

Zoning in olivine xenocryst in hydrous systems

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Chemical zoning in xenocrysts may be inherited, the result of magmatic growth, or diffusive ion exchange with the host magma. To quantify magma residence times of xenocrysts based on diffusion zoning patterns thus requires knowledge of the contribution of diffusion to the zoning patterns and knowledge of appropriate diffusion coefficients. Using olivine xenocrysts (Fo 75-79) from melting experiments run for ca. 1 day, at 1000-1150 °C, 200 MPa, fO_2 near NNO, and 1-5 wt% H₂O, we characterize length-scales of growth versus Fe-Mg diffusion zoning, and suggest that hydrous diffusion coefficients for olivine need to be constrained to reliably model xenocryst residence times in magmatic systems. In the experiments, initially angular, unzoned olivine xenocrysts develop subhedral to euhedral crystal outlines, and continuous Fe-Mg core-rim zoning with rim thicknesses of $\leq 40 \mu\text{m}$. The euhedral crystal outlines and thick rim zones indicate that the zoning patterns partly result from growth. However, abundant healed micro-fractures, originally present in the xenocrysts, extend into the compositional rim zones, and define minimum length scales for zoning as the result of diffusion. The maximum length scale of the diffusion zoning profiles are 9.5 and 17.5 μm in 1000 and 1150 °C experiments, and we suggest that these profiles represent diffusion close to [001]. Estimating the diffusion coefficient D as $\sim l^2/t$ (l = diffusion length scale; t = time) gives $\log(D)$ of ca. -14.8 to -14.2 m^2/s^{-1} at 1000 and 1150 °C, apparently independent of the amount of H₂O present. Using the same approximation to calculate D for olivine xenocrysts in an equivalent dry system (using data from [1]), indicate that diffusion in olivine xenocrysts in low-pressure hydrous systems is over ten times faster than in equivalent anhydrous systems. To reliably quantify magma residence times of xenocrysts based on diffusion zoning patterns thus requires (i) that hydrous diffusion coefficient are rigorously constrained and applied, unless it is evident that the xenocrysts were immersed in dry magmas; and (ii) that growth contributions to xenocryst zoning patterns are constrained (e.g., using markers as above, or comparing zoning patterns for multiple elements).

[1] Costa & Dungan (2005) *Geology* **33**, 837-840.

A novel carbon concentrating mechanism for foraminiferal calcification and its potential effects on paleoceanographic proxies

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We describe a unique carbon concentrating mechanism in foraminifera that serves mainly for calcification and to some extent for symbionts photosynthesis. Observations on the benthic species *Amphistegina lobifera* show intensive seawater vacuolization activity, with two types of vacuoles: Mega-pinocytotic vacuoles (10-20 μm in size) and small spherical vacuoles ($\sim 5 \mu\text{m}$). Using confocal laser microscopy and fluorescent dyes we found that the pH of the mega-vacuoles is close to 9, while the pH of the small spherical vacuoles is below 6. Under these conditions CO_{2(aq)} diffuses from the small vacuoles through the cytosol into the large basic vacuoles. These basic vacuoles are recycled into the calcification site where they exocytose their CO₃²⁻ enriched seawater to the site of biomineralization. Microelectrodes observations of pH and CO₃²⁻ showed that the DIC concentration in the calcifying fluid was at least 4 mM (double than that of seawater). These observations have complex implications for paleoceanographic proxy development: The carbon isotopic fractionation of the symbiotic algae occurs from a semi-closed reservoir. The CO₃²⁻ is higher than that of seawater so that the partition coefficient of other anions in seawater (B, S, P) would be low. High CO₃²⁻ at the calcification site may also lower the $\delta^{18}\text{O}$ of the shell. Planktonic foraminifera may behave differently to some extent because the symbionts are also distributed along the spines, and the system is more open for gas exchange and ions diffusion.