

THE CASE AGAINST OSTWALD RIPENING OF PORPHYROBLASTS: DISCUSSION

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Carlson (1999) pointed out that the coarsening of garnet porphyroblasts due to Ostwald ripening cannot have an appreciable effect as a control of the size of porphyroblasts. However, I found that the values of the appropriate parameters chosen by Carlson (1999) cause serious problem not only for Ostwald ripening, but also for the nucleation-and-growth model of Carlson (1989) and Carlson *et al.* (1995).

Here, I consider a model rock consisting of garnet (grt), chlorite (chl), quartz (qtz) and an aqueous fluid (H₂O). The garnet-forming reaction (2/3) Fe_{4.5}Al₃Si_{2.5}O₁₀(OH)₈ (chl) + (4/3) SiO₂ (qtz) = Fe₃Al₂Si₃O₁₂ (grt) + (8/3) H₂O (H₂O) will take place. Both Ostwald ripening (Miyazaki 1991, 1996) and diffusion-controlled growth (Carlson 1989, Carlson *et al.* 1995) are governed by diffusion of the slowest-diffusing elements. The radial growth-rate is proportional to the influx of the element at the surface of growing minerals. Kretz (1994) formulated the radial growth-rate under diffusion-controlled growth. Using this formulation, the radial growth-rate becomes:

$$D \left(\frac{\partial C_{grt}}{\partial r} \right)_{r=R} = (C_{grt,grt} - C_{grt,eq}) \frac{dR}{dt}, \quad (1)$$

where D is the diffusion coefficient, C_{grt} is the concentration of a garnet component in a diffusive medium, $C_{grt,eq}$ is the equilibrium concentration in a diffusive medium at the interface with the garnet, R is the radius of a spherical grain of garnet, and $C_{grt,grt}$ is the concentration of a garnet component in garnet per unit volume. According to Miyazaki (1996) and Carlson (1999), I assumed that the growth of garnet is controlled by the sluggish diffusion of Al. Therefore, instead of the influx of a hypothetical component of garnet in the left-hand term in Eq. 1, I also assumed that influx of Al is proportional to growth rate. One mole of garnet contains two moles of Al, and $C_{grt,grt} = (1/2) C_{Al,grt}$, where $C_{Al,grt}$ is the concentration of Al in solid garnet per unit volume. Eq. 1 becomes,

$$D \left(\frac{\partial C_{Al}}{\partial r} \right)_{r=R} = (C_{Al,grt} - C_{Al,eq}) \frac{dR}{dt}, \quad (2)$$

where $C_{Al,eq}$ is the equilibrium concentration of Al in the diffusive medium at the interface. Provided that the width of the depleted zone R^{dpl} is large relative to R , then the diffusion of Al to the interface is analogous to the diffusion of Al through a spherical shell of inner radius R and outer radius R^{dpl} . Under these conditions,

$$\left(\frac{\partial C_{Al}}{\partial r} \right)_{r=R} = \frac{C_{Al,m} - C_{Al,eq}}{1/R - 1/R^{dpl}} \frac{1}{R^2}, \quad (3)$$

where $C_{Al,m}$ is the concentration of Al in the diffusive medium in the non-depleted region. Taking

$$R^{dpl} = \beta R, \quad (4)$$

and $C_{Al,grt} = 2C_{grt,grt} = 2/v$, where v is the molar volume of garnet, and combining Eqs. 2, 3 and 4,

$$\frac{dR}{dt} = \frac{\beta}{\beta - 1} \frac{C_{Al,m} - C_{Al,eq}}{(2/v) - C_{Al,eq}} D \frac{1}{R}. \quad (5)$$

Using supersaturation $S = (C_{Al,m} - C_{Al,eq})/C_{Al,eq}$, Eq. 5 becomes,

$$\frac{dR}{dt} = \frac{\beta}{\beta - 1} \frac{C_{Al,eq}}{(2/v) - C_{Al,eq}} SD \frac{1}{R}. \quad (6)$$

Although the concentration of Al in the non-depleted region slowly decreases, the supersaturation S is initially constant, and with increasing t , it is approximately constant. Assuming constant P and T , the radius of the growing grain of garnet can be obtained by integration of Eq. 6,

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$$R = \left(\frac{1}{2} \frac{\beta}{\beta - 1} \frac{C_{Al,eq}}{(2/v) - C_{Al,eq}} SDt \right)^{1/2}. \quad (7)$$

Equation 7 gives a direct estimate of the radius of garnet due to diffusion-controlled growth. The growth rate of Carlson (1989) is proportional to the enlargement of the depleted zone. Carlson *et al.* (1995) assumed that R^{dpl} is given by the diffusion length as follows:

$$R^{dpl} = (Dt)^{1/2}. \quad (8)$$

Comparing Eq. 7 with Eq. 4 and 8, the $C_{Al,eq}$ becomes

$$C_{Al,eq} = \frac{4}{v} \frac{\beta - 1}{S\beta^3 + 2\beta - 2}. \quad (9)$$

Carlson (1989) obtained the value of β by fitting a crystal-size distribution. When one obtains the value of β and S , the value of $C_{Al,eq}$ is automatically fixed by Eq. 9. Therefore, Carlson (1989) and Carlson *et al.* (1995) cannot independently choose a value of $C_{Al,eq}$ with their kinetic model.

I estimated the value of supersaturation S using differences in chemical potential between reactants and products. I assumed that the reactants equilibrated with the diffusive medium in the non-depleted region. The change in Gibbs free energy of dissolution of the reactants, ΔG_{react} , into the diffusive medium becomes

$$\Delta G_{react} = \frac{2}{3} \mu_{chl} + \frac{4}{3} \mu_{qtz} - 2\mathfrak{R}T \ln aC_{Al,m} - \mu_{other} = 0, \quad (10)$$

Here, I assumed that the diffusive medium is an ideal solution, \mathfrak{R} is the gas constant, μ_i is the chemical potential of mineral i , μ_{other} is the chemical potential of chemical species dissolved in the diffusive medium (excluding ideal mixing part of Al), a is a constant that is a factor to convert from concentration to mole fraction ($X_{Al} = a C_{Al}$). The change in Gibbs free energy of the products, ΔG_{prod} , becomes,

$$\Delta G_{prod} = \mu_{grt} + \frac{8}{3} \mu_{H_2O} - 2\mathfrak{R}T \ln aC_{Al,eq} - \mu_{other} = 0. \quad (11)$$

Because growth is controlled by the sluggish diffusion of Al, the concentration of the other elements is constant through the reactants region and the products region. This constancy implies that μ_{other} in Eq. 10 has the same value as that in Eq. 11. Using Eqs. 10 and 11, the concentration of Al becomes,

$$C_{Al,m} = \frac{1}{a} \text{Exp} \left(\frac{(2/3)\mu_{chl} + (4/3)\mu_{qtz} - \mu_{other}}{2\mathfrak{R}T} \right), \quad (12)$$

$$C_{Al,eq} = \frac{1}{a} \text{Exp} \left(\frac{\mu_{grt} + (8/3)\mu_{H_2O} - \mu_{other}}{2\mathfrak{R}T} \right). \quad (13)$$

From Eqs. 12 and 13, the supersaturation S becomes,

$$S = \frac{C_{Al,m}}{C_{Al,eq}} - 1, \\ = \text{Exp} \left(\frac{\Delta\mu}{2\mathfrak{R}T} \right) - 1, \quad (14)$$

where $\Delta\mu = (2/3)\mu_{chl} + (4/3)\mu_{qtz} - \mu_{grt} - (8/3)\mu_{H_2O}$. The value of $\Delta\mu$ was given by Carlson (1999). Using the value of $\Delta\mu$ (1 kJ/mole for $\Delta T = 5^\circ\text{C}$, and 10 kJ/mole for $\Delta T = 50^\circ\text{C}$, where $T = T_{eq} = 490^\circ\text{C}$ at 5 kbar), $S = 0.082$ for $\Delta T = 5^\circ\text{C}$ and $S = 1.095$ for $\Delta T = 50^\circ\text{C}$, were obtained.

With the input of the value of S , $\beta = 2.85$ [from Carlson (1989)] and $v = 1.20 \times 10^5 \text{ mm}^3/\text{mole}$ into Eq. 9, $C_{Al,eq}$ becomes 1.1×10^{-5} and $2.1 \times 10^{-6} \text{ mole/mm}^3$. These values are about seven or eight orders of magnitude greater than the appropriate value of concentration Al in the medium ($C_{Al,eq} = C_{eff\infty} = 1.7 \times 10^{-13} \text{ mole/mm}^3$) according to Carlson (1999). It is clear that Carlson's choice of the value of Al concentration is inconsistent with the kinetic model of Carlson (1989) and Carlson *et al.* (1995). Moreover, there is no reason why one uses a very high concentration for diffusion-controlled growth and does not use such a value for Ostwald ripening. This is the most important flaw in the set of values estimated by Carlson (1999).

Next, I calculated the length of time for diffusion-controlled growth using Carlson's set of appropriate values. Using $\beta = 2.85$ and Carlson (1999)'s set of values of parameters eleven orders of magnitude smaller than that of Miyazaki (1996), $C_{Al,eq} = C_{eff\infty} = 1.7 \times 10^{-13} \text{ mole/mm}^3$, $D = D_{eff} = 5.1 \times 10^{-21} \text{ m}^2/\text{s} = 1.61 \times 10^{-7} \text{ mm}^2/\text{year}$, the time of growth for a grain of garnet 1 mm in radius is given by Eq. 7 as follows: $t = 7.22 \times 10^{14}$ years (for $S = 1.095$) and $t = 9.64 \times 10^{15}$ years (for $S = 0.082$). These results shows that a grain of garnet 1 mm in radius cannot be produced during the geological time-scale by diffusion-controlled growth. Therefore, if one use the Carlson's appropriate set of values, the case is not only against Ostwald ripening, but also against the nucleation-and-growth model of Carlson (1989) and Carlson *et al.* (1995).