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Fluoride in coral aragonite related to seawater carbonate

KENTARO TANAKA and SHIGERU OHDE*

Department of Chemistry, Biology and Marine Science, University of the Ryukyus,
Nishihara, Okinawa 903-0213, Japan

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In order to elucidate the controlling factors for fluoride incorporation into coral aragonite ($CaCO_3$), we determined the ratio of fluorine to calcium (F/Ca) in coral skeletons collected from Pohnpei (Micronesia), Khang Khao (Thailand), Cebu (The Philippines), Tosa Bay (Kochi, Japan), Sakai Port (Wakayama, Japan), Tateyama (Chiba, Japan), Sesoko, Rukan-sho and Mizugama (Okinawa, Japan) using the ion-chromatograph method. The F/Ca (mmol/mol) ratio was highest in Tateyama with an average ratio of 6.04, whereas coral collected from Sakai Port, Tosa Bay, Okinawa, Cebu, Pohnpei and Khang Khao exhibited F/Ca ratios of 5.57, 5.02, 4.49, 4.24, 4.00 and 3.75, respectively. The factor controlling F/Ca ratio is discussed based on the proposed coprecipitation process of F in coral aragonite as the ion-exchange reaction: $CaCO_{3(s)} + 2F^-_{(aq)} = CaF_{2(s)} + CO_3{}^{2-}{}_{(aq)}$. The equilibrium constant for the above equation can be expressed as: $K_F' = [CaF_2][CO_3{}^{2-}]/[CaCO_3][F^-]^2$. In this paper, analyzed F/Ca ratio in coral shows a proportional change to calculated seawater $[F^-]^2/[CO_3{}^{2-}]$. This finding suggests that F/Ca in coral skeletons is possibly controlled by carbonate ion concentration in seawater.

Keywords: coral, fluoride, carbonate, seawater temperature, aragonite

INTRODUCTION

Since the industrial revolution, especially in the latter half of the 20th century, the amount of carbon dioxide in the atmosphere has increased due to a large amount of fossil fuel consumption. This increase in the concentration of atmospheric CO_2 results in global warming. In addition, the change of seawater chemistry, such as decreases of the carbonate ion concentration and pH (seawater acidification), is occurring because a ~50% of anthropogenic CO_2 emission is absorbed into the ocean (Sabine *et al*., 2004). In order to predict the seawater chemistry in the future, it is important to study chemical fossils, such as coral. Coral skeletons possibly provide high-resolution records of past climatic and environmental changes in which the corals grew.

When reef-building corals secrete aragonite, dissolved ions such as strontium and magnesium ions can be incorporated into the skeleton. Using the ratio of incorporated elements to calcium in the aragonite skeletons (e.g., Sr/Ca, Mg/Ca), many researches were performed to estimate the past temperature of seawater in which the coral has grown (Smith *et al*., 1979; Mitsuguchi *et al*., 1996). As well as cations, elements dissolved as anions such as fluoride and borate can be incorporated into the skeleton. The fluoride content in carbonate and its incorporating process were investigated for natural and inorganic calcium carbonate.

Carpenter (1969) measured the fluoride content in marine carbonates such as corals, foraminifera and coccoliths, and found that coral aragonite has a higher concentration than calcite skeletons (foraminifera and coccoliths). Kitano and Okumura (1973) performed carbonate synthesis experiments using a Ca^{2+}–$HCO_3{}^-$–Mg^{2+}–F^- solution and found that the amount of fluoride incorporated into aragonite is larger than that into calcite, but the mechanism of incorporation was not elucidated. Rosenthal and Boyle (1993) and Rosenthal *et al*. (1997) measured the fluoride content of foraminiferal shells (aragonite and calcite), and pointed out that the fluoride coprecipitation was primarily controlled by the biological processes, since the fluoride content has little correlation with seawater temperature. Using SIMS, Hart and Cohen (1996) measured Sr/Ca and F/Ca ratios along the growth axis of a coral skeleton. They reported that the variation of Sr/Ca and F/Ca ratios has a one-year cycle.

Ichikuni (1979) performed a significant research on the coprecipitation experiments of fluoride with aragonite using a $CaCl_2$–Na_2CO_3–NaF solution. He demonstrated that the uptake of fluoride by aragonite is attributed to the ion-exchange reaction, in which one carbonate ion in aragonite is replaced by two fluoride ions. The ion-exchange reaction can be represented as follows:

$$CaCO_{3(s)} + 2F^-_{(aq)} \rightleftarrows CaF_{2(s)} + CO_3{}^{2-}{}_{(aq)} \qquad (1)$$

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*Corresponding author (e-mail: sohde@sci.u-ryukyu.ac.jp) where (s) and (aq) correspond to the solid and liquid phases (Ichikuni, 1979). Using the Ichikuni model, we could consider that fluoride in seawater is possibly incorporated into coral skeletons by the ion-exchange reaction.

The apparent equilibrium constant of reaction (1), K_F', is given as follows:

$$K_F' = [CaF_2][CO_3^{2-}]/[CaCO_3][F^-]^2. \qquad (2)$$

By rearrangement of Eq. (2), the following equation is obtained:

$$[CaF_2]/[CaCO_3] = K_F'[F^-]^2/[CO_3^{2-}]. \qquad (3)$$

The concentration of fluoride ion is constant (68 μM at salinity = 35) in the oceans (Broecker and Peng, 1982) and K_F' is constant when both temperature and pressure are constant. Equation (3) predicts that fluoride content in a coral skeleton is controlled by the concentration ratio of $[F^-]^2/[CO_3^{2-}]$ in seawater. It is important to define the correlation between the fluoride content in coral skeletons and the carbonate concentration in seawater. In this paper, the fluoride content of corals collected from nine locations is determined to elucidate the correlation between the fluoride content and the seawater carbonate ion concentration.

METHODS

Coral samples

Coral samples were collected from Pohnpei (Micronesia, 7°00′ N, 158°15′ E), Khang Khao (Thailand, 13°09′ N, 100°48′ E), Cebu (The Philippines, 15°00′ N, 124°00′ E), Mizugama (Okinawa, Japan, 26°15′ N, 127°45′ E), Rukan-sho (Okinawa, Japan, 26°06′ N, 127°32′ E), Sesoko Island (Okinawa, Japan, 26°38′ N, 127°51′ E), Tosa Bay (Kochi, Japan, 33°30′ N, 133°45′ E), Sakai (Wakayama, Japan, 33°43′ N, 135°18′ E) and Tateyama (Chiba, Japan, 35°00′ N, 139°05′ E). The location of the sampling sites is shown in Fig. 1 and listed in Table 1. After washing the sample ultrasonically using MQ water, the sample skeleton was cut about 1 cm from the surface of the bulk sample of *Porites*, and ~5 cm from surface of *Acropora* and *Pocillopora*, respectively. The cut fragment was washed a few times using MQ water in an ultrasonic bath. The fragment was dried in an oven at 80°C for 7 hours and was then ground using an agate mortar. We also used a coral standard (JCp-1) prepared by the Geological Survey of Japan (GSJ) (Okai *et al.*, 2002).

In order to confirm an annual variation of fluoride content in the coral skeleton, a core sample of coral skeleton was also studied. The core (ø: 6 cm) was collected from Sesoko Island (Okinawa) on 16 August 1996. The core skeleton was drilled along the growth axis and cut into a slab of 5 mm thickness. The density band of this slab was then confirmed by X-ray radiography. The slab was then washed with MQ water in an ultrasonic bath, and dried in an oven (80°C, ~7 h). Every ~1.6 mm of the slab was gradually shaved from the top to a depth of 10 mm as a sub-sample (~10 mg) using a dental drill.

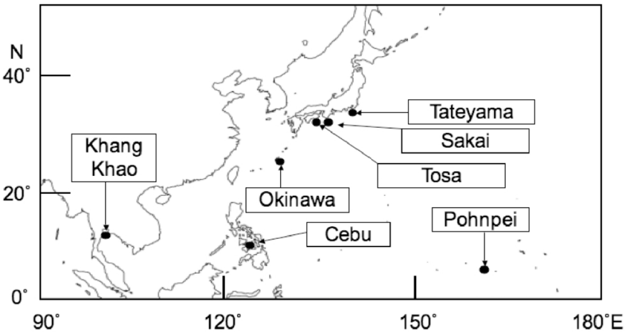

Fig. 1. Map showing sampling locations, Pohnpei, Khang Khao, Cebu, Okinawa (Mizugama, Rukan-sho and Sesoko Island), Tosa Bay, Sakai port and Tateyama.

Analytical methods

A powdered coral sample was dissolved using cation-exchange resin following the procedure outlined by Ichikuni and Tsurumi (1990). About a 0.8 g of cation-exchange resin (acetate H$^+$-form, 20–50 Mesh, MAC-3 produced by Muromachi Technos, Japan) and MQ water (~10 ml) were added together with the powdered sample (~0.1 g) in a 50 ml conical-beaker. This aqueous suspension was stirred for 24 h and then filtered. The resin left in the filter paper was washed using MQ water and the washing was added to the filtered solution. The fluoride concentration of the filtered solution was determined by an ion-chromatograph (IC, DX-120, Dionex, USA). The mixed solution (1.8 mM $NaHCO_3$/1.7 mM Na_2CO_3) was used as the eluent for IC. Data was obtained using an integrator (GR5A chromatpac, Shimazu, Japan). Fluoride standard solutions (1, 2, 3 ppm as F^-) were prepared by diluting sodium fluoride aqueous solution (as F^-: 2000 ppm). Since the fluoride peak was unsymmetrical, the fluoride concentration of the sample solution was calculated using a calibration curve from the peak height to the baseline. The peak height strongly correlated with the standard fluoride concentration to obtain the calibration line (R^2 = 0.999) for the sample analysis. Each sample was measured at least twice. The standard solution (F^-: 2 ppm) was measured at the interval of several measurements to confirm the analytical reproducibility. The reproducibility (RSD, n = 10) of fluoride analysis was 2%.

Calcium content in coral samples was determined using EDTA titration method. About 30 mg of powdered

Table 1. Fluorine and calcium contents in coral skeletons

Sample*	Location	Genus	F (μg/g)	Ca (wt%)	F/Ca (mmol/mol)
88031201	Pohnpei	*Porites*	758	36.5	4.38
88031202	Pohnpei	*Porites*	688	38.2	3.80
880313	Pohnpei	*Porites*	693	38.4	3.81
98111801	Khang Khao	*Porites*	526	37.7	2.94
98111802	Khang Khao	*Porites*	832	38.2	4.60
98111803	Khang Khao	*Porites*	620	38.1	3.43
01031501	Khang Khao	*Porites*	667	38.3	3.67
01031502	Khang Khao	*Porites*	720	38.1	3.99
01031503	Khang Khao	*Porites*	698	38.3	3.85
03040403	Cebu	*Pocillopora*	743	37.2	4.21
03040404	Cebu	*Porites*	677	37.4	3.82
03040405	Cebu	*Porites*	756	38.1	4.19
03040406	Cebu	*Porites*	719	37.0	4.10
03040407	Cebu	*Porites*	668	38.2	3.69
03040409	Cebu	*Porites*	864	38.2	4.77
03040501	Cebu	*Porites*	843	37.8	4.71
03040503	Cebu	*Pocillopora*	790	37.6	4.43
JCp-1**	Ishigaki	*Porites*	773	38.1	4.27
00070401	Mizugama	*Porites*	814	37.4	4.59
00070402	Mizugama	*Porites*	840	37.8	4.69
00070502	Mizugama	*Porites*	796	38.1	4.41
00071601	Mizugama	*Porites*	724	38.2	4.00
00071901	Mizugama	*Porites*	780	38.3	4.30
00071902	Mizugama	*Porites*	797	38.3	4.39
00071903	Mizugama	*Porites*	749	38.5	4.10
00071904	Mizugama	*Porites*	824	38.7	4.49
00081103	Mizugama	*Porites*	651	38.4	3.58
00081208	Mizugama	*Porites*	725	38.2	4.00
00081209	Mizugama	*Porites*	850	38.3	4.68
980923	Rukan-sho	*Acropora*	781	38.2	4.32
03073101	Rukan-sho	*Porites*	839	38.2	4.63
03073102	Rukan-sho	*Porites*	917	38.0	5.09
03073103	Rukan-sho	*Acropora*	826	38.2	4.56
03073104	Rukan-sho	*Pocillopora*	896	38.3	4.94
03073105	Rukan-sho	*Porites*	896	38.8	4.87
03073106	Rukan-sho	*Pocillopora*	737	38.3	4.06
02120601	Tosa	*Porite*	848	37.8	4.73
02120602	Tosa	*Porite*	985	39.0	5.31
83021622	Sakai port	*Porites*	878	37.4	4.95
83021623	Sakai port	*Acropora*	1060	37.8	5.92
83021624	Sakai port	*Acropora*	1070	37.6	6.00
83021625	Sakai port	*Acropora*	1010	38.2	5.58
83021627	Sakai port	*Acropora*	974	38.1	5.39
06111301	Tateyama	*Acropora*	1020	38.3	5.62
06111302	Tateyama	*Acropora*	1070	37.9	5.96
06111701	Tateyama	*Acropora*	1020	38.3	5.62
06111702	Tateyama	*Acropora*	1270	38.3	7.00
06111703	Tateyama	*Acropora*	1110	38.3	6.12
06111704	Tateyama	*Acropora*	1070	38.2	5.91

**Sample code shows sampling date (e.g., 88031201: 12 March 1988).*
***Average value (n = 5).*

sample was dissolved in 4 mL of 2% HNO_3 and diluted to 50 mL. After addition of 0.4 mL of 8 M KOH, the solution was titrated with 0.01 M EDTA solution. The reproducibility (RSD, $n = 10$) of Ca analysis was 0.1%.

Hydrographic data

Salinity was observed at Khang Khao every month from January 2000 to March 2001. Salinity was also measured at Pohnpei, Cebu, Mizugama, Sesoko, Rukan-sho and Tosa when we collected the coral samples (Table 2). Total alkalinity (A_T) was observed at Khang Khao, Cebu, Ishigaki, Mizugama, Ruka-sho and Tosa. A_T is also estimated from salinity using the relationship between A_T and salinity as follows: A_T (mmol/kg) = 2.3S/35 (Broecker and Peng, 1982). Sea surface temperature (SST) was measured at Khang Khao Island from November 1999 to March 2001 and at the Marine Station located in Tateyama from January 2000 to January 2006. We also obtained SST data from NOAA (http://www.noaa.gov/). The growth period of the skeletal part used for measurement (~1 cm for *Porites* and ~5 cm for *Acropora* and *Pocillopora*) is considered to be approximately one year before the sampling date. The annual SST was calculated using data form NOAA. We also estimate $p\mathrm{CO_2}$ data of the sampling stations using atmospheric $\mathrm{CO_2}$ data obtained by Keeling *et al*. (2008), assuming that atmospheric $\mathrm{CO_2}$ is in equilibrium with surface seawater.

It is extremely difficult to measure carbonate concentration in seawater. Seawater $[\mathrm{CO_3}^{2-}]$ can be calculated on the basis of equilibrium system (Morse and Mackenzie, 1990). We calculate seawater $[\mathrm{CO_3}^{2-}]$ using two parameters of A_T and $p\mathrm{CO_2}$. In accordance with the Morse and Mackenzie (1990) method, seawater $[\mathrm{CO_3}^{2-}]$ is given as the function of carbonate alkalinity (A_C) and $p\mathrm{CO_2}$ in seawater as follows:

$$\left[\mathrm{CO_3^{2-}}\right] = \frac{\dfrac{2K_2'A_C^2}{K_0'K_1'p\mathrm{CO_2}}}{1+\dfrac{4K_2'A_C}{K_0'K_1'p\mathrm{CO_2}}+\left(1+\dfrac{8K_2'A_C}{K_0'K_1'p\mathrm{CO_2}}\right)^{1/2}}$$

where K_0', K_1' and K_2' represent the apparent equilibrium constants, the solubility coefficient of $\mathrm{CO_2}$ in seawater, the 1st and 2nd dissociation constant of carbonic acid in seawater, respectively. These apparent constants can be given as a function of temperature, pressure and salinity. The relationship between A_C and A_T is given as follows: $A_T = A_C + [\mathrm{B(OH)_4^-}]$, where $[\mathrm{B(OH)_4^-}]$ is borate ion concentration in seawater. Seawater fluoride ion concentration is estimated from salinity by $[\mathrm{F^-}]$ (μmol/kg) = 68S/35 (Broecker and Peng, 1982).

RESULTS

Analytical results of the fluorine and calcium contents of corals are shown in Table 1. Using the data in Table 1, the average value of coral F/Ca is calculated for each sampling location (Table 2). Fluorine content in coral skeletons varied from ~500 to 1300 ppm (3–7 mmol/mol as

Table 2. Sampling location, number of samples, average value of F/Ca in coral aragonite, salinity, total alkalinity (A_T), sea surface temperature, estimated pCO_2 and calculated $[F^-]^2/[CO_3^{2-}]$

Location	Number of samples	F/Ca (mmol/mol)	Salinity (psu)	A_T[*1] (mmol/kg)	A_T[*2] (mmol/kg)	Temperature (°C)	Temperature[*3] NOAA (°C)	pCO_2[*4] (μatm)	$[F^-]^2/[CO_3^{2-}]$[*5] (μmol/kg)
Pohnpei	3	4.00 ± 0.27	34.5	—	2.27	—	28.7	350	17
Khang Khao	6	3.75 ± 0.51	32.5	2.35	2.10	28.6	28.4	360	18
Cebu	10	4.24 ± 0.36	34.5	2.33	2.27	—	28.3	370	18
Ishigaki (JCp-1)	1	4.27 ± 0.07	34.5	2.28[*6]	2.27	—	26.5	360	18
Mizugama	11	4.29 ± 0.33	34.5	2.30[*7]	2.27	—	23.1	370	19
Rukan-sho	7	4.64 ± 0.34	34.7	2.33[*8]	2.27	—	22.7	380	20
Tosa	2	5.02 ± 0.29	33.8	2.30	2.22	21.7	21.5	370	21
Sakai	6	5.57 ± 0.38	34.5[*9]	—	2.27	—	19.6	340	21
Tateyama	6	6.04 ± 0.47	34.3[*10]	—	2.25	19.0	19.0	380	23

[*1] *Observed total alkalinity is normalized to a constant salinity of 35 psu.*

[*2] *Total alkalinity is calculated to be proportional to salinity as follows: $A_T = 2.3S/35$.*

[*3] *Average temperature of sea surface water during the last one year before collecting the sample. The data are calculated from temperature data from NOAA (http://www.noaa.gov/wx.html).*

[*4] *pCO_2 is estimated from sampling year and data of Keeling et al. (2008).*

[*5] *$[F^-]^2/[CO_3^{2-}]$ in seawater is calculated using hydrographic data (A_T, pCO_2, salinity and SST) as desicribed in the text.*

[*6] *Kawahata et al. (2000b).*

[*7] *Ohde and Hossain (2004).*

[*8] *Ohde and van Woesik (1990).*

[*9] *Ocean Research Institute, The University of Tokyo (1996).*

[*10] *Hagiwara (2003).*

F/Ca). As shown in Table 1, we determined F/Ca ratios in three genera of coral samples (*Porites*, *Acropora* and *Pocillopora*). The average ratio of F/Ca in *Porites* (n = 3), *Acropora* (n = 2) and *Pocillopora* (n = 2) collected from Rukan-sho were 4.87, 4.50 and 4.44 mmol/mol, respectively. The average value of three genera is also calculated at 4.64 ± 0.34 mmol/mol (n = 7) (Table 2). The average values, 4.87, 4.50 and 4.44 mmol/mol are within in the range of the standard deviation (4.64 ± 0.34 mmol/mol) (Table 2). Moreover, the average F/Ca ratios of Cebu corals showed little variations between genera, *Porites* (4.21 mmol/mol) and *Pocillopora* (4.32 mmol/mol). Therefore, the inter-species variations in the F/Ca are not considered in this study.

In turn, the potential errors for calculating seawater $[F^-]^2/[CO_3^{2-}]$ should be checked here before discussion. Seawater $[F^-]^2/[CO_3^{2-}]$ of the sampling locations is calculated from hydrographic data (pCO_2, A_T, SST and salinity) assuming a model condition in which CO_2 is in equilibrium between atmosphere and surface seawater, and A_T and $[F^-]$ have proportional changes to salinity. The calculated value of $[F^-]^2/[CO_3^{2-}]$ is shown in Table 2. For the calculation of seawater $[F^-]^2/[CO_3^{2-}]$, temperature data are obtained from NOAA, while A_T and pCO_2 data are estimated from salinity and atmospheric CO_2 concentration. In order to confirm reliability of the calculation of seawater $[F^-]^2/[CO_3^{2-}]$, we estimate uncertainty of the calculation due to temperature, A_T and pCO_2. As listed in Table 2, the three observed temperature data are consist with those from NOAA (Table 2). We assume the variation in the calculated $[F^-]^2/[CO_3^{2-}]$ due to the temperature data is negligible (<0.2 μmol/kg).

Total alkalinity is estimated from salinity data using the relationship between A_T and salinity (A_T (mmol/kg) = 2.3S/35). The A_T data measured at Khang Khao, Cebu, Ishigaki, Mizugama, Rukan-sho and Tosa are listed in Table 2. These measured A_T values are normalized to a constant salinity of 35 psu. The maximum and minimum value of normalized A_T is calculated at 2.35 and 2.28 mmol/kg (Table 2). Using A_T values of 2.30 (+0.05/–0.02) mmol/kg and the constant parameters (pCO_2 = 360 μatm, Temperature = 25°C and Salinity = 35 psu), seawater $[CO_3^{2-}]$ is calculated at 244 (+9/–3) μmol/kg. The alkalinity value (2.30 (+0.05/–0.02) mmol/kg) results in the value of $[F^-]^2/[CO_3^{2-}]$ of 19.0 (–0.7/+0.2) μmol/kg at salinity of 35 psu. Accordingly, the variation in calculated $[F^-]^2/[CO_3^{2-}]$ due to the alkalinity variation is less than ±0.7 μmol/kg. The potential error is estimated to be ±4%.

We estimate pCO_2 of the sampling stations using atmospheric CO_2 data obtained by Keeling *et al.* (2008), while seawater pCO_2 and atmospheric P_{CO2} were observed in several coral reefs. The difference between pCO_2 and atmospheric P_{CO2} (ΔpCO_2) was reported to be –36, –31, 1, 2 and 18 μatm on Rukan-sho, Great Barrier Reef,

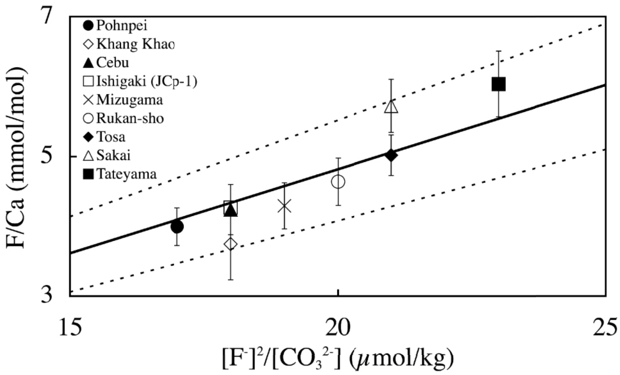

Fig. 2. Relationship between F/Ca in coral and calculated $[F^-]^2/[CO_3^{2-}]$*. Data are shown in Table 2. The regression curve (solid line) is calculated as: F/Ca = 0.24* $[F^-]^2/[CO_3^{2-}]$ *(*R^2 *= 0.76). Two dashed lines have slopes of 0.204 and 0.276 as described in the text.*

Table 3. Salinity, A_T*,* $[F^-]$ *and* pCO_2 *used for the calculation of* $[F^-]^2/[CO_3^{2-}]$ *and constant values of a and b in Eq. (5)*

Salinity (psu)	A_T (mmol/kg)	$[F^-]$ (μM)	pCO_2 (μatm)	*a*	*b*
34.5	2.27	67	340	149	0.630
34.5	2.27	67	350	155	0.636
34.5	2.27	67	360	161	0.642
34.5	2.27	67	370	166	0.648
34.5	2.27	67	380	172	0.652
32.5	2.14	63	360	170	0.660

Sesoko Island (Okinawa), Majuro and Palau (Ohde and van Woesik, 1999; Kawahata *et al.*, 1997; Kitada *et al.*, 2006; Kawahata *et al.*, 2000a). Using pCO_2 (360 (+18/–36) μatm) and the constant parameters (A_T = 2.3 mmol/kg, T = 25°C and S = 35 psu), seawater $[CO_3^{2-}]$ is calculated at 244 (–7/+17) μmol/kg. The pCO_2 value (360 (+18/–36)) μatm results in the value of the calculated $[F^-]^2/[CO_3^{2-}]$ of 19.0 (+0.5/–1.2) μmol/kg at salinity of 35 psu. Accordingly, the variation in calculated $[F^-]^2/[CO_3^{2-}]$ due to pCO_2 is less than ±1.2 μmol/kg. The error is estimated to be ±6%.

We estimate that the variation in the calculated $[F^-]^2/[CO_3^{2-}]$ due to temperature, A_T and pCO_2 is <0.2 μmol/kg, ±0.7 μmol/kg and ±1.2 μmol/kg, respectively. Using such model calculations, we consider that the calculated data for seawater $[F^-]^2/[CO_3^{2-}]$ in Table 2 are reliable for discussion.

DISCUSSION

Fluoride in coral and carbonate in seawater

In order to elucidate factors controlling F/Ca in corals, we apply Eq. (3) to the incorporation of fluoride into coral skeletons. By rearranging Eq. (3), F/Ca ratio in corals can be expressed as follows:

$$\text{F/Ca (mmol/mol)} = 0.5K_F'[F^-]^2/[CO_3^{2-}]\ (\mu\text{mol/kg}). \quad (4)$$

The F/Ca ratio in corals is expressed as a function of K_F' and seawater $[F^-]^2/[CO_3^{2-}]$.

Using the data in Table 2, the average value of F/Ca is plotted against the calculated $[F^-]^2/[CO_3^{2-}]$ in Fig. 2. The error bar in the figure shows the standard deviation of the coral F/Ca data (Table 2). The relative standard deviation (RSD) of the F/Ca ratio in corals from the same locations is calculated to be 5.8–14% (Table 2). As shown in the figure, the F/Ca in corals linearly increases with increasing seawater $[F^-]^2/[CO_3^{2-}]$. Assuming a constant K_F' value, a regression curve analogous to Eq. (4) can be obtained as follows: F/Ca (mmol/mol) = 0.24 $[F^-]^2/[CO_3^{2-}]$ (μmol/kg) ($R^2 = 0.76$). The regression curve (solid line) in Fig. 2 strongly suggests that coral F/Ca is mainly affected by $[F^-]^2/[CO_3^{2-}]$ in seawater. However, the value of K_F' has a temperature dependence. From thermodynamic consideration, relative changes of equilibrium constant associated with temperature can be estimated using the following equation obtained from rearranging the van't Hoff equation: $\log(K_{T2}/K_{T1}) = -\Delta_r H°/2.3R\ (1/T_2 - 1/T_1)$, where K_{Ti}, $\Delta_r H°$ and R represent thermodynamic equilibrium constant at temperature T_i, the standard reaction enthalpy and the gas constant, respectively (Garrels and Christ, 1965). Using the thermodynamic constants listed in Garrels and Christ (1965), $\Delta_r H°$ for Eq. (1) is calculated at –25.61 kJ/mol. Substituting the calculated $\Delta_r H°$ value into the above equation, the relative change in the thermodynamic equilibrium constant of reaction (1) from 19 to 29°C (K_{29}/K_{19}) is calculated at 0.71. Accordingly, when the temperature increases from 19 to 29°C, a 29% decrease in K_F is calculated. Therefore the estimation of the temperature dependence of K_F suggests that K_F' possibly decreases with increasing temperature. Considering that K_F' decreases with increasing temperature, the slope of the regression curve also decreases with temperature. Since K_{29}/K_{19} is calculated at 0.71, we could assume a variation in K_F' of ±15% due to the temperature variation from 19 to 29°C. Based on such an assumption, the slope is calculated to be 0.24 ± 0.036. Two slopes (0.204 and 0.276) of the dashed lines are shown in Fig. 2. The figure clearly shows that the data plots from nine locations are in between the two dashed lines (0.204–0.276). These findings suggest that fluoride uptake into coral skeletons is mainly affected by seawater $[F^-]^2/[CO_3^{2-}]$. In addition, the temperature dependence of K_F' could slightly affect the F/Ca ratio in coral skeletons.

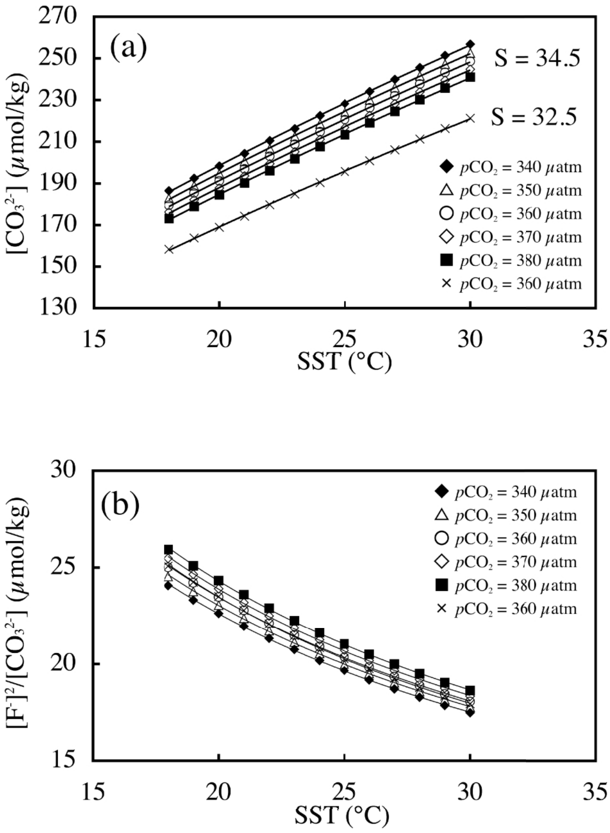

Fig. 3. (a) Relationship between SST and calculated $[CO_3^{2-}]$ using salinity (34.5 psu) and pCO_2 (340–380 μatm). × plot is calculated at salinity (32.5 psu) and pCO_2 (360 μatm). (b) Relationship between SST and calculated $[F^-]^2/[CO_3^{2-}]$ using salinity (34.5 psu) and pCO_2 (340–380 μatm). × plot is calculated at salinity (32.5 psu) and pCO_2 (360 μatm).

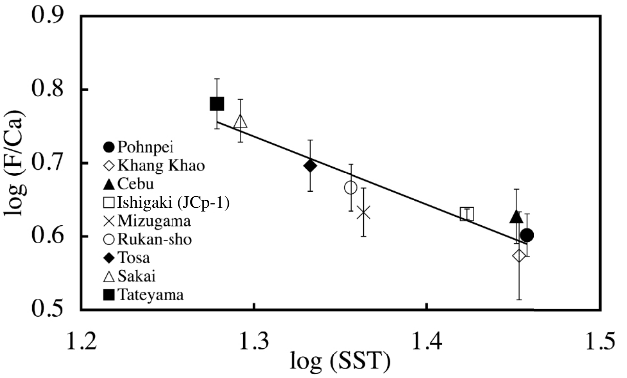

Fig. 4. Logarithmic relationship between F/Ca content in coral and annual average sea surface temperature. The regression line is calculated as: log(F/Ca) = –0.930 logSST + 1.94 (R^2 = 0.876).

Fluoride in coral and seawater temperature

Coral F/Ca ratio shows proportional change to $[F^-]^2/[CO_3^{2-}]$ in seawater (Fig. 2), implying that F/Ca is possibly controlled by seawater $[CO_3^{2-}]$. Since $[CO_3^{2-}]$ in seawater links to seawater temperature, coral F/Ca ratio might be associated with temperature in which corals grew. Using the carbonate equilibrium system (Morse and Mackenzie, 1990), we calculate seawater $[CO_3^{2-}]$ every degree from 18 to 30°C at 1 atm. The parameters (A_T, pCO_2 and salinity in sweater) used for the calculation are listed in Table 3. The temperature dependence of the calculated $[CO_3^{2-}]$ data is shown in Fig. 3a. The calculated $[CO_3^{2-}]$ increases with increasing temperature. When temperature and pCO_2 (360 μatm) are constant, equilibrium $[CO_3^{2-}]$ increases with increasing salinity (Fig. 3a). When temperature and salinity (34.5 psu) are constant, equilibrium $[CO_3^{2-}]$ increases with decreasing pCO_2 (Fig. 3a). Assuming that seawater $[F^-]$ is 63 and 67 μmol/kg for salinity of 32.5 and 34.5 psu, seawater $[F^-]^2/[CO_3^{2-}]$ is also calculated between 18 and 30°C. The calculated $[F^-]^2/[CO_3^{2-}]$ is plotted in Fig. 3b. As shown in the figure, the calculated $[F^-]^2/[CO_3^{2-}]$ decreases with increasing temperature. When temperature and pCO_2 (360 μatm) are constant, the plots of $[F^-]^2/[CO_3^{2-}]$ at salinity of 32.5 psu overlap with the plots at salinity of 34.5 psu (see Fig. 3b). When temperature and salinity (34.5 psu) are constant, Fig. 3b shows a trend of increase in the calculated $[F^-]^2/[CO_3^{2-}]$ with increasing pCO_2 (340–380 μatm). These equilibrium calculations indicate that both temperature and pCO_2 control seawater $[F^-]^2/[CO_3^{2-}]$, but the effect of salinity on seawater $[F^-]^2/[CO_3^{2-}]$ is negligible. Using the corresponding changes in the calculated $[F^-]^2/[CO_3^{2-}]$ and temperature shown in Fig. 3b, regression curves for the plots in Fig. 3b can be represented as the following power function:

$$[F^-]^2/[CO_3^{2-}] = a\mathrm{SST}^{-b} \qquad (5)$$

where a and b are constant. The values of a and b are listed in Table 3. The following logarithm equation is obtained from substituting Eq. (5) into Eq. (4):

$$\log(\mathrm{F/Ca}) = -b\log\mathrm{SST} + \log(0.5K_F') + \log(a). \qquad (6)$$

Using the data shown in Table 2, the logarithm values of F/Ca (mmol/mol) are plotted against the logarithm value of SST in Fig. 4. The regression curve for these plots is obtained as follows: log[F/Ca] = –0.930logSST + 1.94 (R^2 = 0.876). The slope of the regression curve is –0.930 and slightly smaller than negative values of b (0.630–0.660) listed in Table 3. The difference between the slope (–0.930) and the value of $-b$ is calculated at 0.270–0.300. The temperature dependence of K_F' may affect the slope value slightly. It is obscure that the slope value (–0.93) is

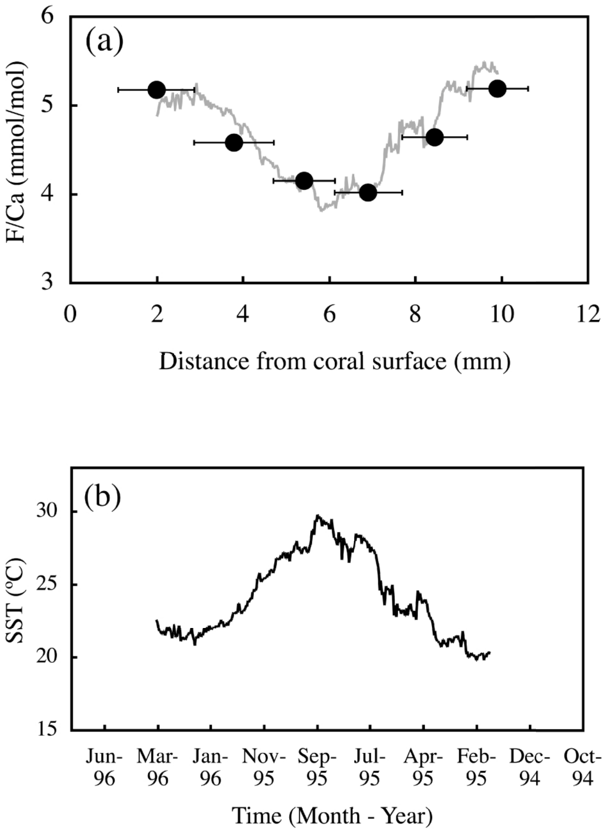

Fig. 5. (a) F/Ca (filled circle) along the growth line (depth: 2–10 mm) of a core sample collected from Sesoko Island, Okinawa. Using the observed SST data and the regression line of Fig. 4, calculated F/Ca data (line) are also plotted in the figure as described in the text. (b) SST observed at the Okinawa Ocean Expo Park from February 1995 to March 1996.

slightly smaller than –*b* value (0.63–0.66). Although the slope of the regression curve is slightly smaller than the value of –*b*, the coral F/Ca ratio decreases with increasing temperature (Fig. 4). As described above, the coral F/Ca ratio is mainly controlled by seawater $[F^-]^2/[CO_3^{2-}]$ (Fig. 2) that is related to temperature (Fig. 3b). Therefore, we consider that coral F/Ca ratio is apparently associated with SST in which corals grew (Fig. 4).

Annual variation of F/Ca in coral

As shown in Table 2 and Fig. 2, we consider that F/Ca in coral skeletons is proportional to seawater $[F^-]^2/[CO_3^{2-}]$ of the sampling locations. Since seawater $[F^-]^2/[CO_3^{2-}]$ is linked to temperature (Fig. 3b), the F/Ca ratio observed in corals from the nine locations is apparently associated with temperature (Fig. 4). The finding possibly suggests that F/Ca in a single coral has a seasonal variation associated with temperature and reflects seawater $[F^-]^2/[CO_3^{2-}]$. In order to observe the seasonal variation of fluoride content in a single coral skeleton, we investigated the relationship between the F/Ca ratio in a core sample collected from Sesoko Island, Okinawa and SST. The analytical data are plotted in Fig. 5a (filled circle). In the figure, the value in the distance from coral surface (*x*-axis) represents the middle point of the shaved part. The F/Ca data vary from 4.02 to 5.19 mmol/mol and show a seasonal variation (Fig. 5a). The observed variation also coincides with a pair of density bands, which corresponds to a one-year growth. Therefore, we assumed that the analyzed part of the core was formed for one year.

Since 1976, SST was observed at the Okinawa Ocean Expo Park (OOEXP) located about 4.5 km to the north-northeast of Sesoko Island. During these twenty-one years, the minimum (21.1 ± 0.5°C) and the maximum (28.1 ± 0.7°C) of SST were observed in Jan.–Mar. and July–Sep., respectively. In particular, when the core sample was collected in 1996, the minimum temperature was observed at 21.5°C in March, and in the previous year, 1995, the minimum temperature was observed at 20.1°C in February (Fig. 5b). Based on the negative correlation between F/Ca and SST, it seems reasonable to propose that the analyzed part of the core skeleton (1.99–9.90 mm) was formed during the period from February 1995 to March 1996. The SST data in this period observed at OOEXP is shown in Fig. 5b. When SST varies between 20.1–28.4°C (Fig. 5b), F/Ca in the core sample varies between 4.02–5.19 mmol/mol (Fig. 5a). This relationship between F/Ca and temperature coincides with the cyclic change of coral F/Ca ratio (0.0018 to 0.0025 in the signal ratio of SIMS) associated with the temperature change (21–27.5°C) (Hart and Cohen, 1996).

The ratio of F/Ca is calculated by substituting the SST data observed at OOEXP (Feb. 95–Mar. 96) into the regression equation shown in Fig. 4. The 424 calculated F/Ca values are plotted in Fig. 5a (see the line). When we plot the calculated F/Ca values in Fig. 5a, the edges of the calculated line are adjusted to the points between the analyzed part (1.99 and 9.90 mm) and the other data are plotted with a regular interval in the figure. The measured coral F/Ca ratios are almost consistent with the calculated F/Ca ratios. This finding suggests that the regression equation in Fig. 4 is also applicable to the single coral and that the fluoride content of a single coral has the negative logarithmic correlation with SST. Considering the relationship between temperature and $[F^-]^2/[CO_3^{2-}]$ (Fig. 3b), the negative correlation between the observed F/Ca ratio and SST reflects that the F/Ca in single coral is mainly controlled by carbonate ion in seawater.

CONCLUSIONS

Factors controlling the fluoride content in coral aragonite were investigated from the analyses of fluoride content in corals collected from the nine locations and in the single core sample using a model assumption in which CO_2 is in equilibrium between atmosphere and surface seawater. The following tentative conclusions are derived from our studies.

(1) The average coral F/Ca ratios from the nine coral reefs clearly showed a linear relationship to the calculated ratio of $[F^-]^2/[CO_3^{2-}]$ in seawater. The coral F/Ca is possibly controlled by seawater $[CO_3^{2-}]$.

(2) The calculated seawater $[F^-]^2/[CO_3^{2-}]$ decreases with increasing temperature. The coral F/Ca decreases with increasing temperature, suggesting that temperature is apparently one of controlling factors for the incorporation of fluoride into coral aragonite.

The present study suggests that the incorporation of fluoride into coral aragonite is primarily controlled by the seawater $[F^-]^2/[CO_3^{2-}]$. In the future, valuable information on surface seawater $[CO_3^{2-}]$ levels may be obtained from analyzing fluoride in coral skeletons.

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