Trimethylsilylation of Linear and Cyclic Tetrameric Silicates

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Summary The suppression of cyclisation side reactions during silicate derivatisation by the method of Tamás *et al.*, using dimethylformamide as solvent, is demonstrated; the cyclic nature of the silicate skeleton in Pb_2SiO_4 is confirmed.

ALTHOUGH the method of trimethylsilylation, in which a silicate ion is converted into an organic (TMS) derivative, is valuable in studying structures, especially of amorphous silicates, there is always a danger of structural change occurring before derivatisation is complete.

Calhoun *et al.*[1] recently reported that when the Lentz method of trimethylsilylation[2] is used to derivatise the silicate skeleton of $Ag_{10}Si_4O_{13}$, known to consist of the linear tetramer ($Si_4O_{13}{}^{10-}$),[3] the product consists mainly of the derivative of the cyclic tetrameric silicate ion, $Si_4O_{12}{}^{8-}$. They devised a modified version of the direct method[4] which largely, although not entirely, suppressed cyclisation. Application of this new technique to lead orthosilicate glass produced no cyclic tetramer derivative, suggesting that its presence, reported by several investigators,[5–9] arises from cyclisation of the linear tetramer. This casts doubt on the presence of the cyclic tetramer in M-, M′- and H-Pb_2SiO_4, previously indicated by trimethylsilylation[6,9] and by the molybdate method and paper chromatography.[7] There is a risk of cyclisation with these latter methods as they also require dissolution of the silicate in acid. Doubts are also cast on the connectivities of Portland cement paste polysilicate fractions determined by trimethylsilylation.[10]

To resolve some of these doubts, $Ag_{10}Si_4O_{13}$ (kindly supplied by M. Jansen) and H-Pb_2SiO_4 (prepared by recrystallising a glass made from PbO and quartz) were trimethylsilylated by the procedure of Tamás *et al.*[11] This procedure is widely used for the study of cement pastes, and has previously been shown[12] to give satisfactory results with artificial mixtures of anhydrous calcium silicates. The products were dried at 110 °C and identified by g l c as described previously[13,14]

The major derivative obtained from $Ag_{10}Si_4O_{13}$ was that of the linear tetramer, eluting 16 25 min after the upper limit of the temperature programme, 265 °C, had been reached It accounted for 99 9% of the total peak area, the remaining 0·1% being due to the cyclic tetramer derivative, eluting at 245 °C The H-Pb_2SiO_4 yielded only the cyclic tetramer derivative

These results confirm the cyclic nature of the silicate skeleton in H-Pb_2SiO_4 The efficient suppression of side reactions by the Tamás method is demonstrated, and it seems unlikely that any gross rearrangement occurs when it is used to derivatise cement pastes This gives some confidence in connectivities derived in this way

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