

Relationship in chemical composition between mother solution and allophane-like aluminosilicate precipitate through neutralization of acid hydrothermal water by seawater

Kenji Nogami

*Kusatsu-Shirane Volcano Observatory, Volcanic Fluid Research Center, Tokyo Institute of Technology,
641-36 Kusatsu, Agatsuma, Gunma 377-1711, Japan*

(Received September 17, 2003; Revised March 12, 2004; Accepted March 12, 2004)

A series of experiments on the formation of allophane-like aluminosilicate precipitates were carried out through neutralization of acid solutions in variety of relative proportions of Si, Fe and Al by seawater. The retrieval and decomposition procedures were available for precise determination of those components in the precipitates. Iron in the mother solutions was completely precipitated and Al was mostly precipitated, however, Si was partly co-precipitated with iron and aluminum. Iron and/or Al coexisting with Si caused a remarkable rise of the precipitated proportion of Si. This was ascribed to co-precipitation of these components on the formation of the precipitates. Difference in effect on the precipitated proportion of Si between Fe and Al was not noticeable. This result indicated equivalence of Fe to Al on the formation of the precipitates through neutralization. The correlations in the $(\text{Fe} + \text{Al})/\text{Si}$ and the Fe/Al molar ratios between the mother solution and the precipitates strongly designated that the relative proportions of Si, Fe and Al in hydrothermal water discharged from submarine volcanoes were able to be determined uniquely through chemical analysis of the precipitates causing discolored seawater.

Key words: Precipitate, co-precipitation, neutralization, acid water, seawater.

1. Introduction

Precipitation of minerals from hydrothermal water is frequently occurred due to change in chemical and physical conditions. Decrease in water temperature makes the solubility of aqueous silica low, which results in formation of silica scale and siliceous sinter. Neutralization is one of the causes of mineral precipitation. Allophane-like iron-bearing aluminosilicates form along the seashore of Satsuma-Iwojima in southern Kyushu, Japan resulting from neutralization of acid thermal water by seawater (e.g. Kamada *et al.*, 1964).

Many active submarine and insular volcanoes are distributed on Izu-Mariana and Ryukyu arcs in the northwestern Pacific Ocean. The surface of the sea above their craters is discolored to white, light blue, yellow and reddish brown, which is frequently observed on submarine volcanic activity. It is owing to suspension of the same allophane-like aluminosilicate precipitates that form at Satsuma-Iwojima (Ossaka, 1975). Further, Ossaka *et al.* (1977) proved that the allophane-like precipitates are formed by coprecipitation of Si, Al and Fe hydroxides through neutralization of acid thermal water by seawater. Although over 90% of Al and Fe in acid thermal water are deposited at pH values of mother solution higher than 6, only about 30% of Si in acid water co-precipitates with Fe and Al (Ossaka *et al.*, 1977; Nogami *et al.*, 1993).

Fukutoku-Oka-no-Ba submarine volcano located on Izu-

Mariana arc at about 1300 km southward from Tokyo is one of most active submarine volcanoes in Japan. Violent eruptions with formation of new islands have often occurred there. A new island was temporally formed on the phreatomagmatic eruption in 1986, however, wave erosion vanished it in about two months and its activity has been dormant since then. The surface of the sea above the crater is always discolored, which indicates that acid hydrothermal water is always discharged from the crater of this submarine volcano even in a dormant period.

Discolored seawater has been collected there several times. In 1977 and 1979 when the volcanic activity was dormant, the precipitates enriched in Si relative to Fe and Al discolored the surface of the sea to milky white and light blue. During the 1986 eruption, color of the surface of the sea was drastically changed into reddish and/or yellowish and the precipitates became enriched in Fe and Al relative to Si. After ceasing the eruption, relative proportions of the components in the precipitates and color of the surface of the sea returned to those in the dormant period (Ossaka *et al.*, 1996).

This example shows good correspondence of chemical composition of the precipitates to submarine volcanism. Although the relative proportions of Si, Fe and Al in the precipitates are different from those in the mother solutions, they designate chemical characteristics of hydrothermal water discharged from submarine volcanoes. Consequently, change in chemical composition of hydrothermal water corresponding to activation of submarine volcanism is detectable through analysis of the precipitates.

In this study, neutralization experiments reproduce alumi-

Table 1. Concentration (in mg/kg) of Si, Fe and Al in acid solutions and seawater prepared for the neutralization experiments.

	Si	Fe	Al
Si solution	172	11.9	60.7
Fe solution	0	913	0
Al solution	0	0	927
Seawater	0.2	0	0

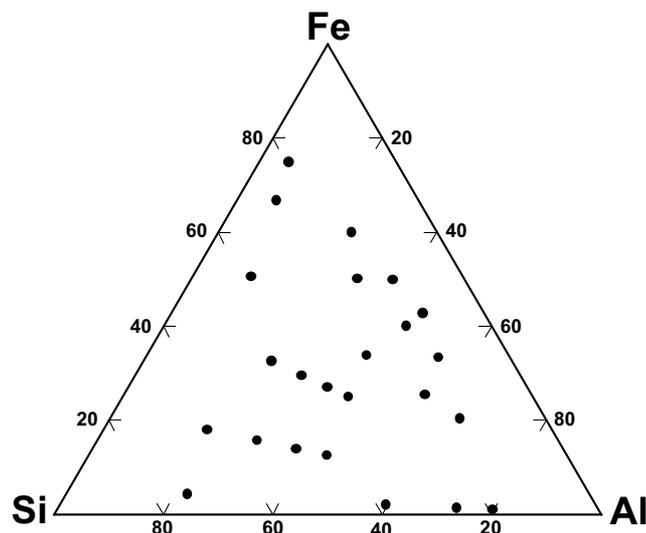


Fig. 1. Relative proportions (in wt.%) of Si, Fe and Al in the mother solutions.

nosilicate precipitates in variety of the relative proportions of Si, Fe and Al. They are aimed to show relationship in the relative proportions of these components between mother solution and aluminosilicate precipitate.

2. Experiments

2.1 Preparation

Si solution: Acid solution of high Si content is very hard for preparation artificially and acid thermal water (95°C, pH 1.61) of high Si concentration collected at Bandaiko hot spring in Kusatsu Spa, Gunma, Japan is used for Si solution.

Fe solution: Iron spices in natural acid thermal water are divalent and trivalent. Oxidation of Fe (II) to Fe (III) is very easy at neutral pH and trivalent iron results in the predominant species in the neutralized solutions. Hence, iron solution is simply prepared by dissolution of FeCl₃ into 0.02 M HCl (approx. 1000 mg l⁻¹).

Al solution: Al solution is prepared by dissolution of Al₂(SO₄)₃·14~18H₂O into 0.02 M HCl (approx. 1000 mg l⁻¹).

Seawater: Seawater filtrated through 5A filter paper has a pH of 8.21.

Concentration of Fe, Al and Si in these solutions and seawater are strictly determined by ICP emission spectrometry (Table 1).

2.2 Experimental procedures

Aluminosilicate precipitates in variety of the relative proportions of Si, Fe and Al are produced through neutralization of acid solutions by seawater. The acid solutions are

Table 2. Formula for preparation of acid solutions and seawater (in ml) for the experiments.

Exp	Si	Fe	Al	Seawater
#1	1.00	0.30	0	200
#2	1.00	0.60	0	200
#3	1.00	0.90	0	200
#4	1.00	0	0.30	200
#5	1.00	0	0.60	200
#6	1.00	0	0.90	200
#7	1.00	0.30	0.30	200
#8	1.00	0.30	0.60	200
#9	1.00	0.30	0.90	200
#10	1.00	0.60	0.30	200
#11	1.00	0.60	0.60	200
#12	1.00	0.60	0.90	200
#13	1.00	0.90	0.30	200
#14	1.00	0.90	0.60	200
#15	1.00	0.90	0.90	200
#16	4.00	0.20	0	500
#17	4.00	0.20	0.20	500
#18	4.00	0.20	0.40	500
#19	4.00	0.20	0.60	500
#20	4.00	0	0	500
#21	4.00	0.60	0.20	500
#22	4.00	0.60	0.40	500
#23	4.00	0.60	0.60	500
#24	4.00	0.60	0.80	500

prepared by mixing of the Si, Fe and Al solutions.

Transfer the Si, Fe and Al solutions to 500 ml beakers according to the formula shown in Table 2. Add the filtrated seawater to the 500 ml beakers correctly using a 100 ml hole pipette. After Osaka *et al.* (1977), these mother solutions are allowed to stand quietly at room temperature for three days, which results in forming a small amount of the precipitates. Figure 1 shows wide variation of the mother solutions in the relative proportions of Si, Fe and Al.

2.3 Analytical procedures

For the experiments from #1 to #15, filtrate the solutions to a 250 ml measuring flask through a 5C filter. Silicon, Fe and Al contents in the filtered solutions are diluted with distilled water and determined and pH values of the solutions are measured. For the other experiments, only pH values of the solutions are measured after filtration through a 5C filter.

The precipitate is subjected to decomposition according to the following scheme. Put the 5C filter paper with the precipitate into a 100 ml beaker. Add exactly five ml of 1 M HCl solution to the beaker with about 5 ml of pure water. Warm this acid solution by a microwave oven for 30 seconds to dissolve the precipitate. Repeat this warming procedure thrice at intervals of 2 minutes. This interval avoids boiling the acid solution. Transfer the solution to a 100 ml measuring flask through a 5A filter paper after cooling. Add correctly five ml of 1M HCl solution to the beaker with about 5 ml of pure water again and repeat the dissolution procedure once

Table 3. Contents (in μg) of Si, Fe and Al in the filtered solutions and the precipitates.

Exp	Filtered solution			Precipitates (direct)			Precipitate (indirect)			Difference (direct-indirect)			
	pH	Si	Fe	Al	Si	Fe	Al	Si	Fe	Al	ΔSi	ΔFe	ΔAl
#1	7.85	100	0	0	100	300	40	120	290	60	-20	10	-20
#2	7.82	100	0	0	100	580	50	120	560	60	-20	20	-10
#3	7.77	110	0	0	110	810	60	110	830	60	0	-20	0
#4	7.88	90	0	110	90	10	190	130	10	230	-40	0	-40
#5	7.80	100	0	12	100	10	490	120	10	500	-20	0	-10
#6	7.76	80	0	100	100	10	790	140	10	790	-40	0	0
#7	7.87	80	0	110	100	290	220	140	290	230	-40	0	-10
#8	7.81	80	0	110	110	280	500	140	290	510	-30	-10	-10
#9	7.41	70	0	100	110	280	800	150	290	790	-40	-10	-10
#10	7.72	90	0	60	110	570	260	130	560	280	-20	10	-20
#11	7.67	90	0	80	110	560	550	130	560	540	-20	0	10
#12	7.58	80	0	70	120	570	850	140	560	830	-20	10	20
#13	7.68	90	0	70	110	840	260	130	830	270	-20	10	-10
#14	7.65	80	0	90	110	850	540	140	830	530	-30	20	10
#15	7.47	80	0	80	120	850	840	140	830	820	-20	20	20
#16	7.74	**	**	**	340	220	120						
#17	7.85	**	**	**	360	220	250						
#18	7.89	**	**	**	370	230	430						
#19	7.86	**	**	**	400	220	620						
#20	7.95	**	**	**	340	40	100						
#21	7.69	**	**	**	370	560	330						
#22	7.74	**	**	**	390	560	480						
#23	7.74	**	**	**	390	560	630						
#24	7.74	**	**	**	410	570	820						

** : not determined.

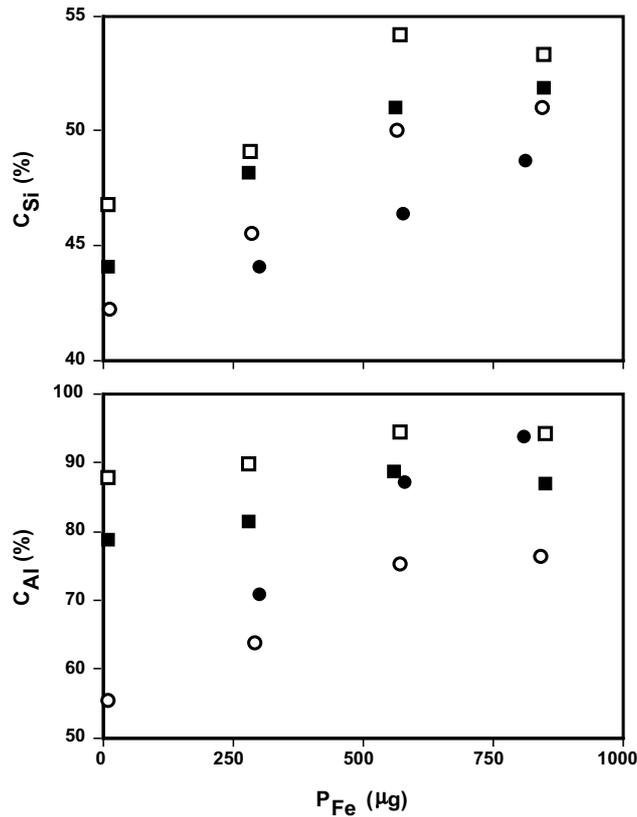


Fig. 2. Change in C_{Al} and C_{Si} plotted against P_{Fe} with variation of I_{Al} . ●: $I_{Al} = 60 \mu\text{g}$. ○: $I_{Al} = 340 \mu\text{g}$. ■: $I_{Al} = 620 \mu\text{g}$. □: $I_{Al} = 900 \mu\text{g}$.

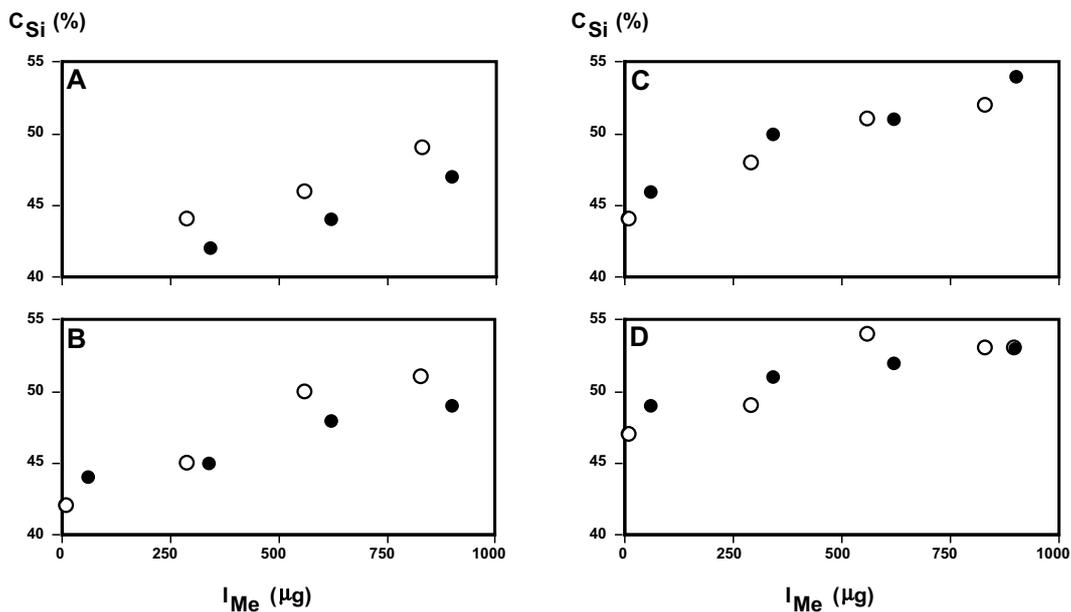


Fig. 3. Change in C_{Si} plotted against I_{Me} . Me = Al and Fe. ○: C_{Si} against I_{Fe} with A) $I_{Al} = 60 \mu\text{g}$, B) $I_{Al} = 340 \mu\text{g}$, C) $I_{Al} = 620 \mu\text{g}$ and D) $I_{Al} = 900 \mu\text{g}$. ●: C_{Si} against I_{Al} with A) $I_{Fe} = 10 \mu\text{g}$, B) $I_{Fe} = 290 \mu\text{g}$, C) $I_{Fe} = 560 \mu\text{g}$ and D) $I_{Fe} = 830 \mu\text{g}$.

more. Wash the beaker and the 5A filter paper thoroughly and diluted with distilled water.

Concentrations of Si, Fe, and Al in the 0.1 M HCl solutions and the filtered solutions are determined by ICP emission spectrometry. Experimental error for determination of Si, Fe and Al is $1 \pm 0.05 \text{ mg l}^{-1}$. A pH meter with a glass electrode is used for pH measurement.

3. Results and Discussion

The pH values of the filtered solutions and the contents of Si, Fe and Al in the filtered solutions and the precipitates are shown in Table 3. Difference in the contents of these components between the prepared solutions and the filtered solutions is also listed in Table 3.

All the solutions have pH values higher than 7. Ferrous ion

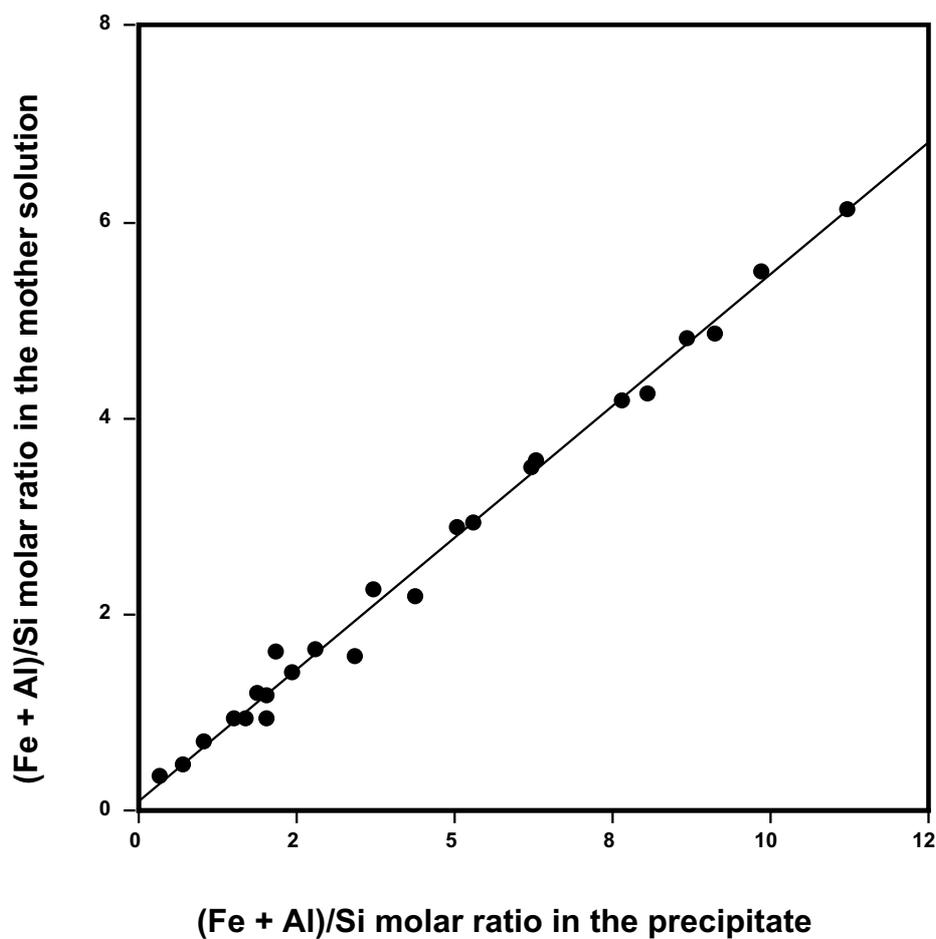


Fig. 4. Relationship in $(\text{Fe} + \text{Al})/\text{Si}$ molar ratio between the mother solution and the precipitate. Regression line is expressed as $(\text{Fe} + \text{Al})/\text{Si}_{\text{mother}} = 0.102 + 0.53 (\text{Fe} + \text{Al})/\text{Si}_{\text{prep}}$.

partly included in the mother solutions must be completely oxidized to ferric ion at these pH values, which makes the solubility of iron ion in the mother solutions extremely low. Difference in the contents of these components in the precipitates between the two determinations listed in Table 3 is $40 \mu\text{g}$ for Si and $20 \mu\text{g}$ for Fe and Al at most. These results show that analytical procedure shown in Section 2.3 enables to determine contents of three components in the precipitates with good precision in the light of the experimental error. Formerly, the precipitates were dissolved into coexistent seawater by addition of conc. HCl in the decomposition procedure on chemical analysis of discolored seawater. Hence, the samples had very high salinity and it made the precise determination of those components difficult. The retrieval and decomposition procedures shown in Section 2.3 help chemical analysis of discolored seawater samples hereafter.

Precipitated proportion of component X , C_x , calculated by the following equation, $C_x = P_x \cdot I_x^{-1} \cdot 100$, where X is Si, Fe and Al. P_x is the content of component X in the precipitate and I_x is the content of component X in the mother solution. Iron in the mother solutions is completely precipitated in all the experiments. Although C_{Al} is slightly lower than C_{Fe} , more than 70% of Al in the mother solutions is precipitated and C_{Al} rises as I_{Al} increases. On the other hand, C_{Si} ranges from 40% to 55% and it is somewhat higher

than the results of the previous works by Oosaka *et al.* (1977) and Nogami *et al.* (1993).

Variation of C_{Al} and C_{Si} with P_{Fe} is shown in Fig. 2. Increase of P_{Fe} raises C_{Si} and C_{Al} markedly. Further, increase of P_{Al} also raises C_{Si} clearly. Coexistence of Fe and/or Al with Si raises C_{Si} markedly, which is attributed to formation of the precipitates by co-precipitation of these components.

Variation of C_{Si} as a function of I_{Fe} is shown in Fig. 3 with changing I_{Al} from 60 to 900 mg. C_{Si} as a function of I_{Al} is also plotted in the same figure with changing I_{Fe} from 10 to 830 mg. These plots of C_{Si} against I_{Fe} and I_{Al} designate that difference in effect on C_{Si} between I_{Fe} and I_{Al} is not noticeable. Trivalent iron is capable of forming octahedrally co-ordinated hydrolyzed species like trivalent Al in weakly alkaline solution (Ichikuni, 1970). Figure 3 clearly shows that trivalent iron is equivalent to aluminum on the formation of the precipitates.

Figure 4 shows a correlation in $(\text{Fe} + \text{Al})/\text{Si}$ molar ratio between the mother solutions and the precipitates. The correlation coefficient is 0.996. This relation strongly indicates that the molar ratio in hydrothermal water discharged from a submarine volcano can be estimated from the ratio in precipitate. This result also designates the equivalence between Fe and Al on the formation of the precipitates. Furthermore, correlation in the molar ratio of Fe to Al between the mother solution and the precipitate is also significant (Fig. 5). The

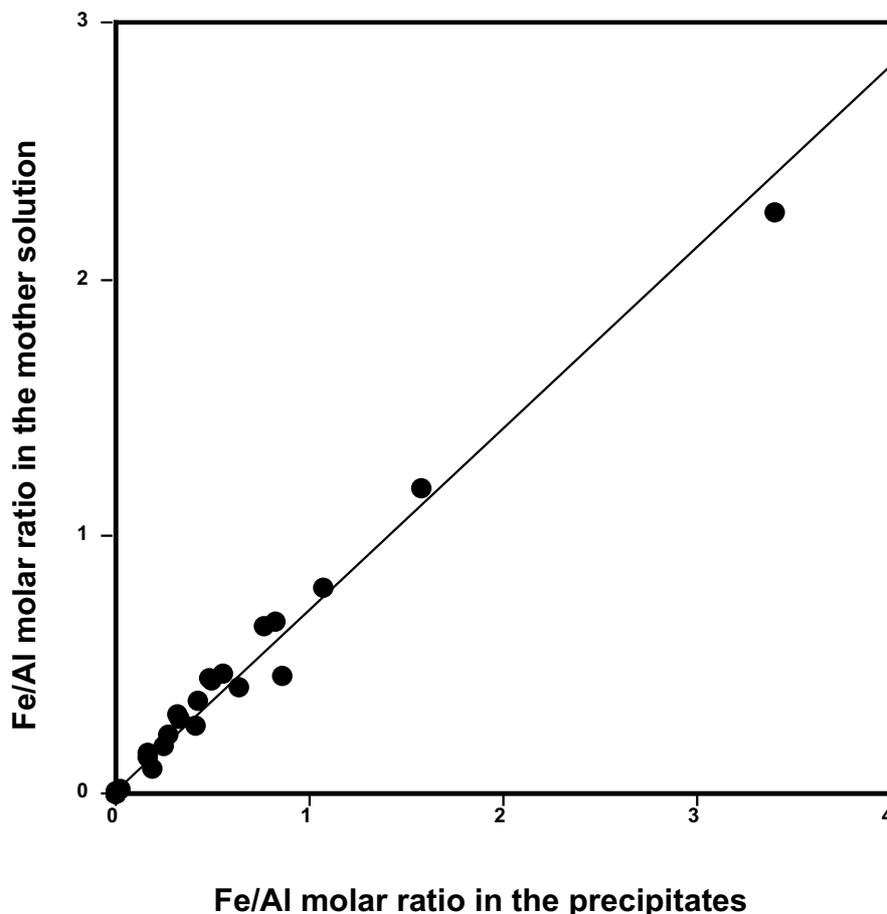


Fig. 5. Relationship in Fe/Al molar ratio between the mother solution and the precipitate. Regression line is expressed as $(\text{Fe}/\text{Al})_{\text{mother}} = 0.041 + 0.67 (\text{Fe}/\text{Al})_{\text{prep}}$.

Fe/Al molar ratios in the precipitates formed on the submarine volcanic activity in the past were less than 4 and the regression line is calculated except the experiments #2 and #3. The correlation coefficient is 0.991. This result shows that the Fe/Al ratio in hydrothermal water can be estimated from the ratio in the precipitate. These correlations in the $(\text{Fe} + \text{Al})/\text{Si}$ and the Fe/Al molar ratios between the mother solution and the precipitates enable us to estimate uniquely the relative proportions of Si, Fe and Al in hydrothermal water through chemical analysis of the precipitates.

4. Conclusions

The experimental study on the formation of the aluminosilicate precipitates provides us with important results on the relationship in the relative proportions of Si, Fe and Al between the mother solution and the precipitate. The analytical procedure originated in this study enables us to determine precisely the relative proportions of Si, Fe and Al in the precipitates with ease. Iron in the mother solutions is completely precipitated and Al is mostly deposited, however, Si is partly co-precipitated with Fe and Al. Iron and/or Al make the precipitated proportion of Si markedly increase and trivalent Fe is equivalent to Al on the formation of the precipitates.

The relationships in the $(\text{Fe} + \text{Al})/\text{Si}$ and Fe/Al molar ratios between the mother solutions and the precipitates give

us that chemical analysis of the precipitates can reveal the relative proportions of Si, Fe and Al in hydrothermal water discharged from submarine volcanoes.

Acknowledgments. I would like to thank the reviewers for helpful comments on this paper.

References

- Ichikuni, M., Incorporation of aluminum and iron into siliceous sinters, *Chemical Geology*, **6**, 273–279, 1970.
- Kamada, M., J. Ossaka, and T. Ozawa, Hydro-alumina-silicate generating from acidic hot spring water along the seashore of Iwojima volcano, Abstract of the Geochemical Soc. Japan, 158–161, 1964 (in Japanese).
- Nogami, K., M. Yoshida, and J. Ossaka, Chemical composition of discolored seawater around Satsuma-Iwojima, Kagoshima, Japan, *Bull. Volcanol. Soc. Japan*, **38**, 71–77, 1993.
- Ossaka, J., The eruption of Nishinosima submarine volcano and geochemical study on the composition of the ejecta and the volcanic activity, *Chemistry Today (Gendai Kagaku)*, **55**, 12–20, 1975 (in Japanese).
- Ossaka, J., Y. Ohira, J. Hirabayashi, and A. Mori, Comparison of amorphous hydro-alumina-silicate, formed in sea water with precipitated allophane, *Jour. Min. Soc. Japan*, **13**, 178–186, 1977 (in Japanese).
- Ossaka, J., J. Hirabayashi, K. Nogami, M. Tsuchide, and N. Adachi, Chemical composition of discolored seawater corresponding to activity of Fukutoku-Oka-no-Ba submarine volcano—as an index of submarine volcanism—, *Bull. Volcanol. Soc. Japan*, **41**, 107–113, 1996 (in Japanese).