

Kinetics of garnet nucleation: Inferences from natural occurrences

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Recent assessments of nucleation and growth of garnet in metamorphic rocks [1-3] invoke divergent controlling mechanisms, and make widely contrasting predictions for nucleation kinetics that are sharply differentiated by the sizes of the thermal intervals over which nucleation is envisioned to extend. Tests of these predictions against chemical and textural features in natural occurrences favor a mechanism in which diffusive impediments to equilibration produce protracted nucleation that extends across a large fraction of the crystallization history.

A set of 371 centered radial concentration profiles on central sections (located by HRXCT) and 468 central compositions for individual garnet crystals in a single sample from the Picuris Range (New Mexico, USA) [4] can be explained only if nucleation of new crystals continued throughout nearly the entire period of garnet crystallization. Mutual consistency among Fe, Mg, and Mn concentrations documents establishment of rock-wide chemical equilibrium for these elements, which allows one to use, for example, Mn content as a proxy for time. A strong correlation exists between crystal size and central Mn content, and central Mn contents in progressively smaller crystals match Mn concentrations in progressively more rimward portions of larger crystals. In these and other rocks, further evidence of protracted nucleation arises when quantitative textural analysis reveals spatial ordering of crystal centers, consistent with suppression of nucleation in diffusionally depleted zones surrounding pre-existing crystals. Such effects have been documented in a suite of 13 garnetiferous pelitic and mafic rocks spanning a wide range of metamorphic conditions.

These chemical and textural observations require that nucleation of garnet is commonly essentially continuous throughout nearly all of its crystallization history: nucleation commonly spans a broad thermal interval (several tens of degrees) and is thus characterized by substantial thermal overstepping and significant departures from chemical equilibrium. The observations are consistent with numerical models of diffusion-controlled nucleation and growth [3] that replicate measured size-composition-isolation correlations, plus spatial ordering and other key textural features; such models require that nucleation intervals span 50-100 °C or more. The observations run strongly counter to the predictions of models that invoke interface-limited precipitation control [2] or reactant-dissolution-limited control [1], for which thermal intervals of nucleation are calculated to be very narrow, ~1 °C or < ~6 °C respectively.

In one exceptional case, chemical data indicate that nucleation was restricted to a short period near the beginning of garnet crystallization [5], but textural measures show that early site-saturation — rather than non-diffusional controls — was responsible.

[1] Schwarz *et al.* (2011) *J Meta Geol* **29**, 497-512. [2] Gaidies *et al.* (2011) *Contrib Mineral Petrol* **162**, 975-993. [3] Ketcham & Carlson (in press) *J Meta Geol*. [4] Chernoff & Carlson (1997) *J Meta Geol* **15**, 421-438. [5] Meth & Carlson (2005) *Can Mineral* **43**, 157-182.

Biological controls on Mn oxide ore formation in east Tennessee, USA

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Field Relationships

Mn oxide ore deposits are commonly found as discrete and disseminated deposits below the middle Ordovician unconformity throughout the Valley and Ridge from GA to VA. Deposits in the Cambrian Erwin, Shady, and Rome Formations in northeast TN are associated with brecciated jasperoid and residual clays of the Shady dolomite and are exposed in the hanging wall of northeast trending thrust faults juxtaposed atop Erwin Formation quartzites. Ore formation postdates jasperoid replacement and occurs primarily as matrix material in jasperoid breccias and as vug infillings with minor occurrences along faults and bedding planes.

Mineralogy and Crystal Morphology

Mn oxides in these ores exhibit a variety of morphologies: loose pellets enclosed in geodes, botryoidal nodules, dendrites and shrubs, drusy coatings on geode interiors, and massive porous and laminated ore with interbedded laminae of Mn oxides and Fe oxyhydroxides. X-ray diffraction (XRD), and scanning and transmission electron microscopy (SEM, TEM) indicate that the shrubs, pellets, and laminae are composed of columnar crystals of a cryptomelane-hollandite solid solution, and are associated with filaments of goethite nodules that form a draped net-like structure. Botryoidal nodules are composed of sheets of romanechite exhibiting stromatolitic layering. The dendritic and drusy Mn oxides are composed of nanoscale acicular cryptomelane needles radiating from irregular chains and interconnected clumps of clay spheres. The dendrites and drusy are microporous with imprints of gas bubbles. The shrubs and laminae resemble stalactites with crystals radiating out from nucleation sites in increasing sizes, and are partially encased by ropes of gravity-draped goethite filaments. Nucleation sites consist of irregular sheets, encrusted ropes, and networked filament structures. TEM and XRD analysis indicate that individual Mn and Fe oxide crystals around the nucleation sites are highly ordered, yet on the μm scale they exhibit unusual morphologies commonly associated with biological mineralization [1,2,3]. Fluid inclusion observations in the jasperoid matrix indicate fluid temperatures < 120°C for the region, which does not rule out biological associations.

Conclusions and Continuing Work

Due to the scale and shape of the nucleation sites, it is likely that small Mn oxide crystals nucleated on negatively charged biological particles (such as extracellular polymeric substances), allowing for abiotic crystal growth, and were not deposited directly on cell surfaces as primary, poorly crystalline biominerals. ⁴⁰Ar/³⁹Ar dating of cryptomelane will constrain the timing of ore emplacement and allow paleoreconstruction of regional sources of ore fluids.

[1] Hofmann and Farmer (2000) *Planet. Space Sci.* **48**, 1077-1086
[2] Chafetz and Guidry (1999) *Sedimentary Geology* **126**, 57-74
[3] Parenteau and Cady (2010) *PALAIOS* **25**, 97-111