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Persistence of shell carbonate and paleo-environmental information under challenging conditions: Time-averaging and aragonite stabilization in modern cold-water seabeds

Susan M. Kidwell, Dept. Geophysical Sciences, University of Chicago

The accumulation of skeletal carbonate is fundamental to many petroleum geologic applications: skeletal debris is strongly associated with marine discontinuities, builds reservoir-scale bodies, and carries diverse proxy information on paleoenvironmental conditions. A first-order latitudinal gradient in rates and pathways of skeletal carbonate alteration almost certainly exists: geologists have reported enhanced preservation in the tropics and suspected enhanced destruction in cold settings. Thus, although low- and mid-latitude shelf seabeds allow millennial-scale persistence of aragonitic shells (work by the PI and others), scales of time-averaging per assemblage are expected to be much lower in high-latitudes, with younger median shell ages and a shorter or sparser tail of shells surviving long-term residence in the surface mixed layer. These differences should have consequences for the paleobiological and geochemical proxy information that skeletal carbonate grains carry. Nonetheless, we still have (1) only scattered radiometric dates for macrobenthic shells from truly cold seabeds and (2) only sparse observations on stages, much less rates, of early-diagenetic modification under such conditions, particularly as it influences aragonite stabilization and survival into the permanent stratigraphic record.

This project focuses on these two unknowns. Module I: Adapt existing methods of bivalve shell age-dating (AMS 14C-calibrated amino-acid racemization) and survivorship analysis (methods already developed with cooperating scientists Tomasovych and Kaufman) to Arctic and subarctic shelves, a new study system for the PI. These data will (a) provide the first direct estimate of the maximum duration of aragonite persistence under such cold-water conditions, and (b) reveal the dynamics of carbonate loss and time to permanent sequestration. Module II: Apply high-resolution imaging (environmental SEM, uncoated material) and compositional analysis (new-to-the-PI) to these shells of known postmortem age to establish the stages, mechanisms, and timing of early-diagenetic microstructural remodeling of bivalve aragonite.

Progress in Module I: We have results on the extent of racemization (D:L ratios for 8 amino acids per shell) from the first 100 Alaskan shells submitted to Northern Arizona University for analysis and are simply awaiting AMS-14C results to calibrate racemization rates (expected January 2020). Shells were drawn from two infaunal aragonitic species, as planned --*Macoma calcarea* and *Nuculana radiata* -- selected for sharing microstructures with already-dated bivalve shells in mid- and low-latitudes. Alaskan shells were acquired from one site in the subarctic North Bering Sea (SLIP 4) and one site in the fully Arctic Chukchi Sea (UTN2; from long-term, NOAA-funded biological observatories DBO1 and DBO3, respectively). We decided against using shells from the cold-temperate Juan de Fuca Strait (WA-BC): further examination revealed that even calcitic scallop shells there had suffered extensive recrystallization.

Even without calibration to calendar years, the shapes of the frequency distributions of D:L ratios shows that (1) *Macoma*, which has persistently large living populations at both sites historically, yields a L-shaped frequency distribution such as found in all other latitudes, indicating rapid loss of shells immediately after death (short initial half-life), but with a small subset (<1%) surviving to form a long tail of older shells. (2) In contrast, *Nuculana*, which is abundant today in the subarctic (main food of diving ducks) but was historically abundant in the Arctic (other work by GRA Meadows), yields a young mode of shells in the subarctic seabed where it is abundant today but an older mode in the Arctic seabed where it is rare today but historically abundant. We see a similar 'young gap' in other study areas where a species has been locally extirpated, supporting confidence in using the shape of such shell-age frequency distributions as proxies of bivalve population sizes. We are submitting an additional 100 *Macoma* shells for AAR analysis to improve our sample size, and look forward to the AMS 14C data that will permit us to quantify their taphonomic half-lives, times to sequestration.

Progress in Module II: SEM of Alaskan shells has revealed that: (1) despite the cold and less-saturated overlying water, the cross-lamellar (XL) aragonite of *Macoma* shells undergoes the same stages of microstructural change as it does in temperate (*Parvilucina*, Southern California) and tropical shelves (*Ctena*, Gulf of Eilat/Aqaba). (2) Also contrary to expectation, damage arises from microbial maceration and loss of the organic matrix of the shell, not from chemical dissolution of the mineral phase. We observe loosening and edge-scalloping of lamellae, not 'karstic' damage to crystallites, despite under-saturated overlying- and pore-waters. This path of microbial disintegration is confirmed by comparison to damage produced on live-collected shells by reagents of known effect (bleach and buffered acetic acid). (3) Older shells (higher D:L ratios) are more pervasively chalky macroscopically, but nevertheless never become karstic under SEM. We suspect that dissolution must be focused on crystallites after they are released from the microstructure by loss of the OM 'mortar'. (4) *Macoma* shells having a vitreous and porcelaneous rather than chalky texture reveal, under SEM, a ~2-3 µm-thick, smooth-topped rind of syntaxial blades that conserve the original dip of lamellae in the original, underlying XL aragonite. These blades are not euhedral but rather biogenic, and probably reflect microbial precipitation. Ramen spectrometry in early 2020 will reveal if this rind is still aragonite or is calcite, which would further increase the shell's ability to persist post-mortem. We have seen a thinner but otherwise identical vitreous skim on some of the older bivalve shells from California and Eilat, also of as-yet-unknown mineralogy. We were extremely surprised to find the growth of this protective rind in cold-water seabeds, and it underscores the unexpected importance of microbial processes here – both in promoting disintegration initially and then, for a very small subset of shells, promoting preservation.

Impacts: Our results so far have met with strong interest from carbonate sedimentologists, biomineralization specialists, and isotopic geochemists who, as hoped, are now open to collaborate with the PI on more sophisticated analyses of these age-dated shells and on experiments of microbial interactions with aragonitic microstructures, a key aim of the project. We have published abstracts for talks at the 2018 and 2019 AGU meetings (PI Kidwell lead author 2018, on stages in microstructural modification common across latitudes; GRA Caitlin Meadows lead author 2019, on age-dating of shells and microstructural effects distinct to Arctic). We plan to prepare our results for journal publication in Spring 2020 once we have the AMS calibration of AAR data.