Regimes of serpentinization and rodingitization in Quebec Appalachian ophiolites

REGIMES OF SERPENTINIZATION AND RODINGITIZATION IN QUEBEC APPALACHIAN OPHIOLITES

BY

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SUMMARY

Two main episodes of serpentinization and rodingitization are observed which have developed through distinct regimes believed to be successively of oceanic and continental origin.

The oceanic episode took place at a distance removed from the spreading axis, under low oxygen activity, temperature falling and static conditions after the peridotite had cooled to below 340°C. It produced pseudomorphic replacements. In contrast, the late episode took place during the tectonic transport and emplacement of the ophiolites, under high oxygen activity, temperature rising (up to 400°C or higher) and dynamic conditions. It produced non-pseudomorphic replacements and extensive developments of asbestos ore in serpentinite and calc-silicate veins in rodingitized rocks.

Mineral parageneses and interpretations are summarized in Table 1.

INTRODUCTION

The chrysotile asbestos-rich peridotites of the Thetford Mines and Asbestos areas (Quebec) are part of a narrow ophiolite belt which extends discontinuously through the Canadian Appalachians from Baie Verte, Newfoundland, to southern Quebec (Church 1972, Laurent 1975*a*, 1977; Williams & St Julien 1978). Locally, the serpentinized peridotites of this belt contain numerous small lenses of massive rodingite and larger bodies of rodingitized granitic rocks. Rodingites are metasomatic rocks enriched in calcium which, because of their widespread occurrence within serpentinites, are regarded as normal by-products of serpentinization (Coleman 1977, p. 108). Hence, to define the conditions of formation of the rodingite and serpentinite mineral parageneses it is necessary to study simultaneously the features of both processes. In the Appalachians the peridotites have undergone a complex evolution,

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they are polymetamorphic and serpentinization developed in two distinct episodes: early oceanic serpentinization and late continental serpentinization (Laurent 1975*b*, Laurent & Hébert 1979). The aim of this paper is to show that there are also two distinct episodes of rodingitization which are closely related to serpentinization. Each episode of serpentinization and rodingitization is defined by a characteristic *regime*.

REGIMES

The process of serpentinization at first glance looks simple since it is mainly an hydration reaction. The impression is wrong however. In fact the petrology of serpentinites is extremely complex due to four main reasons:

(1) Serpentines (lizardite, chrysotile and antigorite) have overlapping fields which are controlled, not only by temperature and pressure, but also by their chemical composition (particularly their content of Al and Fe), by oxygen (ratio Fe^2: Fe^3) and water activities at the time of the reaction, and by the composition of water (pH, CO_2 content). It is well known that the solubility of silica increases with increasing pH, whereas Mg and Ca do not start to precipitate from aqueous solutions before a pH value of 10 is reached (Eitel 1954). Serpentines, consequently, tend to be dissolved by solutions of low pH and precipitated from solutions of high pH. The same is true for the calcium silicates of rodingitic assemblages.

(2) Serpentinites contain, in addition to serpentines, several other constituents: brucite, magnetite, chromite, talc, chlorite, magnesite, sulfides and native metals, etc., which are the products of more than one reaction. Similarly, rodingites consist of multiphase assemblages formed under different conditions.

(3) The process of serpentinization may occur in a *closed* or in an *open* system which may, or may not, initiate significant volume changes. In the case of a reaction in a closed system of the type:

$$\underset{\substack{\text{Olivine}\\ 560\text{ g}\\ 174\text{ cm}^3}}{4Mg_2SiO_4} + 6H_2O \rightarrow \underset{\substack{\text{Serpentine}\\ 552\text{ g}\\ 217\text{ cm}^3}}{2Mg_3Si_2O_5(OH)_4} + \underset{\substack{\text{brucite}\\ 116\text{ g}\\ 49\text{ cm}^3}}{2Mg(OH)_2}$$

the total volume is increased by 53%, whereas if the reaction occurs in the conditions of an open system of the type:

$$\underset{\text{Olivine}}{5Mg_2SiO_4} + 4H_2O \rightarrow \underset{\text{Serpentine}}{2Mg_3Si_2O_5(OH)_4} + \underbrace{4MgO + SiO_2}_{\substack{\text{removed}\\ \text{in solution}}}$$

the total volume remains the same but the bulk composition is modified by losses of Mg and Si. The process of rodingitization, which leads to the formation of a rock denser than its protolith, may also occur either in a closed system, with decrease in volume, or in an open system with metasomatic addition of Ca and H_2O but without significant volume changes.

(4) Finally, the external conditions play an important role. In a static environment serpentinization develops in conditions very different from those of a dynamic environment. In a static environment when temperature decreases progressively, serpentinization produces textures of pseudomorphic replacement. On the contrary, in a dynamic environment when temperature increases progressively, serpentinization is non-pseudomorphic and produces foliated textures and minerals with fibrous habits such as chrysotile.

The various parameters—mineral assemblage, paragenesis, open or closed system—as well as the external conditions of the environment—static or dynamic—must be studied in order to define the *regime of serpentinization and rodingitization*.

I have applied this concept to the study of the serpentinites and rodingites of the Quebec Appalachian ophiolites. These ophiolites have been tectonically emplaced onto the eastern continental margin of North America in Early Ordovician time. They are regarded as fragments of the oceanic crust and mantle that underlay the Proto-Atlantic ocean, or smaller marginal basins (Bird & Dewey 1970; Dewey 1974). If the peridotites represent parts of slices of upper mantle and oceanic crust, the following sequence of events must be considered: (1) the *formation* of the peridotites in an oceanic environment through processes of oceanic lithosphere accretion and sea-floor spreading; (2) the *fragmentation*, and *tectonic emplacement* of the peridotites on the continental margin; and (3) *deformation* of the peridotites with the Cambro-Ordovician country rocks. During this evolution, serpentinization and rodingitization took place in two main episodes of distinct regimes. An early episode characterized by the pseudomorphic replacement of primary minerals by *lizardite* in serpentinites, and by *clinozoïsite*, *diopside* and *hydrogrossularite* in rodingites is assumed to have taken place in the oceanic environment, at temperatures below 340° C and under static conditions. Late serpentinization and rodingitization occurred in a dynamic regime, at higher temperatures than the first episode, and contemporaneous with the tectonic emplacement and transport of the rocks into their present setting. The second episode produced foliated textures and several generations of *antigorite* + *brucite* and *chrysotile* + *brucite veins* in serpentinites, and of *zoïsite*, *grossularite*, *wollastonite*, *prehnite*, *diopside* and *vesuvianite veins* in rodingitized rocks. The peridotites are cut by rootless granitic dikes that by field relationships can be shown to have been emplaced between the two episodes of serpentinization (Laurent 1975*a*, 1975*b*). The dikes have yielded Ordovician ages (Poole *et al.*

1963; Frankel & Clague in prep.). Table 1 gives a summary of the events and parageneses which are described in the next pages.

TABLE 1. — *Summary of events and parageneses*

<table>
<tr><th rowspan="2">Interpretation</th><th colspan="2">Ophiolite formation:</th></tr>
<tr><th>Peridotite</th><th>Dikes of gabbro & diorite</th></tr>
<tr><td rowspan="2">Early oceanic and static episode</td><td colspan="2">Pseudomorphic replacements of primary minerals by:</td></tr>
<tr><td>lizardite + chrysotile + brucite + magnetite + awaruite</td><td>clinozoisite + diopside + hydrogrossularite</td></tr>
<tr><td>Oceanic lithosphere fragmentation</td><td colspan="2">Deformation:
cataclastic structures and textures of rodingite and rodingitized metadiorite</td></tr>
<tr><td>Early phase of obduction</td><td colspan="2">Emplacement of granite dikes and local development of biotite (K metasomatism)</td></tr>
<tr><td rowspan="2">Late continental and dynamic episode (tectonic transport of ophiolite)</td><td colspan="2">Formation of silicate veins:</td></tr>
<tr><td>a) foliated textures with antigorite + brucite + magnetite
b) asbestos veins with chrysotile + brucite + magnetite</td><td>calc-silicates veins with zoisite, grossularite, prehnite, diopside, vesuvianite, wollastonite, etc.</td></tr>
<tr><td>Late alteration (post-emplacement)</td><td colspan="2">talc + chlorites + carbonates + quartz</td></tr>
</table>

MINERAL PARAGENESES

Up to 5 kilometers of serpentinized tectonite peridotite of harzburgitic composition make up the basal part of the Quebec Appalachian ophiolites (Laurent 1975*a*, 1977, 1979). These peridotites contain a complex assemblage of rootless intrusive rocks. Three groups can be distinguished on the base of differences in composition, alteration and deformation. The oldest group consists of isolated lenses a few meters long of massive rodingite with rare relicts of gabbroïc fabric. The second group consists of irregular bodies of hornblende-biotite metadiorite strongly foliated, altered and pervasively rodingitized. The third group consists of younger dikes of granite (De 1972) still relatively undeformed and fresh, although their margins are rodingitized. Bodies of rodingitized gabbro and diorite are consanguineous with the ophiolitic assemblage and were probably emplaced at/or near the spreading axis, whereas the granitic dikes were emplaced later since they postdate a major phase of deformation and alteration of the ophiolitic assemblage.

The early oceanic and static episode

The first episode of serpentinization was pervasive and characterized by the replacement of olivine and orthopyroxene by *lizardite* $\pm$ *chrysotile* $\pm$ *brucite* $\pm$ *magnetite* and, locally, very small amounts of *awaruite* (Ni_3Fe). This reaction occurred at a P_{H_2O} close to 2 000 atm. and at a temperature below 340° C, under low oxygen activity and static conditions (Laurent and Hebert 1979). It produced lizardite pseudomorphs in mesh and hourglass textures with either olivine and orthopyroxene relicts or isotropic and hourglass lizardite in the mesh centers. These textures are illustrated by Wicks *et al.* (1977). In hourglass textures serpentinization advances at right angles to grain boundaries wholly replacing olivine at a uniform rate and constant volume. In mesh textures, the rate of serpentinization progressively slows down and can stop leaving a central core of unaltered olivine, which was replaced or not by randomly oriented serpentine in a later episode. This may indicate that the conditions controlling the reaction were obviously becoming less and less favorable to the continuation of the process, because of relatively rapid temperature falling and decreases in water supplies.

The first episode of rodingitization occurred in the same regime as the early serpentinization. The rodingite locally preserves relicts of gabbroïc fabric, but all primary minerals have been replaced by pseudomorphs of calc-silicate minerals (Olsen 1961). Plagioclase is replaced by *clinozoïsite* and *hydrogrossularite*, and clinopyroxene and hornblende are replaced by *diopside* and smaller amounts of *actinolite* and *chlorite*. Chlorite is concentrated in a thin zone within the serpentinite at the contact with the rodingite. The contact between the rodingite and the chlorite serpentinite is sharp, whereas the contact chlorite serpentinite—serpentinite is gradational and irregular, *chlorite* replacing *lizardite* in this metasomatic reaction zone. The rodingite displays deformation structures—boudinage, brecciation, fractures—and cataclastic and recrystallization textures. Hydrogrossularite, clinozoïsite and diopside are sheared, granulated and partly replaced by mosaïcs of finer-grained neoblasts of zoïsite, calcite, vesuvianite, prehnite, grossularite and diopside.

The irregular bodies, up to 100 m thick, of metadiorite are similarly deformed. They display identical deformation structures and a well developed gneissic (blastomylonitic) texture.

The primary minerals of this rock are, according to De (1972), andesine, poikilitic hornblende, black biotite, apatite and Fe-Ti oxides. They have been partly replaced by calc-silicate minerals and secondary feldspars such as *microcline* and *albite*. The contact with the serpentinite is sharp and even. The degree of rodingitization is maximum in the margins of the metadiorite and decreases towards the core of the body which is richer in feldspars. The calcium-rich margins consist of *clinozoïsite*, *hydrogrossularite*, *diopside*, *tremolite*, *prehnite*, *wollastonite*, *sphene*, etc. Each body differs in mineral composition and extent of rodingitization.

The first episode of serpentinization and rodingitization is characterized by the development of pseudomorphic textures in the absence of shearing and under falling temperature conditions. Pseudomorphic replacements at constant volume are typical of an open system in a static environment. The spreading axis is a dynamic, high temperature environment that does not satisfy these criteria. The regime of this oceanic serpentinization suggests a different environment. Hence I am led to assume that it occurred in the oceanic environment but at a distance removed from the spreading axis. It is only after having cooled to below 340° C that the peridotites were serpentinized under low activity of oxygen and static conditions. Presence of *magnetite—awaruite* suggests conditions of low oxygen fugacities (Moody 1976).

Deformation

The structures and textures of deformation observed in the rodingite lenses and the metadiorite bodies postdate the early episode of serpentinization and rodingitization. This tectonic overprint, however, predates the emplacement of the younger granitic dikes and an episode of potassium metasomatism associated with their emplacement. I interpret this deformation to have occurred during fragmentation of the oceanic lithosphere immediately prior to obduction of the ophiolites onto the continental margin.

Emplacement of granite dikes

The third group of intrusive rocks consists of relatively undeformed and unfoliated dikes, 1 to 10 m thick, of fine to coarse-grained granite with potassium feldspar, oligoclase, quartz, biotite and muscovite as main constituents (De 1972). This rock shows gradual and uneven contacts with the enclosing serpentinites. Granitic material penetrates into the serpentinite to distances that vary from a few millimeters to several centimeters, and xenoliths of serpentinite displaying a reaction rim of *serpentine-talc-anthophyllite* are found within the intrusive rock (Olsen 1961). These observations provide evidence that the youngest dikes were emplaced in peridotites already serpentinized. Serpentinite at the contact with these dikes is cut by chrysotile veins formed during the late episode of serpentinization (see below); therefore the granitic dikes were emplaced between the two episodes of serpentinization. And since they have no roots and no granitic analogs are known to intrude the Cambrian country rock in the vicinity of the ophiolites I have concluded that they have intruded the peridotites before the ophiolites reached their present position (Laurent 1975*a*). Poole *et al.* (1963) have obtained two Early Ordovician K-Ar ages, 477 and 481 m.y., on muscovite from this granite, whereas Frankel and Clague (in prep.) have obtained younger Rb—Sr isochron ages of 451 m.y. for a dark variety and 424 m.y. for a white variety of this granite. I have dated by the K-Ar method a concentrate of 14 mesh unaltered biotite from a pegmatitic facies of fresh granite. The age of this sample which comes from the Lake Asbestos mine at Black Lake is 482.6 $\pm$ 18 m.y. Other K-Ar ages obtained on muscovite (unpubl. data) are significantly younger and close to the Rb-Sr ages ($\sim$ 440 m.y.). There is no doubt that most of the ages obtained do not reflect the time of crystallization and cooling. These granites have been "rejuvenated" during the tectonic emplacement of the ophiolites and the Taconic orogeny. I interpret dike intrusion to have occurred in Early Ordovician time, at the beginning of the process of obduction of the ophiolites onto the continental margin.

Potassium metasomatism was associated with the emplacement of the granite dikes. It is restricted to the metadiorite bodies and the serpentinite at the contact. A widespread development of undeformed reddish brown biotite is observed in the metadiorite. This mica crosses the boundary metadiorite—serpentinite and invades the serpentinite in the contact zone on a width of several centimeters or decimeters. Within the serpentinite stilpnomelane may also develop with biotite (Olsen 1961). Rodingitization and potassium metasomatism have strongly modified the dioritic rocks so that their actual chemical composition does not reflect the characteristics of the original magma.

The late continental and dynamic episode

The late episode of serpentinization produced the commercial chrysotile asbestos that fills a stock work of expansion fractures from 0.5 to 2.5 cm thick within the serpentinized peridotite. *Chrysotile* forms crossfibers in the centers of the veins with *magnetite* and *brucite*, formed during the same reaction, concentrated along the contact between fibers and vein selvages. To explain the mechanism of fiber growth I have applied the principles of incremental strain analysis developed by Durney and Ramsay (1973). Tensile and shear fractures commonly are filled synchronously—as they progressively open—with crystals of fibrous habit derived by solution or diffusion of material from the wall rock. The orientation of the growing fibers in the veins is controlled not by the position of the wall rock but by the direction of minimum shear stress; changes in the orientation of the stress field are expected to produce changes in the direction of fiber growth. Such changes are recorded by fiber bends. The tubular structure of chrysotile can adapt to the deformations. Nevertheless, one can assume that the story of its growth has significant effects on its mechanical properties, which could explain the great variations of its properties observed from one ore body to another, and sometimes within the same ore body. Different generations of veins exhibit cross-cutting relationships. Chrysotile fibers in early veins are bent, kinked, broken and frequently replaced by fibrous *brucite* or *antigorite*, whereas late veins are not deformed. These observations indicate that "chrysotilization" is syntectonic and developed in a dynamic regime.

The relations of wall rock to asbestos veins observed suggest that vein chrysotile was derived from lizardite rather than from fresh relicts of olivine. During the processes of solution, transport, and chrysotile growth, most of the iron accomodated in lizardite was expelled to form additional magnetite. The observed paragenesis is the following:

$$\textit{Lizardite} + H_2O + O_2 \rightarrow \textit{Chrysotile} + \textit{Magnetite} + \textit{Brucite} \pm \textit{excess of Si (removed)}$$

This reaction occurred in a more or less closed system with large volume increases now occupied by the chrysotile veins. The regime was dynamic and characterized by increasing temperatures (up to 400° C or higher) and a high oxygen activity. During the same episode of serpentinization, *antigorite* ± *brucite* developed extensively in shear zones within the peridotite. Non-pseudomorphic platy *antigorite* replaced lizardite producing foliated textures and locally forming antigorite schists (Laurent and Hebert 1979).

The late rodingitization episode, as the "chrysotilization" episode, is characterized by the formation of mineral veins. Rodingite and metadiorite bodies have arrays of calc-silicate veins of *zoïsite*, *zoïsite-prehnite*, *zoïsite-grossularite*, *grossularite*, *grossularite-diopside*, *diopside* and *diopside-grossularite-vesuvianite-margarite-calcite*, as well as crossfibers veins of *wollastonite* and *chlorite*. This episode affected also the younger granite dikes which were rodingitized along their margins and, to various extents, altered to secondary *albite* and *quartz*. Biotite was locally replaced by *potassium feldspar*, *chlorite* and *iron oxides*. Rodingitic minerals and *zeolites* filled vugs and joints. Wares and Martin (this volume) give detailed descriptions of the mineralogy and geochemistry of several examples of this type of rodingitized intrusive rock from the Jeffrey mine at Astestos.

According to my interpretation, this episode of serpentinization and rodingitization developed during the tectonic transport of the ophiolites and their emplacement in the present setting. After emplacement, the serpentinized peridotites were further altered at ambient temperatures by CO_2-SiO_2 bearing ground water.

Serpentine locally was altered to talc and magnesite, and extensive alteration occured along faults between the peridotites and the country rocks where broad zones of *talc-carbonate-chlorite* rock were developed.

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REFERENCES

BIRD, J. M. and J. F. DEWEY (1970). Lithosphere plate-continental margin tectonics and the evolution of the Appalachian orogen. *Geol. Soc. Amer. Bull.*, *81*, 1031-1060.

CHURCH, W. R. (1972). Ophiolite: its definition, origin as oceanic crust, and mode of emplacement in orogenic belts, with special reference to the Appalachians. *In:* The ancient oceanic lithosphere, *Earth Phys. Br. Pub.*, *42*, 3, Dept. Energy, Mines and Resources, Ottawa, 71-86.

COLEMAN, R. G. (1977). Ophiolites, ancient oceanic lithosphere? Springer Verlag, Berlin, Heidelberg, New York.

DE, A. (1972). Petrology of dikes in the ultramafic rocks of southeastern Quebec and origin of the rodingite. *Geol. Soc. Amer. Mem.*, *132*, 489-501.

DEWEY, J. F. (1974). Continental margins and ophiolite obduction: Appalachian-Caledonian system. *In:* The geology of continental margins (C. A. Burk & C. L. Drake eds.), Springer Verlag, New York, 933-950.

DURNEY, D. W. and J. G. RAMSAY (1973). Incremental strains measured by syntectonic crystal growths. *In:* Gravity and Tectonics (K. A. DeJong & R. Scholten eds.), Interscience Pubs., New York, 67-96.

EITEL, W. (1954). The physical chemistry of the silicates. University of Chicago Press, Chicago.

FRANKEL, Ch. S. and D. A. CLAGUE (in preparation). The age and origin of the granitic intrusions of the Thetford Mines ophiolite. *Can. J. Earth. Sci.*

LAURENT, R. (1975*a*). Occurences and origin of the ophiolites of Southern Quebec, Northern Appalachians. *Can. J. Earth Sci.*, *12*, 443-455.

—— (1975*b*). Petrology of the alpine-type serpentinites of Asbestos and Thetford Mines, Quebec. *Schweiz. Mineral. Petrogr., Mitt.*, *55*, 431-455.

—— (1977). Ophiolites of the Quebec Appalachians. *In:* North American Ophiolites (R. G. Coleman & W. P. Irwin, eds.), State of Oregon, Dept. of Geology and Mineral Industries Bull., *95*, 25-40.

—— (1979). Environment of formation, evolution and emplacement of the Appalachian ophiolites from Quebec. Proceedings of the International Ophiolite Symposium, Nicosia, Cyprus (in press).

LAURENT, R. and Y. HEBERT (1979). Paragenesis of serpentine assemblages in harzburgite tectonite and dunite cumulate from the Quebec Appalachians. *Can. Mineral.*, *17*, Part 4, 857-869.

MOODY, J. B. (1976). An experimental study of the serpentinization of iron-bearing olivines. *Can. Mineral.*, *14*, 462-478.

OLSEN, E. J. (1961). High-temperature acid rocks associated with serpentinite in eastern Quebec. *Amer. J. Sci.*, *259*, 329-347.

POOLE, W. H., J. R. BELAND and R. K. WANLESS (1963). Minimum age of Middle Ordovician rocks in Southern Quebec. *Geol. Soc. Amer. Bull.*, *74*, 1063-1065.

WARES, R. P. and R. F. MARTIN (1980). Mineralogical evolution of three rodingite dykes in the Jeffrey Mine, Asbestos, Quebec. This volume.

WICKS, F. J., E. J. W. WITTAKER and J. ZUSSMAN (1977). An idealized model for serpentine textures after olivine. *Can. Mineral.*, *15*, 446-458.

WILLIAMS, H. and P. St. JULIEN (1978). The Baie Verte-Brompton line in Newfoundland and regional correlations in the Canadian Appalachians. Current Research, Part A, *Geol. Surv. Canada*, Paper *78-1A*, 225-229.