Compositions and some properties of opal-CT rocks from the Gamanosawa Formation of Tertiary age, Aomori Prefecture, Japan

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Siliceous hard shales, which were found from the Gamanosawa Formation of Tertiary age, Aomori Prefecture, Japan, are mostly composed of opal-CT. The name of the opal-CT rock is used here instead of the hard shale. The content of SiO_2 is in the range of 83 to 94 wt%. Broad diffused X-ray diffraction patterns correspond to the peaks of opal-CT. The spacing of 4 Å peak is in the range of 4.10 Å to 4.11 Å. Bulk density is in the range of 0.90 to 1.25, and apparent porosity in the range of 40 to 60 volume%. Crystallinity of the opal-CT rock is too poor to reveal phase transition. However, when it is heated over 1250°C in air, the crystallinity is improved and reveal phase transition at temperatures ranging from 182°C to 220°C. The spacing of 4 Å peak progressively decreased from 4.11 Å to 4.05 Å by heating it at high temperatures. By hydrothermal treatments at 500°C and 1000 kg/cm² in a high pressure vessel, the spacing of 4 Å peak also decreased from 4.11 Å to 4.05 Å, and opal-CT gradually transformed into quartz. The opal-CT rocks may be a transitional stage from opal-CT to quartz due to diagenesis in nature.

Introduction

Recent studies on silica minerals have contributed to the problem of diagenesis of siliceous sediments, and significant advance has been made in the interpretation of genesis of silica minerals at earth-surface conditions. Jones and Segnit (1975) found three types of opal such as opal-A, opal-CT and opal-C, in which opal-CT is the most common in nature. Flörke et al. (1975) found that opal-A transformed to chalcedony through opal-CT due to diagenesis in nature. Carr and Fyfe (1958), White and Corwin (1961), Heydemann (1964) and Mizutani (1966) also found that amorphous silica such as silica gel and silica glass transform to quartz through cristobalite stage, corresponding to opal-CT, by hydrothermal treatments. Many reports concerning such as opaline rock found in Tertiary sediments

have been published in Japan (Mitsui et al., 1974, 1975, 1977; Honda, 1978; Mizutani, 1966, 1977, 1978; Kano et al., 1979, 1982; Iijima et al., 1981, 1983; Taguchi et al., 1982).

Siliceous hard shales, which were found from the Gamanosawa Formation at Higashidorimura, Aomori Prefecture, Japan (Kuwano, 1958; Imai, 1961), are mostly composed of opal-CT. The name of the opal-CT rock is used here instead of the hard shale. The purpose of this paper is to provide fundamental data of the opal-CT rocks and some considerations of diagenesis.

Occurrence

The opal-CT rocks studied crop out at Higashidorimura approximately 6 km east of Tanabu Station, Japan National Railway, near Shiriyazaki of Shimokita Peninsula, Aomori Prefecture, Japan (Fig. 1).
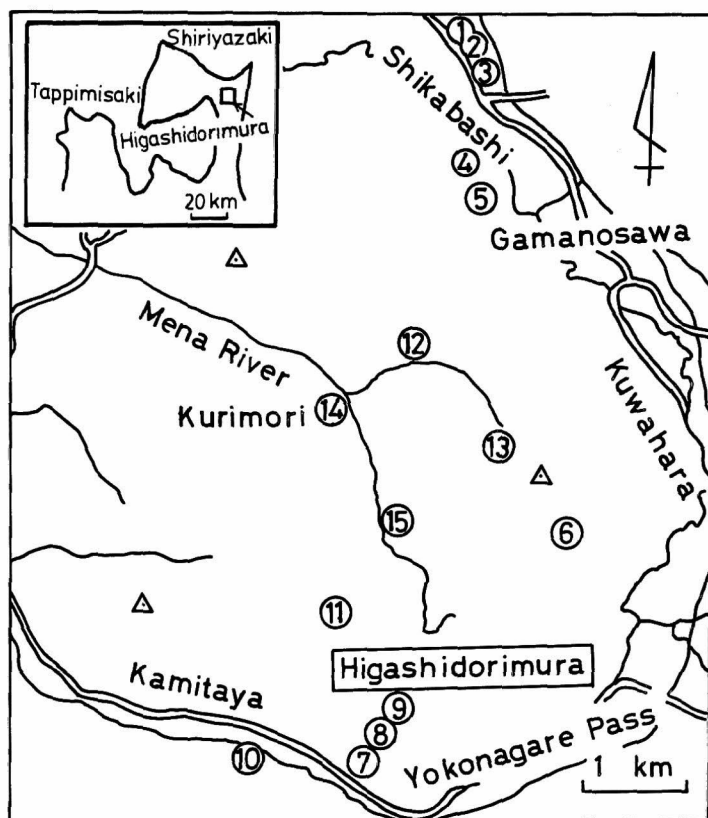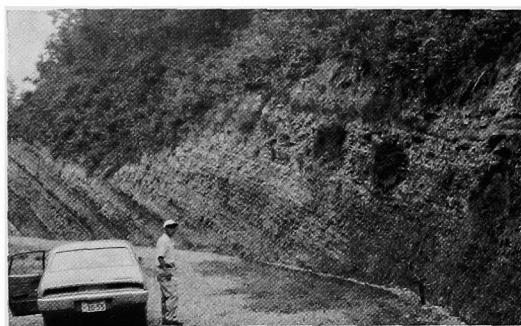
Fig. 1. Locality map of Higashidorimura.
1–15 = Sample locality number.

(a)   **(b)**

Fig. 2. Outcrop of opal-CT rocks at Kamitaya (sample 11 in Fig. 1 and Table 1) consisting of white, grey or dark beds of opal-CT rock alternating with thin yellowish siltstone or dark mudstone layers.

The Gamanosawa Formation of the Tertiary age, which is exposed in the area of Shikabashi to the Yokonagare Pass about 8 km long trending in a north-south direction, and of Kurimori to Kuwahara, Higashidorimura, about 4 km long trending in a west-east direction, consists of siliceous hard shale, siltstone, black mudstone and tuff (Kuwano, 1958; Imai, 1961).

Fig. 2 shows a typical outcrop of the opal-CT rock at Kamitaya (sample 11 in Fig. 1 and Table 1). The opal-CT rock shows alternating of thin siltstone and layers with 0.1 to 20 m in thickness.

Chemical composition

Chemical compositions of the opal-CT rocks dried at 110°C for one day are shown in Table 1. The SiO_2 content is in the range of 83 to 94 wt%. The losses on ignition are in the range of 1 to 4 wt%. Other components such as Al_2O_3, Fe_2O_3, CaO, MgO, Na_2O and K_2O would be from feldspar, clay minerals, iron minerals and others.

X-ray powder study

X-ray powder diffraction patterns of the opal-CT rocks were obtained by a Shimazu X-ray diffractometer using CuKα radiation.

The results are shown in Fig. 3. The opal-CT rocks show a broad diffused X-ray band of opal-CT or opal-C (type I and II, respectively), in which type I is the most common. Flörke et al. (1975) assumed that the opal-CT was built up from a disordered interstratification of cristobalite and tridymite on an atomic scale. The spacing of 4 Å peak of the present rock is in the range of 4.10 Å to 4.11 Å. The spacing which is close to that of tridymite progressively decreases to 4.05 Å (similar to that of cristobalite) with increasing the heating temperature over 1250°C in air. Probably, a tridymite stacking layer is dominant in the opal-CT rock at low temperatures, and a cristobalite stacking layer at high temperatures. Consequently, it has become apparent that the present rocks from the

Table 1. Chemical composition (wt.%) of opal-CT rocks

No.*	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	Ig. loss	Total
1	90.72	4.26	0.83	0.33	0.65	0.27	0.45	3.04	100.91
2	84.98	6.93	0.88	0.17	0.61	0.44	0.73	3.38	98.12
3	83.09	5.86	5.01	0.32	0.58	0.50	0.82	3.69	99.87
4	84.29	6.32	3.27	0.37	0.48	0.47	0.76	3.93	99.89
5	86.20	5.98	1.60	0.58	0.45	0.41	0.67	3.48	99.37
6	90.60	3.43	1.36	1.05	0.52	0.28	0.46	1.96	99.75
7	86.78	3.66	2.31	0.94	0.35	0.30	0.43	3.94	98.71
8	87.96	4.61	1.36	0.75	0.44	0.27	0.39	2.96	98.74
9	88.14	4.20	1.26	0.39	1.10	0.28	0.49	3.74	99.60
10	88.81	3.52	2.02	0.89	0.25	0.33	0.54	2.98	99.34
11	88.27	0.25	1.64	2.86	0.76	0.27	0.82	4.76	99.63
12	88.05	3.42	2.18	0.80	0.21	0.41	0.68	3.48	99.23
13	92.71	2.32	0.67	0.90	0.54	0.20	0.10	2.08	99.52
14	92.35	2.32	0.41	0.04	1.13	0.43	1.08	2.21	99.95
15	93.63	1.70	0.48	1.02	0.31	0.29	0.49	1.81	99.73

*=Sample number.
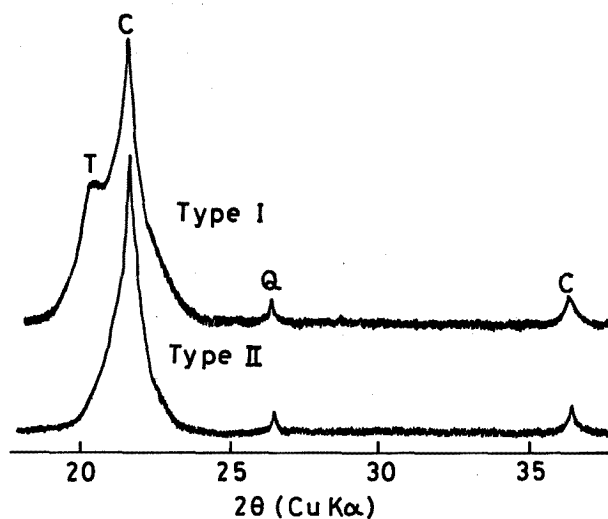
Fig. 3. X-ray diffraction patterns of opal-CT rocks.
C=Cristobalite, T=Tridymite, Q=Quartz.

Gamanosawa Formation are mostly composed of opal-CT.

Density and porosity

The opal-CT rocks were cut to the size of 10 mm×10 mm×10 mm, and dried at 110°C for one day, then weighed (w_1 g). After boiling at 100°C, samples were suspended in water with a steel wire, then weighed (w_2 g). Wiped samples with a wet cloth quickly and weighed (w_3 g). Bulk density and apparent porosity were calculated from the values of w_1, w_2 and w_3. Table 2 shows the bulk density and apparent porosity. The bulk density was in the range of 0.90 to 1.25, and the apparent porosity in the range of 40 to 60 volume %.

Pore size distribution of the opal-CT rocks were measured by the mercury penetration method using a Micrometric mercury porosimeter. Although measurements were carried out for ten samples, the results were almost the same as that of Fig. 4. As shown in Fig. 4, the opal-CT rocks have many small pores, most of which are

Table 2. Bulk density and apparent porosity of opal-CT rock

No.*	Bulk density (g/cm³)	Apparent porosity (vol. %)
1	1.11	51.85
2	1.10	55.37
3	1.19	50.43
4	1.02	56.04
5	1.21	41.92
6	0.98	58.06
7	0.90	63.30
8	1.12	51.92
9	1.11	51.26
10	1.25	43.57
11	0.96	59.77
12	0.93	59.80
13	1.12	51.57
14	1.05	52.35
15	1.10	55.18

*=Sample number.

less than 100 Å in size.

Thermal property

The opal-CT rocks are developed dominantly at Higashidorimura, and the content of SiO_2 is in the range of 83 to 94 wt%. The
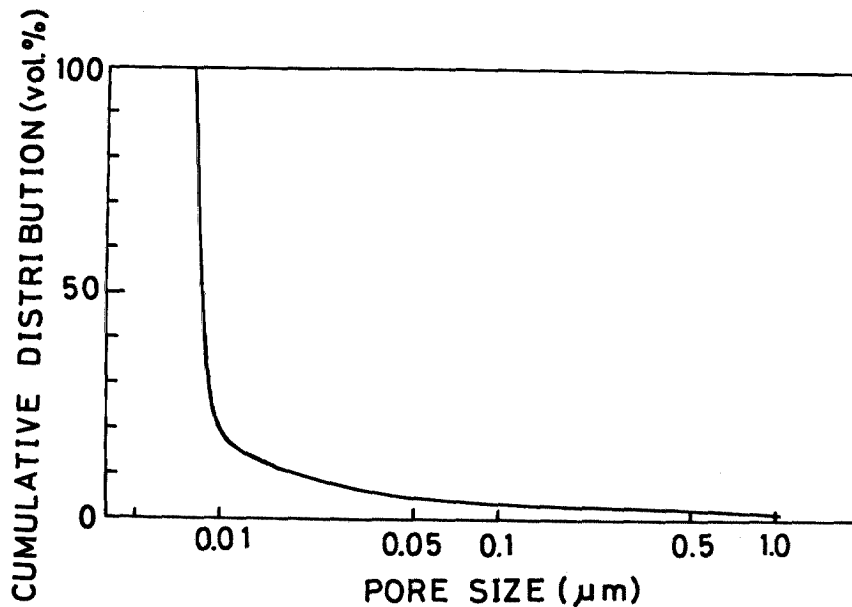
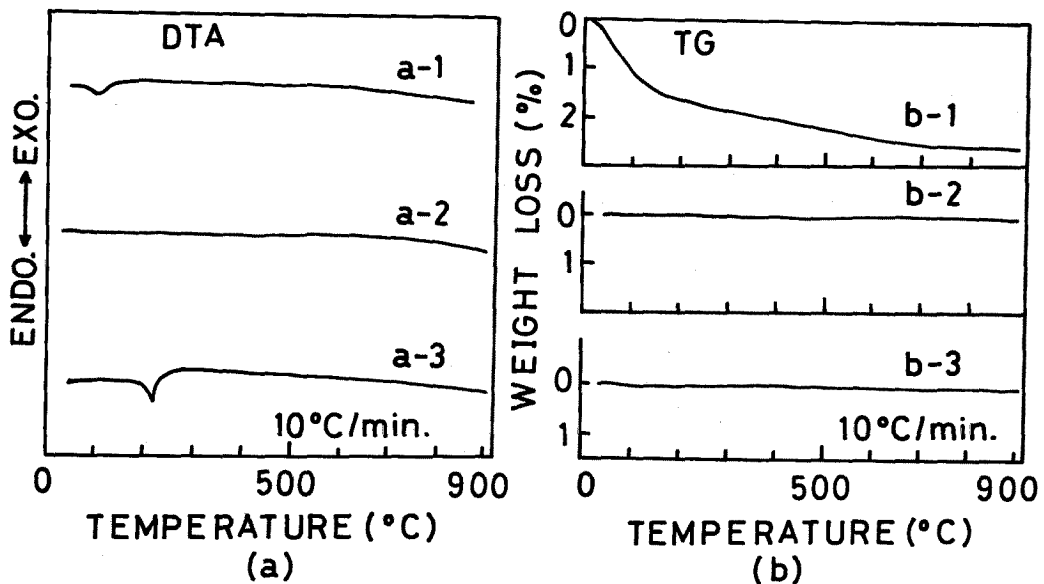Fig. 4. Pore size distribution of opal-CT rock (sample 15).

Fig. 5. DTA and TG curves of opal-CT rocks (sample 11).
a–1 and b–1＝Before calcination, a–2 and b–2＝Calcined at 1200°C for 3 hours, a–3 and b–3＝ Calcined at 1300°C for 3 hours.

opal-CT rocks have been expected to be a ceramic raw material as a source of silica. It has been tried to synthesize zeolite, silicon carbide, silicon nitride, calcium silicate hydrates, etc. from the opal-CT rocks (Hukuo *et al.*, 1983). From the

viewpoint of the study of opal-CT and the
practical study of the opal-CT rocks, follow-
ing thermal properties of the opal-CT rocks
were examined.

Differential thermal analysis (DTA) and
thermogravimetric analysis (TG) curves of
the opal-CT rocks performed with a Rigaku
simultaneous DTA-TG apparatus using
50 mg of specimen are given in Fig. 5.

The opal-CT rocks, which did not in-
clude quartz, had one endothermic peak due
to the loss of the absorbed water around
100°C as shown in Fig. 5a–1. If the opal-
CT rocks include a lot of quartz, there will
be the endothermic peak of phase transition
at 573°C. The weight losses of water and
organic matter, *etc.* were observed at tem-
peratures ranging from 100°C to 800°C
(Fig. 5b–1). The opal-CT rocks calcined
previously at temperatures ranging from
900°C to 1200°C for 3 hours did not show
any peaks on DTA curve (Fig. 5a–2) and
weight losses on TG curve (Fig. 5b–2).
However the opal-CT rocks calcined
previously at temperatures over 1250°C
showed a clear endothermic peak due to
the phase transition around 220°C on DTA
curve (Fig. 5a–3) with no weight losses
(Fig. 5b–3). X-ray diffraction patterns of the
specimens heated at temperatures over
1250°C show X-ray bands of cristobalite
without tridymite, and the spacing of 4Å
peak is 4.05 Å. Therefore, the endothermic
peak around 220°C is due to the phase transi-
tion of cristobalite.

Thermal expansion curves of the
opal-CT rocks, measured by a horizontal
dilatometer with a dial gauge, are given in
Figs. 6 and 7. Sample size for dilatometry
is 30 mm × 8 mmφ. The inflection point
due to the phase transition was not clear.
However, the specimens calcined previously
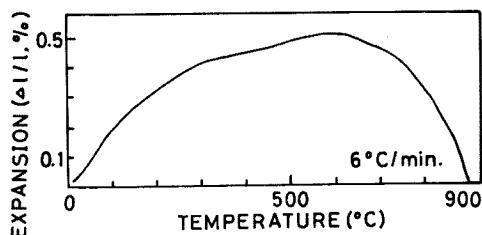at temperatures ranging from 1250°C to

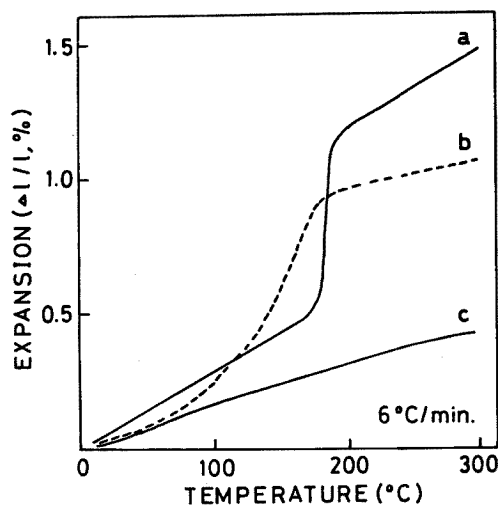Fig. 6. Linear thermal expansion curve of
opal-CT rock (sample 15).

Fig. 7. Linear thermal expansion curves of opal-
CT rocks (sample 15).
a=Calcined at 1300°C for 3 hours, b=
Calcined at 1250°C for 3 hours, c=Calcined
at 1000°C for 3 hours.

1400°C for 3 hours in air showed a clear
inflection point due to the phase transition
of cristobalite at temperatures ranging from
182°C to 188°C (Fig. 7). A well crystallized
cristobalite, usually, shows phase transi-
tion at temperatures ranging from 180°C
to 270°C in air. The differences of transi-
tion temperatures among Fig. 5a–3, Fig. 7–a
and Fig. 7–b would depend on the ex-
perimental conditions.

The opal-CT rocks calcined at tem-
peratures ranging from 100°C to 1450°C for
3 hours were examined by X-ray diffracto-

meter. At temperatures ranging from 100°C to 1100°C, a broad and diffused X-ray band of 4 Å peak became stronger and sharper. The spacing of 4 Å peak also progressively decreased from 4.11 Å to 4.05 Å with increasing the heating temperature over 1250°C in air.

Fig. 8 shows examples of X-ray diffraction patterns of the heated opal-CT rocks.

Consequently, it has made clear that (1) crystallinity of the opal-CT rock is too poor to reveal phase transition, but it can be improved by heating it at temperatures over 1250°C in air, and (2) opal-CT is stable at temperatures below 1100°C, but it progressively changes in cristobalite with increasing heating temperature in air.

Some considerations on diagenesis

Murata and Nakata (1974) described that the porcelanite (opal-CT rock) of the Monterey hard shale of Tertiary system in California showed a decrease in the d(101) spacing from 4.115 Å to 4.040 Å, indicative of a progressive change in its internal structure, with increasing depth of burial. The amount of quartz is larger than that of cristobalite when the depth of burial increases. They concluded that cristobalite would transform gradually to quartz due to the diagenesis. These transformation should occur at comparatively low temperature and pressure in nature (Carr and Fyfe, 1958; White and Corwin, 1961; Heydemann, 1964; Mizutani, 1966, 1977).

The opal-CT rocks of the Gamanosawa Formation also gradually transformed into quartz by hydrothermal treatments at 500°C and 1000 kg/cm², and the spacing of 4 Å peak progressively decreased from 4.11 Å to 4.05 Å.

Consequently, it is suggested that the studied opal-CT rocks will be a transitional stage from opal-CT to quartz due to diagenesis in nature.
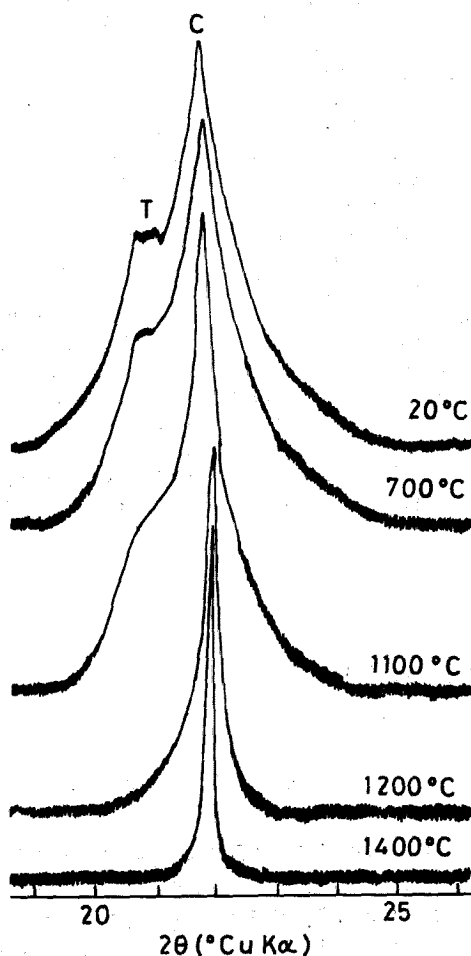

Fig. 8. X-ray diffraction patterns of opal-CT rocks (sample 15). All samples were calined previously at temperatures ranging from 20°C to 1400°C for 3 hours. T=Tridymite, C=Cristobalite.

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青森県の新第三紀蒲野沢層中から産出する Opal-CT 岩の化学組成と諸性質

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青森県下北郡東通村に露出している新第三紀蒲野沢層から産出する，いわゆる硬質頁岩は Opal-CT を主構成物質としていることがわかった。本研究では，この硬質頁岩を Opal-CT 岩とよぶことにする。この岩石中の SiO₂ 成分は 83 から 94 wt. ％ の範囲であり，粉末X線回折図中にみられる最強回折線は Opal-CT によるものであった。回折線ピークは幅広で，4Å ピークの面間隔は 4.10Å から 4.11Å の範囲内であった。Opal-CT 岩の結晶性は悪くて，DTA や熱膨張測定法では，結晶転移を観察できなかった。しかし，1250°C 以上の温度で加熱すると，結晶性がよくなって，4Å ピークの面間隔も 4.11Å から 4.05Å に変わり，結晶転移を示すようになった。また，オートクレーブ処理 (500°C, 1000 kg/cm²，水熱条件) すると，同様に 4Å ピークの面間隔は 4.11Å から 4.05Å に変わり，そののち石英に変化していった。