

### Isotopic Analysis of Silicon by Solid-Source Mass Spectrometry using Negative Ions

AN A.E.I. mass spectrometer, type *M.S.2/S.*, fitted with an electron multiplier and having a triple tungsten filament as source for the thermal ionization of solids is being used for measurements of the abundance of silicon isotopes.

The instrument normally records the amplified current peaks of positive ions. In the case of silicon, it has not been possible so far to detect a positive ion from thermal ionization, but after reversing the polarity of the accelerating voltage and magnetic field of the instrument, negative ions have been measured corresponding to  $\text{SiO}_3^-$  at values of  $m/e$  of 76, 77 and 78.

The filament source is loaded with an alkali silicate, and the best results are obtained from caesium silicate. This is in accordance with the ionization potential of caesium, which is the lowest for the natural alkali element series; thus no ions are obtained from sodium silicate and only small peaks from potassium silicate.

D. C. NEWTON  
J. SANDERS  
A. C. TYRRELL

The Plessey Co., Ltd., Caswell,  
Towcester, Northants.  
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### High-Energy Oxygen Ions in Carbon Dioxide Mass Spectra

MASS spectra of carbon dioxide have been recorded using a low accelerating voltage and magnetic scanning. Under these conditions, a variant of those due to Mohler *et al.*<sup>1</sup>, ions with more than thermal energies will appear as satellite peaks in the spectra. The energies of the ions can then be derived from the separation of the peaks by the use of the mass spectrometer focusing equation.

A high-energy state in oxygen ions has been observed as a satellite on the high-mass side of the main peak due to thermal energy oxygen ions. The energy of this state in oxygen ions was found to be 3.5 V. when the energy of the ionizing electrons was 70 V. The apparent appearance potential was 35 V. (the voltage scale being corrected by the known value for the thermal energy peak of the oxygen ion<sup>2</sup>).

These values would suggest that the ions were due to the dissociation of doubly charged ions<sup>1</sup>; those possible are  $\text{O}_2^{2+}$ ,  $\text{CO}^{2+}$  or  $\text{CO}_2^{2+}$ . It will be seen that the appearance potential is lower than those found for  $\text{O}_2^{2+}$  from oxygen (50 V.) and for  $\text{CO}^{2+}$  from carbon monoxide, namely, 42 V. (ref. 2). Ions of  $\text{O}_2^+$  were not detected under the present conditions; and thus if the mechanism is  $\text{O}_2^{2+} \rightarrow 2 \text{O}^+$ , a previous reaction similar to one suggested by Ogryzlo and Schiff<sup>3</sup>, namely,  $\text{CO}_2 + \text{O} \rightarrow \text{CO} + \text{O}_2$ , seems preferable to a rearrangement reaction involving O or a secondary reaction induced by pressure. The  $\text{CO}_2^{2+}$  mechanism, namely,  $\text{CO}_2^{2+} \rightarrow \text{CO}^+ + \text{O}^+$ , is the most probable, as  $\text{CO}_2^{2+}$  ions exist in the mass spectrum and the appearance potential of the  $\text{O}^+$  ion state is comparable to that of  $\text{CO}_2^{2+}$  ions, about 36 V. by comparison with the known value for  $\text{A}^{2+}$  ions<sup>2</sup>. This

reaction was also postulated by Newton<sup>4</sup> to explain other phenomena in the mass spectra of carbon dioxide. However, if the reaction is indeed  $\text{CO}_2^{2+} \rightarrow \text{CO}^+ + \text{O}^+$ , a definite energy-state would be expected in the  $\text{CO}^+$  ions.

Only the main ion peak, together with high-energy tailing, was apparent in the  $\text{C}^+$ ,  $\text{CO}_2^{2+}$  and  $\text{CO}^+$  ion peaks. The main excitation energy found for  $\text{O}^+$  ions from carbon monoxide under these conditions (70 V. ionizing electrons, 230 V. accelerating voltage) was 2.4 V., compared with Hagstrum's value of 1.5 V. by the retarding potential method and Berry's value of 0.65–2.5 V. by the deflexion method<sup>2</sup>. When ionizing electrons of 70-V. energy were used, the  $\text{O}^+$  ion peak from oxygen showed a high-energy tail but no evidence of a discrete high-energy state.

The ratio between the ions of high-energy state and the thermal energy ions was affected by variations in the ion repeller voltage, which altered the time of residence of the ions in the ion chamber. Low voltages, down to 0.5 V., favoured the high-energy state, presumably because the time available for dissociation was increased, whereas higher voltages, up to 8 V., resulted in the predominance of the thermal-energy ions.

The mass spectrometer is a 10-cm. radius 90° deflexion A.E.I. instrument with a source of Nier type.

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R. M. S. HALL

Central Electricity Research Laboratories,  
Leatherhead, Surrey.

<sup>1</sup> Mohler, F. L., Dibeler, V. H., and Reese, R. M., *J. Chem. Phys.*, **22**, 394 (1954).

<sup>2</sup> Values taken from Field, F. H., and Franklin, J. L., "Electron Impact Phenomena" (Academic Press, New York).

<sup>3</sup> Ogryzlo, E. A., and Schiff, H. I., *J. Chem. Phys.*, **27**, 628 (1960).

<sup>4</sup> Newton, A. S., *J. Chem. Phys.*, **20**, 1330 (1952).

## METALLURGY

### Formation of Fayalite in Roast Reduced Jaspilite

A MAGNETIZING roasting treatment of a fine-grained haematite-quartzite known as jaspilite, occurring in South Australia, is at present being evaluated<sup>1</sup>. When heated in reducing gases at appropriate temperatures, 550–650° C., the haematite in jaspilite is converted to magnetite. Extensive microcracking also occurs in the quartz matrix (Fig. 1A). This cracking allows freer access of reducing gases to the haematite particles undergoing reduction and facilitates grinding prior to magnetic concentration<sup>2</sup>.

In contrast to prior investigations<sup>3</sup>, roast reduction treatments much above 650° C. have led to lower rates of reduction, lower recoveries of magnetite, and less apparent cracking.

One reason for this, other than the effect of increased temperature in reducing the tendency of quartz to crack and part from the haematite, has been found to be the formation of fayalite ( $2\text{FeO} \cdot \text{SiO}_2$ ), by a solid-state diffusion reaction at the operating temperature.

That fayalite will form when haematite is reduced in the presence of silica at higher temperatures, 800–1,000° C., has previously been reported<sup>4,5</sup>. Indeed,