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Distribution coefficients of major and minor elements in coral skeletons: experimental results under variable seawater Ca and carbonate concentrations

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In a search for paleoceanographic proxy for Ca, under the assumption that Na did not change during the past 100 My, we cultured corals under variable seawater (SW) Ca concentrations (10, 15, 20 and 25 mM). Two coral species, *Pocillopora damicornis* and *Acropora cervicornis*, were cultured for ~ 3 months, and the newly precipitated skeleton was analyzed using ICP-OES and compared to the culturing solutions. The results show highly significant linear correlations with zero intercepts between $El/Ca_{Skeletons}$ and El/Ca_{SW} for the following elements: Li, Na, Mg, K, Sr and Ba, from which distribution coefficients (D_{El}) were calculated. These D_{El} values are close to the inorganic D values for aragonite with slightly higher values for Na, Mg and K (elements with $D_{Inorganic} << 1$) and lower values for Sr and Ba ($D_{Inorganic} > 1$). These deviations were fitted with Rayleigh distillation model in which the calcifying fluid is essentially SW. During the experiment, the carbonate chemistry changed and a significant linear correlation was observed between the anions to Ca ratio (An/Ca) in the skeleton and An/CO_3^{2-} of the culturing seawater ($An/CO_3^{2-}{}_{SW}$). Based on these linear fits, we calculated the CO_3^{2-} concentration of the extracellular calcifying fluid (ECF) of the coral ($CO_3^{2-}{}_{ECF}$) that yielded relatively similar $CO_3^{2-}{}_{ECF}$ values for all the anions. For both species, $CO_3^{2-}{}_{ECF}$ values are higher by a factor of 2-3 compared to $CO_3^{2-}{}_{SW}$. Our elevated values of $CO_3^{2-}{}_{ECF}$ are similar to those reported in previous studies based on B and its isotopes and direct measurements using microsensors and fluorescent dyes. These findings provide further evidence that coral calcification occurs from a closed reservoir of SW following Rayleigh process and an increase in pH and DIC of the ECF. Furthermore, these findings suggest that the coral regulates the carbonate chemistry of the ECF to reach a high and relatively constant aragonite saturation (Ω_{Ara}).