

**On the Minor Elements in Ryukyu Limestone from  
Kikai-jima Island, Kagoshima Prefecture, Japan\***

By

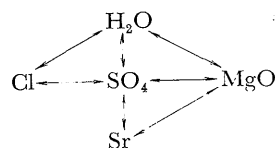
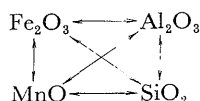
Tadashi FUJINUKI\*\*

Abstract

The mineral composition of Ryukyu limestone from Kikai-jima Island is investigated by X-ray diffraction. As a result, it is confirmed that high magnesium calcite, low magnesium calcite, aragonite and protodolomite are contained in Ryukyu limestone.

By chemical analysis of major components and minor elements, the relation between mineral composition and minor elements is investigated.

Calculating the correlation coefficients ( $\gamma$ ) among the components, the following relations are confirmed, especially in case of  $\gamma > 0.51$ , these relations are noticeable.



It is considered that the correlation in the group of  $\text{Fe}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$  and  $\text{MnO}$  may be caused by the detrital minerals, while that of  $\text{Mg}$ ,  $\text{Sr}$ ,  $\text{SO}_4$ ,  $\text{Cl}$  and  $\text{H}_2\text{O}$  by the carbonate minerals.

**Introduction**

The writer studied previously the minor elements contained in Akasaka limestone (middle to upper Permian age), focusing on the relation between their distribution and the divisions of the limestone by fossil foraminifers. As a result, it was shown that the behavior of a few elements indicated the primary mineral composition and the depositional environment of the limestone (FUJINUKI, 1968). To ascertain the relation of mineral composition to minor elements, Pleistocene Ryukyu limestone, in which various mineral species can be found, has been investigated chemically and mineralogically. The field survey and sampling for this investigation were carried out in Kikai-jima Island, Kagoshima Prefecture.

Kikai-jima Island is situated about 23km eastward of Amami Oshima Island. It is long and narrow in shape and extends about 16km from NE to SW in length and 3.5-6.5km in width.

The basement rock of Kikai-jima Island is Sômachî Formation\*\*\* of Pliocene age, which consists mainly of mudstone and sandstone. Ryukyu limestone occurs over Sômachî Formation and is composed of reefy and deep-sea corals. It contains foraminifers, molluscs, calcareous algae and other calcareous organic remains.

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\*\*\*It belongs to Shimajiri Group distributed in the Ryukyu Islands.

There is a raised coral reef at the coastal lowlands of the island. The sand dune which is composed of fragments of foraminifers, shells and coral, is mainly distributed at the northern and western areas.

This Ryukyu limestone was divided into the following three formations by NAKAGAWA (1964); Hyakunodai Formation, Nagamine Formation and Wan Formation in ascending order. KONISHI (1967) also divided it into the next three formations using the dating of natural alpha-radioactive nuclides in biogenetic carbonate rocks; the older limestone (older than 200 thousand years), the younger limestone (55-70 thousand years) in member of Ryukyu limestone, and Araki limestone (40-45 thousand years) in ascending order. But, according to the latest report of NAKAGAWA (1969), he recognized only two formations, Hyakunodai and Wan. The present study shows that there is no significant difference in minor element contents among the formations divided by KONISHI and NAKAGAWA. Accordingly, in this study these formations are treated in a lump as Ryukyu limestone except for the raised coral reef and sand dune.

The only study of minor elements of Ryukyu limestone in Japan was carried out by KANESHIMA (1965). On the contrary, relating to the minor elements in carbonate rocks of Plio-Pleistocene age and in recent calcareous sediments, there are many reports in the world, and such papers written by FRIEDMAN (1968), KAHLE (1965), KINSMAN (1969), SIEGEL (1960), STEHLI & HOWER (1961) are those examples.

The field surveys for the research of Ryukyu limestone were carried out with the participation of IGARASHI (research target is mineral composition), FUJINUKI (minor elements), WATANABE (organic matter) and TOGASHI (clay minerals), in 1966 and 1968. The samplings for each study were made at the same time. During the survey in 1968, the carbonate minerals were identified by staining in the field, according to FRIEDMAN's method (1959) (FUJINUKI, WATANABE & TOGASHI, 1968).

The present paper describes the result of chemical analysis of major and minor components of Ryukyu limestone. As for the constituent minerals, IGARASHI, a coworker, will report in detail later. Therefore, only the outline of mineral composition is described in the present paper.

### Locality of sampling

The localities in which the samples were collected are shown in Fig. 1.

### Mineral composition

Fifty-eight samples were examined by X-ray diffraction method and confirmed that Ryukyu limestone samples from Kikai-jima Island contained the following minerals; aragonite, high magnesium calcite, low magnesium calcite and protodolomite (calcium excess dolomite). These minerals are equally detected from Hyakunodai Formation and Wan Formation. Aragonite was detected from 29 samples (60.4%), high magnesium calcite from 22 samples (45.8%) and protodolomite from 5 samples (10.4%) out of 48 samples of Ryukyu limestone.

Calculating by the graph shown in CHAVE's report (1952), which illustrates the relation of  $MgCO_3$  content to the major cleavage (100) of calcite,  $MgCO_3$  contained in high magnesium calcite is from the minimum 8.5mol% to the maximum 13mol% and on an average 10.7mol%. These results of calculation are closed to those of 12-13mol% by STEHLI & HOWER (1961), and 10-12

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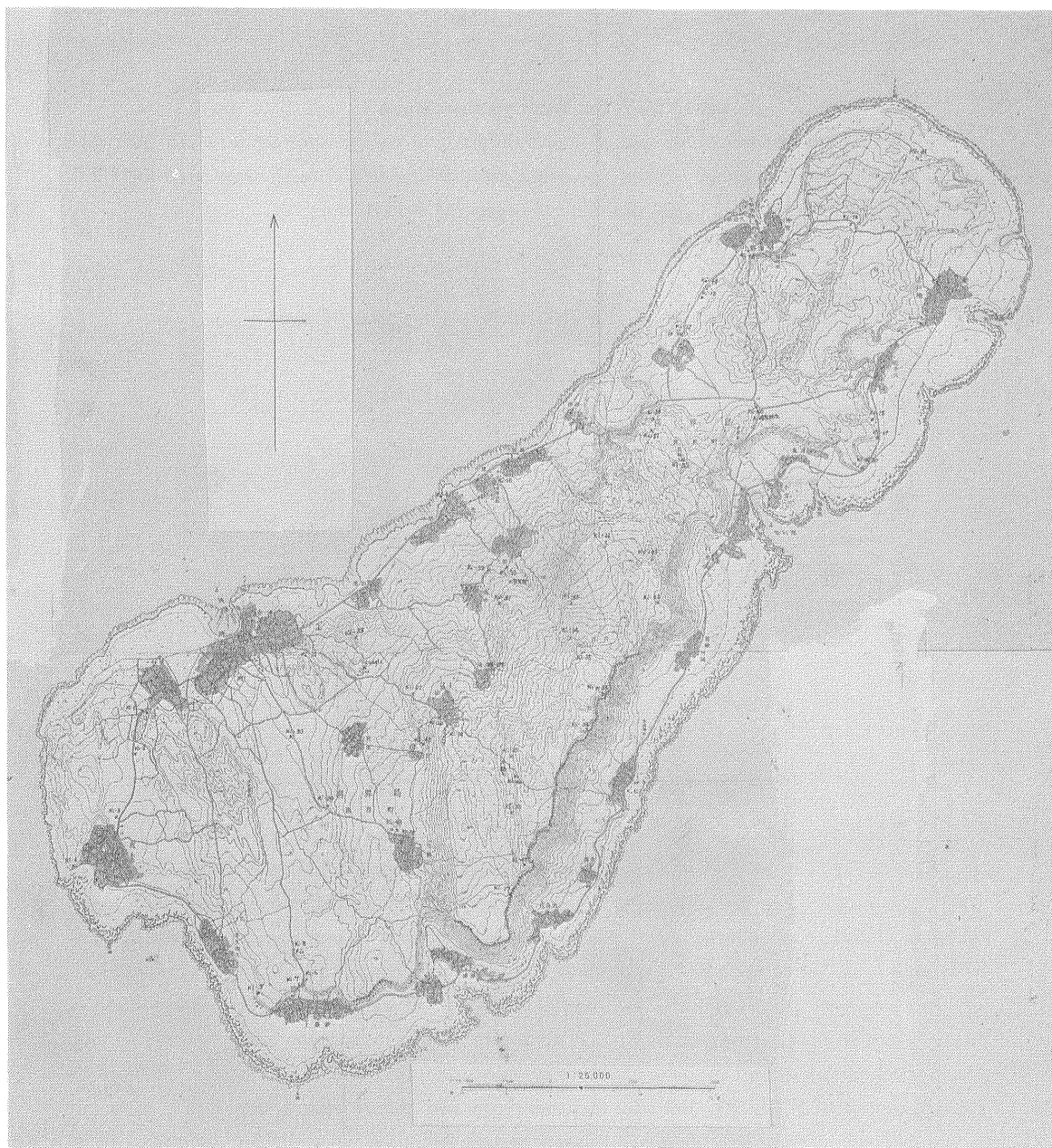


Fig. 1 Locality map of sampling points

mol% by FRIEDMAN (1964).

To separate protodolomite from calcite and aragonite, Ki-22 sample was treated with acetic acid, in which the latter two minerals are soluble. The composition of protodolomite was calculated by the results of DTA, TGA and chemical analysis of the residue. It is considered that the composition of protodolomite is similar to  $\text{Ca}_{0.6}\text{Mg}_{0.4}\text{CO}_3$ .

On the diagenesis of these minerals, there are very significant studies by FRIEDMAN (1964),

MATTHEWS (1968) and LAND (1967). The diagenesis of Ryukyu limestone will be reported at the another chance.

### DTA for Ryukyu limestone

DTA patterns of several samples, of which the mineral composition are different with each other, are shown in Fig. 2. 0.3-0.4g of powdered samples under 150 mesh were used for DTA. The sensitivity of DTA is  $\pm 100\mu\text{V}$  and the rate of heating is  $10^\circ\text{C}/\text{min}$ .

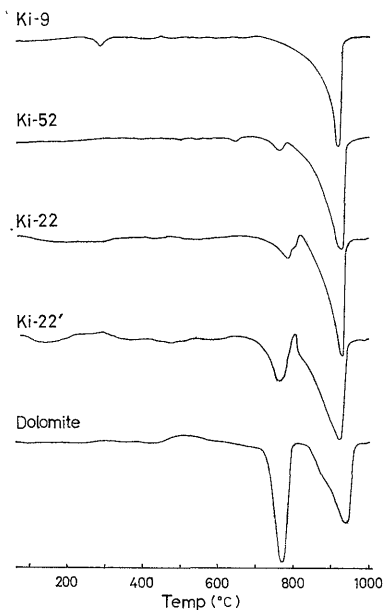


Fig. 2 DTA curves of Ryukyu limestone

Ki-9 in Fig. 2 is reefy coral composed of aragonite only, and its endothermic peak at about  $300^\circ\text{C}$  was produced by dehydration of a specific water (neither combined water nor free water), which is characteristic of aragonitic hexacollara. This phenomenon was already reported by FUJINUKI and IGARASHI (1969). Ki-52 is composed of high magnesium calcite, low magnesium calcite and aragonite and its endothermic peak at about  $750^\circ\text{C}$  was given by the decomposition of  $\text{MgCO}_3$  in high magnesium calcite. Ki-22 is composed of high magnesium calcite, protodolomite, low magnesium calcite and aragonite. Its endothermic peak from  $730$  to  $810^\circ\text{C}$  may be produced by the decomposition of  $\text{MgCO}_3$ , but why the peak shows two steps is inexplicable. Ki-22' is the enriched protodolomite by treating Ki-22 with acetic acid. For a reference, DTA of dolomite (ideal) from Kuzuu ( $\text{MgO}$  19.05%) also is added in Fig. 2.  $\text{MgCO}_3$  and  $\text{CaCO}_3$  in protodolomite are decomposed at lower temperatures than those in ideal dolomite.

### Insoluble residues

The residues of samples treated with hydrochloric or acetic acid were investigated by X-ray diffraction. Some results are shown in Fig. 3. Quartz and feldspar are generally found in insoluble residues, in which clay minerals of kaoline and illite are also contained. Pyrite is a rare constituent in them. Such mineral composition is not so different from that in the insoluble residues of ancient lime-

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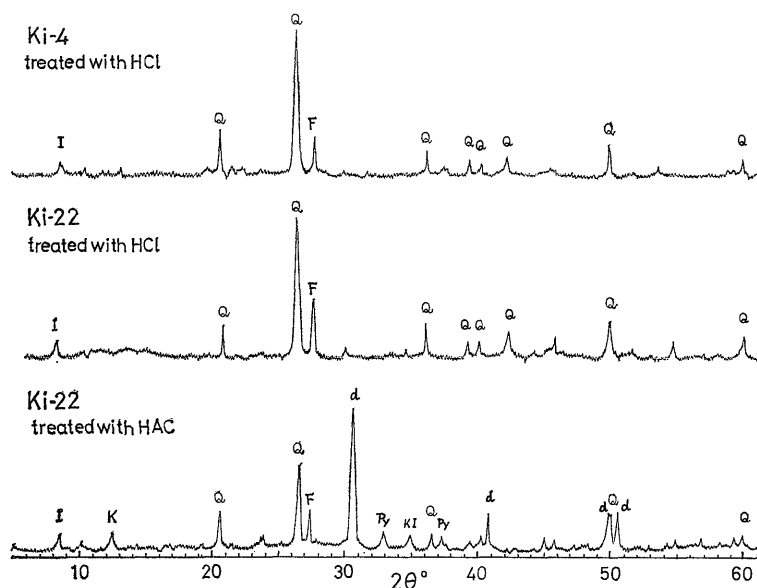


Fig. 3 X-ray diffraction patterns of insoluble residue in Ryukyu limestone  
I : illite, K : kaoline, F : feldspar, d : dolomite, Py : pyrite

stone. When samples are treated with acetic acid, it is often possible to detect protodolomite. Quartz, feldspar, kaoline and illite are the detrital minerals, while pyrite is an authigenetic mineral. It was reported by LOVE (1967) that pyrite might be produced in the stage of early diagenesis.

Relating to the insoluble residues, the detailed study is in progress by TOGASHI. The result will be reported by him later.

**Chemical analysis of major and minor components**

The chemical analysis of major and minor components was performed according to the following procedures;

- CaO, MgO, Al<sub>2</sub>O<sub>3</sub>: chelatometry
- Fe<sub>2</sub>O<sub>3</sub>, MnO, P<sub>2</sub>O<sub>5</sub>, Cl: colorimetry
- Sr: flame photometry (standard addition method)
- SiO<sub>2</sub>, SO<sub>4</sub>, H<sub>2</sub>O: gravimetry

The details of these procedure are given in the report by ISONO, FUJINUKI, NAGAI and KANEKO (1968). Since the sample had decomposed by hydrochloric acid, sulfide-S and organic-S were not contained in SO<sub>4</sub>. After drying sample at 105°C for 2 hrs, H<sub>2</sub>O was analysed by combustion method. The results is shown in Table 1.

Table. 1 Analytical data for carbonate sediments from Kikai-jima Island

Recent coral

specimen	mineral composition				CaO (%)	MgO (%)	Fe (ppm)	Al (ppm)	SiO <sub>2</sub> (%)	Mn (ppm)	Sr (ppm)	P <sub>2</sub> O <sub>5</sub> (%)	SO <sub>4</sub> (%)	Cl (ppm)	H <sub>2</sub> O (%)
	A	MC	C	P D											
<i>Goniastrea sp.</i>	◎				53.47	0.00	160	440	0.27	23	8,450	0.013	0.67	480	1.82
<i>Leptastrea sp.</i>	◎				53.07	0.00	209	730	0.32	46	8,430	0.016	0.62	390	1.66

Reefy coral

sample No.	mineral composition				CaO (%)	MgO (%)	Fe <sub>2</sub> O <sub>3</sub> (%)	Al <sub>2</sub> O <sub>3</sub> (%)	SiO <sub>2</sub> (%)	MnO (%)	Sr (ppm)	P <sub>2</sub> O <sub>5</sub> (%)	SO <sub>4</sub> (%)	Cl (ppm)	H <sub>2</sub> O (%)
	A	MC	C	P D											
Ki-8	⊙				54.01	0.00	0.030	0.076	0.07	0.000	8,409	0.006	0.45	300	1.62
Ki-9	⊙				54.51	0.00	0.047	0.038	0.06	0.002	8,584	0.008	0.47	350	2.01

Sand dune

sample No.	mineral composition				CaO (%)	MgO (%)	Fe <sub>2</sub> O <sub>3</sub> (%)	Al <sub>2</sub> O <sub>3</sub> (%)	SiO <sub>2</sub> (%)	MnO (%)	Sr (ppm)	P <sub>2</sub> O <sub>5</sub> (%)	SO <sub>4</sub> (%)	Cl (ppm)	H <sub>2</sub> O (%)
	A	MC	C	P D											
Ki- 1	○	○	⊙		50.04	2.24	0.219	0.245	2.95	0.007	3,280	0.082	0.52	320	1.96
Ki- 2	○	○	⊙		50.39	2.80	0.245	0.186	1.42	0.005	2,600	0.085	0.45	260	1.69
Ki-13	⊙	○	⊙		51.03	2.65	0.056	0.091	0.38	0.002	4,090	0.071	0.54	220	2.01

Ryukyu limestone

sample No.	mineral composition				CaO (%)	MgO (%)	Fe <sub>2</sub> O <sub>3</sub> (%)	Al <sub>2</sub> O <sub>3</sub> (%)	SiO <sub>2</sub> (%)	MnO (%)	Sr (ppm)	P <sub>2</sub> O <sub>5</sub> (%)	SO <sub>4</sub> (%)	Cl (ppm)	H <sub>2</sub> O (%)
	A	MC	C	P D											
Ki- 3	○		⊙		46.43	1.53	0.630	0.831	10.35	0.010	1,124	0.074	0.21	190	1.20
Ki- 4	○	○	⊙	○	46.35	4.99	0.393	0.434	5.14	0.010	1,082	0.069	0.18	175	0.88
Ki- 5	○		⊙		51.74	0.82	0.278	0.313	3.82	0.006	1,223	0.085	0.14	140	0.83
Ki- 6			⊙		52.73	0.71	0.308	0.246	2.14	0.004	386	0.101	0.07	220	0.82
Ki- 7			⊙		54.45	0.66	0.307	0.315	3.29	0.005	380	0.095	0.06	90	0.52
Ki-10	○		⊙		52.17	0.92	0.210	0.461	2.45	0.005	1,884	0.070	0.22	160	1.26
Ki-11			⊙		52.02	0.71	0.317	0.272	4.13	0.004	538	0.067	0.04	160	0.41
Ki-12	○	○	⊙		50.47	2.14	0.322	0.353	2.83	0.006	2,882	0.344	0.41	260	1.52
Ki-14	○	○	⊙		46.07	1.53	0.658	0.840	11.00	0.018	974	0.100	0.23	160	1.47
Ki-15			⊙		51.24	1.12	0.278	0.344	4.23	0.007	286	0.067	0.04	80	0.87
Ki-16	○	○	⊙		51.24	1.78	0.254	0.281	2.77	0.004	1,170	0.075	0.17	130	1.08
Ki-17			⊙		52.02	0.97	0.280	0.333	3.50	0.004	320	0.111	0.06	130	0.48
Ki-18			⊙		48.83	0.97	0.580	0.626	8.04	0.009	587	0.114	0.09	260	0.98
Ki-19	○	○	⊙		52.17	1.43	0.213	0.312	1.95	0.003	2,324	0.073	0.17	100	0.88
Ki-20			⊙		54.01	0.61	0.126	0.146	0.79	0.002	244	0.084	0.03	50	0.34
Ki-21	○	○	⊙		50.96	2.29	0.203	0.329	1.78	0.003	2,528	0.083	0.43	350	1.33
Ki-22	○	○	⊙	○	44.09	7.80	0.340	0.363	3.34	0.006	1,619	0.037	0.13	190	0.77
Ki-23	○		⊙	○	48.69	2.60	0.460	0.708	5.32	0.008	1,078	0.070	0.11	130	1.31
Ki-24			⊙		48.20	1.12	0.572	0.763	8.56	0.007	436	0.072	0.08	140	1.16
Ki-25	○	○	⊙		52.17	1.48	0.180	0.349	1.72	0.011	1,908	0.083	0.29	160	1.24
Ki-26	○	○	⊙		53.87	1.02	0.100	0.173	0.55	0.002	1,398	0.064	0.17	160	0.64
Ki-27			⊙		53.09	1.58	0.112	0.218	0.85	0.001	422	0.083	0.06	90	0.57
Ki-28			⊙		53.16	0.82	0.184	0.310	1.46	0.001	359	0.064	0.01	90	0.50
Ki-29	○		⊙		51.74	1.43	0.279	0.470	2.66	0.004	1,040	0.111	0.12	90	0.70
Ki-30	○	○	⊙		50.32	2.55	0.312	0.452	2.63	0.007	1,384	0.116	0.42	130	1.02
Ki-31			⊙		53.73	0.87	0.187	0.189	1.33	0.004	502	0.078	0.05	130	0.46
Ki-32			⊙		52.17	0.41	0.330	0.517	3.93	0.008	497	0.098	0.05	110	0.61
Ki-33			⊙		54.01	0.51	0.106	0.175	1.48	0.007	468	0.094	0.04	60	0.20
Ki-34		○	⊙		50.47	1.53	0.780	0.362	3.91	0.010	515	0.110	0.12	100	0.89

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sample No.	mineral composition				CaO (%)	MgO (%)	Fe <sub>2</sub> O <sub>3</sub> (%)	Al <sub>2</sub> O <sub>3</sub> (%)	SiO <sub>2</sub> (%)	MnO (%)	Sr (ppm)	P <sub>2</sub> O <sub>5</sub> (%)	SO <sub>4</sub> (%)	Cl (ppm)	H <sub>2</sub> O (%)
	A	MC	C	PD											
Ki-35	○	○	◎		52.31	2.24	0.073	0.080	0.44	0.004	2,456	0.083	0.27	130	0.68
Ki-36			◎		53.87	1.02	0.107	0.111	0.91	0.004	600	0.100	0.06	60	0.53
Ki-37			◎		50.32	1.12	0.405	0.612	5.78	0.010	448	0.116	0.09	60	0.89
Ki-38	○	○	◎		50.38	2.86	0.071	0.057	0.40	0.001	3,822	0.076	0.45	200	1.42
Ki-39			◎		54.43	0.54	0.065	0.057	0.50	0.001	500	0.058	0.06	40	0.35
Ki-40	○		◎		53.30	0.81	0.148	0.170	1.55	0.003	976	0.085	0.07	40	0.37
Ki-41	○	○	◎		50.68	2.16	0.137	0.155	1.91	0.006	1,755	0.055	0.12	130	0.95
Ki-42	△	○	◎		51.05	2.16	0.315	0.304	3.80	0.005	870	0.107	0.30	125	0.75
Ki-43	○	○	◎		51.65	1.84	0.158	0.175	1.80	0.006	1,720	0.085	0.01	90	0.83
Ki-44	○	○	◎		50.15	2.16	0.203	0.181	1.85	0.007	2,189	0.079	0.23	130	0.65
Ki-45	△	△	◎		47.82	1.78	0.508	0.469	3.76	0.009	876	0.116	0.21	90	0.79
Ki-46	○	○	◎		49.40	2.16	0.306	0.273	7.68	0.005	1,316	0.107	0.22	100	0.65
Ki-47	○	○	◎		49.25	3.67	0.103	0.330	1.69	0.006	1,561	0.102	0.33	170	1.09
Ki-48	○		◎		52.70	1.40	0.110	0.237	3.09	0.006	925	0.053	0.08	80	0.39
Ki-49	○		◎	○	51.05	2.05	0.083	0.351	1.94	0.005	938	0.059	0.09	40	0.59
Ki-50	○	○	◎		49.25	1.84	0.108	0.366	3.67	0.007	1,108	0.111	0.23	60	1.01
Ki-51			◎		50.68	0.81	0.088	0.315	3.55	0.007	639	0.102	0.18	100	0.67
Ki-52	○	○	◎	△	47.90	3.35	0.090	0.408	3.60	0.005	1,843	0.095	0.29	80	1.13
Ki-53			◎		52.55	0.43	0.220	0.335	2.52	0.012	430	0.063	0.05	30	0.71
Average (48 samples)					50.94	1.69	0.263	0.343	3.26	0.006	1,157	0.091	0.16	125	0.82

A : aragonite  
 MC : high magnesium calcite  
 C : low magnesium calcite  
 PD : protodolomite

Amounts  
 ◎ large  
 ○ small  
 △ very small

Discussion

Correlation coefficients between the components

On the basis of the results in Table 1, the correlation coefficients ( $\gamma$ ) among the components except for CaO were calculated. These calculations are shown in Table 2.

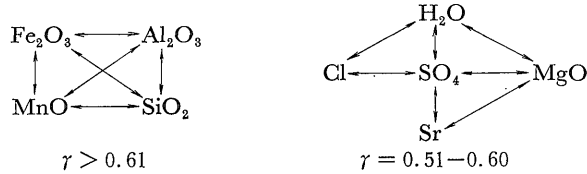
Table 2 Correlation coefficients( $\gamma$ ) among the components

	MgO	Fe <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	MnO	Sr	P <sub>2</sub> O <sub>5</sub>	SO <sub>4</sub>	Cl
H <sub>2</sub> O	<b>0.51</b>	0.34	0.32	0.26	0.32	0.50	0.13	<b>0.70</b>	<b>0.56</b>
Cl	0.26	0.30	0.24	0.19	0.08	0.37	0.12	<b>0.52</b>	
SO <sub>4</sub>	<b>0.66</b>	0.10	0.10	0.04	0.10	<b>0.71</b>	<b>0.28</b>		
P <sub>2</sub> O <sub>5</sub>	-0.12	0.29	0.27	0.23	0.21	-0.14			
Sr	<b>0.57</b>	-0.24	-0.20	-0.29	0.08		-0.24		
MnO	0.07	<b>0.60</b>	<b>0.66</b>	<b>0.82</b>		-0.14	0.20		
SiO <sub>2</sub>	0.06	<b>0.76</b>	<b>0.78</b>		0.28	0.10	0.30		
Al <sub>2</sub> O <sub>3</sub>	0.05	<b>0.72</b>		<b>0.62</b>	0.24	0.12	0.28		
Fe <sub>2</sub> O <sub>3</sub>	0.02		<b>0.58</b>	<b>0.58</b>	<b>0.60</b>	0.00	0.16		
MgO		0.29	0.31	0.35	0.19	-0.18	0.41		

Data in bold line; Ryukyu limestone(48 samples)  
 the others; Akasaka limestone (113 samples)

For a reference, the correlation coefficients between some components of Akasaka limestone are presented in the bottom line of the table.

Among the correlation coefficients of Ryukyu limestone, the particularly large values are shown below;



It is considered that the correlation group of  $\text{Fe}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$  and  $\text{MnO}$  is correspond to the detrital minerals, and the group of  $\text{MgO}$ ,  $\text{Sr}$ ,  $\text{SO}_4$ ,  $\text{Cl}$  and  $\text{H}_2\text{O}$  is to the constituent carbonate minerals in Ryukyu limestone, respectively. The discussion of each component will be described below.

### MgO

When a sample contains a plenty of  $\text{MgO}$ ,  $\text{MgO}$  should exist as high magnesium calcite or protodolomite. The average value of  $\text{MgO}$  content in the samples, from which those minerals were detected by X-ray diffraction, is 2.51% (24 samples), and that of  $\text{MgO}$  content in the others is 0.94% (24 samples). Judging from this average value, it is presumed that low magnesium calcite contains 2mol% of  $\text{MgO}$  on an average. The average value of  $\text{MgO}$ , which the writer calculated from 1496 samples (mainly of Permian age) of ancient limestone of Japan, is 0.77%. This is not so different from the value of low magnesium calcite in Ryukyu limestone. High magnesium calcite was detected from the fossils of foraminifers, calcareous algae and echinoderms. It is not confirmed whether protodolomite is contained or not, but presumably it will be detected from only a specific fossil.

On the correlation between  $\text{MgO}$  and  $\text{SO}_4$ , the writer considers as follows. As  $\text{SO}_4$  has a close correlation to strontium and  $\text{H}_2\text{O}$ , it is easily presumed that  $\text{SO}_4$  is closely related to aragonite. In the samples from which aragonite is detected, high magnesium calcite and protodolomite are often detected together. That is, the average content of  $\text{MgO}$  is 2.19% in 29 samples from which aragonite were detected, and 0.93% in 19 samples from which aragonite were not detected. From the results, it is considered that the correlation between  $\text{MgO}$  and  $\text{SO}_4$  is caused by the result of coexistence of aragonite with high magnesium calcite and protodolomite. Why aragonite coexists with these minerals is an interesting problem related to the diagenesis of Ryukyu limestone. But it is excluded from this paper, for it is not the direct purpose of the present investigation.

### $\text{Fe}_2\text{O}_3$ , $\text{Al}_2\text{O}_3$ and $\text{SiO}_2$

Among  $\text{Fe}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$ , only  $\text{Fe}$  (as  $\text{Fe}^{2+}$ ) is able to replace  $\text{Ca}^{2+}$  in  $\text{CaCO}_3$  (calcite) or  $\text{CaMg}(\text{CO}_3)_2$  (dolomite). In order to discuss iron,  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  must be determined respectively. But it is very difficult to determine the trace amount of  $\text{Fe}^{2+}$  in the sample that contains organic matter and sulfide. Accordingly, total iron is determined for convenience and customarily expressed as  $\text{Fe}_2\text{O}_3$ . In the present paper, total iron is expressed as  $\text{Fe}_2\text{O}_3$ , too.

The close correlation of  $\text{Fe}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$  depends on the existence of some detrital minerals. Calculating  $\text{Al}_2\text{O}_3/\text{Fe}_2\text{O}_3$  eq.ratio, the value of Ryukyu limestone is 2.04, that of Sōma limestone of Jurassic age (FUJINUKI, not published) is 0.89 and that of Akasaka limestone (FUJINUKI, 1968) is 1.15. The value of  $\text{Al}_2\text{O}_3/\text{Fe}_2\text{O}_3$  eq.ratio of Ryukyu limestone is higher than that of ancient limestone. As the reason, the writer supposes as follows. Iron and aluminium are changeable



in their existing state by pH;  $\text{Fe}^{3+}$  changes into stable  $\text{Fe}(\text{OH})_3$  in the range of  $\text{pH} > 3$ , and  $\text{Al}^{3+}$  changes into  $\text{Al}(\text{OH})_3$  in the range from 4 to 10 pH and into  $\text{AlO}_2^-$  in the range of  $\text{pH} > 10$ . Theoretically, the natural waters having an equilibrium with atmospheric  $\text{CO}_2$  and contact with limestone, can reach 9.9 of pH value (GARRELS & CHRIST, 1965). The limit at which  $\text{Al}^{3+}$  begins to have the mobility as  $\text{AlO}_2^-$  is around 10 of pH value. The writer suggests that the main factor controlling the value of  $\text{Al}_2\text{O}_3/\text{Fe}_2\text{O}_3$  eq.ratio is the mobility of aluminium. However, we have to pay attention to the decrease in the value of  $\text{Al}_2\text{O}_3/\text{Fe}_2\text{O}_3$  eq.ratio during the diagenesis of clay minerals.

### MnO

$\text{Mn}^{2+}$  can replace  $\text{Ca}^{2+}$  in calcite like  $\text{Fe}^{2+}$ . In case of Ryukyu limestone, MnO is closely correlated to  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$  and  $\text{Fe}_2\text{O}_3$ . Therefore, detrital minerals must be pointed out as the principal factor of the correlation. In case of Akasaka limestone, MnO is closely correlated to  $\text{Fe}_2\text{O}_3$  only, and not correlated to  $\text{Al}_2\text{O}_3$  ( $\gamma = 0.24$ ) and  $\text{SiO}_2$  ( $\gamma = 0.28$ ). It is due to the fact that lateritic clays are contained within the cracks of limestone and MnO is concentrated in them.

Minerals in the insoluble residue of Ryukyu limestone are quartz, feldspar and clay minerals, and it may be considered that MnO is due to the absorption of clay minerals. KANESHIMA (1965) reported that there was a close correlation between manganese and iron + aluminium in Ryukyu limestone from Ryukyu Islands.

As for Akasaka limestone, ABE, FUJINUKI and FUJIWARA (1966) published a paper in which the state of manganese was investigated with EPR. According to the results  $\text{Mn}^{2+}$  replacing  $\text{Ca}^{2+}$  in  $\text{CaCO}_3$  might be contained in calcite as a mineral like kutnahorite ( $\text{CaMn}(\text{CO}_3)_2$ ).

As an example of the  $\text{CaCO}_3$  with very low concentration of impurity, the writer wants to pick up the reefy coral from the viewpoint of the correlation between mineral constituent and MnO. The reefy coral is mainly composed of aragonite, but often contains shells consisting of high magnesium calcite. Comparing the average MnO content of reefy coral, in which high magnesium calcite is detected by X-ray diffraction, to that of reefy coral with no high magnesium calcite, the considerable

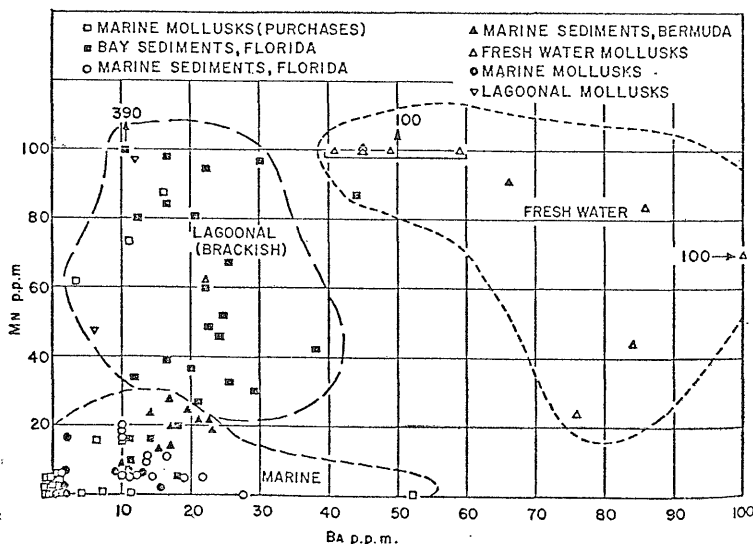


Fig. 4 Plot of barium and manganese for marine, lagoonal (brackish water), and fresh-water carbonate sediments. after FRIEDMAN (1969)

difference is found between the former (0.000%) and the latter (0.006%). But in case of the samples containing much impurity which is impossible to separate from them, it is unable to estimate whether MnO is related to carbonate minerals or detrital ones. Because to determine the minor elements for each fraction is difficult.

FRIEDMAN (1969) stated that manganese as well as barium and iron was an element to indicate the depositional environments of carbonate sediments. The ratios of manganese to barium and to iron indicate clearly under which environment of fresh water, brackish (lagoonal) or marine the carbonate sediments were deposited. The example is shown in Fig. 4.

In case of Ryukyu limestone, if each element is quantitatively determined for fossil and matrix separately, an interesting result can be expected.

#### Sr

As for the state of strontium in limestone, it is assumed that strontium replaces a part of  $\text{Ca}^{2+}$  in  $\text{CaCO}_3$  or strontium is contained in the impure matters. But, since strontium can not detect in the insoluble residue, it is reasonably considered that strontium exists in the former state.

As  $\text{CaCO}_3$  is of ionic bond, the difference of crystal system is an important factor which controls the content of minor elements. The ionic radius of strontium is 1.13A, and crystal system of  $\text{SrCO}_3$  (strontianite) is aragonite type. Forty-eight samples of Ryukyu limestone in Table 1 are divided into two groups; one is the samples with aragonite and the other is without aragonite. Strontium content in each group of samples is as follows;

	number of samples	average Sr content (ppm)	Sr/Ca atom ratio $\times 10^8$
samples containing aragonite	29	1,608	2.05
samples not containing aragonite	19	468	0.58

From the above result, it can be considered that strontium content in limestone is strongly affected by the mineral composition of limestone. Moreover, in case of non-metamorphosed limestone in Japan, it may be possible to decide by the strontium content whether the carbonate minerals in depositional stage were aragonite or calcite.

The tendency that the strontium content in limestone decreases with increasing geologic time has been pointed out by many researchers. MATTHEWS (1966) determined mineral composition and strontium content in various biogenetic carbonates, and according to its strontium content classified aragonite into the following two groups; low strontium aragonite (3,000 ppm and below) and high strontium aragonite (above 3,000 ppm). According to this classification, molluscan shells belong to low strontium aragonite and coral belongs to high strontium aragonite. As the quantitative estimation of mineral composition of limestone is not performed in the present study, the relation of strontium content to amount of aragonite is not yet established.

KINSMAN (1969) stated that the strontium content indicate the mechanism of diagenesis of limestone and emphasized the importance of pore fluid as the factor. But the process that high strontium aragonite transforms into calcite liberating a plenty of strontium has been left unsolved.

#### $\text{SO}_4$ , Cl

$\text{SO}_4$  is closely related with strontium. Since strontium is an element which has clearly correlated

with aragonite, it was assumed that  $\text{SO}_4$  also is a component correlated with aragonite. In fact,  $\text{SO}_4$  contents of recent and reefy coral are 0.65% and 0.46% respectively as shown in Table 1. These values are about three or four times as large as the average  $\text{SO}_4$  content (0.16%) of Ryukyu limestone. Also, there is a considerable difference between the average value of  $\text{SO}_4$  content (0.22%) in the samples containing aragonite and that of  $\text{SO}_4$  content (0.07%) in the samples not containing aragonite. Also,  $\text{SO}_4$  is correlated with  $\text{H}_2\text{O}$ . This fact may suggest that  $\text{SO}_4$  content is influenced by contamination with sea water. But KANESHIMA (1965) denied this assumption by comparing  $\text{SO}_4/\text{Cl}$  ratio of Ryukyu limestone from the Ryukyu Islands with that of sea water. The writer also agrees with his interpretation.

Once the writer tried the following experiment relating to the transformation of aragonite into calcite. Synthesized aragonites were immersed into solutions of various salts. And next, they were soaked in oscillating bath of ultrasonic wave to accelerate the transformation into calcite. From this experiment, it was confirmed that there were differences in the rate of transformation with different kinds of solution.

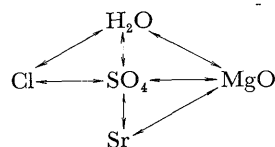
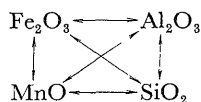
The experiment shows that the solutions of sodium chloride, potassium chloride, ammonium chloride, sodium nitrate, potassium nitrate, ammonium nitrate and calcium chloride prompt the transformation, of aragonite into calcite and the solutions of magnesium chloride, magnesium sulfate, sodium sulfate and sodium citrate inhibit the transformation (FUJINUKI & IGARASHI, 1968). Though the method of experiment was different, the similar conclusion on a role of  $\text{Mg}^{2+}$  was reported by TAFT (1967). In addition, KITANO (1962) reported that relating to the reaction such as  $\text{Ca}(\text{HCO}_3)_2 = \text{CaCO}_3 + \text{H}_2\text{O} + \text{CO}_2$ , if there were magnesium and  $\text{SO}_4$  in mother liquor, aragonite was easily precipitated. From these experiments, the writer supposes that  $\text{SO}_4$  plays a role of stabilizing agent of aragonite.

As for Cl, it is due to the contamination of sea water. Determining the water-soluble part of  $\text{SO}_4$  and Cl, it was clarified that about 50% of Cl is water-soluble while the water-soluble part of  $\text{SO}_4$  is about 5%. If the determination of Na with respect to Cl had been completed, the further definite result could have obtained.

### Conclusion

From X-ray diffraction, DTA and chemical analysis of major and minor components of Ryukyu limestone from Kikai-jima Island, the following facts became clear;

1. The existence of high magnesium calcite, low magnesium calcite, aragonite and protodolomite in Ryukyu limestone was confirmed by X-ray diffraction.
2. The insoluble residue of Ryukyu limestone contains quartz, feldspar, kaoline and illite. It also contains rarely pyrite.
3. By the results of chemical analysis, the correlation coefficients ( $\gamma$ ) among some elements are calculated. The relations of  $\gamma > 0.51$  are as follows;



The group of  $\text{Fe}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{MnO}$  and  $\text{SiO}_2$  is considered to be influenced by detrital minerals. The correlation of the group of  $\text{MgO}$ ,  $\text{Sr}$ ,  $\text{SO}_4$ ,  $\text{Cl}$  and  $\text{H}_2\text{O}$  is correlated to the constituent of carbonate minerals.

4. The value of  $\text{Al}_2\text{O}_3/\text{Fe}_2\text{O}_3$  eq.ratio is higher than that of limestone of the ancient age.

5. Strontium content is different with the difference of mineral composition of limestone. The average Sr content is 1,608 ppm in the samples containing aragonite and 468 ppm in the samples not containing it, respectively.

6. It is likely that  $\text{SO}_4$  is closely correlated to aragonite and plays as the role of stabilizing agent of aragonite.

#### Acknowledgement

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#### References

- ABE, S., FUJINUKI, T. & FUJIWARA, S. (1966): Determination of the State of Manganese in the Akasaka Limestones, "*Nippon Kagaku Zasshi*" vol. 87, no. 4, p. 367—369.
- CHAVE, K. E. (1952): A Solid Solution between Calcite and Dolomite, *Jour. Geol.*, vol. 60, no. 2, p. 190—192.
- FRIEDMAN, G. M. (1959): Identification of Carbonate Minerals by Staining Methods, *Jour. Sediment. Petrol.*, vol. 29, no. 1, p. 87—97.
- FRIEDMAN, G. M. (1964): Early Diagenesis and Lithification in Carbonate Sediments, *Jour. Sediment. Petrol.*, vol. 34, no. 4, p. 777—813.
- FRIEDMAN, G. M. (1968): Geology and Geochemistry of Reefs, Carbonate Sediments, and Waters, Gulf of Aqaba (Elat), Red Sea, *Jour. Sediment. Petrol.*, vol. 38, no. 3, p. 859—919.
- FRIEDMAN, G. M. (1969): Trace Elements as Possible Environmental Indicators in Carbonate Sediments, "Depositional Environments in Carbonate Rocks," Society of Economic Paleontologists and Mineralogists Special Publication, no. 14, p. 193—198.
- FUJINUKI, T. (1968): Geochemical Study of Limestone(1), On the Minor Elements in the Akasaka Limestone, *Bull. Geol. Surv. Japan*, vol. 19, no. 9, p. 603—624 (in Japanese with English Abstract).
- FUJINUKI, T. & IGARASHI, T. (1968): Geochemical Study of the Ryukyu Limestone(3), On Diagenetic Change in the Ryukyu Limestone, Tokyo Conference of the Geochemical Society of Japan, Abstract 3A1.
- FUJINUKI, T., WATANABE, M. & TOGASHI, Y. (1968): Staining Methods of Carbonate Minerals, "*Chishitsu News*", no. 171, p. 35—39.
- FUJINUKI, T. & IGARASHI, T. (1969): On the Water in the Hexacollara, *Jour. the Jap. Assoc. of Min. Petr. and Econ. Geol.*, vol. 62, no. 1, p. 1—17 (in Japanese with English Abstract).
- GARRELS, R. M. & CHRIST, C. L. (1965): Solutions, Minerals, and Equilibria, Harper & Row, Publishers, p. 450.
- ISONO, K., FUJINUKI, T., NAGAI, S. & KANEKO, H. (1968): Total Analysis of Limestone and Dolo-

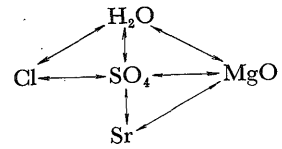
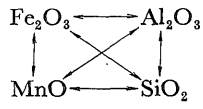
- mite, Methods of Chemical Analysis, Geol. Surv. Japan, no. 40.
- KAHLE, C. F. (1965): Strontium in Oolitic Limestones, *Jour. Sediment. Petrol.*, vol. 30, no. 2, p. 297—304.
- KANESHIMA, K. (1965): Studies on the Various Kinds of the Limestones in the Ryukyu Islands, *Bull. Art & Science Division, Univ. Ryukyus (Mathematics & Natural Sciences)*, no. 8, p. 23—54 (in Japanese with English Abstract)
- KINSMAN, D.J.J. (1969): Interpretation of  $Sr^{2+}$  Concentrations in Carbonate Minerals and Rocks, *Jour. Sediment. Petrol.*, vol. 39, no. 2, p. 486—508.
- KITANO, Y. (1962): The Behavior of Various Inorganic Ions in the Separation of Calcium Carbonate from Bicarbonate Solution, *Bull. Chem. Soc. Japan*, vol. 35, p. 1973—1980.
- KONISHI, K. (1967): Rate of Vertical Displacement and Dating of Reefy Limestones in the Marginal Facies of Pacific Ocean—Application by Natural Alpha-Radioactive Nuclides in Biogenetic Carbonate Rocks up to 150,000 Years Old—*The Quaternary Research*, vol. 6, no. 4, p. 207—223 (in Japanese with English Abstract).
- LAND, L. S. (1967): Diagenesis of Skeletal Carbonates, *Jour. Sediment. Petrol.*, vol. 37, no. 3, p. 914—930.
- MATTHEWS, R. K. (1966): Genesis of Recent Lime Mud in Southern British Honduras, *Jour. Sediment. Petrol.*, vol. 36, no. 2, p. 428—454.
- MATTHEWS, R. K. (1968): Carbonate Diagenesis; Equilibration of Sedimentary Mineralogy to the Subaerial Environments: Coral Cap of Barbados, West Indies, *Jour. Sediment. Petrol.*, vol. 38, no. 4, p. 1110—1119.
- NAKAGAWA, H. (1964): Preliminary Report on Quaternary Formation, Amami Islands, *Jour. Geol. Soc. Japan*, vol. 70, no. 826, p. 405 (in Japanese Abstract)
- NAKAGAWA, H. (1969): Geology of Tokunoshima, Yoronoto and Kikaijima, Amami Gunto, part 2, *Tohoku Univ., Inst. Geol. Pal., Contr.*, no. 68, p. 1—17 (in Japanese with English Abstract).
- SIEGEL, F. R. (1960): The Effect of Strontium on the Aragonite Calcite Ratios of Pleistocene Corals, *Jour. Sediment. Petrol.*, vol. 30, no. 2, p. 297—304.
- STEHLI, F. G. & HOWER, J. (1961): Mineralogy and Early Diagenesis of Carbonate Sediments, *Jour. Sediment. Petrol.*, vol. 31, no. 3, p. 358—371.
- TAFT, W. H. (1967): Physical Chemistry of Formation of Carbonates, CHILINGER, G. V., BISSELL, H. J. & FAIRBRIDGE, R. W. ed., *Developments in Sedimentology*, 9B "Carbonate Rocks" p. 151—167 (Elsevier).

### 鹿児島県喜界島産琉球石灰岩の微量元素について

藤 貫 正

#### 要 旨

鹿児島県喜界島産琉球石灰岩の鉱物組成をX線回折によって調べた。その結果 high magnesium calcite, low magnesium calcite, aragonite, protodolomite の存在が確認された。また主成分および微量元素の化学分析を行ない、微量元素と鉱物組成の関連を検討した。各成分間の相関係数( $r$ )を計算し、特に $r > 0.51$ の関係をまとめるとつぎのようになる。



$\text{Fe}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{MnO}$  のグループは碎屑性鉱物に,  $\text{MnO}$ ,  $\text{Sr}$ ,  $\text{SO}_4$ ,  $\text{Cl}$ ,  $\text{H}_2\text{O}$  のグループは琉球石灰岩の鉱物組成にそれぞれ関連しているものと考えられる。