Trimethylsilyl Derivatives for the Study of Silicate Structures. Part 4.[1] The Conversion of Hemimorphite into Willemite

By **Jiri Götz**, Laboratory for Silicate Research, Czechoslovakian Academy of Sciences, Prague, Czechoslovakia
Charles R. Masson,* Atlantic Regional Laboratory, National Research Council of Canada, Halifax, Nova Scotia, Canada B3H 3Zl

The method of direct trimethylsilylation described previously has been used to follow the change in constitution of hemimorphite, $Zn_4(OH)_2(Si_2O_7){\cdot}H_2O$, on heating at various temperatures up to 1 300 °C. The conversion has also been followed by differential thermal analysis, thermal gravimetric analysis, and *X*-ray diffraction measurements. An abrupt change in the chromatographic pattern occurs at 600—630 °C, corresponding to the disappearance of the Si_2O_7 and emergence of the SiO_4 derivative as the main product of trimethylsilylation. This coincides with the loss of hydroxide groups and the formation of β-Zn_2SiO_4. The initial stage of the reaction at 627 °C shows first-order kinetics. The transformation of β-Zn_2SiO_4 into willemite, α-Zn_2SiO_4, commences at 835 °C and is unaccompanied by further changes in the yield or chromatographic pattern of the products. The results illustrate the use of the method as an adjunct to conventional procedures for studying the change in anionic constitution of silicates having discrete silicate structures.

THE method of trimethylsilylation, described in previous publications,[1-3] is a useful adjunct to more conventional procedures for the study of silicate structures. The technique, originally due to Lentz,[4] has been modified and extended by other workers and has been used to study the constitution of various minerals and glasses [5-10] and to follow the change in constitution of a glass on devitrification.[11] It has also been applied to the study of metallurgical slags.[12]

The method sometimes reveals structural changes which are difficult to detect by other means. An example is the study of aluminium–silicon ordering in melilites, in which changes were observed in the chromatographic pattern of natural melilites which were unaccompanied by changes in the *X*-ray diffraction pattern.[13] An assessment of the method as applied to soluble silicates has been published recently.[14]

The object of the present work was to use the technique to follow the change in constitution accompanying the conversion of hemimorphite into willemite. Hemimorphite, $Zn_4(OH)_2(Si_2O_7){\cdot}H_2O$, has a structure [15] in which the discrete pyrosilicate groups Si_2O_7 are associated with zinc in approximately tetrahedral co-ordination with four oxygen atoms, one of which is from hydroxide. Each hydroxide group is shared by two zinc atoms. One SiO_4 tetrahedron and two ZnO_3-(OH) tetrahedra share one oxygen atom in a common corner. The tetrahedra form layers parallel to 010 and combined with one another through common apices. One molecule of water is present as hydroxide-groups and the other as molecular water in interstices.

The mechanism of conversion of hemimorphite into willemite has been studied by Taylor [16] by single-crystal *X*-ray diffraction, and by Merkulov and Khristoforov.[17] Differential thermal analysis (d.t.a.) studies have been reported by Faust[18] and by Roy and Mumpton.[19] It has been shown that hemimorphite loses its molecular water at $<$ *ca.* 650 °C, with only a slight change in the *X*-ray diffraction pattern, to yield the structurally similar ' modified hemimorphite '.[16] At higher temperatures it loses hydroxide water and is converted into β-Zn_2SiO_4 which, at $<$960 °C, is transformed into willemite. The

---

[1] Part 3, S. K. Sharma, L. S. D. Glasser, and C. R. Masson, *J.C.S. Dalton*, 1973, 1324.

[2] Part 2, J. Götz and C. R. Masson, *J. Chem. Soc.* (*A*), 1971, 686.

[3] Part 1, J. Götz and C. R. Masson, *J. Chem. Soc.* (*A*), 1970, 2683.

[4] C. W. Lentz, *Inorg. Chem.*, 1964, **3**, 574.

[5] B. R. Currell, H. G. Midgley, and M. A. Seaborne, *J.C.S. Dalton*, 1972, 490.

[6] P. D. G. Cradwick, V. C. Farmer, J. D. Russell, C. R. Masson, K. Wasa, and N. Yoshinaga, *Nature, Phys. Sci.*, 1972, **240**, 187.

[7] D. Hoebbel and W. Wieker, *Z. anorg. Chem.*, 1971, **384**, 43.

[8] D. Hoebbel and W. Wieker, *Z. Chem.*, 1972, **12**, 295.

[9] D. Hoebbel and W. Wieker, *Z. anorg. Chem.*, 1974, **405**, 267.

[10] K. E. Kolb and K. W. Hansen, *J. Amer. Ceram. Soc.*, 1965, **48**, 439.

[11] J. Götz, C. R. Masson, and L. M. Castelliz in 'Amorphous Materials,' eds. R. W. Douglas and B. Ellis, Wiley, London, 1972, p. 317.

[12] C. R. Masson, W. D. Jamieson, and F. Mason in ' Physical Chemistry of Process Metallurgy: The Richardson Conference,' eds. J. H. E. Jeffes and R. J. Tait, Institute of Mining and Metallurgy, London, 1974, p. 223.

[13] E. E. Lachowski and F. P. Glasser, *Min. Mag.*, 1973, **39**, 412.

[14] L. S. D. Glasser and S. K. Sharma, *Brit. Polymer J.*, 1974, **6**, 283.

[15] G. A. Barclay and E. G. Cox, *Z. Krist.*, 1960, **113**, 23.

[16] H. F. W. Taylor, *Amer. Mineral.*, 1962, **47**, 932.

[17] A. G. Merkulov and B. S. Khristoforov, *Rentgenogr. Mineral'n. Syr'ya, Vses. Nauchn.-Issled. Inst. Mineral'n. Syr'ya, Akad. Nauk S.S.S.R.*, 1964, **4**, 125 (*Chem. Abs.*, 1965, **63**, 9668e).

[18] G. T. Faust, *Amer. Mineral.*, 1951, **36**, 795.

[19] D. M. Roy and F. A. Mumpton, *Econ. Geol.*, 1956, **51**, 432.

orthosilicate structure of willemite was shown by Bragg and Zachariasen [20] and confirmed by Chin Hang *et al.*[21]

EXPERIMENTAL

Hemimorphite $Zn_4(OH)_2(Si_2O_7)\cdot H_2O$ from Friedensville, Pa., U.S.A. was used. Clean well developed crystals were hand-picked and ground to pass 100 mesh. All the experiments were done with the same batch. To prepare specimens with changed structure small quantities (*ca.* 2 g) of the ground material were heat-treated in air at different temperatures and for various times, in a platinum vessel placed in a crusilite furnace. The temperature was measured by a thermocouple located directly in the powdered sample. After heat-treatment the samples were removed rapidly from the furnace and allowed to cool in air. They were then ground and sieved to pass 100 mesh.

A Geigerflex diffractometer (Rigaku, Denki, Japan) with cobalt-anode radiation filtered by Fe was used for the X-ray diffraction measurements. Specimens for X-ray examination were ground to pass 325 mesh.

Simultaneous d.t.a.–t.g.a. (thermal gravimetric analysis) measurements were made in air with a model 429 STA analyser (Netzsch, West Germany) at 5 °C min^{-1}. Precisely 300 mg of the original hemimorphite powder (<100 mesh) was employed, with Al_2O_3 as the reference material.

The technique of direct trimethylsilylation was similar to that described previously.[2] The powdered solid (*ca.* 4 mg) was stirred vigorously at room temperature with hexamethyldisiloxane (5 cm^3), isopropyl alcohol (0.5 cm^3), and water (0.1 cm^3) in a tightly capped jar, by means of a magnetic stirrer. Chlorotrimethylsilane (3 cm^3) was added and stirring continued for 1 h. The organic layer was removed, clarified by centrifugation, and concentrated by distillation to remove unchanged $SiMe_3Cl$. Hexamethyldisiloxane (15 cm^3) and Amberlyst 15 ion-exchange resin (2 g) were added and the trimethylsilylation completed by stirring at room temperature overnight. The extract was filtered, concentrated by distillation, and examined by gas–liquid partition chromatography in the manner described previously. Peak areas in the chromatograms were measured by an electronic integrator (Hewlett–Packard model 3370A).

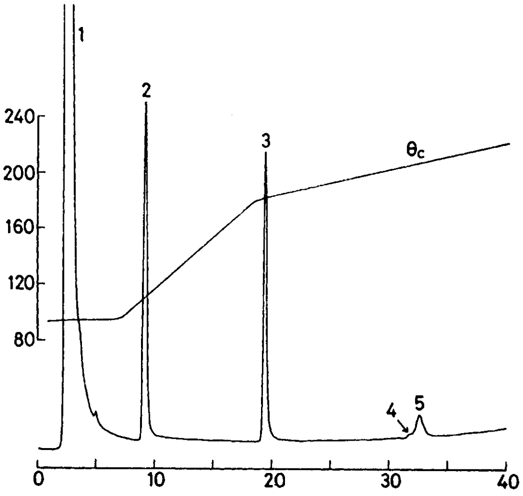

FIGURE 1 Chromatographic pattern for hemimorphite. The peaks are due to (1) solvent and trimethylsilyl derivatives of (2) SiO_4, (3) Si_2O_7, (4) Si_4O_{12}, and (5) Si_3O_{10}

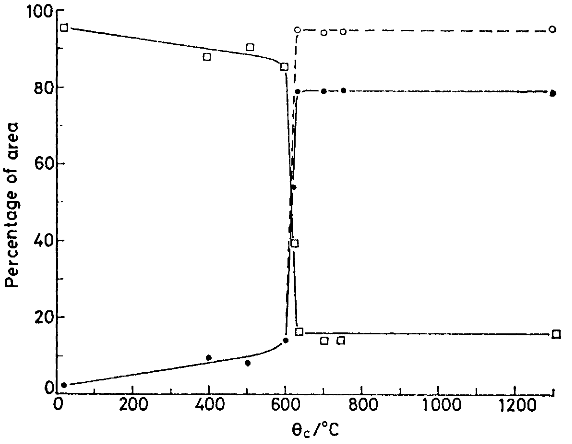

FIGURE 2 Percentage of total area in chromatograms due to derivatives of Si_2O_7 (□) and SiO_4 (●) for specimens of hemimorphite heated for 1 h at various temperatures; (○) 'corrected' values for SiO_4 derivative (see text)

RESULTS

Trimethylsilylation.—Typical chromatograms for hemimorphite under the conditions employed in this work have been illustrated elsewhere.[2,3] In the present study it was found that, of the total area in the chromatogram, 95.4% was attributable to the trimethylsilyl ($SiMe_3$) derivative of the Si_2O_7 group. The remainder was due to small amounts of the $SiMe_3$ derivatives of SiO_4 (2.4), Si_4O_{12} (2.1), and Si_3O_{10} (0.1%) anions. Calibration with standard solutions showed that the yield of the Si_2O_7 derivative was 82.8% of theoretical. The remainder may be due, in addition to the $SiMe_3$ derivatives of SiO_4, Si_3O_{10}, and Si_4O_{12}, to small amounts of $SiMe_3$ derivatives of higher silicate ions not detected chromatographically or to unavoidable losses associated, for example, with the Amberlyst treatment. The yield and pattern were unchanged when the weight of hemimorphite was varied by a factor of three, although the proportion of the Si_4O_{12} derivative in the products increased to *ca.* 5% and that of the SiO_4 derivative decreased to *ca.* 1% when up to 0.5 g of hemimorphite was employed, indicating that these products probably arise from side reactions which are not completely suppressed with the present technique. The absolute yields in this work are comparable with those reported by Sharma *et al.*[1]

Samples of the original hemimorphite powder were heat-treated for 1 h at temperatures between 400 and 1 300 °C, cooled in air, and examined by trimethylsilylation. A typical chromatogram is shown in Figure 1, which shows the pattern obtained for a sample heated for 1 h at 627 °C. The complete results, expressed as percentages of the total area in each chromatogram due to the peak indicated, are shown in Figure 2 for the major products of trimethylsilylation, *i.e.* the SiO_4 and Si_2O_7 derivatives, and for the minor products, Si_3O_{10} and Si_4O_{12}, in Figure 3. The latter values are less accurate due to the small areas of these peaks and their tendency to overlap on the chromatograms, as illustrated in Figure 1.

---

[20] W. L. Bragg and W. H. Zachariasen, *Z. Krist.*, 1930, **72**, 518.

[21] Chin Hang, M. A. Simonov, and N. V. Belov, *Soviet Phys. Cryst.*, 1970, **15**, 387.

The main feature is the abrupt change in the chromatographic pattern for samples which had been heated at 600—630 °C, with the originally dominant Si_2O_7 peak decreasing from >90 to 15—16% of the total area and a corresponding sharp increase due to the SiO_4 derivative (Figure 2). Accompanying these changes is a sharp increase in the percentage area due to the Si_3O_{10} derivative, from virtually zero at <600 °C to $>5\%$ at 627 °C, and a similar although less well defined decrease for the Si_4O_{12} derivative in the same region (Figure 3).

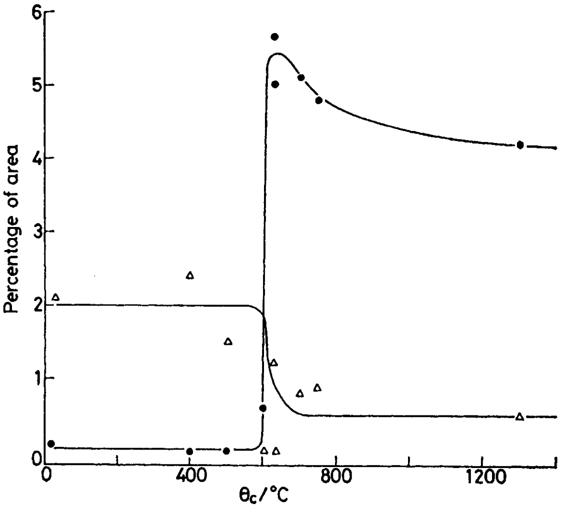

FIGURE 3 Percentage of total area in chromatograms due to derivatives of Si_3O_{10} (●) and Si_4O_{12} (△) for specimens of hemimorphite heated for 1 h at various temperatures

A series of experiments was performed in which small quantities (*ca.* 50 mg) of the original hemimorphite powder were heated for various times at 627 °C. The samples, held in platinum envelopes, were inserted rapidly into the hot zone of a tubular furnace then cooled in air after the time indicated. Figure 4 shows the results obtained for the SiO_4 and Si_2O_7 derivatives as a function of the time of heating. The proportion of Si_2O_7 derivative in the products decreased smoothly with time, accompanied by a corresponding smooth increase in that of the SiO_4 derivative. The curves for the minor products (Figure 5) show that the proportion of Si_3O_{10} derivative in the products was a maximum for samples which had been heated for 1 h at this temperature. The proportion of Si_4O_{12} derivative decreased slightly from *ca.* 2 to 1% of the total area for the same specimens.

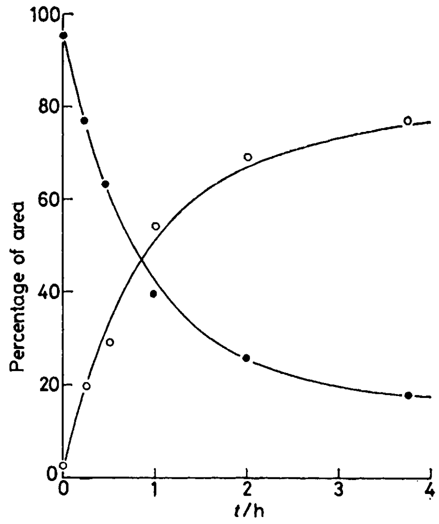

FIGURE 4 Percentage of total area in chromatograms due to derivatives of Si_2O_7 (●) and SiO_4 (○) for specimens of hemimorphite heated for various times at 627 °C

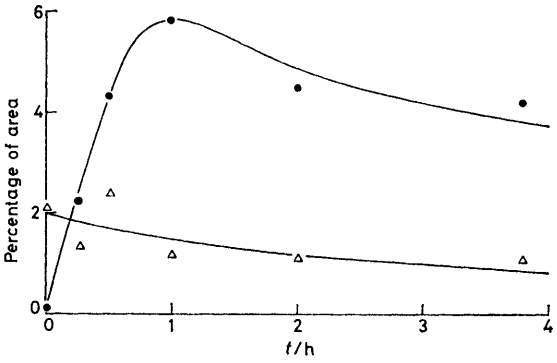

FIGURE 5 Percentage of total area in chromatograms due to derivatives of Si_3O_{10} (●) and Si_4O_{12} (△) for specimens of hemimorphite heated for various times at 627 °C

In Figure 6 the logarithm of the percentage area due to the Si_2O_7 derivative is plotted against the time of heating. The plot is linear for the initial stages, indicating a first-order decomposition, but departs from linearity for samples which had been heated for >1 h.

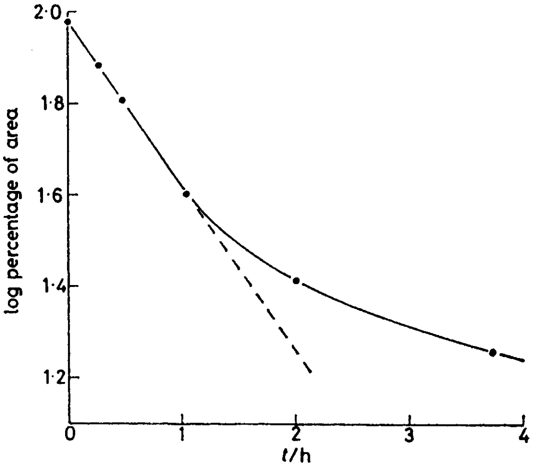

FIGURE 6 Plot of $\log_{10}$ (percentage of area due to Si_2O_7 derivative) against time of heating for specimens of hemimorphite heated at 627 °C

Simultaneous Thermal Analysis.—The results of the simultaneous d.t.a.–t.g.a. experiments are presented in Figure 7 and summarized in Table 1. Between 110 and 175 °C there is a loss by evaporation of adsorbed moisture, which amounts to *ca.* 0.2% by weight of the original material. Between 175 and 600 °C water of crystallization is lost, as indicated by a broad endopeak in the d.t.a. curve and a corresponding decrease in the t.g.a. curve. Quantitative evaluation of the t.g.a. shows a loss of 3.74% by weight of the dry hemimorphite, in agreement with the theoretical value of 3.740%.

Between 620 and 695 °C the dehydroxylation reaction (1)

$$Zn_4(OH)_2(Si_2O_7) \longrightarrow 2\,Zn_2SiO_4 + H_2O \qquad (1)$$

occurs, as indicated by the sharp d.t.a. endopeak at 650—695 °C. The loss of weight on t.g.a. amounts to 3.22% of the original dry hemimorphite, which is somewhat less than the theoretical value of 3.74%. At >695 °C there is no further loss of weight; an exopeak on d.t.a. between 835 and 910 °C, with its maximum at 885 °C, indicates a change in the structure of Zn_2SiO_4.

TABLE 1

Simultaneous d.t.a.–t.g.a. analysis of hemimorphite (300 mg) between 20 and 1 200 °C

θ_c/°C	d.t.a. peaks	t.g.a. curve, loss of weight (mg)	Caused by
110—175	Flat endopeak between 110 and 580 °C	0.70	loss of adsorbed moisture
175—600		11.22	loss of crystalline water
620—690	Sharp endopeak between 650 and 695 °C	9.65	loss of hydroxide water
>690	Exopeak between 835 and 910 °C		change in crystalline structure

X-Ray Diffraction.—The results for powdered samples are presented in Table 2 together with tabulated data for hemimorphite, β-Zn_2SiO_4, and willemite. The powder pattern for the original hemimorphite was identical with the tabulated data.[22] The pattern for hemimorphite heated for 1 h at 600 °C closely resembled that for the original material and may be ascribed to the ' modified hemimorphite ' having slightly altered cell dimensions as reported by Taylor.[16] The specimen heated for 1 h at 630 °C showed reflections identical with the data for β-Zn_2SiO_4,[16] and the sample heated for 1 h at 1 300 °C corresponded to willemite.[22]

TABLE 2

X-ray diffraction data for powdered specimens

Hemimorphite tabulated data [22]		Original hemimorphite		Hemimorphite heated for 1 h at 600 °C	
d/Å	*I*	*d*/Å	*I*	*d*/Å	*I*
6.70	8	6.54	7.7	6.49	8.6
5.40	7	5.35	4.5	5.35	3.7
4.58	6	4.60	1.7	4.55	2.3
4.35	1				
4.16	6	4.16	3.1	4.06	3.2
3.27	10	3.28	5.9	3.27	3.1
3.08	10	3.09	8.2	3.05	4.9
2.92	7	2.92	1.7	2.92	1.2
2.82	3				
2.68	3	2.67	0.5	2.69	0.6
2.63	3				
2.55	8	2.55	2.1	2.54	2.9
2.44	7	2.44	1.6	2.40	1.6
2.39	9	2.39	2.8	2.37	2.8
2.30	2				
2.22	1	2.22	0.7		
2.18	7	2.19	2.5	2.17	1.3
2.09	3	2.09	0.5	2.15	1.0
2.01	4	2.01	0.8	2.04	0.4
1.97	2			2.01	0.3
1.85	3	1.84	0.4	1.85	0.3
1.81	8	1.80	1.0	1.79	1.3
1.78	8	1.78	1.1		
1.75	1				
1.70	3	1.69	0.4		
1.67	4	1.66	0.4		
1.65	3	1.64	0.9		
1.62	4	1.61	0.4		
1.59	5	1.58	0.4		
1.56	5	1.56	0.4	1.54	0.4
1.54	1	1.53	0.2		
1.52	9	1.51	1.1	1.49	0.6
1.47	7	1.46	0.4	1.47	0.3
1.44	10	1.44	1.0	1.43	0.8
1.38	10	1.38	0.9	1.39	0.6
1.30	8	1.30	0.4		
1.28	10	1.29	0.7	1.28	0.4

TABLE 2 (*Continued*)

Hemimorphite heated for 1 h at 630 °C		β-Zn_2SiO_4 observed [16]	
d/Å	*I*	*d*/Å	*I*
4.03	1.3b	4.07	s,b
3.56	1.0b	3.55	vs,b
3.34	1.1	3.29	vw
2.83	0.4b	2.86	ms,b
2.47	1.1b	2.48	vvs,b
		2.31	vvw
		2.12	w
2.02	0.3	2.02	w
		1.8—1.9	vvw,d
1.65	0.2b	1.64	w,b
		1.57	vvw
1.51	0.2	1.52	mw
1.43	0.3	1.43	m
Hemimorphite heated for 1 h at 1 300 °C		**Willemite tabulated data [22]**	
d/Å	*I*	*d*/Å	*I*
4.03	2.8	4.02	4
3.47	6.7	3.48	6
2.81	7.2	2.84	8
2.62	7.6	2.63	9
2.30	3.6	2.32	8
2.13	0.4	2.22	1
2.07	0.8	2.17	1
2.01	0.3	2.01	2
1.99	0.7	1.93	4
1.91	2.6	1.85	8
1.73	0.6	1.74	1
1.68	0.5	1.69	1
1.63	0.8	1.63	2
1.58	0.7	1.60	2
1.55	0.5	1.55	2
		1.52	2
1.45	2.1	1.42	10
1.39	1.1	1.39	2
1.36	1.2	1.36	6

s = Strong, m = moderate, w = weak, b = broad, and d = diffuse.

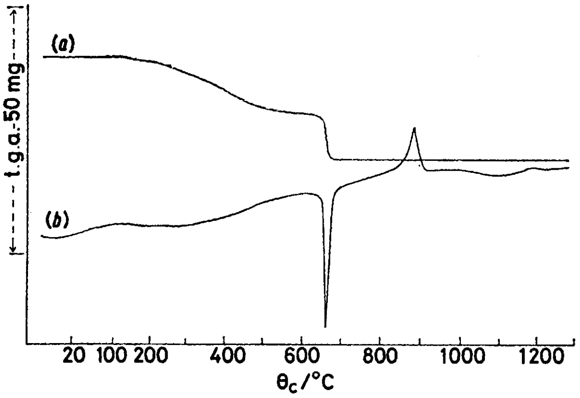

FIGURE 7 Results of simultaneous t.g.a. (*a*) and d.t.a. (*b*) of hemimorphite

---

[22] V. I. Michejev, ' Rentgenometricheskij opredelitel mineralov (*X*-Ray Diffraction Patterns of Minerals),' Gosgeoltechnizdat, Moscow, 1957.

DISCUSSION

The chromatographic data for the minor products of trimethylsilylation (Figures 3 and 5) show that the proportion of Si_4O_{12} derivative in the products was highest when the Si_2O_7 derivative was the main product of trimethylsilylation, suggesting that the former probably arises by side reactions between partially trimethylsilylated Si_2O_7 groups. This is in line with the observation that the yield of Si_4O_{12} derivative from unheated hemimorphite varied with the weight of hemimorphite employed. Under the conditions of this work the area due to this peak rarely exceeded 2% of the total area in the chromatograms, and no further significance is attached to the minor variations in this product observed in Figures 3 and 5.

Although the presence of the Si_3O_{10} derivative in the products may also be ascribed to side reactions of this nature (*i.e.* between incompletely trimethylsilylated SiO_4 and Si_2O_7 groups), it seems probable that the sharp increase in the proportion of this derivative for samples heated for 1 h above 600 °C (Figure 3), the gradual decrease in this product with temperature above 600 °C (Figure 3), and with time on further heating at 627 °C (Figure 5) reflect real changes in the structure of the solid during and after the hemimorphite $\longrightarrow$ β-Zn_2SiO_4 transition. The formation of β-Zn_2SiO_4 from hemimorphite requires the migration of both Si and Zn atoms, as discussed by Taylor,[16] and it is possible that $[Si_3O_{10}]^{8-}$ could be formed as an intermediate product by diffusion of Si into a vacant tetrahedral site adjacent to two others already occupied by Si. The slow decrease in the amount of the Si_3O_{10} derivative with temperature (Figure 3) and time of heating at 627 °C (Figure 5) may then be interpreted as a gradual increase in the ordering of Si and Zn in tetrahedral sites. Some of the Si_2O_7 derivatives observed in the products after heating at $\geqslant 627$ °C (Figures 2 and 4) may also represent groups genuinely present in a slightly disordered material.

Previous work with orthosilicate minerals [2] has shown that the SiO_4 group is particularly difficult to trimethylsilylate quantitatively, due to the highly labile nature of this anion in acidic media. It seems probable that, for the samples heated to >630 °C, the presence of 15—16 area % Si_2O_7 derivative in the chromatograms (Figure 2) is due mainly to dimerization of partially trimethylsilylated SiO_4 groups; this decreases the yield of the SiO_4 derivative for these specimens.

Assuming that the Si_2O_7 derivative in these specimens may be wholly attributed to side reactions of this nature, the areas of the SiO_4 peaks may be ' corrected ' to yield the values indicated by the broken line in Figure 2. Calibration with standard solutions of known concentration showed that the sensitivity (area per μg) is approximately the same for the SiO_4 and Si_2O_7 derivatives. The ' corrected ' values, which are the sum of the areas due to the SiO_4 and Si_2O_7 peaks, are therefore approximately proportional to the weight of derivative in the products. The correction corresponds to 15—16% of the total area in each chromatogram.

Side reactions of this nature probably account also for the non-linearity of the plot in Figure 6. The curve departs from linearity when the proportion of SiO_4 derivative in the products becomes significant. The linearity of the plot is preserved if the areas of the Si_2O_7 peaks for the samples heated for 2 and 3.75 h are corrected by *ca.* 7 and 14% respectively of the total area. Attempts to improve further the accuracy of the technique for orthosilicate minerals without, at the same time, lowering the yield for minerals of other structures, have not, so far, been successful. Similar difficulties have been reported by other workers.[13,14]

The overall pattern of structural changes which result from the heat-treatment of hemimorphite may be summarized as follows. The original disilicate $Zn_4(OH)_2(Si_2O_7)\cdot H_2O$ loses its molecular water between 175 and 600 °C and changes to modified hemimorphite $Zn_4(OH)_2(Si_2O_7)$ which has a slightly altered hemimorphite structure, with the anion $[Si_2O_7]^{6-}$ as the main structural unit. Heating between 600 and 630 °C causes dehydroxylation according to reaction (1) and yields a material with orthosilicate structure, identical with the β-Zn_2SiO_4 described by Taylor.[16] At >835 °C β-Zn_2SiO_4 transforms into willemite, α-Zn_2SiO_4, by an exothermic reaction indicated on d.t.a. curves. Both β- and α-Zn_2SiO_4 contain discrete orthosilicate anions $[SiO_4]^{4-}$ as the structural unit, although their crystalline arrangements differ as indicated by the *X*-ray diffraction patterns.

By means of the trimethylsilylation technique it has been possible to follow the changes in anionic constitution by direct measurement. The results are in excellent agreement with those from *X*-ray diffraction and thermal analysis. They confirm the disilicate structure of modified hemimorphite $Zn_4(OH)_2(Si_2O_7)$ and the orthosilicate structure of β-Zn_2SiO_4. The conversion β-$Zn_2SiO_4 \longrightarrow \alpha$-$Zn_2SiO_4$ occurs without change in the orthosilicate character of these materials.

We thank Dr. V. Seidl, Chemical University, Prague, for very helpful discussions, Mr. G. W. Caines, National Research Council of Canada, for performing some of the trimethylsilylation analyses, and Dr. L. S. D. Glasser for valuable comments on the manuscript and particularly for suggesting that Si_3O_{10} may be a real product of the hemimorphite $\longrightarrow$ β-Zn_2SiO_4 transition.

7/1626 *Received, 12th September*, 1977]