

PREPARATION OF ORGANOSILICATE COMPOUNDS FROM PHLOGOPITE BY TRIMETHYLSILYLATION

KAZUYUKI KURODA AND CHUZO KATO

Department of Applied Chemistry, School of Science and Engineering,
Waseda University, Shinjuku-ku, Tokyo, Japan 160

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Abstract—The reaction of phlogopite with a trimethylsilylating reagent yielded organosilicate compounds which are soluble in various organic solvents. Gas chromatographic analysis of the soluble products indicates that they consist of the trimethylsilylated derivatives of silicic acids which have been formed in the decomposition of phlogopite by hydrochloric acid and that silicic acids formed by the acid attack are monomeric and also oligomeric. The increase of the ratio of GC peak areas of monomer derivative to dimer one with an increase of the reaction time shows that silicic acids in the reaction system tend to depolymerize. The difference between phlogopite and biotite in the ease of trimethylsilylation also is discussed.

Key Words—Biotite, Phlogopite, Trimethylsilylation.

INTRODUCTION

Trimethylsilylation of silicates has been studied for the purpose of the direct elucidation of the silicate structures by preparing the trimethylsilylated derivatives of the silicates.



The trimethylsilylated derivatives of monosilicic acid $[(\text{CH}_3)_3\text{Si}]_4\text{SiO}_4$ * as shown in Figure 1 can be synthesized by the reaction of orthosilicate (such as olivine) with the trimethylsilylating reagent which is trimethylchlorosilane or the mixture of hexamethyldisiloxane, isopropyl alcohol, and hydrochloric acid (Lentz, 1964; Götz and Masson, 1971). Disilicate (such as hemimorphite) yields the derivative of disilicic acid $[(\text{CH}_3)_3\text{Si}]_6\text{Si}_2\text{O}_7$ † (Figure 1) by the trimethylsilylation reaction (Lentz, 1964; Götz and Masson, 1970).

Trimethylsilylation of silicates also has been investigated in order to synthesize new polymers or oligomers retaining a silicate backbone. However, there have been few studies on the preparation of organic solvent soluble products from phyllosilicates by trimethylsilylation.

When biotite was treated with the trimethylsilylating reagent, the trimethylsilylated derivatives of mono- and disilicic acids were formed mainly at reflux temperature and to a lesser degree at room temperature (Kuroda and Kato, 1977). In this paper, trimethylsilylation of phlogopite was studied in order to prepare the oligomeric organosilicate compounds which have been little in-

vestigated except for the research by Currell et al. (1974).

EXPERIMENTAL

Material

The source of the phlogopite used in this work was Madagascar. Clean phlogopite crystals were ground to pass 100 mesh. The purity of the ground material was checked by the method of X-ray powder diffraction. Hexamethyldisiloxane (HMD), isopropyl alcohol, and concentrated hydrochloric acid were reagent grade.

Trimethylsilylation

The procedure described previously (Kuroda and Kato, 1977) was employed for the trimethylsilylation reaction. The reaction temperature was set at (A) room temperature or at (B) reflux temperature (75°C). Organic solvent soluble products and insoluble products were obtained in a similar manner reported elsewhere (Kuroda and Kato, 1977). During the process of the reaction (72 hr), a 2-ml sample of the organic layer of the reaction mixture was taken out at constant intervals (every 12 hr) and the organic solvent soluble product was weighed after the evaporation of HMD under a reduced pressure.

Analyses

Gas liquid partition chromatography was performed with a Shimadzu GC-2C chromatograph with a TCD. The chromatographic conditions were as follows; stainless steel column, 2.25 m long and 3 mm i.d., packed SE-30, 5% on Shimalite W, 60-80 mesh. Oven temperature was 200°C and injection port temperature was 270°C. Hydrogen was used as carrier gas and its flow rate was 20 ml/min. IR spectroscopy, X-ray powder diffractometry, DTA and thin-layer stick chromatog-

* 1,1,1,5,5,5-hexamethyl-3,3-bis(trimethylsilyl)oxytrisiloxane.

† 1,1,1,7,7,7-hexamethyl-3,3,5,5-tetrakis(trimethylsilyl)oxytetrasiloxane.

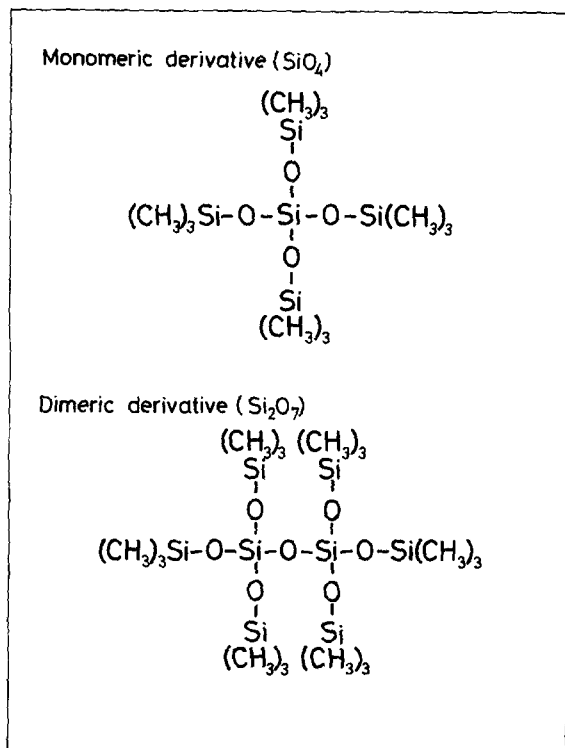


Fig. 1. Trimethylsilylated derivatives of mono- and disilicic acids.

raphy were performed by using the same technique as described in the earlier paper (Kuroda and Kato, 1977).

RESULTS AND DISCUSSION

The trimethylsilylated product of phlogopite formed at room temperature (A) or at reflux temperature (B)

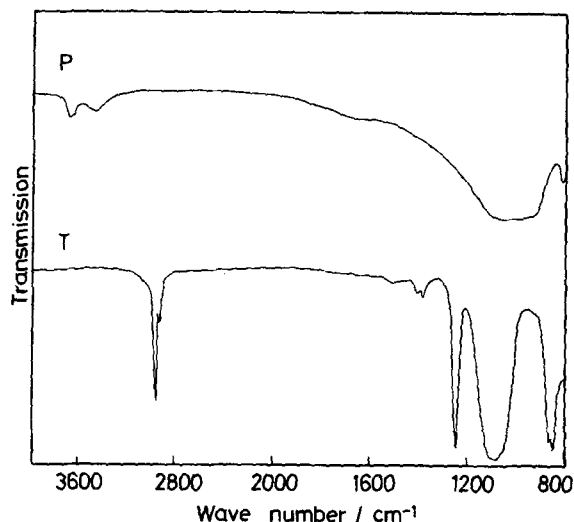


Fig. 2. Infrared spectra of (P) phlogopite and (T) trimethylsilylated derivative formed at reflux temperature.

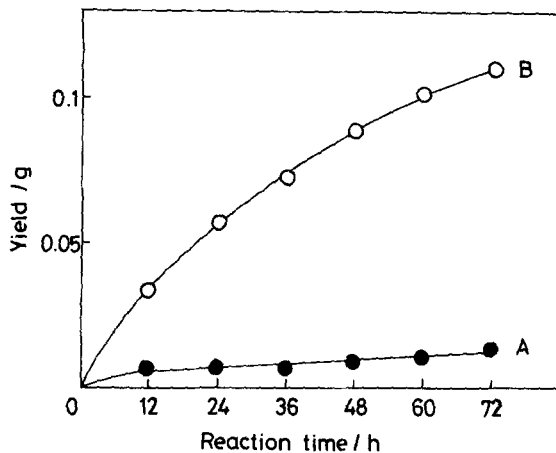


Fig. 3. Yield of the trimethylsilylated products of phlogopite formed at (A) room temperature and (B) reflux temperature.

was a slightly yellow transparent viscous liquid. The yields of the products obtained from 10 g of phlogopite powder were (A) 0.5 g and (B) 5.2 g, respectively. They dissolved in a wide range of organic solvents and were insoluble in water.

Figure 2 shows the infrared spectra of the phlogopite powder and the trimethylsilylated product formed at reflux temperature. The characteristic absorption bands in the product were assigned to trimethylsilyl groups ($2960, 2895 \text{ cm}^{-1}$, $\nu\text{-CH}_3$; 1260 cm^{-1} , $\delta\text{-CH}_3(\text{Si}(\text{CH}_3)_3)$; $1050\text{--}70 \text{ cm}^{-1}$, $\nu\text{-Si-O-Si}$, indicating the trimethylsilylation of silanol groups of silicic acids which were generated in the acid decomposition of phlogopite. The spectrum of the soluble product formed at room temperature was identical with that of the product formed at reflux temperature. Hydroxyl absorption could not be detected, which indicated the

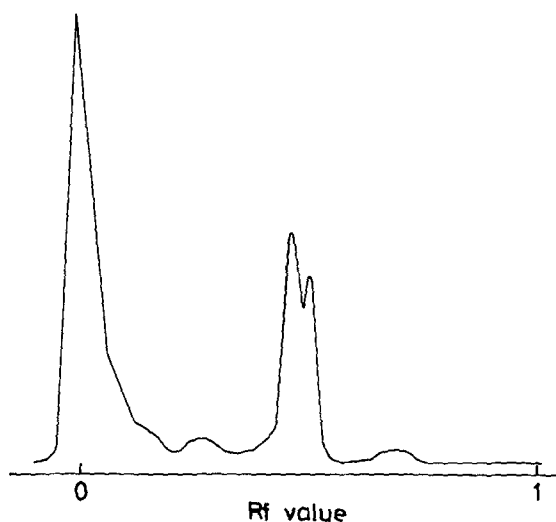


Fig. 4. Thin-layer stick chromatogram of the trimethylsilylated product formed at reflux temperature.

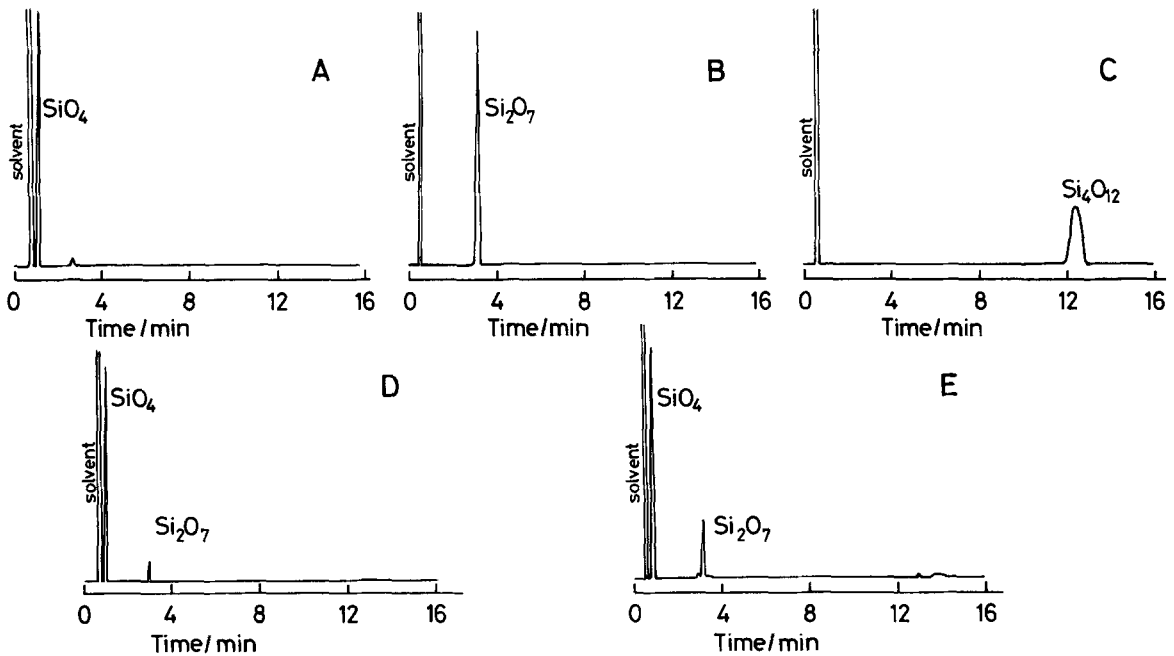
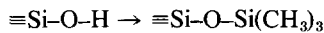


Fig. 5. Gas chromatograms of the trimethylsilylated products from (A) olivine, (B) hemimorphite, (C) laumontite, (D) phlogopite at room temperature, and (E) phlogopite at reflux temperature.

almost complete conversion of silanol groups as expressed by the following formula.



The variation of the yield of the trimethylsilylated soluble products per 2 ml of organic layer in the process of the reaction is given in Figure 3. The increase of the amount of the trimethylsilylated product formed at reflux temperature revealed that the acid decomposition of phlogopite occurred with time at a reasonable rate. On the other hand, the acid attack at room temperature was insufficient to break down the layer structure of phlogopite, so that it can be concluded that the degree of the decomposition at room temperature did not vary so greatly with time.

Figure 4 gives the thin-layer stick chromatogram of the soluble product formed at reflux temperature. This chromatographic pattern was similar to those which were reported for the trimethylsilylated products of biotite (Kuroda and Kato, 1977), indicating the presence of the trimethylsilylated derivatives of mono- and disilicic acids. Higher molecular weight derivatives also were detected at the starting point.

For better separation and identification of the trimethylsilylated products, gas liquid partition chromatography (GLPC) was employed. GLPC of trimethylsilylated derivatives of various silicic acids was reported by Wu et al. (1970) and Garzó and Hoebbel (1976) who analyzed a series of trimethylsilylated de-

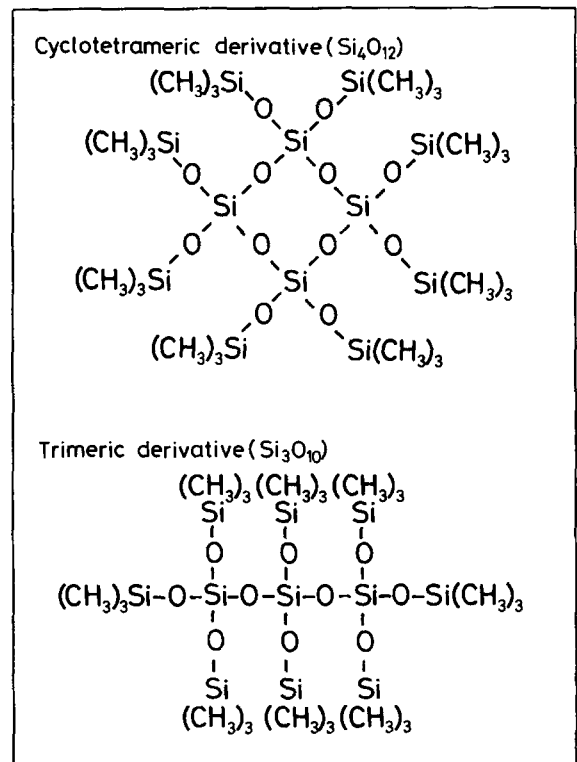


Fig. 6. Trimethylsilylated derivatives of cyclotetra- and trisilicic acids.

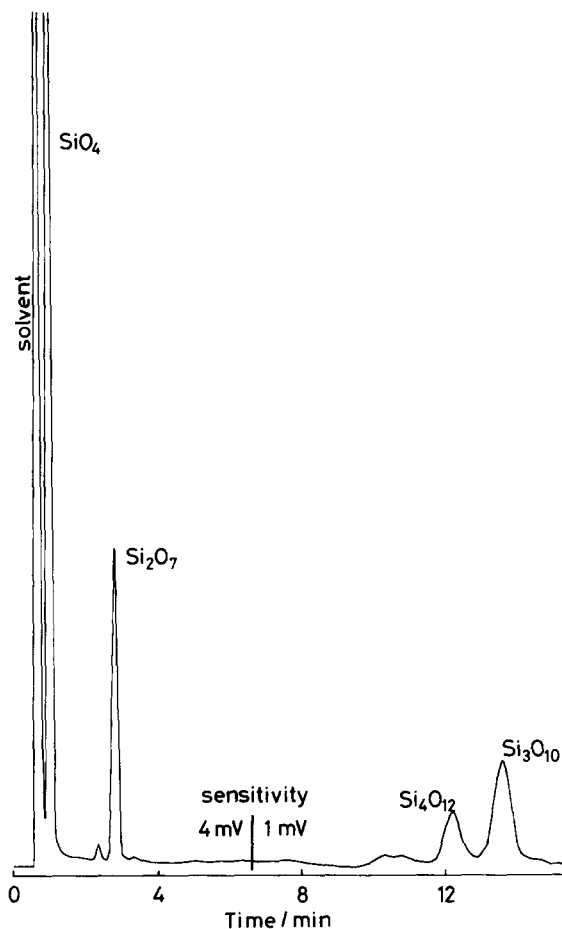


Fig. 7. Gas chromatogram of the trimethylsilylated product formed at reflux temperature.

derivatives and determined their retention characteristics.

Figures 5(A), (B), and (C) show the gas chromatograms of the trimethylsilylated products prepared from olivine ($(\text{Mg,Fe})_2\text{SiO}_4$), hemimorphite ($\text{Zn}_4\text{Si}_2\text{O}_7(\text{OH})_2 \cdot \text{H}_2\text{O}$) and laumontite ($\text{CaAl}_2\text{Si}_4\text{O}_{12} \cdot 4\text{H}_2\text{O}$) by the trimethylsilylation reaction described by Lentz (1964, the Lentz method) or Götz and Masson (1971, the direct method). Monomeric, dimeric, and cyclotetrameric derivatives were obtained as the main products. The chromatograms of the soluble products from phlogopite given in Figures 5(D) and (E) indicated that they contained the trimethylsilylated derivatives of mono- and disilicic acids. The presence of the trimethylsilylated derivatives of cyclotetra- and trisilicic acids illustrated in Figure 6 were detected clearly as shown in Figure 7, when the sensitivity of the GC recorder changed. The presence of the derivative of trisilicic acid was estimated by the retention characteristics (Garzó and Hoebbel, 1976) and other published GC patterns.

Figure 8 shows the effect of the reaction time on the

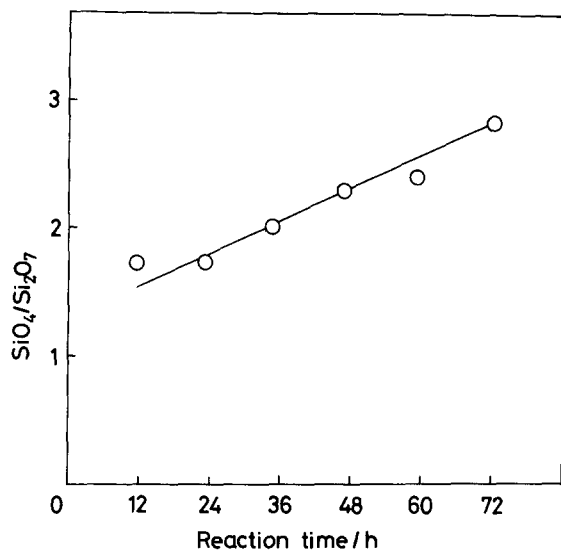


Fig. 8. Ratio of peak areas of monomer to dimer derivatives from phlogopite at reflux temperature.

ratio of peak areas of monomer to dimer derivatives obtained from phlogopite at reflux temperature. The increase of the ratio of $\text{SiO}_4/\text{Si}_2\text{O}_7$ with time reflects the depolymerization of silicic acids in the reaction system. Similar behavior of silicic acids (depolymerization) was reported in the study of trimethylsilylation of hemimorphite by Lentz (1964), who explained the phenomenon of the appearance of the monomeric derivative in a moderate yield by the depolymerization of silicic acids (acid cleavage of siloxane bond). From these findings, it was concluded that hydrochloric acid, which had been considered as a reagent for the removal of interlayer cations and for the attack on Mg in the octahedral layer and Al in the tetrahedral layer, played an important role in the distribution of low molecular weight silicic acids.

X-ray powder patterns of insoluble products (residues) separated from the reaction mixture showed the starting material (phlogopite). The intensity of the powder pattern of the insoluble product formed at room temperature was the same as that of phlogopite, whereas the intensity of the pattern of the insoluble product formed at reflux temperature was slightly diminished. DTA curves of the insoluble products showed no exothermic peaks, so they contained few organic (trimethylsilyl) groups.

In the same reaction time, the proportion of the soluble product may depend on the rate of decomposition of the octahedral layer. If the octahedral layer is decomposed by the acid, silicic acids will appear as a result of the decomposition of the tetrahedral layer. In comparison with the trimethylsilylation of biotite (Kuroda and Kato, 1977), the yield of the soluble product formed at room temperature was considerably lower.

In view of the variation of the yield of the soluble product formed at room temperature (Figure 1), it can be considered that the acid attack by hydrochloric acid on phlogopite at room temperature is not sufficient to decompose the octahedral layer in phlogopite. On the other hand, the insoluble products formed at room temperature and also at reflux temperature were found to be phlogopite on the basis of their X-ray powder patterns.

Consequently, the difference between biotite and phlogopite in the ease of trimethylsilylation seems to be ascribable to the difference in the cations in the octahedral layer. The susceptibility of silicates to acid attack is affected by the presence of Fe (Murata, 1943), so it is suggested that the presence of Fe in the octahedral layer in biotite increases the acid decomposition of phyllosilicate structures.

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REFERENCES

- Currell, B. R., Midgley, H. G., Seaborne, M. A. and Thakur, C. P. (1974) Preparation of polyorganosiloxane from mineral silicates using the method of trimethylsilylation: *Br. Polym. J.* **6**, 229-240.
- Garzó, G. and Hoebbel, D. (1976) Gas chromatographic retention characteristics of trimethylsilylated silicate anions: *J. Chromatogr.* **119**, 173-179.
- Götz, J. and Masson, C. R. (1970) Trimethylsilyl derivatives for the study of silicate structures. Part 1. A direct method of trimethylsilylation: *J. Chem. Soc. Inorg. Phys. Theor.* 2683-2686.
- Götz, J. and Masson, C. R. (1971) Trimethylsilyl derivatives for the study of silicate structures. Part 2. Orthosilicate, pyrosilicate and ring structures: *J. Chem. Soc. (A)* 686-688.
- Kuroda, K. and Kato, C. (1977) Trimethylsilylation of biotite: *Clays & Clay Minerals* **25**, 407-410.
- Lentz, C. W. (1964) Silicate minerals as sources of trimethylsilyl silicates and silicate structure analysis of sodium silicate solutions: *Inorg. Chem.* **3**, 574-579.
- Murata, K. J. (1943) Internal structure of silicate minerals that gelatinize with acid: *Am. Mineral.* **28**, 545-562.
- Wu, F. F. H., Götz, J., Jamieson, W. D. and Masson, C. R. (1970) Determination of silicate anions by gas chromatographic separation and mass spectrometric identification of their trimethylsilyl derivatives: *J. Chromatogr.* **48**, 515-520.

Резюме- В результате реакции флогопита с триметилсилиловыми реагентами образовались органосиликатные соединения, растворимые в различных органических растворах. Газо-хроматографический анализ растворимых продуктов указывал, что они состоят из триметилсилиловых дериватов кремниевых кислот, которые образовывались при разложении флогопита соляной кислотой и что кремниевые кислоты, формировавшиеся под воздействием соляной кислоты, были мономерными и полимерными. Возрастание отношения мономерного деривата к димерному в пиковых зонах газовых хроматограмм с возрастанием времени реакции показывало, что кремниевые кислоты в реакционной системе проявляли тенденцию к деполимеризации. Обсуждается также различие между флогопитом и биотитом по способности к триметилсилилизации.

Kurzreferat- Die Reaktion von Phlogopit mit einem Trimethylsilylierungsreagenz ergab Organosilikatsubstanzen, die in verschiedenen organischen Lösungsmitteln löslich waren. Gas chromatographische Analysen deuteten an, daß sie aus den trimethylsilylierten Derivaten der Kieselsäuren bestehen, welche während des Abbaus von Phlogopit durch Salzsäure geformt wurden und, daß Kieselsäuren, die durch Säureabbau geformt wurden, monomerisch und oligomerisch waren. Die Zunahme des Verhältnisses der GC Signalflächen der monomeren zu denen der oligomeren mit Zunahme der Reaktionszeit, zeigt, daß Kieselsäuren in diesem Reaktionssystem, die Tendenz haben, zu depolymerisieren. Der Unterschied zwischen Phlogopit und Biotit mit Hinsicht auf die Leichtigkeit, mit der Trimethylsilylierung stattfindet, wurde auch diskutiert.

Résumé-La réaction de phlogopite avec un réactif triméthylsilylant a produit des composés organosilicés qui sont solubles dans divers solvants organiques. L'analyse chromatographique à gaz des produits solubles indique que ces derniers consistent en dérivatifs triméthylsilylés d'acides siliciques qui ont été formés par la décomposition de phlogopite par l'acide hydrochlorique, et les acides siliciques formés par l'attaque acide sont monomériques et également oligomériques. Le fait que le rapport des régions des pics de GC du dérivatif monomère à celui du dérivatif dimère augmente avec l'augmentation du temps de réaction montre que les acides siliciques ont tendance à se dépolymériser dans ce système de réaction. La différence entre la facilité de triméthylsilylation de phlogopite et de biotite est aussi discutée.