

A brief retrospective of Bill Carlson's work on metamorphic disequilibrium and kinetics

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Bill Carlson's work has spanned a wide range of metamorphic and mineralogic topics. One overarching theme has been the extension of metamorphic petrology to occurrences dominated by disequilibrium, rather than equilibrium textures. Beginning with his graduate work on calcite-aragonite transition kinetics, continuing with coronal reaction textures, and, for the past 15 years, focusing on the quantitative analysis of porphyroblast textures, Bill has driven the field forward. His advances have been both in the theoretical realm, building on the work of folks like Ralph Kretz, and in the technical realm, in which he pioneered the use of high-resolution computed tomography for the analysis of porphyroblast textures in three-dimensions. While he has not been alone in this effort, his work, along with that of his students and colleagues, has been instrumental in advancing our science from the clean ideality of equilibrium towards the messy but more accurate world of disequilibrium.

Oxygen isotope speedometry in the Biwabik iron-formation

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The Biwabik banded iron-formation (BIF) of northern Minnesota (1.9 Ga), underwent contact metamorphism by intrusion of the Duluth Complex (1.1 Ga). The igneous contact is sub-parallel and intersects the BIF at Dunka Pit.

Apparent temperatures, calculated from $\Delta^{18}\text{O}$ (Quartz-Magnetite) (Clayton and Kieffer, 1991), are precise and decrease smoothly from 700°C at the contact to 375°C at greater than 2.6 km (3-D, normal to the contact). However, measured temperatures are similar to closure temperatures (T_c ; Dodson, 1973) for oxygen diffusion in magnetite at a cooling rate of $\sim 2000^\circ\text{C}/\text{Ma}$ over a gradient in observed grain size of magnetite of 2 mm at the contact to 10 μm at 2.6 km. In the absence of recrystallization, resetting of $\Delta^{18}\text{O}$ (Qt-Mt) is limited by diffusion in magnetite inside the grunerite isograd (2.6 km from the contact). At 1.25 km from the contact, the measured "temperature" is 490°C and T_c is 468°C; at 2.6 km from the contact the temperatures are 375°C and 404°C respectively. If T_c at the contact equals the measured apparent temperature, the cooling rate is defined.

To test whether $\Delta^{18}\text{O}$ (Qt-Mt) is a thermometer or a speedometer in these rocks, additional quartz magnetite pairs were analyzed from two outcrops in Dunka Pit within 10 m of the contact for two grain sizes: 500-350 μm and 150-105 μm diameter. The apparent temperatures are: 669°C, 702°C, and 716°C for 03BIW43B and 601°C, 644°C, and 732°C for 03BIW18C; for 150-105 μm , bulk, and 500-350 μm diameter magnetite grains respectively. Thus magnetites have been reset in $\delta^{18}\text{O}$ as a function of grain size and presumably are zoned in $\delta^{18}\text{O}$ due to diffusion. Inverted pigeonite in BIF at Dunka Pit indicates temperature $> 775^\circ\text{C}$ which further supports the interpretation that $\Delta^{18}\text{O}$ (Qt-Mt) records retrograde exchange.

Thus, measured $\Delta^{18}\text{O}$ (Qt-Mt) values record the rate of retrograde exchange. This suggests that the Biwabik iron-formation at Dunka Pit cooled from $\sim 800^\circ\text{C}$ to T_c (700°C) in 50 kyr. Measured apparent $\Delta^{18}\text{O}$ temperatures are lower than peak temperatures and should not be used to estimate depths of intrusion or peak metamorphic temperatures.

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Effects of reaction kinetics on mixed volatile (CO₂-H₂O) decarbonation reactions in contact aureoles

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One-dimensional models of heat and mass (CO₂-H₂O) transport are used to evaluate the roles of fluid flux, diffusion, and reaction rate during infiltration-driven metamorphism by modeling the reaction: calcite + quartz = wollastonite + CO₂. Incorporation of reaction kinetics (rate constants based on experimental data) produces little change in the rate of advance of a reaction front in up-T flow, but causes reductions of ≤ 20 to 25% in the rate of advance of a reaction front in down-T flow. In contrast, diffusion has no significant impact on the rate of advance or width of a reaction zone in either up- or down-T flow at significant fluid flux (10^{-9} m³ m⁻² sec⁻¹) and for limited timescales ($\leq 50,000$ yrs) of flow and reaction. A significant impact of reaction kinetics in down-temperature flow is to expand reaction fronts to reaction zones. At reaction rates based on experimental studies, reaction zones of > 40 m are quickly developed at significant fluid flux (10^{-9} m³ m⁻² sec⁻¹) and high porosity ($\phi = 0.1$). If fluid flux decreases by decreasing porosity, the width of the reaction zone narrows considerably; at low porosity ($\phi \leq 0.001$) reaction zones are less than 5 m in width. However if reaction rates in contact metamorphic environments are one to two orders of magnitude less than experimental results, then reaction zones of significant width ($> 8-10$ m) could be developed in contact aureoles at porosity of ≥ 0.001 and fluid flux $\geq 10^{-11}$ m³ m⁻² sec⁻¹.

Isograds formed in contact aureoles during down-T flow are typically narrow ($\ll 10$ m; many $\ll 1$ m). Our modeling results indicate that these narrow reaction zones require significant fluid infiltration rates ($\geq 1 \times 10^{-8}$ m sec⁻¹), and either reaction rates faster than experimental values or low porosity (≤ 0.001). Rapid reaction rates appear at odds with an increasing number of reported occurrences of mineralogic and oxygen isotope disequilibrium in metamorphic systems. Alternatively, the narrow reaction zones may indicate that infiltration-driven metamorphism occurs at low porosity (≤ 0.001). If so, the modeling results indicate that equilibrium reaction surfaces may be significantly overstepped for both up- and down-T flow. Such overstepping leads to the possibility that index minerals could be produced in contact aureoles by metastable reactions.

Unreactivity of garnet in low pressure metapelites

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Garnet is one of the most widespread and petrologically important metamorphic minerals in metapelites. Several lines of evidence suggest, however, that in low pressure metamorphism at least, garnet forms at low grade but may not participate modally in subsequent mineral reactions until considerably higher grade is reached: even though it is physically present, it is to a large degree chemically inert due to sluggish kinetics of reaction. The evidence includes: distribution of garnet in individual rocks that is independent of the distribution of later-formed porphyroblasts; euhedral shape of garnet in rocks in which phase equilibrium considerations suggest it should have dissolved significantly (e.g. staurolite-bearing rocks); chemical zoning patterns of garnet in such rocks that show no evidence for reaction; and phase equilibrium systematics of low pressure metapelites that work fine when garnet is ignored.

To test the implications of these observations, we have performed phase equilibrium modelling for isobaric low pressure (3.8 kbar) prograde metamorphism of average metapelite for two end member situations: perfect equilibrium crystallization and perfect fractional crystallization with regard to garnet. The predicted sequence and position of reaction isograds is immaterially different between the two situations, possibly accounting for the success of low pressure phase equilibrium systematics that ignore garnet. These results show that care is required in using garnet in mineral assemblage-based petrogenetic grids, such as for bathozone determinations. Staurolite appears to show some of the same behaviour as garnet, which we have also modelled.

Heat and mass transport modeling and rates of metamorphic processes

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Recent progress in understanding metamorphic processes derives, in part, from advances in our ability to apply computational modeling studies of heat and mass transport to metamorphic systems. Computational modeling of contact metamorphic systems provides a controlled laboratory to investigate the entire thermal history of a metamorphic event and rates of controlling processes. A systematic investigation of the sensitivity of key parameters e.g. permeability structure, fluid flow, fluid production, intrusion temperature, latent heat of crystallization, and multi-stage intrusions, enables examination of their impact on metamorphic processes and on P-T-X-t paths encountered by aureole rocks. Advanced visualization techniques allow the spatial and temporal variability of scalar and vector fields to be analyzed.

For example, one of the fundamental controls on crystal size distribution and porphyroblast growth in metamorphic rocks is the heating rate (dT/dt) experienced by the rocks. Two and three-dimensional heat and mass transport studies suggest that heating rates vary over four orders of magnitude during a single thermal event. While the key parameters control the absolute magnitude of the heating rate, more importantly they affect the spatial and temporal location of high heating rates. As the dominant thermal regime changes from conduction to convection, the spatial distribution of high dT/dt varies markedly. For a conduction dominated regime with isotropic permeability, high heating rates move outward symmetrically with the advance of the diffusive front. In contrast, for the convective case, high heating rates migrate with advance of the convection cell. This results in an asymmetric pattern of high heating around the intrusion.

When combined with data from a natural well-studied contact metamorphic system, thermal models provide the needed temperature-time paths for extracting kinetic data. These studies demonstrate that the assumption of a constant heating rate for extracting kinetic parameters is problematic for most natural settings because of the inherent temporal and spatial variation in thermal paths of metamorphic rocks.

Comparing natural reaction kinetics for isotopic exchange and net-transfer reactions

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Modern research in crustal processes involving metamorphism frequently employs complex physical models wherein some quantification (or assumption) of the rate at which metamorphic reactions, or chemical exchange, proceed. Often, the assumption is made that reaction rates at these conditions are very fast (based largely on lab-based data). To test this, it has proven difficult to extract *quantitative* constraints on metamorphic reaction rates from field based analysis given the inherent complexities of nature and the challenge of constraining timescales. The results of such field based studies (e.g., Carlson et al. 1995; Baxter & DePaolo 2002; Baxter 2003) can be difficult to generalize and compare directly to each other and to lab-based data.

Here, I compare natural rates of bulk fluid-rock isotopic exchange and net-transfer reactions. Given a generalized rate law ($R_{net} = k f(\Delta G)$) where " ΔG " represents the deviation from equilibrium wrt the specific process under consideration - not necessarily expressed as a free energy), " k " is an effective rate constant into which is lumped the long list of factors that may limit or influence rates. While the $f(\Delta G)$ term will differ for every process, both isotopic exchange and net-transfer reaction processes (involving the same phases) should share the same value of " k " because they share the same list of rate-controlling conditions and processes, *excepting* the following: 1) slow product phase nucleation, 2) slow transport of net-transfer reactant species other than the isotope of interest, 3) armoring of stable phases (not consumed by net-transfer reactions) with an isotopically equilibrated rim. Field-based data indicate that differences in " k " related to factors 1 and 2 (which would tend to slow " k " for net-transfer reactions) are less than an order of magnitude. Factor 3 could slow " k " for isotopic exchange, but only in otherwise static P-T-X conditions, especially when solid-solutions are involved. The combined field data suggest that significant disequilibrium (i.e. isotopic disequilibrium and/or net-transfer reaction overstepping) can persist in many metamorphic settings where P-T-X are changing.

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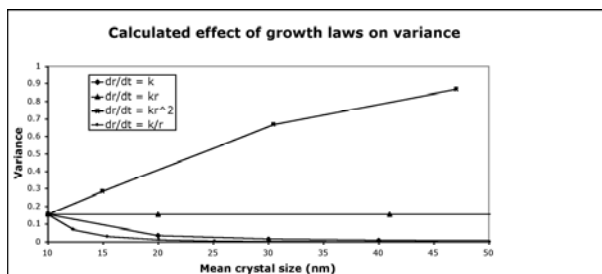
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Crystal growth rate law identified from changes in variance of crystal size distributions

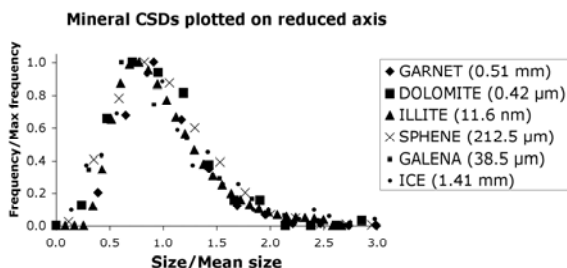
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Rate laws for crystal growth can be identified by the change in the natural log-based variance (β^2) of crystal size distributions (CSDs) during growth. Rate laws proposed for minerals include: $dr/dt = k$ for polynuclear and spiral growth; $dr/dt = k/r$ for diffusion-limited growth; $dr/dt = kr^2$ for mononuclear growth; and $dr/dt = kr$ for proportionate growth, where r is crystal radius, t is time, and k is constant. Computer simulated growth (first figure below) indicates that the first three laws are unlikely: starting with a lognormal CSD having $\beta^2 = 0.16$, CSD variance either approaches zero or increases unrealistically.



Variances for most measured CSDs are small and relatively constant; therefore, the proportionate rate law is favored. For example, mean sizes measured for minerals in the reduced plot below vary widely, from 11.6 nm to 1.41 mm, whereas their variances have a narrow range, from 0.14 to 0.30. In addition, the shapes of these CSDs are approximately lognormal, and only proportionate growth can generate and maintain such lognormal shapes. The other growth mechanisms listed above may occur during crystallization while the overall rate law is proportionate. Experiments with K-alum and calcite crystals indicate that proportionate growth is favored by the advective supply of reactants, whereas constant growth appears when reactant supply is limited by diffusion.



Nucleation and growth mechanisms in phase transformations: Insights from dynamic experiments

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Phase transformations change material physical properties and are thus of fundamental importance to geodynamic models and to probing the Earth with geophysical techniques. Although thermodynamics can be used to predict equilibrium phase assemblages, it tells us nothing about reaction kinetics, the spatial distribution of nuclei, or the grain size distribution and crystallographic orientations of newly developed phases. It is these factors that will control physical properties and physical property anisotropies. In order to understand better phase transformation mechanisms and resultant microstructures, we have been developing and applying techniques for the analysis of microstructures, in an SEM, during high temperature experiments. Experiments on geologically important systems are very difficult. However experiments using metals as rock analogues are possible and give considerable mechanistic insight.

We have observed phase transformations in Ti metal. The structure of Ti transforms at $\sim 882^\circ\text{C}$ from hexagonal close packed (HCP - α) to body centred cubic (BCC - β). The BCC phase nucleates as both intracrystalline plates and grain-boundary allotriomorphs. Electron backscatter diffraction analysis shows that intracrystalline plates have a Burgers orientation relationship with the parent HCP grain ($\{0001\} // \{110\}$ and $\langle 11-20 \rangle // \langle 111 \rangle$). Boundary plane orientations and topography associated with plates suggest that plates nucleate and grow by a shear mechanism. Grain-boundary allotriomorphs have a Burgers orientation with one of their neighbouring HCP grains. The boundary plane orientations are arbitrary and have no associated topography suggesting that allotriomorphs grow by a diffusive process. Direct observations of boundary motion and textural analysis show that, during HCP to BCC transformation, BCC phase microstructure and texture are dominated by the growth of grain boundary allotriomorphs, rather than intracrystalline plates. We will explore the implications of these observations for the kinetics of phase transformations in the Earth.

Application of a continuum diffusion controlled growth model to metamorphic crystallization

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The rate of metamorphic crystallization has been shown to be mainly controlled by diffusion, though other mechanisms have been proposed. The modeling of metamorphic crystal growth has on one hand been advanced using the assumption of local equilibrium and a single controlling component or using coupled diffusion fluxes assuming steady state and local equilibrium throughout the system. Here we present results obtained based on continuum diffusion growth models proposed for igneous crystallization. Equilibrium is maintained on the growing crystal surface, and the matrix buffers the composition to a constant value at a large distance from the porphyroblast.

Simultaneous solution of the coupled diffusion equations and the equilibrium mass action equation at the surface of the growing porphyroblast indicates that concentration ratios between the diffusing species of a factor ten or more (or a variation of the diffusion coefficient of the same order) is enough to allow the system to be controlled by this minor component in the fluid phase. The other concentration profiles show only a small change in concentration towards the porphyroblast surface. A glance at the solubility of typical pelitic assemblages using experimental and thermodynamically estimated values reveals that the chlorine-rich fluids contain Al only as a very minor solute. Hence the common assumption that it is Al diffusion which is limiting diffusional porphyroblast growth in chlorine rich fluids is in agreement with this analysis. Solubility of elements in chlorine poor, alkaline rich fluids is complicated by the complexing of alkalis with Al and Si. Experiments have shown that solubility of Al is similar that of Na, K, and Si. In these solutions no single element is likely to control the diffusional growth of porphyroblasts. The controlling factors are likely one or more of the bivalent cations in the case of e.g. garnet growth. Another interesting consequence of diffusion limiting growth of porphyroblast is that concentration variation in the crystal can also reflect growth velocity variations.

Garnet zoning pattern, growth mechanism and the development of Lu-depleted halos in eclogites

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Radius-rate relationships use major element compositional zoning in minerals to identify the rate-limiting growth mechanisms (e.g. Kretz 1973; Carlson 1989). Application of this concept to garnets of the eclogites of the Zermatt-Saas-Fee ophiolite (ZSFOe, Western Alps, Switzerland/Italy) suggests that all garnets precipitated the same amount of radius per time interval. Hence they grow limited by an interface-controlled mechanism.

Understanding of REE zoning in garnets is the key for interpreting age dates (Lapen et al. 2004). Measured HREE zoning pattern in garnets of the ZSFOe display a prominent change from Gd, which is depleted in the cores and enriched close to the rims, to Lu, which forms a narrow spike in the center.

Most of the HREE including Y behave similar to the major elements which mean that concentration profiles for different garnet sizes from a sample approximately plot on top of each other, if their rims are aligned. This suggests that these elements equilibrated throughout the matrix. However, Lu concentrations in the cores of smaller garnets are always enriched relative to Lu contents at the corresponding distance from the rim of larger garnets. This difference in behavior indicates that Lu incorporation is controlled by another mechanism. The fact that Lu concentrations in small garnets are higher in the center than the composition of Lu in the co-precipitated parts of larger garnets indicates that larger garnets have developed depletion halos surrounding them. Hence Lu-incorporation is diffusion-controlled. Note that trace elements are not abundant enough to influence the rate-limiting mechanism and thus will not hinder nucleation in this diffusion-depleted halos. Similarly, Lu matrix-garnet disequilibrium does not necessarily imply Lu-isotopic disequilibrium, which would invalidate Lu/Hf dating.

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Intergranular diffusion rates in mineral aggregates: Where are we and where do we go from here?

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As noted by Carlson in his recent Presidential Address to the Mineralogical Society of America [1], "the kinetics of intergranular diffusion govern rates of metamorphic crystallization and chemical equilibration in many ordinary circumstances. Unfortunately, those rates remain largely unknown." While intergranular diffusion rates remain largely unknown, significant advances have been made over the past decade.

The results of experimental laboratory studies will be reviewed in light of applications to the kinetics of metamorphic processes. The important role of fluids and the equilibrium fluid distribution during metamorphism will be illustrated through the results of the experimental studies. In addition, the results of recent experiments on the bulk diffusion of Si in feldspar aggregates will be presented. The results of these experiments place valuable constraints on the rate-limiting diffusing species in mineral reactions involving feldspars.

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Can competitive porphyroblast growth lead to size-time correlation?

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Two types of evidence for intergranular diffusion being the rate-limiting process in metamorphic crystallization are spatial ordering of porphyroblasts and radius-rate relationships. However, these are to some extent mutually exclusive in any single situation, as the theoretical radius-rate relationship for thermally-accelerated diffusion is based on growth in isolation, whereas ordering implies competitive growth. However, they both are observed in quartzite schists from the Picuris Mountains of New Mexico.

This paradox provided part of the impetus for creation of a new computer model of metamorphic crystallization in which diffusion is directly quantified as a function of local concentration gradients in the intergranular medium brought about by dissolution of reactants and growth of products. This new treatment allows spatial variability in reactant distribution to be quantitatively taken into account, and its possible effects on final porphyroblast distribution to be studied. As with its predecessor (Carlson et al. 1995), this model successfully reproduces the spatial ordering and crystal size distributions measured in natural samples.

When intergranular diffusion is the only driving force for nutrient transport in these simulations, all growth is competitive. The growth rate of any given porphyroblast is highly dependent on the local nutrient supply and the number of nearby porphyroblasts competing for it. As a result, in the final result there is only a very broad correlation between porphyroblast size and time of nucleation. Conversely, in the Picuris study conducted by Chernoff and Carlson (1997), the correlation between size and time as inferred from central MnO content is relatively tight, a trend that apparently spans several outcrops. This result implies a fairly consistent growth rate that is not achievable in the models as originally posed.

Reproducing this observation requires re-examination of the assumptions behind nucleation and material transport. In particular, fluid advection, possibly driven by fluids produced during dewatering, may provide the missing mechanism.

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**Plenary Address by the
Dana Medalist**

**Rates and mechanisms of
metamorphic processes from natural
occurrences**

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Quantitative analysis of chemical and microstructural features of metamorphic rocks is a powerful and essential tool for kinetic studies. Natural occurrences can be exploited to provide data under conditions inaccessible to laboratory methods, and should be used to validate experimental measurements. The advantage of approaches based on natural rocks stems from the fact that with rare exceptions, direct laboratory replication of the kinetics of metamorphic processes is impossible, because the timescales of nearly all such processes exceed the duration of laboratory experiments by many orders of magnitude. As a result, application of kinetic data determined by experiment commonly requires long extrapolations in temperature or time or both. This problem is particularly acute for the fundamental mechanisms that transform one mineral assemblage to another and that establish chemical equilibrium among coexisting phases and within individual minerals, because rates of these thermally activated processes vary exponentially with temperature.

Extraction of quantitative kinetic data from natural occurrences demands careful identification and verification of the underlying physical mechanisms; creation of a tractable mathematical or numerical model that captures the essential kinetics of the physical mechanisms; diligent efforts to constrain the values of the model's input parameters; and sensitivity analysis to establish the resulting ranges of uncertainty in the output variables.

Examples from the author's past and present research that illustrate the value of kinetic studies based on natural occurrences include: (1) determination of the kinetics of the transformation in nature of aragonite to calcite from analysis of growth-limited replacement microstructures; (2) determination of intergranular diffusion kinetics — from which estimates of rates of equilibration and scales of disequilibrium follow — from diffusion-controlled reaction textures; (3) determination of nucleation-and-growth kinetics from statistical analysis of sizes and locations of crystal arrays; and (4) determination of intracrystalline diffusion kinetics in garnet from modeling of stranded diffusion profiles in partially resorbed crystals.

**Yb and Y diffusion in grossular
garnet**

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Diffusion of ytterbium and yttrium has been measured in natural grossularite (~93% grossular component) under dry, oxygen-buffered conditions. The sources of diffusants for the experiments were microcrystalline Yb and Y aluminate garnets. Experiments were performed by placing the source material and polished garnet slabs in AgPd capsules, and sealing them, along with a solid buffer, under vacuum in silica glass capsules. Prepared capsules were annealed in 1-atmosphere furnaces for times ranging from a few months to 30 minutes at temperatures from 700-1100°C. The Yb and Y distributions in the garnet were profiled with Rutherford Backscattering Spectrometry (RBS). For experiments buffered at QFM, the following Arrhenius relations are obtained:

$$D_{Yb} = 7 \times 10^{-7} \exp(-312 \text{ kJmol}^{-1}/RT) \text{ m}^2\text{s}^{-1}$$
$$D_Y = 1 \times 10^{-6} \exp(-312 \text{ kJmol}^{-1}/RT) \text{ m}^2\text{s}^{-1}$$

Diffusion coefficients for Y and Yb from experiments buffered at IW are about an order of magnitude slower than under QFM-buffered conditions.

The similar diffusivities found for Y and Yb are consistent with earlier observations by Van Orman et al. (2002) that show little variation in diffusivities among the REE in pyrope. The slower diffusivities under IW buffered conditions are also consistent with earlier work showing a positive dependence of cation diffusion on fO_2 .

We are exploring REE diffusion for other garnet compositions, and considering these and previously reported data (van Orman et al., 2002; Tirone et al., 2005) in light of the dependence of diffusivities on garnet unit cell dimensions that has been noted for major element diffusion in garnet (Carlson, 2003).

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Garnet grain distribution along a pelitic eclogite to amphibolite path: Adula Nappe, Switzerland

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Eclogite facies assemblages in the Adula Nappe have been well-documented in mafic and ultramafic lithologies [e.g. 1, 2], but have only been reported for a few pelitic samples [e.g. 3]. Alp de Confín is located within the structurally upper portion of the Adula Nappe and contains an unpublished 30m x 50m paragneiss outcrop that is progressively zoned from eclogite-facies whiteschist in the core to retrograde amphibolite-grade metapelites along the edges.

Preliminary X-ray tomograph analysis of samples from different zones were made at the University of Lausanne to examine garnet size distributions related to the polymetamorphic history of the Adula. Statistical analyses of the tomography results indicate that an even crystal size distribution for garnet is present within the whiteschist, but that a bimodal distribution is exists in the amphibolite-grade paragneisses. This shift in garnet distribution is also mirrored by a reduction in the modal proportion of garnet from ~20% in the whiteschist to <5% in amphibolite-grade samples. The change in garnet modes and crystal size distributions may be due to a reaction involving garnet and the breakdown of paragonite to plagioclase, because no staurolite or biotite is present.

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Breakdown of dolomite in H₂O-rich fluid: An experimental study

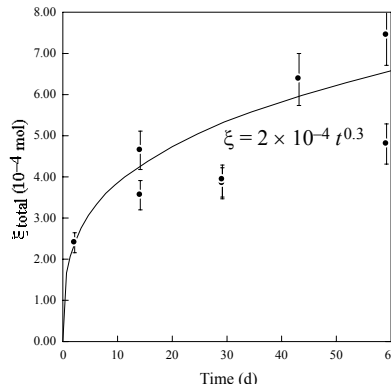
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The existence of calcite + periclase or brucite in contact-metamorphosed dolomite is a potential indicator of reaction in the presence of H₂O-fluid. We have undertaken an experimental study of the breakdown of dolomite to determine the rate of reaction and the minerals that form during cooling. Experiments were conducted with natural and synthetic dolomite powder, dolomite rock, and isotopically characterized H₂O. Samples were heated in cold-seal hydrothermal vessels to temperatures ranging from 650 to 750 °C at pressure of 50 and 100 MPa. In general, we find that dolomite breaks down rapidly in H₂O-rich fluid, that Mg has a high solubility in the fluid, and that magnesite and nesquehonite precipitate from the fluid on quench. The total moles of dolomite reacted over the time of the experiment was found to be proportional to the cube root of time, approximately (Fig. 1). The rate in mol/s is $d\xi/dt = 6.9 \times 10^{-10} t^{-0.7}$.

The overall rate of a heterogeneous reaction is generally found to be proportional to a power greater than one of the affinity of the reaction. Over the duration of our experiments, the affinity changed with time because the fluid composition became more CO₂ rich with the increase in ξ . At constant temperature and pressure, the affinity of the reaction is $A = RT \ln(f^*_{CO_2}/f_{CO_2})$, in which f^* is the equilibrium value of the fugacity of CO₂, 31.7 MPa at $x_{CO_2} = 0.225$. The affinity was determined from the value of x_{CO_2} during experiment. Within error, the instantaneous reaction rate is proportional to the square of the affinity—the least-squares fit gives an exponent of 1.8. In comparison with nature, the lack of brucite and the existence of basic Mg carbonate minerals in our experiments suggest that aqueous fluids encountered in nature are substantially more H₂O rich than those in our closed-system experiments.



Fluid-mediated mineral consumption and growth in polymetamorphosed metapelites of the Black Hills, South Dakota

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Regional Metamorphism in the Black Hills

Late Archean and Early Proterozoic continental margin pelites, graywackes, and quartzites were regionally metamorphosed during collision of the Archean Wyoming and Superior Provinces beginning ~1760 Ma [1]. The metamorphism reached at least garnet-biotite grade conditions. This assemblage occurs in much of the middle portion of the Precambrian core of the Black Hills. It is characterized by inclusion-rich (graphite, quartz, and other phases) unzoned garnets that are $\text{Sps}_{44}\text{Alm}_{44}\text{Pyr}_3\text{Gr}_{59}$. Mn-ilmenite (up to 47% pyrophanite component) also occurs. The broad distribution of the grt-bt assemblage is attributed to the stabilizing effect of Mn.

Mineral growth during contact metamorphism

During late stages of the collision, the rocks were intruded by the Harney Peak leucogranite (HPG) at 1720-1705 Ma. Vigorous fluid flow, evidenced by abundant quartz veins, metasomatic aureoles, and consumption of graphite from metapelites, occurred around the granite. The lowest-grade aureole assemblage includes chlorite that overgrows regional foliation and new, clear, Sps-poor, Alm-rich rims on garnet. Higher-grade facies include staurolite, then sillimanite, and finally second-sillimanite. Mineral compositions suggest 4-4.5 kbar pressure. Within the sillimanite zone, garnet is mostly inclusion free and ~1720 Ma old¹. Textures suggest that this new garnet grew after dissolution of the old garnet, for which the only remaining evidence may be remnant inclusions or quartz-biotite clots in which biotite is coarser than in the matrix. Andalusite typically occurs as euhedral crystals in quartz veins or as poikiloblasts along foliation planes, where it appears to have grown as Si-rich fluids passed through. Most andalusite probably grew during decompression of the fault-bounded HPG block.

Reference

[1] Dahl, P. S. *et al.* (2002) *GSA Abstracts* **34**, 68

Equilibrium and fractional crystallization during prograde metamorphism revisited

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The use of forward thermodynamic modeling to constrain the nature of P-T paths during prograde metamorphism, and in phase equilibrium calculations in general, has become a widely utilized technique. Many studies utilizing this technique to model individual rock samples assume an equilibrium crystallization model with a constant effective bulk rock composition even though it is clear that in many samples, such as garnet-bearing pelites, equilibrium crystallization and constant effective bulk rock composition are not the norm. This study revisits the concept of equilibrium and fractional crystallization in relation to effective bulk rock composition in low-pressure garnet-bearing pelites experiencing isobaric heating paths. The methodology and results from 3 different approaches of modeling fractional crystallization during prograde metamorphism are presented.

Thermodynamic modeling of phase diagram sections in the MnKFMASH and MnNCKFMASHT systems indicate that fractional crystallization of garnet does not, generally, have a significant effect on the stability of non-fractionated phases. However, the results also indicate that it can be extremely important to consider the effect of fractional crystallization on effective bulk rock composition in relation to the stability of the fractionating phase itself. For example, an equilibrium crystallization model along an isobaric heating path for an average low-Al pelite composition from the Nelson Batholith contact aureole, British Columbia, predicts garnet growth, followed by coupled staurolite growth and garnet consumption, in turn followed by coupled staurolite consumption and garnet growth. However, if the effect of garnet fractional crystallization is considered, and garnet is not consumed during staurolite growth, then garnet will not grow during and after staurolite consumption along the prograde heating path. This has important implications on the derivation of garnet-growth P-T paths utilizing garnet chemistry and inferred reaction history. Finally, the effects of fractional crystallization of more than one phase during prograde metamorphism are presented.