The Use of Trimethylsilylation to Study the Structure of Mineral Silicates

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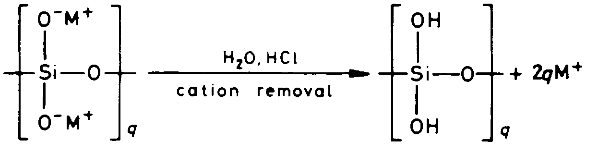
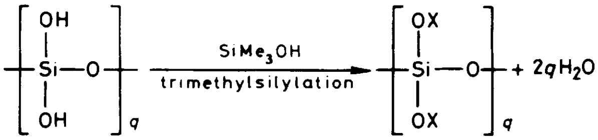
The distribution of aluminium in the tetrahedral layers of a muscovite, a margarite, and a phlogopite has been determined by trimethylsilylation.

The trimethylsilylation of olivine and of natrolite gives predominantly QM_4 ($Q = SiO_{\frac{4}{2}}$, $M = Me_3SiO_{\frac{1}{2}}$) and Q_3M_8 respectively, thus the molecular size of the polyorganosiloxanes produced is a reflection of the silicate anion size and suggests that the technique may be used to study the distribution of the aluminium in the tetrahedral layers of complex silicates. It has been shown that the distribution of aluminium in each of these layers is not random, but that the aluminium atoms are arranged in domains. The kinetics of the trimethylsilylation of the phlogopite have been examined; the results show that the cations are leached out at different rates and that there is no significant variation of silicate anion molecular size during the course of the trimethylsilylation reaction.

The trimethylsilylation reaction may be formally summarised as shown in equations (1) and (2) ($X = {}^{-}SiMe_3$). If it can be assumed that during this reaction the molecular size is unaltered, *i.e.* the value of q remains unchanged, then the method of trimethylsilylation can be used to determine silicate anion size. The polyorganosiloxane product is soluble in organic solvents and molecular size may then be determined by the methods of polymer physics. Since the first report by Lentz[1] in which he described the study of sodium silicates and concretes, trimethylsilylation has been extensively used for the determination of silicate anion size. Currell and Parsonage[2] have reviewed the various applications. More recently Ray and Plaisted[3] described the use of trimethylsilylation to determine the position of aluminium atoms in zeolites. A probable link between the distribution of aluminium atoms in the tetrahedral layer of sheet silicates and the $\bar{M}_n$ (number average molecular weight) distribution of the resulting polyorganosiloxanes was originally indicated by Currell *et al.*[4]



$$\left[-\overset{\displaystyle O^-M^+}{\underset{\displaystyle O^-M^+}{\overset{|}{\underset{|}{Si}}}}-O-\right]_q \xrightarrow[\text{cation removal}]{H_2O,\,HCl} \left[-\overset{\displaystyle OH}{\underset{\displaystyle OH}{\overset{|}{\underset{|}{Si}}}}-O-\right]_q + 2qM^+ \quad (1)$$



$$\left[-\overset{\displaystyle OH}{\underset{\displaystyle OH}{\overset{|}{\underset{|}{Si}}}}-O-\right]_q \xrightarrow[\text{trimethylsilylation}]{SiMe_3OH} \left[-\overset{\displaystyle OX}{\underset{\displaystyle OX}{\overset{|}{\underset{|}{Si}}}}-O-\right]_q + 2qH_2O \quad (2)$$

Experimental

Identification of Minerals and Mineral Analysis.—Margarite, muscovite, natrolite, and olivine were supplied by R. F. D. Parkinson, Shepton Mallet. Phlogopite (tradename Suzorite) was supplied by Marietta Resources Inc. Ltd. The purity of the ground material was checked by *X*-ray powder diffraction. The minerals were analysed by *X*-ray fluorescence spectroscopy for silicon, aluminium, calcium, iron, potassium, and magnesium (Table 1).

Table 1. Analysis of minerals

	Oxide composition (%)					
Mineral	SiO_2	Al_2O_3	CaO	FeO/ Fe_2O_3	K_2O	MgO
Margarite	20	32	34	3	trace	9
Muscovite	43	33	4	6	13	—
Natrolite *	60	32	—	8	—	—
Olivine	36	—	3	18	—	43
Suzorite	41	16	—	10	10	21

* Corrected for a chalk impurity.

Trimethylsilylation.—Propan-2-ol (100 cm^3), hydrochloric acid ($d = 1.18$ g cm^{-3}, 50 cm^3) and hexamethyldisiloxane (66.6 cm^3) were added to the silicate (10 g, 200 or 300 mesh) which had been slurried with water (40 cm^3). The mixture was stirred and heated at a reflux temperature of 72 °C. After the mixture had cooled it was centrifuged to give a hexamethyldisiloxane layer, a water–propan-2-ol layer, and a layer of residual mineral. The organic layer was carefully isolated and excess solvent removed at 60 °C (12 mmHg, 1.6×10^3 N m^{-2}) to yield a mixture of polyorganosiloxanes. The residual mineral after washing with water, propan-2-ol, and diethyl ether was dried to constant weight at an oven temperature of 105 °C. The aqueous layer, hexamethyldisiloxane layer, and the residual mineral were then subjected to a range of analytical procedures.

Analysis.—Molecular weights were determined on a Knauer vapour-phase osmometer calibrated with solutions of benzil in benzene. The aqueous layer produced was analysed for the presence of aluminium, magnesium, and iron by atomic absorption spectroscopy using a Varian Techtron AA6. The polyorganosiloxanes were quantitatively analysed by gel permeation chromatography (g.p.c.) and high performance liquid chromatography (h.p.l.c.).

Gel permeation chromatography was carried out by adding a portion of polyorganosiloxane (*ca.* 2.5 g) to the top of a glass column (32 × 2.2 cm inside diameter), with a porous Teflon disc at the bottom, which had previously been wet packed with Biobeads (SX1 200—45 mesh) and allowed to swell in chloroform–propan-2-ol (3 : 1) mixture for 40 h. The effluent was collected in fractions (*ca.* 2 cm^3) and the eluant allowed to evaporate at 60 °C for 24 h. The residues were weighed and analysed by h.p.l.c.

The polyorganosiloxanes were also analysed directly by h.p.l.c. (with a column bank of seven micro styragel columns with permeability ranges from 1×10^2 to 1×10^4 Å, which was calibrated using Waters Associates polystyrene standards,

Table 2. Yield and composition of polyorganosiloxanes obtained by trimethylsilylation [a]

Mineral	Recovered mineral (g)	Polyorganosiloxanes Yield (g)	QM_4 (%)	Q_2M_6 (%)	Q_xM_8 [b] (%)	Q_xM_{10} [c] (%)	Q_xM_y [d] (%)
Margarite	4.4	1.5	73.4	9.7	15.7	trace	0.7
Muscovite	8.5	1.2	80.8	1.9	6.0	13.1	1.3
Natrolite	*e*	2.5	19.7	1.2	78.5	trace	0.0
Olivine	0.7	4.0	64.3	9.2	11.0	12.8	2.0
Phlogopite	7.0	2.0	48.7	6.0	7.8	7.3	32.7

[a] All reactions were of 3 h duration. [b] $x = 3, 4,$ or 8. [c] $x = 4, 5,$ or 6. [d] Polyorganosiloxanes of molecular weight >1 050 : $x > 6, y > 10$. [e] Figure unreliable due to chalk impurity.

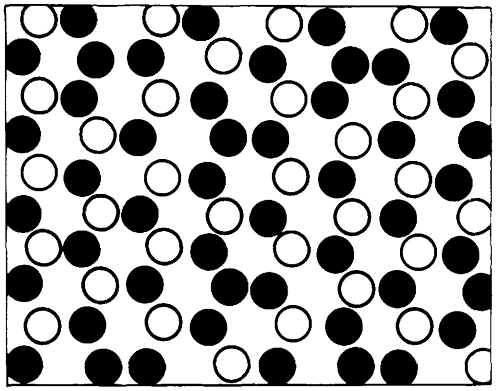


Figure 1. A possible regular distribution in a tetrahedral silicate sheet where Al : Si = 1.5 : 1. Al (●), Si (○)

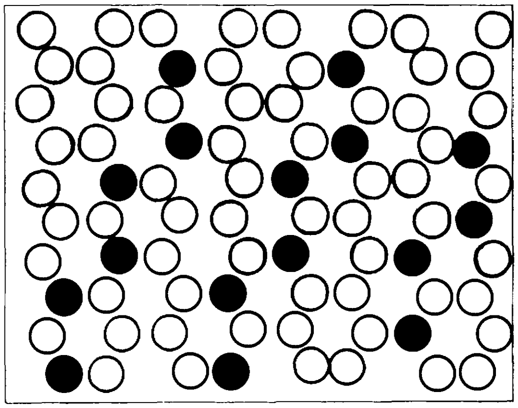


Figure 2. A possible regular distribution in a tetrahedral silicate sheet where Al : Si = 0.25 : 1. Al (●), Si (○)

a range of polydimethylsiloxane fluids, and also a range of Q_xM_y polymers). For quantitative work t-butylbenzene was used as an internal standard.

Results and Discussion

Mineral Structure.—Table 1 gives the oxide composition of the minerals used. Olivine is an orthosilicate containing SiO_4^{4-} ions. Natrolite contains a framework of linked tetrahedra which may be described as closely linked chains; these may be regarded as having a basic unit of five tetrahedra linked by an edge each. Since natrolite contains two aluminium to three silicon ions the tetrahedra may be considered as of two types, those with aluminium and those with silicon. If this is taken into account in the repeat unit it will be found to consist of silica tetrahedra either as isolated SiO_4^{4-} or three linked tetrahedra of $Si_3O_{10}^{8-}$, probably 25% SiO_4^{4-} and 75% $Si_3O_{10}^{8-}$. Both these samples contain impurities, in the case of natrolite the figures given for oxide composition are corrected to allow for chalk impurity. For the mica minerals the data give the elemental formulae given below.

phlogopite: $K_{1.96}Mg_{4.13}Fe_{1.18}[Si_{6.32}Al_{1.68}O_{20}](OH,F)_4$

muscovite: $K_{2.49}Ca_{0.64}Fe_{0.69}Al_{4.12}[Si_{6.46}Al_{1.54}O_{20}](OH,F)_4$

margarite: $Ca_{5.87}Fe_{0.37}Al_{2.1}[Si_{3.23}Al_{4.77}O_{20}](OH,F)_4$

The silicate anion size in these minerals depends on both the overall amount and the distribution of the aluminium in the tetrahedral layers. The aluminium : silicon ratios in the tetrahedral layers are as follows: margarite, 1.5 : 1; phlogopite, 0.3 : 1; muscovite, 0.2 : 1. Different distributions of aluminium atoms (at the same ratio Al : Si) will give the possibility of very different silicate anion size distributions. For example, Figure 1 shows a possible distribution in a sheet where Al : Si = 1.5 : 1; in this case all silicon atoms are isolated, *i.e.* all nearest neighbours are aluminium, and to obtain the linkage of two or more silicon atoms it would be necessary to have a structure involving ' bunching ' or domains.

Figure 2 shows a possible distribution with Al : Si = 0.25 : 1; in this case many silicon atoms are linked together and none is isolated. To obtain isolated silicon atoms, ' bunching ' of aluminium atoms around a single silicon atom is required.

Trimethylsilylation.—Trimethylsilylation of olivine should give only QM_4; similarly natrolite should give a mixture of QM_4 and Q_3M_8 in the ratio of 25 : 75. The yields and the composition of polyorganosiloxanes which are actually produced after a reaction time of 6 h are shown in Table 2. Although the minerals are not 100% pure, olivine gave QM_4 (64.3%) and natrolite gave QM_4 (19.7%) and Q_3M_8 (78.5%). The higher molecular weight products may be present as a result of impurities in the rock samples although polysilicic acid redistribution cannot be ruled out. In the case of the layer silicates, assuming both regular distribution of Al in the layers and the absence of side reactions, margarite (Al : Si = 1.5 : 1) would be expected to give a 100% yield of QM_4 while phlogopite (Al : Si = 0.3 : 1) and muscovite (Al : Si = 0.2 : 1) would be expected to give a high molecular weight material with virtually no QM_4 or other low molecular weight products (see Figures 1 and 2).

Margarite (73.4% QM_4) basically fulfils these expectations

Table 3. The leaching of phlogopite mineral (1 g) by hydrochloric acid (5 mol dm^{-3}; 45 cm^3) at 20 °C

Time	Weight loss	Ions extracted (%)			
(h)	(g)	K	Mg	Al	Fe
3.0	—	9.0	12.0	7.8	7.0
19.5	0.26	25.9	36.6	27.2	21.9
43.0	0.42	60.3	76.6	61.4	43.3
70.0	0.48	57.8	78.5	60.9	42.4
90.0	0.49	64.5	92.1	73.4	51.2

Table 4. The leaching of phlogopite mineral (1 g) during a standard trimethylsilylation reaction

Time	Ions extracted (%)			
(h)	K	Mg	Al	Fe
2.2	35.4	56.3	30.5	35.4
6.0	43.7	64.4	41.2	43.7
13.3	61.0	83.8	53.2	61.0
18.3	61.7	97.8	58.2	61.7
23.3	71.6	98.6	64.7	71.6

Table 5. The statistical analysis of the polyorganosiloxane distribution derived from the mineral phlogopite by h.p.l.c. [a]

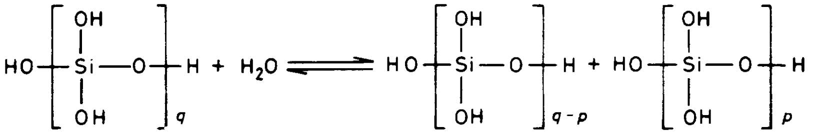
Molecular weight ($\times 10^{-3}$)	Mean weight per cent	Standard deviation
0.4 (QM_4)	51.2	2.0
0.6 (Q_2M_6)	7.1	0.4
0.9 (Q_xM_y) [b]	8.3	0.7
1.0 (Q_xM_y) [c]	6.9	0.3
1.8	2.8	0.7
2.3	2.5	0.7
3.0	2.4	0.7
3.8	2.4	0.6
5.0	2.4	0.7
6.3	2.4	0.6
8.3	2.3	0.5
11.0	2.2	0.5
14.1	2.0	0.4
18.2	1.5	0.2
22.9	1.2	0.2
30.2	0.7	0.3
39.8	0.4	0.2
50.1	0.3	0.2
66.0	0.3	0.2
83.2	0.2	0.2
109.6	0.1	0.1

[a] These analyses were obtained from six different experiments in which reaction mixtures were heated under reflux for times of 1, 2, 3, 4, 5, and 6 h, and one further experiment in which the hexamethyldisiloxane layer was sampled for analysis at reflux times of 10 h, 15 h, and then at five-hourly intervals up to 65 h. [b] $y = 8$. [c] $y = 10$.

but the phlogopite and the muscovite show strong divergence giving high yields of QM_4 (48.7% and 80.8% respectively). It should be noted from Table 2 that (*a*) the muscovite gives the lowest yield of polyorganosiloxane and the highest amount of recovered mineral; and (*b*) the phlogopite gives a higher yield of polyorganosiloxane and that this has a broad spread of components of different molecular weights.

These results can be rationalised on the basis that during trimethylsilylation the tetrahedral sheets fragment at Si–O–Al bonds and that if large areas of the tetrahedral sheets are void of these bonds they will, depending on their size, either give very high molecular weight products (as in the case of phlogopite) and or be relatively non-reactive and give reduced total yields. The distribution of aluminium in the tetrahedral sheets of these micas may be discussed using the notation where, for example, ${}_1Si_3Al_0$ is taken to represent one silicon atom covalently bonded (through oxygen) to three more silicon atoms; similarly ${}_1Si_2Al_1$ represents one silicon atom covalently bonded to two silicon and one aluminium atom. There are in total four possibilities: ${}_1Si_3Al_0$, ${}_1Si_2Al_1$, ${}_1Si_1Al_2$, ${}_1Si_0Al_3$. The distribution of aluminium in the tetrahedral sheets of the three micas may be summarised as follows. (*i*) Margarite is mainly composed of ${}_1Si_0Al_3$ units which arise from a distribution of aluminium atoms similar to that in Figure 1. There is some evidence (formation of Q_2M_6 and Q_3M_8) for the presence of a small number of units containing two and also three silicon atoms. (*ii*) Phlogopite has a distribution of aluminium atoms which gives a gradual progression from ${}_1Si_0Al_3$, through areas with intermediate proportions of aluminium to the void areas, $({}_1Si_3Al_0)_n$. This results in a broader spread of molecular weight species than seen in (*i*) and (*iii*). (*iii*) Muscovite has a distribution of aluminium atoms in which different areas are either very high in aluminium (*i.e.* ${}_1Si_0Al_3$) or completely void [*i.e.* $({}_1Si_3Al_0)_n$]. The areas of high aluminium concentration give rise to QM_4. The void areas do not undergo trimethylsilylation and a low total yield of polyorganosiloxanes is produced. The overall result is a low yield of polyorganosiloxanes which mostly consists of QM_4.

Reliability of trimethylsilylation as a guide to silicate structure. An important potential cause of error is the possibility of polymerisation–depolymerisation reactions occurring at the polysilicic acid stage (see below, for example). However, our results have shown that for natrolite and olivine the structures of the Q_xM_y polyorganosiloxanes do reflect the known structure of the minerals. The removal of the cations is fast in olivine and natrolite and silicic acids will be produced, giving sufficient time for silicic acid redistribution. However, this does not appear to occur to any great extent.



$$HO\left[Si(OH)_2-O\right]_q H + H_2O \rightleftharpoons HO\left[Si(OH)_2-O\right]_{q-p} H + HO\left[Si(OH)_2-O\right]_p H$$

In the case of phlogopite we have shown that there is a significant difference between the rates of leaching out of atoms in different sites. This difference occurs not only during straightforward acid attack (Table 3) but also during trimethylsilylation (Table 4). We have previously suggested [5] that this pattern of atom leaching is compatible with the following model. The interlayer magnesium cations are easily leached and are removed from the structure very quickly along with some iron and aluminium atoms. The potassium and the aluminium ions/atoms are removed much more slowly as their presence is required to maintain ionic neutrality and structural order of the remaining mineral silicate backbone. This maintenance of mineral structural order prevents the excessive build-up of silicic acids in solution and thus decreases the potential for silicic acid redistribution. This reaction, which is extremely fast, results in the production of Q_xM_y polyorganosiloxanes which reflect the aluminium distribution of the tetrahedral layer. This is further confirmed by the fact that the composition of the polyorganosiloxane products does not vary with changes in reaction time. The products obtained from the phlogopite have been completely analysed at reaction times of 1, 2, 3, 4, 5, and 6 h, and also at five-hourly intervals up to 65 h; Table 5 summarises these results, and the statistical treatment indicates the low level of variation.

Acknowledgements

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References

1 C. W. Lentz, *Inorg. Chem.*, 1964, **3**, 574; Special Report 90, Highway Research Board, Washington D.C., 1966, p. 266; *Mag. Conc. Res.*, 1966, **18**, 231.
2 B. R. Currell and J. R. Parsonage, *J. Macromol. Sci. Chem.*, 1981, **16(1)**, 141.
3 N. H. Ray and R. J. Plaisted, *J. Chem. Soc., Dalton Trans.*, 1981, 1260.
4 B. R. Currell, H. G. Midgley, M. A. Seaborne, and C. P. Thakur, *Br. Polym. J.*, 1974, **6**, 229.
5 R. S. Atwal, S. Bicknell, C. B. Cook, B. R. Currell, H. G. Midgley, A. J. Mooney, and J. R. Parsonage, *Br. Polym. J.*, 1979, **11**, 213.

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