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A CHLORINE-BEARING PHASE IN DRILL CORE OF SERPENTINIZED TROCTOLITIC ROCKS OF THE DULUTH COMPLEX, MINNESOTA

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ABSTRACT

Drill core from the troctolitic series of the Duluth Complex, in Minnesota, contains an Fe–Cl-bearing phase in partially serpentinized ultramafic rocks. The phase occurs as vein-filling material in grains up to 200 μm long and 20 μm wide; it has similarities to the phase described by Springer (1989). Analyzed rocks also contain very high concentrations of Cl (up to 3200 ppm) and F (up to 760 ppm), although biotite grains analyzed to date have low halogen contents (< 0.1 wt.% Cl + F). The presence of this Fe–Cl-bearing phase and high whole-rock chlorine values is evidence that these rocks were subjected to invasion by a chlorine-bearing fluid with potential to transport platinum-group elements.

Keywords: iron chloride, serpentinization, biotite, Duluth Complex, Minnesota.

SOMMAIRE

Des carottes prélevées de la série troctolitique partiellement serpentinisée du complexe de Duluth, au Minnesota, contiennent une phase riche en Fe et Cl. On la trouve en remplissage de fissures, en amas 200 μm en longueur et 20 μm en largeur. Elle ressemble au matériau qu'a décrit Springer (1989). Les roches contiennent aussi des teneurs très élevées en Cl (jusqu'à 3200 ppm) et F (jusqu'à 760 ppm), quoique les teneurs des échantillons de biotite analysés jusqu'à maintenant sont très faibles (<0.1% Cl+F en poids). La présence de cette phase riche en Fe et Cl et les teneurs élevées des roches globales font penser que ces roches ont subi l'influence d'une phase fluide riche en Cl capable de transporter les éléments du groupe du platine. Sa présence a des répercussions sur la question de l'altération hydrothermale des roches des fonds océaniques.

(Traduit par la Rédaction)

Mots-clés: chlorure de fer, serpentinisation, biotite, complexe de Duluth, Minnesota.

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INTRODUCTION

Recent investigations of platinum-group-element *(PGE)* deposits have highlighted the importance of a volatile phase in the transport and deposition of the *PGE*s (Kinloch & Peyerl 1990, Ballhaus 1988). Until now, much of the evidence for this process has rested on such data as Cl content of hydrous minerals (Boudreau & Kruger 1990, Boudreau & McCallum 1989, and references therein) and Cl-bearing fluid inclusions (Ballhaus & Stumpfl 1986). This paper describes an occurrence of an Fe–Cl-bearing phase in partially serpentinized mafic rocks from the Duluth Complex, Minnesota (Fig. 1), that may shed further light on the role of Cl-bearing fluids in the transport and deposition of the *PGE*. The wider implications of this occurrence involve the understanding of seafloor alteration by hydrothermal fluids (Berndt *et al.* 1988).

The Fe–Cl-bearing phase (Fig. 2), which resembles that described by Springer (1989), has been observed in drill core from the Duluth Complex, Minnesota (Dahlberg *et al.* 1988, Berndt *et al.* 1988). When drill core surfaces are exposed to air, the phase appears to convert to a rusty brown product of alteration, as described also in Springer (1989). This effect has been observed over intervals ranging in thickness from 30 cm to a few meters and occurs within "zones" up to 44 meters thick. The drill cores bearing the alteration product come from drill holes located in troctolitic rocks in the area of the Maturi, Minnamax, Water Hen, Dunka Road, and Dunka Pit Cu–Ni sulfide occurrences (Table 1, Fig. 1). This paper describes the results of investigations of these drill cores to date.

OCCURRENCE

The drill cores that contain the alteration product occur at distances ranging from 11.3 m to 917.5 m from the footwall of the Duluth Complex. The Cl-bearing phase is associated with partly serpentinized

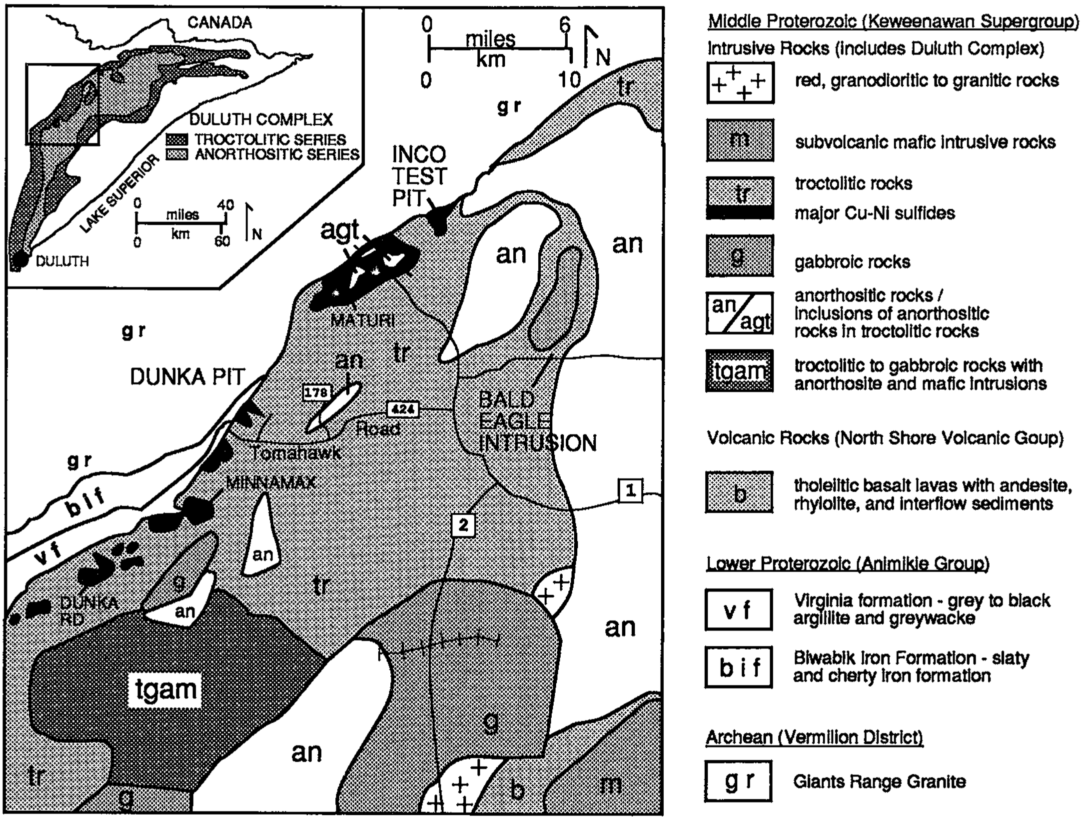

FIG. 1. Generalized geological map of a portion of the Duluth Complex (after Foose & Weiblen 1986).

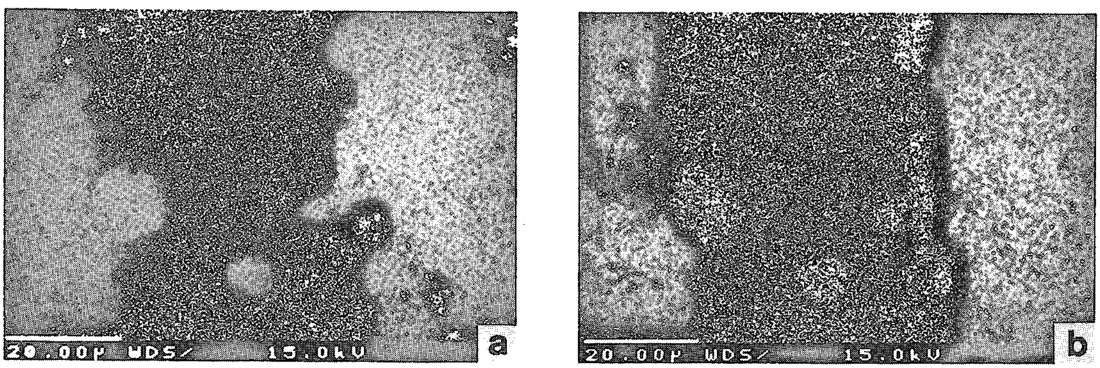

FIG. 2. (a) Cl$K\alpha$, and (b) Fe$K\alpha$ X-ray maps of the Fe–Cl phase surrounded by serpentine. Scale bar is 20 μm. The round, Fe-rich and Cl-free areas are associated grains of secondary magnetite.

cumulates, dominated by one or more of the following minerals: oxides (spinel and ilmenite), olivine, orthopyroxene. Plagioclase-rich to anorthositic patches are commonly observed, and the content of base metal sulfides may average as much as 3 modal %.

The rocks that overlie and underlie these cumulates include pegmatitic gabbro and anorthosite, microgabbro, gabbroic and troctolitic hornfels, and anorthositic troctolite. The degree of serpentinization of the olivine varies from slight to almost complete. The reddish alteration is observed on the sur-

TABLE 1. DRILL–CORE INTERVALS WITH Cl CONTENTS >900 ppm, DULUTH COMPLEX

Drill Hole	Interval (meters)	Cl (ppm)	F (ppm)	Area	Lithology
BA-1	593.45 – 596.46	1100	760	Minnamax	crs. gr. pegmatitic Ol gabbro to troctolite with Ccp and Mag
BA-1	803.15 – 805.59	900	260	Minnamax	partly serpentinized Ol gabbro and norite with Cu-sulfides
BA-2*	1018.64 –1021.69	3000	120	Minnamax	serpentinized mafic to ultramafic cumulate
BA-2*	1026.26 – 1028.09	950	160	Minnamax	feldspathic pyroxenite with Cu-sulfides
BA-2*	996.57 – 997.64	1200	570	Minnamax	f.–med. gr. pyroxenite with Cu-sulfides and up to 20% Ilm
BI-128	585.22 and 598.02	1300	110	Minnamax	Ol and sulfide-bearing gabbro and Mag-Ol cumulate
64048	73.15 – 74.68	1600	740	between Minnamax and Dunka Pit	microgabbro sill (?)
D-10	245.36 – 248.14	1100	60	Dunka Pit	troctolite with peridotite inclusions
DU-14	1188.35 – 1189.09	3200	20	Dunka Pit	oxide cumulate
DU-15*	720.55 - 722.07	1900	20	Dunka Pit	serpentinized ultramafic cumulate

From Dahlberg (1987). Ol = olivine; Ccp = chalcopyrite; Mag = magnetite; Ilm = ilmenite; f. = fine; med. = medium; gr. = grained. Analyses by X-ray Laboratories, Ltd., Don Mills, Ontario. * intervals with iron oxide alteration phase on drill core surfaces.

face of the serpentinized, olivine-rich and the oxide-rich portions of these rocks.

TABLE 2. CHEMICAL COMPOSITION OF WHOLE ROCK AND RED PRECIPITATE*

D-6A whole rock†		D-6A red pcpt.	
	wt%		wt. %
SiO_2	36.20	Si	4.91
TiO_2	0.08	Ti	0.01
Al_2O_3	3.69	Al	0.09
Fe_2O_3**	30.00	Fe	21.43
MnO	0.27	Mn	0.76
MgO	27.20	Mg	10.91
CaO	1.89	Ca	0.15
Na_2O	0.43	Na	0.04
K_2O	0.07	K	0.01
P_2O_5	0.08	P	0.01
Total	99.91		
	ppm		wt. %
Cl	3455	Cl	14.01
Sc	5.4	Br	0.03
V	23	Total	52.36
Cr	118	OH	47.64¥
Co	194		
Ni	1290		
Cu	11		
Zn	174		
Be	0.1		
Sr	58		
Ba	15		

†560.53 –560.74 meters; n.d. : not detected; * analyses by R. Knoche, University of Minnesota. Whole rock: 0.5 g sample, $LiBO_2$ fusion/acid dissolution/DC Plasma-Spectrometry; Cl by D.I. water leach, ion chromatography. Precipitate: 0.015 g sample, acid dissolution/DC Plasma-Spectrometry; Cl, Br by D.I. water leach/ion chromatography. **total Fe as Fe_2O_3. ¥by difference.

Composition of the Chlorine-Bearing Phase, Other Minerals, and the Rocks

Chemical analysis of the reddish alteration collected from the surface of drill core (Table 2) showed high Cl contents. A petrographic examination of partially serpentinized troctolite from drill core D-6A (560.53 - 560.74 m) revealed vein-like intergrowths of an unusual brown-colored phase associated with secondary magnetite and serpentine. The Fe–Cl vein-filling material occurs in domains up to 200 μm long and 20 μm across (Fig. 2), near or in olivine grains that are partly serpentinized. We believe that the residual iron oxide alteration on the surface of the drill core results from dissolution into condensed water and oxidation of the Fe–Cl-bearing phase, upon exposure to air. D. Peterson (pers. comm.) reported that the reddish alteration appears on drill-core surfaces after four months. Similar alteration appears to affect freshly made thin sections bearing the Fe–Cl phase. Electron-microprobe analyses by Sterling Cook of the U.S. Bureau of Mines at its Twin Cities Research Center established that the brown colored phase is an iron chloride (Berndt *et al.* 1988), and results of subsequent analyses of the phase in drill hole D-6A are listed in Table 3. Fe and Cl are the only detectable elements in the chloride phase; stoichiometry and charge balance suggest that $Fe_2(OH)_5Cl$ is a possible formula. This formula implies trivalent iron as opposed to the mineral postulated by Rucklidge & Patterson (1977) and Seyfried *et al.* (1986), and that described by Springer (1989) [$Fe_2(OH)_3Cl$].

Biotite in this sample has among the lowest Cl contents of biotite in the Duluth Complex yet analyzed

TABLE 3. ELECTRON-MICROPROBE DATA ON IRON CHLORIDE*

grain		Fe	Cl	(OH)†	Total
1	wt. %	48.66	14.17	37.17	
	atoms††	1	0.46	2.51	3.97
2	wt. %	46.03	13.16	40.81	
	atoms	1	0.45	2.91	4.36
3	wt. %	47.73	12.99	39.28	
	atoms	1	0.43	2.70	4.13
SF¥	wt. %	53.9	18.2	27.9	
	atoms	1	0.53	1.70	3.23

* Analyses performed by B. Saini-Eidukat at the University of Chicago Dept. of Geophysical Sciences, using a Cameca SX-50 microprobe. Analyses are averages of 4 measurements. †OH content computed by difference from 100. ††Atomic proportions to a basis of Fe = 1. ¥ Fracture filling of Springer (1989).

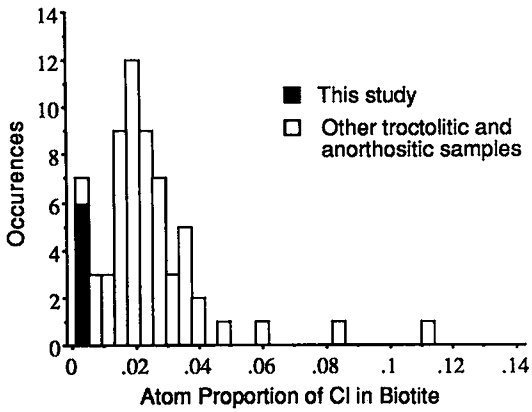

FIG. 3. Histogram of Cl content of biotite from the Duluth Complex. Cl contents of biotite in samples from drill core D-6A (this study), which contains the iron chloride phase, are among the lowest yet analyzed from the Duluth Complex (see Saini-Eidukat *et al.* 1990).

(Fig. 3), even though high whole-rock Cl and F values are reported (Dahlberg 1987) from gabbroic to ultramafic lithologies (Table 1). Several of the Cl-rich samples are either directly associated with the reddish alteration phase or are in close proximity to rocks showing these features. The highest F content found to date is 760 ppm, in coarse-grained gabbroic troctolite.

STRUCTURAL GEOLOGY

There appears to be no relationship between local structures and the occurrence of the alteration phase. High Cl contents do, however, appear to be associated with regional northwest–southeast-trending lineaments and the structurally complex area to the southeast of the Minnamax shaft (Fig. 1). The latter area displays roughly north–south and east–west trending faults which, when projected (Dahlberg 1987), bound the South Kawishiwi intrusion to the northeast and the Partridge River intrusion to the southwest. Six out of ten samples with anomalous Cl values are located in this area. DDH 303 is located to the northeast of the Minnamax shaft, and highly saline waters from this hole assay 11,000 mg/L Cl, and flow at a rate of 567.8 L/min (Morton & Ameel 1985). Only sludge was retrieved from this hole over the interval 426.72 m to 571.20 m, indicating the possible presence of a major fault in this area.

DISCUSSION AND IMPLICATIONS

Observations on serpentinized drill-core from the Duluth Complex have shown that a phase that may be a hydroxychloride is present. This finding has implications for the understanding of the role of Cl-bearing solutions in the transport of platinum-group elements in mafic and ultramafic intrusions (Schiffries 1982, Ballhaus & Stumpfl 1986, Boudreau *et al.* 1986, Boudreau 1988, Saini-Eidukat *et al.* 1990). Further implications of this occurrence are in the understanding of serpentinization (Miura *et al.* 1981, Rucklidge & Patterson 1977), and of seafloor alteration by hydrothermal fluids (Berndt *et al.* 1988, Seyfried *et al.* 1986).

To our knowledge, the occurrence described by Springer (1989) is the only other reported example of an iron chloride phase of this type. Jambor (1975) described deliquescent spots having the formula $NiCl_2 \cdot 6H_2O$, subaerially deposited on drill core from Dumont, Quebec. Rucklidge & Patterson (1977) reported increased Cl content in partially serpentinized rocks, but showed that completely serpentinized rocks contain low Cl levels, comparable to those of their unaltered precursors. They, Seyfried *et al.* (1986), and Berndt *et al.* (1988) suggested the presence of a $Fe_2(OH)_3Cl$ phase from evidence provided by experiments on rock–fluid reaction, and proposed that Cl is introduced and then expelled during the alteration process. Miura *et al.* (1981) reported that high Cl contents are associated with the reaction front of fine-grained serpentine against relict olivine. They discounted the hypothesis of Rucklidge & Patterson (1977) for the presence of a separate hydroxychloride phase and postulated that Cl exists only in a fine-grained serpentine phase and that Fe exists separately as minute grains of less than one nanometer. The lack of Si, the relatively large grain-size and apparent homogeneity of the Fe–Cl-bearing phase described here (Fig. 2) indicate that it is not a fine intergrowth, such as that described by Miura *et al.* (1981).

The ferrous or ferric nature and the hydroxyl content of the phase must be accurately determined before constraints can be placed on its stability and origin; further definition using X-ray and TEM methods is planned. Its presence, however, is clear evidence that rocks of the Duluth Complex were subjected to invasion by Cl-bearing solutions during or after serpentinization. As described by Sabelin *et al.* (1989) and by R. Mogessie (pers. comm.), textures of platinum-group minerals in the Duluth Complex indicate that the *PGE*s were transported and deposited by hydrothermal fluids. These and similar observations from the Merensky reef (Kinloch & Peyerl 1990) give further weight to the suggestion that volatile-rich fluids must be considered in models of the genesis of *PGE* deposits.

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