

The formation process of the cold seep carbonates at the Kuroshima Knoll

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The Kuroshima Knoll is about 26km south of Ishigaki Island in the southern part of the Ryukyu Arc. The area is considered to be the source area of "The 1771 Yaeyama Earthquake Tsunami", which was due to the submarine landslide caused by an earthquake. It has been cleared from some investigations using "Dolphin 3K" and "Shinkai 2000" that there are large-scale dead *Calyptogenia* colonies, many gravels of fallen dolomite chimneys and carbonates on the top of the Knoll (Matsumoto et al., 1999 ; Machiyama et al., 2001). Carbonates of Kuroshima Knoll have various shapes and macroscopic textures. These have been classified into 4 types ; shell crust (pavement), chimney, burrow, and nodule. It is clear that all chimney and burrow carbonates are composed of dolomite, while shell crust and nodule are composed of calcite, sometimes both calcite and dolomite. These carbonates are considered to have been formed by cold seep, because they are characterized by the light carbon isotopic ratio (semi-biogenic) and the heavy oxygen isotopic ratio. This suggests that methane hydrate layers develop under this survey area and the water that has the heavy oxygen and the light carbon isotopic ratio is derived from the dissociation of methane hydrate.

Keywords : Methane hydrate, cold seep, carbonate, dolomite chimney

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1. Introduction

The Kuroshima Knoll is about 26km south of Ishigaki Island in the southern part of the Ryukyu Arc (Fig. 1). The area is considered to be the source area of "The 1771 Yaeyama Earthquake Tsunami", which was due to the submarine landslide caused by an earthquake (Matsumoto and Kimura, 1993). On the other hand, large-scale dead *Calyptogena* communities, many gravels of sand chimneys and calcareous crusts were found on the top of the knoll by driving surveys using deep tow camera system (Matsumoto et al., 1997), ROV "Dolphin-3K", and submersible "Shinkai 2000" (Matsumoto et al., 1999 ; Machiyama et al., 2001). This report presents the preliminary results of the chemical analysis on the carbonates taken by Dolphin-3K (Dive D3K#347, 348, 349, 455, 456, 461, and 462) and Shinkai 2000 (2K#981 and 1179), and discusses the formation process of these carbonates in relation with the dissociation of methane hydrate.

2. Geological setting of the Kuroshima Knoll and seep-related phenomena

The Kuroshima Knoll is isolated from the island shelf. The depth of the flat top of the knoll ranges from 800m to 600m. The knoll is made up of the following Pliocene to Pleistocene sediments : 1) Pliocene to lower Pleistocene Shimajiri Group : (light yellow - to light gray, lithified mudstone), 2) light blue gray semi-lithified sandstone/mudstone correlated with Pleistocene Chinen Formation, and 3) recent sediments : gravels and sandy mud, in ascending order. In the eastern edge of the top of the knoll, many current ripple marks occur in parallel with the NE-SW direction on soft sandy mud substrates, and living *Vesicomya* rarely occurs (Maki et al., 2001). Large-scale dead *Calyptogena* colonies and carbonates occur in the eastern part of the knoll. Many gravels of sand chimneys and calcareous crusts were found in or near dead *Calyptogena* colonies. They consist mainly of fine-grained terrigenous materials and

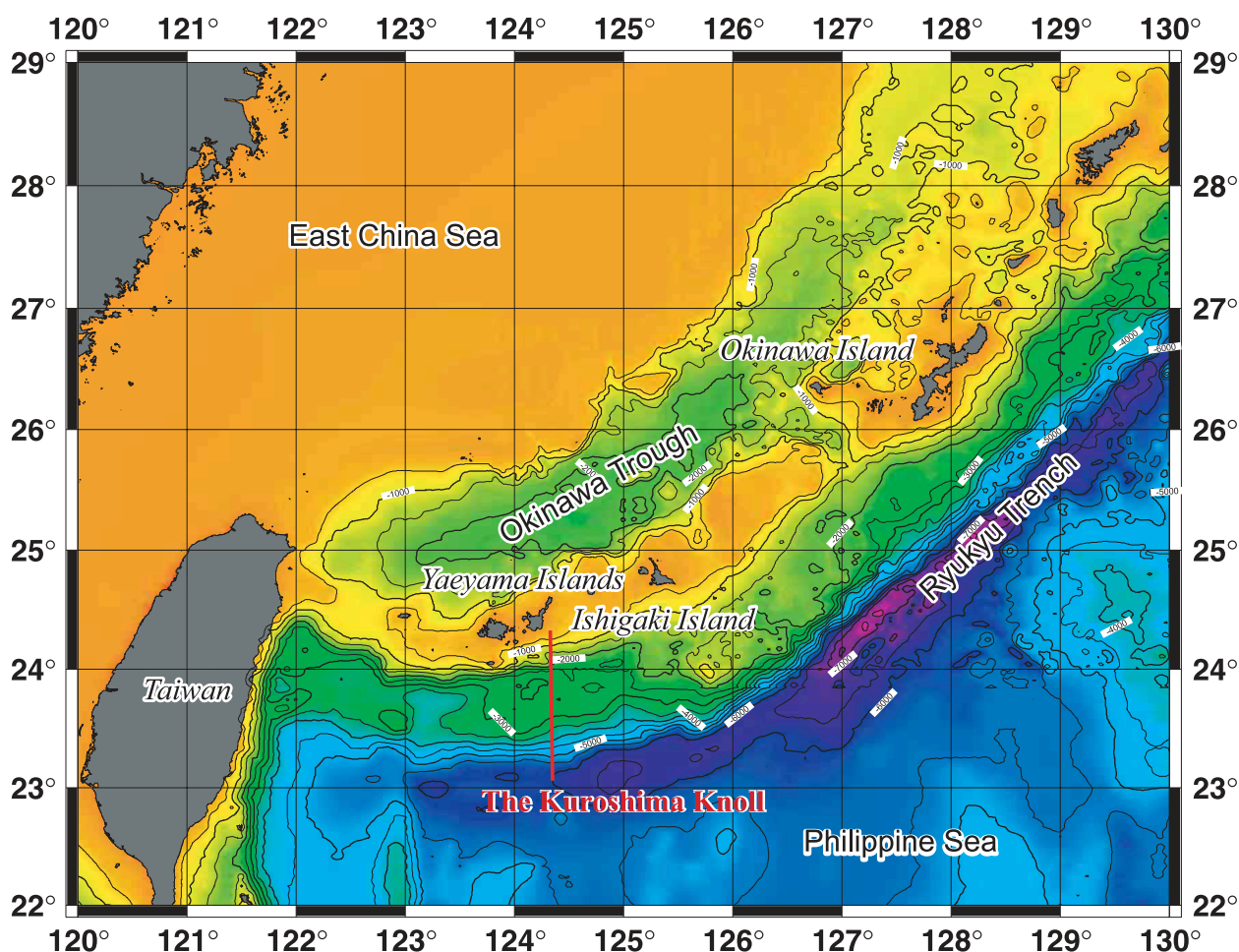


Fig. 1 Location map of the Kuroshima Knoll

micrite or dolomite cements. Moreover, it was recognized that gas bubbles were rising from the cracks of carbonate rock accompanied with *Bathymodiolus* colonies (Shinjo et al., in this vol. ; Machiyama et al., in this vol.). Living *Calyptogena* and tubeworm were also found near the gas bubble spot. The distribution of dead *Calyptogena* colonies and carbonates is limited in the east and west direction, which corresponds to the morphological features of the cracks.

3. Occurrence and types of carbonates

Carbonates recovered from the top of the Kuroshima Knoll have various shapes and consist mainly of fine-grained terrigenous materials, micrite and dolomite cements. In this report, 34 samples of carbonates and mudstone and 3 samples of bottom water were analyzed (Table 1). The locality of each sample is shown in Fig. 2.

On the basis of macroscopic morphological and textural characteristics, these carbonates have been classified into 4 types : shell crust (pavement), chimney, burrow, and nodule (Table 1).

Shell crust (pavement) type (Fig. 3-1) is porous sandstone/mudstone and contains bivalve shells (mostly *Bathymodiolus*). These bivalves may be derived either

from lithification of colonized, unconsolidated sandstone/mudstone or from cementation of individual shell attached to the carbonate crusts. The colors are range from brownish gray to yellowish gray. This type often covers seafloor as pavement and the thickness is up to 80cm. On the other hand, this type sometimes takes a massive form, which varies in size from small to big. For example bigger one is a few meters in height.

Chimney type has a cylindrical shape with a vent hole at the center. A vent hole, which was sometimes filled with cemented sediments, is interpreted to be formed by upward fluid migration (seep activity) from the sub-seafloor. All chimney types are composed of compact pale-gray sandstone/mudstone and fossils are rarely preserved. Chimney types are divided into three different subtypes : cylindrical type, doughnut type, and screw type. The diameter of cylindrical type varies from 5cm (slender one) to 25cm (big one) (Fig. 3-2, 3-3). Though maximum length of the cylindrical chimney is up to one meter, most of this type is a few ten centimeters in length. Doughnut type is thin (about 10cm in thickness) and its diameter is about 30-50cm (Fig. 3-4). This type may be a part of big cylindrical type chimney, because big cylindrical type is easy to separate along the

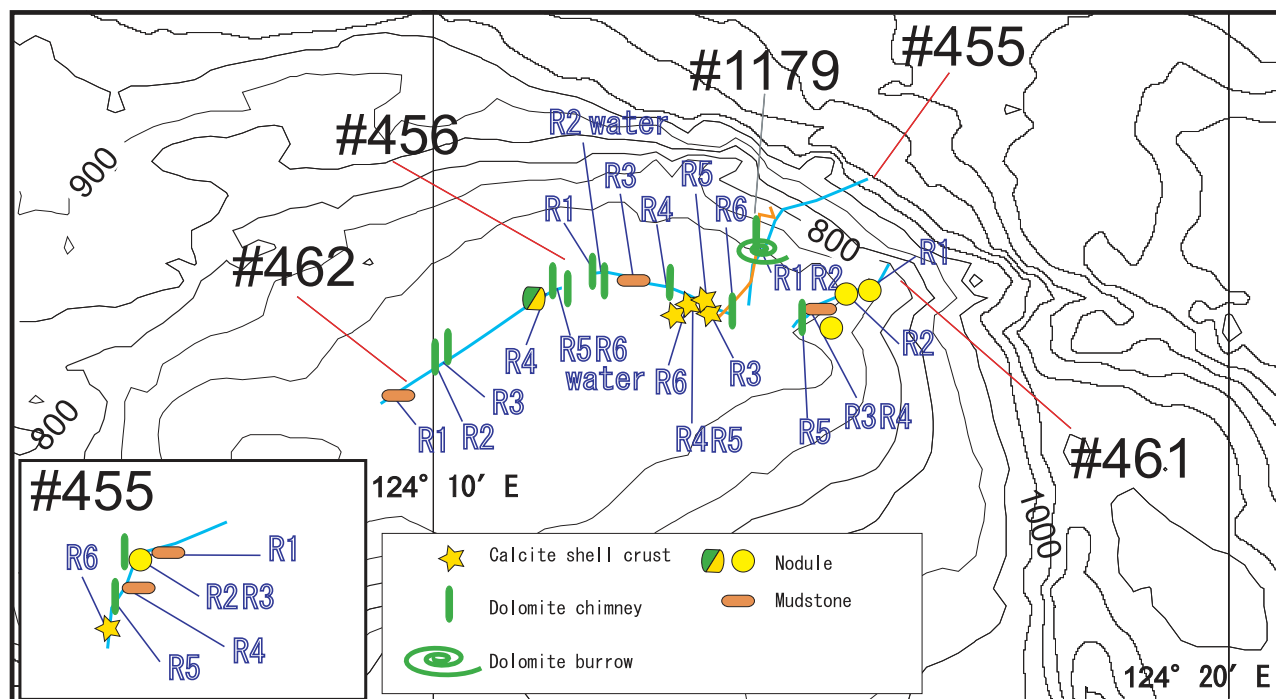


Fig. 2 Locality of analyzed samples

Yellow color means the sample was composed of calcite, and green color means dolomite. Mixed color of nodule mark means the nodule was composed of both calcite and dolomite.

Table 1 Sample list

Carbonate and mudstone							
No	Sample Name	Depth (m)	Type	No	Sample Name	Depth (m)	Type
1	2K#1179-R1	685	burrow	18	D3K#456-R1	654	chimney
2	2K#1179-R2-1	686	chimney	19	D3K#456-R2	656	nodule
3	2K#1179-R3	654	shell crust	20	D3K#456-R3	653	mudstone
4	2K#1179-R4	647	shell crust	21	D3K#456-R4	653	chimney
5	2K#1179-R5	647	shell crust	22	D3K#456-R5	651	shell crust
6	2K#1179-R6	643	shell crust	23	D3K#456-R6-2	666	chimney
7	2K#981-4-1	670	chimney	24	D3K#461-R1	802	nodule
8	D3K#347-6	766	chimney	25	D3K#461-R2	756	nodule
9	D3K#348-3-1	688	chimney	26	D3K#461-R3	713	mudstone
10	D3K#348-5	686	chimney	27	D3K#461-R4	713	nodule
11	D3K#349-6	682	chimney	28	D3K#461-R5	702	chimney
12	D3K#455-R1	772	mudstone	29	D3K#462-R1	656	mudstone
13	D3K#455-R2	755	chimney	30	D3K#462-R2	655	chimney
14	D3K#455-R3	755	nodule	31	D3K#462-R3	655	chimney
15	D3K#455-R4	710	mudstone	32	D3K#462-R4	627	nodule
16	D3K#455-R5	684	chimney	33	D3K#462-R5	639	chimney
17	D3K#455-R6	678	shell crust	34	D3K#462-R6	639	chimney

Shell				
No	Sample Name	Depth (m)	Temp (°C)	Comment
1	2K#1179-B2	7.6	641	living <i>Bathymodiolus</i>

Water			
No	Sample Name	Depth (m)	Temp (°C)
2	2K#1179W3	641	7.5
3	D3K#462	639	8.1

cracks (layer boundaries) (see Fig. 4). A screw type has the parts of a few centimeters bigger in diameter at regular interval, but actually bigger parts are not spiral but parallel (Fig. 3-5).

Sometimes, chimney type has a different feature between upper part and lower part. For example, upper part has holes and is hard, or is coated with manganese. Moreover, most of chimneys are lying on the seafloor, but some are standing. Standing chimneys are fresh and haven't been coated with manganese. Considering chimneys that only upper part is coated with manganese, chimneys may be formed under the seafloor and gradually exposed from the upper part by surrounding layers' erosion, and lastly fall down on the seafloor. Manganese coating has begun after chimneys were cropped out. This may be the reason that the length of chimneys is not so different.

Burrow type (Fig. 3-6) consists of compact mud-

stone/sandstone and is partially coated with manganese. It is like a coiled hose or tube. This type may be a cemented burrow infills.

Nodular type (Fig. 3-7) is massive, round form and consists of compact mudstone/sandstone without organisms, such as shell fragments. The size is up to a few ten centimeters in diameter. In addition to above carbonates, angular mudstone clasts were examined for mineralogy and geochemistry. The clasts are very fragile and porous and not coated with manganese (Fig. 3-8). Therefore, these seem to be derived from mudstone/siltstone of the Shimajiri Group.

4. Methods

The petrography of carbonates was examined with a microscope and a scanning electron microscope (SEM). Elementary analysis of carbonates was also carried out together with the SEM observation.

In the shell crust type, shell fragments were separated from the matrix part, and each fossil and matrix was measured. In the typical samples of three chimney types (big cylindrical, slender cylindrical and doughnut), the analyzed samples were collected from vertical and hori-

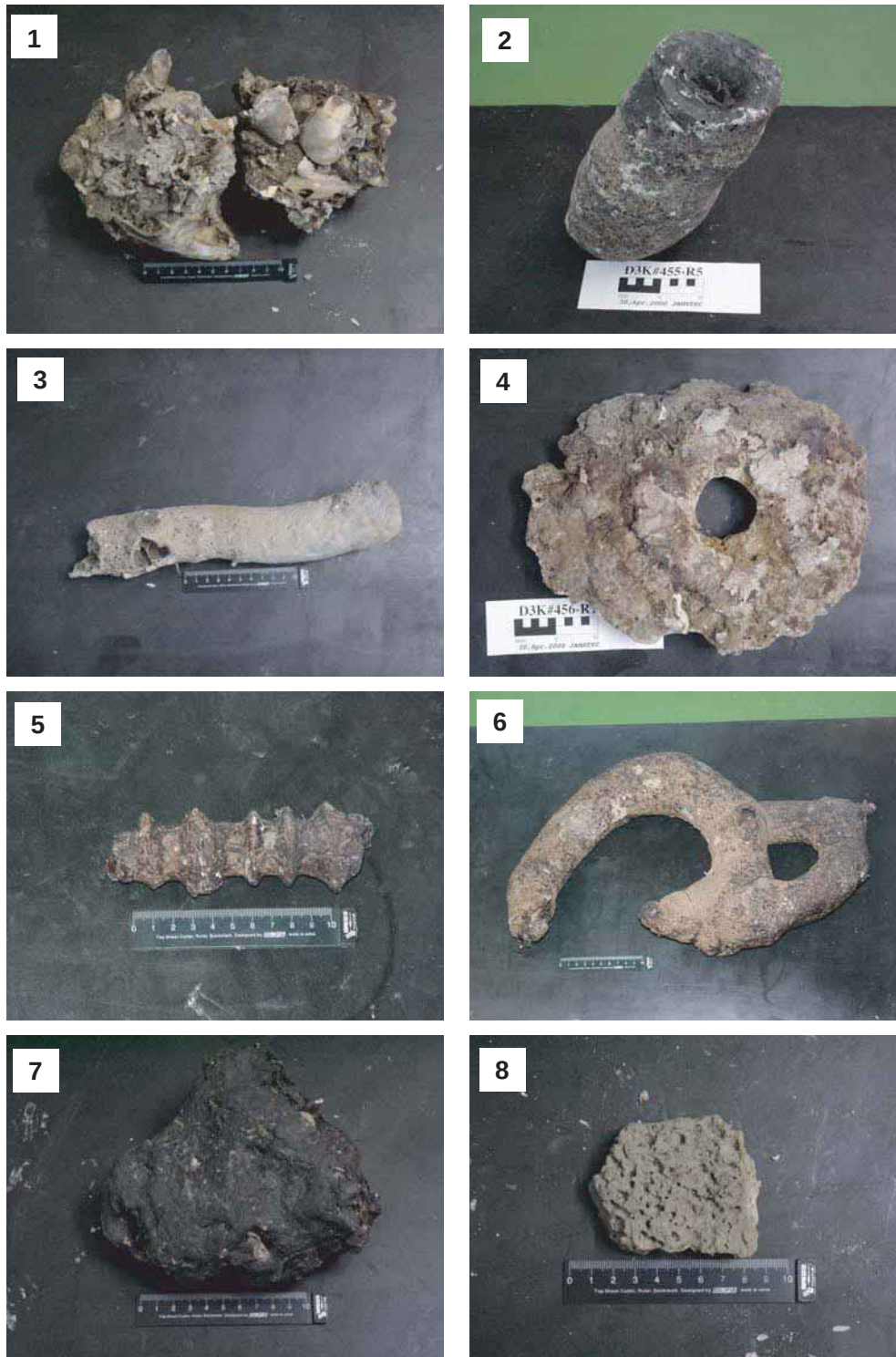


Fig. 3 Photographs of the carbonates and mudstone

1 : Shell crust (pavement) (D3K#456-R5). It is composed of dead *Bathymodiolus* and gray-brown mudstone. 2 : big cylindrical (D3K#455-R5). The upper quarter is coated with manganese and has holes. The lower three quarter is muddy. Its vent hole was clogged. This diameter is 16cm and the length is 33cm. 3 : slender cylindrical (D3K#456-R4). Upper part has holes and is hard, while lower part is a little soft and muddy. This diameter is 5cm and the length is 28cm. 4 : doughnut (D3K#456-R1). It is coated with manganese. The diameter of internal circle is 7cm and the external is about 40cm. The thickness is 7cm. 5 : screw (2K#1179-R2). This diameter is 4.5cm and the length is 14cm. 6 : burrow (2K#1179-R1). It is partially coated with manganese. 7 : nodule (D3K#462-R4). It is coated with manganese. On one side, it has holes probably made by some creatures. 8 : mudstone (D3K#456-R3). It is gray-brown mudstone and a little discolored. It is fragile and one side has holes.



Fig. 4 Doughnut type originates in another chimney. 1 : Sample 2K#1264-R2 is big cylindrical. The diameter is about 15cm. The diameter of its vent hole is 3.5cm and not clogged. 2 : It was half-sized by a cutter. In the position of one thirds from below, the crack reach the vent hole. Spontaneously the lower part separates from the upper part. 3 : This photograph is the lower part. It seems like a doughnut type.

zontal succession of each chimney. All samples were powdered prior to following analyses. Carbonate mineralogy was determined by XRD measurement.

Carbon and oxygen isotopic compositions were measured at University of Tokyo, using Mass Spectrometer, MAT 252 of Finnigan MAT. Carbonates and mudstones sample were separately dissolved to CO_2 by phosphoric acid in a vacuum at 25 °C in a reaction vessel for three days, and collected for measurement using Mass Spectrometer. The results were calculated in per-mil delta notion relative to Peedee formation Belemnite (PDB). The analytical precisions of the delta value are less than ± 0.13 in per mil for both $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values.

Oxygen and hydrogen isotopic compositions are also measured using the same MAT 252. Oxygen isotopic ratio was measured by CO_2 -equilibrium method. 28 mmol (1.0ml) interstitial water was put into small flask and frozen by liquid-nitrogen. And a flask of air was evacuated by vacuum pump. Then, 0.1mmol CO_2 gas of known isotopic composition was introduced into the flask for equilibrium with water, and the flask was kept in the incubator at 25 °C over 12 hours so that oxygen

atoms within the water and CO_2 gas can equilibrate. After this reaction, CO_2 gas has the same oxygen isotopic ratio as the interstitial water and collected for measurement using Mass Spectrometer. The results were calculated in per-mil delta notion relative to Standard Mean Ocean Water (SMOW). The analytical precisions of the delta value are ± 0.05 in per mil SMOW.

5. Results

5.1. Petrography

Shell crust (pavement) type contains many microfossils, authigenic calcite, plagioclase grains in a fine-grained matrix. There are some acicular carbonate crystals that exceed 1mm in length. Moreover, radial fibrous calcite crystals and tiny black pyrite grains are also present.

Chimney type contains few microfossils. Authigenic carbonate minerals are not clear under a polarized microscope. Even with the SEM observation, the identification of individual mineral is difficult under low magnification. Chimneys are composed of micritic

dolomite, which grains are < 1µm in size. Under the SEM observation with high magnification, authigenic dolomite rhombs were clearly observed (Fig. 5). Significant differences in shape, size and color were not observed between the inner and outer parts of chimney. Since no textural evidence of wholesale calcite/aragonite replacement by dolomite was seen, dolomite is considered to be primary micritic cement. Elementary analysis indicates the existence of pyrite, but framboidal pyrite can't be identified (Fig. 6).



Fig. 5 SEM photograph of 2K#1179-R1 (burrow). The rhombic shape of authigenic dolomite is clearly observed.

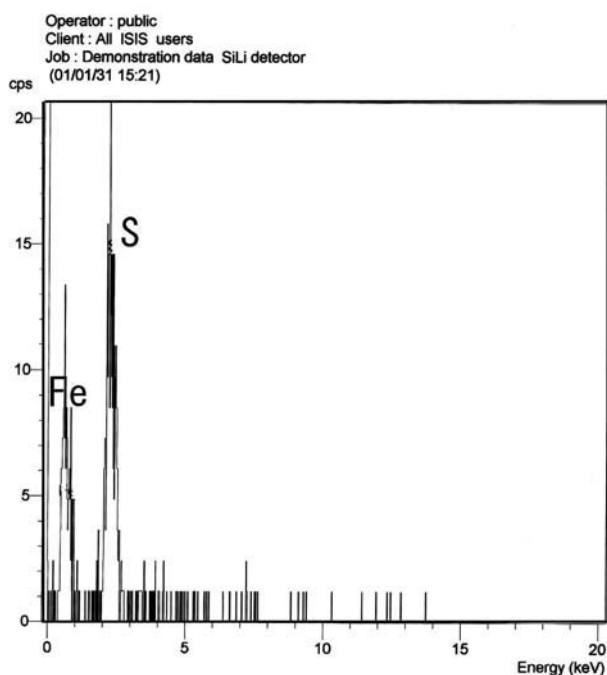


Fig. 6 A graph of the elementary analysis coupled with the SEM. It shows the major diffraction peak of Fe and S.

5.2. Mineralogy

Carbonate mineralogy was determined by XRD measurement (Table 2). Shell crust (pavement) type was composed almost of calcite and the major diffraction peak of calcite was between 3.021 Å and 3.031 Å. On the other hand, chimney type and burrow type were composed exclusively of dolomite and the major diffraction peak of dolomite was between 2.882 Å and 2.908 Å. One sample of nodular type was composed of calcite and dolomite in a ratio of two to one. Each massive mudstone was mainly composed of quartz and contains a small content of carbonate grains such as foraminifers.

The position of the major diffraction peak of calcite varies from sample to sample. The shift of $d(104)$ values away from those of stoichiometric calcite (3.035 Å) can be due to Ca^{2+} substitution by Mg^{2+} and/or Fe^{2+} and Mn^{2+} (Goldsmith and Graf, 1958). Assuming that the shift was caused by Mg substitution, Mg/Ca can be estimated by the following simple equation.

$$\text{Mg (mol\%)} = \frac{1}{0.00298} (3.035 - d)$$

Before above estimation, the peak value of calcite and dolomite was corrected for the major diffraction peak of quartz. The result of XRD and Mg/Ca estimation is shown in Table 3.

Estimated Mg contents fall below zero. This error is may be due to that in inappropriate peak shift correction of quartz not by the combination of quartz and silicon. However, the error of Mg contents may be less than one percent.

5.3. Stable isotopic compositions

The results of the carbon and the oxygen stable isotopic compositions of all measurement are tabulated in Table 4. The oxygen isotopic ratio of dolomite (chimney and burrow) ranges from about 6 to 8 in per mil PDB, and calcite (shell crust and nodule) ranges from 2 to 4.5 in per mil PDB. The carbon isotopic ratio of dolomite ranges from about -50 to -15 in per mil PDB, and calcite (shell crust and nodule) ranges from -20 to 0 in per mil PDB (Fig. 7).

5.4. The condition of the carbonate formation

The oxygen isotopic ratio of the carbonates is deter-

Table 2 The result of XRD measurement of carbonates and mudstonesThe major diffraction peak of quartz, calcite and dolomite are put on the list. Blank columns mean the peak isn't detected.

Sample No.	Qz		Cal		Dol		Qz/Cal/Dol ratio
	d(Å)	INT.(CPS)	d(Å)	INT.(CPS)	d(Å)	INT.(CPS)	
2K#1179R1	3.3360	372			2.8878	1250	1/0/3
2K#1179R2-1	3.3262	418	3.0214	150	2.8933	800	1/0/2
2K#1179R3	3.3311	348	3.0254	182			2/1/0
2K#1179R5	3.3336	338	3.0234	210	2.8897	102	3/2/1
2K#1179R6	3.3360	546	3.0315	212	2.8970	72	3/1/0
D3K#455R1	3.3336	1336	3.0254	196	2.8842	72	6/1/0
D3K#455R3	3.3262	466			2.8842	1174	2/0/5
D3K#455R4	3.3336	1060	3.0274	314			1/0/0
D3K#455R5A1	3.3558	289			2.9080	1219	1/0/4
D3K#455R5A2	3.3533	285			2.9026	1252	1/0/4
D3K#455R5A3	3.3558	244			2.9026	1292	1/0/5
D3K#455R5A4-1	3.3558	227			2.9043	1130	1/0/5
D3K#455R5A4-2	3.3533	237			2.9062	1240	1/0/5
D3K#455R5A5	3.3533	207			2.9043	1179	1/0/6
D3K#455R5A6	3.3558	199			2.9026	1088	1/0/5
D3K#455R5A7	3.3558	242			2.9026	1297	1/0/5
D3K#455R5A8	3.3533	246			2.9062	1132	1/0/5
D3K#455R5A9	3.3558	233			2.9062	1112	1/0/5
D3K#455R5A10	3.3533	204			2.9043	1159	1/0/6
D3K#455R5A11	3.3533	246			2.9026	1190	1/0/5
D3K#455R5A12	3.3558	252			2.9062	1156	1/0/5
D3K#455R5A13	3.3508	272			2.9043	1261	1/0/5
D3K#455R5B1	3.3558	253			2.9099	1270	1/0/5
D3K#455R5B2	3.3533	236			2.9007	1243	1/0/5
D3K#455R5B3	3.3508	246			2.9026	1294	1/0/5
D3K#455R5B4	3.3533	216			2.9043	1235	1/0/4
D3K#455R5B5	3.3533	297			2.9043	1104	1/0/4
D3K#455R5B6	3.3508	262			2.9043	1034	1/0/4
D3K#455R5B7	3.3508	276			2.9043	1027	1/0/4
D3K#455R5B8	3.3533	240			2.9026	1128	1/0/5
D3K#455R5B9	3.3533	219			2.9026	1166	1/0/5
D3K#455R5B10	3.3508	171			2.9026	1255	1/0/7
D3K#455R5B11	3.3508	192			2.9043	1317	1/0/7
D3K#455R5B12	3.3508	240			2.9026	1221	1/0/5
D3K#455R5C1	3.3508	242			2.9026	1195	1/0/5
D3K#455R5C2	3.3558	271			2.9043	1113	1/0/4
D3K#455R5C3	3.3533	288			2.9043	1292	1/0/4
D3K#455R5C4	3.3483	218			2.9007	1132	1/0/5
D3K#455R5C5	3.3262	208			2.8842	1138	1/0/5
D3K#455R5C6	3.3311	220	3.0295	22	2.8897	1192	1/0/5
D3K#455R5C7	3.3336	200			2.8878	1112	1/0/6
D3K#455R5C8	3.3336	220			2.8878	1268	1/0/6
D3K#455R5C9	3.3360	210			2.8915	1216	1/0/6
D3K#455R5C10	3.3311	210			2.8878	1226	1/0/6
D3K#455R5C11	3.3336	266			2.8897	1186	2/0/9
D3K#455R6	3.3262	252	3.0214	246			1/1/0
D3K#455R6Shell			3.0274	366			0/1/0
D3K#456R1	3.3311	440			2.8915	1206	1/0/3
D3K#456R3	3.3336	978	3.0274	340			3/1/0
D3K#456R4A1	3.3287	386	3.0214	60	2.8878	1150	1/0/3
D3K#456R4A2	3.3238	270			2.8842	1282	1/0/5
D3K#456R4A3	3.3287	280			2.8897	1162	1/0/4
D3K#456R4A4	3.3287	328			2.8897	1232	1/0/4
D3K#456R4A5	3.3311	228	3.0154	46	2.8878	1142	1/0/5
D3K#456R4a1	3.3262	330	3.0215	68	2.8860	1314	1/0/4
D3K#456R4a2	3.3287	250	3.0194	52	2.8842	1278	1/0/5
D3K#456R4a3	3.3214	314			2.8842	1218	1/0/4
D3K#456R4a4	3.3287	252			2.8933	954	1/0/4
D3K#456R4a5	3.3214	232	3.0115	58	2.8788	1180	1/0/5
D3K#456R4a6	3.3165	338	3.0116	56	2.8769	1340	1/0/4
D3K#456R4a7	3.3311	380	3.0154	62	2.8897	1194	1/0/3
D3K#456R4B1	3.3311	388	3.0234	98	2.8897	1252	1/0/3
D3K#456R4B2	3.3311	342	3.0214	78	2.8897	1342	1/0/4
D3K#456R4B3	3.3189	300	3.0136	46	2.8806	1118	1/0/4
D3K#456R4B4	3.3311	352	3.0214	58	2.8897	1120	1/0/3

Table 2 の続き

Sample No.	Qz		Cal		Dol		Qz/Cal/Dol ratio
	d(Å)	INT.(CPS)	d(Å)	INT.(CPS)	d(Å)	INT.(CPS)	
D3K#456R4B5	3.3287	330	3.0234	50	2.8878	1288	1/0/4
D3K#456R4B6	3.3311	376	3.0154	76	2.8897	1260	1/0/3
D3K#456R4B-vh	3.3311	434	3.0254	144	2.8897	794	1/0/2
D3K#456R4b1	3.3311	440	3.0234	122	2.8915	1096	1/0/2
D3K#456R4b2	3.3287	354	3.0215	66	2.8897	1404	1/0/4
D3K#456R4b3	3.3287	306	3.0195	46	2.8897	1302	1/0/4
D3K#456R4b4	3.3336	296			2.8897	1182	1/0/4
D3K#456R4b5	3.3385	294	3.0234	48	2.8951	1100	1/0/4
D3K#456R4b6	3.3336	312	3.0175	46	2.8933	1146	1/0/4
D3K#456R4b7	3.3287	324	3.0174	80	2.8878	1334	1/0/4
D3K#456R4b8	3.3311	436	3.0234	132	2.8897	1074	1/0/2
D3K#456R4C1	3.3262	522	3.0194	140	2.8878	1098	1/0/2
D3K#456R4C2	3.3336	400	3.0214	80	2.8933	1274	1/0/3
D3K#456R4C3	3.3238	374	3.0174	68	2.8842	1322	1/0/4
D3K#456R4C4	3.3311	292	3.0195	60	2.8878	1096	1/0/4
D3K#456R4C5	3.3385	422	3.0295	98	2.8933	1206	1/0/3
D3K#456R4C6	3.3360	332	3.0215	54	2.8951	1286	1/0/4
D3K#456R4C7	3.3336	306	3.0234	50	2.8878	1148	1/0/4
D3K#456R4C8	3.3409	288			2.8951	994	1/0/3
D3K#456R4C-vh	3.3287	242	3.0154	50	2.8897	994	1/0/4
D3K#456R5Mx	3.3311	472	3.0254	172			3/1/0
D3K#456R5Shell	3.3385	114	3.0335	258	2.8733	118	1/2/1
D3K#456R6-1	3.3311	768	3.0234	156	2.8989	330	1/0/0
D3K#456R6-2	3.3385	460			2.8915	1392	1/0/3
D3K#461R1	3.3311	376	3.0234	108			1/0/0
D3K#461R3	3.3336	1138	3.0274	270			1/0/0
D3K#461R4	3.3311	1222	3.0214	80			1/0/0
D3K#461R5	3.3311	400			2.8860	1314	1/0/3
D3K#462R1	3.3360	1280	3.0295	336	2.8824	54	4/1/0
D3K#462R3	3.3336	276			2.8878	1534	1/0/6
D3K#462R4	3.3336	500	3.0096	238	2.8988	488	2/1/2
D3K#462R5A1	3.3409	304	3.0295	144	2.9080	860	1/0/3
D3K#462R5A2	3.3360	282	3.0254	110	2.8988	980	1/0/3
D3K#462R5A3	3.3214	298	3.0154	136	2.8951	766	1/0/3
D3K#462R5A4	3.3238	158	3.0115	100	2.8897	732	1/1/5
D3K#462R5A5	3.3336	302	3.0234	124	2.8878	744	1/0/2
D3K#462R5A6	3.3336	276	3.0154	122	2.8878	568	1/0/2
D3K#462R5A7	3.3262	244	3.0194	132	2.8951	624	2/1/5
D3K#462R5A8	3.3262	224	3.0214	118	2.8933	664	2/1/6
D3K#462R5A9	3.3287	262	3.0175	100	2.8915	864	1/0/3
D3K#462R5A10	3.3311	272	3.0215	90	2.8878	666	1/0/2
D3K#462R5A11	3.3287	300	3.0295	92	2.8988	850	1/0/3
D3K#462R5A12	3.3311	274	3.0254	94	2.8934	944	1/0/3
D3K#462R5A13	3.3287	316	3.0194	118	2.8951	1064	1/0/3
D3K#462R5A14	3.3262	302	3.0154	104	2.8951	1010	1/0/3
D3K#462R6	3.3336	244	3.0254	126	2.8988	696	2/1/6

Table 3 The result of Mg content estimationMg of cal is the value of the Mg²⁺ mol% of calcite and Mg of dol is dolomite.

Sample Name.	Cal d	Mg of cal mol%	Dol d	Mg of cal mol%	Sample Name.	Cal d	Mg of cal mol%	Dol d	Mg of cal mol%
2K#1179R1			2.8948	47.0403	D3K#456R4a3			2.9058	43.3456
2K#1179R2-1	3.0382	0.0000	2.9101	41.9228	D3K#456R4a4			2.9076	42.7416
2K#1179R3	3.0373	0.0000			D3K#456R4a5	3.0331	0.6376	2.9004	45.1711
2K#1179R5	3.0329	0.7148	2.8991	45.6074	D3K#456R4a6	3.0381	0.0000	2.9034	44.1477
2K#1179R6	3.0385	0.0000	2.9040	43.9765	D3K#456R4a7	3.0273	2.5738	2.9015	44.7852
D3K#455R1	3.0349	0.0436	2.8936	47.4396	D3K#456R4B1	3.0353	0.0000	2.9015	44.7852
D3K#455R3			2.9010	44.9799	D3K#456R4B2	3.0333	0.5638	2.9015	44.7852
D3K#455R4	3.0369	0.0000			D3K#456R4B3	3.0376	0.0000	2.9046	43.7483
D3K#455R5A1			2.8952	46.9128	D3K#456R4B4	3.0333	0.5638	2.9015	44.7852
D3K#455R5A2			2.8923	47.8859	D3K#456R4B5	3.0378	0.0000	2.9022	44.5772
D3K#455R5A3			2.8898	48.7248	D3K#456R4B6	3.0273	2.5738	2.9015	44.7852
D3K#455R5A4-1			2.8915	48.1544	D3K#456R4B-vh	3.0373	0.0000	2.9015	44.7852
D3K#455R5A4-2			2.8959	46.6779	D3K#456R4b1	3.0353	0.0000	2.9034	44.1745
D3K#455R5A5			2.8940	47.3154	D3K#456R4b2	3.0359	0.0000	2.9040	43.9664
D3K#455R5A6			2.8898	48.7248	D3K#456R4b3	3.0339	0.3826	2.9040	43.9664
D3K#455R5A7			2.8898	48.7248	D3K#456R4b4			2.8991	45.6074
D3K#455R5A8			2.8959	46.6779	D3K#456R4b5	3.0280	2.3624	2.8997	45.4161
D3K#455R5A9			2.8934	47.5168	D3K#456R4b6	3.0270	2.6946	2.9027	44.3826
D3K#455R5A10			2.8940	47.3154	D3K#456R4b7	3.0318	1.0872	2.9022	44.5772
D3K#455R5A11			2.8923	47.8859	D3K#456R4b8	3.0353	0.0000	2.9015	44.7852
D3K#455R5A12			2.8934	47.5168	D3K#456R4C1	3.0362	0.0000	2.9046	43.7584
D3K#455R5A13			2.8965	46.4765	D3K#456R4C2	3.0309	1.3859	2.9027	44.3826
D3K#455R5B1			2.8971	46.2752	D3K#456R4C3	3.0366	0.0000	2.9034	44.1611
D3K#455R5B2			2.8904	48.5235	D3K#456R4C4	3.0314	1.2013	2.8997	45.3960
D3K#455R5B3			2.8948	47.0470	D3K#456R4C5	3.0340	0.3423	2.8978	46.0302
D3K#455R5B4			2.8940	47.3154	D3K#456R4C6	3.0285	2.1745	2.9021	44.5906
D3K#455R5B5			2.8940	47.3154	D3K#456R4C7	3.0329	0.7148	2.8973	46.2181
D3K#455R5B6			2.8965	46.4765	D3K#456R4C8			2.8972	46.2383
D3K#455R5B7			2.8965	46.4765	D3K#456R4C-vh	3.0298	1.7550	2.9040	43.9664
D3K#455R5B8			2.8923	47.8859	D3K#456R5Mx	3.0373	0.0000		
D3K#455R5B9			2.8923	47.8859	D3K#456R5Shell	3.0380	0.0000	2.8779	52.7315
D3K#455R5B10			2.8948	47.0470	D3K#456R6-1	3.0353	0.0000	2.9108	41.6846
D3K#455R5B11			2.8965	46.4765	D3K#456R6-2			2.8960	46.6443
D3K#455R5B12			2.8948	47.0470	D3K#461R1	3.0353	0.0000		
D3K#455R5C1			2.8948	47.0470	D3K#461R3	3.0369	0.0000		
D3K#455R5C2			2.8915	48.1544	D3K#461R4	3.0333	0.5638		
D3K#455R5C3			2.8940	47.3154	D3K#461R5			2.8979	46.0067
D3K#455R5C4			2.8954	46.8456	D3K#462R1	3.0364	0.0000	2.8894	48.8725
D3K#455R5C5			2.9010	44.9799	D3K#462R3			2.8973	46.2181
D3K#455R5C6	3.0413	0.0000	2.9015	44.7852	D3K#462R4			2.9082	42.5369
D3K#455R5C7			2.8973	46.2181	D3K#462R5A1	3.0315	1.1644	2.9101	41.9195
D3K#455R5C8			2.8973	46.2181	D3K#462R5A2	3.0324	0.8658	2.9058	43.3591
D3K#455R5C9			2.8985	45.8188	D3K#462R5A3	3.0371	0.0000	2.9168	39.6745
D3K#455R5C10			2.8997	45.3960	D3K#462R5A4	3.0307	1.4530	2.9089	42.3289
D3K#455R5C11			2.8991	45.6074	D3K#462R5A5	3.0329	0.7148	2.8973	46.2181
D3K#455R6	3.0382	0.0000			D3K#462R5A6	3.0249	3.3960	2.8973	46.2181
D3K#455R6Shell	3.0274	2.5369			D3K#462R5A7	3.0362	0.0000	2.9119	41.3087
D3K#456R1			2.9034	44.1745	D3K#462R5A8	3.0382	0.0000	2.9101	41.9228
D3K#456R3	3.0369	0.0000			D3K#462R5A9	3.0319	1.0537	2.9058	43.3557
D3K#456R4A1	3.0358	0.0000	2.9022	44.5772	D3K#462R5A10	3.0334	0.5302	2.8997	45.3960
D3K#456R4A2			2.9034	44.1611	D3K#462R5A11	3.0438	0.0000	2.9131	40.8960
D3K#456R4A3			2.9040	43.9664	D3K#462R5A12	3.0373	0.0000	2.9053	43.5302
D3K#456R4A4			2.9040	43.9664	D3K#462R5A13	3.0338	0.4161	2.9095	42.1275
D3K#456R4A5	3.0273	2.5738	2.8997	45.3960	D3K#462R5A14	3.0322	0.9362	2.9119	41.3087
D3K#456R4a1	3.0383	0.0000	2.9028	44.3691	D3K#462R6	3.0349	0.0436	2.9082	42.5369
D3K#456R4a2	3.0338	0.4161	2.8985	45.7987					

Table 4 The carbon and the oxygen isotopic ratio of carbonates and mudstones $\delta^{18}\text{O}$ fractionation in magnesian calcite relative to pure calcite precipitated under the same conditions changes in heavy direction by 0.06‰ heavy for each mole-percent MgCO_3 in calcite. The measured $\delta^{18}\text{O}$ of magnesian calcite was corrected by $0.06 (\text{‰}) \times \text{MgCO}_3 (\text{mol}\%)$. *1 : cal : dol = 1 : 2

Sample Name	Type		¹³ C	¹⁸ O	Sample Name	Type		¹³ C	¹⁸ O		
2K#1179-B2-1	living Bathy-modiolus	cal	0.260	3.573	D3K#456-R4-A3			-18.582	7.275		
2K#1179-B2-2			0.573	3.259	D3K#456-R4-A4			-18.301	7.101		
2K#1179-B2-3			0.600	3.348	D3K#456-R4-A5			-19.057	7.022		
2K#1179-R1	burrow	dol	-34.890	7.634	D3K#456-R4-a1			-19.158	6.793		
2K#1179-R2-1	chimney	dol	-33.954	7.120	D3K#456-R4-a2			-17.991	6.777		
2K#1179-R3-Mx	shell crust	cal	-18.813	3.812	D3K#456-R4-a3			-18.269	6.808		
2K#1179-R3-Shell			-0.887	3.439	D3K#456-R4-a4	-18.689	6.836				
2K#1179-R4	shell crust	cal	-10.730	2.955	D3K#456-R4-a5			-17.978	6.901		
2K#1179-R5	shell crust	cal	-17.044	4.124	D3K#456-R4-a6			-19.433	6.995		
2K#1179-R6	shell crust	cal	-16.460	4.545	D3K#456-R4-a7			-21.501	6.936		
2K#981-ST4-1inn	chimney	dol	-19.403	7.361	D3K#456-R4-B1			-19.690	6.894		
2K#981-ST4-1mid			-18.931	7.619	D3K#456-R4-B2			-18.416	7.089		
2K#981-ST4-1out			-17.457	7.537	D3K#456-R4-B3			-18.495	7.071		
D3K#347-ST6	chimney	dol	-41.443	7.206	D3K#456-R4-B4			-18.415	6.734		
D3K#348-ST3-1	chimney	dol	-41.425	7.184	D3K#456-R4-B5			-18.179	7.147		
D3K#348-ST5inn	chimney	dol	-23.937	6.558	D3K#456-R4-B6			-20.364	6.917		
D3K#348-ST5mid			-23.644	6.821	D3K#456-R4-B-vh	chimney	dol	-18.916	6.087		
D3K#348-ST5out			-24.488	6.595	D3K#456-R4-b1			-21.415	6.657		
D3K#349-ST6	chimney	dol	-31.357	7.500	D3K#456-R4-b2			-19.350	6.871		
D3K#455-R1	mudstone	qz	-0.640	-9.238	D3K#456-R4-b3			-17.445	6.876		
D3K#455-R2	chimney	dol	-42.992	7.892	D3K#456-R4-b4			-18.720	6.696		
D3K#455-R3	nodule	dol	-48.296	7.826	D3K#456-R4-b5			-18.911	6.544		
D3K#455-R4	mudstone	qz	-0.081	-2.413	D3K#456-R4-b6			-18.038	6.698		
D3K#455-R5-A1			-42.755	7.701	D3K#456-R4-b7			-18.566	6.717		
D3K#455-R5-A2			-42.668	7.702	D3K#456-R4-b8			-20.197	6.414		
D3K#455-R5-A3			-42.608	7.465	D3K#456-R4-C1			-20.434	6.720		
D3K#455-R5-A4-2			-42.833	7.458	D3K#456-R4-C2			-19.411	6.914		
D3K#455-R5-A4-1			-42.909	7.613	D3K#456-R4-C3			-18.151	6.784		
D3K#455-R5-A5			-43.040	7.414	D3K#456-R4-C4			-18.416	7.052		
D3K#455-R5-A6			-43.029	7.291	D3K#456-R4-C5			-21.079	6.837		
D3K#455-R5-A7			-42.949	7.438	D3K#456-R4-C6			-19.266	6.903		
D3K#455-R5-A8			-42.806	7.665	D3K#456-R4-C7			-18.045	7.092		
D3K#455-R5-A9			-43.021	7.327	D3K#456-R4-C8			-18.885	6.850		
D3K#455-R5-A10			-42.990	7.756	D3K#456-R4-C-vh			-18.292	6.424		
D3K#455-R5-A11			-42.887	7.675	D3K#456-R5-Mx	shell crust	cal	-15.679	2.476		
D3K#455-R5-A12			-42.706	7.834	D3K#456-R5-Shell			-3.078	3.092		
D3K#455-R5-A13	-42.875	7.656	D3K#456-R6-2	chimney	dol			-30.946	7.786		
D3K#455-R5-B1			-43.033	7.640	D3K#461-R1	nodule	qz	-7.621	2.014		
D3K#455-R5-B2			-42.823	7.648	D3K#461-R2-1	nodule	cal	-13.888	3.093		
D3K#455-R5-B3			-42.583	7.218	D3K#461-R2-2			-13.975	3.017		
D3K#455-R5-B4	chimney	dol	-42.656	7.773	D3K#461-R3	mudstone	qz	-0.371	-4.440		
D3K#455-R5-B5			-42.193	7.682	D3K#461-R5	chimney	dol	-38.221	7.698		
D3K#455-R5-B6			-41.848	7.396	D3K#462-R1	mudstone	qz	0.175	-1.004		
D3K#455-R5-B7			-41.588	7.422	D3K#462-R2-1			-28.587	7.230		
D3K#455-R5-B8			-42.708	7.586	D3K#462-R2-2			-26.665	7.474		
D3K#455-R5-B9			-42.675	7.716	D3K#462-R2-3			chimney	dol	-25.725	7.462
D3K#455-R5-B10	-42.995	7.706	D3K#462-R2-4	-25.441	7.729						
D3K#455-R5-B11	-43.087	7.850	D3K#462-R2-5	-25.472	7.657						
D3K#455-R5-B12			-43.052	7.646	D3K#462-R2-6			-26.550	7.495		
D3K#455-R5-C1			-42.512	7.691	D3K#462-R3			chimney	dol	-28.208	7.569
D3K#455-R5-C2			-42.331	7.551	D3K#462-R4					nodule	*1
D3K#455-R5-C3	-42.314	7.632	D3K#462-R5-A1	-30.254	6.633						
D3K#455-R5-C4			-42.769	7.474	D3K#462-R5-A2			-30.212	6.581		
D3K#455-R5-C5			-42.804	7.498	D3K#462-R5-A3			-30.078	6.555		
D3K#455-R5-C6			-43.009	7.475	D3K#462-R5-A4			-30.404	6.671		
D3K#455-R5-C7			-42.550	7.471	D3K#462-R5-A5			-30.208	6.628		
D3K#455-R5-C8			-42.470	7.561	D3K#462-R5-A6			-29.868	6.339		
D3K#455-R5-C9			-42.382	7.192	D3K#462-R5-A7			chimney	dol	-30.116	6.374
D3K#455-R5-C10	-42.287	7.559	D3K#462-R5-A8	-30.410	6.559						
D3K#455-R5-C11	-42.712	6.584	D3K#462-R5-A9	-30.921	6.534						
D3K#455-R6-Mx	shell crust	cal	-16.861	3.073	D3K#462-R5-A10			-30.619	6.706		
D3K#455-R6-Shell			-1.539	3.437	D3K#462-R5-A11			-30.601	6.770		
D3K#456-R1	chimney	dol	-28.922	7.171	D3K#462-R5-A12			-30.788	6.897		
D3K#456-R2	nodule	cal	-17.053	6.301	D3K#462-R5-A13			-30.861	6.815		
D3K#456-R3	mudstone	qz	-0.659	-1.530	D3K#462-R5-A14			-31.056	6.934		
D3K#456-R4-A1	chimney	dol	-21.268	6.999	D3K#462-R6	chimney	dol	-30.002	6.228		
D3K#456-R4-A2			-19.455	7.333							

mined principally by $\delta^{18}\text{O}$ of the water from which the carbonate precipitated, temperature of precipitation, and

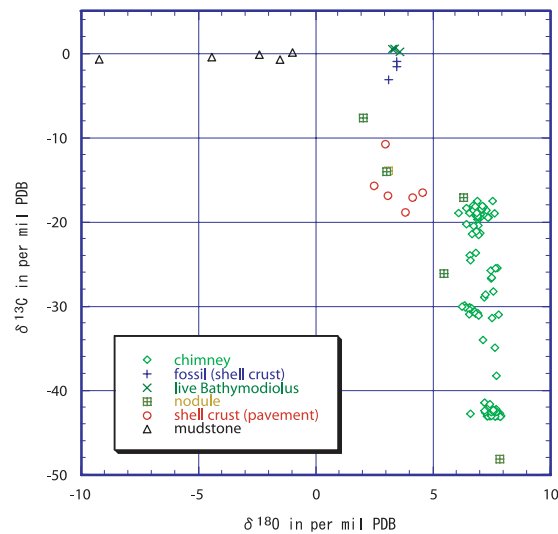


Fig. 7 Isotopic composition of the Kuroshima Knoll

carbonate mineralogy. The relation among $\delta^{18}\text{O}$ of calcite (δc : in per mil PDB), $\delta^{18}\text{O}$ of the ambient water (δw : in per mil SMOW), and the temperature of precipitation (t : $^{\circ}\text{C}$) is given by the following equation.

$$t = 16.5 - 4.3 (\delta c - \delta w) + 0.14 (\delta c - \delta w)^2 \quad (\text{Epstein et al., 1953}) \quad (1)$$

In the case of dolomite precipitation, the oxygen value is subtracted 4 in per mil from its values and is substituted for the above equation (O'Neil and Epstein, 1966). The calculated temperature at each carbonate precipitation is shown in Table 5.

6. Discussion

6.1. The heavy oxygen isotopic ratios

The present oxygen isotopic value of the bottom seawater at the top of the Kuroshima Knoll shows -0.5 to -

Table 5 Estimation of the temperature of precipitation and paleo- $\delta^{18}\text{O}$ of the seawater

Temp is the temperature of the seawater where samples were picked up. δc is the oxygen isotope ratio of the carbonates. Estimated δw is calculated by the equation (1) using the assumption that the temperature of the seawater has not changed and the carbonates position has not moved. The temperature of precipitation is determined by the equation (1) when the δw value is given.

Sample Name	Type	Temp ($^{\circ}\text{C}$)	δc	Estimated δw	$\delta w=2$	Temperature of precipitation			
						$\delta w=1$	$\delta w=0$	$\delta w=-1$	$\delta w=-2$
2K#1179-R1	burrow	8.0	7.634	1.51	-3.28	-5.86	-8.17	-10.19	-11.93
2K#1179-R2-1	chimney	8.0	7.120	1.00	-1.85	-4.57	-7.02	-9.19	-11.07
2K#981-ST4-1	chimney		7.506		-2.93	-5.55	-7.89	-9.95	-11.72
D3K#347-ST6	chimney		7.206		-2.09	-4.79	-7.22	-9.36	-11.22
D3K#348-ST3-1	chimney		7.184		-2.03	-4.74	-7.17	-9.31	-11.18
D3K#348-ST5	chimney		6.658		-0.49	-3.35	-5.92	-8.22	-10.23
D3K#349-ST6	chimney		7.500		-2.92	-5.54	-7.88	-9.94	-11.72
D3K#455-R2	chimney	7.0	7.892	1.50	-3.98	-6.49	-8.72	-10.67	-12.34
D3K#455-R3	chimney	7.0	7.826	5.43	-3.80	-6.33	-8.58	-10.55	-12.23
D3K#455-R5	chimney	8.0	7.540	1.42	-3.02	-5.63	-7.96	-10.01	-11.78
D3K#456-R1	chimney	9.0	7.171	1.31	-1.99	-4.70	-7.14	-9.29	-11.16
D3K#456-R4	chimney	8.7	6.855	0.92	-1.08	-3.88	-6.40	-8.64	-10.60
D3K#456-R6	chimney	8.0	7.786	1.66	-3.69	-6.23	-8.49	-10.47	-12.17
D3K#461-R5	chimney	7.5	7.698	1.44	-3.46	-6.02	-8.31	-10.31	-12.03
D3K#462-R2	chimney	7.4	7.508	1.22	-2.94	-5.55	-7.89	-9.95	-11.73
D3K#462-R3	chimney	7.2	7.569	1.23	-3.10	-5.71	-8.03	-10.07	-11.83
D3K#462-R5	chimney	8.1	6.643	0.55	-0.45	-3.31	-5.89	-8.19	-10.21
D3K#462-R6	chimney	8.1	6.228	0.13	0.82	-2.15	-4.85	-7.27	-9.40
D3K#455-R1	mudstone	6.5	-9.235	-11.77	82.48	75.18	68.15	61.40	54.94
D3K#455-R4	mudstone	7.6	-2.413	-4.64	38.20	32.81	27.69	22.86	18.30
D3K#456-R3	mudstone	8.9	-1.530	-3.41	33.42	28.28	23.41	18.82	14.51
D3K#461-R3	mudstone	7.0	-4.440	-6.84	50.00	44.04	38.35	32.95	27.83
D3K#462-R1	mudstone	7.2	-1.004	-3.35	30.68	25.68	20.96	16.52	12.36
D3K#456-R2	nodule	8.8	6.301	4.39	0.60	-2.36	-5.04	-7.43	-9.55
D3K#461-R1	nodule	6.2	2.014	-0.60	16.44	12.28	8.41	4.81	1.50
D3K#461-R2	nodule	6.5	3.055	0.52	12.12	8.25	4.67	1.37	-1.66
D3K#462-R4	nodule	7.8	5.459	3.28	3.30	0.11	-2.80	-5.43	-7.78
2K#1179-R3-Mx	shell crust	8.3	3.812	1.77	9.17	5.52	2.14	-0.95	-3.76
2K#1179-R3-Shell	shell crust	8.3	3.439	1.40	10.60	6.85	3.37	0.17	-2.75
2K#1179-R4	shell crust	7.6	2.955	0.72	12.52	8.63	5.02	1.68	-1.37
2K#1179-R5	shell crust	7.6	4.167	1.94	7.84	4.29	1.01	-1.98	-4.69
2K#1179-R6	shell crust	7.6	4.545	2.31	6.46	3.02	-0.15	-3.04	-5.65
D3K#455-R6-Mx	shell crust	8.1	3.073	0.98	12.05	8.19	4.61	1.31	-1.71
D3K#455-R6-Shell	shell crust	8.1	3.589	1.49	10.02	6.31	2.87	-0.28	-3.16
D3K#456-R5-Mx	shell crust	8.5	2.476	0.49	14.48	10.46	6.71	3.24	0.06
D3K#456-R5-Shell	shell crust	8.5	3.092	1.10	11.97	8.12	4.54	1.25	-1.77

1.0 in per mil PDB, and the bottom water temperature is about 6 °C to 9 °C. Considering that there is no obvious difference of the oxygen isotopic values between fossil and living *Bathymodiolus*, the seawater environment has not greatly changed. Assuming that the oxygen isotopic ratio of the seawater doesn't vary with times, the temperature of carbonate precipitation must have unrealistically cold value, such as -7 °C. Even was the water temperature colder than now, the heavy oxygen isotopic values of dolomite chimneys couldn't be explained without considering the ambient water had a heavier oxygen isotopic ratio. If the bottom water temperature at the Kuroshima Knoll has not changed, the oxygen isotopic ratio of the ambient water is more than 1.5 in per mil heavy.

6.2. The light carbon isotopic ratios

Shimajiri Group consists mainly of mudstone that contains abundant organic matter. This organic matter would be decomposed in the methane fermentation zone, generating methane with light carbon isotopic ratio (about -90 in per mil PDB), because of the isotopic fractionation by bacteria. This methane supply plays an important role in the sub-seafloor chemical reaction. Methane migrates up to the sulfate reduction zone and is oxidized as shown in the following chemical reaction.



Isotopically light carbon in methane shifts to the bicarbonate on the right (2), and carbonates with light carbon isotopic ratio are precipitated. When upward migration flux of methane is strong, sulfate reduction zone is moved near the seafloor.

6.3. Hydrate-related cold seeps

The existence of methane hydrate depends on the pressure and the temperature conditions. In this study area, methane hydrate layers can exist theoretically, though it may be thin. Methane hydrate is composed of isotopically heavy oxygen water (about +3 in per mil) and light carbon methane (in case of the biogenic origin). Since methane hydrate is very sensitive to the change of pressure and temperature condition, subtle changes would cause dissociation of methane hydrate.

As described above, carbonates were formed by the

cold seep that had the light carbon and heavy oxygen isotopic ratios. There could be another mechanism for $\delta^{18}\text{O}$ enrichment, e.g. the fractionation of the oxygen isotope by evaporation and filtering of the clay layers. Such effects, however, are not suitable for this study area, because the Kuroshima Knoll is under the sea and thick clay layers haven't been found. So, the systematic $\delta^{18}\text{O}$ enrichment of the dolomite chimneys is interpreted as due to methane hydrate dissociation.

6.4. Dolomite chimneys

Isotopic zonation

The carbon and the oxygen isotopic ratios of chimneys show a wide and regular pattern. For example, the carbon isotopic ratios become heavy outwards. Such a phenomenon can be explained as follows. Dolomite chimneys are the result of the expulsion of cold seep. A fluid including ^{13}C -depleted carbonate migrated laterally through a centered vent hole. Concentric precipitation of dolomite occurred by mixing of the fluid penetrating radially outward from the vent hole and pore water (or seawater) in the surrounding sediment. Therefore, the carbon isotopic ratios of dolomite become progressively heavier with increasing distance from the vent hole. The same explanation applies to the case of the oxygen isotopic ratios. The heavy oxygen was supplied from the fluid as in case of the same as light carbon. Big chimney has lightest carbon isotopic ratios, and a slender chimney has heavier values than big chimney (Fig. 8). When the flux of cold seep is high, the power of fluid penetration is also strong and isotopic dilution effect by the pore water should be weak. Therefore, big chimneys may have been formed with stronger cold seep than slender chimneys.

As mentioned above, there is the relation between the flux of cold seep and the carbon isotopic ratios. Cold seep seemed to be derived from the water of methane hydrate dissociation. Therefore, the oxygen isotopic ratios may also become heavier when the flux of the cold seep is high.

Why dolomite?

The carbonate minerals of all chimneys and burrows are composed of dolomite. Ultimate source of SO_4^{2-} in marine sediments is seawater. Mg^{2+} forms ion-complex, MgSO_4^0 , under high concentration of SO_4^{2-} . In semi-

closed system such as burrows or chimneys, however, the supply of SO_4^{2-} is limited. In this case, the amount of MgSO_4^0 decreases and free magnesium ion, Mg^{2+} ,

increases. Hence, Mg/Ca ratio increases and dolomite is easy to precipitate (Baker and Kastner, 1981). In this way, dolomite precipitation occurs within semi-closed system, and forms chimneys.

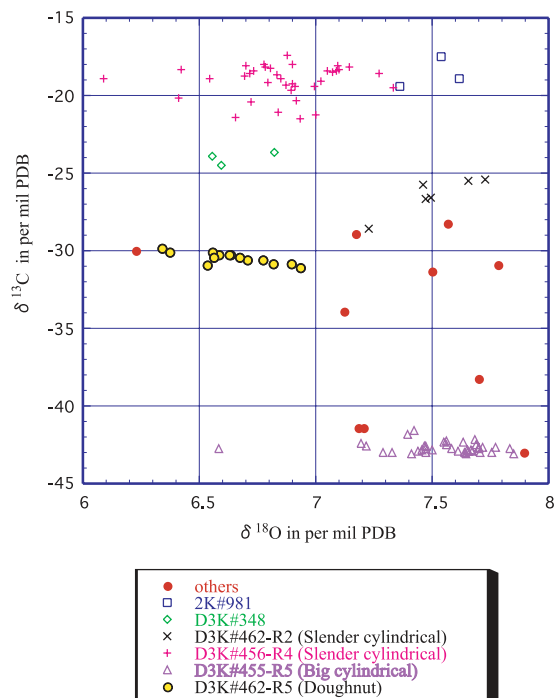


Fig. 8 Isotopic composition of chimneys

7. Conclusion

Cold seep carbonates from the Kuroshima Knoll have various shapes, such as ; (1) shell crust (pavement), (2) chimney, (3) burrow, and (4) nodule. All chimney types and burrow type carbonates are composed of dolomite, while shell crust (pavement) type and nodular type are composed of calcite, sometimes both calcite and dolomite.

Fig. 9 shows the schematic diagram of methane seep-carbonate system on the Kuroshima Knoll. First, methane is produced by bacterial fermentation of the organic matter in the Shimajiri Group. This methane forms methane hydrate layer under the seafloor. When pressure or temperature changes, methane seep with the light carbon and the heavy oxygen isotopic ratio. Secondary, methane reacts with sulfate to form bicarbonate. This bicarbonate which has the light carbon isotopic ratio is precipitated as carbonates. Moreover, HS^- and methane which have not been com-

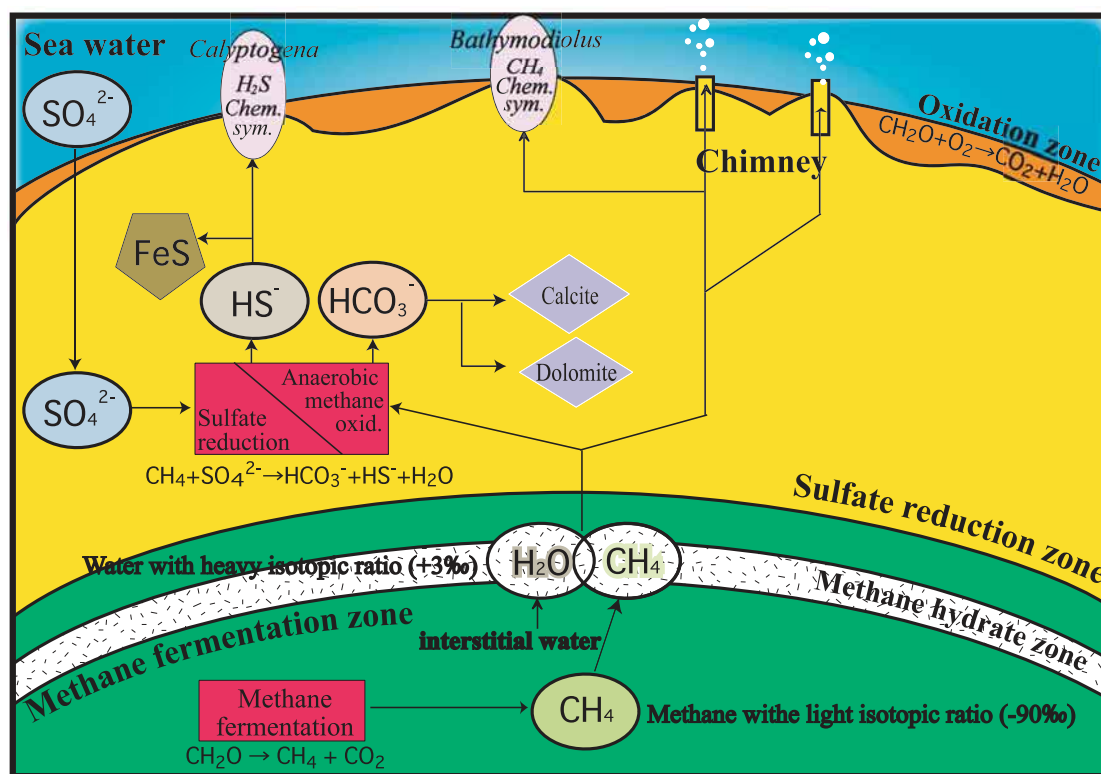


Fig. 9 The schematic diagram of methane seep - carbonate system on the Kuroshima Knoll

pletely consumed reach the seafloor, and feed chemosynthetic communities such as *Bathymodiolus* and *Calyptogena*.

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9. Reference

- 1) P. A. Baker, and M. Kastner, "Constraints on the formation of sedimentary dolomite," *Science*, **213**, 214-216 (1981).
- 2) S.E. Epstein, R. Buchsbaum, H.A. Lowenstam, and H.C. Urey, "Revised carbonate-water isotopic temperature scale," *GSA Bull.*, **64**, 1315-1326 (1953).
- 3) J. R. Goldsmith and D. L. Graf, "Relation between lattice constants and composition of the Ca-Mg carbonates," *Am. Mineral.*, **43**, 84-101 (1958).
- 4) H. Machiyama et al., "Outline of Dolhin-3K dive surveys on the Kuroshima Knoll and in the southern Okinawa Trough -Preliminary report of the NT00-05 Cruise-," *JAMSTEC J. Deep Sea Res.*, **18**, 15-30 (2001).
- 5) T. Matsumoto, C. Uechi, and M. Kimura, "Surface deformation at the origin area of the 1771 Yaeyama Earthquake Tsunami observed by the precise survey off Yaeyama districts, Ryukyu area," *JAMSTEC J. Deep Sea Res.*, **13**, 535-561 (1997).
- 6) T. Matsumoto, M. Kimura, S. Nishida, T. Nakamura, and T. Ono, "Chemosynthetic communities and surface ruptures discovered on the Kuroshima Knoll south of Yaeyama Islands (NT97-14 Cruise)," *JAMSTEC J. Deep Sea Res.*, **14**, 477-491 (1999).
- 7) J.R. O'Neil, and S. Epstein, "Oxygen isotope fractionation in the system dolomite-calcite-carbon dioxide," *Science*, **152**, 3719, 198-201 (1966).
- 8) R. Shinjo, H. Machiyama, I. Motoyama, Y. Maki, G. Toyama, S. Hokakubo, and S. L. Chung, "Outline of SHINKAI-2000 dive surveys at the westernmost part of the Okinawa Trough and the Kuroshima Knoll -Preliminary report of the NT00-06 Leg-1 Cruise-," 17th JAMSTEC Symp. *Deep Sea Res.*, **39** (2001).

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