

# The Formation of Micro-Rodingites from IODP Hole U1309D: Key To Understanding the Process of Serpentinization

**B. RONALD FROST<sup>1\*</sup>, JAMES S. BEARD<sup>2</sup>, ANDREW McCAIG<sup>3</sup> AND ERIC CONDLIFFE<sup>3</sup>**

<sup>1</sup>DEPARTMENT OF GEOLOGY AND GEOPHYSICS, UNIVERSITY OF WYOMING, LARAMIE, WY 82071, USA

<sup>2</sup>VIRGINIA MUSEUM OF NATURAL HISTORY, 21 STARLING AVENUE, MARTINSVILLE, VA 24112, USA

<sup>3</sup>SCHOOL OF EARTH AND ENVIRONMENT, UNIVERSITY OF LEEDS, LEEDS LS2 9JT, UK

RECEIVED JANUARY 31, 2008; ACCEPTED JULY 9, 2008  
ADVANCE ACCESS PUBLICATION AUGUST 2, 2008

*Olivine-rich troctolites of Integrated Ocean Drilling Program hole U1309D contain abundant veins along which the olivine has been serpentinized. Where the serpentinite veins cut plagioclase the plagioclase has been altered to prehnite and in many places the prehnite in the core of the vein has been altered to grossular. We show that these Ca-rich assemblages, which we call micro-rodingites, need not have formed by Ca-metasomatism. Instead the micro-rodingites could have occurred during serpentinization as a nearly closed-system process (apart from the addition of water and release of H<sub>2</sub> and Na<sup>+</sup>). We argue that in these rocks the alteration of plagioclase occurred as a result of the very low silica activity that accompanies serpentinization. The reaction of plagioclase to prehnite and prehnite to grossular provided a source of SiO<sub>2</sub> that allowed olivine to hydrate to serpentine without producing much brucite. Excess Al<sub>2</sub>O<sub>3</sub> produced by the alteration of plagioclase reacted with serpentine to produce chlorite and additional SiO<sub>2</sub>.*

KEY WORDS: *serpentinization; rodingite; Integrated Ocean Drilling Program Expeditions 304 and 304; IODP hole U1309D; ocean floor metamorphism; silica activity*

## INTRODUCTION

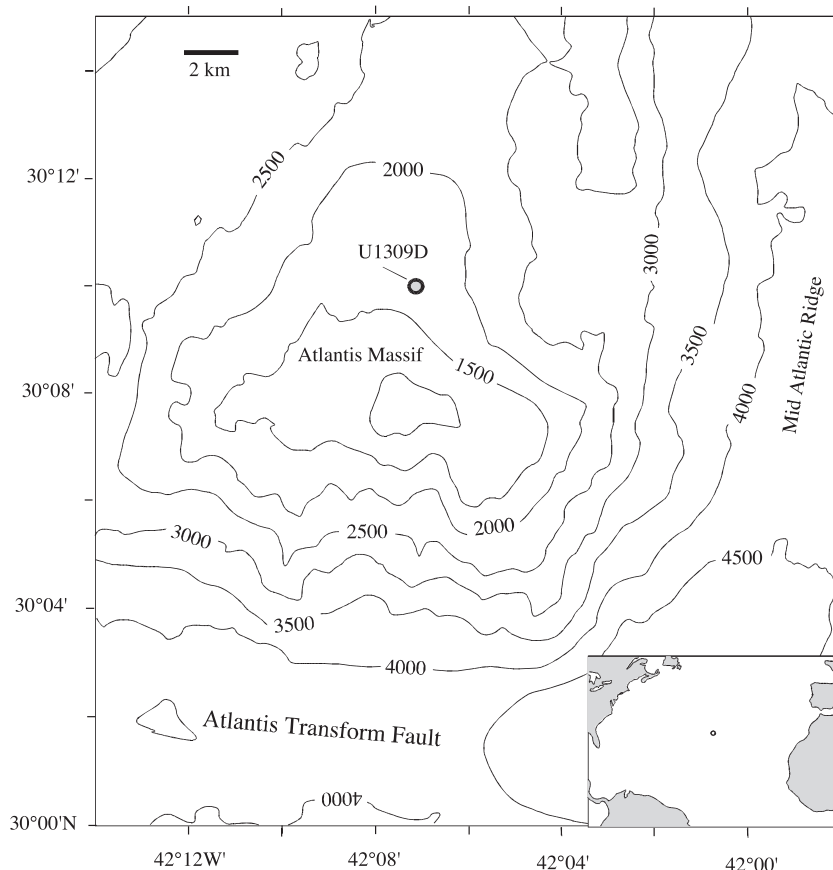
Rodingites are rocks included in serpentinite (typically basalts and gabbros, but in some localities metasedimentary rocks and granites) that contain abundant Ca-rich silicates such as hydrogarnet, prehnite, xonotolite, idocrase, tremolite, and diopside. They are inferred to have

formed via intensive Ca-metasomatism during serpentinization of surrounding peridotite (Coleman, 1963, 1977; Schandl *et al.*, 1989; O'Hanley, 1996). Most petrologists believe that the Ca necessary for this metasomatism was released from pyroxenes during serpentinization of the peridotite. In this paper we describe prehnite–grossular assemblages after plagioclase that formed during serpentinization of olivine-rich troctolite in Integrated Ocean Drilling Program (IODP) hole 1309D. These assemblages, which we call micro-rodingites, provide evidence that some rodingites may form by desilication, rather than addition of Ca. It was the discovery of these micro-rodingites that first alerted us to the importance of silica activity in serpentinization (Frost & Beard, 2007). In this paper we discuss the processes by which the micro-rodingites from hole U1309 formed and use the rock textures to test some of the postulations put forth by Frost & Beard (2007).

## SAMPLE DESCRIPTIONS

IODP hole 1309D was drilled on Atlantis Massif, an inside corner high that is located along the Mid-Atlantic Ridge at 30°N (Ildefonse *et al.*, 2007). (Fig. 1) The hole reached 1415 m below sea floor (mbsf) with a recovery of 75%. The core consists of 92% gabbroic rocks (including gabbro, olivine gabbro, troctolite, and oxide gabbro), 5% olivine-rich troctolite, and 3% basalt (Blackman *et al.*, 2006). The micro-rodingite formed in the olivine-rich troctolite, which occurs in five major horizons in U1309D

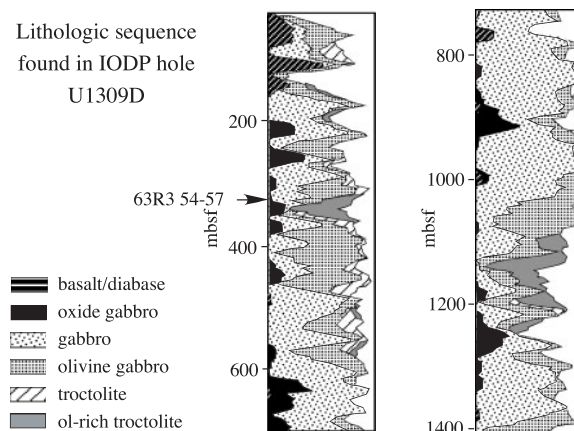
\*Corresponding author. Telephone: 307-766-4290. Fax: 307-766-6679. E-mail: rfrost@uwyo.edu



**Fig. 1.** Location map showing the locations of IODP drill hole U1309D in relation to the Mid-Atlantic Ridge, the Atlantis Transform Fault, and the Atlantis Massif (after Blackman *et al.*, 2006).

(311–340, 1122–1137, 1140–1148, 1155–1168, and 1230–1236 mbsf) (Fig. 2). The olivine-rich troctolite consists of a framework of coarse (up to centimeter-size) olivine crystals that make up 70–90% of the rock. Plagioclase, which makes up 5–20% of the rock, is interstitial to the olivine. Locally, the olivine-rich troctolite contains large centimeter-sized grains of augite, but augite is absent in many samples.

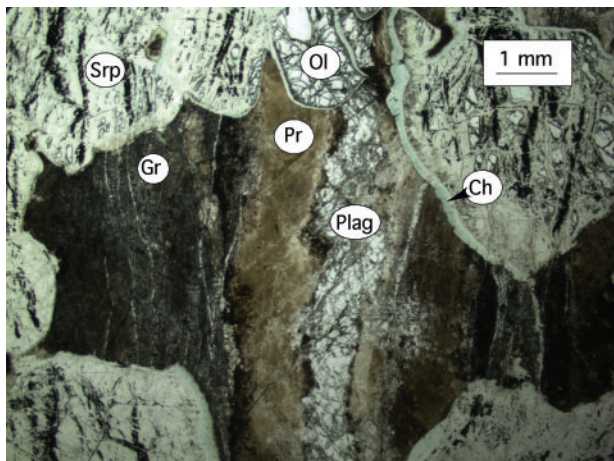
Alteration of the olivine-rich troctolite ranges from minor to extensive. Most of the alteration is seen as serpentinization, although there is generally a chlorite rim around the plagioclase that is inferred to have formed prior to the serpentinization (Blackman *et al.*, 2006). The serpentinization commonly occurs along millimeter-scale veins that are spaced about 1 cm apart. This is most obvious in weakly altered rocks, where the veins are clearly separated by fresh olivine. The veins generally have magnetite centers that are bordered by serpentine margins. Brucite is present in minor amounts at the interface between the magnetite-bearing veins and olivine, but it is absent within the veins themselves. Where the veins cut plagioclase, the plagioclase, which normally is glassy in hand sample, becomes white and pasty. In contrast, the veins seem to have no effect where they cross augite.



**Fig. 2.** Petrological stratigraphy of U1309D hole showing location of sample 63R2 54-57.

### Textural relations

We chose one sample to study in detail (63R2 54-57), which comes from 327.9 mbsf (Fig. 2). It is moderately altered. Olivine is largely serpentinized and the sample is transected by numerous serpentine veins, most of which are



**Fig. 3.** Photomicrograph in PPL showing relations between serpentine, olivine, grossular, prehnite, plagioclase, and chlorite in sample 63R3 54-57. It should be noted that the fresh plagioclase touches fresh olivine.

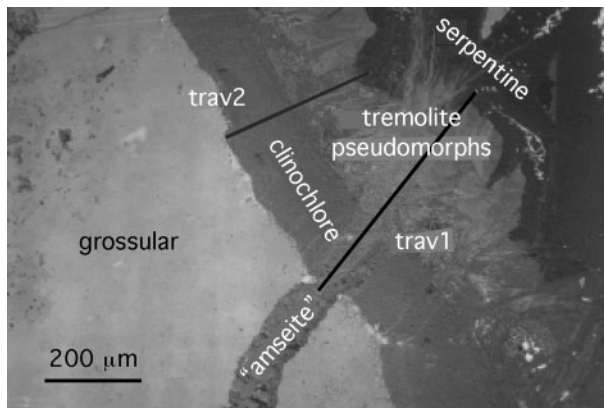
cored by magnetite. In the alteration zones where these veins transect plagioclase, grossular/hydrogrossular commonly occurs proximal to the serpentine vein. The hydrogrossular is generally very fine grained; grain size rarely exceeds 5  $\mu\text{m}$ . A zone of prehnite always separates any relict plagioclase from the hydrogrossular (Fig. 3). In less-altered samples similar textures are found but there is no grossular/hydrogrossular and the alteration zone in the plagioclase consists only of prehnite. Like the hydrogrossular, prehnite is very fine grained, although locally the maximum dimension of the grains may be up to 20  $\mu\text{m}$ .

A somewhat different sequence is seen where plagioclase is (or was) in direct contact with olivine. At this contact, a reaction zone consists of a serpentine rim around the olivine and a chlorite reaction rim surrounding plagioclase. The zone between the chlorite and serpentine appears to be a replacement of the tremolite portion of an original chlorite–tremolite reaction zone (Blackman *et al.*, 2006). In 63R3 54-57, blades and needles of tremolite are pseudomorphed by a mixture of chlorite and serpentine (Fig. 4). The chlorite proximal to the plagioclase, on the other hand, is probably inherited from the original chlorite–tremolite zone. The plagioclase–olivine boundary is locally transected by veins of amesitic chlorite (Fig. 4), which clearly postdate both the chlorite–tremolite reaction zone and the serpentine/prehnite-forming reaction.

## Mineral compositions

### Primary phases

Olivine from sample 63R3 54-57 is  $\text{Fo}_{87}$  (Table 1). It is homogeneous and unzoned. Augite is calcic ( $\text{Wo}_{46-48}$ ) and magnesian ( $\text{En}_{46-48}$ ). It contains about 3.0 wt %  $\text{Al}_2\text{O}_3$  and 0.5 wt %  $\text{Na}_2\text{O}$ . Plagioclase is unzoned and ranges from  $\text{An}_{75}$  to  $\text{An}_{78}$ .



**Fig. 4.** Backscattered SEM image showing the trace of microprobe scans across a reaction rind between grossular (after plagioclase) and serpentine (after olivine).

### Prehnite

Prehnite is close to stoichiometric  $\text{Ca}_2\text{Al}_2\text{Si}_3\text{O}_{10}(\text{OH})_2$  (Table 1) with a small amount of excess tetrahedral aluminum and minor (0.2 wt %) iron. It contains minor amounts of  $\text{MgO}$  (~0.2%), consistent with prehnite from mafic or ultramafic systems (Deer *et al.*, 1962).

### Grossular/hydrogrossular

The garnet that replaces plagioclase is a mildly hydrated grossular with 1–7% andradite component (Table 1). The hibschite (hydrogrossular) component of the garnet ranges from 6 to 11%. The water content of the garnet was determined by difference and is subject to large systematic errors. Perfect stoichiometry for these samples would require addition of an additional 1–2%  $\text{H}_2\text{O}$ , yielding a garnet total of between 101 and 102 wt %.

### Chlorite and serpentine

Chlorite is the alteration mineral that forms in direct contact with plagioclase in the reaction zone between olivine and plagioclase. Compositions near clinchlore are most common, but alumina-rich varieties that approach amesite occur in composition in veins that transect the reaction zone (Table 2; Fig. 5). The Mg-number is variable, ranging from <70 to 95, with most values between Mg-number 70 and 90. The lowest Mg-numbers are found adjacent to prehnite after plagioclase. Most chlorite analyses contain detectable Cl, usually <0.2 wt %. Al-poor serpentine is the primary alteration mineral of olivine in these samples. It is more magnesian than either olivine or chlorite, having Mg-number 90–98, with most values >95. It contains detectable Cl, with values ranging from 0.1 to 0.4 wt %.

There is a nearly complete continuum in Si, Al, and  $\text{R}^{2+}$  cations between serpentine [ $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$ ], clinchlore [ $\text{Mg}_{2.5}\text{AlSi}_{1.5}\text{O}_5(\text{OH})_4$ ], and amesite [ $\text{Mg}_2\text{Al}_2\text{SiO}_5(\text{OH})_4$ ]

Table 1: Analyses of minerals from 63R3 54-57

	olivine	augite	plagioclase	prehnite	grossular	grossular
SiO <sub>2</sub>	40.20	52.62	48.61	42.84	35.19	34.96
TiO <sub>2</sub>	0.01	0.72	0.01	0.04	0.02	0.00
Al <sub>2</sub> O <sub>3</sub>	0.01	2.58	32.27	24.70	22.40	20.90
Cr <sub>2</sub> O <sub>3</sub>	n.d.	0.81	n.d.	n.d.	n.d.	n.d.
Fe <sub>2</sub> O <sub>3</sub> *	n.d.	0.50	0.11	0.22	0.43	2.58
FeO	12.80	2.83	n.d.	n.d.	n.d.	n.d.
MnO	0.19	0.11	0.04	0.03	0.17	0.51
NiO	0.26	n.d.	n.d.	n.d.	n.d.	n.d.
MgO	46.52	16.48	0.06	0.27	0.14	0.19
CaO	0.05	22.90	15.51	26.81	38.02	37.66
Na <sub>2</sub> O	n.d.	0.40	2.77	0.11	0.15	0.02
K <sub>2</sub> O	n.d.	n.d.	0.01	0.03	n.d.	n.d.
H <sub>2</sub> O				4.33	3.27	3.31
Total	100.04	99.94	99.40	99.37	99.79	100.13
<i>Cation proportions</i>						
Oxygens	4	6	8	24	24	24
Si	0.999	1.921	2.237	5.931	5.568	5.562
Ti	0.000	0.020	0.000	0.005	0.003	0.000
Al	0.000	0.111	1.750	4.030	4.178	3.919
Cr	—	0.023	—	—	—	—
Fe <sup>3+</sup>	—	0.014	0.004	0.023	0.051	0.309
Fe <sup>2+</sup>	0.266	0.086	—	—	—	—
Mn	0.004	0.003	0.002	0.003	0.023	0.069
Ni	0.005	—	—	—	—	—
Mg	1.724	0.897	0.004	0.056	0.034	0.046
Ca	0.001	0.896	0.765	3.976	6.447	6.420
Na	—	0.028	0.247	0.029	0.023	0.002
K	—	—	0.001	0.005	—	—
OH	—	—	—	3.998	1.726	1.754
Total	3.000	3.999	5.009	18.055	18.052	18.080
<i>n</i>		16	4	5	1	1

\*Fe<sub>2</sub>O<sub>3</sub> for augite is calculated based on stoichiometry; for plagioclase, prehnite, and grossular Fe<sub>2</sub>O<sub>3</sub> = Fe<sub>total</sub>. n.d., not determined. H<sub>2</sub>O calculated on basis of stoichiometry.  
*n*, number of analyses.

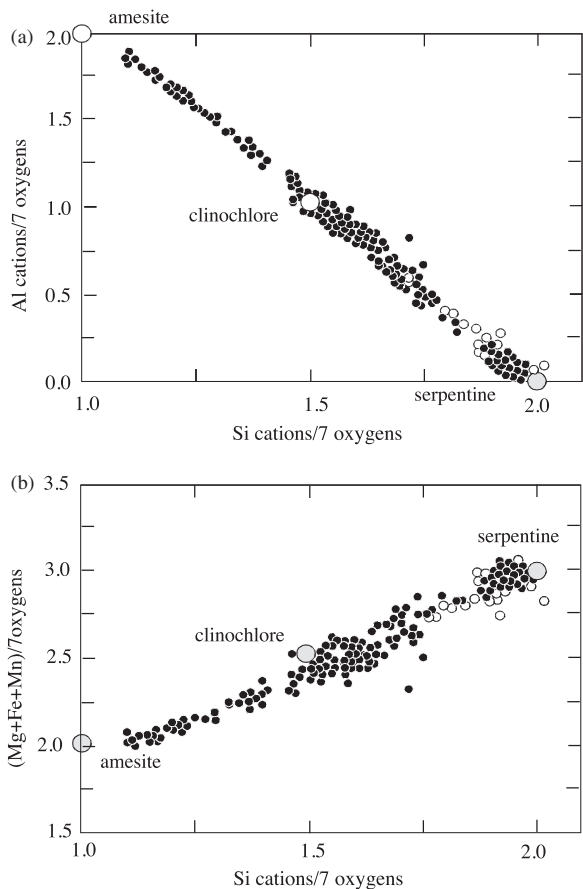
in the samples examined for this study (Fig. 5a and b). In traverses through the reaction zone separating plagioclase from olivine, we found that analyses close to the olivine are uniformly Al-poor and typical of serpentine (probably lizardite), whereas the mineral proximal to the plagioclase contact is very close to stoichiometric clinocllore (Fig. 6). Another traverse tracks the composition of a vein of amesitic chlorite as it transects the reaction zone. In both traverses, the region between serpentine associated with olivine and chlorite associated with plagioclase is marked by an erratic, but more or less

Table 2: Analyses of serpentine and chlorite from sample 63R3 54-57

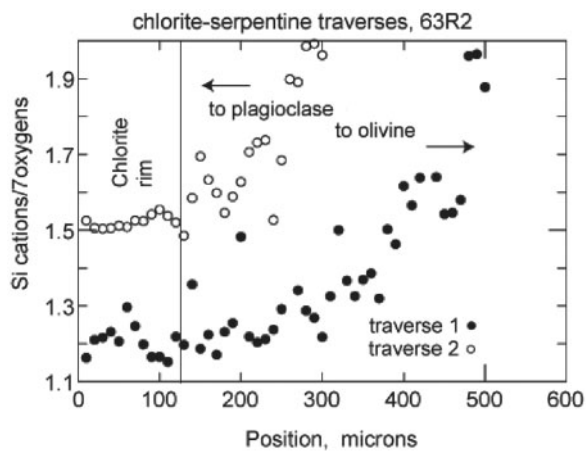
	1	2	3	4	5	6	7	8	9
SiO <sub>2</sub>	41.43	41.52	40.08	40.61	36.52	33.94	32.93	30.74	23.71
TiO <sub>2</sub>	0.01	0.03	0.00	0.04	0.02	0.00	0.05	0.00	0.03
Al <sub>2</sub> O <sub>3</sub>	0.58	0.83	2.15	4.08	8.70	11.76	14.54	17.51	30.09
Cr <sub>2</sub> O <sub>3</sub>	0.00	0.00	0.05	0.00	0.01	0.00	0.00	0.02	0.03
FeO	2.22	1.94	3.09	4.27	5.23	4.74	6.70	5.61	8.15
MnO	0.05	0.07	0.09	0.18	0.10	0.03	0.10	0.06	1.77
MgO	40.58	40.42	38.85	37.91	34.98	34.42	30.98	31.24	22.63
CaO	0.01	0.02	0.05	0.09	0.00	0.00	0.07	0.08	0.06
Na <sub>2</sub> O	0.02	0.02	0.03	0.09	0.03	0.01	0.32	0.04	0.03
K <sub>2</sub> O	0.00	0.00	0.01	0.02	0.02	0.02	0.18	0.02	0.01
H <sub>2</sub> O	12.51	12.53	12.37	12.73	12.42	12.31	12.33	12.30	12.23
Cl	0.10	0.10	0.11	0.10	0.04	0.10	0.03	0.11	0.01
OH = Cl	-0.02	-0.02	-0.03	-0.02	-0.01	-0.02	-0.01	-0.03	0.00
Total	97.46	97.45	96.85	100.09	98.06	97.31	98.23	97.71	98.74
<i>Cation proportions calculated on the basis of 36 O, OH, and Cl</i>									
Si	7.928	7.934	7.756	7.635	7.046	6.600	6.402	5.981	4.647
Ti	0.001	0.004	0.000	0.005	0.003	0.001	0.007	0.000	0.004
Al	0.130	0.186	0.491	0.905	1.979	2.695	3.332	4.015	6.951
Cr	0.000	0.000	0.007	0.000	0.001	0.000	0.000	0.003	0.005
Fe <sup>2+</sup>	0.356	0.310	0.501	0.671	0.844	0.770	1.089	0.913	1.336
Mn	0.007	0.011	0.015	0.028	0.017	0.005	0.017	0.010	0.293
Mg	11.578	11.515	11.208	10.626	10.062	9.977	8.980	9.061	6.614
Ca	0.002	0.005	0.011	0.018	0.000	0.001	0.014	0.017	0.013
Na	0.007	0.009	0.011	0.034	0.011	0.002	0.120	0.015	0.013
K	0.000	0.000	0.001	0.005	0.004	0.005	0.045	0.005	0.003
OH	15.969	15.966	15.963	15.969	15.988	15.968	15.991	15.963	15.997
Cl	0.031	0.034	0.037	0.031	0.012	0.032	0.009	0.037	0.003
Total	36.010	35.973	36.001	35.927	35.968	36.056	36.007	36.020	35.879
X <sub>Mg</sub>	0.970	0.974	0.957	0.941	0.923	0.928	0.892	0.908	0.832

consistent trend of increasing Al and decreasing Si as one moves toward plagioclase. When all analyses are compiled, it is clear that there are strong maxima at the compositions of serpentine and clinocllore and a distinct minimum that corresponds to the interval separating minerals identified as chlorite from those identified as serpentine (Fig. 7). A few analyses in the zone of chlorite pseudomorphing tremolite show elevated CaO up to 3 wt %, suggesting that relict tremolite may be present, which adds to the scatter in Si contents.

It must be borne in mind that in the exceptionally fine-grained world of serpentinites virtually all microprobe analyses are mixtures that occur on a submicron scale, which may grade imperceptibly into atomic interlayered structures. Given this, we tentatively interpret analyses that lie within the minimum in Fig. 7 as physical mixtures,

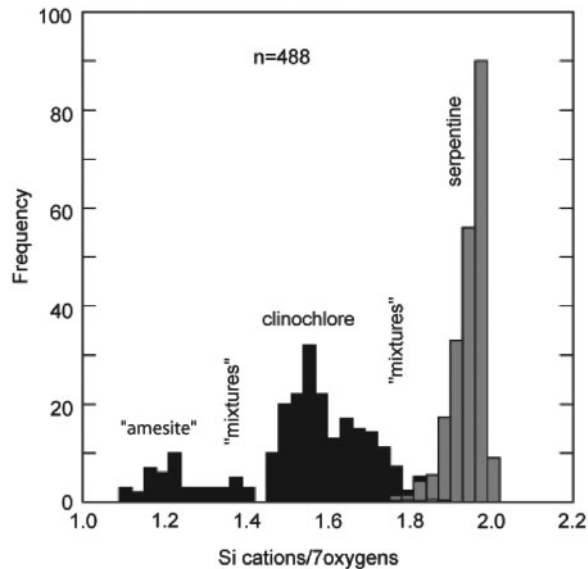


**Fig. 5.** Compositional range of serpentine and chlorite from 63R3 54-57. (a) Variation of Al ions p.f.u. with silica; (b) variation of R<sup>2+</sup> ions p.f.u. with silica.



**Fig. 6.** Variation of chlorite and serpentine compositions along the two transects shown in Fig. 4.

those that lie between clinocllore and amesite as solutions, and those that lie in the region between true chlorite and true serpentine as mixtures on either the submicron or interlayer scale.



**Fig. 7.** Histogram showing the composition range of serpentine and chlorite from 63R3 54-57. We interpret the area with only a few analyses to represent mixtures between serpentine and clinocllore and between clinocllore and amesite, whereas the range of compositions in chlorite and to a lesser extent that in serpentine are interpreted as solid solutions.

**DISCUSSION**

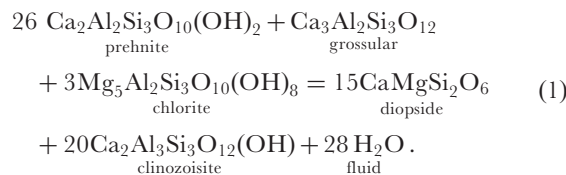
**Calculation procedures and standard states**

In our calculations we used the THERMOCALC database of Holland & Powell (1998) and chrysotile as our serpentine mineral, despite the fact that chrysotile is probably metastable (Evans, 2004). In actuality, the choice of which serpentine polymorph we used is moot; the free energy change involved in the hydration reactions studied vastly overwhelms the small energy differences between lizardite, chrysotile, and antigorite.

When discussing aqueous silica, we reference silica activity to the standard state of the solubility of pure quartz at the *T* and *P* of interest (i.e. activity of H<sub>4</sub>SiO<sub>4</sub>, or SiO<sub>2</sub> (aqueous)). This variable we will call *a*<sub>SiO<sub>2</sub>(aq)</sub>. Similarly, for reactions open to alumina we symbolize alumina as Al<sub>2</sub>O<sub>3</sub>(aq) to emphasize that it is a mobile component.

**Reactions in the model system CaO–MgO–Al<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub>–H<sub>2</sub>O**

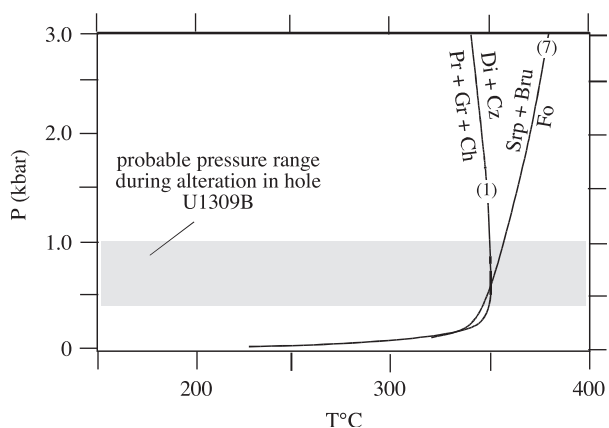
The association of grossular, prehnite, and chlorite in the alteration zone, and the absence of diopside and clinzoisite, allows us to conclude that the alteration must have taken place at temperatures below the reaction



We calculated the location of this reaction (Fig. 8) using end-member compositions for the phases and clinocllore as the chlorite because it appears to be directly related to the metasomatic reactions; the amesite appears to be a later vein (Fig. 4). We used end-member compositions because we have no composition data for diopside or clinzoisite, which would be the high-*T* products of the reaction. Of the minerals in this reaction, clinzoisite is likely to deviate most from end-member composition. Not only that, it has a large stoichiometric coefficient in reaction (1). Because decreasing the activity of  $\text{Ca}_2\text{Al}_3\text{Si}_3\text{O}_{12}(\text{OH})_2$  will drive reaction (1) to lower temperatures, we are confident that the location of this reaction in Fig. 8 indicates the maximum temperature at which the micro-rodingite alteration could have taken place.

The base of the core today lies at a pressure of less than 0.5 kbar, but this is after a considerable amount of the overlying rock was tectonically excised (Ildefonse *et al.*, 2007). At the time of alteration the pressure was not likely to have been hydrostatic because the huge volume change involved in serpentinization would have closed fractures as soon as they opened. Therefore, we presume that at the time these veins formed the rocks were at a pressure between 0.5 and 1 kbar. At these pressures, the maximum temperature for the formation of the veins would have been 350°C.

The alteration of the plagioclase to prehnite and grossular involves assemblages similar to those found in rodingites, so it is tempting to postulate that these micro-rodingites, like other rodingites, formed through Ca-metasomatism. However, there is no local source for additional CaO. Olivine contains only 0.05 wt % CaO and augite in the rock is unaltered; the only other calcic phase is plagioclase. It is possible that CaO was added from a cryptic source outside the system, but if so it would have had to traverse more than 300 m of gabbroic rock and leave no trace of its presence in the overlying rocks. We contend



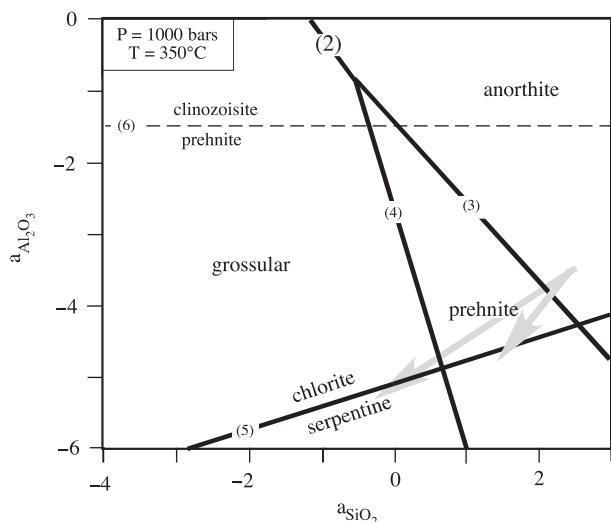
**Fig. 8.** *P-T* diagram showing the minimum temperature for the formation of the microrodingites.

that it is more plausible that, instead of CaO-metasomatism, the micro-rodingites formed by extraction of silica and aluminum from the plagioclase, leaving a residue enriched in CaO. To model this process we have written the reactions that relate the stable phases in the micro-rodingites so that CaO is conserved, which means that  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$  are mobile components (Table 3). We chose to calculate relations at 350°C and 1 kbar, because these are the maximum *T* and *P* at which the reactions are likely to have taken place. We included clinzoisite in these calculations because it is a Ca–Al silicate that is common in rodingites but is conspicuously missing in the micro-rodingites from U1309D. The relation between these reactions is shown in Fig. 9.

Several observations are critical to modeling the how the micro-rodingites formed. First is that grossular never touches unaltered plagioclase; prehnite always lies between them. Second is that chlorite always lies between serpentine and anorthite, prehnite, and grossular. This means that the zoning from unaltered plagioclase, through prehnite, then grossular to chlorite and serpentine was driven by activity gradients in both silica and alumina (see gray arrows in Fig. 9), although the gradient in alumina activity may have been low. Figure 9 also shows that epidote is absent from the micro-rodingites because at the *P* and *T* of this diagram; it is stable only at relatively high alumina activities.

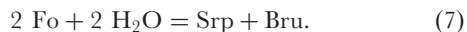
**Table 3:** *Open-system reactions between phases in altered olivine-rich troctolites*

Composition	Phase (abbreviation)
$\text{CaAl}_2\text{Si}_2\text{O}_8$	Anorthite (An)
$\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$	Grossular (Gr)
$\text{Ca}_2\text{Al}_2\text{Si}_3\text{O}_{10}(\text{OH})_2$	Prehnite (Pr)
$\text{Ca}_2\text{Al}_3\text{Si}_3\text{O}_{12}(\text{OH})$	Clinzoisite (Cz)
$\text{CaMgSi}_2\text{O}_6$	Diopside (Di)
$\text{Mg}_2\text{SiO}_4$	Forsterite (Fo)
$\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$	Serpentine (Srp)
$\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$	Talc (Tlc)
$\text{Mg}_5\text{Al}_2\text{Si}_3\text{O}_{10}(\text{OH})_8$	Chlorite (Ch)
$\text{Mg}(\text{OH})_2$	Brucite (Bru)
Reaction	Reaction number
$26 \text{ Pr} + \text{Gr} + 3 \text{ Ch} = 15 \text{ Di} + 20 \text{ Cz} + \text{H}_2\text{O}$	(1)
$3 \text{ An} = \text{Gr} + 3 \text{ SiO}_{2(\text{aq})} + 2 \text{ Al}_2\text{O}_{3(\text{aq})}$	(2)
$2 \text{ An} + \text{H}_2\text{O} = \text{Pr} + \text{SiO}_{2(\text{aq})} + \text{Al}_2\text{O}_{3(\text{aq})}$	(3)
$3 \text{ Pr} = 2 \text{ Gr} + 3 \text{ SiO}_{2(\text{aq})} + \text{Al}_2\text{O}_{3(\text{aq})} + 3 \text{ H}_2\text{O}$	(4)
$5 \text{ Srp} + 3 \text{ Al}_2\text{O}_{3(\text{aq})} + 2 \text{ H}_2\text{O} = 3 \text{ Ch} + \text{SiO}_{2(\text{aq})}$	(5)
$2 \text{ Pr} + \text{Al}_2\text{O}_{3(\text{aq})} = 2 \text{ Cz} + \text{H}_2\text{O}$	(6)

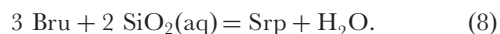


**Fig. 9.** Activity  $\text{Al}_2\text{O}_3$ –activity  $\text{SiO}_2$  diagram calculated at 1000 bars and  $350^\circ\text{C}$  showing the stability relations between anorthite, chlorite, grossular, prehnite, serpentine, and clinozoisite. Gray arrow shows approximate activity path followed from unaltered plagioclase into the serpentine vein.

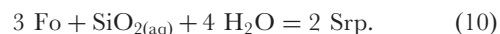
The hydration of olivine is usually written as the reaction



Brucite, however, is a mineral that is stable only at very low silica activity. If reaction (7) was the major hydration reaction the product would contain about 18 vol. % brucite and 82 vol. % serpentine. Although brucite is commonly present cryptically in serpentinites (Hostetler *et al.*, 1966), it is seldom present in abundances approaching 18%. One reason for this is that, if any silica is available brucite will alter to serpentine by the reaction



As a result, a reasonable version of the olivine hydration reaction is



Reaction (10) shows that alteration of olivine to serpentine without producing brucite involves the addition of both water and silica. The silica presumably is extracted from the surrounding rock.

We suggest that the alteration reaction in the olivine-rich troctolites involved hydration of olivine to serpentine that operated at the same time as desilication of plagioclase to prehnite and grossular. We have written model reactions (Table 4) for this process using three assumptions. First, we assumed that  $\text{SiO}_2$  was a mobile component. Second, we assumed that the  $\text{SiO}_2$  released by the desilication of anorthite or prehnite [reactions (14)–(17)] was consumed by the serpentinization of olivine [reaction (10)],

**Table 4:** Silica-dependent alteration reactions in olivine-rich troctolite

Reaction	Reaction number
$2 \text{Fo} + 3 \text{H}_2\text{O} = \text{Srp} + \text{Bru}$	(7)
$3 \text{Bru} + 2 \text{SiO}_2(\text{aq}) = \text{Srp} + \text{H}_2\text{O}$	(8)
$2 \text{Bru} + \text{SiO}_2(\text{aq}) = \text{Fo} + 2 \text{H}_2\text{O}$	(9)
$3 \text{Fo} + \text{SiO}_2(\text{aq}) + 4 \text{H}_2\text{O} = 2 \text{Srp}$	(10)
$3 \text{Fo} + 5 \text{SiO}_2(\text{aq}) + 2 \text{H}_2\text{O} = \text{Tlc}$	(11)
$6 \text{Fo} + \text{Tlc} + 9 \text{H}_2\text{O} = \text{Srp}$	(12)
$\text{Tlc} + \text{H}_2\text{O} = \text{Srp} + 2 \text{SiO}_2(\text{aq})$	(13)
$5 \text{Fo} + 4 \text{An} + 10 \text{H}_2\text{O} = 2 \text{Pr} + 2 \text{Ch} + \text{SiO}_2(\text{aq})$	(14)
$6 \text{An} + \text{Srp} + 5 \text{H}_2\text{O} = 3 \text{Pr} + 3 \text{Ch} + 4 \text{SiO}_2(\text{aq})$	(15)
$6 \text{Pr} + 5 \text{Fo} + 2 \text{H}_2\text{O} = 4 \text{Gr} + 2 \text{Ch} + 5 \text{SiO}_2(\text{aq})$	(16)
$9 \text{Pr} + 5 \text{Srp} = 6 \text{Gr} + 3 \text{Ch} + 10 \text{SiO}_2(\text{aq}) + 7 \text{H}_2\text{O}$	(17)

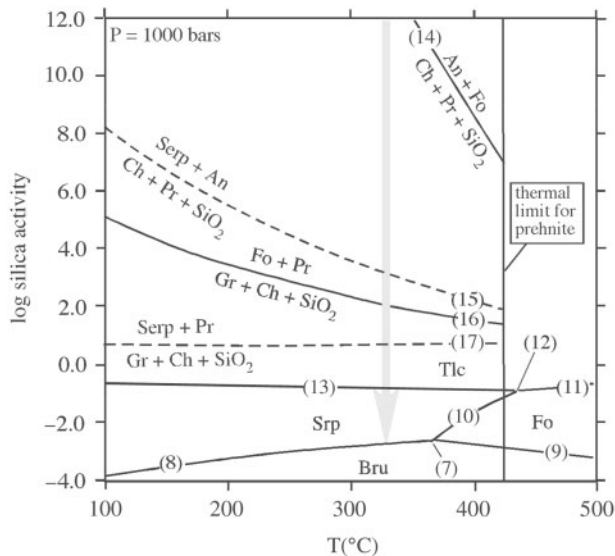
despite the fact that olivine in some samples may be separated from prehnite or plagioclase by a millimeter or more of serpentine or chlorite. Third, we assumed that  $\text{Al}_2\text{O}_3$  produced in the alteration reactions reacted with serpentine to make chlorite.

Figure 10 shows that, although the log of the silica activity for the serpentine–brucite and olivine–serpentine buffers [reactions (8) and (10)] are negative, the log for the silica activities of olivine + anorthite or olivine + prehnite [reaction (14) or (16)] are strongly positive. At first glance such extreme values for silica activity seem unrealistic, because silica activity cannot exceed 0.0, the value at which the system is saturated in quartz. The reactions that lie at  $\log a_{\text{SiO}_2} > 0.0$ , such as reactions (14)–(17) in Fig. 10, can be stable if the water activity is very low. These high values for  $\log a_{\text{SiO}_2}$  indicate that once water gained access to the rock an intense chemical potential gradient existed between the assemblage olivine–plagioclase and the serpentine-bearing portions of the rock. This extreme gradient clearly provided the chemical work necessary for silica to diffuse from the plagioclase alteration front to the olivine alteration front. In Fig. 10 we show the plagioclase alteration reactions containing olivine [reactions (14) and (16)] as continuous lines and their serpentine-bearing equivalents [reactions (15) and (17)] as dashed lines.

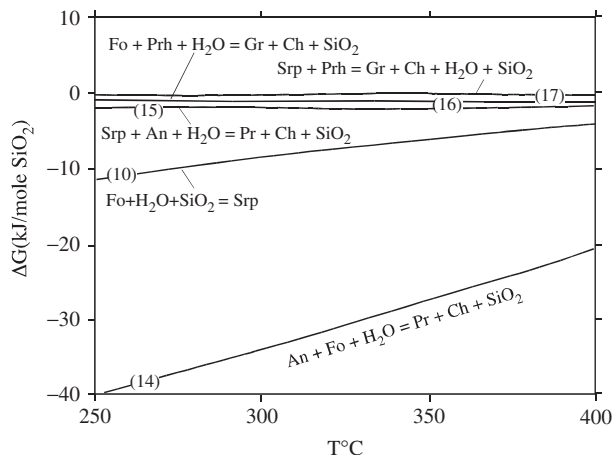
Another way to express what is shown in Fig. 10 is to realize that in a system involving a pure phase undergoing hydration (i.e. where water activity is near unity), the free energy of the reactions can be expressed as

$$\Delta G = \frac{-RT \log(a_{\text{SiO}_2})}{2.303}.$$

Figure 11, which has been calculated from Fig. 10 using the expression above and normalizing each reaction to 1 mole



**Fig. 10.**  $T$ - $\log a_{\text{SiO}_2}$  diagram showing the relation between the serpentinization reactions and the alteration reactions in the plagioclase. Gray arrow shows approximate activity gradient between serpentinized olivine and fresh plagioclase (+ olivine).



**Fig. 11.**  $\Delta G$ - $T$  diagram comparing the alteration reactions in the olivine-rich troctolites. Free energy is normalized per mole of aqueous silica released by the reactions.

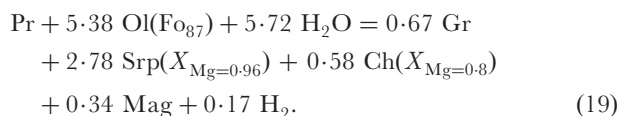
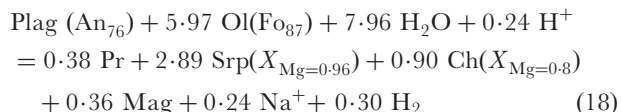
of  $\text{SiO}_{2(\text{aq})}$  shows dramatically how much energy is released by the alteration of anorthite to prehnite + chlorite. Petrologists generally consider that the free energy change accompanying serpentinization is so great that olivine readily hydrates whenever it gets a sniff of  $\text{H}_2\text{O}$ . Figure 11 shows that the alteration of olivine + plagioclase to prehnite + chlorite is even more energetic, which explains why plagioclase in the troctolite has been altered to prehnite wherever it has been in contact with a fracture. In contrast, the alteration of prehnite to grossular

does not have nearly as high a free energy change, which explains why grossular is present only in the more highly altered rocks, where higher fluxes of fluid probably were present.

**Reactions in the natural rocks**

The presence of additional components in the natural rocks, most specifically  $\text{FeO}$  and  $\text{Na}_2\text{O}$ , means that the minerals in the natural rocks, particularly olivine and plagioclase, will have slightly different compositions from those used in the model system above. This has several effects on the reactions modeled above. First, it changes the stoichiometry of the reactions. Second, it adds three more components— $\text{Na}_2\text{O}$ ,  $\text{FeO}$ , and  $\text{O}_2$ —and one additional phase, magnetite (Mag). Finally, the minerals in the natural rocks will not have end-member compositions, and therefore will have reduced activity. This might displace the model reactions somewhat compared with what is shown in Figs 9–11.

Using stoichiometric prehnite and grossular, and the compositions of olivine, plagioclase, serpentine (analysis 1 in Table 2), and chlorite (analysis 8 in Table 2), and adding the olivine hydration reaction in the proper proportion to consume the silica released, we obtain the following reactions for the alteration of plagioclase to prehnite and of prehnite to grossular:



Unlike the model reactions, which can be combined to conserve silica, neither reaction (18) nor (19) is closed. Small amounts of  $\text{H}_2$  are produced by the formation of magnetite, and nearly all  $\text{Na}_2\text{O}$  in the plagioclase has been lost from the system. We have chosen to write reaction (18) in terms of naked ions, although, considering that serpentine from these rocks contains up to 0.1% Cl, it is likely that the ions were complexed with Cl. As written, reaction (19) will lead to reduction and reaction (18) will lead to reduction and an increase in alkalinity, properties that are common in fluids associated with serpentinites.

Because reactions (18) and (19) are different from the model reactions shown in Figs 9 and 10 it is fair to ask whether the reactions in the model system have any relevance to the natural reactions. Although the activity–composition relations for most phases at these low temperatures are unknown we can approximate an answer to this question from the law of mass action. For conditions



where water activity is unity the equilibrium constant for reaction (14) is

$$\log K_{14} = \log K_s + \log(a_{\text{SiO}_2}) \quad (20)$$

where

$$K_s = \frac{(a_{\text{Pr}})^2 (a_{\text{Ch}})^2}{(a_{\text{Fo}})^5 (a_{\text{An}})^5}. \quad (21)$$

If we assume that the activity of prehnite = 1, that  $a_{\text{An}} = X_{\text{An}}$ , and take the usual convention that the activity of forsterite and chlorite equals  $X_{\text{Mg}}$  raised to the power of the number of sites available,  $K_s$  becomes

$$K_s = \frac{(X_{\text{Ch}})^{10}}{(X_{\text{Fo}})^{10} (X_{\text{An}})^5}. \quad (22)$$

Because at fixed  $T$  and  $P$ ,  $K_{14}$  is constant, then

$$[\log K_s + \log(a_{\text{SiO}_2(\text{aq})})]_1 = [\log K_s + \log(a_{\text{SiO}_2(\text{aq})})]_2 \quad (23)$$

where condition 1 is the pure system and condition 2 is the natural system. The effect of natural components on the silica activity of the reaction becomes

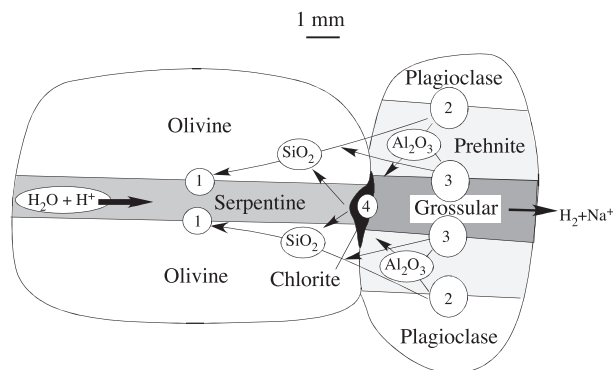
$$[\log(a_{\text{SiO}_2})]_1 - [\log(a_{\text{SiO}_2})]_2 = (\log K_s)_1 - (\log K_s)_2. \quad (24)$$

$\log(K_s)_1$  of course equals zero and by substituting equation (23) into equation (24) and solving for the mineral compositions in the rocks we obtain

$$\Delta[\log(a_{\text{SiO}_2})] = -0.80. \quad (25)$$

Although a difference in 0.8 log units seems large, for most temperatures more than 10 log units of silica activity separate serpentinization reactions from reaction (14). By applying the same reasoning to reaction (17) (and normalizing the stoichiometry to 1 mole of silica produced) we obtain a displacement  $-0.4$  log units. These calculations imply that it is safe to say that compositional effects will not strongly affect the conclusions of this paper.

As noted above, reactions (18) and (19) are the sums of reactions that took place in single cells in various places along a fracture (Fig. 12). Where the fracture cut olivine, the olivine hydrated to serpentine (and minor amounts of magnetite), while consuming water and silica from the surroundings (cell 1). The small amounts of  $\text{H}_2$  produced from the magnetite-forming reaction leave the system. Where the fracture cut plagioclase there were three cells. The plagioclase altered to prehnite at cell 2, liberating  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ , and  $\text{Na}_2\text{O}$ . The  $\text{Na}_2\text{O}$  was lost from the system. The prehnite altered to grossular at cell 3, liberating  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ , and  $\text{H}_2\text{O}$ . The  $\text{Al}_2\text{O}_3$  liberated from cells 2 and 3 reacted with serpentine on the margins of the original plagioclase grain to produce chlorite and  $\text{SiO}_2$  (cell 4). The  $\text{SiO}_2$  liberated by cells 2, 3 and 4 was consumed by cell 1 in the production of serpentine.



#### Reaction Cells in altered olivine-rich troctolite

1. Olivine +  $\text{H}_2\text{O}$  +  $\text{SiO}_2(\text{aq})$  = Serpentine
2. Plagioclase +  $\text{H}_2\text{O}$  = Prehnite +  $\text{Al}_2\text{O}_3(\text{aq})$  +  $\text{SiO}_2(\text{aq})$
3. Prehnite = Grossular +  $\text{SiO}_2(\text{aq})$  +  $\text{Al}_2\text{O}_3(\text{aq})$  +  $\text{H}_2\text{O}$
4. Serpentine +  $\text{Al}_2\text{O}_3(\text{aq})$  +  $\text{H}_2\text{O}$  = Chlorite +  $\text{SiO}_2(\text{aq})$

**Fig. 12.** Diagram showing the reaction cells that operated during the alteration of olivine and plagioclase in the olivine-rich troctolites.

As noted above, brucite in this rock is restricted to the interfaces between the veins and olivine, which means that silica mobility must have been on a sufficient scale to consume brucite along the fractures by reaction (8). Because the average grain size for olivine from this rock is about 10 mm (Blackman *et al.*, 2006), we contend that silica needed to move 5 mm or less to close reactions (18) and (19). Alumina mobility was much lower. Chlorite is restricted to within 0.2–0.4 mm of the relict plagioclase (Figs 4 and 6). The grain size for plagioclase in this rock is 1–2 mm (Blackman *et al.*, 2006). This implies that  $\text{Al}_2\text{O}_3$  mobility was of the order of 1 mm or less.

## CONCLUSIONS

The micro-rodingites from U1309D are evidence for the strong desilication effects of serpentinization. Desilication was progressive, with plagioclase initially desilicating to prehnite and the prehnite further desilicating to form grossular garnet. The driving force for desilication was the hydration of olivine to serpentine plus brucite. Brucite stability requires silica activities that are among the lowest observed in geological systems (Frost & Beard, 2007). Because of this, plagioclase (and, later, prehnite) in the troctolite donated silica for the reaction brucite + silica = serpentine.

These results suggest that a re-examination of rodingites and rodingite petrogenesis in general might be in order. Rodingites have been generally considered the product of the metasomatic addition of Ca and, indeed, Ca addition can be demonstrated in many rodingites. However, an equally common and important component of the metasomatism is Si depletion (e.g. Coleman, 1963). In a typical gabbroic rodingite, plagioclase is replaced by Si-poor Ca–Al silicates, with grossular (and/or hydrogrossular)

and prehnite being among the commonest. Hydrogrossular, in particular, is a virtually diagnostic rodingite mineral. As we have shown here, the formation of grossular and prehnite from plagioclase does not require any addition of Ca, as long as silica and  $\text{Al}_2\text{O}_3$  are mobile. Ca addition, when it occurs, probably reflects, at least in part, the replacement of Na–Ca plagioclase by Ca-silicates (e.g. prehnite), with the result that Na is lost to the local system and probably precipitated elsewhere as sodic plagioclase or zeolites (Whitmarsh *et al.*, 1998; Blackman *et al.*, 2006).

## ACKNOWLEDGEMENTS

The authors would like to thank the Joint Oceanographic Institutions for allowing us to sail on Integrated Ocean Drilling Program (IODP) Expeditions 304 and 305 and providing us access to the samples. This work was supported by the grant JOI 48299 to B.R.F. and by the Virginia Museum of Natural History to J.S.B. We wish to acknowledge helpful reviews by Kurt Bucher, Bernard Evans, John Shervais, and Bruce Yardley, which markedly improved the quality of the paper.

## REFERENCES

- Blackman, D. K., Ildefonse, B., John, B. E., Ohara, Y., Miller, D. J., MacLeod, C. J. & the Expedition 304/305 Scientists (2006). Ocean core complex formation, Atlantis Massif. *Proceedings of the Integrated Ocean Drilling Program, v. 304/305*. doi:10.2204/iodp.proc.304305.2006.
- Coleman, R. G. (1963). *Serpentinities, Rodingites, and Tectonic Inclusions in Alpine-type Mountain Chains*. Geological Society of America, *Special Papers* 73.
- Coleman, R. G. (1977). *Ophiolites, Ancient Oceanic Lithosphere?* Berlin: Springer.
- Deer, W. A., Howie, R. A. & Zussman, J. (1962). *Rock Forming Minerals, Vol. 3, Sheet Silicates*. London: Longman.
- Evans, B. W. (2004). The serpentinite multisystem revisited; chrysotile is metastable. *International Geology Review* **46**, 479–506.
- Frost, B. R. & Beard, J. S. (2007). On silica activity and serpentinization. *Journal of Petrology* **48**, 1351–1368.
- Holland, T. J. B. & Powell, R. (1998). An internally consistent thermodynamic dataset for phases of petrologic interest. *Journal of Metamorphic Geology* **16**, 309–343.
- Hostetler, P. B., Coleman, R. G., Mumpton, F. A. & Evans, B. W. (1966). Brucite in Alpine serpentinites. *American Mineralogist* **51**, 75–98.
- Ildefonse, B., Blackman, D., John, B. E., Ohara, Y., Miller, D. J., MacLeod, C. J. & Integrated Ocean Drilling Program Expeditions 304/305 Science Party (2007). Oceanic core complexes and crustal accretion at slow-spreading ridges. *Geology* **35**, 623–626.
- O'Hanley, D. S. (1996). *Serpentinities: Records of Tectonic and Petrological History*. *Oxford Monographs on Geology and Geophysics* **34**, 277 pp.
- Schandl, E. S., O'Hanley, D. S. & Wicks, F. J. (1989). Rodingites in serpentinized ultramafic rocks of the Abitibi greenstone belt, Ontario. *Canadian Mineralogist* **27**, 579–591.
- Whitmarsh, R. G., Beslier, M.-O., Wallace, P. & the Leg 173 Shipboard Scientific Party (1998). Sites 1065–1070, Iberia Abyssal Plain. *Proceedings of the Ocean Drilling Program, Initial Reports, 173*. College Station, TX; Ocean Drilling Program, pp. 65–294.