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Micro-scale trimethylsilylation for the characterisation of some silicate ions

During the study in 1983 of the new mineral mattheddleite, $Pb_{20}(SiO_4)_7(SO_4)_4Cl_4$, from Leadhills, Scotland (Livingstone *et al.*, 1987), we wanted to confirm that only monomeric silicate anions were present, but the available material was limited to microgram quantities. It is possible to distinguish between SiO_4^{-4}, $Si_2O_7^{-6}$, and other low molecular weight silicate ions in minerals by treatment with acids in the presence of trimethylsilylation reagents. The various silicic acid species released from the solid samples are converted into neutral, volatile trimethylsilyl (TMS) derivatives, $Si[OSi(CH_3)_3]_4$ ('Si_1'), $Si_2O[OSi(CH_3)_3]_6$ ('Si_2'), etc., which can be isolated and quantified by gas chromatography (GC). The major TMS product in each case corresponds to the anion originally present, although hydrolysis and condensation of the silicic acids before they are trapped as TMS derivatives may give rise to small amounts of TMS derivatives not characteristic of the parent silicate. The trimethylsilylation technique, in various modifications, has been used extensively to speciate silicate ions (see review by Currell and Parsonage, 1981) but the published methods require relatively large samples, from a few to 500 mg. However, it was found that the method of Kalmychkov (1982), which employs trimethylchlorosilane, a base (pyridine) and an optional co-solvent such as dimethylformamide, can be adapted to a micro-scale if, as is common practice for the trimethylsilylation of organic compounds, the reaction mixture is injected into a gas chromatograph without further treatment.

A few crystal fragments of mattheddleite (<10 µg) were treated at 20°C with trimethylchlorosilane (2 µl), dry pyridine (1.5 µl) and dry dimethylformamide (1.5 µl), typically for 1 hour, then 0.5 µl of the mixture was analysed by GC (for GC conditions see Table 1). The chromatogram showed a large peak due to Si_1, and a small peak due to Si_2 formed as a byproduct. No peak due to the TMS derivative of SO_4^{-2} was present in the chromatograms of mattheddleite and ellestadite, nor was one seen when ammonium sulphate, which is readily trimethylsilylated, was treated in the same way. This, the sulphate TMS derivative appears to be unstable under the analytical conditions employed (cf. Mawhinney, 1983).

The results for mattheddleite and some refer-

Table 1. Gas chromatographic analysis of trimethylsilylated silicates

Mineral	Anion present	Ratio of peak areas, Si_1/Si_2
Mattheddleite		15.7
Ellestadite	SiO_4^{-4}	9.0
Bultfonteinite	SiO_4H^{-3}	19.0
Thaumasite	$SiO_6H_6^{-2}$	10.1
Barysilite	$Si_2O_7^{-6}$	0.01
Hemimorphite	$Si_2O_7^{-6}$	<0.11

GC conditions. 25 m silica capillary column coated with methyl-phenyl-silicone CPSil8; 100°C for 6 min, then rising at 10° per min; flame ionisation detector. Retention indices: Si_1, 1180; Si_2, 1670 (n-alkane calibration, undecane = 1100, dodecane = 1200, etc.)

Samples used. Ellestadite, Ettringer, Bellerberg, Laacher See, Germany (BM 1980,648). Bultfonteinite, Nchwaning, Hotazel, Cape Province, S. Africa. Thaumasite, Paterson, New Jersey, USA. Barysilite, Harstig mine, Pajsberg, Varmland, Sweden (BM 64352). Hemimorphite, Rutland Cavern, Matlock Bath, Derbyshire, UK.

ence minerals of known structure are compared in Table 1. Since mattheddleite and the nesosilicates ellestadite (Sudarsanan, 1980) and bultfonteinite (McIver, 1963) give comparable, high $Si_1:Si_2$ ratios, while the sorosilicates barysilite (Lajzerowicz, 1964) and hemimorphite (Barclay and Cox, 1960) give low $Si_1:Si_2$ ratios, it was concluded that mattheddleite contains only monomeric silicate anions. Trimethylsilylation cannot distinguish between unprotonated and protonated SiO_4^{-4} ions such as those in bultfonteinite, and Table 1 also shows that the unusual ion $Si(OH)_6^{-2}$ in thaumasite (Edge and Taylor, 1971) yields the orthosilicate TMS derivative, with loss of two OH^- groups. Forsterite, idocrase and zoisite failed to produce more than traces of TMS derivatives under the same conditions. Some non-silicate minerals can also be analysed in this way, for example pyromorphite and mimetite, which give GC peaks at retention indices 1280 and 1370, respectively, attributed to the phosphate and arsenate TMS compounds (cf Butts and Rainey, 1971). Further work is clearly needed to test the scope and potential of this promising diagnostic micro-technique, but lack of facilities have prevented the author from continuing the investigation.

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