Protodolomite in Daito-jima, Okinawa

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This report describes protodolomites found in Daito-jima to the east of the Okinawa Islands, Japan. To investigate the conditions for sedimentary protodolomite formation, the distribution and chemical composition of protodolomites were studied through field observations and laboratory analyses. From the thin section studies of carbonate rocks, it was observed that porous parts of coral were cemented by protodolomite crystals and that aragonite in hard tissue of coral was transformed into protodolomite. These observed facts may show that protodolomite was formed through the transformation from aragonite and magnesian calcite in magnesium rich solution. The distribution and chemical composition of protodolomite in Minami-daito-jima suggest that protodolomites may be formed in concentrated seawater.

INTRODUCTION

Carbonate rocks are widely distributed on the surface of the earth. Most carbonate rocks are formed through diagenetic processes of the skeletal parts of calcareous marine organisms. Although the skeletons consist mainly of aragonite and high-magnesian calcite, carbonate rocks are composed of low-magnesian calcite and dolomite (CHAVE, 1952; 1954; LOWENSTAM, 1954; KITANO, 1964; KITANO *et al.*, 1969; MILLIMAN, 1974). Since aragonite and high-magnesian calcite are metastable, they are recrystallized into more stable minerals such as low-magnesian calcite. Although dolomite is more stable than calcite in marine environment, dolomite is not formed directly in this environment inorganically or biologically but is formed through diagenetic processes. The mechanism for the formation of sedimentary dolomites is not well understood. This is one of the most interesting problems in carbonate geochemistry.

Many researchers have reported on the occurrence of protodolomite in Quaternary dolomites (ALDERMAN and SKINNER, 1957; WELL, 1962; BERNER, 1965). Protodolomites will no doubt provide a key to the question on the

dolomite formation. The authors have studied this problem through (a) field observations of protodolomites and estimations of environmental conditions under which protodolomites were formed, and (b) laboratory experiments on the syntheses of protodolomites from simple aqueous solutions conditioned close to seawater (OHDE and KITANO, 1978). The result of syntheses suggested that protodolomites are formed possibly from concentrated seawater.

Natural protodolomites were collected from Minami and Kita Daito-jima. These islands are typical emerged atolls. Observations in this study and also drilling at Kita-daito-jima (SUGIYAMA, 1934) suggest that the thickness of carbonate sediments is over one thousand meters. The occurrence of Pleistocene dolomites and associated carbonate minerals has been described by many researchers: some of them showed that Daito-jima was one of the best areas in the Pacific for studies on protodolomite formation (OHTA, 1938; SCHLANGER, 1965; BERNER, 1965; KONISHI *et al.*, 1972; KASHIMA, 1974, 1975). However, no detailed geochemical information and studies have yet been available on protodolomites in these islands. The main purpose of the present paper is to describe the distribution

and chemical composition of protodolomite in Daito-jima.

EXPERIMENTAL

The present authors have surveyed the lateral distribution of protodolomites in Daito-jima and have determined the chemical compositions of the protodolomites. As seen from Fig. 1, the island is located about four hundred kilometers to the east of Okinawa and is separated by the Ryukyu Trench from Okinawa.

Samples About five hundred carbonate samples were collected. Figure 2 shows some of the sampling stations on the western and eastern shore slopes of Minami-daito-jima.

Analytical method After the sample was dissolved with 6N HCl solution, silica, sulfate and insoluble residue were determined by gravimetry, calcium and magnesium by EDTA titration, phosphorus by spectrophotometry, and Sr, Na, K, Mn and Zn by the atomic absorption method. Neutron activation method developed by the authors (OHDE *et al.*, 1978) was employed for the determination of fourteen trace elements: F, Cl, Sc, Br, I, Ba, La, Ce, Sm,

Eu, Tb, Yb, Th and U.

Protodolomite, which is a solid solution of magnesite (48-40mol%) and calcite (52-60 mol%), was identified by the X-ray powder diffraction method. Thin sections of some samples were examined to check the texture and cementation of protodolomites.

RESULTS AND DISCUSSION

Distribution of protodolomites Carbon-

Fig. 2. Sampling stations at western and eastern sides in Minami-daito-jima.

Fig. 1. Location of Daito-jima.

ate rocks in Daito-jima are composed exclusively of low-magnesian calcite and protodolomite. Figure 3a shows their lateral distribution in Minami-daito-jima. The lack of data in the central part of the island is due to the geological feature that reddish soil covers the surface of this area. Figure 3b shows the geomorphological classification of the island by TAKENAGA (1972). These two figures have a good correlation: protodolomite is not observed on the western side of the island where fairly young ridges such as R1 and R2 (consisting of protodolomite, see Figs. 3a and 3b) are lacking, as seen from Fig. 3b. In addition, the lack of young ridges in the western area seems to have some connection with the fact that the western area was always on the lee side during the atoll formation. There seems to exist a significant correlation between the geomorphological feature of the islands and the protodolomite distribution. It is not clear, however, how the correlation mentioned above corresponds to the physical and chemical change in the environment of protodolomite formation.

The results of X-ray and chemical analyses

showed that protodolomites in Daito-jima contained 40-48mol% magnesium carbonate as a solid solution between calcite and magnesite. There was no obvious correlation between the magnesium carbonate content of protodolomites and their geographycal location, for example, elevation from the sea level.

Thin sections of carbonate samples

Figure 4 shows a thin section photomicrograph of a protodolomite sample collected from station 5 (see Fig. 2) in the Saitominato area (see Fig. 3a). The photograph clearly shows fossilized coral skeleton (*Galaxea* sp.) as the dark area and also rhombohedral protodolomite crystal as cementing material in the porous parts of the coral. X-ray analysis of this sample reveals that both the skeleton and the porous portions are composed of protodolomite. However, it is well known that living *Galaxea* secretes pure aragonite. Thus, it is clear that aragonite in the hard tissue of the coral was transformed into protodolomite. Furthermore, the authors also observed in Daito-jima that the magnesian calcite of a calcareous alga was transformed into proto-

Fig. 3a. Distribution of protodolomite in Minami-daito-jima. Large and small circles denote average and individual values, respectively.

Fig. 3b. Geomorphological classification of Minami-daito-jima (TAKENAGA, 1972), T: terrace, R: ridge, L: lagoon.

dolomite. These observations indicate that the formation of protodolomite had proceeded from aragonite and/or magnesian calcite in magnesium rich solution.

Chemical compositions of protodolomite and calcite To estimate the chemical composition of the parent magnesium rich solution, major and natural protodolomite formation, major and minor elements in natural protodolomites and calcites were determined by the methods described in the experimental section. Table 1 shows the concentrations of chemical elements in protodolomites (4 samples) and calcites (4 samples). TOKUYAMA *et al.* (1972) reported that the silica content of Ryukyu limestones ranged from 0.27 to 27.3%. The silica and insoluble residue contents of carbonate rocks in Daito-jima are extremely low, as seen from Table 1. Table 2 shows the average concentrations of some constituents in protodolomites (20 samples) and calcites (10 samples) with

standard deviation, minimal and maximal values. The following results are obtained from Tables 1 and 2.

Fluoride content of protodolomites Figure 5 shows a good correlation between fluoride content and proportion of protodolomite in Daito-jima carbonates (correlation coefficient = 0.90). KITANO and OKUMURA (1973) reported

Fig. 4. Thin section photomicrograph of protodolomite cement (open nicol).

Table 1. Chemical composition of carbonate rocks from Minami-daito-jima

Sample No.	Sai-6	Sai-25	Ni-4	Ni-18	A-1	A-3	L-1	K-5
Location	Reef*	Reef*	Reef*	Reef*	Lagoon**	Lagoon**	Lagoon**	Lagoon**
Mineral	Protodolomite	Protodolomite	Calcite	Calcite	Protodolomite	Protodolomite	Calcite	Calcite
Ca (%)	23.98	24.23	38.92	39.02	23.79	24.07	39.06	39.74
Mg (%)	11.40	11.26	0.48	0.46	11.73	11.44	0.27	0.21
SiO ₂ (%)	n.d.	0.04	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Insoluble residue (%)	0.04	0.13	0.09	0.07	0.11	0.08	0.04	0.06
SO ₄ (ppm)	1420	1230	800	680	850	1210	500	70
P (ppm)	150	160	360	180	200	150	400	84
F (ppm)	610	590	74	56	520	550	140	21
Na (ppm)	1000	350	380	98	290	330	93	32
Cl (ppm)	1400	41	490	59	25	28	17	13
K (ppm)	24	22	27	22	32	24	20	24
Sc (ppm)	1.6	12	38	22	45	22	21	25
Mn (ppm)	1.6	13	4.8	9.5	21	24	20	17
Zn (ppm)	6.9	6.3	6.5	6.2	7.9	7.1	7.2	6.6
Br (ppm)	0.55	0.28	1.2	0.94	0.59	0.35	5.8	0.86
Sr (ppm)	190	220	200	220	200	200	400	310
I (ppm)	5.0	5.6	4.9	4.8	3.2	3.0	8.5	2.0
Ba (ppm)	tr.	tr.	1.8	1.5	tr.	tr.	3.3	tr.
La (ppb)	n.d.	38	140	100	47	n.d.	56	140
Ce (ppb)	56	110	260	140	230	220	85	120
Sm (ppb)	n.d.	14	41	23	38	n.d.	11	34
Eu (ppb)	1.4	2.7	6.5	3.0	12	tr.	tr.	6.5
Tb (ppb)	n.d.	n.d.	n.d.	19	20	tr.	n.d.	tr.
Yb (ppb)	n.d.	17	29	23	63	24	26	30
Th (ppb)	n.d.	n.d.	13	14	tr.	tr.	tr.	tr.
U (ppm)	0.61	0.31	0.15	0.13	1.5	2.7	0.17	0.15

*: Sampling point is shown in Fig. 2.

**: Sampling point is shown in Fig. 3.

n.d.: not detected, tr.: trace.

that in coprecipitation experiment in the solution system " $\text{Ca}(\text{HCO}_3)_2 + \text{F}^- + \text{Mg}^{2+} + \text{Na}^+ + \text{Cl}^-$ " the amount of fluoride coprecipitated with calcite (low Mg calcite) increases with increasing concentration of magnesium ions in the parent solution. KITANO and OKUMURA (1973) and OHDE and KITANO (1980) also studied the coprecipitation of fluoride and magnesium ions with carbonates (low Mg calcite, high Mg calcite and protodolomite) synthesized in $\text{CaCl}_2 + \text{MgCl}_2 + \text{NaHCO}_3 + \text{NaF} + (\text{NaCl}) - \text{H}_2\text{O}$ solutions at 25°C , and obtained a result similar to that in Fig. 5. The fluoride content of carbonate sediments seems to be controlled by the concentration of magnesium ions in the parent solution and also by the magnesium carbonate content of carbonate sediment. Accordingly, fluoride ions will be incorporated into calcitic carbonates more easily from magnesium rich brine than from fresh water. These results on the field observations and laboratory experiments suggest that the protodolomites were formed from magnesium-rich brine.

Uranium content of protodolomites Figure 6 shows the relation between uranium content and proportion of protodolomite, indicating that the uranium contents of protodolomites

from lagoons are higher than those from reefs. Since the protodolomites were autogenous, the above result may suggest the difference in sedimentary environment between lagoons and reefs. However, the chemical form of uranium in carbonate rocks has not yet been known. Uranium in protodolomites is not simply incorporated through diagenetic processes after the formation of protodolomite in Daito-jima, because the uranium content of protodolomites in reefs and that of calcites in lagoons are very small. SUGIMURA (1970) reported that uranium should be deposited into sediment in an anaerobic environment. Modern lagoons of atolls are more anaerobic than reefs (SMITH *et al.*, 1978). Therefore, the high uranium content of the protodolomites in the ancient lagoon of Daito-jima may suggest that anaerobic environment prevailed during the formation of protodolomites.

Sodium, chloride, sulfate, strontium, barium, manganese and phosphorus contents of protodolomite Sodium, chloride and sulfate are more concentrated in protodolomites than in calcites, as seen from Tables 1 and 2. The ratios among these elements are different from those in seawater. TOKUYAMA *et al.* (1972)

Table 2. Average contents of some constituents in protodolomite and calcites in reef and lagoon (ppm)

Constituent	Reef		Lagoon	
	Protodolomite	Calcite	Protodolomite	Calcite
Nos. of samples	14	4	6	6
F	530±70 (440-660)	73±26 (53-110)	540±40 (500-590)	70±44 (21-140)
U	0.30±0.13 (0.18-0.61)	0.16±0.09 (0.08-0.29)	1.7±0.6 (1.0-2.7)	0.20±0.06 (0.15-0.29)
Na	680±340 (290-1500)	320±320 (48-760)	310±70 (160-400)	48±24 (29-93)
Cl	690±660 (41-2300)	390±460 (19-1000)	27±5 (20-34)	13±3 (9.7-17)
SO ₄	1300±300 (790-1720)	730±470 (150-1300)	1000±200 (700-1210)	280±150 (n.d.-500)
Sr	190±30 (120-230)	230±30 (200-260)	200±20 (160-220)	340±50 (280-400)
Br	1.1±0.5 (tr.-1.6)	1.4±0.4 (tr.-1.8)	tr. (-)	2.1±1.4 (tr.-3.3)
Mn	11±5 (1.6-21)	9.4±6.9 (4.1-19)	23±2 (20-25)	25±15 (17-38)
P	160±50 (100-300)	190±120 (110-360)	180±100 (100-250)	300±170 (84-460)

reported that average concentrations of sodium, chloride and sulfate are 120, 30 and 170ppm, respectively, in calcitic Ryukyu limestones. They are a little lower than those in Daito-jima limestones. As seen from Table 2, strontium, barium and phosphorus are less concentrated in protodolomites than in calcites. The average manganese content of lagoon samples is higher than that of reef samples.

It is highly probable that some of the elements in the protodolomites were lost or gained through diagenetic processes. In addition, there is no sufficient information on the chemical behavior of these elements during protodolomite formation in magnesium-rich brine. Thus the trial for estimating the chemical composition of parent solution has been obscured.

Rare earth element contents of protodolomites No detailed studies have yet been made on the coprecipitation of rare earth elements with marine carbonates and on their

diagenetic behaviors. Table 3 shows the average concentrations of rare earth elements in the carbonate rocks and corals from Minami-daito-jima. Rare earth elements were not detected in primary carbonates such as corals, while they were detected in secondary carbonate rocks. These elements may have been incorporated into the carbonate rocks through diagenetic processes. Figure 7a shows the relationship between Sc content, of which detection limit is quite low, and silica content of carbonate rocks. Similarly, Fig. 7b shows the relation of Eu and silica contents. These two figures show a similar trend. KITANO *et al.* (1979) suggested that silica incorporated in marine carbonates is supplied mostly from terrigenous materials. Significant fractions of rare earth elements in the samples may have been incorporated as silicates during and after the formation of the carbonate rocks in the islands.

Parent solution for the formation of proto-

Fig. 5. A plot of fluoride content against the weight percent of protodolomite in carbonate rocks.

Fig. 6. A plot of uranium content against the weight percent of protodolomite in carbonate rocks. ○: Reef, ●: Lagoon.

Table 3. Average contents of rare earth elements in carbonate rocks and corals from Minami-daito-jima

	Mineral composition	Nos. of samples	La (ppb)	Ce (ppb)	Sm (ppb)	Eu (ppb)	Tb (ppb)	Yb (ppb)	Sc (ppb)
Dolostone	Protodolomite	15	62±34	110±74	21±8	4.1±3.1	n.d.	19±16	12±11
	Protodolomite > Calcite	4	76±15	78±15	23±2	3.3±2.3	n.d.	11±9	7.2±5.1
	Protodolomite < Calcite	9	98±100	140±130	26±19	5.1±5.5	tr.	19±21	13±20
Limestone	Calcite	8	97±40	120±70	24±10	4.5±1.8	n.d.	21±8	21±10
Coral	Aragonite	3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	1.0±0
	Detection limit		10	20	2	0.8	4	3	0.6

n.d.: not detected, tr.: trace.

dolomite The $^{18}\text{O}/^{16}\text{O}$ ratio is useful for the discussion on the chemical composition of the parent solution for the protodolomite formation. According to BERNER (1965), GROSS and TRACEY (1966) and FONTES *et al.* (1969), the $\delta^{18}\text{O}$ values of protodolomites in Pacific atolls are higher than those of calcites. BERNER (1965) pointed out that the protodolomites were formed in isotopically heavy seawater through evaporation. A similar result was reported by KONISHI *et al.* (1972) for protodolomites from Okinawa Island.

Field observations and stable isotope data suggest that protodolomite is formed from concentrated seawater in lagoon. This is supported by the experimental results on protodolomite

syntheses in aqueous solutions (OHDE and KITANO, 1978). Synthesis experiments show that the very high concentrations of magnesium ions and dissolved carbonate materials and the fairly high concentration of calcium ions in parent solution are needed for the protodolomite formation. The transformation of magnesian calcite and aragonite to protodolomite is expected from field observations in magnesium rich brine. The origin of magnesium and calcium in protodolomite is considered to be seawater concentrated through intensive evaporation in shallow lagoons. However, many problems concerning the parent solution still remain unsolved: For example, how an arid climate had continued for a sufficiently long

Fig. 7a. Relation between scandium and silica contents of carbonate rocks. ●: Protodolomite, ◐: Protodolomite + Calcite, ○: Calcite.

Fig. 7b. Relation between europium and silica contents of carbonate rocks. ●: Protodolomite, ◐: Protodolomite + Calcite, ○: Calcite.

period of time to maintain concentrated seawater for protodolomite formation? What is the origin of the very large amounts of carbonate ions for the protodolomite formation? How did the transformation from magnesian calcite and aragonite to protodolomite occur in magnesium rich brine? How is the observed correlation between geomorphological feature and distribution of protodolomite related to the chemical composition of the parent solution? Nevertheless, our observations will provide a better understanding of the nature of sedimentary protodolomite and of the environment, in which it was formed.

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REFERENCES

- ALDERMA, A. R. and SKINNER, H. C. W. (1957) Dolomite sedimentation in the south-east of South Australia. *Am. J. Sci.* **255**, 561–567.
- BERNER, R. A. (1965) Dolomitization of the Mid-Pacific atolls. *Science* **147**, 1297–1299.
- CHAVE, K. E. (1952) A solid solution between calcite and dolomite. *J. Geol.* **60**, 190–192.
- CHAVE, K. E. (1954) Aspects of the biogeochemistry of magnesium. *J. Geol.* **62**, 266–283, 587–599.
- FONTES, J. C., KULBICKI, G. and LETOLLE, R. (1969) Les sondages de l'atoll de Mururoa; aperçu géochimique et isotopique de la série carbonate. *Cahiers. Pacif.* **27**, 69–74.
- GROSS, M. G. and TRACEY, J. I., JR. (1966) Oxygen and carbon isotopic composition of limestones and dolomites, Bikini and Eniwetok Atolls. *Science* **151**, 1082–1084.
- KASHIMA, N. (1974) Insoluble residues from the Daito Limestone of Minamidaito-Jima. *Mem. Ehime Univ., Sci., Ser. D. (Earth Sci.)* **7**, No. 3, 79–88 (in Japanese with English abstract).
- KASHIMA, N. (1975) A note on the Daito Limestone of Minamidaito-Jima with special concern to its dolomitization. *Mem. Ehime Univ., Sci., Ser. D. (Earth Sci.)* **7**, No. 4, 95–101 (in Japanese with English abstract).
- KITANO, Y. (1964) On factors influencing the polymorphic crystallization of calcium carbonate found in marine biological systems. In Recent researches in the fields of hydrosphere, atmosphere and nuclear geochemistry, 305–319. Maruzen Co., Ltd., Tokyo.
- KITANO, Y., KANAMORI, N. and TOKUYAMA, A. (1969) Effects of organic matter on solubilities and crystal form of carbonates. *Am. Zoologist* **9**, 681–688.
- KITANO, Y. and OKUMURA, M. (1973) Coprecipitation of fluoride with calcium carbonate. *Geochem. J.* **7**, 37–49.
- KITANO, Y., OKUMURA, M. and IDOGAKI, M. (1979) Behavior of dissolved silica in parent solution at the formation of calcium carbonate. *Geochem. J.* **13**, 253–260.
- KONISHI, K., KANESHIMA, K., NAKAGAWA, K. and SAKAI, H. (1972) Pleistocene dolomite and associated carbonates in south Okinawa, the Ryukyu Islands. *Geochem. J.* **6**, 17–36.
- LOWENSTAM, H. A. (1954) Factors affecting the aragonite: calcite ratio in carbonate secreting marine organisms. *J. Geol.* **62**, 284–322.
- MILLIMAN, J. D. (1974) *Marine carbonates*. Springer-Verlag, Berlin-Heidelberg-New York.
- OHDE, S. and KITANO, Y. (1978) Synthesis of protodolomite from aqueous solution at normal temperature and pressure. *Geochem. J.* **12**, 115–119.
- OHDE, S., OHTA, N. and TOMURA, K. (1978) Determination of trace elements in carbonates by instrumental neutron activation analysis. *J. Radioanal. Chem.* **42**, 159–167.
- OHDE, S. and KITANO, Y. (1980) Incorporation of fluoride into Ca-Mg carbonates. *Geochem. J.* **14**, 321–324.
- OHTA, Y. (1938) Chemical analysis and microchemical tests on the boring cores obtained from the deep well in Kita-Daito-Zima and Daito Limestone. *Contr. Inst. Geol. Paleont., Tohoku Imp. Univ.*, n. 30, 1–30 (in Japanese).
- SCHLANGER, S. O. (1965) Dolomite-evaporite relations on Pacific Islands. *Sci. Rept. Tohoku Univ., 2nd Ser. (Geol.)* **37**, 15–29.
- SMITH, S. V., JOKIEL, P. L. and KEY, G. S. (1978) Biogeochemical budgets in coral reef systems. *Atoll Res. Bull.*, n. 220, 1–11.
- SUGIMURA, Y. (1970) Natural radioactive elements. In *Chemistry of seawater*. 350–363, Tokai Univ. Press. Tokyo (in Japanese).
- SUGIYAMA, T. (1934) On the drilling in Kita-Daito-Zima. *Contr. Inst. Geol. Paleont., Tohoku Imp. Univ.* **11**, 1–44 (in Japanese).

- TAKENAGA, K. (1972) Geomorphological significance of limestone caves in Minami-daito-jima. *Japan Caving* 4, 57-65 (in Japanese).
- TOKUYAMA, A., KITANO, Y. and KANESHIMA, K. (1972) Geochemical behavior of chemical species in the processes of limestone formation. Part I. Chemical composition of corals and limestones in the Ryukyu Islands. *Geochem. J.* 6, 83-92.
- WELL, A. J. (1962) Recent dolomite in the Persian Gulf. *Nature* 194, 274-275.