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Biomineralization and proxies of $CaCO_3$ in the oceans: It is all about seawater...

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Calcium carbonate precipitation in today's ocean is a major process in the global carbon cycle that control atmospheric CO_2 and climate. Almost all the $CaCO_3$ precipitation in the ocean is biological and most invertebrates that calcify transport seawater (SW) directly into their calcification site. The only exception to the SW mechanism is the coccolithophores that transport calcium and bicarbonate ions and calcify intracellularly. In contrast, foraminifera, corals, echinoderms, mollusks, sponges and other minor groups, bring bulk seawater directly into their privileged space where calcification occurs. The SW hypothesis is supported by several different lines of evidence: 1. The incorporation of cell impermeable fluorescent dyes (calcein and FITC-Dextran) into the skeletons. 2. The skeletal chemistry contain most of the major, minor and trace elements and their stable isotopes present in seawater with slight deviations compared to inorganic $CaCO_3$ precipitated from seawater. 3. Direct microscopic observations at the calcifying fluid of corals, foraminifera and echinoderms show seawater labeled with cell impermeable fluorescent dyes at the calcification sites. Pulse-chase experiments with calcein demonstrate SW transport dynamics that is fast enough to support the observed calcification rates for corals and foraminifera. Seawater with Ca^{2+} >10 mM, DIC of 2mM and pH above 8.0 such that it is supersaturated with respect to both calcite and aragonite. Because of the excess Ca^{2+} over CO_3^{2-} the main organismal modifications of the SW are pH and DIC elevations, achieved by protons removal in exchange for alkalinity transport, most likely Na, K, and possibly Ca-ATPases, into the calcifying seawater. Recent experimental studies on the partition of elements in corals and foraminifera skeletons under variable calcium and carbonate concentrations show clear Rayleigh distillation behavior with a mechanism to increase the CO_3^{2-} concentrations by a factor of 2-3. Our experiments support the seawater model as opposed to the trans-membrane alternative and explain well why foraminifera and corals are excellent archives for past seawater chemistry, improve the reliability of existing proxies and introduce new ones. A special novel focus of our recent studies is the development of proxies for the past carbonate system involving anion elements (B, S, I, Br, As, Mo).