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An Investigation of Dust Particles Found in a Ceramic Processing Environment

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Abstract

Clean rooms have potential advantages for ceramic powder processing. In order to determine the degree of contamination by air-borne particles present in a normal processing environment, and therefore, to give an indication of the possible benefits of a clean environment, a survey of samples taken from clean-room prefilters was carried out. Based on a qualitative analysis using EDAX peak height, particles have been grouped, according to the major elements present, and microstructural correlations made. The effect of contaminants on ceramic processing is examined.

Die Verarbeitung keramischer Pulver unter Reinraumbedingungen läßt Vorteile erwarten. Um den Grad der Verunreinigung durch die in normaler Umgebung vorhandenen Staubpartikel zu bestimmen und damit einen Aufschluß über die möglichen Vorteile einer reinen Umgebung zu erhalten, wurden Proben aus Reinraum-Vorfiltern untersucht. Auf Grund qualitativer EDAX-Intensitäts Analysen wurden die Teilchen gemäß der Hauptelemente zusammengefaßt und mikrostrukturelle Beziehungen aufgestellt. Auf die Auswirkungen der Verunreinigungen auf die Keramikherstellung wird eingegangen.

Les salles blanches présentent des avantages potentiels lors l'élaboration céramiques. Dans le but de déterminer le degré de contamination par les particules contenues dans l'atmosphère lors de l'élaboration dans un environnement normal et, par conséquent pour donner des indications sur les avantages potentiels du travail en salle blanche, on a examiné des échantillons provenant des pré-filtres de la salle blanche. On a groupé les particules selon les principaux éléments présents, déterminés par la hauteur de pics en analyse quantitative EDAX, et on a effectué des corrélations microstructurales. On examine ici l'effet des produits de contamination sur le traitement des poudres lors de l'élaboration des céramiques.

1 Introduction

The use of 'clean-rooms' is standard practice within the semi-conductor, micro-electronics and optical fibre industries. 'Clean' in this context normally means using atmospheres having controlled numbers of air-borne particles of specified dimension. Abbreviated examples of common standard conditions are given in Table 1. (The class description contains further restrictions with regard to numbers of larger particle sizes, sampling floor area, and room positive pressures.) Class D level of cleanliness is widely used in commercial practice.

In the ceramic powder processing industries the use of clean environments has the potential advantage of preventing contamination by particles of dimensions larger than the anticipated sintered grain size and thus the ability to create damaging microstructural defects. Much air-borne dust is organic in nature, but this nonetheless may create large voids in a compacted powder during burn-out when the powder is heated to sintering temperature. Such large voids may not readily be removed during sintering.[2] Inorganic dusts can give rise to metallic contamination which will be of significance in, for example, the production of thin films of multilayer capacitor dielectric materials, where film thicknesses may not be much greater than the contaminant particle dimensions. The use of clean processing areas in the ceramics industries is in consequence being evaluated for a range of material types

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Table 1. Examples of 'clean' environments[1]

Class of environmental cleanliness	*Maximum permitted number of particles m^{-3}*	
	Size 0·3 μm	*Size 0·5 μm*
D	1 000	350
E	10 000	3 500
F	ns	3 500
H	ns	35 000
J	ns	350 000

ns = Not specified.

including alumina, barium titanate and transformation-toughened zirconia. The Division of Ceramics, University of Leeds, has a clean-room facility which allows work to be carried out at dust count levels down to 3500 m^{-3} of particles $>0{\cdot}5\,\mu m$ in dimension using Class 100 Federal Standard[3] (class F BSI) laminar air-flow cabinets.[1,4] The clean-rooms themselves normally have particle counts of $<35\,000\,m^{-3}$ (particles $>0{\cdot}5\,\mu m$), as determined by a continuous reading, laser particle count analyser (Malvern LPC-500).

There is a considerable amount of information concerning atmospheric dust concentration and composition in urban and rural environments, including that from sampling carried out within the urban Leeds environment.[5] Sampling is normally divided into coarse (2·5 to 15 μm) and fine (<2·5 μm) particle fractions. Particles of sizes 15 μm and below are inhaled by the human respiratory system, while particles below 2·5 μm can penetrate the alveoli.[6] Such sampling has shown that particles containing the ions Cl, NO_3, SO_4 and NH_4 are each present in air-borne dusts at greater than the one percent level. The cations, Na, K, Mg, Ca, Fe, Pb, Cu, Zn and Mn were found to be present in smaller quantities.[7] A mean particle concentration of 35·5 $\mu g\,m^{-3}$ was measured in the Leeds urban environment of which 12 $\mu g\,m^{-3}$ consisted of smoke particles.[5] Sulphate concentrations of 8–10 $\mu g\,m^{-3}$ are typical in urban UK areas.[8] Seasonal variations in atmospheric pollution content have been shown by many studies[9,10] with notable decreases in, for instance, SO_2 in the summer.[11]

While these studies can give some guide to external atmospheric conditions, they reveal little about particle sizes, concentrations and compositions within an enclosed environment, especially one containing the specialised chemical powders of a ceramics laboratory or industry. As part of an evaluation of the use of clean environments for ceramic processing, a study has been made of the types of contaminant, air-borne particles present in unfiltered air adjacent to the clean-room. The air to the clean-rooms is filtered in two stages. Initially a glass-fibre net filter, with relatively wide interstices, is used to remove particles by interception and inertial impaction. Electrostatic attraction also allows these filters to remove at least some of the finer particles of sizes down to around 0·5 μm. A high efficiency particulate filter (HEPA), a fibrous mat of submicrometer-sized fibres, is used for the second filtering stage. For this evaluation, samples of used prefilter material were examined by scanning electron microscopy, to give a qualitative assessment of particle morphology and chemical composition.

2 Experimental

Sections of filter material were taken from unused glass-fibre prefilters (Filter Supply and MFG Company Ltd) and a prefilter used for seven days between 4 October 1989 and 11 October 1989. The clean-room air system delivers between 0·8 and 1 $m^3\,s^{-1}$ of filtered air through a 300 × 300 × 50 mm filter. Therefore, an estimated volume of 500 000 m^3 of air had passed through the filter volume of $4{\cdot}5\times10^{-2}\,m^3$. Special care was taken in mounting the sections for SEM to avoid contamination from handling. Fibres were taken only from the inside of the filters.

Filter fibres were examined using CAMSCAN Series 4 SEM, with Link Systems EDAX analysis. Particles chosen at random from three areas of the used prefilter were analysed. Because of difficulties in satisfactorily coating the filter and their adhering particles, gold had to be used. Information on the sulphur content of particles at low S peak heights, and information on P and Zr was lost. Large S peaks could be seen as shoulders on the Au peak. Elements of lower atomic number than Na could not be analysed.

3 Results

Figure 1 shows a section of unused prefilter, with the corresponding EDAX analysis in Fig. 2. The background consists of two Au peaks with a small Si peak from the glass fibre.

Figure 3 shows a low magnification micrograph of an area of a used filter. Three sites were chosen for analysis from this area; marked A, B and C, they are shown at higher magnification in Figs 4, 5 and 6 respectively. The particles subjected to analysis are identified on the figures.

EDAX analyses were sorted by dominant peak

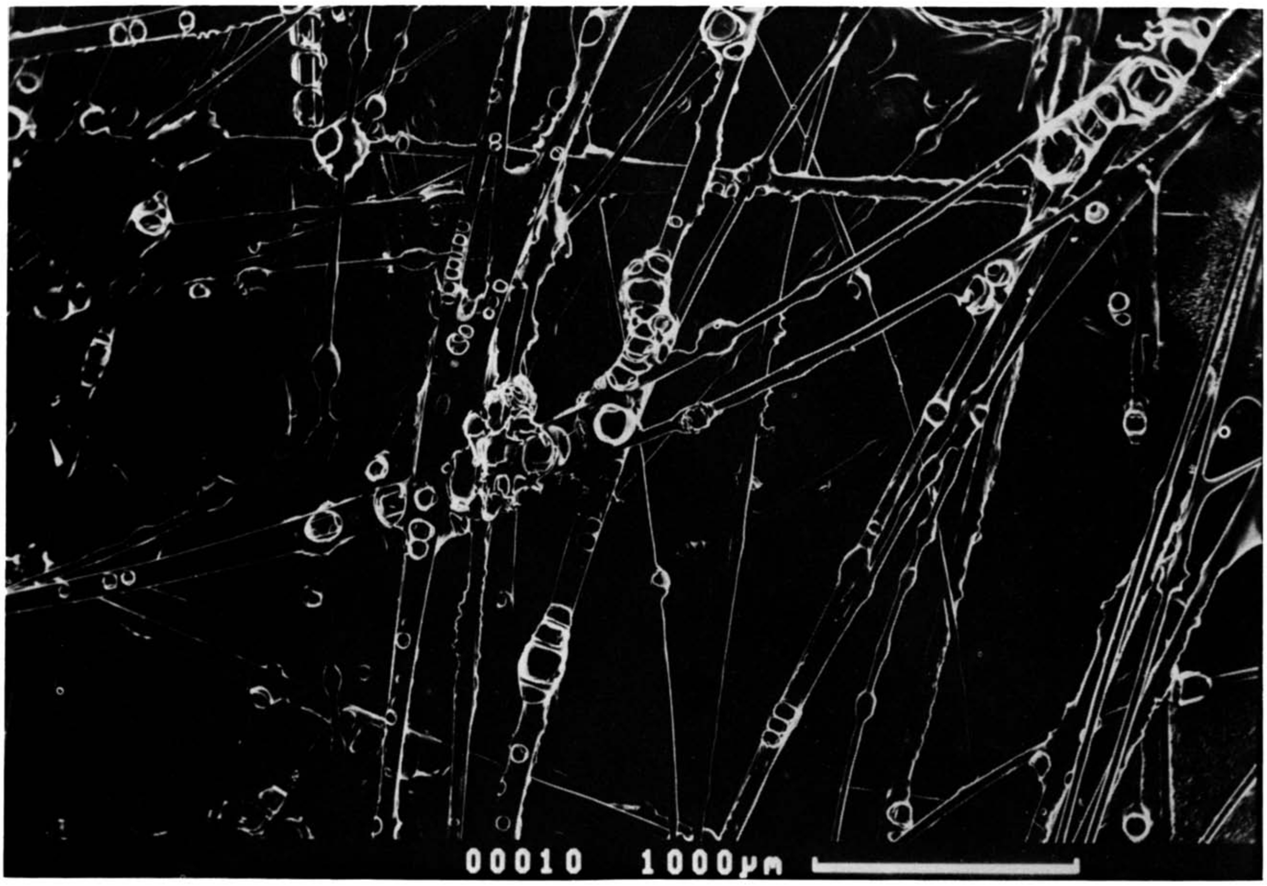

Fig. 1. SEM micrograph of unused prefilter.

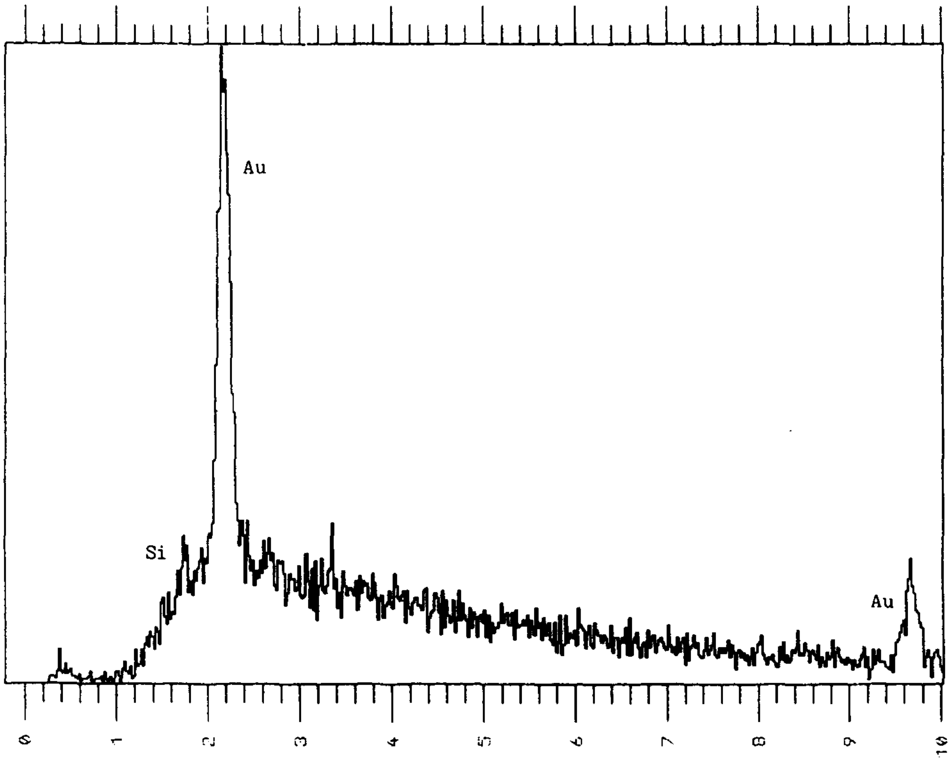

Fig. 2. EDAX analysis of unused prefilter.

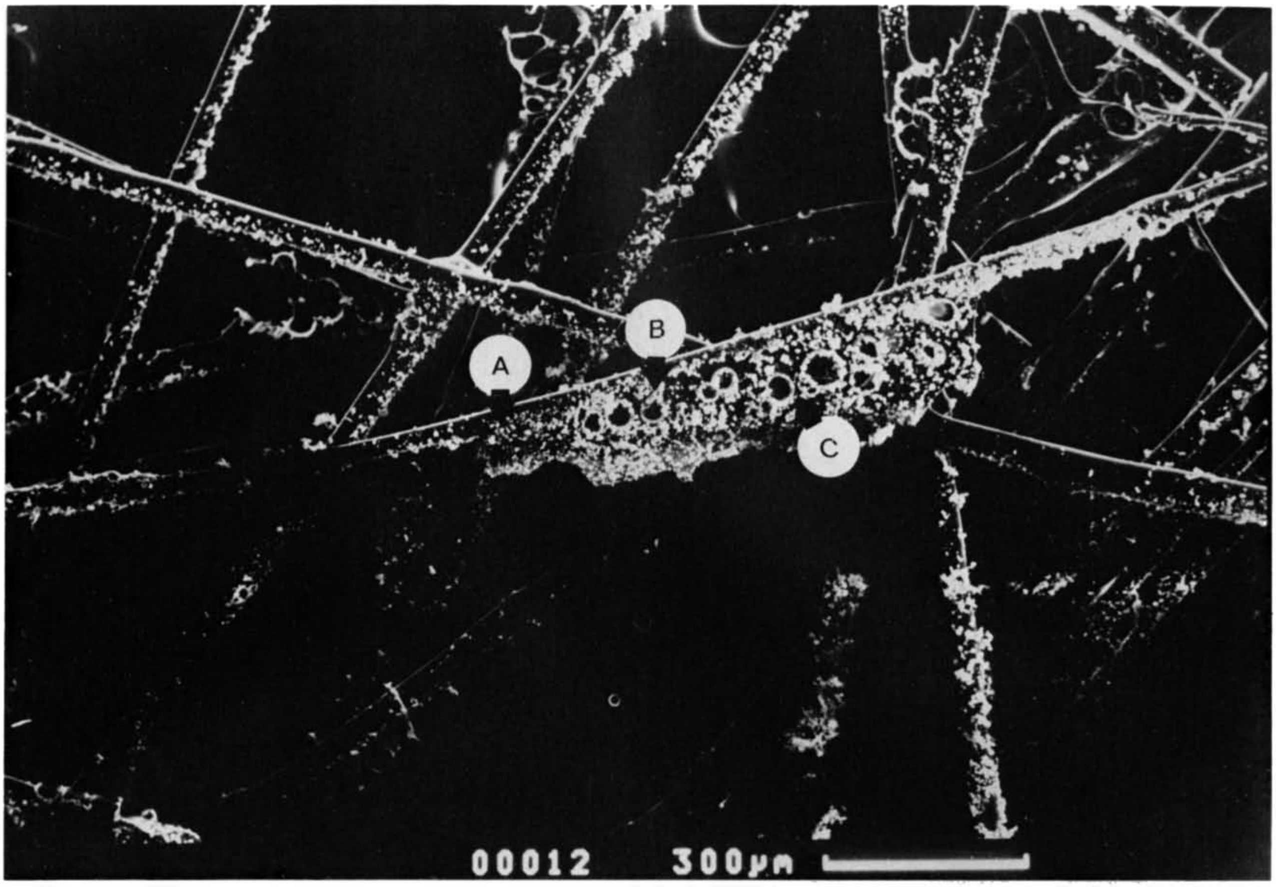

Fig. 3. SEM micrograph of used prefilter. Analyses of particles were made at sites A, B and C.

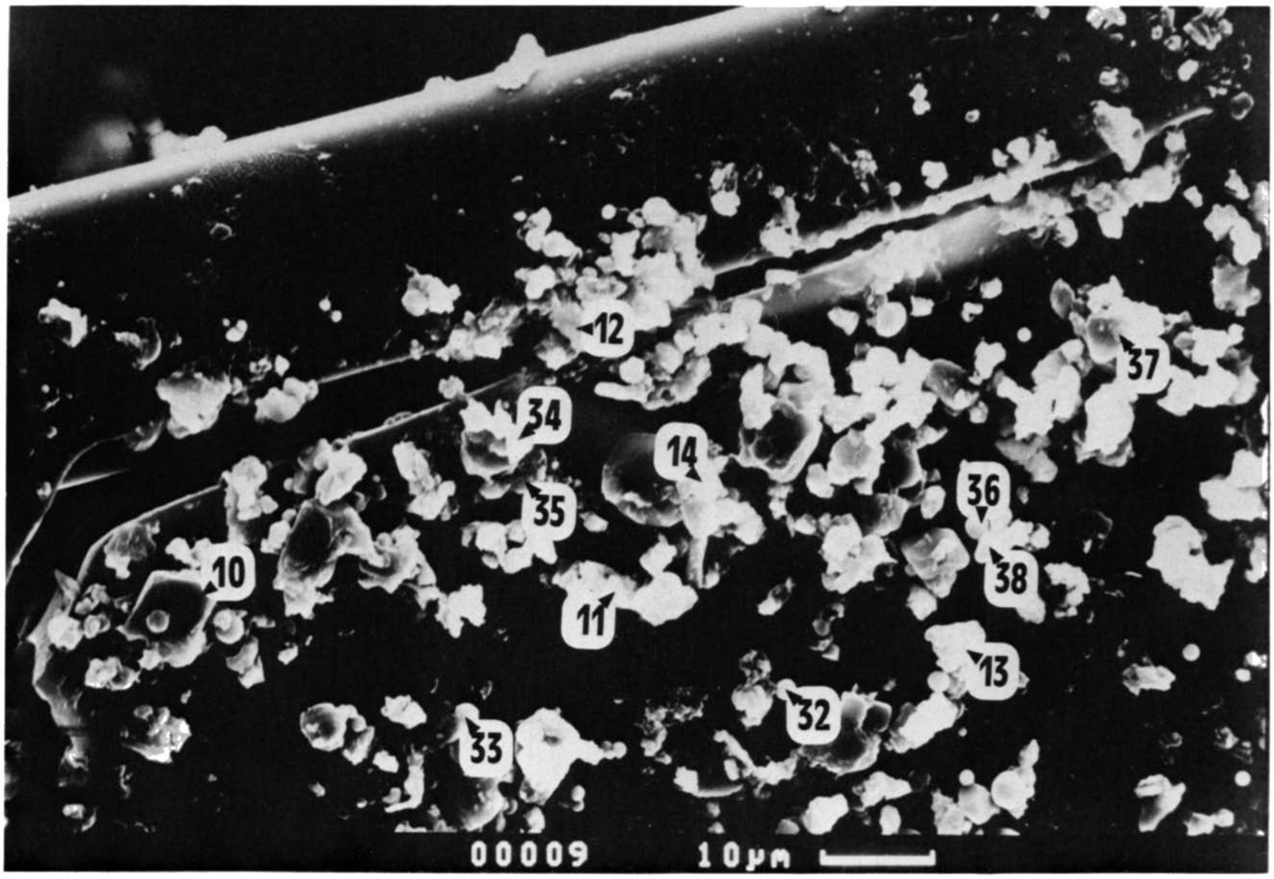

Fig. 4. SEM micrograph of used prefilter at site A. Analysed particles are marked.

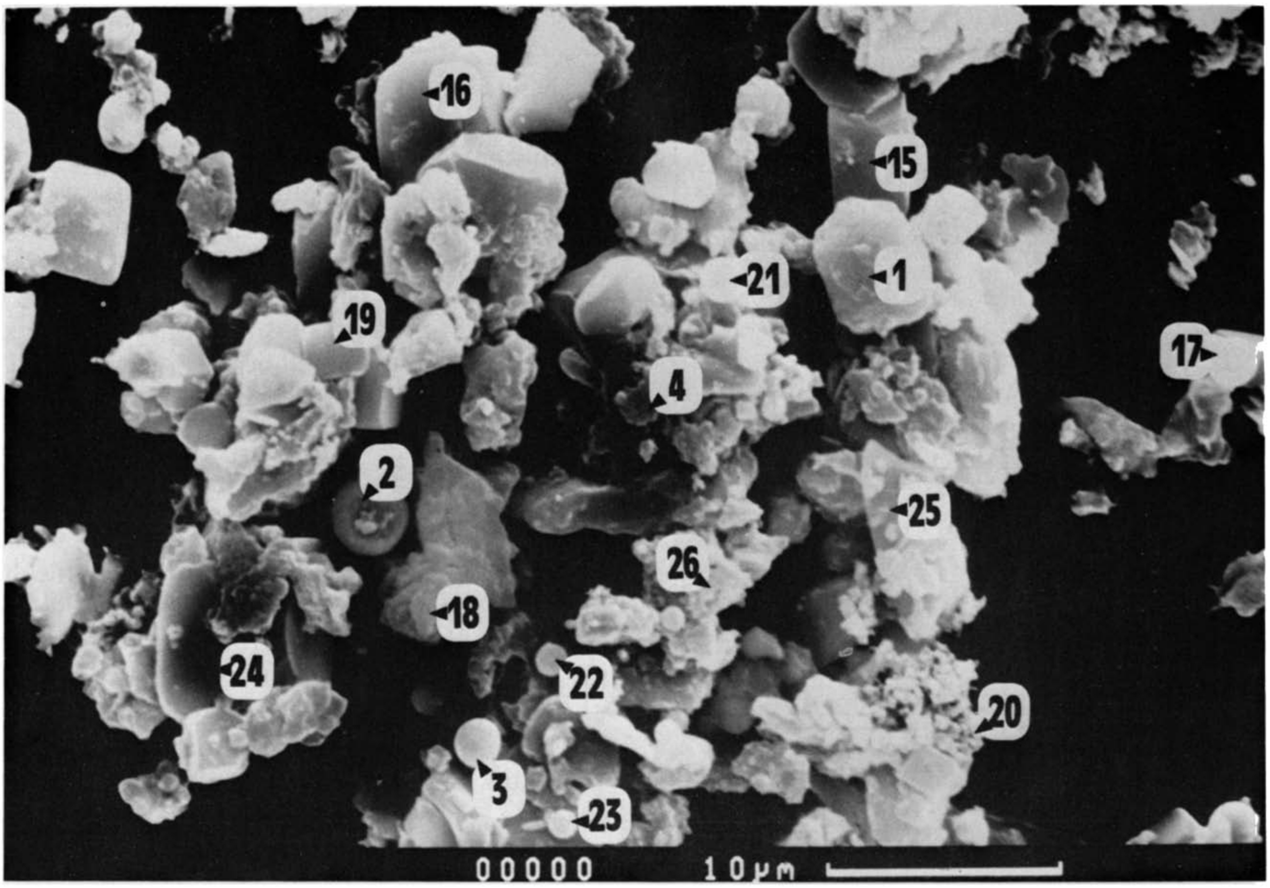

Fig. 5. SEM micrograph of used prefilter at site B. Analysed particles are marked.

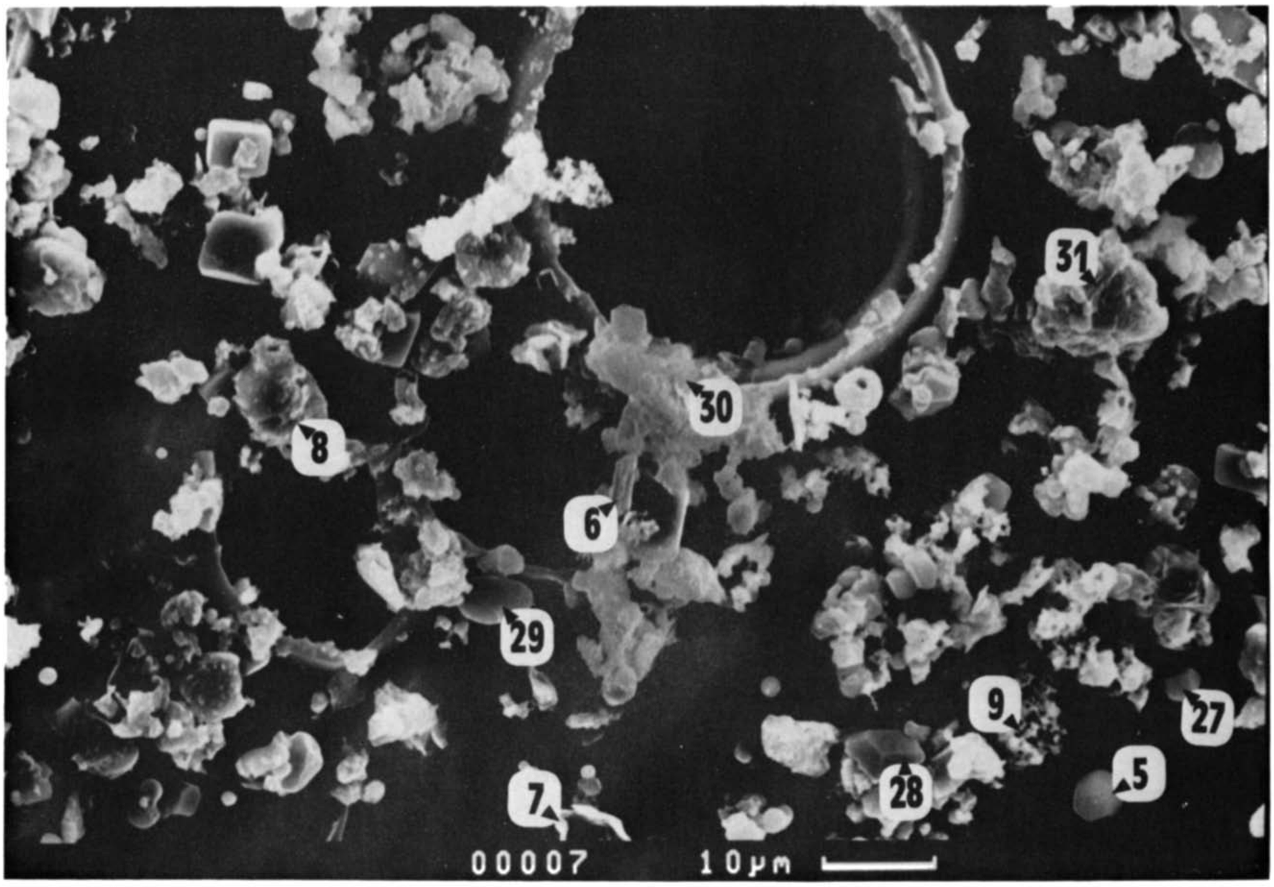

Fig. 6. SEM micrograph of used prefilter at site C. Analysed particles are marked.

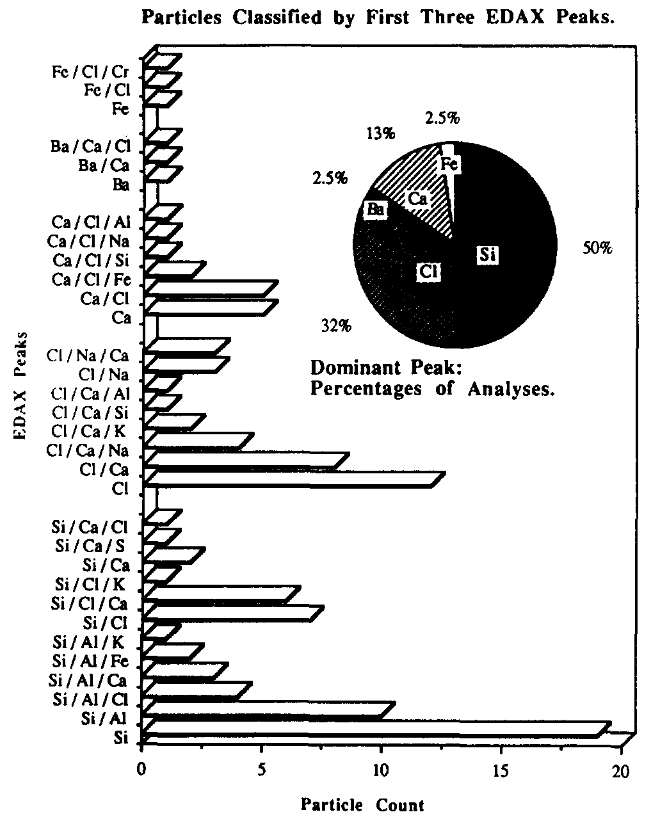

Fig. 7. Bar chart of particle elemental compositions analysed by the three major EDAX peak heights.

height above background, leading to five categories for which the major peaks were Si, Cl, Ca, Ba or Fe. The percentages of particles examined which fall into these or their subgroups are given in the text. While these figures are in no sense quantitative, they give some guide to the ranking of the elements observed.

These analyses are summarised in Fig. 7.

3.1 Silicon dominant

These comprised 50% of the particles observed. This might be expected from the prevalence of silicon containing crustal minerals. An earlier study has shown that quartz can comprise up to 25% of the mass of the coarse aerosol fraction.[12] This category further divides into three subcategories, rich in Al, Cl and Ca. A typical, representative EDAX analysis is given in Fig. 8.

3.1.1 Aluminium second peak

These comprise 26% of the total particles and further subdivide into four categories: Cl as the third peak (10%), particles 8, 17, 23 and 30; Ca as the third peak (8%), particles 2, 22 and 32; Fe as the third peak (5%), particles 3 and 36; and K as the third peak, particle number 12.

The morphology of these particles—except 8 and 30, both with Cl as the third peak, and 11 with K as the third peak—is unexpectedly spherical, as can be seen in Figs 9, 10 and 11 which show particles 2, 3 and 22 and 36 respectively with a size range of 1·1 to 3·4 μm. Particles 8, 11 and 30 are parts of irregular masses of material of the order of 10 to 20 μm in length. Particles 8 and 30 are shown in more detail in Figs 12 and 13.

Al is present at 8·13% by mass in igneous rocks,[13]

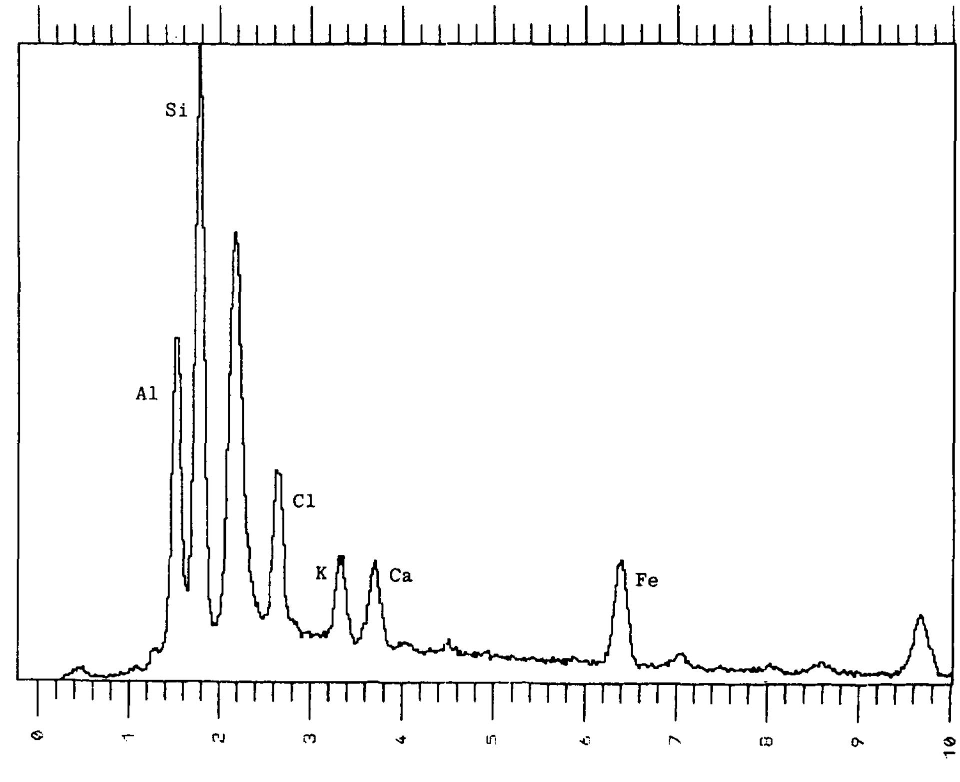

Fig. 8. Representative analysis from Si-dominant particle.

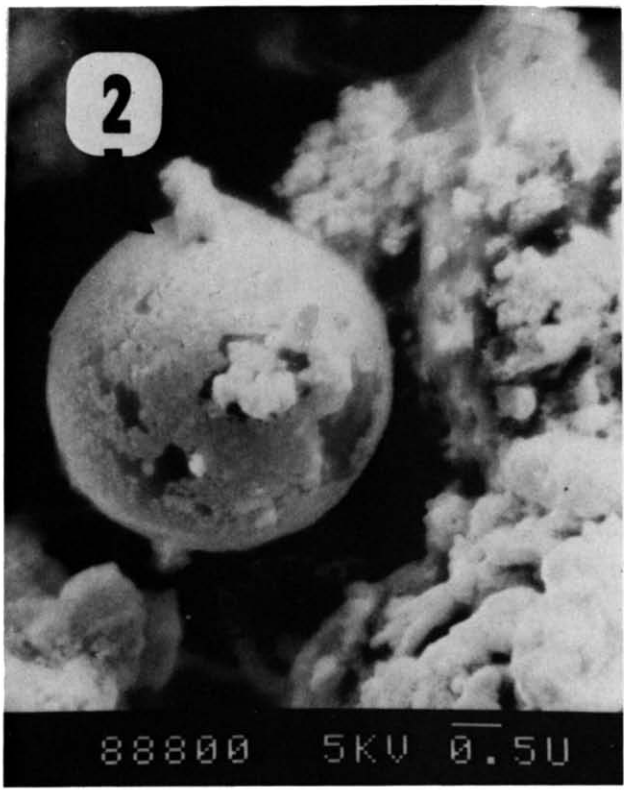

Fig. 9. High-resolution SEM micrograph of particle 2.

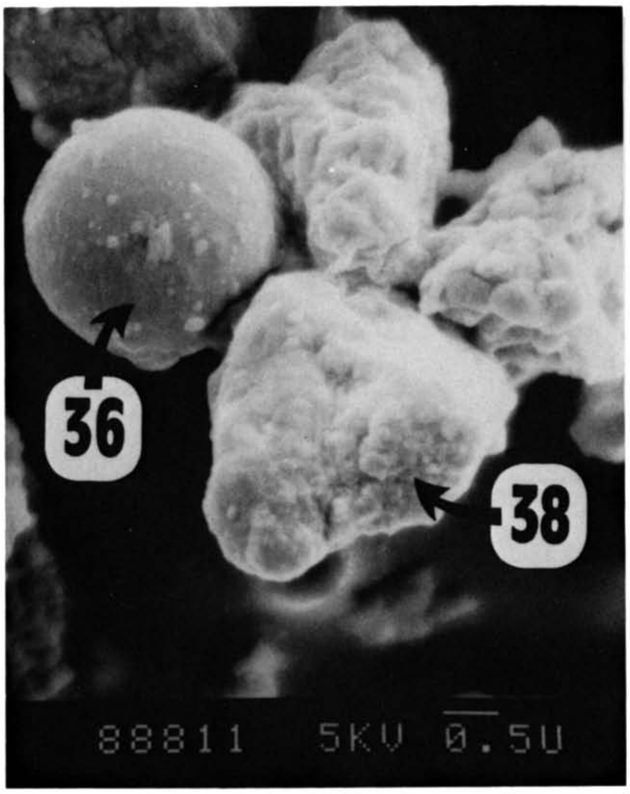

Fig. 11. High-resolution SEM micrograph of particles 36 and 38.

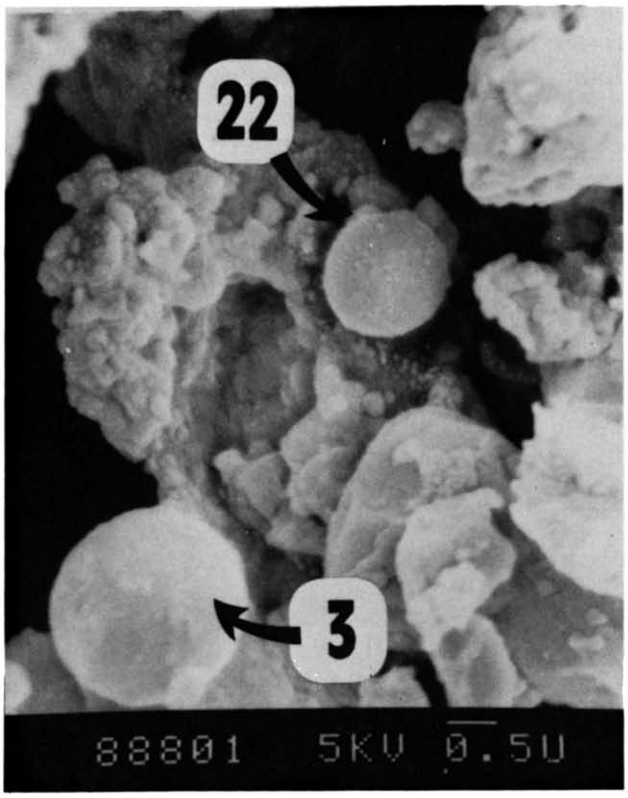

Fig. 10. High-resolution SEM micrograph of particles 3 and 22.

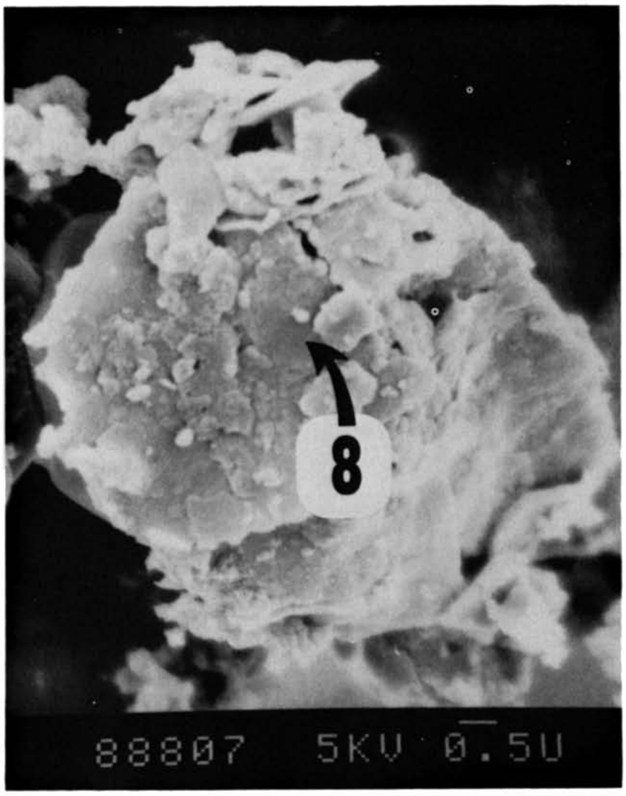

Fig. 12. High-resolution SEM micrograph of particle 8.

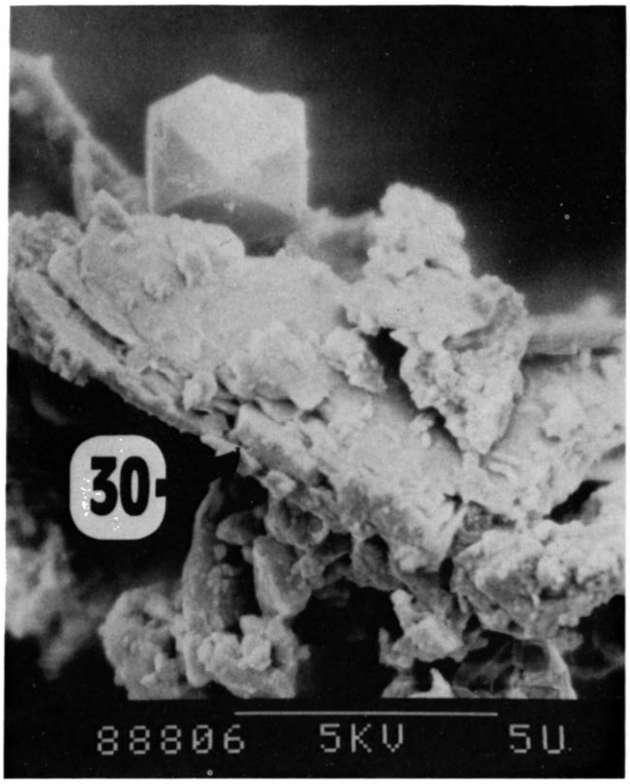

Fig. 13. High-resolution SEM micrograph of particle 30.

and it would be expected that particles originating in mineral dusts and having silicon as the dominant element would have aluminium as a major second component. On the other hand, the spherical morphology of the majority of these particles suggests strongly that they are ash particles from the combustion of coal.

3.1.2 Chlorine second peak

These comprise 18% of the total particles, and there are only two further subdivisions: Ca as third peak (16%), particles 12, 16, 21, 24, 33 and 34; and K as third peak, particle number 25. Particles 16, 24 and 25 are large and faceted, ranging in size from 6·3 to 7·5 μm, and 34 is smaller (3·7 μm) and faceted, whereas 21 and 33 are both spherical particles approximately 2 μm in diameter. Particle 12 has an irregular morphology of 7·5 μm overall dimension.

3.1.3 Calcium second peak

Two particles in this category have Ca as the second peak. Both are complex mixtures, particle 4 of S, Cl, K, Al, Fe and possibly Ba, and particle 18 of Cl, Al, Fe and K. Both are from complex irregularly shaped clusters of material of lengths 2·7 and 3·9 μm, respectively.

3.2 Chlorine dominant

EDAX traces with Cl dominant comprise 31% of the total. This was an unexpectedly high value, but the prevalence of chlorine was confirmed in an analysis of particles adhering to a second used prefilter. A representative EDAX analysis is shown in Fig. 14.

3.2.1 Calcium second peak

Particles with Ca as the second peak comprise 21% of the total (66% of those with the Cl peak dominant). These further subdivide into those with

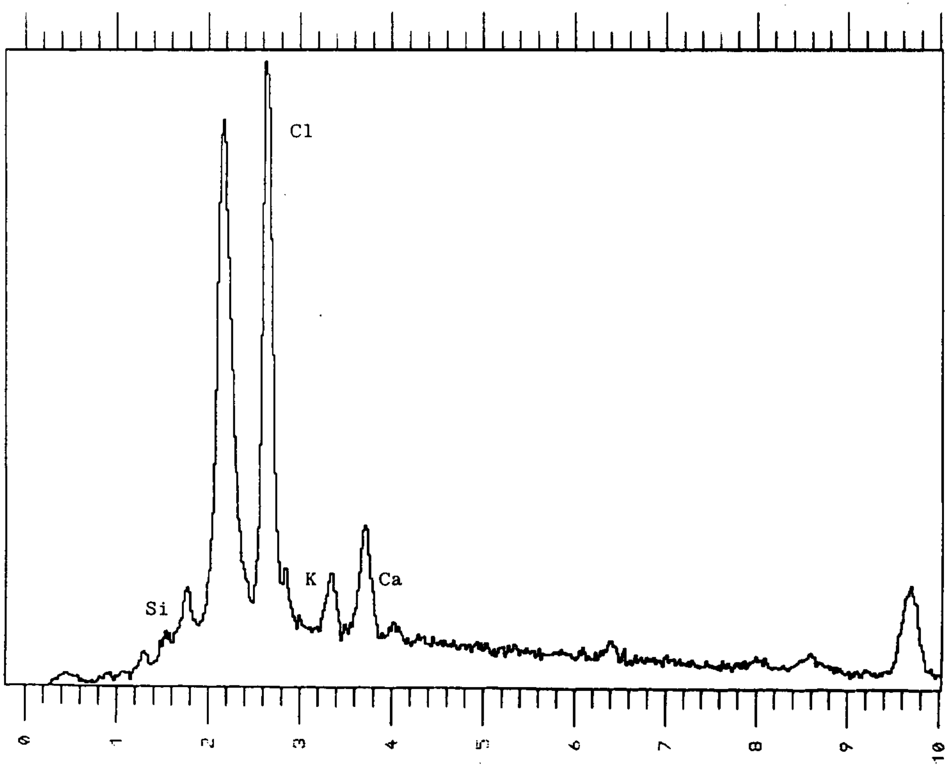

Fig. 14. Representative analysis from Cl-dominant particle.

Na as the third peak (10·5%), particles 5, 10, 19, 37; those with K as the third peak (5%), particles 29 and 31; Si as the third peak, particle number 9; and Al as the third peak, particle 15. (The Na peak height is likely to be least reliable because of the low energy of the characteristic X-rays.)

All those with sodium as the third peak are faceted particles, ranging from cuboid to more complex shapes, and are 4·5 to 7·5 μm in size. They are likely to be sodium chloride from deposited human tissue. The human body contains about 2% Ca and 0·23% K by mass together with 0·1% Na and Cl.[14] C, H and O, in association with Ca, P, K, Na and Cl form the major constituents of skin tissue.[15] Na and Cl concentrations are increased by perspiration which can contain up to 4·68 g litre^{-1} of Cl and 3·12 g litre^{-1} of Na.[16]

Particles 29 and 31 have widely different morphologies, as shown in Figs 15 and 16, one being an ovoid, 5 μm in length, and the second irregularly shaped, about 12 μm at its greatest extent. The higher resolution micrograph of Fig. 15 shows the ovoid to be coated with a fine deposit of the order of 0·1 μm. Particle 9 has a very fine structure of about 8 μm diameter, wheras 15 is similar to the Na third peak particles. None are spherical.

3.2.2 Sodium second peak

These comprise 8% of the total (particles 1, 27 and 28) and all have Ca as the third peak, suggesting again that they come from human tissue; they are all faceted, and range from 3·5 to 6·5 μm in length.

3.2.3 Sulphur second peak

One particle, about 5 μm in length, has sulphur as the second peak, number 26. This has a complex, very fine morphology and also contains Si, Ca, K, Ba (or Ti) and Fe.

3.3 Calcium dominant

All have Cl as the second highest peak and comprise 13% of the total, indicating a human skin source. A representative trace is given in Fig. 17. 5% have Fe as the third peak, particles 6 and 7; again these are both faceted and are 8 and 7 μm in length. The two more complex particles, 13 and 14 (5 and 4 μm) have Si and Na as the third peaks respectively. The fine particle aggregate, ~5 μm in diameter, comprising particle number 20, has Al as the third peak.

3.4 Barium dominant

One particle, almost certainly the product of an electroceramic processing area, had Ba as the dominant element (particle 35). The particle is of a

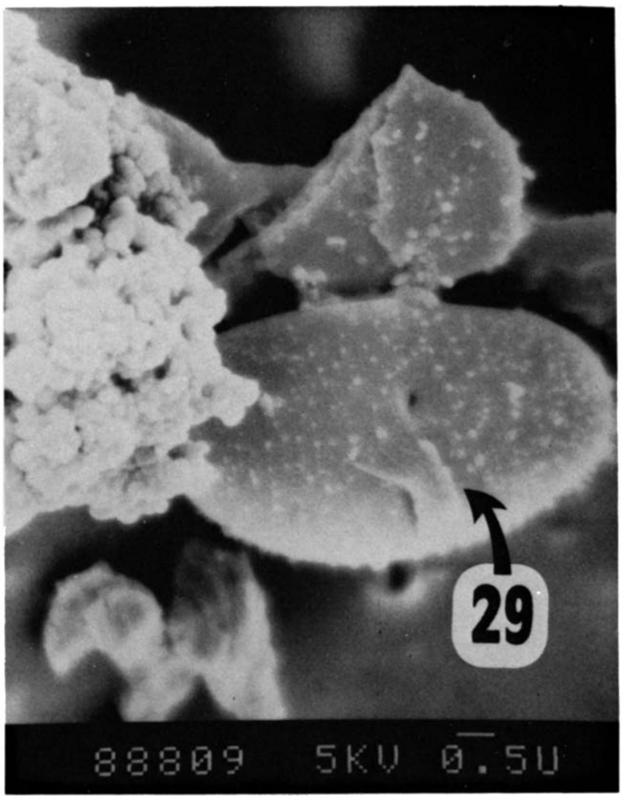

Fig. 15. High-resolution SEM micrograph of particle 29.

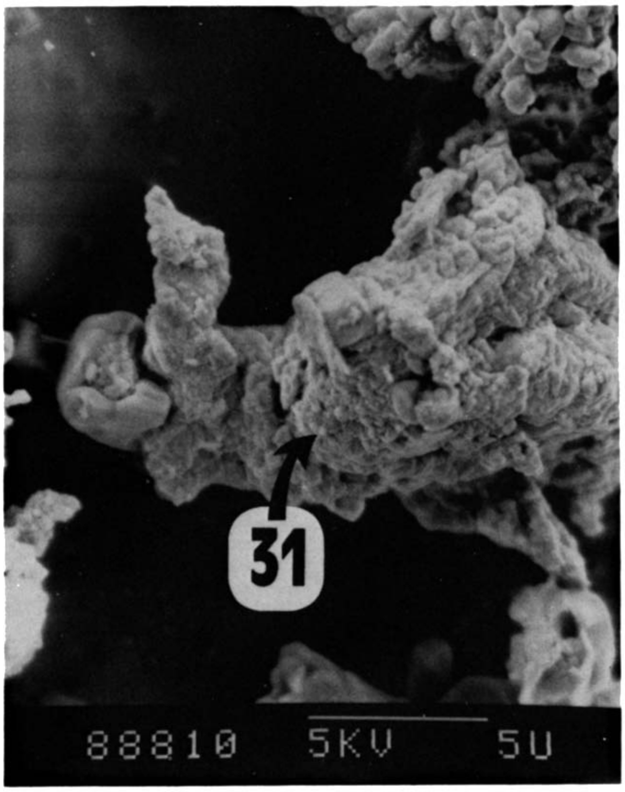

Fig. 16. High-resolution SEM micrograph of particle 31.

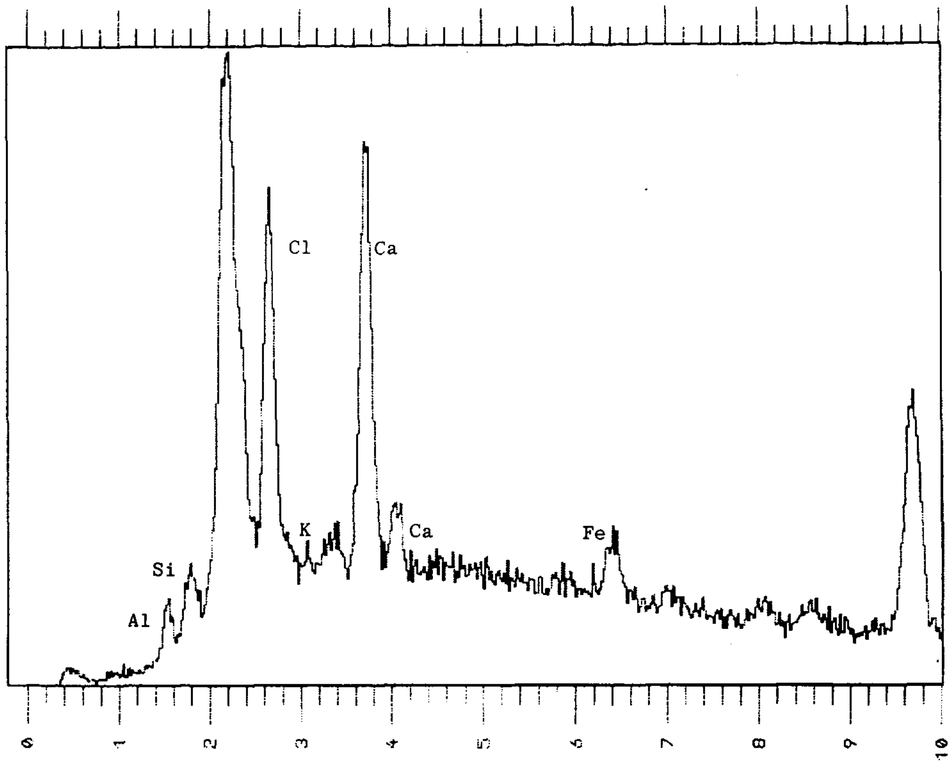

Fig. 17. Representative analysis from Ca-dominant particle.

small complex deposit, 6 μm in length, found to contain also Ca, Cl, Si, Fe and Al (Fig. 18).

3.5 Iron dominant

One particle, 38 (the larger non-spherical particle in Fig. 11), with a dominant Fe peak was observed. This 2 μm particle also contained Cl, Cr, Si, Ca and K suggesting either that it was originally from a ferrous alloy (Fig. 19) or that it is a particle of foundry dust. The clean-room is sited adjacent to metallurgy workshops.

4 Conclusions

This analysis has shown the very wide range of particle compositions and morphologies of air-borne dust particles existing in a university ceramics

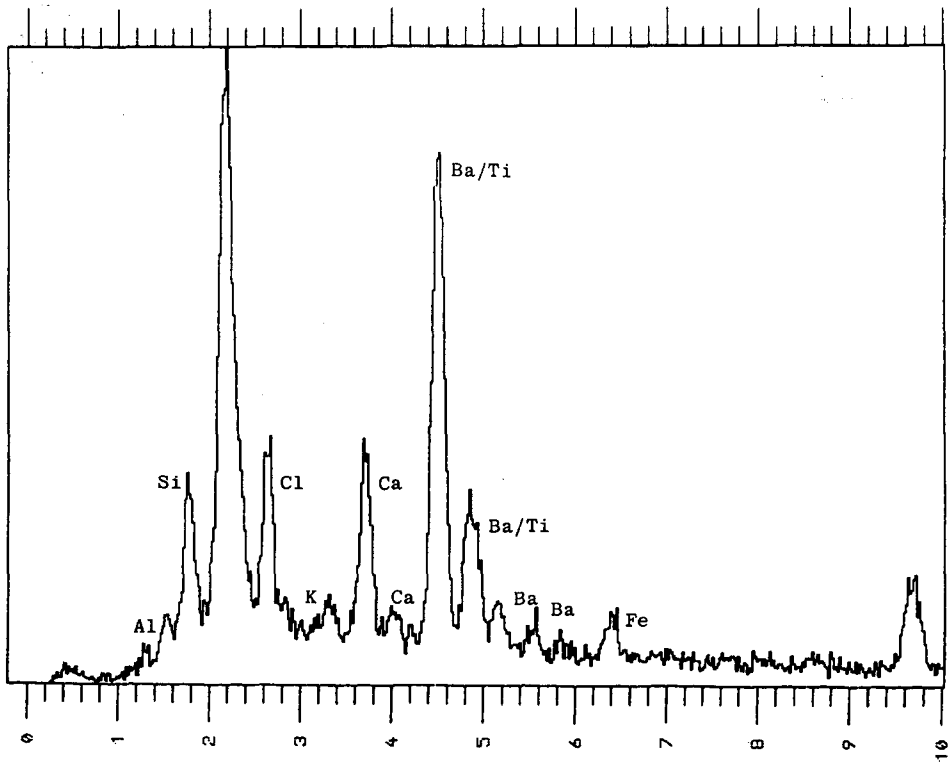

Fig. 18. Representative analysis from Ba-dominant particle.

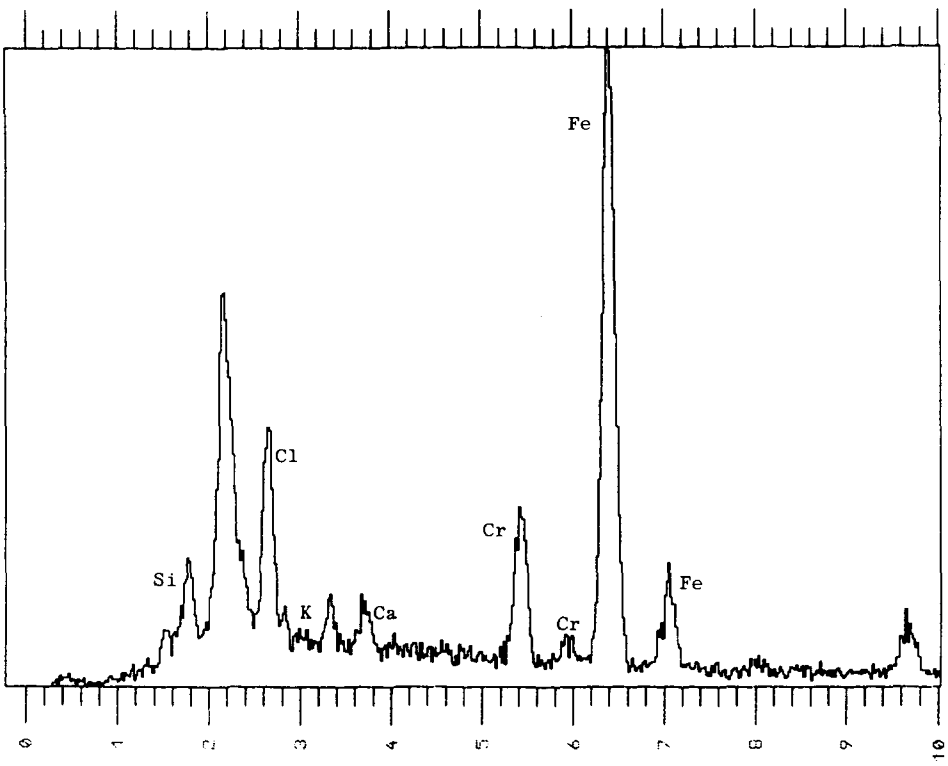

Fig. 19. Representative analysis from Fe-dominant particle.

laboratory environment. In the context of the processing of high-purity technical ceramic powders, a significant feature is the size of many of these dust particles, which is in the 1–10 μm range, and thus of the same order of magnitude as the grain size of the sintered materials being prepared. It may be surmised that metal oxide or halide-containing particles much larger than this do not remain airborne for a sufficiently long period to become important as contaminants; particles much finer are certainly trapped by the filters, but at this size they are unlikely to create serious microstructural problems.

The origins of the dust particles appear to fall into two main divisions. One is industrial, and includes most probably the spherulised material from power station or other type of solid fuel combustion systems. This would account for much of the alumino-silicate-rich material. It is likely that many of the calcium-rich particles originate in lecture theatre chalk; sulphur would then also have been present but in this examination could not be detected with confidence. The second is probably human tissue and organic fabric debris, accounting for much of the chloride contamination as well as the irregularly shaped material which appears to be free from the heavier metallic elements. Because of the volatility of most chlorides it is likely that most of this type of contamination will be removed during the early stages of the sintering process and before pore closure occurred at 80–85% density. The alumino-silicate particles would remain, probably to generate alumino-silicate intergranular phase glass, some of which might trap a proportion of the other contaminant metals. Material which is predominantly organic would create correspondingly sized voids in a compacted fine powder after heating in air. Such particles could have important consequences for the production of very thin films of material as, for example, in multilayer components in which the film thickness after sintering can approach 20 μm and thus be of the same magnitude as the dust particle dimension. A more serious consequence for the production of thin films of tape-cast materials as precursors for multilayer electroceramic applications would be the settling of dust particles on newly prepared plastic tape before stacking and sintering.

The potential benefits of clean-room working for the processing of ceramic powders are thus easiest to identify in the area of thin film production. This is the area of interest for the microelectroceramics industries using thin film materials. There is also likely to be interest in the context of processes requiring the development of a ceramic–metal bond, where clean surfaces are desirable.

Acknowledgements

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