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IRON- AND ALUMINUM-RICH SERPENTINE AND CHLORITE FROM THE BOUNDARY ULTRAMAFIC COMPLEX, CAPE SMITH BELT, NEW QUEBEC

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ABSTRACT

Iron- and aluminum-rich serpentines (maximum 15.8% Al_2O_3 and 17.1% FeO, by weight) are common in the Boundary ultramafic complex, a komatiitic intrusive–extrusive body in the eastern part of the Aphebian Cape Smith Belt, northern Quebec. Most of the pervasive serpentinization occurred during peak (biotite-grade) metamorphism, which was contemporaneous with regional thrusting. Later retrogression, locally accompanied by CO_2 metasomatism, was associated with later phases of deformation. Early-formed serpentines are typically pseudomorphic, whereas later serpentines include interpenetrating or vein antigorite and, lastly, vein chrysotile. Formation of the nonpseudomorphic serpentine textures is associated with other features indicative of element migration, including tremolitization of serpentine, serpentinization of clinopyroxene, and replacement of sulfides by silicates, and *vice versa.* Aluminum contents of lizardite are variable; nonpseudomorphic multilayer varieties have the highest Al contents. In contrast to the highly variable compositions of the serpentine-group minerals, chlorite compositions are relatively constant (Fe-rich clinochlore). Elevated abundance of Fe is most clearly associated with sulfide accumulations. Formation of Al- and Fe-enriched serpentine may be a function of the relatively aluminous bulk-composition (as much as 10 wt.% Al_2O_3) of the komatiitic rocks, and a later metamorphic history that involved considerable migration of elements on a local scale.

Keywords: lizardite, antigorite, chrysotile, chlorite, aluminous serpentine, serpentinization, peridotite, electron-microprobe analyses, Cape Smith Belt, New Quebec.

SOMMAIRE

Les minéraux du groupe de la serpentine enrichis en fer et en aluminium (jusqu'à 17.1% de FeO et 15.8% de Al_2O_3, en poids) sont répandus dans le complexe ultramafique de Boundary, massif intrusif et extrusif d'affinité komatiitique affleurant dans la partie orientale de la ceinture aphébienne du Cap Smith, au Nouveau-Québec. La majeure partie de la serpentinisation, répandue, a eu lieu aux conditions maximales d'un épisode de métamorphisme dans le sub-facies à biotite, qui a accompagné un chevauchement régional. Un métamorphisme rétrograde, aussi bien qu'une métasomatose locale due à l'infiltration du CO_2, ont accompagné les phases tardives de la déformation. La serpentine précoce est typiquement pseudomorphique, tandis que la serpentine tardive est faite d'antigorite en interpénétrations ou en veines. Les veines de chrysotile se sont formées en dernier. La formation de la serpentine en texture non pseudomorphique est associé à d'autres manifestations de mobilisation des éléments, y compris la trémolitisation de la serpentine, la serpentinisation du clinopyroxène, et le remplacement des sulfures par des silicates et *vice versa.* Les teneurs en Al de la lizardite sont variables; les variétés non pseudomorphiques à feuillets multiples sont les plus alumineuses. En contraste avec cette grande variabilité, la chlorite (une clinochlore ferreuse) est relativement invariable. Les teneurs les plus élevées en fer dans la serpentine sont typiquement associées aux accumulations de sulfures. La formation de serpentine enrichie en Al et en Fe pourrait bien résulter du caractère relativement alumineux des roches komatiitiques (jusqu'à 10% de Al_2O_3 en poids) et des épisodes subséquents de métamorphisme, qui ont impliqué une mobilité importante des éléments sur une échelle locale.

(Traduit par la Rédaction)

Mots-clés: lizardite, antigorite, chrysotile, chlorite, serpentine alumineuse, serpentinisation, péridotite, données à la microsonde électronique, ceinture du Cap Smith, Nouveau-Québec.

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INTRODUCTION

Serpentine-group minerals, with an idealized formula of $Mg_3Si_2O_5(OH)_4$, are the most abundant constituents of low-grade metaperidotites, although the stability relationships of the serpentine polymorphs are still imperfectly understood. Significant advances have recently been made (Chernosky *et al.* 1988, O'Hanley *et al.* 1989). The importance of components other than those in the ideal formula, especially Al, in stabilizing lizardite to higher temperatures, has been discussed by Frost (1975) and investigated experimentally by Caruso & Chernosky (1979). The purpose of this paper is to describe the occurrence and composition of coexisting aluminous lizardite, antigorite and chlorite from greenschist-facies metaperidotite and metapyroxenite. The compositions reported here are among the most iron- and aluminum-enriched serpentine reported as rock-forming phases from ultramafic rocks, and their occurrence may shed some light on controls of serpentine composition.

X-ray diffraction and electron-microprobe analyses were carried out on secondary minerals from a sequence of komatiite flows and related subvolcanic intrusions that host high-grade Ni–Cu sulfide mineralization. This sequence of ultramafic rocks, the Boundary ultramafic complex (Fig. 1), is located near the eastern end of the Cape Smith – Wakeham Bay Foldbelt (Hynes & Francis 1982). This work summarizes part of a broader study of Ni deposits in the area (Albino 1984), and was initiated to determine the conditions under which the mineralized ultramafic body was metamorphosed.

GEOLOGICAL SETTING

The Boundary ultramafic complex consists of a suite of komatiite flows and subvolcanic sills, located at the contact between an underlying sequence of tholeiitic basalt and fine-grained clastic sedimentary rocks (Povungnituk Group) and a thick overlying pile of komatiitic and tholeiitic basalts (Chukotat Group). The rocks have been metamorphosed under conditions of the low- to mid-greenschist facies (the biotite isograd is

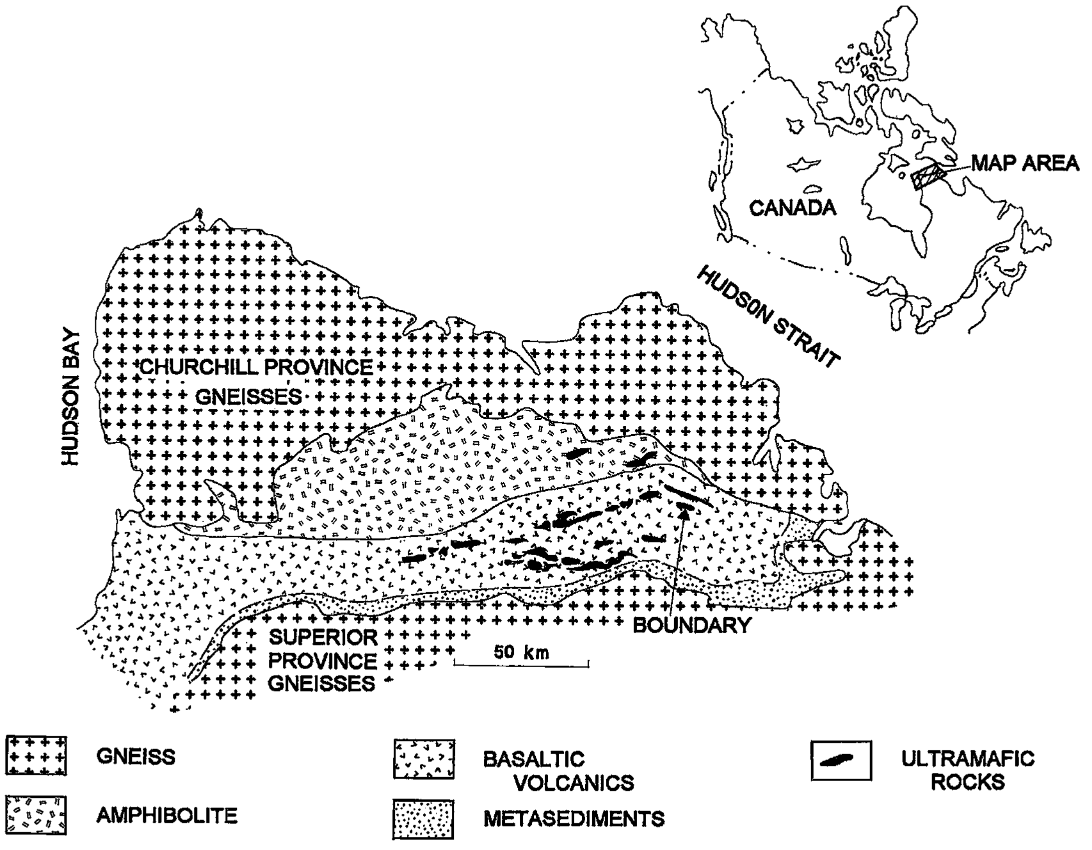

FIG. 1. Location map and generalized geological map of the Cape Smith Belt (from Barnes *et al.* 1982), showing the Boundary area.

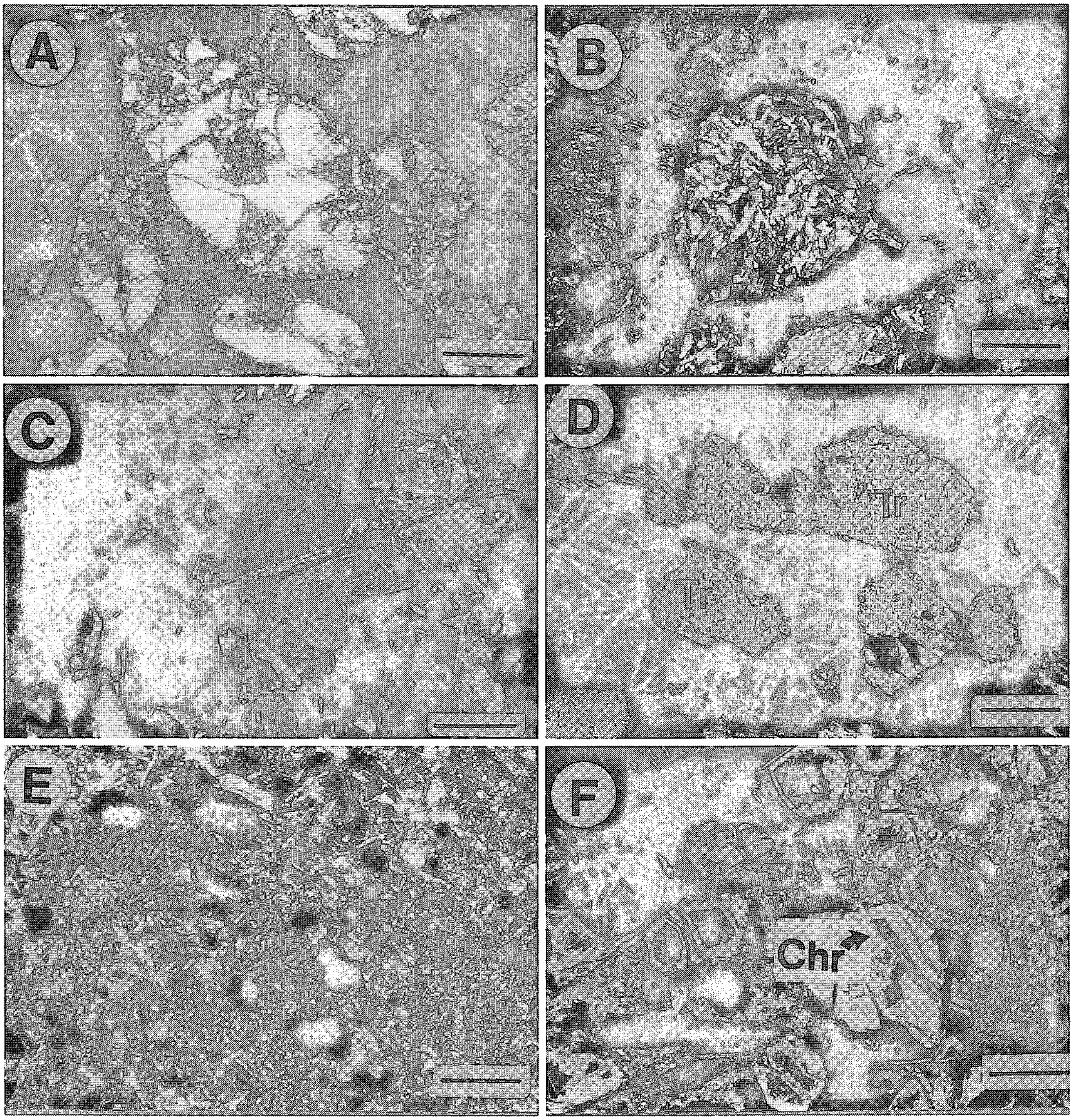

FIG. 2. Textures of serpentine-group minerals of the Boundary area. A. Hourglass-textured lizardite pseudomorphous after olivine. Scale bar 0.1 mm. B. Thorn-textured antigorite after olivine. Scale bar 0.2 mm. C. Lizardite "bastite" after orthopyroxene(?). Scale bar 0.1 mm. D. Tremolite (Tr) partly replacing serpentine after olivine. Scale bar 0.1 mm. E. Nonpseudomorphous lizardite with magnetite. Scale bar 0.2 mm. F. Chrysotile veins (Chr) cutting dolomite pseudomorph after olivine. Scale bar 0.2 mm.

within a few hundred meters of the study area) and subjected to localized retrogression along moderately to steeply dipping faults (Albino 1984). Peak metamorphism was synchronous with the main phase of deformation (*D*1), which produced penetrative fabrics near the (tectonic) contact between the Cape Smith Belt supracrustal rocks and the Archean basement gneisses and in the less competent sedimentary rocks (Hynes & Francis 1982, Albino 1984). Later retrograde metamorphism was contemporaneous with movement along high-angle reverse faults (*D*2), parallel to the belt, and subvertical normal faults, perpendicular to its trend (*D*3). Previous investigators (Hynes & Francis 1982) considered the Belt to be an *in situ* rift sequence, but more recent work (Hoffman 1985, Picard *et al.* 1990, St-Onge *et al.* 1989, 1992) has suggested that the entire Cape Smith Belt is allochthonous with respect to the underlying Archean rocks.

PETROLOGY OF THE ULTRAMAFIC ROCKS

Two groups of ultramafic rocks were examined, the Ni-sulfide-bearing Boundary ultramafic complex, and a suite of barren layered sills and flows (Albino 1984). The barren units consist of lowermost chilled zones, overlain by olivine and olivine–clinopyroxene cumulates and thick zones of massive (and locally layered) gabbro. The ultramafic rocks of the Boundary ultramafic complex originated as thick, ponded flows and as a subvolcanic sill complex. They consist of peridotite, poikilitic peridotite and pyroxenite, with lesser porphyritic komatiite and flow breccias. The primary phases were magnesian olivine (nowhere preserved), oikocrysts of magnesian augite, and a fine-grained groundmass that probably consisted of glass and quench-textured clinopyroxene and plagioclase. The Mg content of the rocks ranges from 19 to 34% MgO (wt.), and the Al content, from 2.5 to over 13% Al_2O_3 on an anhydrous basis (Albino 1984).

Metamorphism under greenschist-facies conditions has led to the development of serpentine – tremolite – diopside – calcite – chlorite ± pyrrhotite – pentlandite assemblages. Varying intensity of alteration is marked by the replacement of primary minerals by compositionally contrasting phases, *e.g.*, tremolite pseudomorphous after olivine, and serpentine after clinopyroxene or tremolite. The degree of preservation of igneous textures is variable: in most areas the textures are clearly visible, but locally they range from obscure to totally destroyed. This is especially true in the part of the ultramafic body that hosts ore-grade Ni–Cu sulfides.

OCCURRENCE OF SERPENTINE MINERALS

Barren ultramafic rocks

The serpentine-group minerals occur principally in basal olivine-rich zones, mostly poikilitic peridotite, of the layered sills intrusive into metasediments of the Povungnituk Group, and flows of the Chukotat Group. Different serpentine-group minerals were recognized using a combination of optical characteristics (mainly sign of elongation), morphology, and the results of X-ray diffraction. Although relict augite and chromite are commonly preserved, olivine and the fine-grained groundmass are completely altered, and the rocks now consist of lizardite, antigorite, chlorite, magnetite, diopside, and minor tremolite, in addition to the relics.

Serpentine after olivine is dominantly pseudomorphic (all serpentine textural terms are after Wicks & Whittaker 1977), comprising hourglass and mesh lizardite (Fig. 2a), with interlocking antigorite mesh-centers. Minor nonpseudomorphic antigorite, mostly interpenetrating (Fig. 2b), postdates the main episode of serpentinization, and probably reflects a minor event involving late heating (Wicks & Whittaker 1977). In a few samples, coarse-grained prismatic tremolite has replaced mesh or hourglass lizardite (Fig. 2d).

Serpentine veins are common throughout most of the ultramafic rocks and include early varieties, consisting of interlocking antigorite, late pseudofibrous Al-rich lizardite (Fig. 2d), and very late fine-grained fibrous chrysotile veinlets (Fig. 2e). Chrysotile is indicative of serpentinization at relatively low temperatures (Evans 1977, p. 408), and here it may be related to minor retrograde metamorphism associated with *D*3 deformation.

Augite oikocrysts are fresh to severely altered. The alteration products include diopside, either very fine-grained or coarsely prismatic, minor tremolite and rare antigorite or lizardite "bastite" (Fig. 2c). Antigorite typically replaces augite along cleavage planes in more heavily altered samples. The degree of alteration, as revealed by replacement of early minerals by chemically dissimilar phases (*e.g.*, tremolite after serpentine, antigorite after augite) tends to increase near the contacts between the ultramafic and the gabbro zones. This may be the result of increased flow of fluids along this contact (commonly sheared).

Other less abundant alteration-related minerals include magnetite and chlorite. The chlorite has extremely low, typically anomalous interference-colors, and is commonly zoned. Carbonate and sulfide minerals, extremely common in ultramafic rocks of the Boundary ultramafic complex, are very rare in the barren ultramafic bodies and seem to be restricted to cross-cutting veinlets. Carbonate minerals are, however, abundant in the vicinity of *D*2 thrust faults and in minor *D*3 structures near their intersection with *D*2 faults. In these areas, extensive infiltration of CO_2 and K has converted the ultramafic rocks to chromian muscovite – dolomite – chlorite – pyrite assemblages, which in a few instances have preserved primary igneous textures. The normal absence of carbonate minerals, however, and the common assemblages antigorite–diopside and antigorite–tremolite indicate that metamorphic fluids were water-rich, with $X(H_2O)$ in excess of 0.99.

The Boundary ultramafic complex

In ultramafic rocks of the Boundary ultramafic complex, antigorite is the dominant metamorphic mineral. In contrast to the unmineralized ultramafic rocks in the area, however, Al-rich lizardite and weakly pleochroic chlorite are common, diopside is rare, and tremolite and carbonates are the dominant calcic phases. Diopside is present only in the least altered rocks, which tend to occur remote from ore. Secondary magnetite, ilmenite and Fe–Cu and Fe–Ni sulfides are ubiquitous. The relative proportions of the secondary minerals, as well as the compositions of the individual phases, are quite variable over distances of a few centimeters.

TABLE 1. STAGES OF SERPENTINIZATION IN ULTRAMAFIC ROCKS OF THE BOUNDARY AREA, CAPE SMITH BELT, NEW QUEBEC

STAGE	MINERALOGY	TEXTURE
1	Lizardite	Hourglass replacement of olivine
2	Antigorite (-diopside)	Mesh and hourglass replacement of olivine; some alteration of augite
3	Antigorite-lizardite (tremolite-dolomite)	Interlocking and interpenetrating antigorite; lizardite in groundmass. Antigorite replaces early pseudomorphous lizardite
3a	Lizardite (tremolite-dolomite)	Veinlets of pseudofibrous Al-rich lizardite with minor tremolite and calcite, rare dolomite
3b	Antigorite	Coarse interpenetrating thorn-textured antigorite recrystallization of earlier serpentines
4	Chrysotile	Minor veinlets and rare replacement of antigorite and lizardite around edges of olivine pseudomorphs

As in the barren ultramafic rocks, several generations of serpentine after olivine are present in the rocks of the Ni-sulfide-bearing Boundary ultramafic complex (Figs. 2a–f, Table 1). These include early (stage 1) pseudomorphic lizardite after olivine (Fig. 2a), slightly later fine-grained lizardite in the altered mesostasis, and mesh- and hourglass-textured antigorite pseudomorphous after olivine (stage 2), followed by interpenetrating and vein antigorite (Figs. 2b, e) and, lastly, minor chrysotile in veins and replacing antigorite (Fig. 2f). The proportion of nonpseudomorphic textures is much higher in the Boundary ultramafic complex than in the barren peridotites of the layered sill and Chukotat Group layered flows. As well, weakly mineralized peridotite tends to have better preserved igneous textures than do samples in well-mineralized parts of the Boundary ultramafic complex.

During stage-3 serpentinization, CO_2 was introduced locally, giving rise to various ophicarbonate assemblages (Trommsdorff & Evans 1977). The assemblages antigorite – calcite, tremolite – calcite and tremolite – dolomite – antigorite – calcite are common in the Boundary ultramafic complex and indicate that the $X(CO_2)$ in the metamorphic fluids attained a maximum of 0.05 in most areas. In addition, considerable alteration accompanied stage-3 serpentinization, in which serpentine replaced pyroxene and tremolite, and carbonate and Ca-bearing silicates replaced serpentine pseudomorphous after olivine.

ANALYTICAL METHODS

X-ray-diffraction patterns were obtained using a 57.3-mm Gandolfi camera and a Philips X-ray generator. A total of 10 diffraction patterns were obtained during this study, including serpentine and chlorite patterns. Standard operating conditions were 35 kV, and 15 mA, with Ni-filtered Cu radiation; exposure times ranged from 6 to 18 hours. The samples chosen for X-ray-diffraction analysis were removed from specific textural sites (*e.g.*, veinlets, pseudomorphs after olivine and pyroxene) in thin and polished

TABLE 2. REPRESENTATIVE COMPOSITIONS OF SERPENTINE-GROUP MINERALS FROM ULTRAMAFIC ROCKS OF THE BOUNDARY AREA

Sample	E6-86	E6-86	95	95	95	95	116	116	116	116	116	116	116	116	116	116	116
Number			-65	-65	-115	-115	-165	-165	-210	-210	-230	-230	-270	-270	-296	-296	-311
Lithology	Dn	Dn	PPd	PPd	PPd	PPd	Pd	Pd	Pd	Pd	Pd	Pd	PPd	PPd	SZ	SZ	SZ
Habit	1	2	3	4	4	5	1	1	4	1	3	5	4	1	4	1	4
SiO_2	38.89	36.60	38.68	37.30	39.29	38.14	36.03	36.89	33.36	37.69	39.64	38.15	40.80	33.00	37.23	36.46	38.38
Al_2O_3	4.25	7.67	3.66	3.25	2.72	4.38	7.66	7.31	14.08	5.72	2.85	4.10	1.40	15.14	2.68	7.11	2.77
FeO	6.32	6.08	9.64	11.74	9.91	10.33	12.61	12.49	11.42	11.53	12.51	13.12	13.43	12.49	17.09	13.38	15.29
MgO	34.22	33.59	33.94	32.74	33.81	33.10	30.76	31.25	30.41	32.81	32.91	31.99	32.41	29.27	29.09	27.79	30.46
Total	83.68	83.84	85.92	85.03	85.73	85.95	87.06	87.94	89.27	87.75	87.91	87.36	88.04	89.90	86.09	84.74	86.90
Cations on the basis of 14 oxygen atoms																	
Si	3.846	3.611	3.801	3.758	3.872	3.760	3.552	3.593	3.188	3.663	3.858	3.756	3.977	3.146	3.809	3.696	3.842
Al	0.495	0.892	0.424	0.386	0.316	0.509	0.890	0.839	1.586	0.655	0.327	0.476	0.161	1.701	0.323	0.850	0.327
Fe	0.523	0.502	0.792	0.989	0.817	0.852	1.040	1.018	0.913	0.937	1.018	1.080	1.095	0.996	1.462	1.134	1.280
Mg	5.043	4.939	4.970	4.916	4.966	4.864	4.520	4.537	4.331	4.753	4.774	4.694	4.709	4.159	4.435	4.199	4.545

Notes: each composition represents the average of 3 to 7 spots on a single grain. Units: Dn dunite, Pd peridotite, PPd poikilitic peridotite, SZ sulfide zone. Habit: 1 veinlet, 2 nonpseudomorphic serpentine, 3 lizardite after olivine, 4 thorn-textured antigorite intergrown with sulfide, 5 thorn-textured antigorite, 6 lizardite after pyroxene. All samples except E6-86 have the prefix BC. Oxides expressed in wt.%.

TABLE 3. COMPOSITION OF CHLORITE FROM ULTRAMAFIC ROCKS OF THE BOUNDARY AREA, CAPE SMITH BELT, NEW QUEBEC

Sample*	210	311	311	311	296	296	296	296	230
SiO_2 wt.%	31.91	32.34	33.51	32.40	33.36	30.72	31.90	32.90	32.45
Al_2O_3	15.77	14.39	12.16	13.48	11.98	13.15	14.00	14.33	14.53
FeO	13.05	12.17	13.72	12.82	14.56	13.27	13.74	13.68	12.06
MgO	29.51	29.33	29.83	28.59	28.63	26.50	28.06	28.61	29.70
Total	90.24	88.23	89.22	87.29	88.53	83.64	87.70	89.52	88.74
cations on the basis of 14 oxygen atoms									
Si	3.164	3.226	3.279	3.240	3.265	3.207	3.198	3.210	3.227
Al	1.843	1.692	1.402	1.589	1.382	1.618	1.654	1.648	1.703
Fe	1.082	1.015	1.123	1.072	1.192	1.158	1.152	1.116	1.003
Mg	4.361	4.361	4.350	4.261	4.176	4.123	4.193	4.160	4.402

* Sample number bears the prefix BC116- in each case.

thin sections with a sharpened tungsten carbide needle. The use of the Gandolfi camera allowed normal powder photographs to be made using samples as small as 0.05 × 0.05 mm, and the thickness of a normal thin section.

The serpentine polymorphs were identified using the criteria listed in Whittaker & Zussman (1956), supplemented by data in Coats (1968) and Wicks & O'Hanley (1988). The small size of some samples resulted in rather poor exposures, but identification of different serpentine minerals was nevertheless possible.

Electron-microprobe analyses were done on a MAC (Materials Analysis Company) model 400 microprobe, equipped with a Kevex 7000 energy-dispersion analyzer, located at the University of Colorado, Boulder. Normal operating conditions were 15 kV accelerating potential, emission current of 150 μA, and a counting time of 100 seconds. Standards used included natural olivine, orthopyroxene, augite and biotite; on-line ZAF corrections were applied. Mineral compositions reported here (Table 2, 3) represent the averages of two to seven analyses of individual grains. Compositions of individual grains are typically very similar, with intragrain variations less than approximately 10%. Early sessions included analyses for minor elements, including Mn, Cr, and Ni. These components were uniformly present at very low levels (<0.05–0.10 wt.%) of the oxides; in later sessions, the minerals were analyzed for Mg, Si, Fe, and Al only.

MINERALOGY OF THE SERPENTINE AND CHLORITE GROUPS

Chlorite-group minerals have a basal repeat distance (d_{001}) of about 14 Å, which varies with composition; the normal d_{001} of the serpentine-group minerals is slightly greater than 7 Å. Amesite and berthierine are Al- and Fe-rich members, respectively, of the serpentine (7 Å) group. It has been suggested (Roy & Roy 1955, Yoder 1952) that they are stable at low temperatures (≤500°C), with serpentine and 14 Å chlorites stable at higher temperatures. Wicks & O'Hanley (1988) proposed that there is complete solid-solution between serpentines [$Mg_6Si_4O_{10}(OH)_8$] and amesite [$(Mg_4Al_2)(Si_2Al_2)O_{10}(OH)_8$], although Bailey (1988a) reviewed evidence for a significant miscibility gap. Regardless, the most Al- and Fe-rich members of the serpentine group are typically found in rocks other than ultramafic rocks, most commonly low-grade aluminous metasedimentary rocks (*e.g.*, Jahanbagloo & Zoltai 1968, Brindley & Brown 1980).

Antigorite has traditionally been regarded as the stable high-temperature member of the serpentine group (Frost 1975, Evans 1977), but a considerable body of experimental data (Chernosky 1971, Caruso & Chernosky 1979) indicates that Al-rich lizardite is stable to higher temperatures than is antigorite. The relations among Al-rich and Al-poor serpentine and chlorite are still very poorly known, but Caruso & Chernosky (1979) have proposed a topology for relevant reactions in the system SiO_2–Al_2O_3–MgO–H_2O based on theoretical considerations and limited experimental data.

RESULTS OF X-RAY-DIFFRACTION ANALYSIS

Chlorite and several varieties of serpentine, all with a strong reflection at approximately 7 Å, were identified in the X-ray-diffraction patterns. Three different varieties of serpentine were identified, although there were difficulties in comparing the present patterns to most published serpentine patterns because of the small apparent d_{001} (7.14–7.23 Å) values.

Lizardite is the most common serpentine mineral, and was identified in five samples. It is found in veinlets, as orthopyroxene(?) "bastite", as hourglass-textured pseudomorphs after olivine (Wicks & Whittaker 1977), and in the matrix of volcanic breccia of the Boundary ultramafic complex. The basal repeat-distance (*ca.* 7.14 Å) suggests that the lizardite is aluminous (Gillery 1959). Several of the lizardite samples have broad, poorly resolved peaks in the 3.8 to 5.2 Å range, suggesting that they are multilayer varieties. Wicks & Plant (1979) reported that multilayer lizardite is typically the most Al-rich of the serpentine-group minerals. This is consistent with the Al-rich nature of the serpentines considered here (see below), and the X-ray-diffraction data that suggest that multilayer lizardite is common in the Boundary complex serpentinites.

Antigorite occurs in thorn textures (Wicks & Whittaker 1977) and in veinlets. The relative paucity of peaks in the 6–7 Å range suggests that *a* for these samples is less than the typical ~43 Å (Whittaker & Zussman (1956).

MINERAL CHEMISTRY

Serpentine

All of the serpentine samples investigated in this study are Al- and Fe-bearing varieties, with Al_2O_3 ranging from 1.4 to more than 14 wt.%, and FeO^T (total iron expressed as FeO), from 5.1 to 17.1 wt.% (Table 2).

Iron content is lowest in late chrysotile (identified by optical properties) veinlets and highest in blade-like antigorite intergrown with Fe–Ni sulfides. A continuum of serpentine compositions is evident on a FeO–MgO–SiO_2 diagram (Fig. 3). Vein serpentines, which include antigorite, chrysotile and lizardite, typically have the greatest variation in iron content. Antigorite pseudomorphous after olivine and later "thorn" antigorite have intermediate iron contents, ranging from 9 to 13 wt.% (Fig. 3). Antigorite intergrown with sulfides has variable but high levels of iron (Fig. 3).

Because Fe^{2+}, which substitutes in the octahedrally coordinated site, tends to increase the structural mismatch between the sheets of octahedra and tetrahedra in the serpentine structure (Wicks & Whittaker 1975), it has been suggested that iron must either occur in the Fe^{3+} state, or as Fe^{2+} accompanied by vacancies in the octahedral sites (Wicks & Plant 1979). The overall reduced nature of the rocks [estimated log $f(O_2)$ based on opaque assemblages is about 10^{-25}–10^{-26}: Albino (1984)] argues against the presence of significant Fe^{3+}, as do the cation totals very close to 10 (on the basis of 14 atoms of oxygen) calculated on the assumption of all iron as Fe^{2+}. Therefore, the most likely solution involves a substitution of the type $2Fe^{2+} \rightleftharpoons \square + Al^{3+}$ (where $\square$ represents a vacancy) for Mg^{2+} in the layer of octahedra in the serpentines, coupled with Al-for-Si substitution in the layer of tetrahedra, although O'Hanley & Offler (1992) suggested significant Fe^{3+} contents in lizardite with modest (2.1 to 4.2 wt.%) FeO contents.

The large variation in Al contents of the serpentines in this study is evident on a MgO–Al_2O_3–SiO_2 plot (Fig. 4), where they form a continuous trend from 1 to 19 wt.% Al_2O_3. The high Al contents are probably responsible for the small d_{001} value (7.14–7.23 Å) discussed above.

The range of Al content is greatest in the vein serpentines, which include all of the serpentine polymorphs. The highest aluminum is likely in lizardite, especially the multilayer lizardite (Wicks & Plant 1979). The Al contents of some of the veinlet serpen-

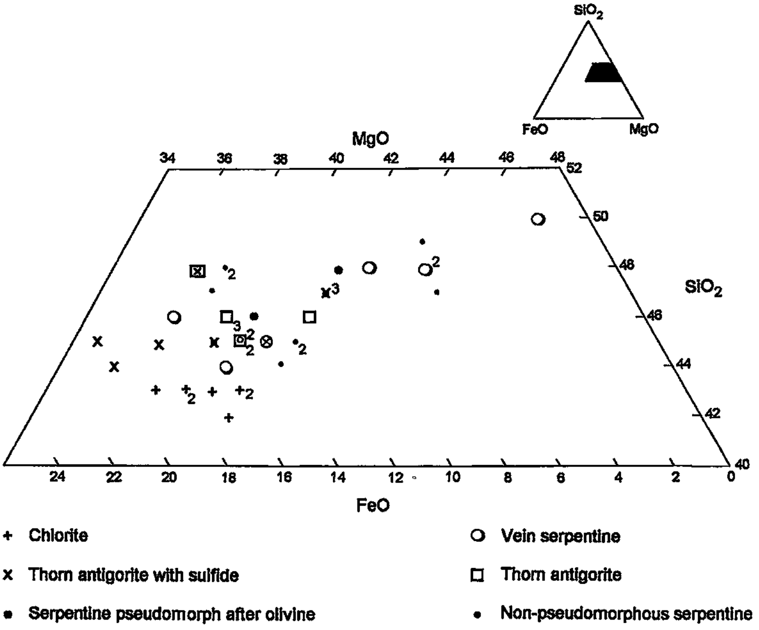

FIG. 3. MgO–FeO–SiO_2 diagram showing compositions of serpentine-group minerals and chlorite from the Boundary area. Numbers refer to multiple analyses with the same composition in terms of MgO–FeO–SiO_2.

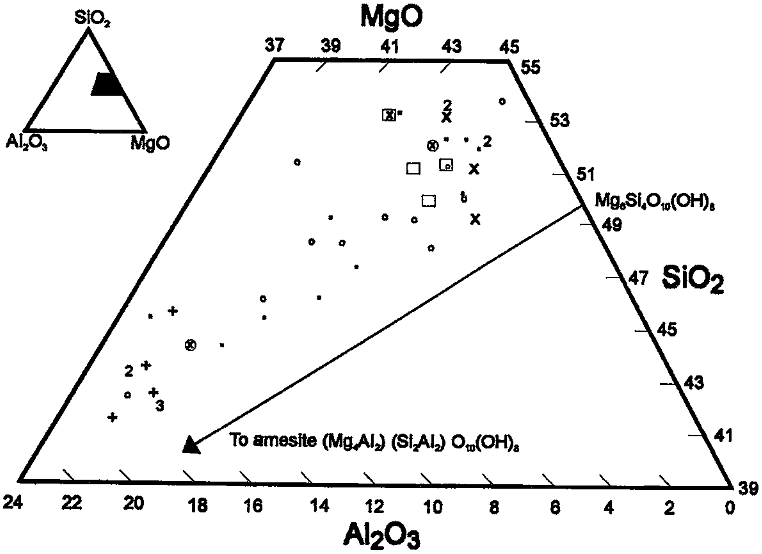

FIG. 4. $MgO–Al_2O_3–SiO_2$ diagram showing compositions of serpentine-group minerals and chlorite from the Boundary area. Symbols as in Figure 3.

tines are among the highest reported to date from natural ultramafic-rock-derived serpentines (Wicks & Plant 1979). The range of values in antigorite is much smaller, and it appears that antigorite was able to accommodate a maximum of about 5 wt.% Al_2O_3 (Fig. 4, Table 2), which is similar to the maximum level of Al in antigorite reported by Dungan (1979) and Wicks & Plant (1979). Note that the results of Blais & Auvray (1990), in a study of serpentine from Finnish komatiites, are virtually the opposite of those presented here. Although the maximum Al content in antigorite that they reported is similar to that documented here, the lizardite in their study has much lower Al contents, with a much smaller range than they observed in associated antigorite.

Chlorite

In contrast to the serpentines, the composition of the chlorite analyzed in this study is quite constant (Table 3). Chemically, the chlorite is classified as iron-bearing chlinochlore (Bayliss 1975, Bailey 1988b). On an $MgO–Al_2O_3–SiO_2$ plot, the chlorite compositions overlap considerably with serpentine (Fig. 4), but on the $FeO–SiO_2–MgO$ diagram, they form a distinct field, with lower Si than in serpentines with a similar iron content (Fig. 3). This, combined with a lower ^{IV}Si occupancy in the chlorite, suggests that $a(SiO_2)$ may have determined whether chlorite or serpentine formed.

DISCUSSION

The system $MgO–FeO–Al_2O_3–SiO_2–H_2O$

The unusual abundance of high-Al serpentines in this study may simply be due to the aluminous nature of the komatiite flows (as much as 10 wt.% Al_2O_3), relative to the better-studied alpine-type serpentinites (*e.g.*, lizardite containing ~1.0% Al_2O_3 in serpentinites from Quebec: Cogulu & Laurent 1984). The maximum value for x [where the structural formula of lizardite is given by $(Mg_{6-x}Al_x)(Si_{4-x}Al_x)O_{10}(OH)_8$: Caruso & Chernosky 1979] encountered in these samples, approximately 0.8, is close to the value predicted to minimize the mismatch between sheets of octahedra and tetrahedra in the serpentine structure. An alternative explanation for the great abundance of highly aluminous serpentine is the Barrovian-type thermal gradient inferred for the rocks of the area (Schimann 1978, Albino 1984), as high pressure apparently leads to the stabilization of Al-rich lizardite, with respect to Mg–Al chlorite (Wicks & O'Hanley 1988). It also is possible that the Al- and Fe-rich compositions reported here reflect physical mixtures of more than one phase. Additional micro-analytical work (*e.g.*, analytical transmission electron microscopy) would allow testing of this last alternative.

Conditions of metamorphism

It was hoped that the coexistence of Al-rich lizardite, Al-poor antigorite and chlorite would allow some estimates to be made of the conditions of metamorphism in the study area. The absence of metamorphic olivine in the area, including in some brucite-bearing rocks, limits the temperature of peak metamorphism to below that of the reaction:

antigorite + brucite = forsterite + water (1)

Examination of Figure 4a of Caruso & Chernosky (1979) and the apparently stable coexistence of Al-rich lizardite, Al-poor antigorite, and chlorite indicate that pressure must have exceeded that of the invariant point at the intersection of the reactions:

antigorite = forsterite + talc + water (2)

aluminous lizardite =
chlorite + talc + forsterite + water (3)

This appears to limit the metamorphic conditions to a pressure greater or equal to 2.5 kbar, and possibly considerably higher, and temperatures in the range of 425–450°C. The small amount of Al present in the antigorite of this suite may increase the equilibrium temperature of reaction (1), so temperatures may possibly have been as high as 500°C. This would, of course, have the effect of lowering the pressure of the invariant point as well. The intermediate pressures suggested here are consistent with pressure estimates and field gradients suggested by other workers in the eastern Cape Smith Belt (Bégin & Carmichael 1992).

CONCLUSIONS

Highly aluminous lizardite, with variable, but commonly elevated abundances of iron, is a major rock-forming mineral in serpentinized komatiites of the Cape Smith Belt. Lizardite formed during retrograde serpentinization, and was later followed by prograde antigorite and chlorite. The abundance of very Al-rich serpentine may reflect a combination of bulk composition and metamorphic history, including both partly open-system behavior during the crystallization of nonpseudomorphic serpentine, and relatively elevated pressure.

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