

Rates and scales of metamorphic equilibration: The importance of intergranular solubility controlled by fluid composition

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Summary

Variations over time in the character of compositional zoning in garnet from Harpswell Neck, Maine, resulting from a shift in composition of the metamorphic fluid from CO₂-rich to H₂O-rich, demonstrate that differential solubility of cations in fluids of variable composition is a fundamental control on the time scales and length scales of chemical equilibration in metamorphic rocks.

Introduction: What produces the unusual zoning in garnets from Harpswell Neck, Maine?

Garnet is widespread in pelitic schist of the Jewell Formation exposed in coastal outcrops at the southernmost point of the Harpswell Neck peninsula, Maine. The character of chemical zoning in the inner portions of many of these garnets is strikingly different from that in their outer portions, and the zoning of Mn, Fe, and Mg is unlike that of Ca and Y. For Mn, Fe, and Mg, many crystals have irregular, patchy distributions in their cores that give way to smooth, concentric zoning in their outer rims. In contrast, zoning of Ca and Y is comparatively smooth and concentric throughout these crystals. Rims of all crystals share equivalent concentrations of all elements.

The interiors of some crystals have overgrown a planar foliation, which is invariably at an angle to the exterior foliation, and is occasionally crenulated. In some crystals, this included foliation is deflected in the outer portions of the garnet, rotating toward parallelism with the external foliation. In rare cases that display transitions in both zoning character and inclusion-trail orientation, the transition between the regions containing a planar foliation and the regions displaying curved inclusion trails is found at approximately the same position as the transition from patchy to concentric zoning in Mn, Fe, and Mg.

Initial explanations for these features focused on the interpretation of Mn distributions. Daniel and Spear (1998) and Spear and Daniel (1998) relied on an equilibrium model in which isolated maxima in Mn were regarded as separate sites of nucleation, from which it was inferred that the patchy zoning of Mn, Fe, and Mg resulted from coalescence during growth of separately nucleated crystals.

Subsequent EBSD study by Hirsch et al. (2003) revealed, however, that most garnet crystals comprise only a single crystallographic orientation, and that the relatively rare misorientations that do exist within crystals are spatially unrelated to compositional variations, ruling out the multiple-nucleation hypothesis for the origin of the patchy zoning. Hirsch et al. instead explained the patchy Mn zoning in garnet cores as the result of overprinting during growth, a process in which the garnet incorporates into its chemistry much of the pre-existing heterogeneity of the precursor matrix. This is a disequilibrium process that will occur if the rates of intergranular diffusion of some components (e.g., Mn) are slow in comparison to the growth rate of the garnet, so that a portion of the surface of a garnet crystal adjacent to a high-Mn precursor grain grows in a local, restricted, Mn-rich environment and creates a small region of spessartine-rich garnet at that spot. The transition from this disequilibrium zoning in garnet cores to the smooth, concentric equilibrium zoning in garnet rims was attributed by Hirsch et al.

to increasing temperature during garnet crystallization: the sub-micron scale of intergranular transport and equilibration during growth of garnet cores was thought to expand to centimeter-scale during growth of garnet rims, owing to the exponential dependence of rates of intergranular diffusion on temperature. The uncommon occurrence of such features was attributed to an unusually low temperature for garnet growth (rim growth at 450-470 °C; Spear and Daniel, 1998) in the Mn-rich compositions at Harpswell Neck.

In both previous studies, the origin of concentric zoning for Ca and Y in garnet cores was not considered in detail, and no attempts were made to explain the difference in the zoning patterns of these elements from those of Mn, Fe, and Mg. The apparent long-length-scale equilibration for Ca and Y throughout the entire crystallization interval — particularly during early growth when Mn, Fe, and Mg exhibit extremely short length scales for equilibration — is exactly the inverse of what is expected from Carlson's (2002) analysis of a suite of localities in which Fe and Mg commonly equilibrate widely even at low temperatures, but Mn, Ca, and Y commonly fail to equilibrate at centimeter-scale until amphibolite-facies or even granulite-facies conditions are attained.

New data on variations in temperature and fluid composition during garnet growth at Harpswell Neck are reported here and interpreted in the context of overprint zoning for slow-diffusing elements; they demonstrate that temperature increases cannot account for the observed transition in zoning character, but that this transition is instead correlated with a major shift in the composition of the intergranular fluid during garnet crystallization.

Results I: Temperatures during garnet crystallization

An attempt was made to quantify the range of temperature during garnet crystallization, using Fe-Mn exchange equilibria between host garnet and inclusions of ilmenite at varying distances from garnet cores outward to rims, for garnets spanning the largest possible range of central Mn contents, and thus the largest possible ranges of nucleation and growth temperatures. The results revealed no appreciable differences in temperatures between cores and rims, and no dependence on Mn concentration of the garnet immediately surrounding the inclusion; this could result either from preservation of a narrow range of crystallization temperatures or from progressive prograde re-equilibration that causes all temperatures to converge to some near-peak value. Temperatures retrieved from 167 garnet-ilmenite pairs are quite uniform, with a mean and standard deviation of 546 ± 28 °C.

Further thermometry utilized Fe-Mg exchange equilibria between garnet rims and neighboring matrix biotite. Using the calibration of Holdaway (2000), which was judged to be most suitable for dealing with the high-Mn garnets found at Harpswell Neck, temperatures retrieved from 26 garnet-biotite pairs yielded a mean and standard deviation of 548 ± 10 °C, identical within error to the garnet-ilmenite results. (Recalculation of temperatures using the calibration of Ferry and Spear (1978) — the same calibration employed by Spear and Daniel (1998) — yielded temperatures of 455 ± 22 °C. This is consistent with Spear and Daniel's previously reported range of 450-470 °C, demonstrating that the discrepancy is solely the result of using different calibrations.)

Together, these findings suggest the need for an upward revision of the temperatures for garnet growth at Harpswell Neck by approximately 90 °C, and they provide no support for an unusually low temperature for the onset of crystallization nor for a protracted range of temperature during growth. This in turn casts doubt upon the explanation for the transition from short-range to long-range Mn-equilibration advanced by Hirsch et al. (2003), namely increases in distances of diffusional equilibration as the result of initially low but increasing temperature.

Results II: Fluids during garnet crystallization

Because rates of intergranular diffusion are strong functions not only of temperature but also of the solubility of diffusing components in the intergranular medium, the above result focused attention on the fluids attending garnet crystallization at Harpswell Neck. Fluids were characterized by a combination of field study of multiple generations of ubiquitous quartz veins and their relationships to garnet crystallization, and microchemical analysis by Raman spectrometry of fluid inclusions in quartz and in garnet.

Regionally, folding about NNE-trending axes preceded NNE-directed dextral transpression along km-scale strike-slip faults. The planar foliation included in most garnets likely formed during the folding event, and the subsequent deflection of the foliation in garnet rims and the discordance between interior and exterior foliations likely record the effects of the later shearing. The earliest generation of quartz veins was emplaced during and after folding, and contemporaneously with early garnet growth, as garnets are found both within these veins and lining their edges. Garnet growth continued during the emplacement of a second generation of quartz veins that record the regional shear event. In both generations of veins, two distinct assemblages of fluid inclusions are found, one H₂O-rich and one CO₂-rich. However, in the first generation of veins, CO₂-rich inclusions are decidedly more abundant; in the second generation, H₂O-rich inclusions predominate. Multiple CO₂-rich fluid inclusions were found in quartz crystals captured in garnet interiors, but there was no evidence for H₂O-rich fluid inclusions in such crystals. No fluid inclusions could be analyzed in garnet cores, but two fluid inclusions in a garnet rim were found to be rich in H₂O with minor CO₂.

The data from fluid inclusions in quartz veins, in quartz inclusions in garnet, and in garnet itself therefore document a distinct shift in fluid composition from CO₂-rich to H₂O-rich during garnet growth, accompanying a transition from regional folding to regional shearing. Growth of garnet cores took place in the presence of the CO₂-rich fluid, but growth of garnet rims took place in the presence of the H₂O-rich fluid.

Interpretation: Solubility as a control on rates of intergranular diffusion

The recognition that changes in the character of garnet zoning correlate with changes in the composition of fluids attending garnet growth leads to a novel alternative explanation for the unusual zoning in the garnets of Harpswell Neck: low solubility for Mn, Fe, and Mg and high solubility for Ca and Y in a CO₂-rich fluid restricted the length-scales of equilibration for the former and expanded them for the latter during the growth of garnet cores; transition to an aqueous fluid with relatively high solubility for all elements then led to rock-wide equilibration for all during growth of garnet rims.

Although few data are available on solubilities at metamorphic conditions, information gleaned from low-temperature regimes and hydrothermal systems suggests that such an explanation is plausible. The complexation of Ca and REE (and thus Y) by carbonate and bicarbonate ligands is well-documented in geological fluids, and a CO₂-rich fluid that lacked chloride (and fluoride) for complexation of other cations would be a suitable intergranular medium for enhancement of the intergranular diffusion of Ca and Y, but not Mn, Fe, and Mg. Transition to an aqueous fluid with even relatively low salinity would introduce ligands that would be effective in complexation of all the cations, leading to more rapid intergranular diffusion of all components and more extensive diffusional equilibration.

Conclusions

The garnets at Harpswell Neck provide a striking example of the importance of intergranular solubilities as a control on rates of intergranular diffusion, and consequently on the time scales and length scales of chemical equilibration during metamorphic crystallization. Carlson's (2002) synthesis of the relative rates of chemical equilibration for various cations, which emphasizes temperature as the dominant factor, may apply to crystallization in the most commonly

encountered range of fluid compositions (i.e., somewhat saline aqueous fluids), but significant departures from that framework must be expected as fluid composition varies. The implication of the Harpswell Neck example is that in some circumstances, the effects of relative solubility can become the determining factors controlling the type and extent of partial chemical equilibration during metamorphic crystallization.

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References

- Carlson, W. D., 2002, Scales of disequilibrium and rates of equilibration during metamorphism: *American Mineralogist*, 87, 185-204.
- Daniel, C. G., and Spear, F. S., 1998, Three-dimensional patterns of garnet nucleation and growth: *Geology*, 226, 503-506.
- Ferry, J. M., and Spear, F. S., 1978, Experimental calibration of the partitioning of Fe and Mg between biotite and garnet: *Contributions to Mineralogy and Petrology*, 66, 113-117.
- Garber, J., 2008, Impact of fluid evolution on garnet growth in pelitic rocks from Harpswell Neck, Maine [BS Thesis]: University of Texas at Austin, 64 pp.
- Halick, M. A., 2005, Tests of an overgrowth model of disequilibrium crystallization in garnets from Harpswell Neck, Maine [BS Thesis]: University of Texas at Austin, 68 pp.
- Hirsch, D. M., Prior, D. J., and Carlson, W. D., 2003, An overgrowth model to explain multiple, dispersed high-Mn regions in the cores of garnet porphyroblasts: *American Mineralogist*, 88, 131-141.
- Hixon, J. D., 2006, Controls on scales of chemical equilibration during metamorphism: Insights from garnet zoning patterns [MS Thesis]: University of Texas at Austin, 227 pp.
- Holdaway, M. J., 2000, Application of new experimental and garnet Margules data to the garnet-biotite thermometer: *American Mineralogist*, 85, 881-892.
- Spear, F. S., and Daniel, C. G., 1998, Three-dimensional imaging of garnet porphyroblast sizes and chemical zoning: Nucleation and growth history in the garnet zone: *Geological Materials Research*, 1, 1-44.