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ON CHLORINE IN SERPENTINIZED DUNITE*

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ABSTRACT

Serpentinized Precambrian dunites from Ontario, Canada, contain several tenths of a per cent chlorine while peridotites and pyroxenites, which are associated, show a nearly normal amount of chlorine, about 0.04 per cent. The chlorine in dunite is fairly soluble in hot water and readily soluble in cold sulphuric acid, except for a few hundredths of a per cent. It is suggested that the readily soluble chlorine was introduced into the rock during serpentinization by chloride-rich solutions from adjacent sediments and tuffs. The difficultly soluble chlorine is probably entrapped in silicate crystals.

INTRODUCTION

The chlorine content of igneous rocks including grabbo, basalt and diabase averages about 0.02 per cent and varies only a few hundredths of a per cent. In contrast the ultramafic rocks, particularly dunite and serpentinized dunite, are quite variable in chlorine content, the amount ranging from a few thousandths of a per cent to several tenths of a per cent.

Although the reason for the variability of chlorine content in serpentinized dunite is controversial, it is believed generally that most of the chlorine is introduced by deuteric or hydrothermal solutions which permeated the rock after primary crystallization. A small amount is undoubtedly introduced as a part of the parent material. If this origin of chlorine in dunites is correct, one would expect the primary chlorine to be more or less uniformly distributed while chlorine introduced by solution would be distributed somewhat unevenly. The present study was undertaken to provide additional analyses of chlorine in serpentinized Precambrian rocks and to determine the distribution of this element in such rock masses.

ANALYTICAL METHOD

Diamond drill core samples[1] from serpentinized ultrabasic rocks in Ontario, Canada, Fig. 1, were used in all of the determinations except for one sample of olivine from a bomb in Hawaiian basalt. Grab samples of clean core which weighed approximately 25 grams were taken at approximately 50 or 100 foot intervals through the rock mass. These samples were crushed and ground to minus 120 mesh in a porcelain mortar.

All of the chlorine determinations were made by a potentiometric

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[1] Courtesy Dominion Gulf Company, Toronto, Canada.

method in which one gram of the sample is fused with six grams of sodium carbonate. The fused product is leached on a steam bath for one hour, and the leachate filtered and washed. The filtrate is neutralized with dilute sulphuric acid and excess acid is added to make the solution 7.5 normal. The sample is titrated potentiometrically with standard silver nitrate using silver/silver chloride and glass electrodes.

Care was taken to avoid possible chlorine contamination although it is recognized that some contamination may have occurred during the drilling operation. Owing to the substantially impermeable nature of the rock,

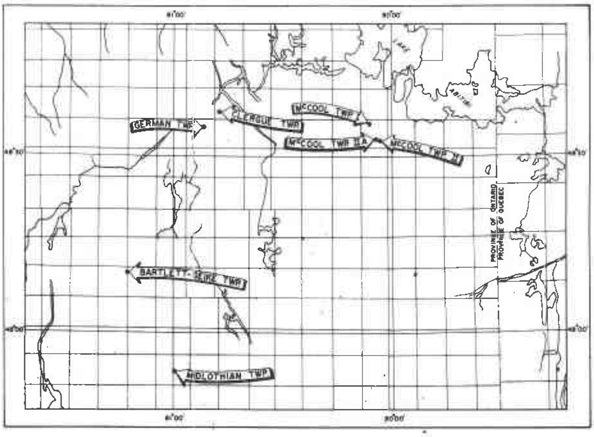

Fig. 1. Location of drill holes.

it is believed that this source of chlorine contamination does not introduce a serious error in the analyses. Blank determinations were made through the whole procedure. Deionized and triple distilled water was used in all of the determinations.

Data and Results

The chlorine contents of samples from eight diamond drill holes are given in Table 1. The analyses show that the amount of chlorine in dunite[2] varies from about 0.1 to 0.7 per cent and averages 0.23 per cent for all of the samples. In contrast the next most common rock type in this suite of samples, peridotite,[2] averages 0.049 per cent chlorine. The metamorphosed sediments in the lower portion of the German Township drill hole average 0.048 per cent chlorine with the suggestion of a slightly higher chlorine content near the contact with the pyroxene bearing

[2] Highly serpentinized.

periodotite. The tuff which is in contact with the dunite in the Clergue Township drill hole shows 0.19 per cent chlorine while the dunite immediately adjacent to the contact contains 0.70 per cent chlorine. Where dunite is in contact with peridotite the chlorine content of the dunite is greater by approximately one order of magnitude. Table 1 and Fig. 2 show that the chlorine content of the peridotite is significantly less than that of the dunite. The contact zone may grade over one hundred feet or more. There is also a suggestion that within the dunite mass the chlorine content decreases away from the contact with the peridotite. Dunite

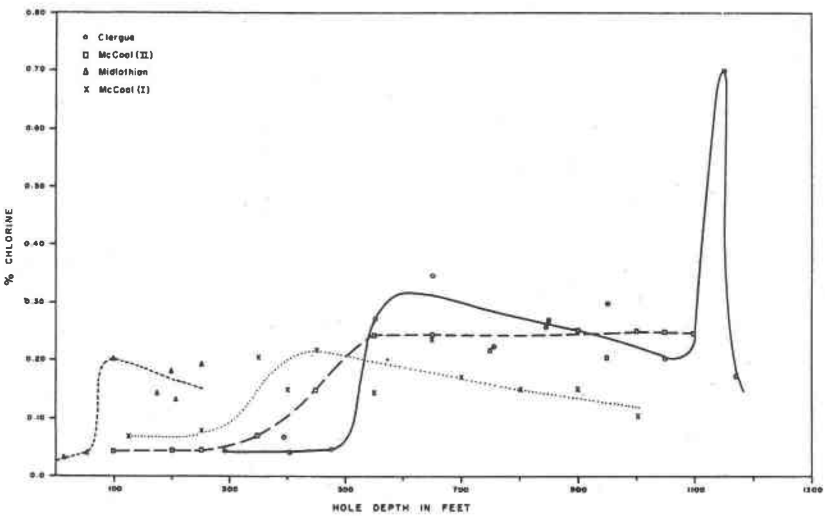

FIG. 2. Per cent of chlorine as a function of depth.

from the McCool II drill hole does not show a decrease in chlorine content similar to the other sections but rather remains substantially constant over the length of the section examined. The Clergue dunite, which is in contact with metamorphosed sediments, shows a sharp increase in chlorine content near the contact.

Fluorine determinations were carried out on samples from the McCool II drill hole at 450 feet, the McCool IIA drill hole at 950 feet and the Clergue Township drill hole at 753 feet. None of these samples showed more than 0.01 per cent fluorine, using the method wherein distilled fluosilicic acid at pH 3.0 is titrated with thorium nitrate using sodium alizarin sulfonate as an indicator. Time would not permit fluorine determinations on all of the samples and as a result it can only be assumed that the other high chlorine samples had a low fluorine content.

TABLE 1. CHLORINE CONTENTS OF DRILL CORES*

German Township			Bartlett-Geike Township			Clergue Township		
Depth	Rock	% Cl	Depth	Rock	% Cl	Depth	Rock	% Cl
170	Perid.	0.098	86	Perid.	0.076	296	Perid.	0.043
225	Perid.	0.077	141	Basalt	0.015	396	Pyrox.	0.070
275	Perid.	0.060	238	Lamp.	0.023	404	Pyrox.	0.038
375	Perid.	0.017	404	Perid.	0.034	471	Perid.	0.046
475	Perid.	0.090	515	Perid.	0.023	551	Dunite	0.27
625	Perid.	0.039	614	Basalt	0.015	651	Dunite	0.37
725	Perid.	0.036	720	Perid.	0.015	753	Dunite	0.22
830	Perid.	0.090				842	Dunite	0.26
925	Pyrox.	0.028				949	Dunite	0.30
1095	Seds.	0.078				1050	Dunite	0.21
1150	Seds.	0.057				1150	Dunite	0.70
1190	Seds.	0.021				1170	Tuff	0.19
1250	Seds.	0.036						
Midlothian Township			McCool Township I			McCool Township II		
Depth	Rock	% Cl	Depth	Rock	% Cl	Depth	Rock	% Cl
5	Perid.	0.03	130	Perid.	0.07	100	Gabbro	0.04
50	Perid.	0.04	250	Perid.	0.08	200	Perid.	0.04
100	Dunite	0.20	350	Dunite	0.21	250	Perid.	0.04
175	Dunite	0.14	400	Dunite	0.15	350	Perid.	0.07
200	Dunite	0.18	450	Dunite	0.22	450	Perid.	0.15
202	Dunite	0.13	550	Dunite	0.14	550	Dunite	0.24
250	Dunite	0.19	650	Perid.	0.24	650	Dunite	0.24
			700	Dunite	0.17	750	Dunite	0.22
			800	Dunite	0.15	850	Dunite	0.27
			900	Dunite	0.15	900	Dunite	0.25
			1000	Dunite	0.11	950	Dunite	0.21
						1000	Dunite	0.25
						1050	Dunite	0.25
						1100	Dunite	0.24

Note: Perid.—Serpentinized peridotite; Pyrox.—Serpentinized Pyroxenite; Lamp.—Lamprophyre; Seds.—metamorphosed graywacke and argillite; Basalt—Olivine basalt dike.

* Analysts—B. B. Osthaus and J. A. Solomon

RELATIONSHIP OF CHLORINE TO WATER CONTENT

It seems reasonable to suggest that there may be a relationship between the high chlorine content of ultramafic rocks and their water content. Analyses of composite samples of anorthosite, altered peridotite and altered dunite which are given in Table 2 show that although the water content of the anorthosite is approximately one-quarter of the water content of the peridotite which underlies it, the chlorine contents of both rocks are approximately the same. On the other hand the water contents of the peridotite and dunite are similar but the chlorine content of the dunite is several times greater.

Further, the determination of chlorine in a fresh olivine bomb in recent basalt from Hawaii shows 0.01 per cent chlorine in the olivine and 0.04 per cent chlorine in the basalt. The water content of the volcanic material was not determined but in view of the fresh nature of the rock and

Table 2. Analyses of McCool Township IIA Composite Core Samples†

Depth, Feet	Rock Type	Per Cent Cl	Per Cent Total H_2O
92– 112	Anorthosite	0.01	4.18
225– 296	Peridotite*	.01	12.54
332	Peridotite*	.07	11.82
463– 493	Dunite*	.26	13.70
585– 607	Dunite*	.23	13.15
756– 760	Dunite*	.23	13.80
962– 995	Dunite*	.21	13.00
1126–1226	Dunite*	.21	12.59

* Highly serpentinized.

† Analysts—B. B. Osthaus and J. A. Solomon.

the lack of alteration of the olivine it is reasonable to suppose that the total water content of either the olivine or basalt was less than one per cent.

Analyses of a variety of ultramafic rocks reported by Kuroda and Sandell (1953) suggest that high chlorine content is associated with high water content, although there are notable exceptions as evidenced, for example, by Harzburgite from Lewis Hill, Newfoundland, which shows 0.06 per cent chlorine and 10.05 per cent water. However, none of the ultramafic rocks reported by Kuroda and Sandell or by the author shows a high chlorine content and a low water content. In contrast, the water content of alkaline lavas reported by Bowen (1937) is low while the chlorine and fluorine contents are relatively large. From published data and the data given in this report, one can suggest that a high chlorine content in dunite is associated with a high water content but a high water content does not necessarily indicate a high chlorine content.

Distribution of Chlorine in Altered Dunite

Since all of the dunites were highly serpentinized with the development of chrysotile veinlets, samples at depths of 651 and 753 feet in the

Clergue Township hole which contained chrysotile fiber and massive serpentinized dunite were separated and each fraction was analyzed for chlorine. The chlorine contents of the chrysotile fiber and serpentinized dunite were 0.46 per cent and 0.36 per cent, respectively, for the sample at 651 feet and 0.27 and 0.19 per cent, respectively, for the sample at 753 feet. Although the chlorine content of the chrysotile fiber fraction is larger in each sample the difference is not great and one must conclude that chlorine is more or less evenly distributed throughout the whole rock mass.

TABLE 3. SOLUBILITY OF CHLORINE IN DUNITE AT 1150 FEET IN CLERGUE TOWNSHIP DRILL HOLE

Solvent	Digestion Time	Temperature	Per Cent Cl
H_2O	1 hour	85° C.	0.20
7.5N H_2SO_4	5 mins.	25° C.	0.62
7.5N H_2SO_4	1 hour	85° C.	0.65
Total chlorine as determined by fusion procedure			0.70

An attempt was made to determine the location of the chlorine in the rock mass by carefully hand-picking the various mineral components for study. Although the Clergue Township sample at 1150 feet showed 0.70 per cent chlorine, suggesting the presence of one or more per cent of a chlorine bearing mineral and possibly isomorphous substitution of chloride ions for hydroxyl ions, no *x*-ray diffraction evidence could be found for either of these conditions. One must, therefore, suspect that the chlorine is present in an amorphous phase and/or that it occurs in minute fluid inclusions. Small and undetectable amounts of crystalline chlorides may be present as discrete particles located along grain boundaries.

The solubility of the chlorine bearing component was determined in water and in 7.5N sulphuric acid as shown in Table 3. These results indicate that a portion of the chlorine is soluble in water and this may be derived from soluble metal chlorides which are intergranular or present as minute particles along grain boundaries. The amount of chlorine dissolved in cold acid in five minutes is substantially the same as that dissolved in hot acid for one hour indicating that the chlorine bearing component is readily soluble in acid. The difference between the amount of chlorine which is soluble in hot acid and the total chlorine as determined by sodium carbonate fusion, 0.05 per cent, may be accounted for in part by analytical error, sample variation or actual chlorine which is held tightly by the less soluble part of the rock. Some combination of these possibilities seems to be the most likely explanation.

Although the samples were studied by *x*-ray and chemical methods, the location of chlorine in serpentinized dunite remains unknown. However, as one would suspect, the bulk of the chlorine does not occur as chloride ions in isomorphous substitution for hydroxyl ions in chrysotile or antigorite or for that matter in any of the common hydrous silicates found in serpentinized dunite.

Discussion

Dunite is a nearly pure forsteritic rock, and by virtue of its composition, formation by simple magmatic processes is practically precluded. From a geochemical viewpoint, Bowen and Tuttle (1949) concluded that ultramafic rocks can be intruded only in a solid state. This condition can be met by crystallization of olivine from a basic magma with subsequent filter pressing and intrusion of the olivine as a crystal mush. Subsequently dunite may be altered by metamorphic and/or hydrothermal processes to serpentinized dunite. Alternatively, serpentinized dunite may be formed by metasomatic processes involving desilication of basic rocks by water vapor which is undersaturated with SiO_2.

The real problem at hand is one of accounting for several tenths of a per cent chlorine. Several explanations can be offered for the high chlorine content of these serpentinized Precambrian dunites but it must be remembered that there is no proof for any.

Firstly, one can propose that the parent olivine crystals formed in a closed system, a magma, at high temperature and pressure and as a result a portion of the volatiles in the system was trapped during primary crystallization. Inclusion of trace amounts of various elements can be accounted for by this means. Normally gaseous elements such as chlorine seldom amount to more than a few hundredths of a per cent of the rock. Furthermore, appreciable amounts of fluorine are generally present in magmas and as a result entrapped magmatic gases should contain comparable amounts of fluorine and chlorine. However, the dunites included in this study do not show unusual amounts of fluorine. For these reasons it seems impossible to account for the high chlorine content of the rocks on a basis of entrapped magmatic volatiles, although it is quite reasonable to suggest that the few hundredths of a per cent chlorine which is difficultly soluble and the fluorine can be attributed to such an origin.

Secondly, if the chlorine in the dunite was not introduced as entrapped material, it must have been introduced later by deuteric or hydrothermal solutions or by imbibition of fluids from adjacent rocks. Any of these fluids or solutions must have had a high concentration of chlorine but a low concentration of fluorine. Without entering into a long discourse on the character of hydrothermal solutions it is probably sufficient to point out that hydrothermal solutions usually follow channel ways. However, it must be remembered that metasomatism affects large rock masses and it is entirely possible that serpentinization in these rocks is the result of metasomatic processes involving chloride-rich fluids.

Since dunites are frequently associated with orogenic belts and are found associated with sedimentary rocks, is it possible that these Precambrian dunites were formed in zones containing sediments saturated with a high chloride brine? Cores from only two of the basic rock masses studied showed that there were sediments in contact with altered peridotite in German Township and with altered dunite in Clergue Township. The altered peridotite in contact with graywacke and argillite in German Township shows a slightly higher chlorine content than most peridotites, approximately 0.060 per cent as compared with an overall average of 0.049 per cent. Here the metamorphosed sediments show a high chlorine content near the contact with the ultrabasic rocks. The relationship between the chlorine content of the Clergue Township dunite and the tuff is more striking in that the dunite immediately adjacent to the contact contained 0.70 per cent chlorine while the tuff adjacent to the contact contained 0.19 per cent chlorine. Away from the contact the chlorine content of the dunite is only about half of that near the contact. Although this is rather scant evidence on which to base a hypothesis, there is a suggestion that the water necessary for serpentinization of the dunite was derived from adjacent sediments which were saturated with a chloride brine. It is conceivable that such a brine permeated the rock mass either during or shortly after formation. Water was used up in the formation of serpentine and the resultant fluid was concentrated to a point where chlorides were precipitated either along grain boundaries or in interstices of the rock. If metal chlorides or oxychlorides were precipitated it is difficult to see why there is no evidence for such compounds in the rock. One would expect these compounds to be readily soluble and this is consistent with the observations. Further, one would expect the chlorine content of the rock to increase away from the contact with the sediment since the fluids would be concentrated as they migrated through the rock. There is evidence of this in the Clergue, Midlothian and McCool rock masses.

Other interpretations may be equally valid. It is the author's sincere hope to interest someone in undertaking a comprehensive study of chlorine rich ultrabasic rocks including processes of serpentinization.

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