# Wilbur and Ague, Data Repository Material Figure DR1



Figure DR1. Simplified geologic map of the study area modified from Ague (2002). Sample locations for garnets shown in Figs. 1 and DR2 denoted with filled circles. Metamorphic zones: Chlorite; Biotite-Garnet (Bt-Grt); Staurolite-Kyanite (St-Ky).



Figure DR2. Chemical profiles for garnets. Chemical constrasts across core-rim boundaries less distinct than for exampes in Fig. 2. Staurolite-Kyanite zone of the Wepawaug Schist. Sample locations shown in Fig. DR1.



Figure DR3. Supersaturation as a function of normalized bond strength. Minimum value for  $\Phi_1/kT$  of 4 for silicates shown with vertical line. Approximate morphology boundary between open, "branched" cyrstal forms and compact, euhedral, facetted forms shown with dashed line. Crystallization path indicated with blue arrow.

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### WILBUR AND AGUE; APPENDIX DR1

### MINERAL ANALYSES

Two-dimensional chemical maps as well as chemical profiles were done at 15 kV using the JEOL JXA-8600 electron microprobe at Yale University using wavelength-dispersive spectrometers, natural and synthetic standards, mean atomic number (MANB) and off-peak background corrections, and  $\varphi(\rho z)$  matrix corrections. Peak *T* was insufficient to homogenize compositions by diffusion, so the chemical zonation patterns provide a valuable record of reaction histories (cf. Kohn and Spear, 2000; Spear and Daniel, 2001; Carlson, 2002). Chemical maps were done with MANB and either 100 nA beam current and 1.5 second dwell times, or 200 nA beam current and 0.25 second dwell times. High spatial resolution profiles indicate similar concentrations for Ti and Y across core-rim boundaries in WepS garnets (not shown).

## NOTES ON MONTE CARLO CRYSTAL GROWTH SIMULATIONS

We use the Monte Carlo (MC) method of Xiao et al. (1988) to model crystal growth at constant *P*. The treatment includes diffusion of nutrient through the fluid phase to the growing crystal, surface attachment kinetics, and diffusion along crystal faces (a form of surface relaxation). We extend the method to allow for variable amounts of equilibrium overstepping during growth. The goal of the modeling is to investigate whether crystal morphology transitions in metamorphic rocks can be related to the degree of reaction overstepping, not to reproduce crystal shapes and sizes exactly. The simulations are done on a two-dimensional, trigonal lattice (1000 x 1000 grid size). Nutrient aqueous species dissolved in the fluid are generated in a circular source region at some distance from the growing crystal. Diffusion through the fluid takes place according to a random-walk process through the grid. Intervening mineral grains

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could modify diffusion pathways, but we note that if nutrient supplies were strongly anisotropic, then the natural crystals would have grown with marked asymmetries (cf. Xiao et al., 1990). Although diffusion rates are not quantified, lattice units in the crystal have the same length as the mean free path for diffusion, appropriate for growth from a liquid (Xiao et al., 1990). The probability that nutrient diffusing through the fluid will bond to the crystal surface on contact at site  $i (P_i)$  is given by the rate of impingement of nutrient ( $K^+$ ) relative to the sum of the rates of impingement and detachment (K):

$$P_{i} = \frac{K^{+}}{K^{+} + K^{-}} = \frac{K_{eq}^{+} \exp(\Delta \mu / kT)}{K_{eq}^{+} \exp(\Delta \mu / kT) + \nu \exp(-E_{i} / kT)} \quad (1)$$

where *k* is the Boltzmann constant, *T* is absolute temperature,  $E_i$  is the interaction energy for the growth unit and its nearest and next-nearest neighbors in the solid, and  $\nu$  is a vibration factor.  $\Delta \mu / kT$  is the thermodynamic driving force for crystallization that acts to bond growth units to the crystal. The chemical potential difference  $\Delta \mu$  reflects the average Gibbs free energy difference between the compositions of the supersaturated fluid and the fluid in equilibrium with the solid directly at the solution-crystal interface. Crystallization at low  $\Delta \mu / kT$  near chemical equilibrium favors growth of compact, facetted, euhedral crystals whereas high  $\Delta \mu / kT$  corresponds to strong disequilibrium and results in anhedral or "branched" forms (Xiao et al., 1988).  $E_i = \Phi_i n_i + \Phi_2 m_i$ ;  $\Phi_1$  and  $\Phi_2$  are the interaction energies per molecule between a given site in the lattice and its  $n_i$  nearest neighbors and  $m_i$  next-nearest neighbors, respectively. The "normalized bond strength"  $\Phi_1 / kT$  increases as bond strength increases or *T* decreases.  $K_{eq}^+$  is the equilibrium value of  $K^+$  and is evaluated assuming local equilibrium directly at the crystal surface (rates of attachment and removal are equal). The nutrient may bond to the crystal, diffuse along the surface, or return to the fluid phase. If the nutrient does not bond, the jump rate from site *i* on the crystal to site *j* is:

$$K_{i \to j} = v_s \exp(-\Delta E_{ij} / kT) \tag{2}$$

where  $v_s$  is a vibration factor.  $\Delta E_{ii}$  is the activation energy approximated by

 $\Phi_1(n_i - n_j) + \Phi_2(m_i - m_j)$ ; *n* and *m* denote numbers of nearest and next-nearest neighbors, respectively, for site *i* and the potential jump site *j*. The probability of a jump from site *i* to a particular neighbor site *j* on the crystal or in the fluid is given by the ratio of the  $K_{i\rightarrow j}$  value for the jump relative to the sum of the  $K_{i\rightarrow j}$  values for all possible nearest-neighbor jumps. Computer solution follows the flow chart given in Figure 2 of Xiao et al. (1988), with the exception that we account for variable  $\Delta \mu/kT$  during model crystal growth. We found that  $\Phi_2/\Phi_1$  values less than ~ ±0.2 were best for replicating the observed garnet morphologies.

There are scale-dependent aspects to crystal growth (Xiao et al., 1988), but the general conclusions regarding overstepping and morphology will be appropriate for macroscopic crystals. For example, the transition from "branched" to compact, euhedral crystal forms will shift to slightly smaller  $\Delta \mu/kT$  and larger  $\Phi_1/kT$  as model crystal size increases (Xiao et al., 1990), but growth in the 3<sup>rd</sup> dimension, which we neglect, tends to have the opposite effect and stabilizes compact, euhedral forms at larger  $\Delta \mu/kT$  (Xiao et al., 1991). Thus we infer that these two effects will tend to cancel.

Early growth at large  $\Delta \mu/kT$  followed by growth at lower  $\Delta \mu/kT$  is successful at qualitatively reproducing the observed garnet morphologies. We examine two possibilities for variations in  $\Delta \mu/kT$  during crystal growth. In the first, growth occurs initially at large  $\Delta \mu/kT$  and then drops to a low value at a prescribed stage of the growth history. In the second, the

 $\log_{10}(\Delta \mu/kT)$  decreases linearly from an initial large value to a final small one. Many other possible  $\Delta \mu/kT$  paths are possible, but the two examined here both capture the basic morphological characteristics of the crystals. Future refinement of the crystal growth models may allow  $\Delta \mu/kT$  -time paths to be accurately determined based on crystal morphologies. In all examples shown, the model crystals comprise 100,000 molecular growth units.

## **REFERENCES CITED IN APPENDIX AND FIGURES**

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