both up to 2.8 wt.% Cl). On the basis of results from TEM–AEM analyses, however, the retrograde amphibole (grunerite) was found to contain inclusions of Cl-rich annite (1.7–2.8 wt.%) and talc (about 1 wt.%), with the amphibole itself containing no detectable Cl (*i.e.*, <0.1–0.2 wt.%). Such data indicate that high Cl values in some amphiboles can be ascribed to submicrometer inclusions of Cl-rich phases. The Cl-rich amphibole analyzed in this study exhibits some variation in Cl contents (2.5 to 4.0 wt.% Cl in one grain, 2.7 to 3.3 wt.% Cl in another). An X-ray map of Cl*K*α X-rays from one Cl-rich grain presented previously (Fig. 7) clearly demonstrates that Cl is homogeneously distributed throughout the grain. As the distribution of Cl is relatively homogeneous and the grain itself is not characterized by minute regions of extreme enrichment or depletion, the Cl cannot be derived from inclusions. Further support for the fact that artifacts (*e.g.*, included phyllosilicates, fluid inclusions) are not the source of Cl in these Cl-rich amphiboles is evident in binary plots of Cl *versus* K, $^{[4]}$Al and Mg# (Figs. 8, 9, 10), which indicate regular variations with respect to these elements. Lastly, optical microscopy and an XRD analysis indicate that the amphiboles are, for the most part, single-phase. Therefore, we conclude that the Cl present in the Cl-rich amphiboles from this study is structurally bound. The within-grain Cl variation may likely reflect local variations in Cl concentration within the fluid during growth, or variation in the flux of fluid through the sulfides.

High concentrations of Cl in amphiboles (predominantly those belonging to the calcic subgroup) are found in a variety of geological environments including moderate- to high-grade metamorphic rocks, igneous rocks, submarine metasediments and metabasites, skarns and active geothermal systems (Ito & Anderson 1983, Suwa *et al.* 1987, Enami *et al.* 1992, Léger *et al.* 1996). The Cl content of these amphiboles is typically less than 2 wt.%, and rarely exceeds 3 wt.% (Suwa *et al.* 1987). The fact that such Cl-rich amphiboles crystallize over such a wide range in *T* (~350–800°C) and *P* (0–8 kbar) suggests that neither of these variables is a strong factor in controlling the growth or stabilizing these particular minerals. On the basis of data from Cl-rich amphiboles observed in a number of diverse geological environments, Enami *et al.* (1992) concluded that in low-chlorinity environments, the Cl content of an amphibole increases with the chlorinity of the coexisting fluid, as well as crystal-chemical constraints imposed the proportion of (Na + K), Fe and $^{[4]}$Al. In high-chlorine environments, this same content is most strongly dependent on $X(\mathrm{Fe}^{2+})$ and the edenite content (*i.e.*, the substitution $\{^{[A]}(\mathrm{Na,K})^{[4]}\mathrm{Al}\square_{-1}\mathrm{Si}_{-1}\}$) of the amphibole.

A comparison of Cl-bearing amphiboles from igneous, high-grade metamorphic, skarn and geothermal metamorphic rocks with those from this study is presented in Figures 14(a–d). A slight overlap between halogen-poor amphiboles from this study and those from igneous and high-grade metamorphic rocks is evident. There is a small amount of overlap between Cl-rich amphiboles from our work and those from high-grade metamorphic rocks, but trends in the two populations are quite different. There is slightly better agreement (in terms of compositional trends) between our Cl-rich amphiboles and those from skarns, but the majority of our data do not lie within the field ascribed to skarns. In fact, the Cl-rich amphiboles from this study overlap to the greatest extent (in terms of both composition and trend) with those from the Salton Sea geothermal system. The major implication of this observation is that the Cl-rich amphiboles from the Footwall Breccia may have developed under conditions similar to those that gave rise to amphiboles in the Salton Sea. Amphiboles from this environment are believed to have crystallized at temperatures of approximately 350°C and pressures of 0.3 kbar (Enami *et al.* 1992). A temperature of formation of 400 ± 50°C was obtained in this study using actinolite–albite pairs along the margin of a Cl-rich biotite vein and the geothermometer proposed by Spear (1980). This value is consistent not only with that determined for the Salton Sea amphiboles, but is also within the range of 130–435°C obtained by microthermometric studies of fluid inclusions from the Deep Copper zone at Strathcona mine, on the North Range (Farrow & Watkinson 1992, Li & Naldrett 1993a, Molnár *et al.* 1998).

As has been noted earlier in this report, Cl-rich amphiboles observed in this study are intimately associated with Ni–Cu mineralization, which suggests that a genetic link between the two may exist. The important role of halogen-rich fluids (notably those rich in Cl) in the formation of comagmatic, Footwall Cu–Ni–PGE ore deposits in Sudbury is well known and has been established through numerous studies, as noted earlier. Therefore, it is not unreasonable to conclude that geochemically similar fluids may have also played a part in the formation of magmatic, contact Ni–Cu orebodies, although there do not seem to have been any published studies on the matter. However, given the low modal abundance of Cl-rich amphibole and biotite, and the absence of Cl-rich apatite in Footwall Breccia, the implication is that the saline fluids associated with contact Ni–Cu deposits did not play the same role as those involved in formation of Footwall Cu–Ni–PGE deposits.

There is much debate as to the whether the fluids associated with Footwall Copper orebodies arose from magmatic (*e.g.*, exsolution from a sulfide-rich silicate magma as it approached its solidus; Li *et al.* 1992, Li & Naldrett 1993a, b, Jago *et al.* 1994) or hydrothermal processes (*i.e.*, heated Footwall fluids; Farrow & Watkinson 1992, Molnár *et al.* 1998). Likewise, the source of saline fluids within the Footwall Breccia is not known. In considering potential sources for Cl throughout the Sudbury Structure, we have analyzed whole-rock samples of the gneiss from the Archean Levack Gneiss Complex Footwall rock, and have noted anomalous Cl concentrations in excess of 700 ppm (McCormick *et al.* 1999), suggesting that these rocks may have been important contributors to the fluids associated with mineralization. Further evidence to support this hypothesis comes from a study conducted by Marshall *et al.* (1999). On the basis of results from fluid inclusion, ^{40}Ar–^{39}Ar and both stable (O, H) and radiogenic (Rb, Sr) isotope analyses, these authors have been able to document a mixing trend between an 1800 Ma magmatic fluid (temporally consistent with the ~1850 Ma age determined for the SIC; Krogh *et al.* 1984) and a 2400 Ma high-temperature fluid. The latter fluid has an age corresponding to that of peak metamorphism of the Levack Gneiss (*i.e.*, ~2640 Ma; Krogh *et al.* 1984), thus suggesting that it may have been a product of the breakdown of hydrous minerals during melting of this complex. The SIC Sublayer also contains Cl-bearing amphiboles, apatite (Warner *et al.* 1998; up to 3.7 wt.%, McCormick *et al.* 1998) and micas (McCormick *et al.* 1998, M. Reich, pers. commun.), suggesting that it too may have been a potential source for Cl. At this time, it is not clear if either the Footwall or Sublayer was the dominant (or perhaps only) source for these fluids, and mixing of the two fluid sources cannot be ruled out.

Conceptual Model for Amphibole Formation

Results from this study have demonstrated that on the basis of halogen content, three populations of amphiboles are recognized in the Footwall Breccia (*i.e.*, halogen-poor, Cl-rich and F-rich). Considering the crystal-chemical behavior of F, Cl and OH, at least two chemically distinct fluids must have been involved in the crystallization of these minerals. Temporally, it is apparent that a halogen-poor fluid was responsible for the formation of primary, halogen-poor pale green amphibole. Such amphiboles likely acted as nucleation sites for the crystallization of a secondary growth of Cl-rich blue-green amphibole (occurring predominantly as a rim), which could have developed by influx of a completely unrelated second fluid, or possibly through a modified primary fluid. Since Cl will preferentially

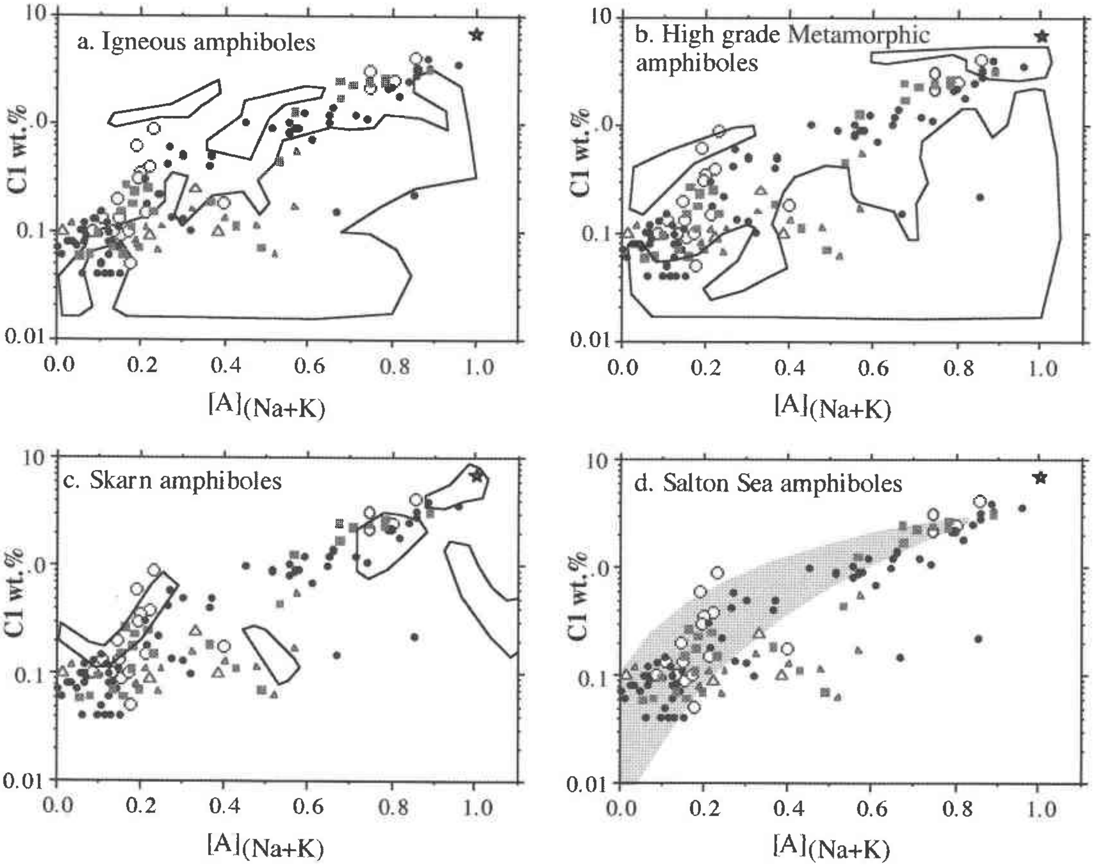

FIG. 14. Amphibole data from this study compared to information for Cl-bearing amphibole from four different geological environments, as compiled by Enami *et al.* (1992). All data have been recalculated on the basis of 23 anions per formula unit. The star indicates the composition of the "ideal" chlorohastingsite. a. Igneous amphiboles ($n = 136$), b. high-grade metamorphic amphiboles ($n = 189$), c. skarn amphiboles ($n = 27$), and d. Salton Sea amphiboles. The data from amphiboles examined in this study overlap to the greatest degree with those from the Salton Sea geothermal field.

remain in a fluid over OH during amphibole crystallization, (Boudreau *et al.* 1986, Markl & Piazolo 1998), the presence of Cl-rich amphiboles indicates that the ratio $a_{Cl}^{fluid}/a_{H2O}^{fluid}$ was high when they formed.

The temporal relationship between both the halogen-poor and Cl-rich amphiboles and those that are F-rich is difficult to ascertain, considering the latter amphiboles are not observed in direct contact with either of the former two. Given that: (i) the F-rich amphibole is found most commonly to occur as single grains or clusters of grains rather than as a rim, and (ii) that two distinct populations of halogen-bearing amphiboles exist (*i.e.*, F- and Cl-bearing, Fig. 13), the implication is that a distinct, F-rich fluid, presumably unrelated to the other fluid(s) (from which the halogen-poor and Cl-rich amphiboles grew), was involved. The influx of a F-rich fluid is also supported by the presence of F-bearing apatite, which occurs in both mineralized zones (where it is intergrown with sulfides) and unmineralized zones (where it has nucleated on, and is overgrown by, halogen-poor amphibole). The crystals of F-bearing apatite that are intergrown with the sulfides are typically rounded and fractured, suggesting that the apatite was not in equilibrium with the surrounding assemblage. The crystals of F-bearing apatite within the unmineralized breccia are typically more equant and unfractured. The presence of amphiboles containing both F and Cl imply that these F-rich fluids also contained some Cl.

Through petrographic examinations conducted in this study, an alteration assemblage characterized by epidote + chlorite (+ albite) has been identified in both mineralized and unmineralized zones. This assemblage clearly postdates formation of Cl-rich amphiboles. It commonly rims or occurs in various stages of replacement of both Cl-rich and halogen-poor amphibole. The conditions under which this assemblage formed are not

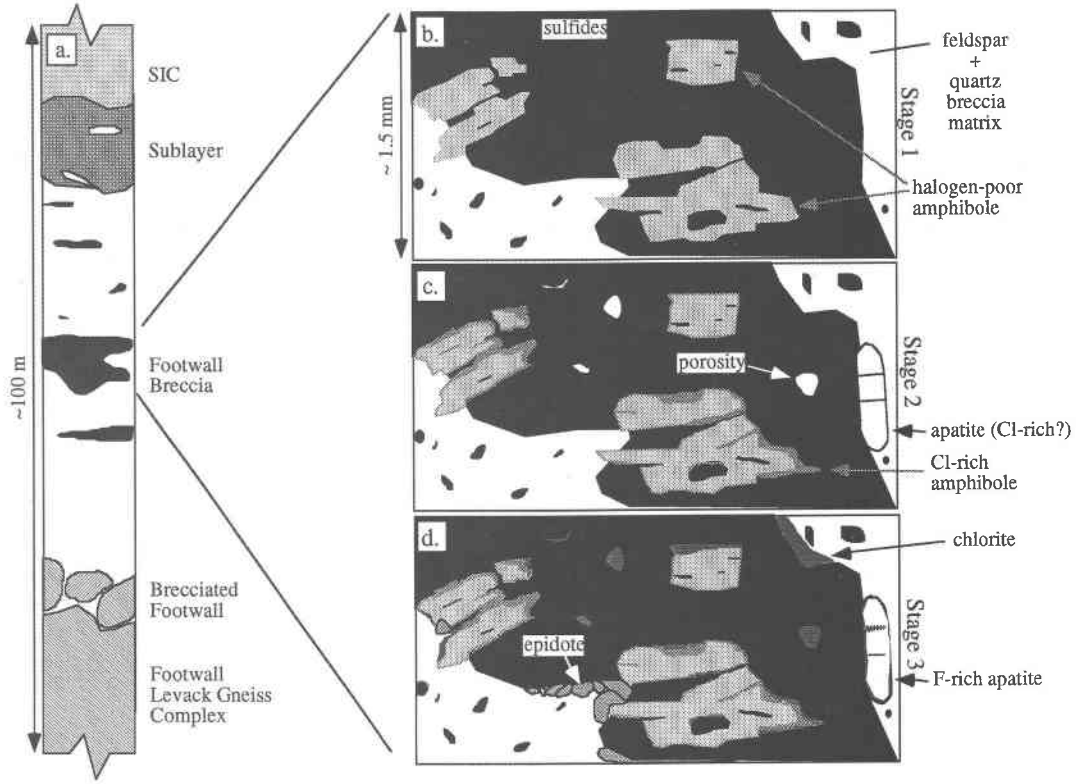

FIG. 15. A conceptual model of the growth of phases associated with mineralization in the Footwall Breccia. a. A generalized schematic log through the Footwall breccia in the North Range, from the SIC main mass to the Footwall Levack Gneiss. b. Stage 1, in which halogen-poor amphibole grew from hot fluids associated with the ore emplacement in the breccia. c. Stage 2, in which hot, highly saline fluids percolate through the breccia, following the same pathways as the sulfides. Cl-rich amphibole grew during this stage; we speculate that Cl-rich apatite could also have grown at this time within the breccia. d. Stage 3, in which possible cooler, H_2O- and F-rich fluids could have filtered through the breccia pile, resulting in the formation of F-rich amphibole, re-equilibration (or formation) of apatite, which is F-rich, and formation of epidote and chlorite (+ albite).

known, but it is possible that it was produced through a separate period of fluid influx. Epidote and chlorite ("ripidolite") also commonly nucleate on the margins of the sulfides (mainly pyrrhotite, *e.g.*, Fig 7a). The presence of epidote, as it is a Fe^{3+}-dominant phase, suggests that the fluids associated with this alteration assemblage were relatively oxidizing. Consistent with this speculation is the modal increase of ilmenite relative to magnetite outside the mineralized breccia zones (the ilmenite: magnetite ratio can vary from 0 in massive sulfide to >12 in barren breccia), which is suggestive of a reaction involving the oxidation of titanian magnetite to magnetite + ilmenite in the unmineralized breccia.

Furthermore, the crystal-chemical preference of F over Cl in the OH site of amphibole (as well as in biotite and apatite; Boudreau *et al.* 1986, Markl & Piazolo 1998), and the fact that F- and Cl-bearing amphiboles exist in mutually distinct populations (Fig. 14), together suggest that the concentration of F present during formation of the Cl-rich amphiboles must have been extremely low.

A conceptual model relating to the formation of the halogen-poor and halogen-bearing amphiboles in Footwall Breccia is diagrammatically represented in Figure 15. This model requires at least two fluids to have circulated through the ore zones. Two models could account for the halogen-poor and Cl-bearing amphiboles, and their textural relationship (*i.e.*, cores and rims, respectively). Model 1 is a two-fluid model, with an aqueous fluid preceding a saline fluid. In this model, we speculate that a hot (≥650°C, based on the presence of exsolved pentlandite in the sulfide assemblage) aqueous fluid, likely contemporaneous with sulfide emplacement, was present proximal to and within the ore zones, from which the halogen-poor, pale green amphibole crystallized (Fig. 15b). This hypothesis is based on the fact that the halogen-poor amphibole: (i) occurs intergrown with sulfides, (ii) typically is idiomorphic, and (iii) commonly contains inclusions of sulfides that are elongate parallel to growth planes (schematically shown in Fig. 15b). This aqueous fluid was followed by a second, relatively hot fluid (≥350°C, based on both plagioclase–amphibole geothermometry and on chemical similarities between amphiboles characterized in this study and those from the Salton Sea geothermal system) that was highly saline. This saline fluid percolated through the ore zones, likely following the same preferred pathways as did the sulfides themselves. Growth of Cl-bearing phases may have been facilitated within the ore zones because of the increased void space generated by contraction of pentlandite (and a concomitant reduction in volume) during cooling. From this second fluid, the blue-green Cl-rich amphibole crystallized, preferentially nucleating on and around grains of halogen-poor amphibole (Fig. 15c). The localization of the Cl-bearing phases around the ore zones may be a function of both permeability and the availability of Fe^{2+}. In particular, the availability of Fe^{2+} proximal to, and within, ore zones would be expected to have been quite high, whereas that within unmineralized Footwall Breccia would be considerably lower, on the basis of the relatively lower modal abundance of Fe-bearing phases in such areas. The availability of Al and the alkalis (Na and K) could have been supplied through the alteration of feldspar in combination with a saline fluid.

Model 2 is a desiccation model similar to that presented by Kullerud (1996) and Markl *et al.* (1998) to explain the presence of Cl-rich amphiboles in metamorphic terranes. In the case of Footwall Breccia, this model requires the influx of an initially halogen-poor fluid, likely contemporaneous with the emplacement of the sulfides (Fig. 15b). This aqueous fluid stagnated and slowly became enriched in Cl relative to H_2O *via*: (i) the hydration–alteration of pyroxene to amphibole, (ii) the growth of hydrous phases (*i.e.*, amphibole and biotite). As in model 1, we speculate that this aqueous fluid was initially quite hot (≥650°C). With time, this fluid became saturated with salt (*i.e.*, became a brine), and the volume of the fluid phase decreased, resulting in the loss of permeability in the system. The Cl-rich phases were formed by local equilibration of the hydrous phases (amphibole and biotite), and produced a rim around them (Fig. 15c). The Cl-rich amphibole growth likely occurred at temperatures ≥350°C (as in model 1). This desiccation model is consistent with petrographic observarions and fluid-inclusion studies (*e.g.*, Molnár *et al.* 1998), but does require that the system remained closed for a sufficient amount of time to permit evolution of the fluid to a highly saline brine. The permeability of the Footwall Breccia during the time of formation of these amphiboles is unknown. Thus, the probability of maintaining a closed system within and proximal to mineralized breccia for long periods of time cannot be evaluated.

Data from the mineralogical characterization of the Footwall Breccia from the ore zones outward into unmineralized regions suggest that a separate F-rich, aqueous fluid was present that presumably was more oxidizing (on the basis of the presence of epidote, as noted earlier), and that moved through the breccia. The temporal relationship between the F-rich, aqueous fluid, which gave rise to the F-rich amphibole (and F-bearing apatite) and the fluid(s) that produced the halogen-poor and Cl-rich amphiboles is not known, owing to the absence of direct spatial associations (*e.g.*, overprinting, cross-cutting relationships *etc.*) among the three populations of amphibole. However, on the basis of disequilibrium textures observed in F-bearing apatite that are intergrown with sulfides, we speculate that the apatite may have re-equilibrated with a F-rich fluid. Therefore, the F-rich fluid likely postdated that which formed the Cl-rich phases. It is not clear at present if the fluid from which the F-rich amphiboles crystallized and that which produced the alteration assemblage were one and the same, or if two distinct fluids were responsible. As such, they are treated as a single fluid in our model. On the basis of petrographic evidence previously outlined, it is clear that the epidote + chlorite (+ albite) assemblage postdates the Cl-rich and halogen-poor amphiboles (Fig. 15d).

As previously mentioned, F-bearing phases (apatite and amphibole) and the epidote + chlorite assemblage are not limited to mineralized breccia; thus it is possible (although no cross-cutting relationships have been documented) that this fluid(s) was more regional in extent. The modal increase in ilmenite relative to magnetite in the Footwall Breccia outside of ore zones, suggestive of significant changes in $f(O_2)$, also supports this interpretation. The growth of these phases could have resulted from an influx of cooler H_2O- and F-rich fluid. Whole-rock data show that levels of F in amphibolite samples of the Levack Gneiss Complex can exceed 2500 ppm (McCormick *et al.* 1999), indicating that F-rich fluids have been present in the Sudbury region prior to the development of the Sudbury Structure, and thus might have been a potential source of the F-rich fluid that circulated through the breccia pile.

CONCLUSIONS

1. Three chemically distinct populations of amphibole have been recognized in Footwall Breccia at the Fraser mine, Sudbury, Ontario: (a) Halogen-poor (<0.5 wt.%), Fe-rich, pale green amphibole (typically actinolite or magnesiohornblende in composition), (b) Cl-rich (>0.5 wt.%), Fe-rich, blue-green amphibole (hastingsite to potassic-chlorohastingsite in composition), which most commonly occurs as a thin rim on (a), and (c) rare, F-rich (up to 1.1 wt.% F), Cl-poor amphibole (magnesiohornblende).

2. Strong positive correlations between K and $^{[4]}$Al (respectively) *versus* Cl and a negative one between Mg# *versus* Cl exist for the Cl-rich amphibole.

3. Two paragenetic models are proposed that could have led to the development of the halogen-poor and halogen-rich amphiboles noted in this study: (i) A two-fluid model, in which an earlier halogen-poor aqueous fluid formed the actinolite and magnesiohornblende, and a separate, saline fluid produced the Cl-rich amphibole, and (ii) a dessication model, in which a single, initially halogen-poor aqueous fluid formed the actinolite and magnesiohornblende, and, in time, evolved to a saline brine that equilibrated with the local mineral assemblage and formed the rims of Cl-rich amphibole.

4. An intimate spatial relationship exists between sulfides in the Footwall Breccia environment and the Cl-rich amphibole. However, there is little evidence at this point to support a temporal relationship, and they may not be cogenetic. Instead, the fluids from which the Cl-bearing amphibole grew may have followed the same preferred pathways as did the sulfides.

5. Cl-bearing phases have also been noted in other mineralized environments within the Sudbury Structure (*e.g.*, Deep Copper zone, Sublayer). Documentation of trends toward halogen enrichment may be important in the recognition of ore zones in a variety of potentially mineralized environments (*e.g.*, Jago *et al.* 1994, Boudreau 1995).

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