RODINGITIZATION OF IRANIAN BASIC ROCKS: A NEW INTERPRETATION

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Abstract

Mineral paragenesis of rodingitized basic rocks of Iranian ophiolites are presented and metasomatic reactions between Ca^{+2} bearing aqueous fluids issued during serpentinization of host ultramafic rock − with magmatic minerals of basic rocks leading to present paragenesis of rodingites are discussed. It is concluded that Ca^{+2} rich aqueous fluid in equilibrium with serpentinite has high Ca^{+2} chemical potential to react with magmatic minerals of basic dykes resulting in lowering the free energy of system, appearance of a new mineral paragenesis and total or partial conversion of basic dykes to rodingites. A feedback mechanism is proposed to account for inter-relationship of serpentinization and rodingitization.

Keywords: Rodingite; Ophiolite; Iran; Basic Rock; Rodingitization

List of Abbreviations

Ab = Albite = $NaAlSi_3O_8$
An = Anorthits = $CaAl_2Si_2O_8$
Ca = Calcite = Co_3Ca
Ca-Ts = Tschermak's molecule = $CaAl_2SiO_6$
Dp = Diopside = $CaMgSi_2O_6$
En = Enstatite = SiO_3Mg
Fo = Forsterite = SiO_4Mg_2
Grs = Grossular = $Ca_3Al_2Si_3O_{12}$
Hgrs = Hydrogrossular = $Ca_3Al_2Si_{2.5}O_{10}(OH)_2$
M-cpx = Magmatic Clinopyroxene
Mgch = Mg-chlorite = $Mg_5Al_2Si_3O_{10}(OH)_8$
Opx = Orthopyroxene = $MgSiO_3$ = Enstatite
Pmp = Pumpellyite = $Ca_4MgAl_5O(OH)_3(Si_2O_7)_2(SiO_4)_2,2H_2O$
Prh = Prehnite = $Ca_2Al_2Si_3O_{10}(OH)_8$

Pt = Pectolite = $Ca_2NaH(SiO_3)_3$
Q = Quartz = SiO_2
Se = Serpentine = $Mg_3Si_2O_5(OH)_4$
Tc = Talc = $Mg_3Si_4O_{10}(OH)_2$
Tr = Tremolite = $Ca_2Mg_5Si_8O_{22}(OH)_2$
Vs = Vesuvianite = $Ca_{10}Mg_2Al_4(Si_2O_7)_2(SiO_4)_5(OH)_4$
Vt = Vuagnatite = $CaAlSiO_4(OH)$
Xo = Xonotlite = $Ca_6Si_6O_{17}(OH)_2$
Zo = Zoisite = $Ca_2Al_3O(Si_2O_7)(SiO_4)OH$

Introduction

Rodingites are calcium rich rocks composed principally of hydrogrossular, grossular-andradite garnet, diopside, vesuvianite, epidote prehnite, pectolite, xonotlite, etc. They occur as metasomatically altered dykes and other lithic tectonic inclusions within the

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serpentinite bodies. They also occur at the serpentinite country rock boundary [4]. It is believed that serpentinization of olivine and orthopyroxene liberates calcium which can not be accommodated in serpentine crystal structure [4,10]. The liberated calcium is concentrated in the fluids associated with serpentinization thus reacting with basic or other lithic inclusions in serpentinized ultramafic bodies or any other rocks such as greywacks, shales, volcanic, metamorphic and plutonic rocks in contact with serpentinite bodies. The product of reaction of calcium rich fluids with lithic inclusions in the serpentinites is the formation of calcium rich minerals in lithic inclusion which brings about metasomatic rocks at the expense of lithic inclusions. These rocks are generally called rodingites and the process is called rodingitization.

These are several interesting thermodynamical and kinetical problems in the evaluation of metasomatic reactions leading to the formation of rodingites. These problems can be formulated as follows:

1. What is the nature of rodingitizing fluids?

2. What is the nature of metasomatic reactions between rodingitizing fluid and the various types of rocks in contact with serpentinite bodies?

3. What are thermodynamic and kinetic factors which act as deriving mechanism for rodingitization?

In this article I try to find some tentative solutions to these problems. My main task is to present these solutions for rodingitized basic rocks (gabbros, diabasic dykes, pillow lavas) of Iranian ophiolites.

Mineral paragenesis of Iranian rodingitized basic rocks are first presented and then I try to derive mineral paragenesis of rodingites by metasomatic reaction of Ca^{+2} rich fluid and magmatic minerals and finally I try to discuss on petrogenesis of these reactions by thermodynamic and kinetic reasoning.

Geological Information

Most of Iranian rodingites are in fact rodingitized pegmatitic gabbro dykes, diabasic dykes and minor basaltic pillow lavas. The host serpentinite bodies are mainly serpentinized harzburgites, dunite and lherzolites. Serpentinite bodies show two distinct stages of serpentinization.

1) Static serpentinization which is attributed by Sabzehei [8] to the ocean floor metamorphism. 2) Polyphasic dynamic serpentinization which is attributed by Sabzehei [9] to the emplacement of ophiolites. Static serpentinization is materiaitzed by massive nonfoliated serpentinite with chrysotile, antigorite and bastite as main serpentine minerals in order of abundance. Dynamic serpentinization produced various types of foliated, sheared and crushed serpentinites with antigorite as main serpentine mineral.

Rodingites are found as dismembered, boudined, isolated bodies of different sizes in the serpentinite bodies. They have following peculiarities:

1. There are systematic zonings from completely rodingitized rock at direct contact with the host serpentinite to partially rodingitized basic rock leading finally to basic original rock weekly touched by rodingitization.

2. In spite of rodingitization the nature of original rocks can be identified in the field.

The original rocks are diabasic dykes, gabbro (norite, cpx-plagioclase pegmatitic gabbros, layered cumulate gabbros), pyroxenite dykes in order of abundance.

3. Many original rocks are converted to masses of monomineralic rocks such as garnetites, vesuvianitite etc.

4. In some cases small masses of albitite or albite rich rocks are found in serpentinite body not too far from the rodingitization site.

5. Many rodingites show two stages of rodingitization: (a) Static rodingitization which produces rodingites of typical granoblastic texture. (b) Dynamic rodingitization which produces veined rodingites. Static and dynamic rodingitization can well be correlated with relevant static and dynamic serpentinization. During dynamic serpentinization the rigid brittle dykes of basic rocks are strongly deformed and a gradient of permeability is created between plastic serpentinite and brittle basic dykes so the activated fluid rush into the basic dykes. Such a circumstance creates a favourable condition for the reaction of fluids with minerals of dykes as deformation creates more reaction sites. Dynamic emplacement of serpentinite bodies acts therefore as a kinetic factor for metasomatic reactions.

6. Iranian rodingite is heterogenous – with respect to mineral paragenesis.

Mineral Paragenesis

Following mineral paragenesis are found in Iranian rodingites [1,3,6,9,11,12]:

- Grs + Mgch + Relict magmatic Cpx
- Vs + Hgrs + Mgch
- Dp + Grs
- Prh + Grs + Dp + Mgch
- Grs + Vt + Prh
- Tr + Grs
- Vt + Pt + Mgch
- Tc + Ca + Zo
- Vs + Mgch + Tr + Grs
- Hgrs + Mgch

- Prh + Dp + Grs
- Dp + Hgrs + Pt + Zo
- Grs + Prh + Xo
- Tr + Hgrs
- Tr + Hgrs + Mgch
- Pt + Mgch + Prh
- Parawollastonite + Grs + Ca + Magnesite
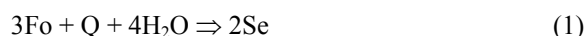- Dp (Metasomatic) + Cpx (relict)

Petrographic observations show that:

a) Grossular-Hydrogrossular and zoisite-epidote are mostly formed at the expense of plagioclase [8].

b) Mg-chlorite, tremolite, and talc are mostly formed at the expense of magmatic clinopyroxenes.

c) Magmatic cpx is transformed into pure metasomatic diopside.

d) Pectolite, vuagnatite, prehnite and xonotlite are mostly formed in the veins during dynamic rodingitization of basic rocks.
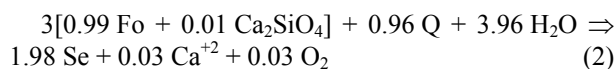
Petrogenesis

It is universally understood that rodingitization is a type of metasomatic process spatially and temporally associated with the process of serpentinization. Textural and mineralogical studies clearly demonstrate a type of calcic metasomatism for conversion of basic dykes to rodingites. The essential problem is the source of calcium. We know that serpentinization of olivine and orthopyroxenes in harzburgites and lherzolites may release Ca^{+2} into serpentinizing aqueous fluids. Deer *et al*. [5] demonstrated that forsterite from ultramafic peridotite may contain up to 0.42 percent CaO which is equivalent to 1.39 percent SiO_4Ca_2.
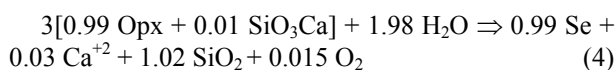
For serpentizaiton of olivine we may write following reaction:

$$3Fo + Q + 4H_2O \Rightarrow 2Se \qquad (1)$$

If we assume %1 of SiO_4Ca_2 the reaction (l) can be written in following form:

$$3[0.99\ Fo + 0.01\ Ca_2SiO_4] + 0.96\ Q + 3.96\ H_2O \Rightarrow 1.98\ Se + 0.03\ Ca^{+2} + 0.03\ O_2 \qquad (2)$$

Orthopyroxenes of peridotite - according to Deer *et al*. [5] – have up to 2.14 percent CaO which is equivalent of 4.40% SiO_3Ca. If we assume only %1 of SiO_3Ca in orthopyroxenes of harzburgites we may write two similar reactions:

$$3Opx + 2H_2O \Rightarrow Se + Q \qquad (3)$$

$$3[0.99\ Opx + 0.01\ SiO_3Ca] + 1.98\ H_2O \Rightarrow 0.99\ Se + 0.03\ Ca^{+2} + 1.02\ SiO_2 + 0.015\ O_2 \qquad (4)$$

In the reactions (2) and (4) which lead to serpentinization of olivines and orthopyroxenes, Ca^{+2} are liberated into the fluids. Coleman [4] already stated that water issuing from serpentinized terrains are rich in $Ca(OH)_2$ and have unusually high pH (11+) values. He stated that water rich in Ca^{+2}, $(OH)^{-1}$ are incompatible with rocks surrounding serpentinite and that Ca^{+2} can not be accommodated into the crystal structure of serpentine minerals. In contrast, the fluid rich in Ca^{+2} have high tendency to react with the magmatic mineral of basic dyke which are either cutting ultramafic bodies or as gabbroic bodies Juxtaposed to serpentinizing bodies by a tectonic process (Fig. 1).

This circumstance creates a favorable thermodynamic atmosphere for rodingitization. In fact in this circumstance a gradient of chemical potential ($\mu\ Ca^{+2}$) is created between serpentinizing peridotite and metasomatically transforming basic rocks.

This gradient should be somehow leveled. This is achieved by the reactions occurring between Ca^{+2} rich fluids and basic rocks until following condition is fulfilled:

$$\mu_1\ Ca^{+2} = \mu_2\ Ca^{+2}$$

Chemical potential of Ca^{+2} in Serpentinite

= Chemical potential of Ca^{+2} in basic dyke

In this circumstance the free energy of system is minimized and new paragenesis appears at the expense of magmatic minerals. Appearance of new paragenesis implies the set up of a few reactions. Coleman [4] has already cited two reactions of this type as follows:
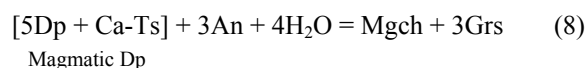
$$3An + Ca^{+2} + H_2O \Rightarrow Zo + 2H^+ \qquad (5)$$

$$Zo + 5Ca^{+2} + 13H_2O \Rightarrow 3Hgrs + 1.5\ SiO_2 + 10H^+ \quad (6)$$
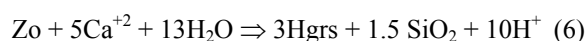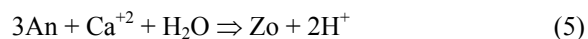
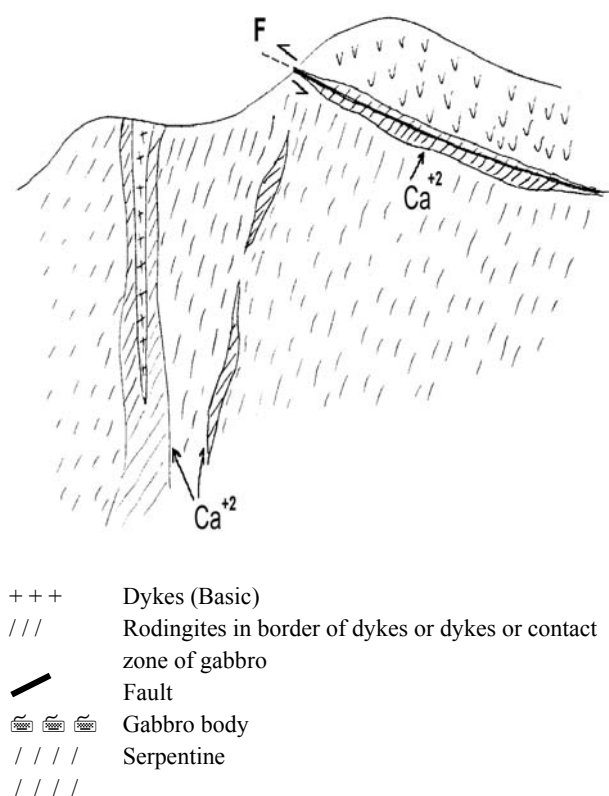I tried to write other reactions of this type based on the real paragenesis of rodingites:

a. Mg-chlorite + Hydrogrossular

In many Iranian rodingites, Mg-chlorite + hydrogrossular is formed at the expense of An rich plagioclase and magmatic cpx. We may write following reaction:

$$[5Dp+2Ca\text{-}Ts]+An+Ca^{+2} + 11H_2O = Mgch + 3Hgrs \quad (7)$$
Magmatic Dp
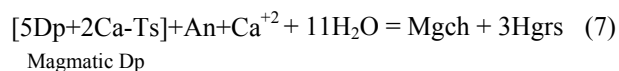
If Ca^{+2} activity is considerably decreased we may have grossular formed by following reaction:

$$[5Dp + Ca\text{-}Ts] + 3An + 4H_2O = Mgch + 3Grs \qquad (8)$$
Magmatic Dp

+ + +   Dykes (Basic)

/ / /   Rodingites in border of dykes or dykes or contact
              zone of gabbro

⟋   Fault

▦ ▦ ▦   Gabbro body

/ / / /   Serpentine
/ / / /

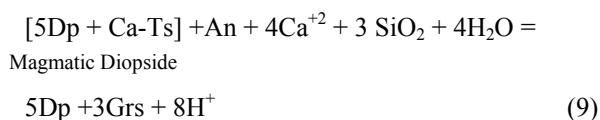**Figure 1.** Diagrammatic   presentation   of   rodingite–
serpentinite relation.

b. Metasomatic Diopside + Grossular or Hydrogrossular

It is often seen that magmatic diopside is recrystallized into pure diopside $(CaMgSi_2O_6)$ plus grossular. We may write following reaction for this paragenesis:

$[5Dp + Ca\text{-}Ts] + An + 4Ca^{+2} + 3\ SiO_2 + 4H_2O =$
Magmatic Diopside

$5Dp + 3Grs + 8H^+$ (9)

Hydrogrossular is formed when SiO_2 activity is decreased:

$Grs + 2H_2O = Hgrs + 0.5SiO_2 + 2H^+ + 1/2\ O_2$ (10)

Hydrogrossular can be directly formed at the expense of plagioclase by following reaction:

$6An + 6Ca^{+2} + 18H_2O + 3SiO2 = 6Hgrs + 24H^+$ (11)
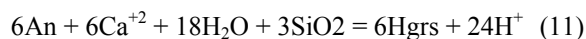
c. Zoisite bearing assemblages:

Zoisite can be formed by following reaction:

$6An + 2Ca^{+2} + 4H_2O = 4Zo + 2H^+$ (12)
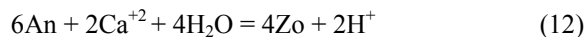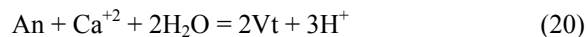
d. Pectolite + Prehnite bearing assemblage:

These two minerals can be formed by following reaction:

$4Ab + An + 5Dp + 6Ca^{+2} + 14H_2O =$
$4Pt + 2Prh + Mgch + 3SiO_2 + 12H^+$ (13)

$[5Dp + Ca\text{-}Ts] + An + 6Ca^{+2} + 10H_2O + 6SiO_2 =$
Magmatic Dp

$4Prh + 5Dp + Grs + 12H^+$ (14)
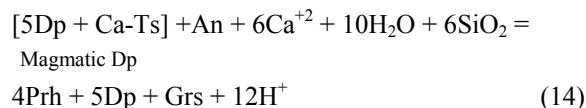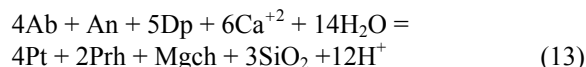
Vuagnatite (Vt) is reported by Adib et al. [1] from Neiriz rodingites. It can be formed by following reactions:

$6An + 8Ca^{+2} + 14H_2O + 3SiO_2 =$
$4Vt + 2Prh + 2Hgrs + 16H^+$ (15)
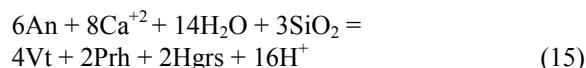
It should be noted that vuagnatite is reported in presence of prehnite and hydrogrossular. Other reactions for pectolite + prehnite association with or without vuagnatite can be summarized as follows:

$2Ab + An + 10H_2O + 7Ca^{+2} + 4SiO_2 =$
$2Pt + 2Prh + 16H^+$ (16)

$Ab + An + 4Ca^{+2} + 6H_2O + SiO_2 =$
$3Vt + Pt + 8H^+$ (17)

$2An + 2Ca^{+2} + 2SiO_2 + 4H_2O = 2Prh + 4H^+$ (18)

$Prh = 2Vt + SiO_2$ (19)

$An + Ca^{+2} + 2H_2O = 2Vt + 3H^+$ (20)
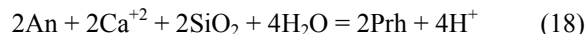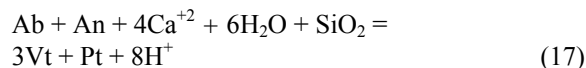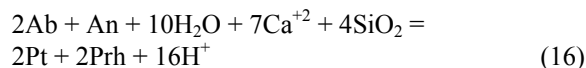
Xonotlite $[Ca_6Si_6O_{17}(OH)_2]$ is observed to appear with prehnite and grossular for which we may propose following reaction:

$6An + 15Ca^{+2} + 12SiO_2 + 19H_2O =$
$Xo + 3Prh + 3Grs + 3OH^+$ (21)
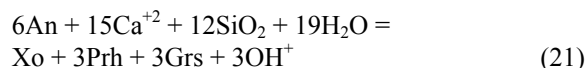
Prehnite can be formed at the expense of zoisite by following reaction:
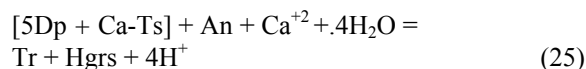
$2Zo + 2Ca^{+2} + 4H_2O + 3SiO_2 = 3Prh + 2H^+$ (22)
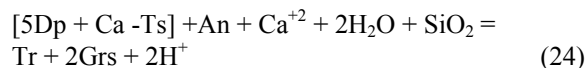
The appearance of vuagnatite in presence of prehnit and grossular may be visualized by following reaction:

$3An + 4Ca^{+2} + 6H_2O + 2SiO_2 =$
$2Vt + Prh + Grs + 8H^+$ (23)
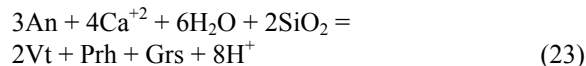
e. Tremolite bearing assemblages

Tremolite bearing assemblages may be the result of following reactions:

$[5Dp + Ca\text{-}Ts] + An + Ca^{+2} + 2H_2O + SiO_2 =$
$Tr + 2Grs + 2H^+$ (24)

$[5Dp + Ca\text{-}Ts] + An + Ca^{+2} + .4H_2O =$
$Tr + Hgrs + 4H^+$ (25)

$$2[5Dp + Ca\text{-}Ts] + 7An + 2Ca^{+2} + 12H_2O =$$
$$Tr + Mgch + 2Grs + 5Prh + SiO_2 + 4H^+ \qquad (26)$$

$$[5Dp + Ca\text{-}Ts] + 4An + 2Ca^{+2} + 6H_2O =$$
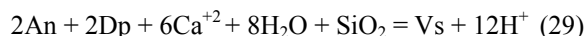$$Tr + 2Zo + 2Grs + 8H^+ \qquad (27)$$
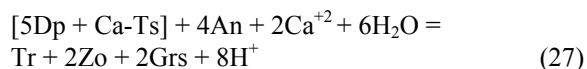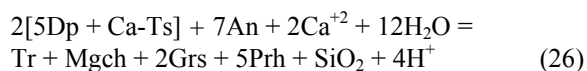
f. <u>Vesuvianite bearing assemblages</u>

For vesuvianite bearing assemblages following reactions can be written:

$$[7Dp + Ca\text{-}Ts] + 3An + 2Ca^{+2} + 8H_2O =$$
$$Vs + Mgch + Grs + 6SiO_2 + 4H^+ \qquad (28)$$

$$2An + 2Dp + 6Ca^{+2} + 8H_2O + SiO_2 = Vs + 12H^+ \quad (29)$$
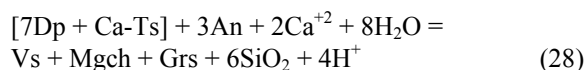
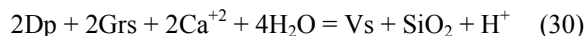By comparison of (28), (29) we may conclude that monomineralic rocks composed of vesuvianite is formed by increased activity of SiO_2 in Ca^{+2} rich fluid. We may also write following reaction for formation of monomineralic vesuvianite bearing rocks:

$$2Dp + 2Grs + 2Ca^{+2} + 4H_2O = Vs + SiO_2 + H^+ \quad (30)$$

$$2Mgch + 7Grs + 26Ca^{+2} + 18H_2O = 5Vs + 16H^+ \quad (31)$$
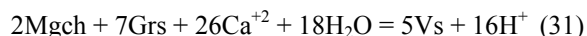
g. <u>Talc bearing assemblages</u>

If CO_2 is present in minor amount in Ca^{+2} rich fluids, talc + calcite can be formed according to following reaction:

$$3Dp + 4CO_2 + Ca^{+2} + 2H_2O =$$
$$Tc + 4Ca + 2SiO_2 + 2H^+ \qquad (32)$$
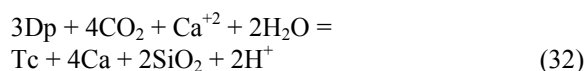
h. <u>Pumpellyite bearing assemblages</u>

Pumpellyite is formed together with grossular by following reactions:

$$2[5Dp + Ca\text{-}Ts] + 25An + 9Ca^{+2} + 64H_2O =$$
$$l0Pmp + 2Grs + 6SiO_2 + 58H^+ \qquad (33)$$
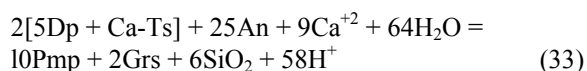
If the activity of all pure minerals in all the reactions is taken as unity we may have two types of equilibrium constants as follows for all the reactions (1) to (33):

$$K_1 = \frac{[fH^+]^m}{[aCa^{+2}]^n \cdot [fH_2O]^o \cdot [aSiO_2]^p}$$

$$K_2 = \frac{[fH^+]^{m_1} \cdot [aSiO_2]^{p_1}}{[aCa^{+2}]^{n_1} \cdot [fH_2O]^{o_1}}$$

It means that in the process of rodingitization the essential factors are $_aCa^{+2}$, f(H) + and f(H_2O). In some of the reactions, SiO_2 is liberated and in some is consumed. It can be visualized that the liberated SiO_2 in some reactions are consumed in other reactions. For example SiO_2 liberated in reaction (28) may be consumed by reaction (29) which converts the whole original rock to pockets of pure vesuvianite. The reason why rodingites are so heterogenous are: (1) Different activity of Ca^{+2} in different parts of environment. (2) Different fugacity of H_2O in different parts. (3) Presence or absence of SiO_2 in invading solutions of different reaction sites. It is interesting to note that in K_2 type reactions, SiO_2 is liberated. This SiO_2 along with H_2O enhances the serpentinization of host peridotite which in turn - as a feed back mechanism - liberates more Ca^{+2} into fluid which either facilitate rodingitization or converts the early paragenesis of rodingites to other paragenesis which needs different proportions of Ca^{+2} and H_2O. In Figure 2 the feed back mechanism is schematically illustrated.
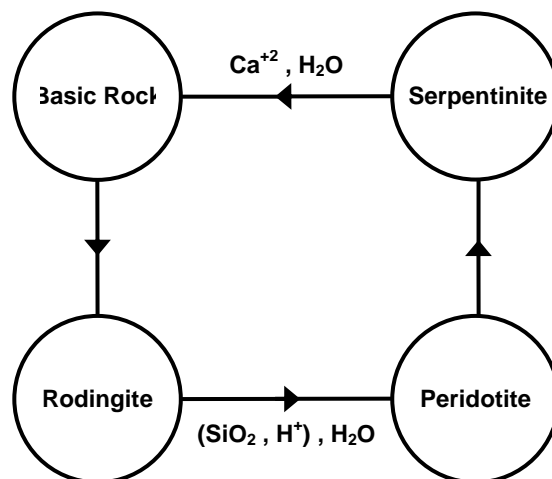

Figure 2. Schematic representation of feed back mechanism in the process of serpentinization and rodingitization.

As K_1 and K_2 strongly depend on fH^+ and $_aCa^{+2}$, a series of $fH^+ - {_a}Ca^{+2}$ diagrams can be constructed to illustrates, the stability of rodingite paragenesis. Therefore we suggest to experimental petrologists to run a series of experiments by using natural gabbro samples in presence of Ca^{+2} rich aqueous solutions.

A serious question arises concerning the absence of sodic minerals in rodingitized basic rocks. Gabbroic

dykes have considerable amount of high calcian plagioclase. It is quite logic to expect the appearance of sodic minerals when the plagioclase is converted to grossular, prehnite or other calc-silicates. In some parts of Iranian rodingite we know the occurrence of pectolite which is a calcium - sodium hydrosilicate but it is not widespread. In some instances lenses of albitite and quartz albitites are found in the serpentinite [8]. This may account for liberated albite from crystal structure of plagioclase during the process of rodingitization. We can conclude that sodium of plagioclase may be accommodated into the structure of pectolite or migrate from the site of rodingitization to form albitite masses.

Conclusion

From all the aforementioned data we can conclude that:

1. Rodingitization of basic rocks in contact with serpentinite bodies is achieved by metasomatic reaction of Ca^{+2} rich fluid issued during the serpentinization of peridotite.

2. Rodingitization obeys the law of chemical potential. Serpentinization creates a fluid in which Ca^{+2} has high chemical potential. Lowering the free energy of system is achieved by reaction of Ca^{+2} rich fluids with magmatic minerals of basic rocks until μCa^{+2} for fluid equals μCa^{+2} in basic rocks. Rodingites with a complex association of calc-silicate are then created by equalization of μCa^{+2} in serpentinites and enclosing basic rocks.

3. Equilibrium condition for rodingite paragenesis is strongly sensitive to aCa^{+2} and $f(H^+)$.

4. In some of the reactions leading to rodingite paragenesis SiO_2 is liberated and in some of them it is consumed. It is suggested that a feed back mechanism may exist in which liberated SiO_2 in aqueous solution, may enhance serpentinization which in turn produce more Ca^{+2} that is absorbed by basic rock for development of a new type of rodingite paragenesis.

5. The presence of monomineralic rodingites and heterogenous aspect of rodingites attributed to different stoichiometry of Ca^{+2}, SiO_2, H^+, $(OH)^-$ in aqueous solution in different parts of rodingitization site.

6. The 33 presented reactions are realistic reactions based on a) Petrographic observations, b) Analysis of natural water from the springs in serpentinites [4] which are rich in $Ca(OH)_2$, and c) Chemical balance. Therefore we suggest to run experimental studies based on such a realistic conditions.

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