Forum

Chemical disequilibrium during garnet growth: Monte Carlo simulations of natural crystal morphologies

COMMENT: doi: 10.1130/G23441C.1

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Wilbur and Ague (2006) presented a detailed Monte Carlo model for chemical zonation in garnets, using texturally sector-zoned porphyroblasts. Two aspects of their article left me puzzled.

1) It is unclear why Wilbur and Ague do not regard textural sector zoning as 'true' sector zoning (even if it was not in the original definition). Sector zoning requires that adjacent sectors (or growth pyramids, the bases of which are the crystal faces) develop to some extent 'independently' of each other. In chemical sector zoning, this enables sectors of different crystallographic form to have different chemical compositions (e.g., staurolite; Hollister, 1970) while, in twin sector zoning, adjacent pyramids of the same form are twinned (e.g., grandite garnets; Jamtveit, 1991). In textural sector zoning, matrix-derived inclusions (type 1 inclusions) lie along and define sector boundaries (Andersen, 1984). In contrast, elongate quartz rods that form during garnet growth (type 2 intergrowths; Fig. 1B; Burton, 1986) lie perpendicular to the crystal face forming the base of a particular growth pyramid (sector) and indicate the lineage growth direction. These attest to the 'independence' of the growth direction of each sector. In crystals of homogenous form, such as rhombdodecahedral and icositetrahedral garnets, no chemical sector zoning can be present, even if twin and/or textural sector zoning is developed.

2) In the model proposed by Wilbur and Ague, garnet growth is concentrated at crystal edges, leading to hopper and dendritic habits. In 2-D sections, this gives 're-entrants' in crystal faces (here termed 'face re-entrants' for simplicity) (Fig.1A; Wilbur and Ague's Fig. 3, hereafter called WAFig. 3). Wilbur and Ague correlate these to re-entrants between growth branches seen in photographs and chemical maps of their porphyroblasts (WAFigs. 1 and 2).

In textural sector zoning, sector patterns are defined by the type 1 inclusions and type 2 intergrowths (as described above); observed patterns vary in complexity, depending on the crystal habit and section orientation
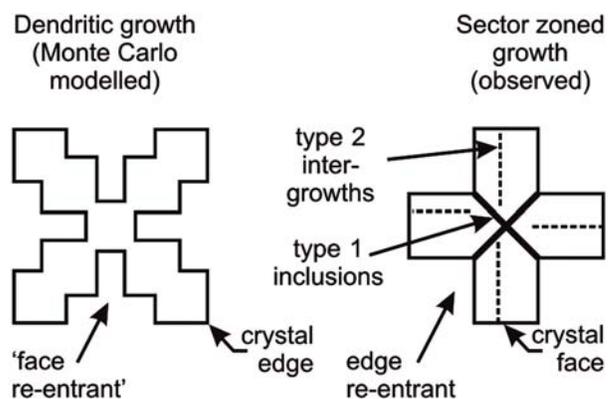

Figure 1: Schematic drawings comparing 'face re-entrants' on hopper/dendritic crystals and edge re-entrants on textural sector-zoned crystals.

through the crystal (see http://homepage.univie.ac.at/alexander.hugh.rice/). In WAFig. 1A, sector boundaries are particularly well defined by type 1 inclusions, and in WAFig. 1E, they are defined by type 2 intergrowths.

Texturally sector-zoned crystals may develop re-entrants at the boundaries of crystal faces ('edge re-entrants;' Fig. 1B). Thus, by definition, these occur at places where type 1 inclusions intersect an edge of the crystal (or an edge of a particular growth-zone, since subsequent growth can fill re-entrants). Edge re-entrants form when sectors on opposite sides of a sector boundary grow too quickly perpendicular to their faces for growth parallel to the faces to fill the incipient re-entrant (cf. Andersen, 1984); that is, through slow-edge growth.

Although all the garnets in WAFig. 1A–1E have re-entrants, these occur at points where type 1 inclusions reach the rim of the central growth zone (organic matter-free zone) and are thus edge re-entrants, typical of textural sector zoning, rather than the face re-entrants of dendritic growth. Comparison of the textural and chemical development of the porphyroblasts (Fig. 2A-F; WAFigs. 1 and 2) shows that the chemical branches mapped lie between these edge re-entrants and therefore reflect enhanced growth on the crystal faces, rather than at the crystal edges.
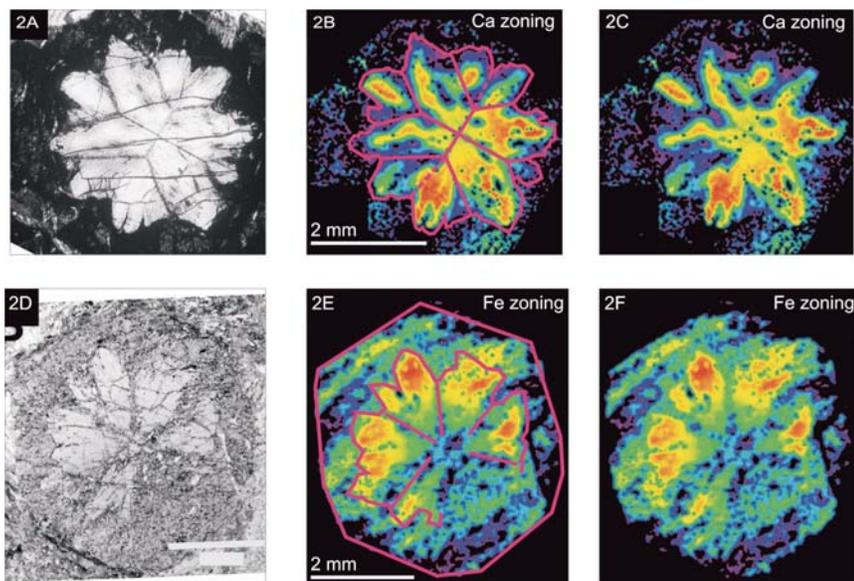

Figure 2: Comparison of photographs and chemical maps of garnets from Wilbur and Ague (2006). Figures 2A and 2C are WAFigure 1A and WAFigure 2D. Figures 2D and 2F are WAFigures 1B and WAFigure 1F. Figures 2B and 2E show the geometry of the garnets (taken from Figures 2A and 2D) superimposed on the chemical maps (Figures 2C and 2F). Solid red lines show garnet shapes and observed textural sector zone boundaries; dashed lines show probable textural sector zone boundaries. Figures 2A and 2C have been rotated 27° clockwise and 2° counterclockwise, respectively, to give them the same orientations as the chemical maps. For each set of pictures, the scale is constant.

Thus the modeled chemistry, which has enhanced crystal edge growth, resulting in face re-entrants, differs entirely from the observed chemistry with enhanced crystal face growth and edge re-entrants. The former, as noted by Wilbur and Ague, is consistent with dendritic growth, which would seem to lie at the opposite end of a textural spectrum from textural sector zoning (Fig. 1), the one characterized by rapid edge growth and the other by inhibited edge growth.

ACKNOWLEDGMENTS

I thank Jay Ague for details concerning the relative orientations of the textural figures and chemical maps.

REFERENCES CITED

Andersen, T.B., 1984, Inclusion patterns in zoned garnets from Magerøy, north Norway: Mineralogical Magazine, v. 48, p. 21–26, doi: 10.1180/minmag.1984.048.346.03.

Burton, K.W., 1986, Garnet-quartz intergrowths in graphitic pelites: The role of the fluid phase: Mineralogical Magazine, v. 50, p. 611–620, doi: 10.1180/minmag.1986.050.358.06.

Hollister, L.S., 1970, Origin, mechanism, and consequences of compositional sector-zoning in staurolite: American Mineralogist, v. 55, p. 742–766.

Jamtveit, B., 1991, Oscillatory zoning patterns in hydrothermal grossular-andradite garnet: Non-linear dynamics in regional immiscibility: American Mineralogist, v. 76, p. 1319–1327.

Wilbur, D.E., and Ague, J.J., 2006, Chemical disequilibrium during garnet growth: Monte Carlo simulations of natural crystal morphologies: Geology, v. 34, p. 689–692, doi: 10.1130/G22483.1.
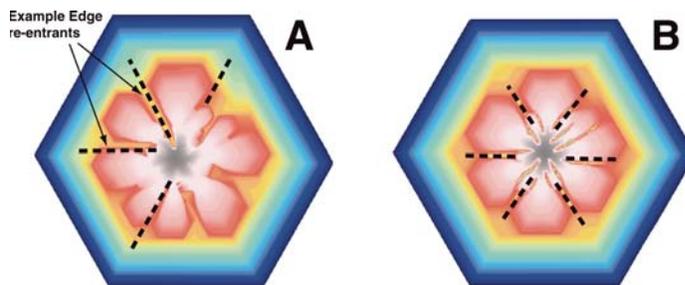
Figure 1. Monte Carlo (MC) crystal growth simulations showing formation of edge re-entrants. A: Transitional case with edge and face re-entrants. Dashed lines trace out positions of edge re-entrants during growth. Degree of supersaturation decreases during growth, such that $\Delta\mu/kT = 9.25$ for first 5% of growth history, decreasing to 5 for the next 20%, and then to 10^{-2} for the remaining 75% ($\Delta\mu$ = chemical potential difference; k = Boltzmann's constant; T = absolute temperature). Nutrient aqueous species generated at edge of circular source region at some distance from crystal; normalized bond strength = 8; and interaction energy ratio = 0.1. See Wilbur and Ague (2006) for detailed discussion. B: Similar to Figure 1A, but $\Delta\mu/kT = 9.7$ for first 5% of growth history, decreasing to 5 for the next 20%, and then to 10^{-2} for the remaining 75%. Nutrient aqueous species generated throughout circular source region surrounding crystal.

REPLY: doi: 10.1130/G23787Y.1

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We thank Rice (2007) for insightful comments on our work (Wilbur and Ague, 2006) and for highlighting important issues in metamorphic crystallization. However, Rice's comments do not affect our conclusions regarding disequilibrium during garnet growth.

The first issue Rice raises concerns terminology. To many in the community, any term that includes "sector zonation" implies that different crystal faces grew with different chemical compositions. We were simply emphasizing that the term "textural sector zonation" does not refer to such differences (for crystals of any symmetry, cubic or otherwise).

The second set of issues centers on dendrites and crystal growth morphology. Following conventions in solid-state physics, we use the term "dendritic" in a broad sense to describe a crystal that develops with a branching form (cf. Ben-Jacob and Garik, 1990). This would include both of the branched morphologies in Rice's Figure 1. Rice argues that the branching in our models produces face re-entrants, whereas edge re-entrants are observed in the natural examples. It is true that the natural examples we show have large numbers of edge re-entrants, although face re-entrants are also found. Without detailed crystallographic measurements, we are not convinced that Rice's interpretations of chemical zonation are diagnostic of growth morphology in all cases. Regardless, it was not our intention to argue that all growth far from chemical equilibrium is characterized by face re-entrants. Rather, our goal was to show in a general way how branching morphologies can develop during such growth. We highlight two points in this regard.

1) Most importantly, the interplay between rates of surface diffusion, bonding, and the propagation of crystallographic perturbations is complex and is a strong function of the saturation state and the transport of nutrients to growing crystals. Space did not permit us to show a large number of examples of how these phenomena relate to each other. However, we show in this Reply that at very high initial supersaturation, there is a transition to growth characterized by edge re-entrants (Fig. 1). Here, the bonding rate is fast relative to surface diffusion, and regions of larger surface area (e.g., faces) can propagate rapidly. Given the model simplifications, we emphasize that very detailed comparisons between natural crystals and models should be done with caution. Nonetheless, the models in Figure 1 of this Reply are similar in morphology to garnets in our study, such as the crystal in our original Figures 1B and 2E–2H. We illustrate a transitional case here in Figure 1A to show that edge re-entrants and face re-entrants both can develop during growth relatively far from chemical equilibrium. The directions of dendrite propagation are critically dependent on the dynamics of disequilibrium growth such that growth branches can follow *either* of the general orientations shown in Rice's Figure 1 (see also Figure 4 in Ben-Jacob and Garik, 1990).

2) Natural garnet is cubic and three-dimensional, whereas our models are based on a two-dimensional, trigonal lattice. There will be unavoidable differences between observed and model morphologies because of the model simplifications. We note that simplifications are not limited to our Monte Carlo models. The qualitative models of Rice's Figure 1 are also highly simplified and fail to capture some of the characteristic morphological features of the growth branches, particularly the curved or irregular tips that are observed in many specimens (Wilbur and Ague, 2006; Fig. 1C, 1F).

We conclude that edge re-entrants and face re-entrants do not represent opposite ends of a "textural spectrum" as envisioned by Rice, but instead are both manifestations of the same underlying phenomenon: growth relatively far from chemical equilibrium.

ACKNOWLEDGMENTS

REFERENCES CITED

Ben-Jacob, E., and Garik, P., 1990, The formation of patterns in non-equilibrium growth: Nature, v. 343, p. 523–530, doi: 10.1038/343523a0.

Wilbur, D.E., and Ague, J.J., 2006, Chemical disequilibrium during garnet growth: Monte Carlo simulations of natural crystal morphologies: Geology, v. 34, p. 689–692, doi: 10.1130/G22483.1.

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