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PYROSMALITE IN CANADIAN PRECAMBRIAN SULFIDE DEPOSITS: MINERAL CHEMISTRY, PETROGENESIS AND SIGNIFICANCE

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ABSTRACT

Pyrosmalite-series minerals [$(Fe,Mn)_8Si_6O_{15}(OH,Cl)_{10}$] are reported from metamorphosed sulfide deposits in three Canadian Precambrian mining camps: Matagami, Quebec (Archean, Zn–Cu–Ag–Au), Manitouwadge, Ontario (Archean, Cu–Zn–Ag–Au) and Thompson Nickel Belt, Manitoba (Proterozoic, Ni–Au–PGE). As a result of electron-microprobe data, pyrosmalite is found to form a continuous solid-solution series from a value of Mn/(Fe + Mn) of 0.08 to 0.85, and is a sink for Cl. Textural characteristics and element partitioning indicate that pyrosmalite crystallized during both regional metamorphism and late-stage hydrothermal activity. However, the initial Cl-enrichment in the host lithologies may have occurred during seafloor hydrothermal alteration as an integral part of the syngenetic ore-forming processes for the associated base-metal mineralization. Identification of pyrosmalite in volcanogenic massive sulfide (VMS) deposits provides further support for a brine-pool model for ore genesis and suggests that the precious-metal mineralization commonly associated with these sulfide deposits may have been related to Cl-rich fluids.

Keywords: pyrosmalite-series minerals, (Fe,Mn) solid solution, Cl-enrichment, Canadian Precambrian sulfide deposits, brine-pool model, precious-metal mineralization.

SOMMAIRE

Nous avons découvert des membres de la série de la pyrosmalite [$(Fe,Mn)_8Si_6O_{15}(OH,Cl)_{10}$] dans des gisements métamorphisés de sulfures dans trois camps miniers précambriens canadiens: Matagami, Québec (archéen, Zn–Cu–Ag–Au), Manitouwadge, Ontario (archéen, Cu–Zn–Ag–Au), et la ceinture nickelifère de Thompson, Manitoba (protérozoïque, Ni – Au – éléments du groupe du platine). A la lumière des données obtenues par microsonde électronique, la pyrosmalite est une solution solide continue [Mn/(Fe + Mn) entre 0.08 et 0.85] et concentre le Cl présent dans ces roches. Les textures caractéristiques et la répartition des éléments montrent que la pyrosmalite a cristallisé à la fois au cours d'un métamorphisme régional et pendant une activité hydrothermale tardive. Toutefois, l'enrichissement initial des lithologies hôtes en Cl aurait pu se produire au cours d'une altération hydrothermale lors de la minéralisation syngénétique en métaux de base, sur les fonds océaniques. La présence de la pyrosmalite dans des gisements volcanogéniques de sulfures massifs étaye l'hypothèse d'un bassin de saumures impliqué dans la minéralisation; la présence d'une accumulation des métaux précieux couramment associée à ce genre de gisement de sulfures témoignerait de l'implication d'une phase fluide riche en chlore.

(Traduit par la Rédaction)

Mots-clés: minéraux du groupe de la pyrosmalite, solution solide (Fe, Mn), enrichissement en Cl, gisements de sulfures précambriens canadiens, modèle de bassin de saumures, minéralisation en métaux précieux.

INTRODUCTION

Pyrosmalite was originally established as a single mineral species (Zambonini 1901, Dana 1920, Frondel & Bauer 1953, and references therein), but presently refers to minerals within the solid-solution series $(Mn,Fe)_8Si_6O_{15}(OH,Cl)_{10}$, including the end-members manganpyrosmalite and ferropyrosmalite (Vaughan 1987). In this paper, "pyrosmalite" will be used to refer to the solid-solution series. The structure of pyrosmalite consists of brucite-type layers of octahedra alternating with sheets of tetrahedra, both upward- and downward-facing in six-membered Si_6O_{15} rings (Kashaev 1968, Takéuchi *et al.* 1969, Kato & Takéuchi 1983), with Cl preferentially located at OH(1) positions (Kato & Takéuchi 1983). Similar sheet silicates include "brokenhillite" (Czank 1987, questionable status in Nickel & Nichols 1991), friedelite (*cf.* Bauer & Berman 1928, Frondel & Bauer 1953), mcgillite (Donnay *et al.* 1980), nelenite (Dunn & Peacor 1984) and schallerite (*cf.* Bauer & Berman 1928, Frondel & Bauer 1953), and are collectively referred to as minerals of the friedelite group. Peacor & Essene (1980) suggested that caryopilite has a gen-

TABLE 1. OCCURRENCES OF THE PYROSMALITE SERIES

References	Occurrences	Composition	Metamorphic Grade
Zambonini 1901, Dana 1920	Nordmark, Sweden (Fe, Proterozoic)	X_{Mn}= 0.41-0.49 Cl = 3.79-4.88	amphibolite facies
Zambonini 1901, Dana 1920	Dannemora, Sweden (Fe, Proterozoic)	X_{Mn}= 0.51 Cl = 3.52-3.70	amphibolite facies
Bauer & Berman 1928, Frondel & Bauer 1953	Sterling Hill, New Jersey, USA (Zn-Fe-Mn, Proterozoic)	X_{Mn}= 0.76 Cl = 3.80	granulite facies
Hutton 1956, Stillwell & McAndrew 1957, Plimer 1984	Broken Hill, Australia (Pb-Zn-Ag, Proterozoic)	X_{Mn}= 0.42-0.85 Cl = 3.78-3.80	granulite facies
Watanabe & Kato 1958, Watanabe et al. 1961	Kyurazawa mine, Tochigi, Japan (Fe-Mn, Paleozoic)	X_{Mn}= 0.53-0.82 Cl = 5.00-5.63	(metamorphosed)
Kayupova 1964	Dzhumart and Ushkatyn deposits, Kazakhstan (Fe-Mn)	X_{Mn}= 0.60 Cl = 3.62	(metamorphosed)
Oftedal & Saebø 1965	nordmarkite druses, Grorud, Oslo, Norway	no information	?
Sundius et al. 1966	Hällefors, Sweden (Ag-Fe-Mn, Proterozoic)	no information	amphibolite facies
Kazachencko et al. 1979	Primorye, Russia (Pb-Zn-Au-Ag, Cretaceous)	X_{Mn}= 0.55-0.64 Cl = 5.35	(metamorphosed)
Vaughan 1986	Pegmont, Australia (Pb-Zn, Proterozoic)	X_{Mn}= 0.08 Cl = 4.00-4.25	amphibolite facies
Fan et al. 1992	Wafangzi, Liaoning, China (Mn-Fe, Proterozoic)	X_{Mn}= 0.65 Cl = 3.49	contact metamorphosed
Costa et al. 1983, this study	Mattagami Lake mine, Matagami, Quebec (Zn-Cu-Ag-Au, Archean)	X_{Mn}= 0.33-0.85 Cl = 0.79-5.42	greenschist facies
Pan & Fleet 1992, this study	Geco & Willroy mines, Manitouwadge, Ontario (Cu-Zn-Ag-Au, Archean)	X_{Mn}= 0.17-0.62 Cl = 0.12-5.93	amphibolite to granulite facies
this study	Thompson mine, Thompson, Manitoaba (Ni-Au-PGE, Proterozoic)	X_{Mn}= 0.10-0.15 Cl = 2.73-4.87	amphibolite to granulite facies

X_{Mn} = Mn/(Fe + Mn) atomic ratio.

eral formula of $(Mn,Fe,Mg)_8Si_6O_{15}(OH)_{10}$ and also is a member of the friedelite group.

Although pyrosmalite was originally considered to be exceedingly rare, it has since been observed with increasing frequency in metamorphosed polymetallic sulfide deposits and Fe–Mn deposits worldwide (Table 1). However, identification of pyrosmalite-series minerals has undoubtedly been obscured by its optical resemblance to white micas (Pan & Fleet 1992). The discovery of the pyrosmalite-series minerals in the Geco Cu–Zn–Ag–Au massive sulfide deposit of the Manitouwadge mining camp, Ontario (Pan & Fleet 1992, E.U. Petersen, pers. commun. 1992) was made only through a combination of electron-microprobe analysis and X-ray powder diffraction. Similarly, manganpyrosmalite in the Mattagami Lake Zn–Cu–Ag–Au massive sulfide deposit, Matagami, Quebec (Costa 1980, Costa *et al.* 1983) was recognized by partial electron-microprobe analysis (without a determination of Cl) and single-crystal X-ray diffraction. More recently, we have identified pyrosmalite-series minerals in two other Canadian Precambrian sulfide deposits: the Willroy Cu–Zn–Ag–Au massive sulfide deposit of the Manitouwadge mining camp, Ontario, and the Thompson nickel sulfide deposit of the Thompson Nickel Belt, Manitoba.

In this paper, we report on the textures and chemical compositions of pyrosmalite-series minerals in the above three Canadian Precambrian mining camps. Results of electron-microprobe analyses establish a continuous solid-solution between ferropyrosmalite and manganpyrosmalite. Textural characteristics and element partitioning are used to elucidate the paragenesis and origin of pyrosmalite in these metamorphosed sulfide deposits; assemblages of coexisting minerals and available fluid-inclusion data are analyzed to constrain its conditions of formation. In addition, we discuss the significance of pyrosmalite, and particularly its high Cl content, in metamorphosed massive sulfide deposits in the light of syngenetic models (Friesen *et al.* 1982, Costa 1980, Costa *et al.* 1983, Large 1992). Finally, the occurrence of pyrosmalite with associated Cl-rich fluids is related to precious-metal mineralization commonly associated with Precambrian sulfide deposits (*cf.* Friesen *et al.* 1982, Costa 1980, Costa *et al.* 1983, Hannington & Scott 1989, Large *et al.* 1989, Chen *et al.* 1993, Large 1992).

OCCURRENCES AND PETROGRAPHY

Matagami, Quebec

The Mattagami Lake mine exploits an Archean volcanic rock-hosted Zn–Cu–Ag–Au massive sulfide deposit located in the Matagami mining camp of northwestern Quebec, within the Abitibi subprovince of the Superior Province (Costa 1980, Costa *et al.* 1983, and references therein). It consists of two ore zones (a pyrite – sphalerite unit and a pyrite – pyrrhotite – magnetite unit) and is underlain by vitroclastic rhyolite and basalt of the Watson Lake Group and overlain by the Key Tuffite (Fig. 1; Costa 1980, Costa *et al.* 1983, and references therein).

Pyrosmalite at the Mattagami Lake mine is restricted to the uppermost portion of the pyrite–sphalerite unit, just below the hanging-wall Key Tuffite (Fig. 1). The pyrosmalite-bearing rocks are composed of pyrite, sphalerite, pyrrhotite, magnetite, chalcopyrite, carbonates (calcite, dolomite, ankerite and siderite), talc, cummingtonite–dannemorite, actinolite–tremolite, chlorite, stilpnomelane, pyrosmalite, and caryopilite (Costa 1980, Costa *et al.* 1983).

Pyrosmalite locally makes up 30–40% by volume of the pyrite – sphalerite ore, commonly occurring as large grains or flakes (up to 0.5 × 0.3 mm) with well-developed basal cleavage, in close association with carbonates and disseminated within the ore minerals (Fig. 2a). Mutual contacts with amphiboles (*i.e.*, cummingtonite–dannemorite and actinolite–tremolite) and other silicate minerals are common, but no replacement texture involving pyrosmalite after any other mineral phases

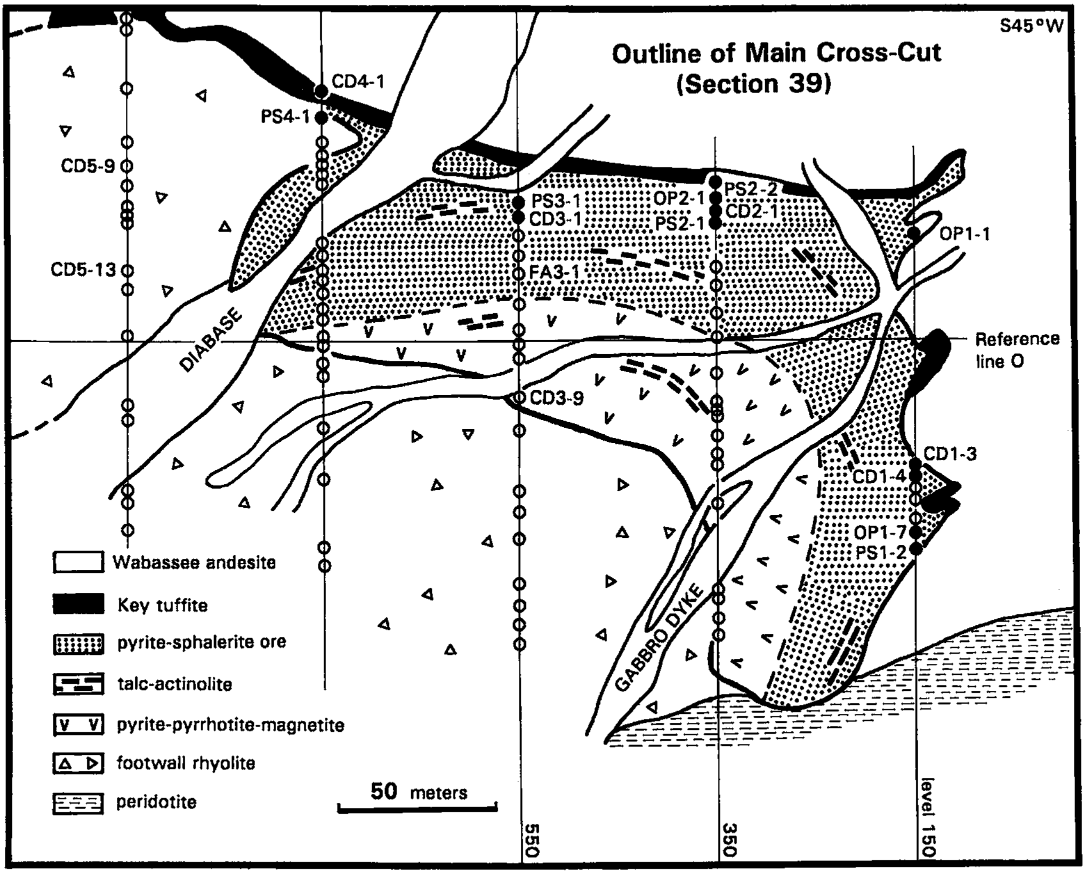

FIG. 1. Geological outline of section 39 of the Mattagami Lake Zn–Cu–Ag–Au orebody, with sample locations (after Costa *et al.* 1983). Only numbers for the pyrosmalite-bearing samples (filled circles) and those cited in Tables 2 and 3 are given.

has been observed. Instead, individual grains of pyrosmalite are commonly rimmed by caryopilite (Fig. 2b).

Manitouwadge, Ontario

Pyrosmalite has been observed in the Geco and Willroy mines, two of the four Archean Cu–Zn–Ag–Au massive sulfide deposits at the Manitouwadge mining camp of northwestern Ontario, which is located at the northern edge of the Wawa subprovince of the Superior Province (Friesen *et al.* 1982, Petersen 1986, Pan & Fleet 1992). These deposits are stratigraphically underlain by garneti-

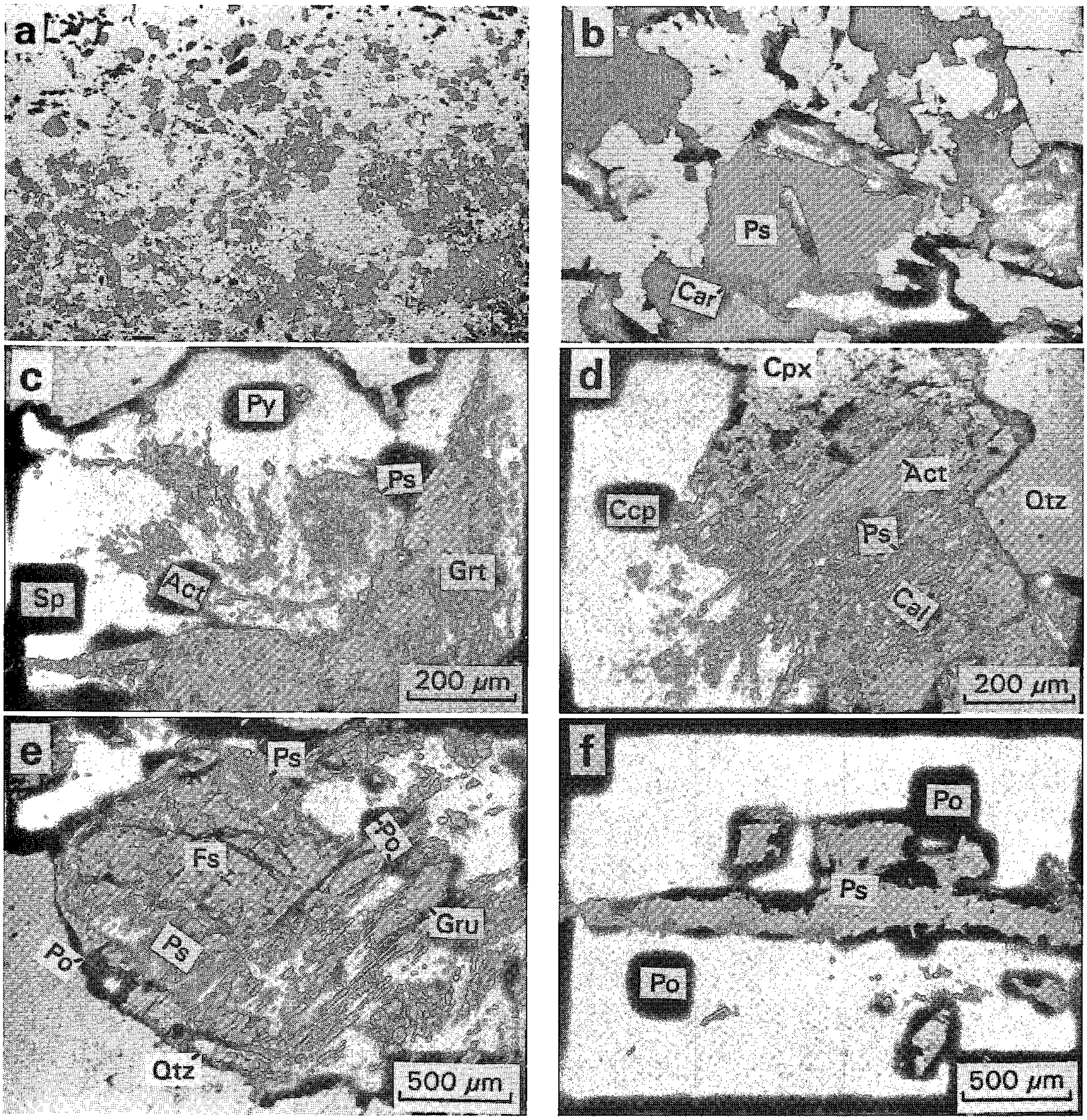

FIG. 2. Electron back-scattered images (a and b) and photomicrographs (c, d, e and f) illustrating occurrences and textures of pyrosmalite (Ps): a) as a major phase (grey) associated with ore minerals (white: including pyrite, sphalerite, pyrrhotite and magnetite) from the Mattagami Lake mine; note several crystals of pyrosmalite showing a hexagonal outline (scale bar: 100 μm); b) partly replaced by caryopilite (Car), from the Mattagami Lake mine (scale bar: 10 μm; c) in association with garnet (Grt), actinolite (Act), pyrite (Py), and sphalerite (Sp) as characteristic radiating clusters, from the Geco mine (from Pan & Fleet 1992); d) in association with actinolite (Act), calcite (Cal) and quartz (Qtz) as an aggregate replacing clinopyroxene (Cpx) in chalcopyrite(Ccp)-rich ore from the Willroy mine; e) in association with grunerite (Gru), quartz and pyrrhotite (Po) as aggregates replacing ferrosilite (Fs) from the Thompson mine, and f) in association with pyrrhotite as cross-cutting vein from the Thompson mine.

ferous cordierite – orthoamphibole gneisses that are interpreted as altered mafic to intermediate volcanic rocks, and are overlain by quartz – biotite – feldspar gneisses, interpreted as metasediments with intercalated volcanic rocks (Friesen *et al.* 1982). The massive sulfide deposits and supracrustal country-rocks have undergone multiple periods of deformation and have been subjected to a regional metamorphism of upper amphibolite to granulite facies (Petersen 1986, Pan & Fleet 1992).

Pyrosmalite in the Geco mine appears to be restricted to the lower, smaller 4/2 Copper Zone (for metal zonation, see Friesen *et al.* 1982). It occurs both as extremely fine-grained inclusions (<15 μm in maximum dimension) within spessartine-rich garnet porphyroblasts and as radiating clusters associated with actinolite (Fig. 2c), epidote, chlorite, plagioclase, K-feldspar, biotite, calcite, sphalerite, and pyrite in skarn-like calc-silicates (Pan & Fleet 1992).

In the Willroy mine, pyrosmalite was observed in several samples of chalcopyrite-rich ore. It is commonly present in association with actinolite, quartz, calcite, epidote, and chlorite as aggregates replacing clinopyroxene (Fig. 2d) and garnet.

Thompson Nickel Belt, Manitoba

The Thompson Nickel Belt is located at the boundary between the Superior and Churchill provinces. The zone of nickel mineralization at the Thompson mine is associated with sequences of metasedimentary rocks, including metapelite (biotite schist) and related granitic pegmatite, quartzite, skarn and iron formation. Serpentinites occur in the pelitic member as small lenses (Peredery *et al.* 1982). The main Ni-sulfide mineralization is found in metapelite, and minor disseminations of sulfides are present in ultramafic lenses. Regional metamorphism of the Thompson Nickel Belt includes an earlier granulite-facies event, followed by an amphibolite-facies event of the Hudsonian Orogeny and a late-stage hydrothermal alteration (Peredery *et al.* 1982).

Pyrosmalite was observed at the Thompson mine in only one sample of banded iron formation (BIF) that was collected within the footwall and about 3 to 15 meters below the nickel sulfide orebodies; the footwall is characterized by alternating layers rich in iron silicates + magnetite and rich in quartz. The layers rich in iron silicates + magnetite consist of mainly garnet,

TABLE 2. COMPOSITIONS OF THE PYROSMALITE SERIES

Location	Mattagami Lake mine				Manitouwadge			Thompson	
Sample	PS4-1	PS2-1	OP1-7	OP1-7	8383[a]	8383[b]	9360	TS18[c]	TS18[d]
SiO_2 (wt. %)	34.42	35.19	34.84	35.44	35.29	31.42	34.56	34.12	34.48
TiO_2	0.03	0.00	0.00	0.00	0.00	0.03	0.00	0.00	0.11
Al_2O_3	0.13	0.02	0.08	0.06	0.06	2.43	0.40	0.24	0.24
Cr_2O_3	0.00	0.02	0.03	0.00	0.00	0.00	0.03	0.04	0.05
MnO	28.04	43.66	23.25	17.39	20.36	31.70	12.85	7.04	5.76
FeO*	24.61	8.07	28.88	35.09	34.47	21.18	40.23	46.77	46.73
MgO	1.01	1.78	0.81	1.40	0.25	0.42	0.02	0.54	0.58
ZnO	0.00	0.02	0.46	1.03	0.00	0.00	0.00	0.00	nd
CaO	0.04	0.02	0.00	0.00	0.04	0.21	0.29	0.03	0.09
Na_2O	0.05	0.01	0.00	0.00	0.00	0.04	0.01	0.02	0.03
K_2O	0.02	0.00	0.00	0.01	0.00	0.04	0.00	0.01	0.12
Cl	5.14	4.54	4.00	0.79	0.92	3.70	4.19	4.87	3.17
H_2O**	7.32	7.59	7.58	8.61	8.51	7.59	7.49	7.35	7.77
O≡Cl	1.16	1.02	0.90	0.18	0.21	0.86	0.94	1.10	0.71
Total	99.65	99.90	99.03	99.64	99.69	97.90	99.13	99.93	98.42
	Chemical formulae calculated on the basis of 14 cations								
Si	5.98	6.03	6.07	6.02	6.04	5.52	6.05	5.95	6.02
^{IV}Al	0.02	0.00	0.00	0.00	0.00	0.48	0.00	0.05	0.00
^{VI}Al	0.01	0.00	0.01	0.01	0.01	0.02	0.08	0.01	0.06
Cr	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02
Fe	4.08	1.16	4.21	4.95	4.92	3.10	5.89	6.81	6.82
Mg	0.26	0.45	0.21	0.35	0.06	0.11	0.05	0.14	0.16
Mn	3.62	6.34	3.43	2.47	2.95	4.71	1.91	1.04	0.86
Zn	0.00	0.00	0.06	0.13	0.00	0.04	0.00	0.00	----
Ca	0.01	0.00	0.00	0.00	0.01	0.00	0.05	0.00	0.01
Na	0.01	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.01
K	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02
Cl	1.51	1.32	1.18	0.23	0.27	1.10	1.24	1.44	0.94
OH	8.49	8.68	8.82	9.77	9.73	8.90	8.76	8.56	9.06

see Fig. 1 for sample numbers and locations of the Mattagami Lake mine; 8383 and 9360 are samples of the Geco and Willroy mines, respectively; TS18 is a banded iron formation sample of the Thompson mine; a, in radiating cluster; b, as inclusion in garnet porphyroblast; c, in cross-cutting vein; d, replacing ferrosilite; wt. %, weight percent;
*, total iron content as FeO; **, H_2O calculated from OH = (10 − Cl).

TABLE 3a. COMPOSITIONS OF PYROXENES, CARYOPILITE AND BIOTITE

Mineral	pyroxenes		caryopilite			biotite		
Sample^a	9360	TS18	PS2-2	CD4-1	FA3-1	CD5-9	CD5-13	TS18
SiO_2 (wt. %)	50.86	47.10	37.27	37.39	37.09	36.72	38.04	33.29
TiO_2	0.00	0.08	0.00	0.00	0.02	1.74	0.17	1.68
Al_2O_3	0.20	0.39	0.03	1.12	0.11	14.70	13.43	16.36
Cr_2O_3	0.00	0.01	0.00	0.03	0.04	0.00	0.02	0.00
MnO	4.13	1.85	6.98	10.40	4.12	0.28	0.17	0.22
FeO*	14.63	46.48	41.54	32.70	43.98	17.53	18.13	32.31
MgO	6.94	4.27	3.45	8.87	4.61	12.62	15.25	3.73
ZnO	0.00	nd	0.24	nd	0.07	nd	nd	nd
CaO	23.48	0.26	0.00	0.11	0.02	0.04	0.04	0.08
BaO	nd	nd	nd	nd	nd	0.06	0.02	0.19
Na_2O	0.21	0.01	0.01	0.00	0.00	0.02	0.05	0.07
K_2O	0.00	0.01	0.00	0.01	0.02	9.80	9.80	8.91
F	0.00	0.00	0.00	0.00	0.00	2.08	2.83	0.48
Cl	0.00	0.00	0.61	0.76	0.54	0.13	0.06	0.19
O≡F,Cl	0.00	0.00	0.14	0.17	0.12	0.95	1.28	0.26
Total	100.45	100.46	89.99	91.22	90.50	94.77	96.73	97.25
	6 oxygens		(Si + Al) = 6**			22 oxygens		
Si	1.99	1.99	5.99	5.80	5.98	5.69	5.79	5.36
^{IV}Al	0.01	0.01	0.01	0.20	0.02	2.31	2.21	2.64
^{VI}Al	0.00	0.01	0.00	0.00	0.00	0.37	0.20	0.46
Ti	0.00	0.00	0.00	0.00	0.00	0.20.	0.02	0.20
Cr	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Fe	0.48	1.65	5.59	4.23	5.92	2.27	2.31	3.25
Mg	0.40	0.27	0.83	2.05	1.11	2.91	3.46	0.89
Mn	0.14	0.07	0.95	1.36	0.56	0.04	0.02	0.03
Zn	0.00	----	0.03	----	0.01	----	----	----
Ca	0.00	0.01	0.00	0.02	0.00	0.01	0.01	0.01
Ba	----	----	----	----	----	0.00	0.00	0.01
Na	0.02	0.00	0.00	0.00	0.00	0.01	0.02	0.02
K	0.00	0.00	0.00	0.00	0.00	1.93	1.90	1.83
F	0.00	0.00	0.00	0.00	0.00	1.02	1.36	0.24
Cl	0.00	0.00	0.17	0.20	0.15	0.03	0.02	0.05

a, see Table 2 and Fig. 1; wt. %, weight percent; *, total iron content as FeO; **, after Peacor & Essene (1980).

biotite, and magnetite, with variable amounts of pyroxene, grunerite, pyrosmalite, ilmenite, and pyrrhotite. Two distinct textural varieties of pyrosmalite are present. More commonly, pyrosmalite occurs as aggregates with grunerite, quartz and pyrrhotite after ferrosilite (Fig. 2e). Although replacement along or parallel to the cleavage of ferrosilite is observed locally (Fig. 2e), most aggregates occur around grain boundaries and show no preferred crystallographic orientation to the host ferrosilite, indicating the absence of any epitaxic relationship between these two minerals (see also Hutton 1956). Secondly, pyrosmalite also is present in association with pyrrhotite in cross-cutting veins (Fig. 2f).

MINERAL CHEMISTRY

The chemical composition of pyrosmalite and associated minerals from the three Canadian Precambrian mining camps is presented in Tables 2 and 3. All chemical analyses were made with a JEOL JXA–8600 electron microprobe fitted with four automated wavelength-dispersion spectrometers, at the University of Western Ontario. Operating conditions included an

TABLE 3b. COMPOSITIONS OF AMPHIBOLES

Location	Mattagami Lake mine						Manitouwadge		Thompson
Sample^a	PS4-1	OP1-7	PS4-1	OP1-7	CD3-9	CD3-9	8383	9360	TS18
Mineral	Dan	Dan	Act	Act	Edn	Par	Act	Act	Gru
SiO_2 (wt. %)	54.01	53.37	54.06	51.75	44.88	39.77	49.63	54.33	50.16
TiO_2	0.00	0.00	0.00	0.00	0.28	0.04	0.00	0.00	0.00
Al_2O_3	0.04	0.15	1.15	1.33	10.78	16.69	0.04	0.06	1.12
Cr_2O_3	0.00	0.02	0.00	0.00	0.01	0.00	0.06	0.00	0.01
MnO	10.54	11.14	4.33	3.14	1.24	1.38	7.12	2.01	1.50
FeO*	17.68	20.29	11.07	20.57	16.23	19.13	28.69	15.07	36.29
MgO	15.30	12.53	15.56	8.66	10.93	7.80	0.78	13.18	7.42
ZnO	nd	0.57	nd	1.20	nd	nd	0.00	0.00	0.00
CaO	0.67	0.39	11.96	11.37	10.33	10.87	11.47	12.48	0.03
Na_2O	0.01	0.05	0.12	0.34	2.05	2.25	0.05	0.07	0.45
K_2O	0.01	0.00	0.00	0.13	0.19	0.36	0.07	0.01	0.10
Cl	0.00	0.00	0.00	0.02	0.69	1.50	0.00	0.00	0.20
O≡Cl	0.00	0.00	0.00	0.00	0.16	0.34	0.00	0.00	0.05
Total	98.26	98.55	98.26	98.51	97.46	99.45	97.91	97.21	97.23
	Chemical formulae calculated on the basis of 23 cations								
Si	8.00	8.02	7.81	7.83	6.75	6.02	7.98	7.99	7.93
^{IV}Al	0.00	0.00	0.19	0.17	1.25	1.98	0.01	0.01	0.07
^{VI}Al	0.00	0.03	0.01	0.07	0.64	1.00	0.00	0.00	0.14
Ti	0.00	0.00	0.00	0.00	0.03	0.00	0.00	0.00	0.00
Cr	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Fe	2.19	2.55	1.34	2.60	2.03	2.42	3.86	1.85	4.79
Mg	3.38	2.81	3.35	1.95	2.44	1.76	0.19	2.89	1.75
Mn	1.32	1.42	0.53	0.40	0.16	0.18	0.97	0.25	0.20
Zn	----	0.06	----	0.13	----	----	0.00	0.00	0.00
Ca	0.11	0.06	1.85	1.85	1.66	1.77	1.98	1.97	0.00
Na	0.00	0.01	0.03	0.10	0.60	0.66	0.01	0.02	0.14
K	0.00	0.00	0.00	0.03	0.04	0.07	0.01	0.00	0.02
Cl	0.00	0.00	0.00	0.00	0.17	0.38	0.00	0.00	0.05

Act, actinolite; Dan, dannemorite; Edn, edenite; Gru, grunerite; Par, pargasite; a, see Table 2 and Fig. 1; wt. %, weight percent; *, total iron content as FeO.

accelerating voltage of 15 kV, beam current of 10 nA, beam diameter of 2–3 mm, 20-second counting time, and minerals and synthetic glasses as standards. Matrix corrections were performed using the Tracor-Northern ZAF program.

Pyrosmalite

Although pyrosmalite from the Mattagami Lake, Geco, and Willroy mines is extremely heterogeneous in chemical composition from sample to sample, it is generally homogeneous within individual grains, and exhibits only minor grain-to-grain variations within most samples in all three Precambrian mining camps examined in this study. Pyrosmalite in only one sample (OP1–7) of the Mattagami Lake mine shows wide variations in both Cl content and Mn/(Fe + Mn) ratio, which are positively correlated (Fig. 3). A similar correlation between Cl and Mn/(Fe + Mn) ratio was reported for pyrosmalite in skarn-like calc-silicates from the Geco mine (Pan & Fleet 1992).

Most compositions of pyrosmalite-series minerals in the literature have an Mn/(Fe + Mn) atomic ratio ranging from 0.41 to 0.85 (Table 1, Fig. 4). An Fe-rich end-member with Mn/(Fe + Mn) = 0.08 was described only recently from the Pegmont deposit, Australia (Vaughan 1986). The two texturally distinct varieties of pyrosmalite in the banded iron formation of the Thompson mine (Figs. 2e,f) show no compositional difference and have an Mn/(Fe + Mn) ratio ranging from 0.10 to 0.15 (Table 1), consistent with the high whole-rock Fe/Mn ratio and similar to that of the most Fe-rich end-member from the Pegmont deposit (Vaughan 1986). Pyrosmalite from the Geco, Willroy and Mattagami Lake mines varies widely in Mn/(Fe + Mn) ratio (Tables 1, 2) and encompasses both ferropyrosmalite and manganpyrosmalite. Of particular interest are the intermediate compositions of ferropyrosmalite from the Geco and Willroy mines, indicating a continuous solid-solution series from 0.08 to 0.85 (Fig. 4). However, pure end-member compositions of either ferropyrosmalite or manganpyrosmalite have not yet been found (Table 1, Fig. 4).

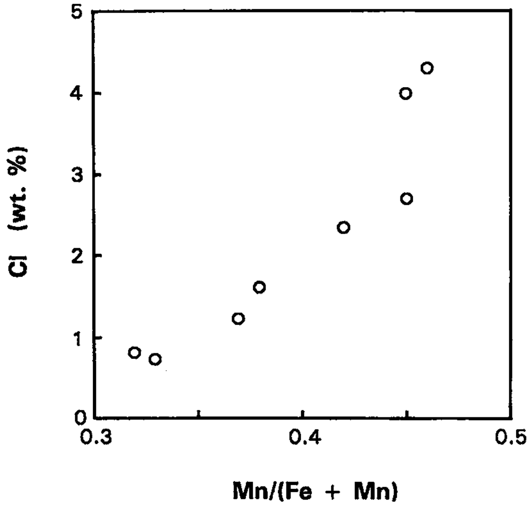

FIG. 3. Plot of Cl *versus* Mn/(Fe + Mn) showing compositional variation of pyrosmalite in sample OP1–7 from the Mattagami Lake mine, Quebec (see Fig. 1).

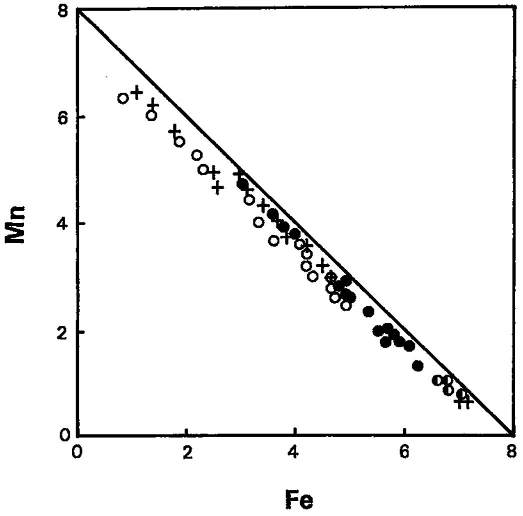

FIG. 4. Plot of Mn *versus* Fe showing a complete solid solution in the pyrosmalite series from a Mn/(Fe + Mn) value of 0.08 to 0.85. Crosses represent data from the literature, open circles, from the Mattagami Lake mine, Quebec, filled circles, from the Geco and Willroy mines, Ontario, and half-filled circles, from the Thompson mine, Manitoba. The solid line indicates the ideal correlation.

Chlorine is present in all pyrosmalite grains analyzed to date (Tables 1, 2). Although most pyrosmalite compositions established in the present study have a Cl content within the range in the literature (3.58 to 5.63 wt.% Cl; *cf.* Vaughan 1986), chlorine-depleted compositions (less than 3.58 wt.% Cl) also have been obtained for some pyrosmalite grains from all three Canadian Precambrian mining camps (Table 2).

Significant amounts of Zn and Mg have been detected in pyrosmalite from the Mattagami Lake mine (Table 2; *cf.* Frondel & Bauer 1953, Hutton 1956, Stillwell & McAndrew 1957). Zinc is typically below detection limit in ferropyrosmalite from the Thompson mine. Although sphalerite is abundant in all pyrosmalite-bearing samples from both the Geco and Willroy mines, and gahnite is present in the skarn-like calc-silicates of the Geco mine, zinc has not been detected in pyrosmalite from these two deposits.

Associated silicate minerals

Most silicates, oxides, carbonates and sulfides associated with pyrosmalite in all three mining camps studied have been analyzed in some detail (Costa 1980, Costa *et al.* 1983, Pan & Fleet 1992, Chen 1993). Additional compositional data on pyroxenes, caryopilite, biotite and amphiboles are presented here (Tables 3a, b).

The pyroxene that is replaced by ferropyrosmalite in the banded iron formation from the Thompson mine is ferrosilite, with an Fe/(Fe + Mg + Mn) ratio of about 0.83 (Table 3a). The clinopyroxene in the Willroy mine varies significantly within the diopside–hedenbergite series and has a variable content of the johannsenite component (Table 3a). The manganese content of pyrosmalite is directly related to that of the host clinopyroxene at the Willroy mine (Fig. 5).

Caryopilite from the Mattagami Lake mine has an Fe/(Fe + Mn + Mg) ratio greater than 0.55 (Table 3a), and represents a new Fe-rich member (work in progress). These compositions of Fe-rich caryopilite also contain minor amounts of Zn and Cl (Table 3a).

The biotite associated with Cl-depleted ferropyrosmalite from the Geco mine is F-rich but does not contain detectable Cl (Pan & Fleet 1992). The biotite from the Thompson mine contains minor amounts of both F and Cl (Table 3a). Costa *et al.* (1983) recognized two varieties of the phlogopite–biotite series (Ti-rich and Ti-poor) in the footwall rhyolite and basalt of the Mattagami Lake mine. The present study shows that significant amounts of F, but only background values of Cl, are present in both varieties. However, neither phlogopite nor biotite has been observed in the pyrosmalite-bearing samples of the Mattagami Lake mine.

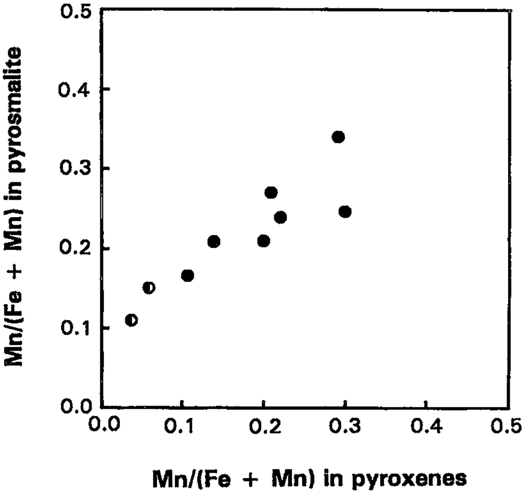

FIG. 5. Mn/(Fe + Mn) distribution between pyrosmalite and host clinopyroxene from the Willroy mine (filled circles); data for pyrosmalite and ferrosilite from the Thompson mine (half-filled circles) are shown for comparison.

According to the classification of Leake (1978), the Fe–Mg–Mn amphibole associated with ferropyrosmalite in the banded iron formation of the Thompson mine is grunerite (Table 3b). The Fe–Mg–Mn amphibole at the Mattagami Lake mine belongs to the cummingtonite–dannemorite series (Table 3b; see also Costa *et al.* 1983). It is noteworthy that both cummingtonite and dannemorite from the pyrosmalite-bearing samples of the Mattagami Lake mine contain measurable Zn contents (up to 1.8 wt.% ZnO; *cf.* Klein & Ito 1968).

Calcic amphiboles associated with pyrosmalite at the Geco and Willroy mines vary from actinolite to ferroactinolite (*cf.* Leake 1978), with variable amounts of Mn. The highest Mn content (up to 7.1 MnO wt.%; Table 3b) was found in grains in direct association with manganoan ferropyrosmalite at the Geco mine. Calcic amphibole in pyrosmalite-bearing samples from the Mattagami Lake mine invariably belongs to the actinolite–tremolite series, and contains variable amounts of Mn (Table 3b). Similar to their Ca-poor counterparts, both actinolite and tremolite from the Mattagami Lake mine contain significant contents of Zn (up to 1.2 wt.% ZnO: Table 3b; *cf.* Klein & Ito 1968).

In this study, large grains of calcic amphibole (up to 2 mm in diameter) also have been observed in several samples from the pyrite – pyrrhotite – magnetite ore unit and the altered footwall rhyolite of the Mattagami Lake mine. These grains of calcic amphibole commonly contain a Cl,Al,Na-rich core (up to 1.5 wt. % Cl; Table 3b) rimmed by Cl-absent actinolite. The Cl-rich core is extremely heterogeneous with respect not only to Cl content but also to Fe/Mg ratio and contents of Al and Si (Table 3b), and ranges from edenite to pargasite. Calcic amphiboles rich in Cl and K that are not associated with pyrosmalite have been observed also in skarn-like calc-silicates from the main orebody of the Geco mine (Pan & Fleet 1992).

DISCUSSION

In addition to the occurrences of pyrosmalite in the three Canadian Precambrian mining camps considered here, the Sullivan mine, Kimberley, British Columbia (a Proterozoic, sediment-hosted Zn–Pb–Ag sulfide deposit) is the type locality of mcgillite, a polytype of manganpyrosmalite (Donnay *et al.* 1980). We have examined samples from many other well-known Canadian sulfide mining camps (*e.g.*, Bathurst, New Brunswick; Kidd Creek and Sturgeon Lake, Ontario; Noranda, Quebec; and Snow Lake, Manitoba) but have failed to detect pyrosmalite or any other member of the friedelite group. However, given the difficulty in identification of these minerals by optical means and limited number of samples examined (less than 10 each), the present study is by no means exhaustive.

Partitioning of Fe and Mn between pyrosmalite and coexisting silicate minerals

The most important criteria used to interpret the paragenesis and origin of pyrosmalite in the metamorphosed Precambrian sulfide deposits of this study are textural characteristics (see below). Element partitioning also provides invaluable information on coexisting minerals during the crystallization of pyrosmalite (*cf.* Mueller 1961, Pan & Fleet 1989). Figure 6a shows that the Mn/Fe ratios in pyrosmalite and Fe–Mg–Mn amphiboles at the Mattagami Lake mine correlate positively, giving a distribution coefficient (K_D) of 1.44 with a standard deviation of 0.12; hence Mn is only slightly enriched in pyrosmalite relative to coexisting Fe–Mg–Mn amphiboles. Similarly, systematic distributions of Fe and Mn between pyrosmalite and calcic amphiboles occur at both the Mattagami Lake mine (Fig. 6b) and the Geco and Willroy mines (Fig. 6c). However, the calculated distribution coefficients of 2.6 for the Mattagami Lake mine and 2.4 for the Geco and Willroy mines are considerably higher than that for pyrosmalite and Fe–Mg–Mn amphiboles at the Mattagami Lake mine. Although biotite and chlorite from the Geco and Willroy mines are much less enriched in Mn than the coexisting amphiboles (Pan & Fleet 1992), the patterns of distribution of Fe and Mn between pyrosmalite and each of these two former minerals are also almost linear (not presented here). From textural evidence and these data on element partitioning, we tentatively conclude that pyrosmalite crystallized in chemical equilibrium with calcic amphibole, Fe–Mg–Mn amphibole, biotite, and chlorite, albeit on a very local scale (*e.g.*, within aggregates of grains). The distribution of Fe and Mn between pyrosmalite and host pyroxenes also is systematic (Fig. 5) and is interpreted to reflect cation proportions inherited during replacement processes (Figs. 2d, e).

Paragenesis and origin of pyrosmalite

All examples of pyrosmalite in the literature, with the possible exception of the Norwegian occurrence (Oftedal & Saebø 1965), which is without either chemical or X-ray data, are found in metamorphosed Fe–Mn and massive sulfide deposits (Table 1). The Mattagami Lake, Geco and Willroy mines of the present study also have been interpreted to be volcanogenic massive sulfide (VMS) deposits (Friesen *et al.* 1982, Costa 1980, Costa *et al.* 1983, Pan & Fleet 1992, and references therein). There is no general agreement concerning the origin of the Thompson nickel sulfide deposit, for which the "volcanogenic exhalative" model is only one among many proposed

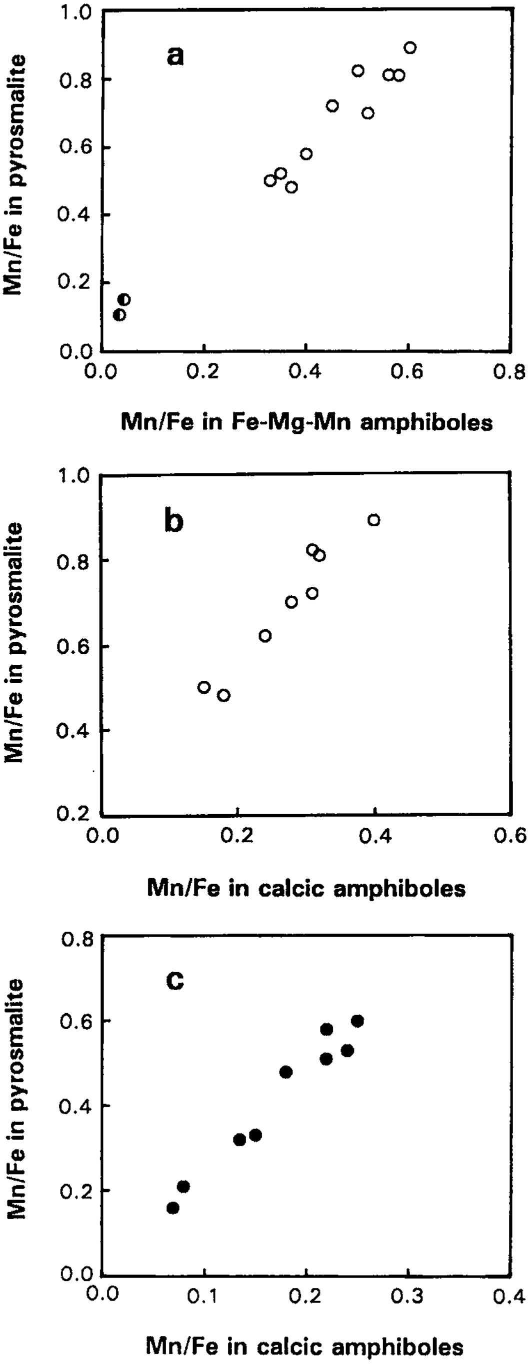

FIG. 6. Mn/Fe distribution between pyrosmalite and: a) Fe–Mg–Mn amphiboles of the Mattagami Lake mine (open circles) and the Thompson mine (half-filled circles); b) calcic amphiboles of the Mattagami Lake mine (open circles), and c) calcic amphiboles of the Geco and Willroy mines (filled circles).

genetic models (*e.g.*, volcanogenic or Kambalda type, hydrothermal replacement and massive sulfide flow; *cf.* Peredery *et al.* 1982). However, the ferropyrosmalite at the Thompson mine is restricted to the banded iron formation (*i.e.*, metamorphosed chemical sediments). Despite its exclusive occurrence in Fe–Mn and massive sulfide deposits, there is no evidence for the direct precipitation of pyrosmalite from hydrothermal fluids on the seafloor. Pyrosmalite has not been observed in modern sulfide deposits or Fe–Mn deposits on the seafloor, and the ancient Fe–Mn and massive sulfide deposits have all been metamorphosed (Table 1).

It is peculiar therefore that talc, carbonates, Mn-bearing serpentine, Mn-bearing amphiboles and the sulfide ore minerals at the Mattagami Lake mine were considered by Costa *et al.* (1983) to be directly precipitated during hydrothermal activity on the seafloor. Talc, an important gangue mineral at the Mattagami Lake mine, is indeed present as a primary mineral in some presently active seafloor hydrothermal systems (see Rona 1988 for a review), and the present descriptions and discussion indicate that pyrosmalite was most likely part of the main silicate assemblage in the Mattagami Lake mine. However, a greenschist-facies regional metamorphism has been documented in the Mattagami Lake area by Jolly (1978), and the silicate mineral assemblages within the Mattagami Lake mine (Costa 1980, Costa *et al.* 1983, see above) are not inconsistent with it (*cf.* Gole 1980, Miyano & Klein 1989). More importantly, silicate minerals such as talc, chlorite, amphiboles and pyrosmalite in the ore units and chlorite in the altered rhyolite of the footwall do exhibit a degree of preferred orientation. It is possible, therefore, that pyrosmalite in the Mattagami Lake mine was a product of the greenschist-facies regional metamorphism, and not a direct precipitate from the hydrothermal fluids responsible for the ore deposit. A prograde metamorphic origin has been proposed by Vaughan (1986) for the ferropyrosmalite in the Pegmont deposit, Australia. Similarly, manganpyrosmalite occurs as mineral inclusions in garnet porphyroblasts in skarn-like calc-silicates of the Geco mine; these most likely crystallized during regional metamorphism or perhaps even earlier (Pan & Fleet 1992).

However, most examples of pyrosmalite in the literature are considered to have originated as a metasomatic replacement of earlier anhydrous silicates or as aggregates in cross-cutting veins (Hutton 1956, Stillwell & McAndrew 1957, Watanabe & Kato 1958, Watanabe *et al.* 1961, Fan *et al.* 1992), pointing to a late-stage hydrothermal origin (Kayupova 1964, Plimer 1984). This is the most plausible origin for the ferropyrosmalite in the Geco, Willroy and Thompson mines (Figs. 2c, d, e, f).

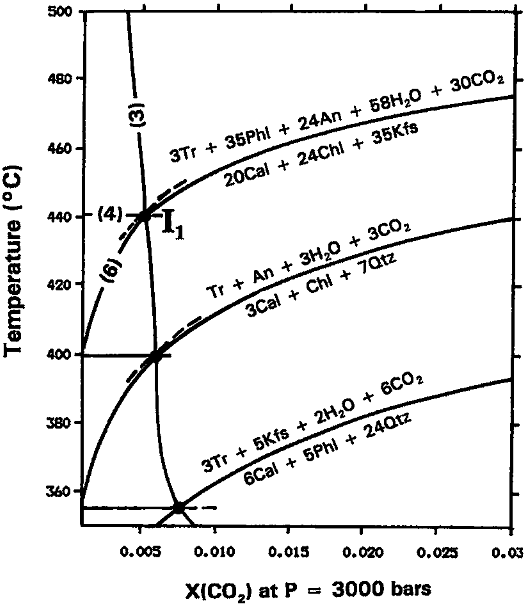

FIG. 7. Isobaric T–*X*(CO_2) diagram for the system K_2O – CaO – MgO – FeO – Al_2O_3 – SiO_2 – H_2O – CO_2 calculated using the GE0–CALC software package of Brown *et al.* (1988) and internally consistent thermodynamic data of Berman (1988) at a total pressure of 3 kbar for assemblages of alteration minerals in skarn-like calc-silicates at the Geco mine (mineral data from Pan & Fleet 1992): An, anorthite; Cal, calcite; Chl, clinochlore; Kfs, K-feldspar; Phl, phlogopite; Qtz, quartz, and Tr, tremolite. For reactions (3), (4) and (6) see text.

Pyroxene is by far the most common mineral to be replaced by pyrosmalite (Hutton 1956, Stillwell & McAndrew 1957, Watanabe & Kato 1958, Watanabe *et al.* 1961, this study). Reactions involving metasomatic replacement may be quantified by mass-balance calculations using mineral compositions and data on specific gravity (Gresens 1967). Calculated reactions for ferropyrosmalite after ferrosilite at the Thompson mine and after hedenbergite at the Willroy mine are as follows (in weight units):

(1) 100 ferrosilite + 1.9MnO + 1.9Cl + 4.7H_2O =
59 ferropyrosmalite + 22 grunerite + 19.1SiO_2 +
10.5FeO + 2.3MgO,

and

(2) 100 hedenbergite + 2.3MnO + 9FeO + 0.5MgO +
1.8Cl + 4.3H_2O = 44 ferropyrosmalite + 49 actinolite
+ 9SiO_2 + 17CaO.

The first reaction is consistent with not only the presence of quartz and pyrrhotite (addition of S_2) but also the observed volume ratio (3 to 1) of ferropyrosmalite and grunerite after ferrosilite at the Thompson mine (Fig. 2e). Similarly, the second reaction is in agreement with the presence of quartz and calcite (addition of CO_2) in aggregates of ferropyrosmalite and actinolite after hedenbergite at the Willroy mine. It is noteworthy that the metasomatic replacement of manganpyrosmalite after rhodonite at the Kyurazawa mine, Japan (Watanabe *et al.* 1961) also includes the crystallization of a manganiferous amphibole, quartz and manganoan calcite, similar to the case in the second reaction above.

Conditions of formation of pyrosmalite

Although thermodynamic data are not available for accurate evaluation of the stability of pyrosmalite, the extensive ranges of chemical substitutions of Fe^{2+} for Mn^{2+}, and of Cl^- for OH^-, indicate that pyrosmalite may have a large field of stability in terms of P and T. Consequently, the critical parameters for its formation probably are not temperature or pressure but composition. A rather special bulk-rock composition is required for formation of pyrosmalite, and this appears to be supported by the exclusive occurrence of pyrosmalite in Fe–Mn deposits and Fe–Mn-rich rocks within massive sulfide deposits (Table 1).

The preceding discussion has demonstrated that a close approach to chemical equilibrium between pyrosmalite and associated minerals appears to have been achieved within individual aggregates of grains. Thus, the conditions of crystallization of pyrosmalite in the three Precambrian sulfide mining camps examined in this study may be estimated from a thermodynamic analysis of the assemblages of coexisting minerals. For example, the stability of the assemblage actinolite + chlorite + phlogopite + plagioclase + K-feldspar + epidote associated with ferropyrosmalite in skarn-like calc-silicates of the Geco mine (Pan & Fleet 1992) is constrained by the following model reactions:

(3) 2 clinozoisite + CO_2 = 3 anorthite + calcite + H_2O,

(4) 3 tremolite + 35 phlogopite + 114 anorthite + $88H_2O$ =
24 clinochlore + 35 K-feldspar + 60 clinozoisite,

(5) 3 tremolite + 35 phlogopite + 24 anorthite + $58H_2O + 30CO_2$ =
30 calcite + 24 clinochlore + 35 K-feldspar,

and

(6) 16 clinozoisite + 3 tremolite + 35 phlogopite + $50H_2O + 38CO_2$ =
38 calcite + 24 clinochlore + 35 K-feldspar.

In the system $K_2O - CaO - MgO - FeO - Al_2O_3 - SiO_2 - H_2O - CO_2$, the above four model reactions define an invariant point I_1 at a temperature of 440 ± 10°C and $X(CO_2)$ of 0.005 ± 0.001 at a total pressure [$P_{total} = P(H_2O) + P(CO_2)$] of 3 kbar (Fig. 7).

The temperature of formation of pyrosmalite at the Mattagami Lake mine can be estimated from the cal-

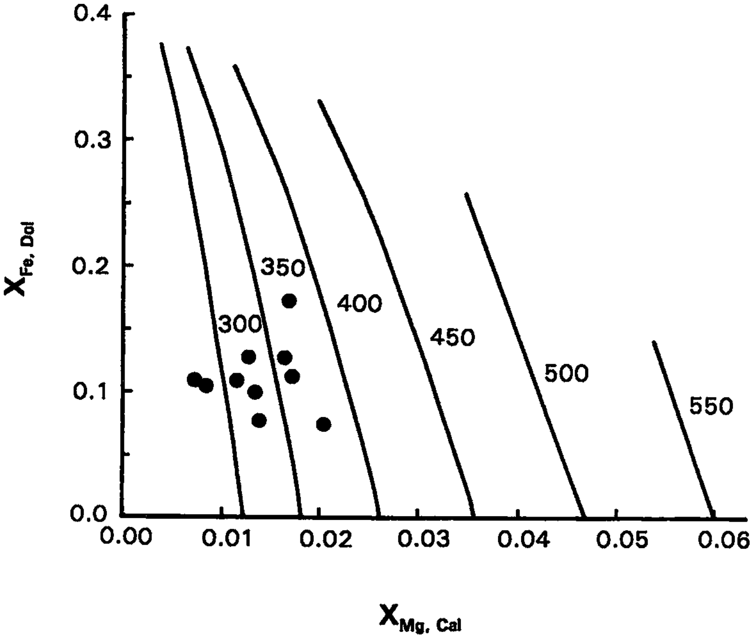

FIG. 8. Calcite–dolomite geothermometer of Powell *et al.* (1984) for coexisting calcite and dolomite of the Mattagami Lake mine (data from Costa 1980, Costa *et al.* 1983): $X_{Mg,Cal}$ = Mg/(Ca + Mg + Fe + Mn) in calcite; $X_{Fe,Dol}$ = Fe/(Ca + Mg + Fe + Mn) in dolomite.

cite–dolomite geothermometer (*cf.* Powell *et al.* 1984, Anovitz & Essene 1987). The high Mn contents of both calcite and dolomite at the Mattagami Lake mine (Costa *et al.* 1983) may have a significant effect on the applicability of this geothermometer (Powell *et al.* 1984). However, the compositions of coexisting calcite + dolomite pairs in various rocks, including the pyrosmalite-bearing samples, of the Mattagami Lake mine yielded temperatures of less than 400°C (Fig. 8), which are in fair agreement with the uncorrected filling temperatures (240°–320°C) of fluid inclusions in grains of quartz and sphalerite of this deposit (Costa *et al.* 1983, 1984).

The chemical compositions of pyrosmalite also imply a high activity of Cl but low fugacity of oxygen in the ambient fluids. Indeed, salt-bearing, hypersaline fluid inclusions (up to 38 wt. % NaCl equivalent) have been observed in quartz grains from the Mattagami Lake mine (Costa *et al.* 1984). The average 0.2 wt.% Cl content in biotite from the banded iron formation of the Thompson mine (Table 3a) indicates that the coexisting ferropyrosmalite crystallized from a fluid with $\log(f_{Cl}/f_{OH})$ of about –3.56 at 450°C (*cf.* Munoz 1984). A low fugacity of oxygen for the formation of pyrosmalite during regional metamorphism is readily provided by the reduced sulfide and oxide assemblages (*e.g.*, the pyrite + pyrrhotite + magnetite assemblage at the Mattagami Lake mine). Similarly, pre-existing metamorphic assemblages would also effectively buffer the redox environment for the formation of pyrosmalite by late hydrothermal activity in the metamorphosed Fe–Mn and massive sulfide deposits. For example, reduced conditions for crystallization of the pyrosmalite-bearing calc-silicates of the Geco and Willroy mines are indicated by the compositions of garnet (extremely high almandine/andradite ratio), and have been constrained quantitatively from the mineral assemblage of garnet + clinopyroxene + quartz + magnetite to be at about ± 1 log unit from the fayalite – magnetite – quartz (FMQ) buffer at 650°C (Pan & Fleet 1992, *cf.* Zhang & Saxena 1991). Similarly, the chemical compositions of coexisting magnetite and ilmenite in the banded iron formation at the Thompson mine indicate that the oxidation state prevailing there also was close to the FMQ buffer (Chen 1993; *cf.* Andersen & Lindsley 1988).

Source of chlorine

The high Cl contents of pyrosmalite (Tables 1, 2) and other members of the friedelite group, such as mcgillite (Donnay *et al.* 1980) and caryopilite (above), are of particular interest. Pyrosmalite appears to be the sink for Cl in the three Precambrian mining camps examined in this study. *Note added in proof*: Ferropyrosmalite (5.66–6.54 % Cl) has recently been reported in the Deep Copper Zone of the Strathcona deposit, Sudbury, Ontario (Springer 1989, Li & Naldrett 1993). The timing of the crystallization of pyrosmalite during regional metamorphism and late hydrothermal alteration (Plimer 1984, Vaughan 1986, and above) indicates two possible sources for Cl: a pre-existing Cl-rich fluid within the Fe–Mn and massive sulfide deposits, and a metasomatic Cl-rich fluid introduced from an external source. The exclusive occurrences of pyrosmalite in Fe–Mn and massive sulfide deposits seem to favor the former source (Vaughan 1986, Pan & Fleet 1992). Seyfried *et al.* (1986) demonstrated experimentally that a chloride enrichment occurs in seafloor hydrothermal alteration at elevated temperatures (> 400°C). Moreover, high-temperature, highly saline fluids have been documented in presently active seafloor hydrothermal systems (Delaney *et al.* 1987). Therefore, the initial Cl enrichment in the present Precambrian sulfide deposits may have occurred during seafloor hydrothermal alteration as an integral part of the syngenetic ore-forming processes for the associated mineralization (see below). Similarly, the occurrence of Cl-rich scapolite in metamorphosed evaporites and argillites has been attributed to primary concentration in sedimentary salts (Mora & Valley 1989 and references therein).

The Cl-rich calcic amphibole in the skarn-like calc-silicates of the Geco mine is almost certainly a product of hydrothermal activity during the waning stage of the regional metamorphism (Pan & Fleet 1992) and therefore does not provide any unique constraint on the timing or source of the Cl-enrichment. In contrast, the Cl,Al,Na-rich calcic amphibole at the Mattagami Lake mine could not have been produced by low-grade regional metamorphism (*cf.* Jolly 1978, Robinson *et al.* 1982) and may be relict and igneous in origin. Therefore, the occurrence of such Cl,Al,Na-rich calcic amphibole may indicate that the host volcanic rocks of the massive sulfide deposit at the Mattagami Lake mine were unusually enriched in Cl. Costa *et al.* (1984) have attributed the highly saline ore-forming solutions of the Mattagami Lake mine to either a contribution by magmatic fluid or seawater–basalt interactions (see also Seyfried *et al.* 1986). It is noteworthy that the Ti-rich biotite from the footwall rhyolite at the Mattagami Lake mine also has been interpreted to be a relict igneous phase (Costa *et al.* 1983), but it only contains a minor amount of Cl (Table 3a).

Significance of pyrosmalite associated with ore deposits

Costa and coworkers (Costa 1980, Costa *et al.* 1983) proposed a brine-pool model for the genesis of the Mattagami Lake mine Zn–Cu–Ag–Au massive sulfide deposit, based on whole-rock geochemistry, oxygen isotopes, and mineral chemistry. Subsequently, Costa *et al.* (1984) recognized salt-bearing, hypersaline fluid inclusions in quartz grains from this deposit. A brine-pool model has been proposed for the genesis of sheet-style volcanogenic massive sulfide (VMS) deposits in general (Sato 1972, Large 1992, and references therein). As pointed out by Large (1992), the major weakness in this genetic model is the lack of supporting evidence from fluid inclusions for salinities as high as 15 to 25% by weight of NaCl. This is undoubtedly due to the fact that most of the VMS deposits worldwide have been subjected to intense deformation and metamorphism subsequent to their formation (Franklin *et al.* 1981, Large 1992). Consequently, primary fluid inclusions are rarely preserved. It is also well known that Cl is strongly partitioned into an aqueous fluid rather than coexisting hydrous minerals at low P–T hydrothermal conditions (Volfinger *et al.* 1985, Zhu & Sverjensky 1991). Therefore, chemical analysis of most hydrous silicate minerals, such as amphibole and chlorite, provides little information on the composition of the ambient fluid. However, the presence of pyrosmalite, which preferentially incorporates Cl into its structure (Kato & Takéuchi 1983) during regional metamorphism or late-stage hydrothermal alteration, probably indicates that the coexisting fluid was highly saline. This may be attributed to Cl-enrichment related to seafloor hydrothermal alteration (see discussion above). Thus, the occurrence of abundant pyrosmalite in massive sulfide deposits can also be considered as evidence for the brine-pool model (*cf.* Sato 1972, Costa 1980, Costa *et al.* 1983, Large 1992).

It is well known that precious-metal (particularly Au and Ag) mineralization is associated with massive sulfide deposits throughout geological time (Hannington & Scott 1989, Large *et al.* 1989). Significant Au and Ag values are present in both the Geco mine (Friesen *et al.* 1982) and the Mattagami Lake mine (Costa 1980, Costa *et al.* 1983). Recently, Chen *et al.* (1993) reported native gold and several platinum-group minerals (PGM) in As-rich nickel ore hosted by metapelite and granitic pegmatite in the Thompson mine.

Experimental studies (Henley 1973, Seward 1973, 1984) have demonstrated that gold is transported in hydrothermal solution mainly as either thio or chloro complexes. H_2S-rich fluids are most likely dominant in seafloor hydrothermal systems; the thio complexes, particularly $Au(HS)_2^-$, therefore, are considered by many to be the most important species involved in gold transport and deposition in massive sulfide deposits. Based on thermodynamic calculations, Large *et al.* (1989) recognized a "switchover" in the importance of chloro and thio complexes with change in physicochemical conditions: gold transport as $AuCl_2^-$ or $AuCl^0$ is favored in relatively high-temperature fluids (>300°C) with low pH ($\leqslant 4.5$), low concentration of H_2S, high salinity and moderate to high $f(O_2)$, whereas gold transport as $Au(HS)_2^-$ is favored in lower-temperature fluids (150–300°C), with moderate to alkaline pH, high concentration of H_2S, low salinity and moderate $f(O_2)$. The documentation of pyrosmalite in the Manitouwadge and Matagami mining camps indicates that chloro complexes may have been important for gold mineralization during seafloor hydrothermal alteration (*cf.* Hannington & Scott 1989, Large *et al.* 1989) in those VMS deposits. Most interestingly, Large and his coworkers (Large *et al.* 1989, Large 1992) recognized that gold in the Australian VMS deposits is concentrated in either the upper parts, in association with Zn, Ag ± Pb ± Ba, or the lower massive and stringer zones, in association with Cu. This is similar to the occurrence of pyrosmalite in the uppermost part of the Mattagami Lake mine (Fig. 1), where it is associated with the pyrite – sphalerite ore, and in the 4/2 Copper Zone of the Geco mine (*cf.* Friesen *et al.* 1982). Unfortunately, no systematic study on the distribution of Au with stratigraphy in these sulfide deposits is available.

Similarly, recent field and experimental studies have highlighted the importance of chloride complexes in the transport and deposition of the platinum-group elements (PGE; Boudreau *et al.* 1986, Sassani & Shock 1990, Hsu *et al.* 1991, Fleet 1992). Chen *et al.* (1993) also suggested that the unusual occurrence of PGM in metasedimentary rocks of the Thompson mine was most likely associated with late-stage hydrothermal alteration, albeit of pre-existing magmatic sulfides. Although pyrosmalite was not observed in PGM- and Au-bearing samples, a Cl-rich fluid is indicated by the presence of Cl-rich allanite (up to 0.8 wt.% Cl; Chen *et al.* 1993; *cf.* Pan & Fleet 1990) and was probably involved in the formation of the PGM (*cf.* Boudreau *et al.* 1986, Sassani & Schock 1990, Hsu *et al.* 1991).

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