The Distribution Coefficients of Major and Minor Elements in Coral Skeletons Under Variable Calcium Seawater Concentrations

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Coral skeletons are one of the best archives for past ocean seawater (SW) chemistry and isotopes. However, the distribution coefficients of major and minor elements in coral skeletons are not well determined. In this study, we launched an experiment to determine the distribution coefficients of multiple elements in corals' skeletons by changing Ca concentrations in SW (Ca_{SW}). Two scleractinian corals, *Pocillopora damicornis* and *Acropora cervicornis* were cultured in modified Gulf of Eilat water (Red-Sea) with Ca_{SW} of approximately 10, 15, 20, and 25 mM. After almost three months, the newly grown skeletons were analyzed for the following elements: Li, Na, Mg, K, Sr, and Ba. Their ratios to Ca in the coral skeleton (El/Ca_{coral}) increased linearly with El/Ca_{SW} (with R^2 values above 0.98), crossing the origin and thus indicating constant distribution coefficient for each element over the experimental range of El/Ca_{SW}. The values of D_{El} were in good agreement with values reported for corals collected in natural seawater. However, differences were observed between the two species, and both were slightly deviating from inorganic aragonite D values. These deviations are well explained by Rayleigh fractionation process in the calcifying fluid (assuming it is mainly seawater). This was observed both for elements with $D > 1$ (Ba and Sr) and $D < 1$ (Li, Mg, Na, and K). *P. damicornis* showed open system behavior (~20% of its Ca utilized) while *A. cervicornis* showed more closed calcifying reservoir (~50% of its Ca utilized). The finding that the distribution coefficients of the six minor and trace elements are constant for a given species, should help in the reconstruction of past seawater chemistry based on multielement measurements in fossil corals. In particular, Na/Ca_{coral} can be used to reconstruct past ocean Ca concentrations and with El/Ca_{coral} ratios for other elements, their concentrations for the Cenozoic can be reconstructed.

Keywords: coral calcification, trace elements, distribution coefficient, Rayleigh fractionation, seawater paleochemistry

INTRODUCTION

The changes in the elemental composition in Scleractinian corals skeletons, provide important archive and proxies for reconstructing ancient seawater (SW) chemistry. It is recognized, that the uptake and partition of elements that coprecipitate with $CaCO_3$ of coral skeleton, changes in response to biotic and abiotic factors e.g., temperature (Beck et al., 1992; Mitsuguchi et al., 1996;

Cohen et al., 2001; Gaetani and Cohen, 2006; Gaetani et al., 2011), calcification rates (Livingston and Thompson, 1971; Mitsuguchi et al., 2003), and particularly SW chemistry (Goreau, 1959; Swart, 1981; Shen and Boyle, 1987, 1988; Lough and Barnes, 1990; Fallon et al., 2002; Alibert et al., 2003; Giri et al., 2018). Thus coral skeletons provide an important archive on long-term changes in SW chemistry (e.g., Gothmann et al., 2015), together with fluid inclusions in marine evaporites (Hardie, 1996; Horita et al., 2002). The majority of previous coral trace element studies have concentrated on Sr/Ca, Mg/Ca, and Ba/Ca that have long residence time (1–10 Ma) and are part of the conservative elements that show a constant ratio in SW. Therefore, changes in their ratios were ascribed mainly to abiotic factors e.g., Sr/Ca and Mg/Ca for sea surface temperature (Beck et al., 1992; McCulloch et al., 1994; Cohen et al., 2001; Marshall and McCulloch, 2002; Fallon et al., 2003), Ba/Ca for SW barium, oceanic upwelling and rivers runoff (Lea et al., 1989; Sinclair, 2005; LaVigne et al., 2011, 2016). On longer time scales (>10 Ma) these elemental ratios depend on SW chemistry that has changed over the phanerozoic (Ries, 2004; Gothmann et al., 2015 and references therein). Contrary to Sr/Ca, Mg/Ca, and Ba/Ca the ratios of Li/Ca, K/Ca and Na/Ca in coral skeletons received much less attention (Amiel et al., 1973; Mitsuguchi et al., 2010; Mitsuguchi and Kawakami, 2012; Rollion-Bard and Blamart, 2015; Yoshimura et al., 2017; Marchitto et al., 2018) even though they are the major or minor elements in SW and have measurable abundances in the skeletons. Combining both Li/Ca and Mg/Ca increased the significance of Mg/Li as a paleothermometer in corals (Hathorne et al., 2013b; Montagna et al., 2014; D'Olivo et al., 2018; Marchitto et al., 2018; Cuny-Guirriec et al., 2019). Recently a new palaeoceanographic proxy for reconstructing Ca concentration in ancient SW was introduced based on Na/Ca in foraminiferal calcitic shells (Hauzer et al., 2018). It was shown that the partition of Na into foraminifera shells is primarily related to the SW Na/Ca ratio, with no resolvable temperature sensitivity. In view of this novel potential proxy in foraminifera, and the measurements of Na/Ca in recent and fossil coral skeletons (e.g., Bar-Matthews et al., 1993; Mitsuguchi et al., 2010; Gothmann et al., 2015; Yoshimura et al., 2017), in the present study, we investigated the effect of elevated Ca_{SW} concentration on the partition of Li, Na, Mg, K, Sr, and Ba into the skeletons of the hermatypic corals *Pocillopora damicornis* and *Acropora cervicornis*.

MATERIALS AND METHODS

Laboratory Culturing

Pocillopora damicornis and *Acropora cervicornis* mother colonies (raised for 8 years at Red Sea Fish Ltd. aquaculture facility) were cultured in the laboratory for 1 month before the experiment. The corals were held in 500 L recirculated system, running with filtered (1 μm polystyrene filter) Gulf of Eilat SW (salinity 40.65 ‰ diluted to a salinity of 35 ‰). Once a week, 10% of the system water was renewed to sustain chemical stability. The system was illuminated by LED lights (Reef Led 90, Red Sea) providing irradiance of 350 μmol photons m^{-2} s^{-1} for a light dark cycle of 12:12 h. Two experiments (labeled as exp1 and

exp2) were conducted for 80 and 87 days, respectively. Each experiment included four groups, cultured in different calcium concentrations (Ca_{SW}) of ∼ 10, 15, 20, and 25 mM (**Table 1**). In the first experiment, each group included five *P. damicornis* fragments (∼ 1 cm in length; mean wet weight 187 ± 11 mg fragment^{-1}) and five *A. cervicornis* (∼ 1 cm in length; mean wet weight 205 ± 12 mg fragment^{-1}). In the second experiment, each group included ten *P. damicornis* fragments obtained from different mother colony than those of the first experiment (∼ 1 cm in length; mean wet weight 201 ± 25 mg fragment^{-1}) (**Table 1**). Each fragment, after weighing, was glued with ethyl cyanoacrylate glue (Scotch super glue gel, 3M United States) to the center of a microscope glass slide (**Figure 1A**). The slides were wet weighed again in order to subtract the cyanoacrylate and primary fragment weight, to assess the new skeleton growth at the end of the experiment. Each group was placed in an individual 75 L aquarium system, running with modified Gulf of Eilat SW (S = 35 ‰, Ca_{SW} ∼10.3 mM). Corals were fed weakly with liquid coral food (Reef Energy, Red Sea) and the water of each aquarium was circulated through a foam fractioner to remove excess DOC and aerate intensively the water. The first group was set as a control, and the Ca_{SW} level in each experimental group was modified using $CaCl_2$ anhydrous powder (99.99% trace metal basis, Sigma Aldrich) to a final concentration of approximately 15, 20 and 25 mM (**Table 1**). The carbonate chemistry was not modified, except for the dilution of alkalinity and DIC proportionally to the salinity and exchange with air CO_2. During the experiments, the aquaria were tightly covered with transparent plastic foil to minimize evaporation and the salinity was monitored daily with conductivity meter (WTW, multi 3620 IDS, Tetracon 325C conductivity probe, $K = 0.475$ cm^{-1}). The salinity of the aquaria was slightly elevated by the addition of $CaCl_2$ (**Table 1**). All other experimental conditions were kept approximately the same. O_2 and pH were measured weekly using WTW multi 3620 IDS (WTW optical IDS dissolved oxygen FDO 925; WTW IDS pH- electrodes Sentix 940, calibrated with Radiometer NBS certified buffers and the values are reported using the NBS scale). Note that the system was essentially open to the atmosphere (with aeration) and this kept the O_2 and pH relatively constant (**Table 1**). Total alkalinity (A_T) measurements were done weekly using an automatic potentiometric Gran titration beyond the second endpoint (Schneider and Erez, 2006) of roughly 5 g SW sample accurately weighed. The acid used was 0.025M HCl (ACS reagent 37%, Sigma Aldrich), and the titrator used was Metrohm 848 Titrino plus (Metrohm, Switzerland) with a precision of 0.008 mmol/Kg. Standard seawater reference solution (Scripps Institution of Oceanography, batch 173) was used to calibrate the A_T measurements. Using CO2SYS (Pierrot et al., 2006) we calculated the relevant carbonate chemistry parameters, including $\Omega_{aragonite}$ taking into account the Ca concentrations and the salinity changes caused by the addition of anhydrous $CaCl_2$. The data is summarized in the **Supplementary Table 1**.

Calcification Rates Measurements

Once a week, water samples were taken from each aquarium for elemental analysis and alkalinity measurement (in experiment 2

TABLE 1 | Variable Ca_{SW} experimental conditions for coral culture (Ac is *Acropora cervicornis*; Pd is *Pocillopora damicornis*).

Exp (days)	Corals	Initial Ca_{SW} (mM)	Initial A_T (mM)	Temp (°C)	Salinity ‰	pH	DO (mg/L)	Survived corals	Final Ca_{SW} (mM)	Δ Ca_{SW} (%)	Final A_T (mM)	Calcification rate (mg gr^{-1} day^{-1})
1 (80)	5 Ac 5 Pd	10.3 ± 0.11	2.109 ± 0.018	25.3 ± 0.1	35 ± 0.1	8.11 ± 0.01	8.16 ± 0.01	5 Ac 5 Pd	10.06 ± 0.11	2.3		
	5 Ac 5 Pd	15.1 ± 0.15	2.105 ± 0.016	25.2 ± 0.1	35.3 ± 0.1	8.06 ± 0.01	8.17 ± 0.01	5 Ac 5 Pd	14.3 ± 0.14	5.4		
	5 Ac 5 Pd	20.1 ± 0.21	2.105 ± 0.017	25.2 ± 0.1	36.1 ± 0.1	8.06 ± 0.01	8.15 ± 0.01	5 Ac 5 Pd	19.6 ± 0.20	2.5		
	5 Ac 5 Pd	25 ± 0.25	2.103 ± 0.017	25.1 ± 0.1	36.9 ± 0.1	8.06 ± 0.01	8.14 ± 0.01	5 Ac -*	23.7 ± 0.23	5.2		
2 (87)	10 Pd	10.3 ± 0.12	2.106 ± 0.016	25.3 ± 0.1	35 ± 0.1	8.12 ± 0.01	8.14 ± 0.01	10 Pd	10.0 ± 0.17	2.5	1.502 ± 0.012	19.98 ± 2.93
	10 Pd	15.0 ± 0.15	2.106 ± 0.018	25.7 ± 0.1	35.2 ± 0.1	8.09 ± 0.01	8.17 ± 0.01	10 Pd	14.6 ± 0.11	2.7	1.367 ± 0.01	21.47 ± 1.05
	10 Pd	20.1 ± 0.21	2.107 ± 0.018	25.5 ± 0.1	36.1 ± 0.1	8.11 ± 0.01	8.14 ± 0.01	10 Pd	19.7 ± 0.16	2	1.488 ± 0.013	15.76 ± 0.23
	10 Pd	25.0 ± 0.24	2.106 ± 0.017	25.6 ± 0.1	36.8 ± 0.1	8.16 ± 0.01	8.14 ± 0.01	10 Pd*	24.7 ± 0.19	1.2	1.505 ± 0.014	10.23 ± 3.3

The values are average ± SD of all measurements during the experiments . (*) P. damicornis did not survive at Ca_{SW} of 25 mM and deceased after 2 days in experiment 1 and after 28 days in experiment 2.

only). Calcification rates were calculated from the difference in A_T measured at the beginning and the end of the experiment. Calcification rates were calculated according to the calcification equation (Schneider and Erez, 2006) and reported in units of μmol $CaCO_3$ gr^{-1} day^{-1} :

$$Calcification \left(\mu mol\ CaCO_3 gr^{-1}\ day^{-1}\right)$$
$$= \frac{\frac{\triangle A_T}{2} \times (V_{chamber} - V_{coral}) \times 1.0264}{T \times CWW} \quad (1)$$

Where $V_{chamber}$ (L), is the volume of the experimental chamber and V_{coral} (L) is the displacement volume of the coral, T is time in days and C_{WW} is the live coral wet weight (mg). Since culturing aquarium is ∼ 20,000 times larger than the coral fragments, the fragments volume is negligible.

Sample Preparation

At the end of the experiment (80 and 87 days), the slides were cleaned from any residual algae or bio-film with fine brush, without disturbing the newly grown horizontal section of the skeleton. After cleaning, the slides were wet weighed again and the tissue was removed with an airbrush and collected for further analysis. The slides with the remaining skeletons were treated with 5% NaOCl solution (Reagent grade 4.99%, Sigma Aldrich) for 8 h. to remove any residual organic tissue. Thereafter, the slides were thoroughly rinsed with DDW (18.18 MΩ cm) and finally moved to sonication bath containing DDW for 5 min. Finally, the slides were left for further 12 h. in DDW to remove residual SW and NaOCl solution from its cavities. After drying the slides in the oven (70°C for 24 h) the newly grown flat skeleton (**Figure 1B**) was carefully removed from the glass with a scalpel and spatula under a binocular. Part of the collected skeleton fragments were weighed, crushed and homogenized with a mortar and pestle. Roughly 50 mg of the homogenized skeleton powder (accurately weighed), was then dissolved in 10 ml 5% HNO$_3$ ($\geq$ 99.999 Trace metal basis, Sigma Aldrich) for elemental analysis.

Elemental Analysis SW and Skeleton

Trace elements concentrations in the newly grown skeleton and the SW were analyzed by ICP-OES (Spectro Arcos II, Ametek Germany) for major and minor elements (Li, Na, Mg, K, Ca, Sr, and Ba). All samples were measured in duplicates without any further dilution using specific methods developed for enriched Na and enriched Ca matrixes. SW Elemental concentrations were determined from calibration curves validated by external standards (OSIL IAPSO standard P139, United Kingdom and High Purity Standards SW reference, United States) and by an internal Sc standard, once every 5 samples. Coral skeleton's elemental analysis was determined from calibration curves generated from 5 multi element standard solutions containing 2000 mg/L Ca as matrix to match the CaCO$_3$ samples (Custom blends, High Purity Standards, United States). The Standard solutions minor and trace elements ranges included the average concentration of the elements in coral skeletons as described in the literature (**Table 2**). Complete analytical conditions
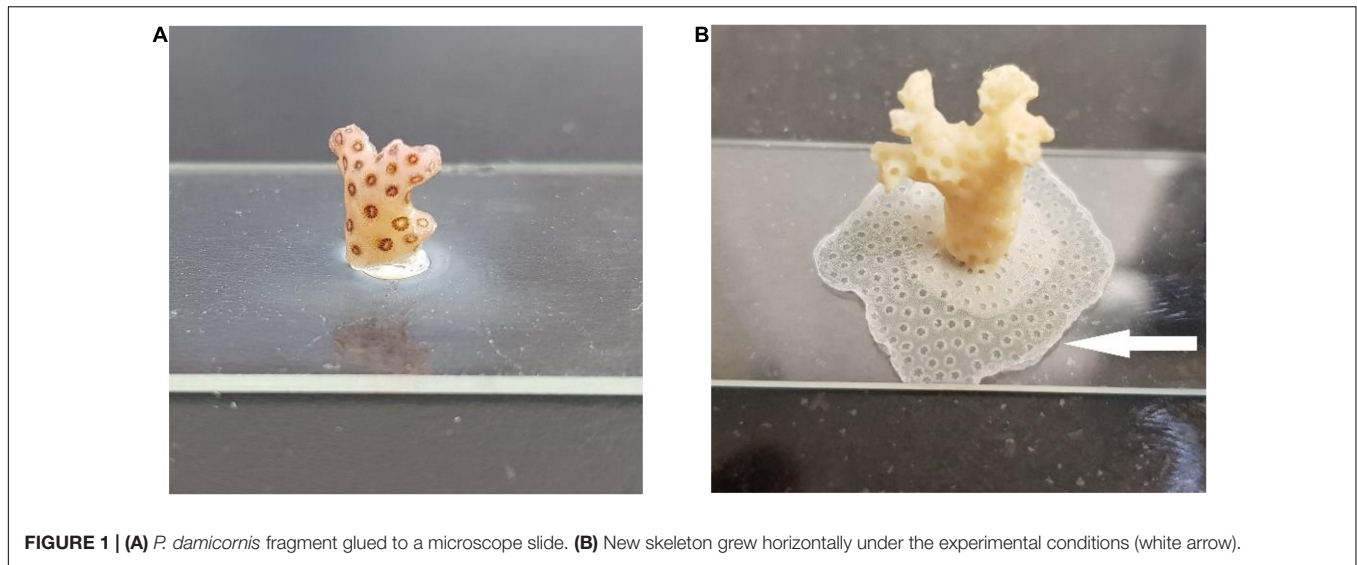
FIGURE 1 | (A) *P. damicornis* fragment glued to a microscope slide. **(B)** New skeleton grew horizontally under the experimental conditions (white arrow).

including wavelengths, interferences, standard deviations and errors, as well as ICP-OES parameters are summarized in the **Supplementary Table 2**. The standard errors of the ratios to Ca in the SW and corals were Li/Ca = 0.927%, Na/Ca = 1.01%, Mg/Ca = 1.01%, K/Ca = 1.03%, Sr/Ca = 0.906%, Ba/Ca = 1.19% calculated from the duplicates.

Statistical Analysis

The influence of changing Ca_{SW} on the partition of elements in the coral skeleton was determined by linear correlation using Pearson correlation coefficients (r). *P*-Values below 0.05 were considered statistically significant unless otherwise noted. The variance in calcification rates and the variance in D_{El} between the two coral species and literature inorganic aragonite were determined by one-way ANOVA (Tukey-Kramer). Statistical analyses were performed using Origin Pro software for Windows (Version 2017, OriginLab, Inc.).

RESULTS

Calcification Rate

Total growth and calcification rates were measured only in experiment 2 and were estimated by cumulative alkalinity depletion and by the change in the total coral fragments weight. Both methods were well correlated ($R^2 = 0.989$; $p < 0.01$) for *P. damicornis* fragments that were grown in Ca_{SW} of 10.3, 15.0, and 20.1 Mm (**Table 1** and **Figure 2**). Based on weekly A_T measurements, the corals calcification rates were quite uniform throughout the experiment despite the decrease in A_T (**Supplementary Table 1** and **Supplementary Figure 1**). The average calcification rates were significantly different between the Ca groups with highest daily $CaCO_3$ addition at Ca_{SW} of 15.0 mM (21.47 ± 1.05 mg gr^{-1} day^{-1}), followed by 10.3 mM (19.98 ± 2.93 mg gr^{-1} day^{-1}), 20.1 mM (15.76 ± 0.23 mg gr^{-1} day^{-1}) and the lowest $CaCO_3$ addition was observed at 25.0 mM (10.23 ± 3.3 mg gr^{-1} day^{-1}) (**Figure 2**). Further to the low calcification rates, at Ca_{SW} of 25.0 mM corals fragments did not survive beyond the 28th day into the experiment. Note, however, that alkalinity depletion in this high calcium experiment was 5 times greater than the weight increase caused by inorganic precipitation of $CaCO_3$ in the aquarium. CO2SYS calculations showed that $\Omega_{aragonite}$ has changed during the experiment as A_T decreased. While this could have affected the values we report, we have no way to separate the effects of $\Omega_{aragonite}$ on the results using our sampling method. Therefore, our results represent an average of the $\Omega_{aragonite}$ for the entire experiment.

Skeleton Chemistry and Distribution Coefficients

Corals skeletal El/Ca (El/Ca_{Coral}) of the cultured groups and the culturing SW El/Ca (El/Ca_{SW}), are presented in **Table 2** and **Figure 3**. The distribution coefficients for these elements (D_{El}) are the slopes of the linear regressions in **Figure 3**. These experimental values are compared to published natural and experimental coral values and to inorganic experimental values, are shown in **Table 3**. The natural coral D_{El} were normalized for $25 \pm 2°C$ as both Sr and Mg are influenced by temperature. All conservative elements (Li, Na, Mg, K, Sr, and Ba) in the coral skeleton (El/Ca_{coral}) were positively correlated with Ca_{SW} for both species (**Figure 3**). The regression curves are linear, cross the origin and are highly significant with R^2 values of 0.99–0.98 (ρ values lower than 0.01 or 0.001; **Figure 3**). The distribution coefficients (D_{El}) are therefore constant and equal to the slope of El/Ca_{coral} and El/Ca_{SW} line. It is significant that the two separate experiments gave very close values for *P. damicornis*. which could be fitted with one linear equation. For both coral species, the obtained D_{El} values for Li, Mg, Na and K were lower than 1, in the range of 10^{-4} to 10^{-3}, while for Sr and Ba, D_{El} values were higher than 1 (**Table 3**). D_{El} values between the two species shows significant difference (ρ > 0.05) between *A. cervicornis* and *P. damicornis*, with higher values for *A. cervicornis* for most elements excluding Ba

TABLE 2 | El/Ca ratios in SW, new skeleton precipitated under the experimental conditions and the comparison to reported ratios in the literature.

El/Ca	Exp	Ca$_{SW}$ (mM)	SW	*A.cervicornis*	*P.damicornis*	Lit. corals (10.3 mM 25 ± 3°C)	Average lit. corals	References
Li/Ca	1	10.3	2.54 ± 0.02	5.24 ± 0.17	4.73 ± 0.2	6.27 (*Porites sp.*)	6.38 ± 1.3	Cuny-Guirriec et al., 2019
		15.1	1.75 ± 0.02	3.56 ± 0.2	3.11 ± 0.2	5.37 (*S. siderea*)		Fowell et al., 2016
		20.1	1.19 ± 0.03	2.90 ± 0.19	2.40 ± 0.2	6.97 (*Acro. sp.*)		Montagna et al., 2014
		25.0	1.03 ± 0.02	2.10 ± 0.1		6.19 (*Porites sp.*)		Hathorne et al., 2013a
	2	10.3	2.48 ± 0.02		4.76 ± 0.1			
		15.0	1.70 ± 0.02		3.26 ± 0.19			
		20.1	1.25 ± 0.01		2.37 ± 012			
		25.0	0.99 ± 0.01		1.90 ± 0.09			
Na/Ca	1	10.3	46.1 ± 0.8	23.8 ± 0.88	20.4 ± 0.75	22.5 (*A. digitifera*)	20.80 ± 1.1	Bell et al., 2017
		15.1	32.3 ± 0.3	16.2 ± 0.65	13.5 ± 0.89	21 (several sp.)		Yoshimura et al., 2017
		20.1	23.6 ± 0.2	12.2 ± 0.95	8.0 ± 0.66	19.55 (*P. lutea*)		Rollion-Bard and Blamart, 2015
		25.0	19.5 ± 0.2	8.4 ± 0.71		20 (several sp.)		Mitsuguchi et al., 2010
	2	10.3	46.3 ± 0.5		18.8 ± 0.75			
		15.0	31.7 ± 0.3		12.5 ± 0.75			
		20.1	23.5 ± 0.2		9.1 ± 0.63			
		25.0	18.7 ± 0.2		6.1 ± 0.3			
Mg/Ca	1	10.3	5.36 ± 0.05	6.88 ± 0.41	5.14 ± 0.07	4.9 (*P. damicornis*)	4.49 ± 0.26	Giri et al., 2018
		15.1	3.74 ± 0.03	4.95 ± 0.25	3.16 ± 0.13	4.2 (*Porites sp.*)		Hathorne et al., 2013a
		20.1	2.72 ± 0.02	3.63 ± 0.21	2.27 ± 0.18	4.5 (several sp.)		Mitsuguchi et al., 2010
		25.0	2.23 ± 0.03	2.61 ± 0.18		4.38 (*P. lutea*)		Allison and Finch, 2007
	2	10.3	5.3 ± 0.02		5 ± 0.09			
		15.0	3.63 ± 0.02		3.32 ± 0.12			
		20.1	2.68 ± 0.01		2.12 ± 0.06			
		25.0	2.14 ± 0.01		1.69 ± 0.05			
K/Ca	1	10.3	1.03 ± 0.04	0.21 ± 0.01	0.18 ± 0.01	0.171 (*Porites sp.*)		Mitsuguchi and Kawakami, 2012
		15.1	0.72 ± 0.08	0.13 ± 0.01	0.12 ± 0.007			
		20.1	0.52 ± 0.13	0.1 ± 0.005	0.08 ± 0.005			
		25.0	0.4 ± 0.22	0.07 ± 0.004				
	2	10.3	1.01 ± 0.05		0.17 ± 0.01			
		15.0	0.69 ± 0.09		0.12 ± 0.01			
		20.1	0.5 ± 0.07		0.08 ± 0.001			
		25.0	0.39 ± 0.08		0.06 ± 0.003			
Sr/Ca	1	10.3	8.87 ± 0.08	9.6 ± 0.19	9.67 ± 0.23	9.5 (*P. damicornis*)	9.14 ± 0.26	Giri et al., 2018
		15.1	6.17 ± 0.05	6.0 ± 0.22	6.72 ± 0.37	9.26 (*A. digitifera*)		Bell et al., 2017
		20.1	4.48 ± 0.04	5.24 ± 0.31	4.87 ± 0.17	8.84 (*Porites sp.*)		Hathorne et al., 2013a
		25.0	3.7 ± 0.03	4.15 ± 0.29		9 (several sp.)		Mitsuguchi et al., 2010
	2	10.3	8.69 ± 0.02		9.59 ± 0.22			
		15.0	5.94 ± 0.02		6.61 ± 0.36			
		20.1	4.38 ± 0.01		5.1 ± 0.21			
		25.0	3.49 ± 0.01		4.37 ± 0.39			
Ba/Ca	1	10.3	4.83 ± 0.05	7.59 ± 0.24	8.43 ± 0.13	12.4 (*F. fargum*)	7.35 ± 3.1	Gonneea et al., 2017
		15.1	3.37 ± 0.03	5.07 ± 0.1	6.2 ± 0.14	4.72 (*P. lobata*)		LaVigne et al., 2016
		20.1	2.4 ± 0.03	3.05 ± 0.09	4.37 ± 0.08	7.5 (*Porites sp.*)		Hathorne et al., 2013b
		25.0	1.97 ± 0.02	2.64 ± 0.12		4.8 (*P. lutea*)		Allison and Finch, 2007
	2	10.3	4.83 ± 0.06		8.68 ± 0.57			
		15.0	3.31 ± 0.03		5.99 ± 0.22			
		20.1	2.44 ± 0.02		4.54 ± 0.18			
		25.0	1.95 ± 0.02		3.85 ± 0.28			

El/Ca$_{SW}$ ratios are given in mol mol^{-1} for Na, Mg and K, mmol mol^{-1} for Li and Sr, and μmol mol^{-1} for Ba. El/Ca$_{coral}$ ratios are given in mmol mol^{-1} for Na, Mg, K and Sr, and μmol mol^{-1} for Li and Ba.

and Sr (**Figure 3**). The significant difference between species is seen also for literature values (see values and references in **Table 3**). Coral D$_{El}$ values show similar values for most elements as determined from inorganic experiments, excluding Li that shows D$_{inorganic}$ > D$_{Coral}$ and K that shows D$_{inorganic}$ < D$_{Coral}$ (**Figure 4**). These small but significant differences between the inorganic D$_{El}$ values and the corals in our and other experiments may well be explained using Rayleigh fractionation model (see discussion).

DISCUSSION

Ca$_{SW}$ Influence on Calcification Rates

A few studies have investigated the effect of Ca$_{SW}$ on corals calcification rates (Yamazato, 1966; Chalker, 1976; Swart, 1979). They found that calcification rates increased with Ca$_{SW}$ but Giri et al. (2018) did not observe such effect. This study demonstrates that calcification in *P. damicornis* increased up to 15 mM, but further increase to 20.1 and 25 mM decreased the
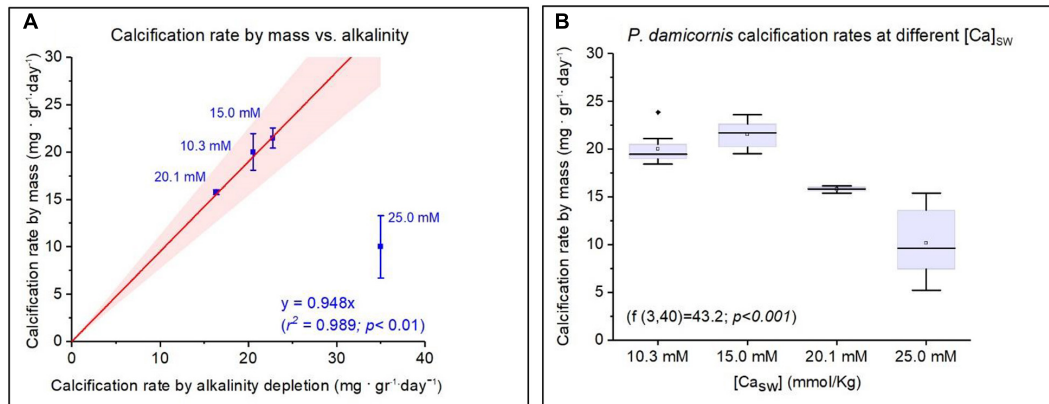
FIGURE 2 | Calcification rates of *Pocillopora damicornis* under variable Ca$_{SW}$. **(A)** Calcification rate measured by mass addition compared to alkalinity depletion. Corals cultured under Ca$_{SW}$ of 25 mM are excluded from the regression due to mortality on 28th day. **(B)** The Mean, median, and deviations of growth rate as a function of Ca$_{SW}$ with maximum values showed at 15 mM (21.5 ± 1.05 mg. gr^{-1}. day^{-1}).

calcification (**Figure 2**). Furthermore, it seems that the highest Ca$_{SW}$ concentration caused severe stress that led to mortality of all corals after 28 days (experiment 2). In experiment 1 all the *P. damicornis* fragments deceased after 2 days in 25 mM Ca but *A. cervicornis* fragments survived at that concentration but the growth rates were not measured and visual observation of the horizontal growth was minimal. The inhibitory effect of high Ca$_{SW}$ (> 15 mM) on calcification was documented also for *A. cervicornis, A. formosa* and *A.squamosa* (Chalker, 1976; Swart, 1979). Similar observations were made on the foraminifer *O. ammonoides* (Hauzer et al., 2018). Our experiment suggests that calcification rates do not influence coral D$_{El}$ for Li, Na, Mg, K, Sr, and Ba.

The Effect of El/Ca$_{SW}$ on El/Ca$_{coral}$

It is well documented that alkaline earth metals (Mg, Sr, and Ba) coprecipitate into corals skeletons as cations substituting for Ca (Livingston and Thompson, 1971; Amiel et al., 1973; Howard and Brown, 1984; Shen and Boyle, 1987, 1988; Sholkovitz and Shen, 1995; McCulloch et al., 2003). Alkali elements (Na, K, and Li) in coral skeletons were also measured (Mitsuguchi et al., 2010; Mitsuguchi and Kawakami, 2012; Hathorne et al., 2013a,b; Rollion-Bard and Blamart, 2015; Yoshimura et al., 2017). However, except for the early work of Swart (1979; 1981 for Sr, Mg, and Na) and the recent work of Giri et al. (2018 for Sr and Mg), we present here the most comprehensive experimental study to determine D values for Li, Na, Mg, K, Sr, and Ba in coral skeleton by changing El/Ca$_{SW}$. This experiment was carried out on two species, *P. damicornis* and *A. cervicornis*, over a large range of Ca$_{SW}$ (10.3–25 mM). El/Ca$_{coral}$ and El/Ca$_{SW}$ in the control group (10.3 mM), were similar to those from field collected corals (**Table 2**) except for Li/Ca$_{coral}$ where our values ($\sim$ 5 μmol mol^{-1}) were lower than average field data (6.38 ± 1.3 μmol mol^{-1}). The source of this discrepancy is not clear but part of it may be related to the analytical procedure of the skeleton. It is also possible that this may be temperature related response of the two species used in this experiment

(Montagna et al., 2014; D'Olivo et al., 2018; Cuny-Guirriec et al., 2019). For all elements we observe highly significant positive correlation between El/Ca$_{coral}$ and El/Ca$_{SW}$ under increased Ca$_{SW}$ (**Table 2** and **Figure 3**). These results agree with previous study showing such correlations under variable Ca$_{SW}$ (Giri et al., 2018). The pioneering work of Swart (1981) who cultured four species under four variable Ca$_{SW}$ and measured Sr, Mg, and Na in their skeletons agrees with our results, mainly for Sr (given the use of EPMA for the skeletal analysis with low sensitivity for concentrations lower than 1%). In inorganic precipitation experiments for aragonite, the El/Ca ratio increased for the alkali ions Li, Na, and K, with increasing their concentrations relative to Ca in the parent solution (Kitano et al., 1975; Okumura and Kitano, 1986). These results agree with our data for both species (**Table 2** and **Figure 3**). However, the actual concentrations in the aragonite were similar to the coral values only for Na while for Li the inorganic values were higher, and for K, they were lower. Given that the inorganic experiments were not done in seawater and that kinetic effects are also possible there is a general agreement between the corals and the inorganic experiments.

D$_{El}$ Values

For all the elements measured in this study (Li, Na, Mg, K, Sr, and Ba) we observe significant linear regression between El/Ca$_{coral}$ and El/ Ca$_{SW}$ going through the origin (**Figure 3**) suggesting constant distribution coefficients in their aragonitic skeletons. Although D$_{El}$ values varied between *P. damicornis* and *A. cervicornis,* the values are in close proximity to those calculated from field values for various coral species and laboratory inorganic experiments (**Figures 3, 4** and **Table 3**). While D$_{El}$ for Na, Mg, Sr, and Ba were consistent with the average D$_{El}$ of inorganic aragonite, D$_{Li}$ for both species were significantly lower than the inorganic ones while D$_K$ was significantly higher. Note, however, that all our experiments were done at constant temperature of 25.4 ± 0.2°C while natural corals are exposed to $\sim$ 10°C variability in their natural environment and D$_{Sr}$ and D$_{Mg}$ are temperature sensitive. For our corals, D$_{Ba}$ was 1.79 ± 0.02
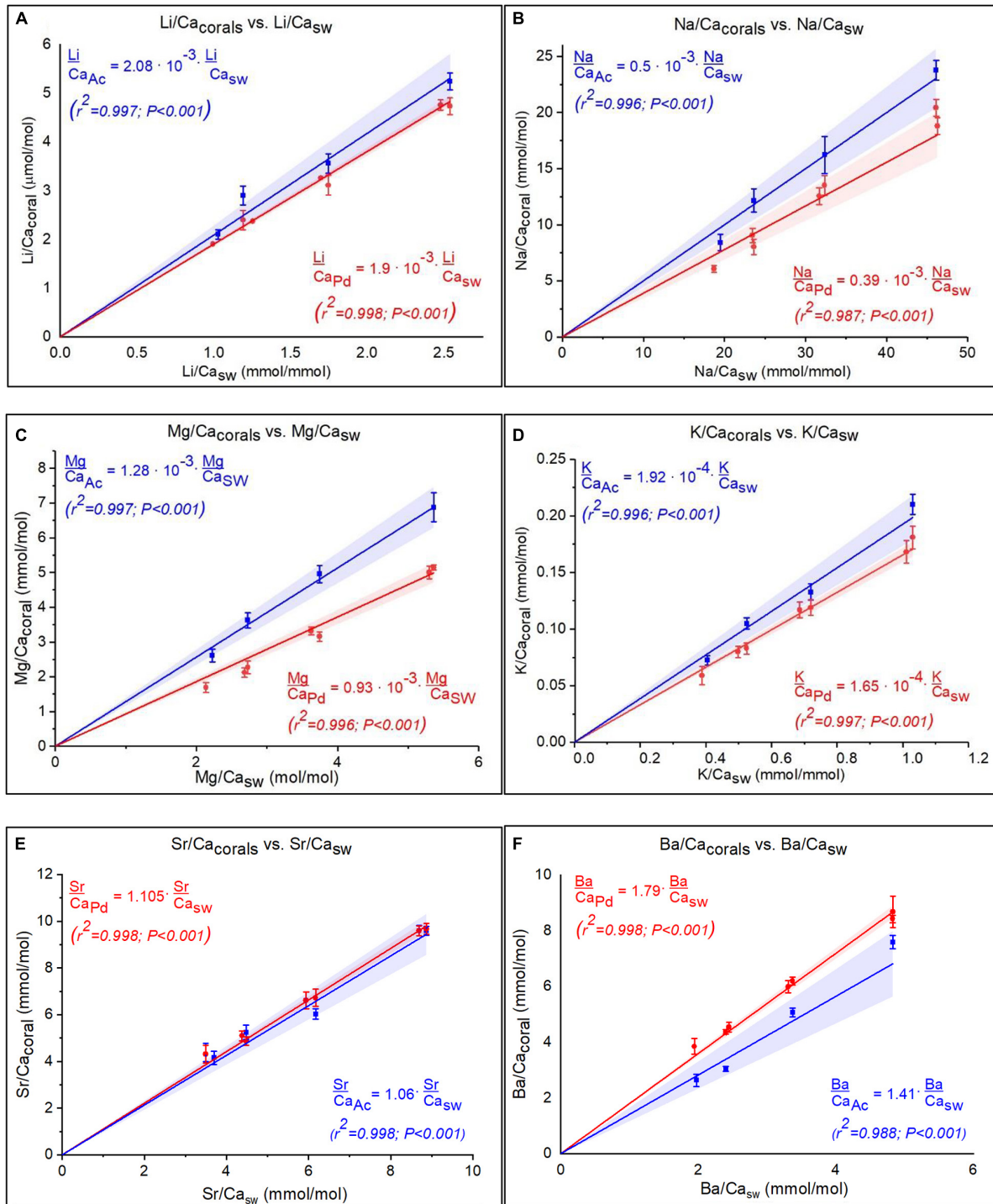
FIGURE 3 | (A–F) El/Ca$_{coral}$ as function of El/Ca$_{SW}$ under variable Ca$_{SW}$ for both species, for six elements (*Pocillopora damicornis* in red and *Acropora cervicornis* in blue). The regressions show linear positive correlations for all elements. Note that for *P. damicornis* data for two separate experiment are shown with slight differences that are within the error on the replicates. The linear regressions that cross the origin imply constant distribtion coefficient for all elements. The shaded area is the 95% confident bands.

and 1.41 ± 0.08 for *P. damicornis* and *A. cervicornis*, respectively. D$_{Ba}$ for *Favia fargum* was determined experimentally by Gonneea et al. (2017) by changing Ba/Ca$_{SW}$ over a range of 7.3 to 43.9

μmole mole^{-1} and temperatures of 22.4 to 27.7°C. Their average D$_{Ba}$ was 1.75 ± 0.14 over all the experimental range (temperature and Ba/Ca) and 1.76 ± 0.18 in the temperature experiment at

TABLE 3 | D_{El} values for experimental corals compared to various coral species (field collected and experimental normalized to 25 ± 3°C) and inorganic studies.
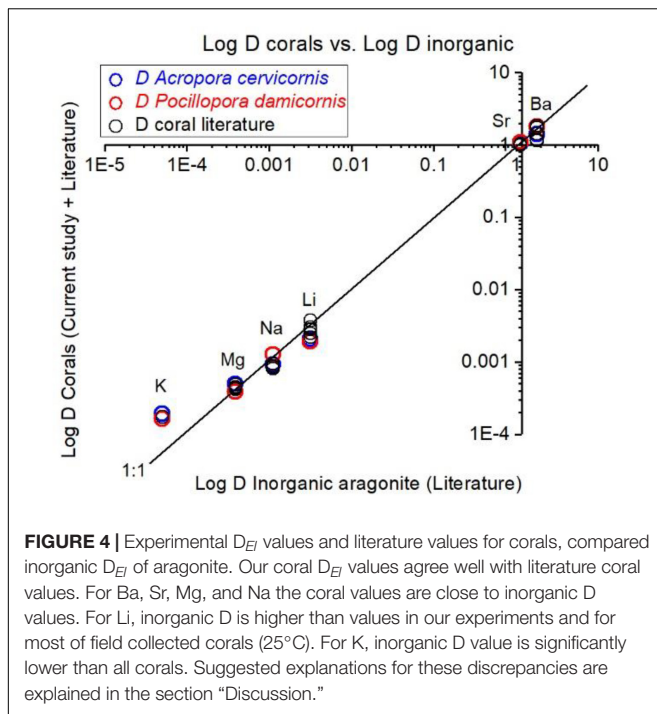
D	A. cervicornis	P. damicornis	Lit. corals	Average lit. coral	Lit. inorganic	Average lit. inorganic	References
$D_{Li}(\times 10^{-3})$	2.08 ± 0.08	1.9 ± 0.02	2.20	2.49 ± 0.01	3.15	3.15 + 0.06	Marriott et al., 2004a,b
			2.46				Cuny-Guirriec et al., 2019
			2.11				Fowell et al., 2016
			2.79				Montagna et al., 2014
			3.00				Hathorne et al., 2013a
$D_{Na}(\times 10^{-3})$	0.5 ± 0.02	0.39 ± 0.02			0.37	0.385 ± 0.001	Kitano et al., 1975
					0.4		Kinsman, 1970
			0.48	0.446 ± 0.0003			Bell et al., 2017
			0.45				Yoshimura et al., 2017
			0.42				Rollion-Bard and Blamart, 2015
			0.43				Mitsuguchi et al., 2010
$D_{Mg}(\times 10^{-3})$	1.28 ± 0.03	0.93 ± 0.02		0.87 ± 0.05	0.89	0.89	AlKhatib and Eisenhauer, 2017
			0.95				Giri et al., 2018
			0.81				Hathorne et al., 2013a
			0.87				Mitsuguchi et al., 2010
			0.85				Allison and Finch, 2007
$D_{K}(\times 10^{-4})$	1.92 ± 0.06	1.65 ± 0.02			0.5	0.5	Okumura and Kitano, 1986
			1.74	1.74			Mitsuguchi and Kawakami, 2012
D_{Sr}	1.06 ± 0.03	1.105 ± 0.01			1.11	1.13 ± 0.01	AlKhatib and Eisenhauer, 2017
					1.13		Gaetani and Cohen, 2006
					1.15		Kinsman and Holland, 1969
			1.01	1.01 ± 0.02			Giri et al., 2018
			0.99				Hathorne et al., 2013a
			1.01				Mitsuguchi et al., 2010
D_{Ba}	1.41 ± 0.08	1.79 ± 0.02			1.59	1.85 ± 0.3	Dietzel et al., 2004
					2.11		Gaetani and Cohen, 2006
			1.76	1.5 ± 0.31			Gonneea et al., 2017
			1.18				LaVigne et al., 2016
			1.86				Hathorne et al., 2013a
			1.19				Allison and Finch, 2007

Ba/Ca$_{SW}$ closest to our experimental value. Yamazaki et al. (2021) measured D_{Ba} for initial settled polyps of *A. gutatus* as a function of Ba concentration and light intensity. Their D_{Ba} values were higher than all previous values ranging from 1.3 to 7.5 with higher values at lower light levels. In the latter paper, however (their **Figure 1** and **Table 1**) the reported D_{Ba} values cannot be considered as distribution coefficients, because the linear plots of El/Ca$_{Coral}$ vs El/Ca$_{SW}$ have significant intercept with the Y axis. Surprisingly, if we combine all the data of this experiment and force the linear regression through the origin, we get a single D_{Ba} value of 1.91 ± 0.18 with R^2 of 0.88. This value is close to those reported in previous studies (**Table 3**). The behavior of the distribution coefficient between species relative to the inorganic ones and relative to each other may be well explained using a Rayleigh fractionation model as we show below.

Rayleigh Fractionation

Several geochemical models have been suggested to explain the elemental and isotopic composition of biogenic skeletal carbonates, based on thermodynamic and kinetic principles. These models in combination with biological calcification mechanisms can eventually be used to explain the chemical and isotopic composition of marine calcifyers in order to use them as environmental proxies (McConnaughey, 1989; Elderfield et al., 1996; Cohen et al., 2001; Gaetani and Cohen, 2006;

Sinclair et al., 2006; Gagnon et al., 2007, 2012). The geochemical and biological models demonstrate that in corals, calcification proceeds from a calcifying fluid within semi-closed privileged space below the calicoblastic epithelium, often defined as the Extra Cellular Fluid (ECF). The major component of this fluid is SW that is supplied to the ECF by either paracellular pathways (Tambutte et al., 2012; Venn et al., 2020) or by another as yet unknown mechanism. Throughout calcification, some elements with $D_{El} > 1$ (e.g., Ba and Sr) are depleted in the ECF relative to Ca and these elements may be enriched in the skeleton. Other elements with $D_{El} < 1$ (e.g., Mg, Na, K, and Li) are enriched in the ECF while CaCO$_3$ is precipitated because more Ca is consumed relative to these elements. As a result, the apparent distribution coefficients measured in corals for these elements should be higher than their inorganic ones. This process can be described by a Rayleigh fractionation process, that explains the biogenic distribution coefficients of these elements in coral skeleton. This model was first introduced by Elderfield et al. (1996) to explain the variability of trace elements in foraminifera, and afterward was readily used also for corals (Gaetani and Cohen, 2006; Gagnon et al., 2007; Gaetani et al., 2011; Sinclair, 2015; Giri et al., 2018). The Rayleigh model was widely used to explain Ca and Sr isotopes in corals (Raddatz et al., 2013; Inoue et al., 2015; Gothmann et al., 2016). The use of Rayleigh model to explain the distribution coefficients of all elements in our study

FIGURE 4 | Experimental D_{El} values and literature values for corals, compared inorganic D_{El} of aragonite. Our coral D_{El} values agree well with literature coral values. For Ba, Sr, Mg, and Na the coral values are close to inorganic D values. For Li, inorganic D is higher than values in our experiments and for most of field collected corals (25°C). For K, inorganic D value is significantly lower than all corals. Suggested explanations for these discrepancies are explained in the section "Discussion."

is very well justified, mainly because we measured experimentally the D values for two elements with D > 1 (Ba and Sr) and four elements with D < 1 (Li, Na, Mg, and K). In **Figure 5** we show the expected Rayleigh functions for all six elements based on their inorganic D_{El} values (**Table 3**), as a function of f - the fraction of Ca utilized from the closed calcifying reservoir (as fully explained by Elderfield et al., 1996), where:
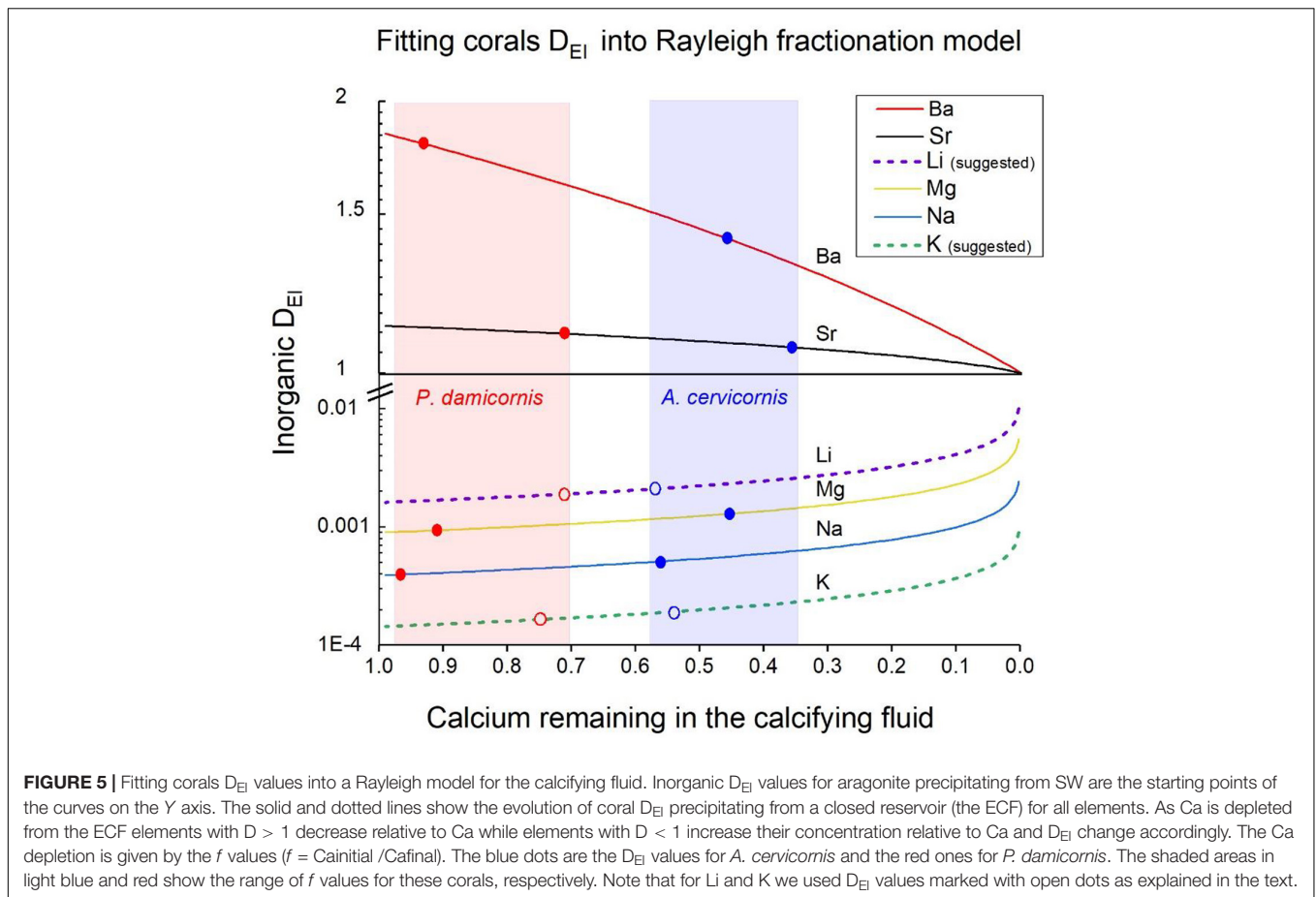
$$D_{Coral} = (1 - f^{D\ inorg.})/(1 - f) \qquad (2)$$

Next, we fitted our measured D_{Coral} values into Rayleigh fractionation curves for the two species (*P. damicornis* and *A. cervicornis*) as shown (**Figure 5**). Based on this model we conclude that *P. damicornis* behaves as relatively open system with f values between 0. 98 and 0.7 and for *A. cervicornis* f values range between 0.58 and 0.35 i.e., behaving as a half-open system for the various elements (**Figure 5**). For both species we marked the f ranges in light blue and red shades (**Figure 5**). As discussed above, D_{El} values of corals in experimental studies and many field studies show values that are very similar to our two species (normalized to 25°C). Unfortunately, the inorganic experimental D_{El} values show relatively wide range either similar to the corals or larger (e.g., Sr, Mg, **Table 3** and **Figure 4**). For the Rayleigh model we used inorganic average values for Na, Sr and Ba (**Table 3**) for Mg we used the values of AlKhatib and Eisenhauer (2017). For two elements (Li and K) the reported inorganic D value fall out or the Rayleigh model shown in **Figure 5**: For Li the inorganic D value of 3.15×10^{-3} (Marriott et al., 2004a,b) is significantly higher than both corals (2.08×10^{-3} and 1.9×10^{-3}) and all the field corals (**Figures 3, 4**). But D_{Li} of Okumura and Kitano (1986) is 0.27×10^{-3} and the average D_{Li} of both inorganic experiments is 1.7×10^{-3}, a value

that fits well our Rayleigh calculations (see below). Inorganic D_K is 0.5×10^{-4} (Okumura and Kitano, 1986) a factor of 3 lower than the coral's values (1.65×10^{-4}, 1.92×10^{-4}) yielding f values that are close to 1 for both species. We propose two possibilities to resolve the discrepancy in Li and K between the reported inorganic values and our Rayleigh model: The first is that D inorganic values for Li and K are inaccurate and should be modified. If we try to fit both species into their Rayleigh Ca utilization ranges, we need to assume D_{Li} to be 0.16×10^{-3} instead of 0.315×10^{-3} (Marriott et al., 2004b) i.e., a factor of 2 lower. We note that our Li/Ca$_{coral}$ values (~5 μmol mol^{-1}) are lower compared with average literature field corals (6.38 μmol mol^{-1}) as we discussed above (**Table 3**). Even if we take this field corals average it will require a lower inorganic D_{Li} (~ 0.28 $\times 10^{-3}$) to explain the field coral values. For potassium the inorganic D_K value needs to be 1.43×10^{-4} instead of 0.5×10^{-4} i.e., 3 times higher than reported (Okumura and Kitano, 1986) in order to fit our Rayleigh model (Open markers in **Figure 5**). A second possibility is that the corals concentrate K and reduce Li in the ECF. This explanation opens wide possibilities that cannot be resolved without further experiments dedicated to this specific question. For the present study, we chose the first possibility and suggest that more experimental work is needed to determine accurately D_{Li} and D_K in inorganic experiments. If we use the D_{El} values proposed above, we get a good fit to the Rayleigh model for both species (**Figure 5**) as well as for all the other elements (Na, Mg, Sr, and Ba). The use of the Rayleigh model to explain the various D_{El} for the two species strongly support the hypothesis that SW is the main source for ions at the ECF (Gaetani and Cohen, 2006; Gagnon et al., 2007; Gothmann et al., 2016; Giri et al., 2018). While these studies do not specifically spell this out, their use of the Rayleigh models, like ours, starts from SW composition at the ECF. Most of the Ca ions needed for calcification is available directly from SW as Ca$_{SW}$ = 10.3 mM, and similarly part of the DIC (DIC$_{SW}$ = 2 mM, see discussion on modification of DIC below). Bulk transport of SW is also the source for all the other trace and minor elements found in the skeleton, as can be concluded from their fit to the Rayleigh model. Obviously, the SW in the ECF is replenished once it is depleted of Ca and CO$_3$ during the calcification process. More evidence for SW at the ECF is discussed in relation to the calcification process is given below.

Implications for Calcification Mechanisms in Corals

We propose that the fluid in the ECF is essentially SW that arrives to the privileged calcifying space below the calicoblastic epithelium, probably by paracellular pathways (Tambutte et al., 2012). One of the main supports for bulk SW transport to the ECF is coming from observations on Calcein labeling of coral skeletons (Braun and Erez, 2004; Erez and Braun, 2007; Tambutte et al., 2012). Calcein, is a membrane-impermeable fluorescent dye and its presence in large parts of the ECF indicates the presence of SW. The newly precipitated coral aragonite crystals that grow in the flat coral preparation (e.g., Raz-Bahat et al., 2006) are homogeneously labeled with Calcein and provide

FIGURE 5 | Fitting corals D_{EI} values into a Rayleigh model for the calcifying fluid. Inorganic D_{EI} values for aragonite precipitating from SW are the starting points of the curves on the Y axis. The solid and dotted lines show the evolution of coral D_{EI} precipitating from a closed reservoir (the ECF) for all elements. As Ca is depleted from the ECF elements with D > 1 decrease relative to Ca while elements with D < 1 increase their concentration relative to Ca and D_{EI} change accordingly. The Ca depletion is given by the f values (f = Cainitial /Cafinal). The blue dots are the D_{EI} values for *A. cervicornis* and the red ones for *P. damicornis*. The shaded areas in light blue and red show the range of f values for these corals, respectively. Note that for Li and K we used D_{EI} values marked with open dots as explained in the text.

an evidence that bulk SW is actually the calcifying fluid (e.g., Ohno et al., 2017; Venn et al., 2020). Further support of SW at the ECF is coming from the experiment of Gagnon et al. (2012) that studied the short-term incorporation of isotopes of Ca, Sr, Ba, and Tb into coral skeleton. The measurements using nanoSIMS showed that SW bulk transport is the main source of Ca (and all the other elements) in the ECF. Other pathways that can bring SW to the ECF such as mega-pinocytosis or SW vacuoles as seen in foraminifera (Bentov et al., 2009), or other leaky pathways are also possible. These may include tissue retraction between polyps as seen at the start of polyp bailout (e.g., Domart-Coulon et al., 2004), or through skeleton exposure due to physical or biological tissue damage (e.g., parrotfish injuries, worms, and mollusks burrowing). There are three major modifications of the SW at the ECF which are: (1) an increase in pH (e.g., Al-Horani et al., 2003; Venn et al., 2011; Gagnon, 2013). (2) Accumulation of DIC as a result of CO_2 diffusion and/or bicarbonate transport (e.g., McCulloch et al., 2012, 2017; Sevilgen et al., 2019). (3) Release of organic macromolecules (perhaps including proteins) that serve as an organic matrix which directs the growth patterns, texture, and crystallography of the skeleton (Allemand et al., 1998; Tambutté et al., 2011). Based on our Rayleigh model *P. damicornis* is more open system i.e., it utilized lower fraction of its Ca (∼ 20 %) while *A. cervicornis* behaves as a semi-closed system that utilizes higher fraction of Ca from its ECF (∼50%). Both

strategies may influence the calcification rates: *A. cervicornis* may invest more energy in elevating the pH and DIC and therefore can utilize higher fraction of the SW Ca (**Figure 5**). *P. damicornis* on the other hand, exchanges its SW at the ECF faster and its pH and DIC elevations may therefore be lower. This may explain the difference in their calcification rates suggesting that the closed system strategy of *A. cervicornis* is more efficient. Based on the growth of *P. damicornis* in the second experiment, and the total growth in the first experiment we can estimate that *A. cervicornis* grew at least twice faster than *P. damicornis* (see **Supplementary Table 3**).

Independent evidence for our Rayleigh calcification model comes from B/Ca and $\delta^{11}B$ in laboratory and field studies. $\delta^{11}B$ is used to calculate the pH and B/Ca to calculate the CO_3 concentration at the ECF. These two parameters of the carbonate system allow calculation of the DIC in the calcifying fluid (Allison et al., 2014; DeCarlo et al., 2017, 2018). In addition, DeCarlo et al. (2017) suggested that Raman spectra of the skeleton correlate well with $\Omega_{aragonite}$ and this allows to calculate the Ca at the ECF. Similar approach was used by Ross et al. (2019) where the authors compared skeleton derived chemistry at the ECF for different species collected in several locations in Australia. In both studies, the data on *Acropora* species and *P. damicornis*, support our results i.e., *Acropora* calcifies faster than *P. damicornis*. Furthermore, their estimated DIC and $\Omega_{aragonite}$ yielded higher

values for *Acropora* compared to *Pocillopora* which may explain *Acropora*'s faster calcification rate. In both papers mentioned above, the Ca estimates at the ECF for the *Acropora* species is lower than those of *P. damicornis* in agreement with our *f* values suggesting higher Ca utilization for *Acropora*. The geochemical ECF estimates represent longer time averages (days, weeks or months) and may show steady state chemical compositions of the ECF. There is good agreement of these values with the previous short-term microelectrode and fluorescent dyes experiments, that represent short term values of pH, DIC, and Ca (e.g., Al-Horani et al., 2003; Venn et al., 2011; Sevilgen et al., 2019 and references therein). Both types of studies support each other, and biological direct observation increase the confidence of the calcification mechanisms that are proposed based on geochemical data. The most significant process in the calcification mechanism is that the ECF is essentially seawater that is modified by the coral mainly to increase its pH, DIC, and $\Omega_{aragonite}$. High $\Omega_{aragonite}$ values are needed to start precipitation of the skeleton, but during the precipitation process Ca, CO_3, DIC, and pH are all decreasing until calcification stops. The dynamics of these processes may be controlled by the diurnal cycle as light enhanced calcification is well documented in hermatypic corals (e.g., Cohen et al., 2016 and references therein).

Implications for Paleoceanographic Reconstructions

Corals are successfully applied as paleoceanography recorders mainly for paleotemperature based on $\delta^{18}O$, Sr/Ca, and Mg/Ca (e.g., Smith et al., 1979; Beck et al., 1992; Mitsuguchi et al., 1996; Felis et al., 2004; D'Olivo et al., 2018 and references therein). Reconstructions of ocean chemistry based on corals is scarce (Bender, 1973; Ries et al., 2006), but recently, the study of Gothmann et al. (2015), showed the high potential for such reconstructions over the past 200 Ma. Our findings strengthen the confidence of these paleo-studies have important implications for past ocean chemistry reconstruction. One of the main hurdles of proxies used in coral was the "vital effects" i.e., the deviation of coral skeletons from expected thermodynamic values of aragonite precipitation from seawater (e.g., McConnaughey, 1989; Adkins et al., 2003; Gagnon et al., 2007; Gothmann et al., 2016). In this study we show that seawater is the initial calcifying fluid at the ECF and fractionation of trace elements in the skeleton is constant for each species following a Rayleigh process from a semi-closed ECF reservoir. D_{coral} values are therefore constant (i.e., intercept 0 in the El/Ca plots) for each of the two species we studied (**Figure 3**). We propose that the closure of the ECF is mainly in order to modify its carbonate chemistry i.e., elevation of pH, DIC and $\Omega_{aragonite}$ and this closure is the main cause for Rayleigh process that we observe in coral skeletons trace elements.

Reconstruction of past seawater chemistry based on coral skeletons may be more reliable by measuring elements with D > 1 (Ba and Sr) and D < 1 (Na and Mg) and compare it to inorganic values. This may help to remove the vital effects related to the Rayleigh process. The most important ratio in these reconstructions is Na/Ca$_{skeleton}$ as proposed by Hauzer et al. (2018) and Houedec et al. (2021) for foraminifera

during the Cenozoic. This follows from the assumption that Na concentration is constant over the last 50–100 Ma and Ca$_{SW}$ may be calculated from Na/Ca$_{coral}$. Na concentration in coral skeletons is relatively high (e.g., Mitsuguchi et al., 2010; the present study) and since Kawabata et al. (2021), suggested that Na substitutes Ca in the lattice of aragonite based on K-edge X-ray absorption near edge structure (XANES) measurements, the Na/Ca$_{coral}$ may indeed be used as a proxy for Ca$_{SW}$. Once we know the past Ca, with information on temperature, it is also possible to calculate Sr, Mg, K, Li, and other elements that have shorter residence times (Mg ∼14 Ma; K ∼ 7 Ma; Sr ∼ 6 Ma; Li and Ca ∼ 1Ma; Pilson, 2013). Thus, despite the complex biological processes involved in the calcification of corals, their skeletons provide a unique and reliable archive for paleoceanoraphic reconstructions.

SUMMARY

In this study two scleractinian corals species, *Pocillopora damicornis* and *Acropora cervicornis* were cultured under variable seawater calcium (Ca$_{SW}$) ranging from ∼10 to 25 mM. The results demonstrate that the incorporation of the conservative elements Li, Na, Mg, K, Sr and Ba into the coral's skeletons, is directly related to the El/Ca$_{SW}$ ratio. The significant linear regression between El/Ca$_{coral}$ and El/ Ca$_{SW}$, going through the origin, suggests constant distribution coefficients (D$_{coral}$) for each element. For both coral species, D$_{El}$ values for Na, Mg, Sr, and Ba were in close proximity to the inorganic D$_{El}$ values, however, D$_{Li}$ were slightly lower and D$_K$ higher than the inorganic values. Rayleigh fractionation model explains well the variation in D$_{El}$ between the two species and the inorganic D$_{El}$ yielding the following conclusions:

SW is the main source for ions at the ECF, which shows precipitation from a semiclosed reservoir, that can be modeled using Rayleigh fractionation process.

Different coral species demonstrate different strategies with respect to their Ca utilization from the ECF. *P. damicornis* behaves like relatively open system while *A. cervicornis* is a half-open system, that may be more efficient as it shows higher calcification rate.

For Li and K the published inorganic D$_{El}$ values are inconsistent with the Rayleigh model based on the coral D$_{El}$. We propose that D$_{Li}$ and D$_K$ may be inaccurate and suggest hypothesized alternative values, however, this needs direct experimental study.

Finally, this study shows that coral skeletal trace elements may serve as highly reliable archive for paleoceanographic reconstructions. Na/Ca$_{coral}$ may be used to calculate past Ca$_{SW}$ for the Cenozoic (as Na$_{SW}$ was probably constant). Other elemental concentrations may thus be calculated based on their skeletal values and D$_{El}$ values of this paper.

DATA AVAILABILITY STATEMENT

The original contributions presented in the study are included in the article/**Supplementary Material**, further inquiries can be directed to the corresponding author.

AUTHOR CONTRIBUTIONS

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SUPPLEMENTARY MATERIAL

The Supplementary Material for this article can be found online at: https://www.frontiersin.org/articles/10.3389/feart.2021.657176/full#supplementary-material

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