Geochemical Behavior of Fluorine during the Formation of Pleistocene Limestones in Yoron-jima Island, Southwestern Japan

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The distribution and the mode of occurrence of fluorine in Holocene (mainly high-Mg calcite), Pleistocene (low-Mg calcite), and Paleozoic (low-Mg calcite) limestones of Yoron-jima Island were investigated, and the geochemical behavior of F during the formation of Pleistocene limestones is discussed. The average F contents of Holocene (n=3), Pleistocene (n=20), and Paleozoic (n=8) limestone samples are 680, 99, and 45 ppm, respectively, showing a marked decrease of this element during early diagenetic processes of marine carbonates. A positive correlation between the F and Mg contents of Pleistocene limestones indicates that F might have been removed together with Mg^{2+} from high-Mg calcite into interstitial waters during these processes. A main mode of occurrence of F (about 50%) in Pleistocene limestones is confirmed to be carbonate fluorapatite (francolite), and the rest is thought to be fluorite.

Fluorine contents of high-Mg calcite (calcareous algae) and aragonite (corals) are rather high (about 0.1 wt%), considering its low concentration (about 1.3 ppm) in seawater.[1—4] In general, fluoride ion is easily incorporated into marine high-Mg calcite (calcite with more than 1.05 wt% Mg)[5] and aragonite during the formation of these minerals. However, thus incorporated F in these minerals gradually decreases during the transformation of high-Mg calcite or aragonite to low-Mg calcite.[4,6] To make the behavior of F clear, Rude and Aller[4] estimated that a portion of released F^- through the transformation is fixed again as fluorapatite in carbonate sediments. If this is the case, $PO_4{}^{3-}$ ion may be responsible for the behavior of F during carbonate diagenesis. Such a mechanism of fluoride fixation has been rationalized by the existence of fluorapatite in relatively old (older than 2×10^6 years) (Tertiary, Mesozoic, and Paleozoic) limestones.[7,8] However, at present, the mode of occurrence of F in Holocene (younger than 1×10^4 years) unconsolidated carbonate sediments or Pleistocene (1×10^4—2×10^6 years) limestones remains unsolved.

On the other hand, most of the released F from high-Mg calcite may return to seawater. Taking into account that about 50% of dissolved F^- is present as MgF^+ in seawater,[9,10] it seems reasonable to consider that F^- behaves like Mg^{2+} during the transformation of high-Mg calcite to low-Mg calcite, namely, the formation of limestone.

Yoron-jima Island, located in southwestern Japan, is largely covered with Middle and Upper Pleistocene limestones of foraminiferal shell (high-Mg calcite) origin. This island therefore offers an excellent field for investigating the F behavior during the transformation of carbonate minerals at a recent stage.

In this work, we tried to investigate the factors controlling the geochemical behavior of F during the carbonate transformation using the Yoron Pleistocene limestone as a representative of relatively recent carbonates.

Experimental

Geological Setting and the Description of Samples. Samples were taken from Yoron-jima Island, southwestern Japan (Fig. 1). Yoron-jima is located at 27°00′N latitude, 128°20′E longitude, about 20 km northeast from the main island of Okinawa. The island is surrounded by barrier reefs, and shallow-water sediments consist of foraminiferal shells with subordinate amounts of corals, echinoids, and calcareous algae.[11] The area is 20.8 km^2, and the highest point is 97.2 m. Most of the island is flat and covered with Pleistocene limestone layers (the Nama and Gusuku Formations) with max. 70 m in thickness. The Nama Formation unconformably overlies the Gusuku Formation. Most of the Pleistocene limestones consist of foraminiferal shells with subordinate amounts of corals, calcareous algae, molluscs, and other calcareous organic remains.[11] These limestones are white and contain small amounts of impurities. Twenty Pleistocene limestone samples were collected from the Nama and Gusuku Formations (Fig. 1).

The basement of the Pleistocene limestones, the Ritcho Formation, outcrops in the southern part of the island. This formation is composed of limestone, slate, chert, sandstone, and tuff. Geological age is the Paleozoic (older than 2.48×10^8 years) and estimated to be the Permian.[11] Eight limestone samples were taken from this formation. In addi-

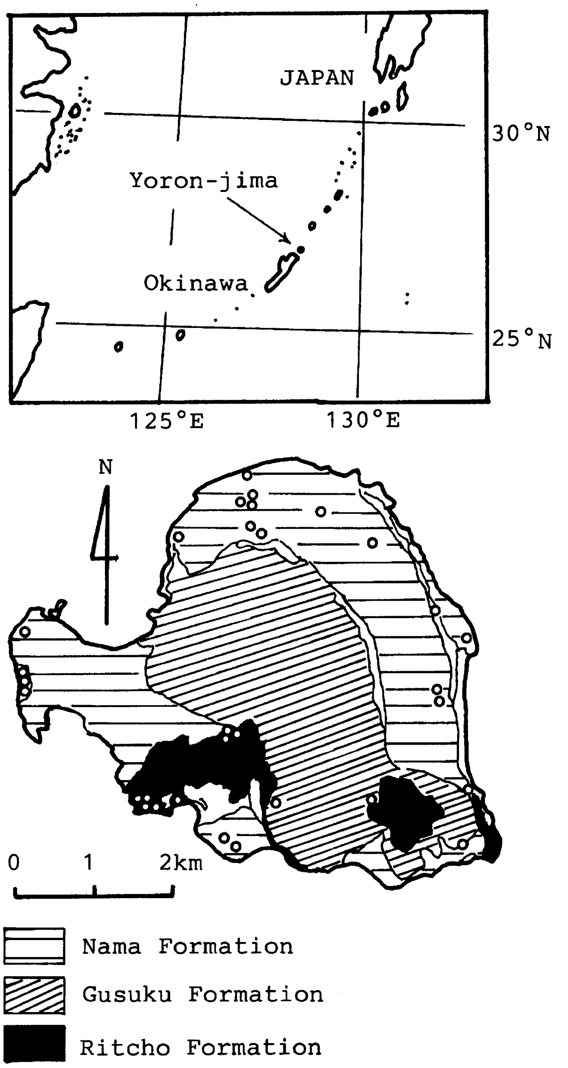

Fig. 1. Sampling locality (three formations were figured on the basis of the study of Nakagawa (1967).

tion, 3 limestone samples (classified as foraminiferal grainstone) mainly composed of loosely cemented foraminiferal grains (1—2 mm in diameter) were taken from the western shoreline of the island. The geological age of these limestones is estimated to be the Holocene, since fragments of *Homotrema rubrum* (benthic foraminifera) are still reddish violet in color.

Preparation of Samples. A sample was broken into small pieces (about 1 cm in diameter), and immersed in diluted nitric acid. After sufficient rinsing with deionized water, the sample was air-dried at room temperature for a week, and then pulverized to < 0.15 mm in an agate mortar. According to powder X-ray diffractometry (XRD) of bulk samples, the Pleistocene and Paleozoic limestone samples gave no peaks of any minerals other than low-Mg calcite, but the Holocene ones gave peaks of high-Mg calcite and aragonite (Fig. 2).

Methods of Chemical Analysis. Powdered samples (1.00—2.00 g) were dissolved with 3 mol dm^{-3} $HClO_4$. After it was separated from samples by steam distillation in the presence of $HClO_4$, F^- was determined photometrically by using alizarin fluorine blue (1,2-dihydroxyanthraquinone-3-yl-methylamino-*N*,*N*-diacetic acid). The accuracy of the method was certified by analyzing standard reference rock samples (JLs-1: limestone and JDo-1: Dolostone) issued from the Geological Survey of Japan.[12] The relative standard deviations ($n=3$) were 2.2% and 0.47% for JLs-1 (av. F; 38 ppm) and JDo-1 (av. F; 260 ppm) samples, respectively, the detection limit (sample weight: 2.00 g) being 5 ppm F. Our values agree with the reference values, 38.3±1.8 ppm[13] (JLs-1) and 245±9 ppm[13] (JDo-1), suggesting that this method is suitable for the determination of F in carbonate rocks.

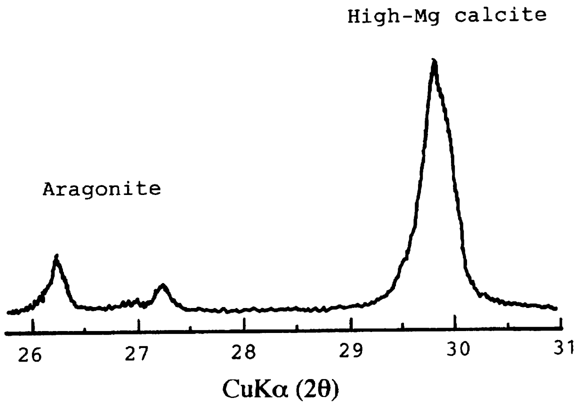

Fig. 2. Powder X-ray diffractogram of Holocene limestone sample (82-KYL-30) from Yoron-jima Island.

After the decomposition of the powdered sample (1.000 g) with a mixture of HNO_3 and $HClO_4$, Ca was determined by EDTA (ethylenediamine tetraacetic acid) titrimetry. Magnesium, Sr, Fe, Mn, and K were determined by flame atomic absorption spectrometry. Aluminum was determined by the 8-quinolinol extraction-photometry. The determination of P was also done by phosphorus vanadomolybdate extraction-photometry.

Identification of F-Bearing Minerals. Powdered samples (about 200 g) were dissolved with 1 mol dm^{-3} acetic acid at room temperature (about 298 K) or at low temperature (< 283 K) by cooling with ice, and then insoluble minerals were identified with X-ray diffraction. Peak displacements were measured relative to the (101) reflection peak of quartz, which was contained as an insoluble residue.

Results and Discussion

The analytical results for F and associated elements are summarized in Table 1.

Contribution of F in Silicates to Total F in Bulk Limestones. Fluorine-bearing minerals in carbonate rocks are generally fluorite, apatite, and clay minerals. Proportions of these minerals depend mainly upon the mode of origin.[14] As Table 1 shows, a prominent feature of these samples is low concentrations of SiO_2, Al_2O_3, and Fe_2O_3, which are one or two orders of magnitude lower than those for ordinary limestones.[15] Accordingly, the amount of coexisting silicate minerals such as quartz, feldspars and clays is very small, suggesting that the contribution of F in these silicates to the total F content of a bulk limestone sample may be negligible. The most common clay mineral with

Table 1. Arithmetic Means of Major, Minor, and Trace Elements in Limestone Samples from Yoron-jima Island (Concentrations in ppm Unless Noted as %)

Geological age	No. of samples	SiO$_2$ %	CaO %	MgO %	Fe	Al	Mn	Sr	Na	K	P$_2$O$_5$	F
Pleistocene	20	0.13[a)]	54.95	0.63	200	200	10	300	130	31[a)]	570	99
		0.12	*0.31*	*0.16*	*160*	*170*	*6*	*91*	*73*	*23*	*140*	*38*
Holocene	3	<0.02	49.42	3.84	72	71	3	2900	3300	73	430	680
		—	*0.49*	*0.20*	*3*	*6*	*0*	*280*	*140*	*3*	*8*	*24*
Paleozoic	8	0.06	55.28	0.34	160	72	19	240	39	11	380	45
		0.07	*0.24*	*0.07*	*200*	*88*	*12*	*100*	*16*	*6*	*230*	*20*

Italic: Standard deviation. a) Means were calculated by using detection limits (SiO$_2$: 0.02%, K: 5 ppm) with respect to the samples having values less than these detection limits.

a high F content is illite.[1)] Muscovite, whose structure is similar to illite, is represented as $K_2Al_4(Si_6Al_2)O_{20}(OH)_4$,[16)] and hence the Al content of illite is estimated to be 20 wt%. From the average Al content (0.02 wt%), Yoron Pleistocene limestones may contain about 0.1 wt% illite. Assuming that the F content of illite is 1000 ppm,[1)] the contribution of the F in illite to the total F in Yoron Pleistocene limestone samples is about 1 ppm, which is about 1/100 of the average F content of these samples. Most of F in Yoron Pleistocene limestone samples are therefore contained in sparingly soluble F-bearing minerals other than silicates.

Change in F Content during the Formation of Yoron Limestones. The F content of Pleistocene limestone samples composed of low-Mg calcite ranges from 43 ppm to 180 ppm, the average being 99 ppm (Table 1). This average value is about 1/7 of the F content of Holocene limestone samples composed of high-Mg calcite and subordinate amounts of aragonite. Ichikuni[17)] reported that, in an aragonite lattice, one CO_3^{2-} is replaced by two touching F^- by ion exchange. The similar mode of occurrence of F^- in both high-Mg calcite and aragonite may reasonably be assumed. Such an unstable mode of occurrence of F^- in these minerals renders F^- easily removed by interstitial waters during the transformation process. On the other hand, an appreciable amount of F^- remains in the Paleozoic limestones (av. 45 ppm) as compared with that (99 ppm) of Pleistocene limestones (Table 1). This indicates that only a slight amount of F has been removed during the recrystallization process of low-Mg calcite.

Factors Controlling the Geochemical Behavior of F during the Formation of Yoron Pleistocene Limestones. As Fig. 2 shows, Yoron Holocene limestone samples contain small amounts of aragonite. Since the average Sr contents of Yoron coral aragonites, foraminiferal high-Mg calcites, and the Holocene limestones are 8000,[3)] 2150,[18)] and 2900 ppm (Table 1), respectively, the weight ratio of aragonite to high-Mg calcite in the Holocene limestones is calculated to be 13:87. Furthermore, the average F content of Yoron coral aragonites and the Holocene limestones are 910[3)] and 680 ppm, respectively (Table 1). On the basis of the above ratio, the F content of high-Mg calcite in the limestones is calculated to be 650 ppm. Considering that the contribution of the F in aragonites to the total F content may therefore be small, most of F in the Holocene limestones may be contained in high-Mg calcite.

As Table 2 shows, the F content of Yoron Pleistocene limestone samples is positively correlated with that of MgO and the correlation is clearly seen in Fig. 3. Moreover, the plots of the F vs. MgO contents fall along the solid line which indicates the average ratio of the F and MgO of Holocene limestones. This indicates the removal of F^- together with Mg^{2+} during the transformation of high-Mg calcite to low-Mg calcite. Due to the strong affinity for Mg^{2+}, F^- may be leached out in the form of MgF^+.

Table 2 also shows a positive relationship between F and P_2O_5 contents of Pleistocene limestone samples. This implies that ${PO_4}^{3-}$ acts as an important fixing agent of F^- to form fluorapatite. Rude and Aller[4)] have also estimated that a portion of F released during the transformation of high-Mg calcite and aragonite to low-Mg calcite is fixed as fluorapatite. However, the presence of fluorapatite in Holocene unconsolidated carbonate sediments or Pleistocene limestones has not been confirmed so far.

Mode of Occurrence of F in Yoron Pleistocene Limestones. The minerals identified in 1 mol dm^{-3} acetic acid-insoluble residues in Yoron limestone samples are summarized in Table 3. Both apatite and fluorite were found in most of the Paleozoic limestones,

Table 2. Correlation Matrix for Concentration of Chemical Species in Pleistocene Limestone Samples (n=20) from Yoron-jima Island

	MgO	Sr	Na	P$_2$O$_5$	F
MgO	—	0.40	0.20	$\underline{0.53}$	$\underline{\underline{0.82}}$
Sr		—	0.10	0.24	0.49
Na			—	0.06	0.13
P$_2$O$_5$				—	$\underline{\underline{0.77}}$
F					—

=: Significance at 1% level. –: Significance at 5% level.

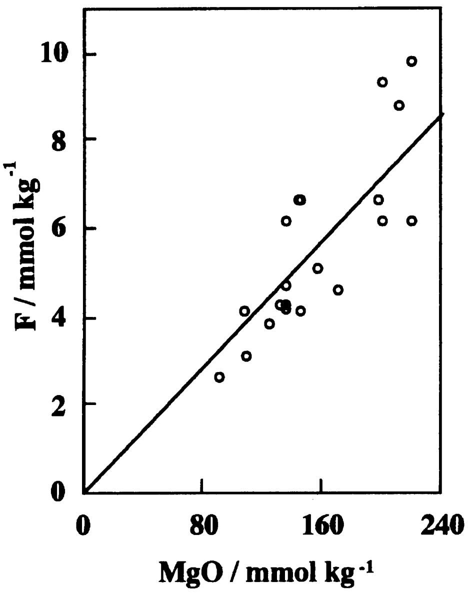

Fig. 3. Relationship between F and MgO contents of Pleistocene limestone samples from Yoron-jima Island. Solid line shows the average ratio of F and MgO contents of Holocene limestone samples from Yoron-jima Island.

and apatite was also found in a Pleistocene limestone sample (82-KYL-06). Although XRD peaks of apatite identified in the 82-KYL-06 sample were weaker and smaller than those of apatite in the Paleozoic limestone composite sample (Fig. 4), a large portion of apatite in Pleistocene limestones might have been dissolved during 1 mol dm^{-3} acetic acid treatment due to its small crystal size. We therefore consider that apatite is a main common F-bearing mineral in Yoron Pleistocene limestones.

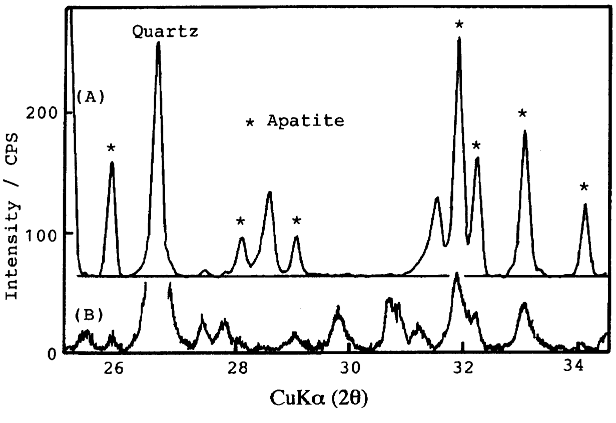

Fig. 4. Powder X-ray diffractograms of 1 mol dm^{-3} acetic acid-insoluble residues in limestone samples from Yoron-jima Island. (A) Composite sample of 8 Paleozoic limestone samples, (B) 82-KKL-06 (Pleistocene limestone). Measurement conditions for X-ray diffraction: Voltage; 40 V, Current; 20 mA, Scan rate; 0.1° 2θ/min.

Table 3. 1 mol dm^{-3} Acetic Acid-Insoluble Minerals in Limestone Samples from Yoron-jima Island

Sample No.	Mineral[a)]					
	Qtz	Fel	Ill	Chl	Apt	Flr
[Holocene]						
82-KYL-31[c)]	+					
[Pleistocene]						
82-KYL-03	+++[b)]	++	++	+		
82-KYL-04	++	+	+	++		
82-KYL-06[c)]	++	+	++	+	+	
82-KYL-08	++	+	+	+		
82-KYL-11[c)]	++	+	++	+		
82-KYL-13	++	+	++	++		
82-KYL-14	+	++	+	+		
82-KYL-22	++	+	+	+		
82-KYL-24	+	+	+	++		
82-KYL-28	+++	+	++	+		
82-KYL-29[c)]	+	+	+	+++		
[Paleozoic]						
82-KYL-17	++	+	+	+++		
82-KYL-18	+		+	++	++	+
82-KYL-21	++		+	++	++	+
82-KYL-25	+			++	++	+
82-KYL-26				+	++	+
82-KYL-27	+		+		++	+
Composite[c,d)]	+	+	+	++	++	+

a) Qtz: Quartz, Fel: Feldspars, Ill: Illite, Chl: Chlorite, Apt: Apatite, Flr: Fluorite. b) Semi-quantitative expression of X-ray intensity of XRD; +: weak, ++: medium, +++: strong. c) Dissolved under low temperature (< 283 K). d) Composite sample of 8 samples.

Fluorine and PO_4 contents were then plotted to clarify the contribution of $PO_4{}^{3-}$ to the geochemical behavior of F during the formation of limestones (Fig. 5). A positive correlation can be seen between the F and PO_4 contents, though the molar ratio of F to PO_4 does not agree with that of fluorapatite [$Ca_{10}(PO_4)_6F_2$], which is shown as a solid line in Fig. 5.

Sedimentary apatite generally appears as francolite (carbonate fluorapatite), which differs in composition from pure fluorapatite.[19)] The structure of francolite can be written as $Ca_{10}(PO_4)_{6-x}(CO_3)_xF_{0.4x}F_2$ ($x \leq 1.5$),[20)] indicating that the F content depends upon the amount of CO_3. The accurate mineralogical composition of the apatite in 82-KYL-06 sample was identified to evaluate the F content of this mineral. The CO_3 content of the apatite was estimated by the XRD method. Schuffert et al.[21)] proposed an empirical equation that defines the relation between CO_3 content and $\Delta 2\theta$ for the (300) and (002) XRD reflections of francolite (CO_3 wt%$=38.381\ \Delta 2\theta_{(300)-(002)} - 276.343$). The 2θ values for the (300) and (002) XRD reflections of the apatite in 82-KYL-06 sample are 33.04 and 25.80, respectively. The CO_3 content is thus calculated as 1.5 wt%. The molecular weight of francolite is expressed as 1008.64$-$7.75 (wt% of CO_2 in apatite).[19)]

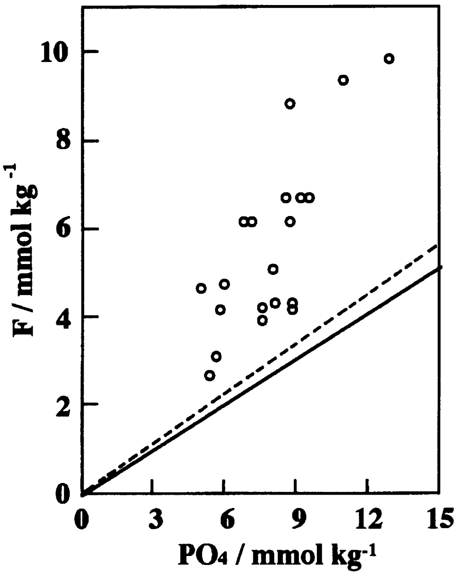

Fig. 5. Relationship between F and PO$_4$ contents of Pleistocene limestone samples from Yoronjima Island. Solid and dotted lines show the amount of F assuming that the element is contained as fluorapatite [$Ca_{10}(PO_4)_6F_2$] and francolite [$Ca_{10}(PO_4)_{5.74}(CO_3)_{0.26}F_{2.1}$] with 1.5 wt% CO$_3$, respectively.

The molecular weight of the francolite in 82-KYL-06 sample is about 1000. Since 1.5 wt% CO$_3$ in francolite corresponds to 0.25 mol kg^{-1}, the chemical formula of the francolite with 1.5 wt% of CO$_3$ is expressed as $Ca_{10}(PO_4)_{5.75}(CO_3)_{0.25}F_{2.1}$. The dotted line in Fig. 5 indicates the molar F/PO$_4$ ratio of francolite with 1.5 wt% of CO$_3$. Assuming that all the francolites in Yoron Pleistocene limestones contain about 1.5 wt% CO$_3$, the francolites may contain about half of the total F in these samples.

Possible F-bearing minerals other than francolite are sellaite (MgF$_2$) and fluorite (CaF$_2$). The good positive correlation between the F and MgO contents of Yoron Pleistocene limestone samples (Fig. 3) implies the possible presence of sellaite. However, the solubility product ($10^{-8.1}$; 291 K)[22] of MgF$_2$ is far greater than that ($10^{-11.75}$; 298 K)[23] of CaF$_2$. Even though MgF$_2$ is for a short time present as a F-bearing compound, F$^-$ will be finally fixed as CaF$_2$ during the diagenetic processes. Unfortunately, we could not find fluorite in the Pleistocene limestone samples (Table 3). However, the lack of identification of fluorite by X-ray diffraction may be due to the large difference of molecular weight of CaF$_2$ (78.08) and $Ca_{10}(PO_4)_6F_2$ (1008.64). The weight ratio of fluorite to fluorapatite with the same F content is 1/13. This may be a main reason why fluorite was not identified. We therefore concluded that the rest of the F may be contained as fluorite.

Conclusions

1. Fluorine is greatly decreased during the transformation of high-Mg calcite to low-Mg calcite. The average F content of Yoron Pleistocene limestones consisting of low-Mg calcite is about 100 ppm.

2. Fluorine might have been leached out in the form of MgF$^+$ from high-Mg calcite into interstitial waters during this process. A good positive correlation also exists between the F and MgO contents of Pleistocene limestones.

3. The presence of carbonate fluorapatite (francolite) in Pleistocene limestones was experimentally identified with XRD. About half of F is contained as carbonate fluorapatite in Yoron Pleistocene limestones and the rest is probably contained as fluorite.

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