

## Metastable phases in foraminifer *Amphistegina sp.* shells and implications for biomineralisation

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Different planktic and benthic foraminifer species have been shown to contain vaterite and/or amorphous calcium carbonate (ACC) in their shells (Jacob et al., 2017). These metastable phases are interpreted to be remnants of a stepwise non-classical crystallization pathway that terminates with crystallization of calcite in the 'mature' shell. Studying the phase composition of biominerals containing such metastable components is very challenging in terms of artefact-control as phases are often nano-granular, fragile under the e-beam and transform easily upon drying or prolonged storage. We present here the first FIB Transmission Electron Microscopy results on shells of benthic foraminifers *Amphistegina lobifera* and *Amphistegina lessonii* that were sacrificed immediately prior to analysis and thus present the freshest natural material we have studied with these methods to date.

All shells studied consisted mainly of calcite, but in addition, vaterite was found in each of the samples, and ACC was observed in some. These metastable phases were present as nanometre sized grains (ca. 5-10 nm), distributed randomly (i.e. not representing a cohesive layer), and closely associated with calcite grains and/or organic-rich areas. Different to earlier observations on dry-stored material (Jacob et al., 2017) we could identify and fully crystallographically index two different polytypes of vaterite, namely hexagonal vaterite (P3<sub>2</sub>1) and 2-layer monoclinic vaterite (C2). Both polytypes have been postulated based on crystallographic modelling (Demichelis et al., 2013; Makovicky 2016; Christy 2018) and represent the least energy structures of vaterite. Monoclinic vaterite (C2) is reported here for the first time in natural biominerals. Our findings suggest that also *Amphistegina sp.*, form their shell via a stepwise crystallization pathway, thus superseding the long-standing paradigm that planktic foraminifera construct their shells by direct precipitation of calcite from seawater.

Jacob et al. (2017) *Nat Comm* 8, 1265; Demichelis et al. (2013) *Cryst Gr&Des* 12, 2247; Makovicky (2016) *Am Mineral* 101, 1636; Christy (2017) *Cryst. Gr&Des* 17, 3567;