# Trimethylgermyl Derivatives for the Study of Silicate Structures

By H. P. Calhoun and C. R. Masson*

(*Atlantic Regional Laboratory, National Research Council of Canada,* 1411 *Oxford Street, Halifax, N.S., Canada* B3H 3Z1)

*Summary* Silicate minerals react with trimethylchlorogermane in the presence of water to yield trimethylgermyl derivatives $Si_xO_y(GeMe_3)_z$; the method is a useful adjunct to the technique of trimethylsilylation for the study of silicate structures.

THE method of trimethylsilylation[1] has been applied by many investigators to the study of silicate structures. The basis of the method is the chemical conversion of silicate anions present in the silicate material into their trimethylsilyl (TMS) derivatives. In complex extracts the derivatives of lower molecular weight are sufficiently volatile to be separated by g.l.c. One difficulty encountered with the method is the occurrence of side reactions which prevent accurate representation of the original silicate structure. Possible side reactions include polymerization and depolymerization of silicate anions before trimethylsilylation is complete and hydrolysis of the TMS derivatives themselves. Another limitation is our frequent inability to obtain high absolute yields in trimethylsilylation reactions with silicate glasses and some minerals. This may be due to a variety of factors including: (a) polymerization of silicate anions to high molecular weight species, which are undetectable chromatographically, before trimethylsilylation is complete, (b) trapping of low molecular weight silicate anions in a polymeric silicate matrix, and (c) insolubility of the silicate material in the trimethylsilylation medium. A further limitation arises from the presence of silicon atoms in both the silicate framework and in the TMS 'capping' groups, making study of the insoluble trimethylsilylated residues (presumably silicate polyions which are partially trimethylsilylated) difficult.

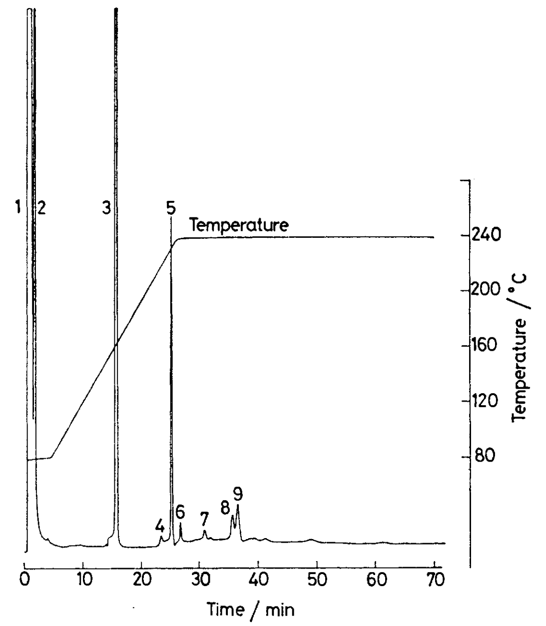

FIGURE. Chromatogram of calcium orthosilicate trimethylgermylation product on a packed column (SE 30 on Chromosorb W, 3·6 m long × 3·2 mm diameter). Peaks correspond to: (1), $O(SiMe_3)_2$; (2), $O(GeMe_3)_2$; (3), $SiO_4(GeMe_3)_4$; (4), unknown; (5), $Si_2O_7(GeMe_3)_6$; (6), $Si_3O_9(GeMe_3)_6$; (7), unknown; (8), $Si_4O_{12}(GeMe_3)_8$; and (9), $Si_3O_{10}(GeMe_3)_8$.

We now report a new method of investigating silicate structures in which trimethylgermyl derivatives of silicate anions are formed. It is expected that this method will obviate some of the difficulties inherent in the trimethylsilylation procedure.

Silicate minerals react with trimethylchlorogermane in the presence of water to yield trimethylgermyl (TMG) derivatives, $Si_xO_y(GeMe_3)_z$. With the minerals investigated, the presence of water was essential for reaction to take place. In a typical reaction 0·1 g of the mineral, 0·1 ml of $H_2O$, 0·6 ml of $Me_3GeCl$, and 3·0 ml of $O(SiMe_3)_2$ were stirred together at room temperature for 1 h. The hexamethyldisiloxane (upper) layer was separated and analysed by g.l.c. In contrast with the method of trimethylsilylation, propan-2-ol was found to be unnecessary for reaction to take place and was usually omitted from the reaction medium. Hexamethyldisiloxane was used as a solvent for convenience, but was not essential for reaction to occur. In some experiments acetone was used as solvent. TMG derivatives of the anions $SiO_4^{4-}$, $Si_2O_7^{6-}$, $Si_3O_9^{6-}$, $Si_4O_{12}^{8-}$, and $Si_3O_{10}^{8-}$ were observed in the chromatograms. These had longer retention times and were expelled from the column at higher temperatures than the analogous TMS derivatives. A typical chromatogram is shown in the Figure. The products obtained from various minerals and their relative yields expressed as percentages of the total peak area in the chromatograms are given in the Table. Incompletely derivatized products (*e.g.*, hydroxy derivatives) were formed only in very small amounts.

TABLE. Percentage peak areas [excluding $O(SiMe_3)_2$ and $O(GeMe_3)_2$].

| | Mineral | | |
|---|---|---|---|
| Derivative | $Ca_2SiO_4$ | $Na_2H_2SiO_4\cdot 8H_2O$ | $Ca_3Si_2O_7$ |
| $SiO_4(GeMe_3)_4$ | 79·6 | 68·2 | 25·3 |
| $Si_2O_7(GeMe_3)_6$ | 14·9 | 17·8 | 62·1 |
| $Si_3O_9(GeMe_3)_6$ | 0·8 | 2·4 | 2·9 |
| $Si_4O_{12}(GeMe_3)_8$ | 2·1 | 1·3 | 3·4 |
| $Si_3O_{10}(GeMe_3)_8$ | 2·1 | 5·4 | 2·8 |
| Sum of unidentified peaks | 0·5 | 4·9 | 3·5 |

In the trimethylsilylation technique reaction does not proceed to completion, so that stirring of a hexamethyldisiloxane solution of the product with Amberlyst 15 cation exchange resin is necessary to achieve complete derivatization. We have found that this process can contribute to the occurrence of side reactions in some cases. For example, recent studies in our laboratory have shown that $Si_3O_9(SiMe_3)_6$ is completely converted into $Si_3O_{10}(SiMe_3)_8$ when stirred for several days at room temperature with Amberlyst 15 and hexamethyldisiloxane. The trimethylgermylation method avoids this problem as the reaction proceeds to completion without the use of Amberlyst 15.

(*Received*, 17*th April* 1978; *Com.* 389.)

---

[1] C. W. Lentz, *Inorg. Chem.*, 1964, **3**, 574; J. Götz and C. R. Masson, *J. Chem. Soc.* (*A*), 1970, 2683; 1971, 686; S. K. Sharma, L. S. D. Glasser, and C. R. Masson, *J.C.S. Dalton*, 1973, 1324; J. Götz, D. Hoebbel, and W. Wieker, *J. Non-Cryst. Solids*, 1976, **20**, 413.