

Hydrothermal Changes of Silica Gels, part XXIV
--Effect of the double salts of Ca and Mg, part 3, with special reference to chert diagenesis--*

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Abstract

Hydrothermal changes of silica gels adding the single and/or mixture of the double salts of Ca and Mg such as the hydroxides and oxides were clarified for 24--240 hours at 250°C--350°C. On the case of the single addition, Mg(OH)₂ made silica gel change into only broad peak (opal-A), and Ca(OH)₂ into α -cristobalite (opal-CT), however the amount of the mixed additions was much, silica gel was changed into α -cristobalite (opal-CT) with calcium silicate of truscottite Ca₄Si₂O₁₈(OH)₈·2H₂O and talc (magnesium silicate, Mg₃Si₄O₁₀(OH)₂).

Apparently the double salts effects of the mixed additions are observed, and the stage of transformation from amorphous silica gel and the formation of chert were discussed.

Introduction

In nature, chert of siliceous sediments occurs, and its origin is thought to be deposited from radiolarian ooze. Then since 1977, Mitusio (1977-1996) has been studying the transformation of amorphous silica gels into α -cristobalite (opal-CT) and α -quartz through broad peak (opal-A) with his colleagues. And he used such cations as follows: H⁺, NH₄⁺, K⁺, Na⁺, Ca²⁺, Mg²⁺, Co²⁺, Mn²⁺, Fe³⁺ and Al³⁺, as well as artificial sea water and some organic matters of glycine, urea and ethylene-diamine.

Then the starting materials of silica gels changed into α -cristobalite (opal-CT) and/or α -quartz through broad peak (opal-A) by many cations, as well as artificial sea water and some organic matters of glycine, urea and ethylene-diamine..

So this time, the writers experimented with the mixtures of Ca(OH)₂ and Mg(OH)₂ additions by different concentrations and hours at the same temperature of 300°C and on some case at 350°C for single additions. And they clarified the mixed additions were better than the single ones, and discussed the formation of chert according as the Mitusio's results for nearly 30 years.

Method

2-1 Materials

The silica gels of fine-grained amorphous type of Wako gel 300 produced by Wako Chemical CO. LTD were used (Photo-1A). And Ca(OH)₂ and Mg(OH)₂ were the special class reagents of the Nakarai Chemical CO. LTD, and CaO and MgO were the first class reagents of also the Wako Chemical CO. LTD.

2-2 Procedure

The starting material of 0.400g of silica gels mixed with distilled water 1.3ml each concentration of oxides and hydroxides as 0.100g and 0.010g were placed in a special devised micro-autoclave (9.7ml) which was lined with Hasteloy-C. Then it was put in an electric furnace reserved as the desired temperature of 250°C, 300°C and 350°C. And after each hour passed, it was taken out from the furnace, and it was cooled down to the room temperature by an electric fan. And the micro-autoclave was opened and the contents were washed out by distilled water. Then by filtration it was separated into the solid phase and the liquid one diluted by 100ml. Then the solid part was analyzed by X-ray diffractometry (XRD), optical microscope (OM) and scan-

*Reported in the Geological Society of Japan, Kansai and Nishi-nihon Branches Joint Meeting in Kagawa University (1993)

ning electron microscope(SEM).

XRD condition is as follows: 30KV 40mA Cu K α scannig speed=4° /min. slit= DS,0.1 RS,0.3 SS,0.1.

As for the liquid phase, the cations of Si, Ca and Mg were measured by ICP-AES Seiko spectronics 8000. Then the real concentration is to be multiplied by 30 times.

Results

Here the results are reported as follows.

3-1 Effect of the hydroxides mixture of Ca(OH)₂ and

Mg(OH)₂

When these two additions of Ca(OH)₂ and Mg(OH)₂ were mixed together with amorphous silica gel, the results are shown in Table 1.

Thus the results obtained by the additions of Ca(OH)₂ and Mg(OH)₂, and the mixture of them are described below.

3-1-1. Addition of 0.100g (Fig.1-Fig.3)

When the weight of Ca(OH)₂ and Mg(OH)₂ was 0.100g respectively, the results are shown as follows in Table 1.

Tab.1 Results of hydrothermal experiments for amorphous silica gel 0.400g reacted for 24-240 hours at 250°C-350°C with the additions of Ca(OH)₂ and Mg(OH)₂.

No	Add'n (g)	Temp (°C)	Time (h)	Products	Si (ppm)	Ca (ppm)	Mg (ppm)
CM 1	0.100	350	24	Ts(r)	10.5	7.6	0.17
CM 2	"	"	72	T(r) Ts(r)	9.9	5.3	0.11
CM 3	"	"	240	T(r) Ts(c) C(r)	2.7	4.8	0.05
CM 4	0.100	300	24	Ts(r)	9.4	9.3	0.15
CM 5	"	"	72	T(r) Ts(r)	8.7	6.7	0.14
CM 6	"	"	240	T(r) Ts(c) C(r)	8.2	7.1	0.20
CM 7	0.100	250	24	Ts(r)	4.7	5.2	0.14
CM 8	"	"	72	Ts(r)	10.5	9.2	0.19
CM 9	"	"	240	T(r) Ts(r)	10.2	7.9	0.19
CM10	0.010	350	24	bp	5.5	1.4	0.06
CM11	"	"	72	C(c)	2.2	1.7	0.07
CM12	"	"	240	C(a)	4.8	2.1	0.05
CM13	0.010	300	24	bp	7.7	3.5	0.13
CM14	"	"	72	bp	5.5	2.8	0.12
CM15	"	"	240	C(c)	6.4	4.9	0.14
CM16	0.010	250c	24	bp	9.2	0.3	0.05
CM17	"	"	72	bp	6.8	3.2	0.08
CM18	"	"	240	bp	10.1	3.7	0.09

bp:broad peak C: α -cristobalite(opal-CT) T:talC Ts:truscottite (a):abundant (c):common (r):rare Hereafter the real cocentration is x30.

3-1-1-1. Reactions at 250°C (Fig.1)

At 250°C, the results are shown in Fig.1. As is clear, X-ray powder pattern of the starting material with silica gel 0.400g and the mixture of hydroxides of Ca(OH)₂ and Mg(OH)₂ 0.100g respectively, shows the sharp peaks of Ca(OH) and Mg(OH)₂, and that of broad one respectively at 0 hour which is the starting time.

And for 24 hours, the starting material showed the small peaks of truscottite(calcium silicate, Ca₁₄Si₂₄O₁₈(OH)₈·2H₂O).

And as 72 hours have passed, these peaks grew up a little more than those for 24 hours.

Finally, the peaks of talc(magnesium silicate, Mg₃Si₄O₁₀(OH)₂) were added to the peaks of truscottite.

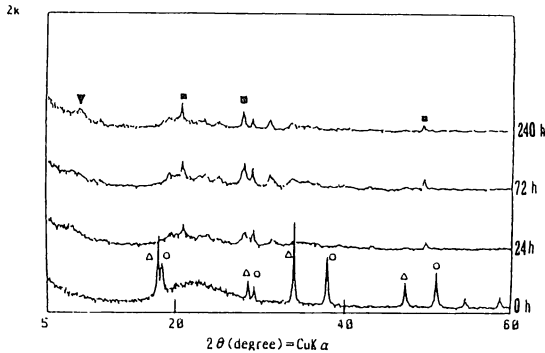


Fig.1 X-ray diffraction patterns of reacted products at 250°C for 24-240 hours. Silica gel=0.400g Ca (OH)₂=0.100g Mg(OH)₂=0.100g

▼:talc ■:truscottite △:Ca(OH)₂ ○:Mg(OH)₂

3-1-1-2. Reactions at 300°C (Fig.2)

As the reaction temperature became more high as at 300°C(Fig.2), and treated for 24 hours, the starting material showed the small peaks of truscottite(calcium silicate).

And the peaks became more higher for 72 hours.

Finally, the silica gel changed into α-cristobalite (opal-CT). And moreover, the peaks of talc(magnesium silicate, Mg₃Si₄O₁₀(OH)₂) were also produced.

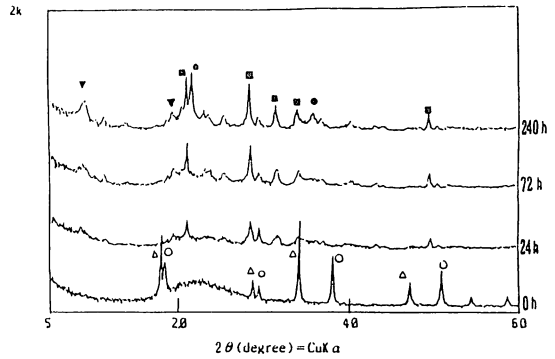


Fig.2 X-ray diffraction patterns of reacted products at 300°C for 24-240 hours. Silica gel=0.400g Ca(OH)₂=0.100g Mg(OH)₂=0.100g

▼:talc ■:truscottite ●: α-cristobalite(opal-CT)
△:Ca(OH)₂ ○:Mg(OH)₂

3-1-1-3. Reactions at 350°C (Fig.3)

As the reaction temperature became highest as 350°C (Fig.3), and treated for 24 hours, the small peaks of truscottite(calcium silicate) were observed.

And for 72 hours, the peaks became more higher, and this time the small peaks of talc were also found.

Finally for 240 hours, the silica gel also changed into α-cristobalite(opal-CT). And moreover, the peaks of both truscottite(Photo-1E) and talc were produced.

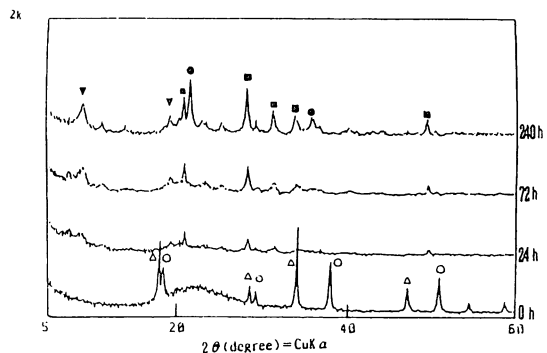


Fig.3 X-ray diffraction patterns of reacted products at 350°C for 24-240 hours. Silica gel=0.400g Ca(OH)₂=0.100g Mg(OH)₂=0.100g

▼:talc ■:truscottite ●: α-cristobalite(opal-CT)
△:Ca(OH)₂ ○:Mg(OH)₂

3-1-2. Addition of 0.010g (Fig.4-Fig.6)

When the weight of the addition of $\text{Ca}(\text{OH})_2$ and $\text{Mg}(\text{OH})_2$ was 0.010g respectively, the results are shown in Table 2.

3-1-2-1. Reactions at 250°C (Fig.4)

On this case that the addition of $\text{Ca}(\text{OH})_2$ and $\text{Mg}(\text{OH})_2$ 0.100g respectively became less at 250 °C, the starting material showed only a broad peak of silica gel as $2\theta = 22^\circ \text{ CuK}\alpha$, without the peaks of $\text{Ca}(\text{OH})_2$ and $\text{Mg}(\text{OH})_2$. And when 24 hours have passed, this starting material was changed and showed a broad peak of $2\theta = 22^\circ \text{ CuK}\alpha$, which was depicted as "bp" in the text figures, that was something like opal-A, however this is not a solid material, so that Mitusio always named this as "broad peak" which is the pre-existing mineral of silica mineral(Photo-1B). As described below, this is called as broad peak(opal-A).

Then this broad peak(opal-A) grew up for 72 hours, and after 240 hours have passed, this peak became a little more sharper, that was clearly the pre-existing mineral of silica mineral of α -cristobalite(opal-CT).

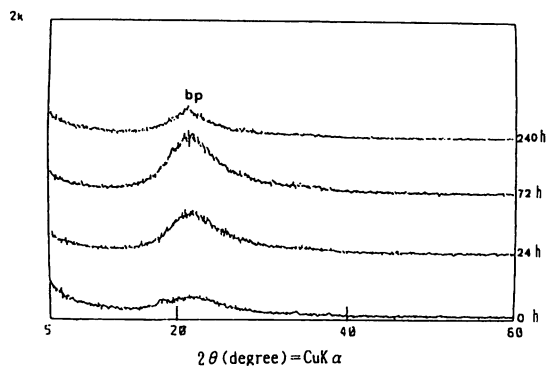


Fig.4 X-ray diffraction patterns of reacted products at 250°C for 24-240 hours. Silica gel=0.400g $\text{Ca}(\text{OH})_2=0.010\text{g}$ $\text{Mg}(\text{OH})_2=0.010\text{g}$
bp:broad peak(opal-A)

3-1-2-2. Reactions at 300°C (Fig.5)

Then at 300 °C and treated for more than 24 hours, the starting material of silica gel showed the broad peak(opal-A). And elapsing time of 72 hours, the peak of this material grew up a little more than that for 24 hours (Fig.5).

Finally after 240 hours, the peaks of this material grew up clearly and showed α -cristobalite(opal-CT).

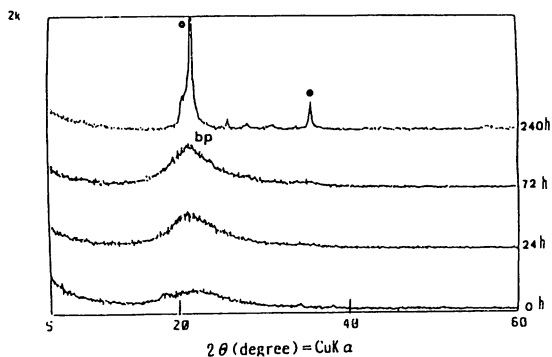


Fig.5 X-ray diffraction patterns of reacted products at 300°C for 24-240 hours. Silica gel=0.400g $\text{Ca}(\text{OH})_2=0.010\text{g}$ $\text{Mg}(\text{OH})_2=0.010\text{g}$

bp:broad peak ●: α -cristobalite(opal-CT)

3-1-2-3. Reactions at 350°C (Fig.6)

Then the reaction temperature became highest as at 350 °C, the broad peak(opal-A) showed a little peak. However on this case after 72 hours, the sharp peaks of α -cristobalite(opal-CT) occurred already as was shown in Photo-1C, although the other cases less than 300°C needed for 240 hours.

After 240 hours the peaks of α -cristobalite(opal-CT) showed more clear, and the second peak became more sharper, that means the transformation and crystallization of amorphus silica gel have occurred and that it changed into silica mineral of α -cristobalite(opal-CT)(Photo-1D).

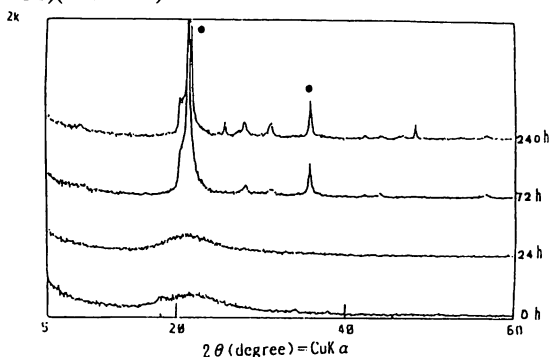


Fig.6 X-ray diffraction patterns of reacted products at 350°C for 24-240 hours. Silica gel=0.400g $\text{Ca}(\text{OH})_2=0.010\text{g}$ $\text{Mg}(\text{OH})_2=0.010\text{g}$

bp:broad peak(opal-K) ●: α -cristobalite(opal-CT)

3-2 Effect of the oxides mixture of CaO and MgO

When these two additions of CaO and MgO were mixed together with amorphous silica gel, the results are shown in Table 2.

Thus the results obtained by the additions of CaO and MgO, and the mixture of them are described below.

3-2-1. Addition of 0.100g (Fig.7-Fig.9)

When the weight of CaO and MgO was 0.100g respectively, the results are shown as follows in Table 2.

3-2-1-1. Reactions at 250°C (Fig.7)

At 250°C, the results are shown in Fig.7. As is clear,

X-ray powder pattern of the starting material with silica gel 0.400g and the mixture of CaO and MgO were mixed together, the results are shown in Table 2.

The original starting material of silica gel with the mixture of CaO and MgO, which shows some peaks at 0 hour of starting time, is shown in Fig.7.

Then after 24 hours the peaks of the starting material already disappeared, and both two peaks of truscottite and talc occurred for only 24 hours. And for 72 hours the peaks of two products showed not so much change as those for 24 hours.

After 240 hours the peaks of two products of truscottite and talc showed clearly, however talc is not so clear.

Tab.2 Results of hydrothermal experiments for amorphous silica gel 0.400g reacted for 24-240 hours at 250°C-350°C with the additions of CaO and MgO.

No	Add'n (g)	Temp (°C)	Time (h)	Products	Si (ppm)	Ca (ppm)	Mg (ppm)
CM19	0.100	350	24	Ts(r)	12.0	10.6	0.20
CM20	"	"	72	T(r) Ts(r)	8.4	8.7	0.15
CM21	"	"	240	T(r) Ts(c) C(r)	7.4	3.4	0.07
CM22	0.100	300	24	Ts(r)	15.3	9.4	0.28
CM23	"	"	72	T(r) Ts(c)	15.8	3.3	0.36
CM24	"	"	240	T(r) Ts(c)	8.4	0.3	0.33
CM25	0.100	250	24	Ts(r)	10.1	7.3	0.26
CM26	"	"	72	T(r) Ts(r)	14.1	6.0	0.07
CM27	"	"	240	T(r) Ts(c)	9.2	6.0	0.07
CM28	0.010	350	24	bp	6.7	2.3	0.08
CM29	"	"	72	C(c)	7.7	3.2	0.17
CM30	"	"	240	C(a)	8.9	8.3	0.06
CM31	0.010	300	24	bp	9.4	0.6	0.12
CM32	"	"	72	C(c)	10.4	1.0	0.27
CM33	"	"	240	C(a)	11.6	2.0	0.09
CM34	0.010	250c	24	bp	5.8	1.8	0.15
CM35	"	"	72	bp	9.1	3.7	0.18
CM36	"	"	240	C(c)	2.5	1.4	0.41

bp:broad peak C: α -cristobalite(opal-CT) T:talc Ts:truscottite (a):abundant (c):common (r):rare

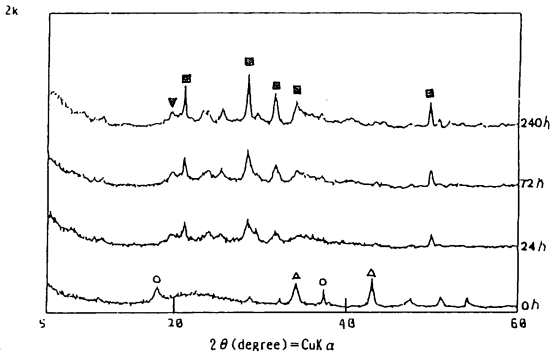


Fig.7 X-ray diffraction patterns of reacted products at 250°C for 24-240 hours. silica gel=0.400g CaO=0.100g MgO=0.100g
 ▼:talc ■:truscottite △:CaO ○:MgO

3-2-1-2. Reactions at 300°C (Fig.8)

Fig.8 shows the results when the reaction temperature was at 300°C.

After 24 hours the peaks of truscottite and talc also occurred for only 24 hours as the same case as that at 250°C.

Then after 72 hours, the peaks of two products became a little sharper, and finally the peaks of talc also became clear, while those of truscottite occurred at most.

As the reaction hours became longer, the products became more.

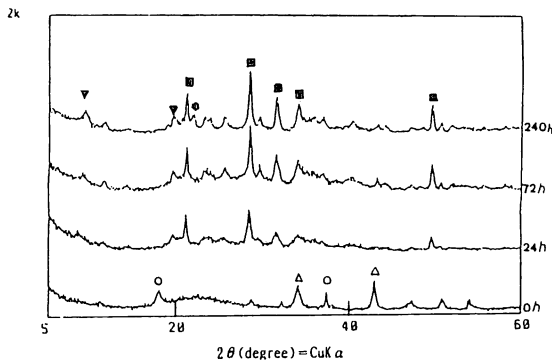


Fig.8 X-ray diffraction patterns of reacted products at 300°C for 24-240 hours. Silica gel=0.400g CaO=0.100g MgO=0.100g
 ▼:talc ■:truscottite ●: α-cristobalite(opal-CT)
 △:CaO ○:MgO

3-2-1-3. Reactions at 350°C (Fig.9)

Finally, the results hydrothermally treated at 350°C are shown in Fig.9.

Then only after 24 hours treatment, the peaks of truscottite occurred clearly, and those of talc were not so clear as those at truscottite.

And after 72 hours the peaks of both products of truscottite and talc became clear.

Then after 240 hours, the small peak of α-cristobalite(opal-CT) could be observed, while both products also became clear and the photograph was shown in Photo-1F.

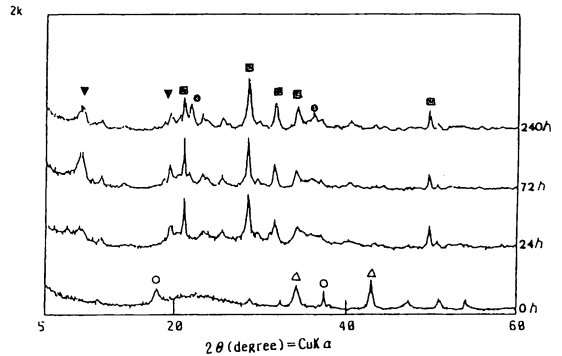


Fig.9 X-ray diffraction patterns of reacted products at 350°C for 24-240 hours. Silica gel=0.4g CaO=0.100g MgO=0.100g
 ▼:talc ■:truscottite ●: α-cristobalite(opal-CT)
 △:CaO ○:MgO

3-2-2. Addition of 0.010g (Fig.10-Fig.12)

When the additions weight of CaO and MgO were 0.010g, respectively, the results of X-ray diffractory powder patterns are shown as follows in Table 2 and Fig.10-Fig.12.

3-2-2-1. Reactions at 250°C (Fig.10)

At 250°C, the results are shown in Fig.10. As it is clear, the peak of "broad peak(opal-CT), bp" was found for 24 hours.

And after 72 hours also the peak was nearly the same as that of 24 hours.

However the peak of α-cristobalite(opal-CT) grew up well for 240 hours.

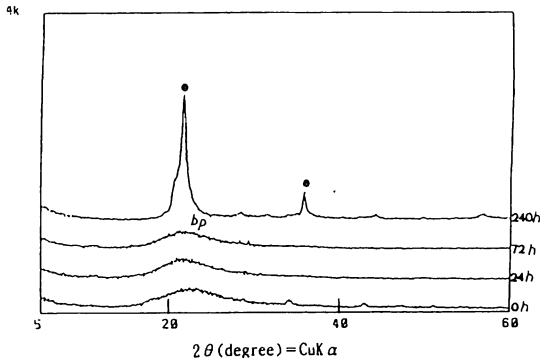


Fig.10 X-ray diffraction patterns of reacted products at 250°C for 24-240 hours. Silica gel=0.400g CaO=0.010g MgO=0.010g bp:broad peak ●: α-cristobalite(opal-CT)

3-2-2-2. Reactions at 300°C (Fig.11)

The results at 300°C are shown in Fig.11. As it is clear, the peak of "broad peak(opal-CT), bp" was observed for 24 hours.

And after 72 hours the clear but small peaks of α-cristobalite (opal-CT) grew up, and it is more sharper than that of 24 hours.

And finally for 240 hours, the peaks of α-cristobalite(opal-CT) grew up abundantly.

Then on this case at 300°C, α-cristobalite(opal-CT) was crystallized at first for 72 hours.

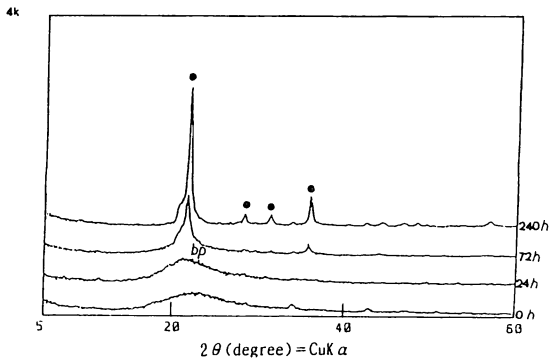


Fig.11 X-ray diffraction patterns of reacted products at 300°C for 24-240 hours. Silica gel=0.400g CaO=0.010g MgO=0.010g bp:broad peak ●: α-cristobalite(opal-CT)

3-2-2-3. Reactions at 350°C (Fig.12)

The results experimented at 350°C are shown in Fig.12. As it is clear, the peak of "broad peak(opal-CT), bp" was found for 24 hours(Photo-1B).

And after 72 hours the peaks grew up as nearly the same as that of 240 hours at 300°C.

Then after 240 hours the peaks of α-cristobalite(opal-CT) grew up best of all these experiments.

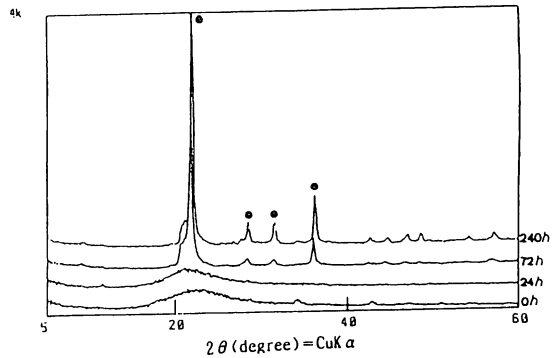


Fig.12 X-ray diffraction patterns of reacted products at 350°C for 24-240 hours. Silica gel=0.400g CaO=0.010g MgO=0.010g bp:broad peak ●: α-cristobalite(opal-CT)

3-3. Variations of cations in the liquid phase (Fig.13-Fig.16)

Next the variations of cations such as Si, Ca and Mg included in the liquid phase were measured as x1/30 dilution. These were shown in Tab.1 and Tab.2, and all the results are shown generally in Tab.3. Also the results were depicted in Fig.13 to Fig.16, and the real concentration is to be multiplied by 30 times.

3-3-1. Effect of hydroxides of Ca(OH)₂ and Mg(OH)₂

The concentration of the cations of Si, Ca and Mg was as follows:

3-3-1-1. Addition of 0.100g (Fig.13)

The results in the liquid phase of these conditions are described as below:

Tab.3 Concentration variation of Si, Ca and Mg in the liquid phase after each reaction hours (ppm).

A: 0.100g of Ca(OH)₂ and Mg(OH)₂

		24	72	240
Si	250° C	4.7	10.5	10.2
	300° C	9.4	8.7	8.2
	350° C	10.5	9.9	2.7
Ca	250° C	5.2	9.2	7.9
	300° C	9.3	6.7	7.1
	350° C	7.6	5.3	4.8
Mg	250° C	0.14	0.19	0.19
	300° C	0.15	0.14	0.20
	350° C	0.17	0.11	0.05

B: 0.010g of Ca(OH)₂ and Mg(OH)₂

		24	72	240
Si	250° C	9.2	6.8	10.1
	300° C	7.7	5.5	6.4
	350° C	5.5	2.2	4.8
Ca	250° C	0.3	3.2	3.7
	300° C	3.5	2.8	4.9
	350° C	1.4	1.7	2.1
Mg	250° C	0.05	0.08	0.09
	300° C	0.13	0.12	0.14
	350° C	0.06	0.07	0.05

C: 0.100g of CaO and MgO

		24	72	240
Si	250° C	10.1	14.1	9.2
	300° C	15.3	15.8	8.4
	350° C	12.0	8.4	7.4
Ca	250° C	7.3	6.0	6.0
	300° C	9.4	3.3	0.3
	350° C	10.6	8.7	3.4
Mg	250° C	0.26	0.29	0.16
	300° C	0.28	0.36	0.33
	350° C	0.20	0.15	0.07

D: 0.010g of CaO and MgO

		24	72	240
Si	250° C	5.8	9.1	2.5
	300° C	9.0	10.4	11.6
	350° C	6.7	7.7	8.9
Ca	250° C	1.8	3.7	1.4
	300° C	0.6	1.0	2.0
	350° C	2.3	3.2	8.3
Mg	250° C	0.15	0.18	0.41
	300° C	0.12	0.27	0.09
	350° C	0.08	0.17	0.06

The real concentration is x30.

3-3-1-1-1. Concentration of Si (Fig.13 upper)

The concentration of Si is shown in Fig.13, and the maximum of it is less than about 11ppm.

At 250°C, however it increased suddenly since 72 hours after 24 hours, and it became nearly saturated for 240 hours.

At 300°C, the curve became nearly straight down to about 8ppm as the elapsing time.

However at 350°C, the Si concentration decreased down to about 3ppm from 24 hours as the elapsing time.

it became nearly saturated for 240 hours like the Si concentration.

However at 300°C, the Ca concentration was the maximum for 24 hours, and it decreased as the reaction time elapsed with nearly saturated condition since 72 hours increasing a little for 240 hours.

And at 350°C the curve decreased down to about 3ppm nearly linearly.

3-3-1-1-3. Concentration of Mg (Fig.13 lower)

The results of the Mg concentration measured at each temperature are shown in Fig.13. As it is clear, the maximum concentration is very low below 0.2ppm.

When at 250°C it increased at 72 hours, and after then it became nearly saturated.

And at 300°C it increased a little as elapsing of time.

At 350°C the curve fell down nearly straight as the time elapsing as much as Ca .

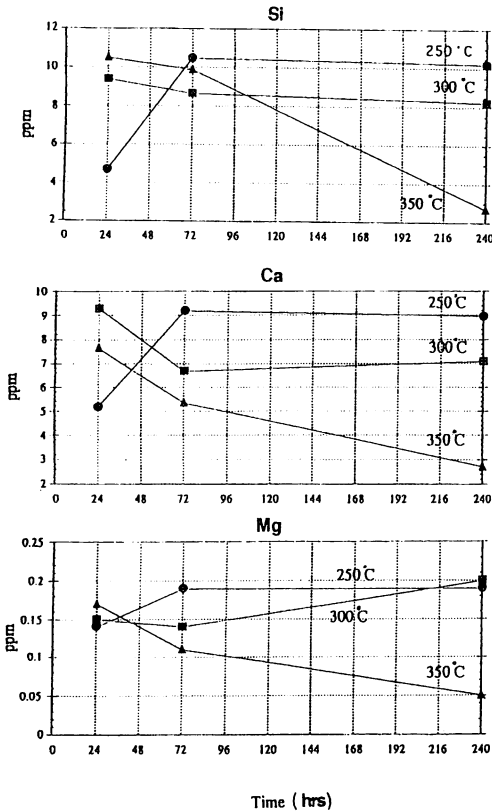


Fig.13 Concentration of Si, Ca and Mg in the liquid phase after reaction for 24-144 hours.

Silica gel=0.400g Ca(OH)₂=0.100g Mg(OH)₂=0.100g
 ●:250°C ■:300°C ▲:350°C

Hereafter the real concentration is X30.

3-3-1-1-2. Concentration of Ca (Fig.13 middle)

The Ca concentration is shown in Fig.13, and the maximum of it is less than about 10ppm.

And at 250°C, it increased suddenly for 72 hours, and

3-3-1-2. Addition of 0.010g (Fig.14)

On the case when the addition of Ca(OH)₂ and Mg(OH)₂ was 0.010g respectively, the results are shown in Fig.14. Under this condition, the additions were less, and the solved cations of Ca and Mg were less than those of the additions 0.100g.

3-3-1-2-1. Concentration of Si (Fig.14 upper)

The Si concentration is also less than 10ppm, that is shown in Fig.14.

As it is clear in Fig.14, all the concentration of Si have the same tendency that the curves were nearly the same and parallel with the concave apex at 72 hours, and that the Si concentration was higher as the temperature became lower.

3-3-1-2-2. Concentration of Ca (Fig.14 middle)

The Ca concentration is also less than 5ppm, that is shown in Fig.14.

As it is clear in Fig.14, the concentration of Ca increased as the reaction hour passed at 250°C. And at 300°C it was nearly the same tendency of the curves of Si contents at 250°C.

And at 350°C, the value of Ca increased a little with the temperature increasing, however it lied between about 1.5 ppm and 2.0ppm.

3-3-1-2-3. Concentration of Mg (Fig.14 lower)

The Mg concentration is also very low and the maxi-

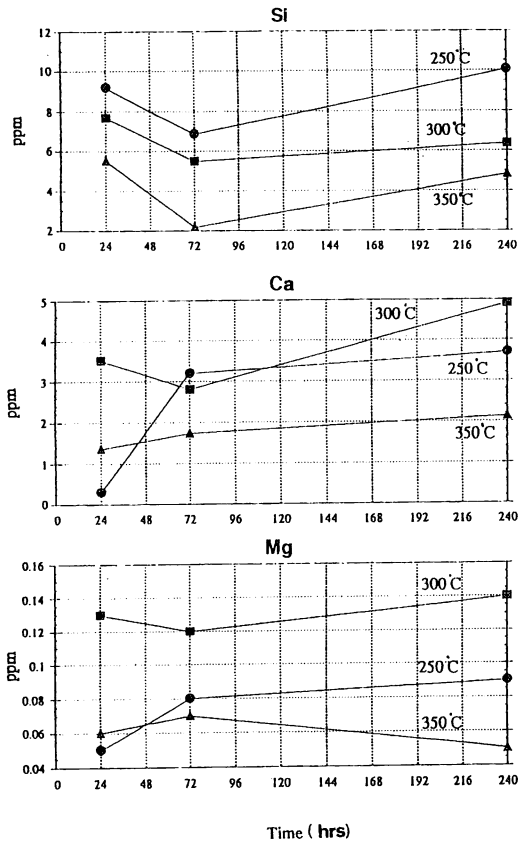


Fig.14 Concentration of Si, Ca and Mg in the liquid phase after reaction for 24-240 hours.

Slica gel=0.400g Ca(OH)₂=0.010g Mg(OH)₂=0.010g
 ●:250°C ■:300°C ▲:350°C

imum is below 0.2ppm.

At 250°C it increased a little as the reaction time elapsed. However the curve at 300°C was highest and it was between 0.14ppm and 0.12ppm, and it seems like a bow-shape that the minimum point was at for 72 hours.

And that at 350°C was nearly between 0.07ppm and 0.05ppm, and it also seemed like an inverted bow-shape that the maximum point was at for 72 hours.

3-3-2. Effect of oxides of CaO and MgO

On this case, the oxides of CaO and MgO were added, and then the results were treated as below.

3-3-2-1. Addition of 0.100g (Fig.15)

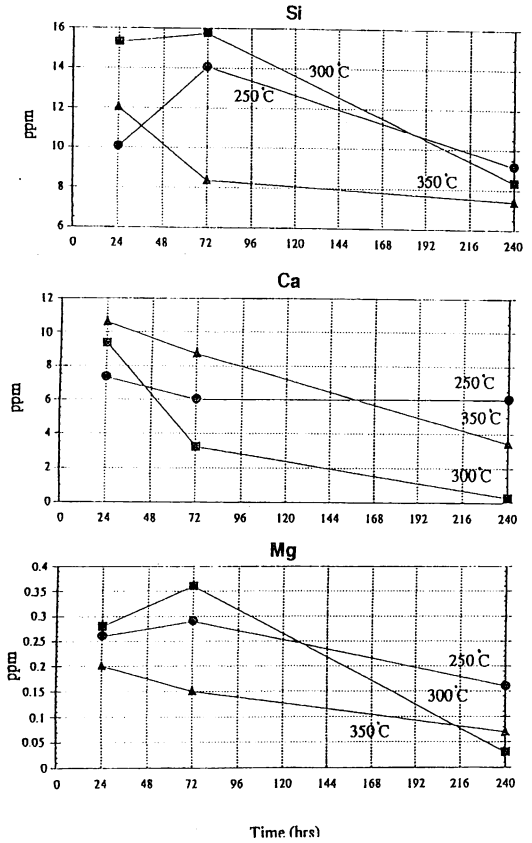


Fig.15 Concentration of Si, Ca and Mg in the liquid phase after reaction for 24-240 hours.

Slica gel=0.400g CaO=0.100g MgO=0.100g
 ●:250°C ■:300°C ▲:350°C

When the additions are 0.100g of both CaO and MgO, the results are shown in Fig.15.

3-3-2-1-1. Concentration of Si (Fig.15 upper)

The Si concentration on this case was as in Fig.15. As it is clear in the Figure, the concentration of Si was below 16ppm which was a little more than those of the hydroxides additions.

At 250°C the value changed something like a bow-shaped with concave apex at 72 hours, that is the maximum value 14ppm. And at 300°C the values both at 24 hours and 72 hours were nearly same, while the Si concentration decreased down to about 8.2ppm. However at 350°C the value decreased as the reaction time

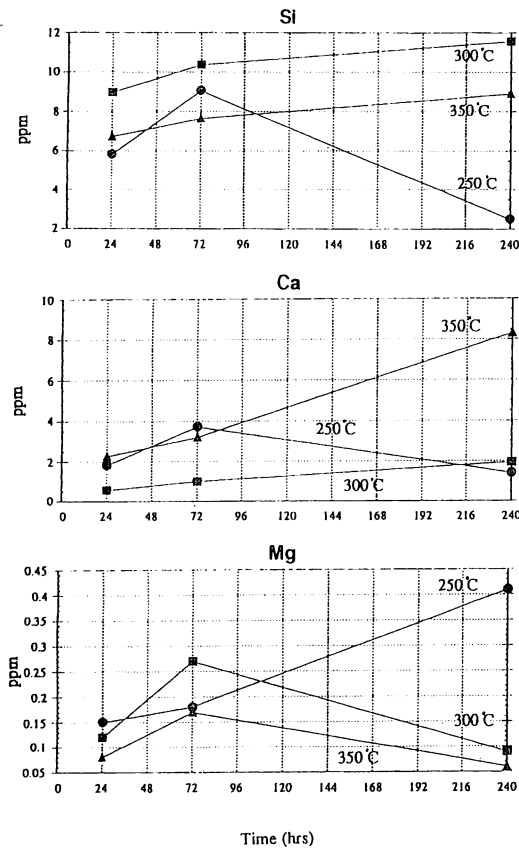


Fig.16 Concentration of Si, Ca and Mg in the liquid phase after reaction for 24-144 hours.

Silica gel=0.400g CaO=0.010g MgO=0.010g
 ●:250°C ■:300°C ▲:350°C

elapsed.

3-3-2-1-2. Concentration of Ca (Fig.15 middle)

As for the Ca concentration, all the values decreased as the time of experiments passed, and the maximum one was about 10.5ppm with minimum one about 0.3ppm, as is shown in Fig.15.

At 250°C the value changed not so much between 7.3ppm and 6.0ppm. However at 300°C the Ca concentration decreased down for 72 hours, and for 240 hours the value became the minimum of 0.3ppm. And the values decreased down linearly in proportion to the time elapsed at 350°C.

3-3-2-1-3. Concentration of Mg (Fig.15 lower)

The Mg concentration is as in Fig.15. As it is clear in the Figure, all the concentration of Mg is very low and below 0.36ppm.

At 250°C the value changed something like a little bow-shaped with concave apex at the maximum value 0.29ppm for 72 hours.

However the concentration curve at 300°C was also something like a bow-shaped with concave apex with the maximum value 0.36ppm at 72 hours also.

And the values at 350°C decreased down almost linearly in proportion to the time elapsed.

3-3-2-2. Addition of 0.010g (Fig.16)

On the case of the addition of CaO and MgO is 0.010g, respectively, the results of the concentration curves are shown in Fig.16.

3-3-2-2-1. Concentration of Si (Fig.16 upper)

Fig.16 shows the results of Si concentration. On this case the concentration of Si lies between 11.6ppm and 2.5ppm.

At 250°C, the concentration curve became a bow-shaped form with the concave apex at 72hours of the maximum value 9.1ppm. And the curves of both at 300°C and 350°C, the former was more higher value than the latter, were pararell and increased with the elapsing times.

3-3-2-2-2. Concentration of Ca (Fig.16 middle)

Fig.16 shows the results of the concentration of Ca, which lies between 8.3ppm and 0.6ppm.

On this case at 250°C, the curve is also a little concaved bow-shaped form with the apex for 72 hours of the maximum value 3.7ppm.

However at both 300°C and 350°C, the values became nearly linear with increasing concentration in proportion to the time elapsing. The concentration at 350°C is always higher than those at 300°C.

3-3-2-2-3. Concentration of Mg (Fig.16 lower)

The Mg concentration is very low and the maximum is below 0.41ppm.

At 250°C it increased as the reaction time elapsed. However the curves both at 300°C and 350°C were nearly pararell and like a bow-shape that the maximum point at for 72 hours, and the concentration at 300°C

was always higher than those at 350°C.

To sum up, the changes in the liquid phases are summarized as follows comparing the data obtained by the writers: When crystallization of broad peak(opal-A) and α -cristobalite(opal-CT) occurred, the concentrations of Si, Ca and Mg decreased.

Discussion

First to compare the data for 72 hours obtained above with those by the writers and their colleagues, they will discuss the effects of single additions of various kinds of cations, and next the effects of additions of double cations will be discussed except the changes in the liquid phases because of some limitations.

4-1. Effects of single salts

The effects of single additions will be discussed here mainly focusing on the salts of Ca and Mg.

4-1-1. Ca salts

When the additon was Ca salts, the results are as follows:First, Mitusio(1986,1988,1989,1991,1996) mentioned the changes of silica gel using calcium compounds of Ca(OH)_2 , CaCl_2 , CaCO_3 and CaO under various hydrothermal conditions.

As for Ca(OH)_2 , Mitusio(1991) and Mitusio and Hirano(1991), and Hirano and Mitusio(1991) clarified that it made amorphous silica gel by Mallinocrodt CO. LTD change into only broad peak(opal-A) even at 300°C and 350°C for 72 hours, but into α -cristobalite(opal-CT) for 120 hours, if the addition was 0.010g, because of the stability of this gel. If the addition was 0.100g, truscottite occurred at 300 °C and 350°C only for 24 hours.

As for CaO , silica gel changed into α -cristobalite (opal-CT) at 350 °C for 72 hours(Mitusio and Watanabe, 1996).

Then at 350 °C by 4- Mole CaCl_2 , that was the equivalent concentration with sea water at a room temperature and pressure by NaCl , silica gel changed into broad peak(opal-A) for 24 hours, and α -cristobalite (opal-CT) and silica-K for more than 120 hours (Mitusio, 1989). And at 350°C by 1.75- Mole CaCl_2 , that was the equivalent concentration with sea water at an elevated temperature and high pressure by NaCl , it changed into also α -cristobalite(opal-CT) for more than 288 hours.

Moreover, Mitusio(1986, 1988) made clear that limestone CaCO_3 also had effects to make silica gel change into broad peak(opal-CT) and α -cristobalite (opal-CT) for more than 144 hours at 300°C and 350 °C. This means that silica gel and CaCO_3 make mutual crystallization each other, and that therefore chert and limestone have close relationship in some outcrops in nature.

When the additions were much, calcium silicates of truscottite $\text{Ca}_7(\text{Si}_4\text{O}_{10})(\text{Si}_8\text{O}_{19})(\text{OH})_4 \cdot \text{H}_2\text{O}$ and xonotlite $\text{Ca}_6(\text{Si}_6\text{O}_{17})(\text{OH})_2$ were occurred. However when the additions were few, then silica gel was changed into broad peak(opal-A) and α -cristobalite (opal-CT).

Next, Hirano and Mitusio(1992) showed more details on the formation of calcium silicates such as truscottite and xonotlite, using more amounts of Ca(OH)_2 . When Ca(OH)_2 was less than 0.100g, only truscottite occurred for 24 hours, and for 72h it was changed into xonotlite without broad peak(opal-A). Finally, α -cristobalite (opal-CT) occurred a little for 144 hours. However, Ca(OH)_2 was more than 0.150g for 24 hours only truscottite and for 72 hours it was changed into xonotlite, and α -cristobalite(opal-CT) occurred commonly. Finally for 144h, α -cristobalite(opal-CT) occurred abundantly, and xonotlite was not so much changed.

4-1-2. Mg salts

Then when the additon was Mg salts of Mg(OH)_2 , MgO and MgCl_2 , the results were reported by Mitusio(1991). Later on, the results of MgO and Mg(OH)_2 with the mixture of them were discussed by Mitusio and Watanabe(1996).

The brief results are shown as follows : If MgO and Mg(OH)_2 were less, silica gel changed only into broad peak(opal-CT) on the case of less addition of 0.010g, however if the additions were the least of 0.001g, then α -quartz occurred both at 300°C and 350°C for 192 hours. And as for MgCl_2 both with 4-Mole and 1.75-Mole, only broad peak(opal-CT) was observed at 250°C-350°C for 48-240 hours.

4-1-3. Other single cations

Since 1977, Mitusio(1977--1996) has been reporting the process of crystallization of amorphous silica gels and the catalytic ability of single additions of various metals compounds, as well as NH_4^+ and artificial sea water. These make amorphous silica gels change into

mainly some crystallized silica minerals such as broad peak(opal-A), α -cristobalite(opal-CT) and α -quartz, and silica-K on some case. As the main reaction making silica gels crystallization needs (OH)⁻ ion, cations are necessary to add as catalyzers which act as next three:

- 1)Hydrolysis, solubility to solutions,
- 2)Dehydration and polymerization, in order to make up huge structures of some crystals, and
- 3)Nomal salt effects.

And metal oxides are better catalyzer than hydroxides and single metals. And as for 1) and 2), the mono-valent cations are the best catalyzer, and the next is bi-valent ones, and the last is tri-valent ones except Fe³⁺.

The mono-valent cations such as K and Na are excellent to transform silica gels into α -quartz(Mitusio *et al.*,1981;1984), however NaCl is into α -cristobalite (opal-CT) for nomal salt effect(Mitusio *et al.*, 1981). And also NH₄⁺(Mitusio and Umehara,1991) can change silica gels into α -cristobalite(opal-CT). H₂O needs much more times(Mitusio *et al.*,1978).

Next, bi-valent cations such as Ca, Fe(Mitusio *et al.*,1979;1980) and Co(Mitusio and Mori,1987) also change silica gels into α -cristobalite(opal-CT). Mg also change into α -cristobalite(opal-CT) and into α -quartz for longer time(Mitusio,1992). However, Mn compounds inhibited the transformation of silica gels (Mitusio,1984).

Tri-valent cation of Al₂O₃ can change silica gels into only broad peak(opal-A), however Al(OH)₃ was into α -cristobalite(opal-CT) at the high temperature of 350°C.

To sum up, the order of making amorphous silica gels transformation by metal ions is: K>Na>Ca>Mg>Fe>Co>NH₄⁺>Al>H>Mn.

As for 3), this depends upon the alkalinity of solutins when metals ions are dissolved. Then the order of reaction for better catalyzer is: KCl>NaCl>CaCl₂>MgCl₂>AlCl₃>Fe(SO₄)₂>>MnCl₂.

4-1-4. Artificial sea water.

Next, on the special cases to use artificial sea water, amorphous silica gels made β -hydrogen silicate H₂Si₂O₅ and anhydrite CaSO₄(Mitusio and Kanamori, 1985), and the former is thought to be changed into α -cristobalite(opal-CT) for a long period. This suggests that the many cations in natural sea water accelerate

such amorphous silica as the ooze of diatom and radiolaria change into α -cristobalite(opal-CT)/and α -quartz.

4-1-5. Organic matters

In addition to these cations, organic matters such as ethylene-diamine, urea and glycine that are also good catalyzers to make dolomite(Mitusio *et al.*, 1982; Nisahizawa *et al.*,1987), can transform amorphous silica gels into α -cristobalite (opal-CT)(Mitusio, 1991). This means that radiolaria made up of amorphous silica contains some amounts of orgnic matters such as glycine and other amnio-acids as life-substances, and that orgnic matters played important roles to the transformation of α -cristobalite (opal-CT) and α -quartz for long periods of geologic times.

4-2. Effects of double salts

Next, the effects of double salts should be discussed.

4-2-1. Effects of Ca(OH)₂ and Al₂O₃

Mitusio and Hirano(1993) clarified that on the case of the mixture of both Ca(OH)₂ and Al₂O₃ added, they accelerated silica gel transformation of even to α -quartz at 300°C for 72 hours. Apparantly, the mixture of Ca and Al is a better catalyzer that can more accelerate to produce α -quartz(Mitusio and Hirano, 1993), although the single addition could change only into broad peak(opal-A) under the same condition.

4-2-2. Effects of Ca and Mg

This is now the writers are reporting, and the results are already shown in Chapter 2. Apparantly the double salts effects to accerate the transformation of silica gels could be observed.

Judging from these facts, the followings are considered:The double salts can make silica gel change into α -cristobalite (opal-CT) and on some case even into α -quartz.

4-3 Transformation stage of silica gel (Fig.17 and Photo-1)

As it is clear from these facts as above-mentioned, the followings are concluded, and Fig.17 and Photo-1 show each transformation stage of silica gel as follows:

A ; starting material, amorphous silica gel with sharp

edges(Photo-1 A)

B ;Stage I, broad peak(opal-A) with fracture/crack and dull edges (Photo-1 B)

C ;Stage II, α -cristobalite(opal-CT), spherule with framboidal structure (Phto-1 C/D)

D ;Stage III, α -quartz, needle-like micro-crystalline structure(On this experiment, this was not attained)

First, the starting materials of amorphous silica gel change into broad peak(opal-A), and that is stage I.

Next, as the stage II, α -cristobalite (opal-CT) occurred.

And as the third stage of stage III, α -quartz with micro-crystal could be produced.

4-4 Origin and mechanism of chert

The chemical composition of chert is occupied by mainly silica and a few amounts of accessory elements such as Al, Fe, Mg, Ca, Na, K and etc.

On the other hand, the crystal of chert is α -quartz and α -cristobalite on some case.

Then circumfering sea-water including various kinds of cations has been affecting on the crystallization of dead/alive skeltons of radiolaria (Mori and Mitusio, 1988) or diatom. And also the organic matters such as glycine, serine, glutamine acids and etc. may contain in diatom and radiolaria.

Then these organic matters also accelerate the transformation of silica gel as described in the section of the effects by organic matters.

Concluding remarks

The results are summarized as follows:

- 1)The addition of the mixture of hydroxides of $\text{Ca}(\text{OH})_2$ and $\text{Mg}(\text{OH})_2$ has the effect that changed amorphous silica gel into broad peak(opal-A) and α -cristobalite(opal-CT)..
- 2)The oxides of CaO and MgO also accelerated amorphous silica gel into α -cristobalite(opal-CT).
- 3)The oxides are better than hydroxides to make silica gel change into α -cristobalite(opal-CT).
- 4)When the addition of oxides and hydroxides was rich, calcium silicates of truscottite and magnesium silicates of talc respectively were produced.
- 5)The solved ions of Si, Ca and Mg varied as the conditions of treatments, and when the crystallization occurred they decreased as reported before.
- 6)These facts show the effects of double cations.
- 7) Moreover, organic matters also are the catalyzer for the transformation of silica gel, and mechsam of chert was concluded.

Next, many mixtures of cations are to be reported on the other chances.

Acknowledgement

The writers would like to express their sincere thanks to the Director Nakamichi Yamasaki, Associate Professor Kazumichi Yanagisawa and Dr.Hyuu Ki of the Hydrothermal Reseach Laboratory of Kochi University for their kind advices. And special thanks

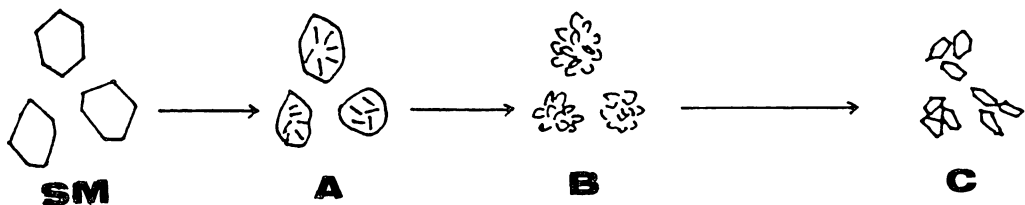


Fig.17 Transformation stage of silica gel (Mitusio, 1989)

SM; starting material, amorphous silica gel with sharp edges

A; Stage I, broad peak(opal-A) with fracture/crack and dull edges

B; StageII, α -cristobalite(opal-CT), spherule with framboidal structure

C; StageIII, α -quartz, micro-crystalline structure

are also due to the members of the Research Society of Human and Environmental Changes (RSHEC) for their kind helps.

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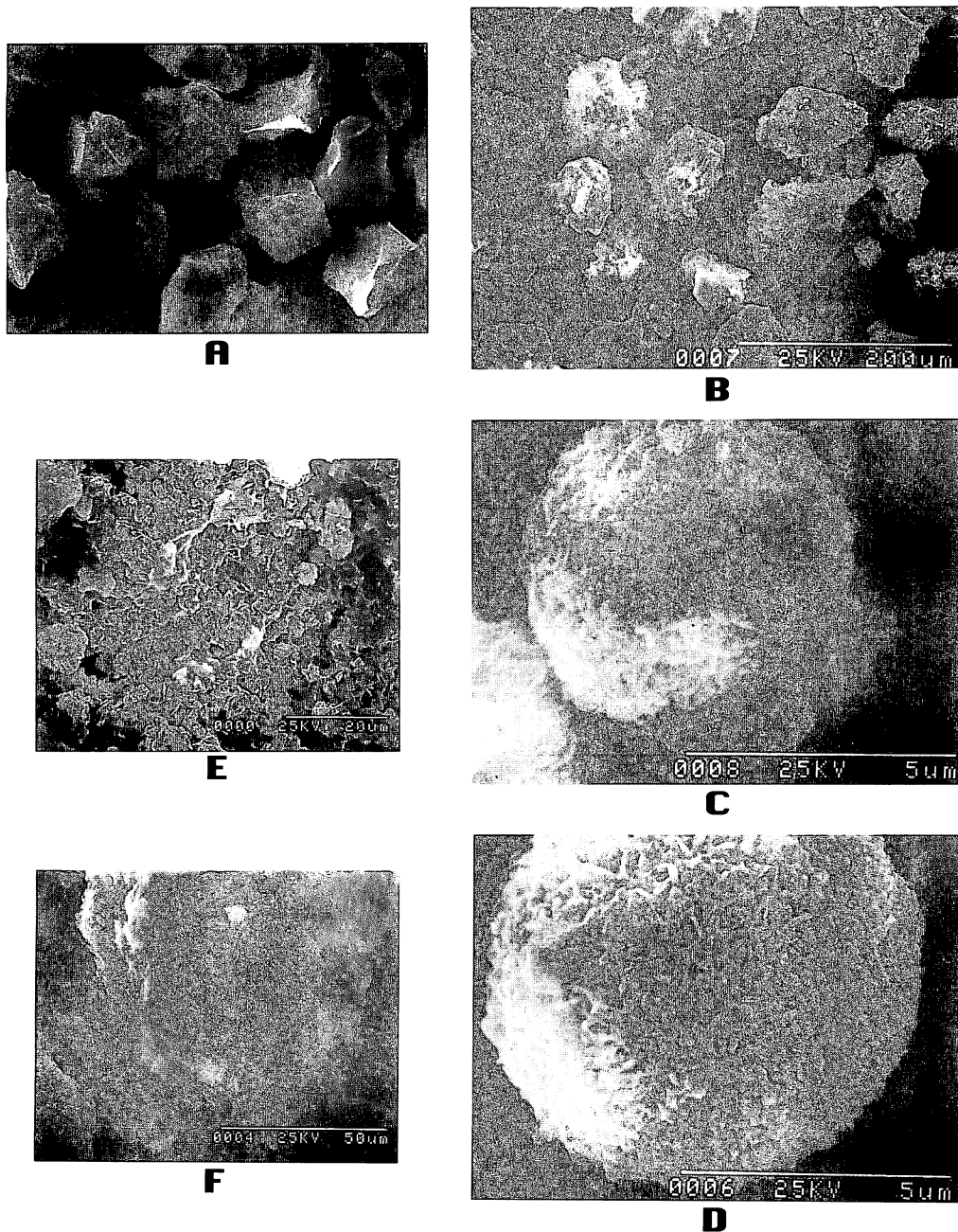


Photo-1 Each stage of transformation of amorphous silica gel
 A, starting material of amorphous silica gel x200
 B, broad peak (opal-A) $\text{CaO} \cdot \text{MgO} = 0.010\text{g}$, 24hr, 350°C x200
 C, α -cristobalite (opal-CT) $\text{Ca}(\text{OH})_2 \cdot \text{Mg}(\text{OH})_2 = 0.010\text{g}$, 72hr, 350°C x10,000
 D, α -cristobalite (opal-CT) $\text{Ca}(\text{OH})_2 \cdot \text{Mg}(\text{OH})_2 = 0.010\text{g}$, 240hr, 350°C x10,000
 E, truscottite $\text{Ca}(\text{OH})_2 \cdot \text{Mg}(\text{OH})_2 = 0.100\text{g}$, 240hr, 350°C x5,000
 F, talc $\text{CaO} \cdot \text{MgO} = 0.100\text{g}$, 240hr, 350°C x5,000