UR1991_12

1/16

Tasmania Department Of Resources and Energy

Division of Mines and Mineral Resources — Report 1991/12

Silica fume analysis — A preliminary report

by R. S. Bottrill

Abstract

Silica fume, a by-product of some pyrometallurgical furnaces, has been suspected of causing deleterious health effects when inspired. Thermal behaviour is discussed and several methods of analysis are reviewed, all of which may be inadequate for determinations at the ACGIH-recommended TLV.

INTRODUCTION

Silica Fume is the name given to the very fine-grained dust given off as a by-product of high temperature furnaces which reduce silica to silicon and/or silicon alloys. It is essentially amorphous silica, with small amounts of quartz, cristobalite and other phases.

Several crystalline forms of silica are known to produce the fibrotic reactions in lung tissue known as silicosis or pneumoconiosis (Bye *et al.*, 1984), so silica fume has understandably been investigated for similar reactions (Vitums *et al.*, 1977; Jahr, 1981). Data to hand at present indicate the possibility of some short-lived deleterious health effects, although probably not silicosis itself, associated with silica fume (Jahr, 1981). Pending the results of further epidemiological research, a Threshold Limit Value (TLV) of 0.2 mg/m^3 has been proposed by the American Conference of Governmental Industrial Hygienists (ACGIH) (ACGIH, 1989), although a TLV of 2 mg/m^3 has been proposed by Jahr (1981). This relatively low proposed TLV for silica fume (compared with 0.1 mg/m^3 for quartz) has caused considerable consternation amongst the governmental authorities and industry personnel involved with the monitoring and analysis of silica fume, because of difficulties in the accurate determination of small quantities of this silica fume.

This report summarises presently-known methods of determination of amorphous silica (with emphasis on X-ray diffraction methods), the present state of knowledge of the composition of silica fume produced in Tasmania, and some related issues.

SILICA

This compound (SiO_2) has a complex phase diagram (fig. 1). There are three major stable crystalline states (polymorphs) at atmospheric pressure: quartz, cristobalite and tridymite. All of the above phases have at least two structural modifications, stable at different temperatures (e.g. alpha-quartz and beta-quartz). Some workers consider tridymite to be an unstable phase for pure silica at atmospheric pressure, in the absence of other "mineralising" components (Wahl *et al.*, 1961). Other crystalline states occurring under different physico-chemical conditions include coesite, keatite (silica-K), silica-O and stishovite.

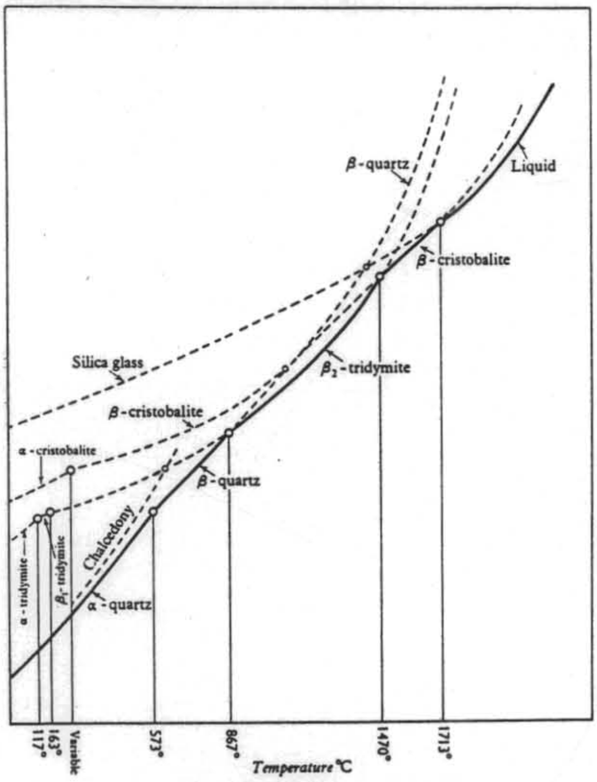


Figure 1

The stability relations of the silica minerals (after Fenner, 1913)

Unless otherwise indicated, "quartz" refers to alpha-quartz, the polymorph stable under atmospheric temperatures and pressures, in this report and in most other publications. Cristobalite likewise usually refers to alpha-cristobalite.

Amorphous silica is a term used to describe a number of related solid phases, natural and synthetic, which are non-crystalline (i.e. with no regular X-ray diffraction pattern) and consist predominantly (>90%) of silica. It includes silica glass, fused silica, precipitated silica, diatomite, opal-A, fumed silica and silica fume (Jones and Segnit, 1971; Jahr, 1981). All amorphous silica is metastable.

Sluggish phase transformations give problems in interpretation of the phase changes: for example amorphous silica will recrystallise metastably, at temperatures of a few hundred degrees Celsius or less, firstly to cristobalite ± tridymite, then to alpha-quartz (the stable phase below 573°C), in a matter of hours under suitable conditions (Campbell and Fyfe, 1960; Kastner *et al.*, 1977). Natural amorphous silica (opal-A) forming on the sea floor will recrystallise, at temperatures <20°C, to crystalline silica (cristobalite ± tridymite, then to alpha-quartz), probably by a solution-reprecipitation mechanism, over a period of thousands or millions of years (Kastner *et al.*, 1977). The rates and temperatures of the transformations are also dependant upon the grainsize, pH and other chemical components present (Campbell and Fyfe, 1960; Wahl *et al.*, 1961).

SILICA FUME

Silica fume is the term used to describe the amorphous silica dust formed by oxidation of SiO vapour escaping from the Electrolytic Submerged Arc (ESA) furnaces used to produce metallic silicon and silicon alloys by reduction of quartz (fig. 2). It is not to be confused with fumed silica, which is amorphous silica formed by combustion of silicon-halogen compounds and has slightly different properties (Jahr, 1981). Silica fume is composed of extremely fine-grained (0.01–1 µm) spherical particles of amorphous silica which are usually flocculated into larger clumps of material.

A typical dust sample collected from these ESA furnaces is usually dominated by silica fume, but small and variable amounts of other phases, particularly from the feed or by-products, are usually present. Quartz is usually present as a minor constituent. Some incipient recrystallisation to cristobalite is also commonly present, while partial recrystallisation to tridymite is much rarer.

SILICOSIS

The medical condition called silicosis is usually related to the entry of quartz (or other forms of crystalline silica) into the lungs. The coarser dust particles seldom reach the lungs, but the respirable size fraction (1–10 µm) of dusts can, and may then travel down the bronchial tubes into the bronchial alveoli, where they are engulfed by macrophages. These micro-organisms, part of the body's defence mechanisms, are damaged or killed by the crystalline silica particles, leading to the release of enzymes and mediators, causing fibrosis and scarring of the lungs (Vallyathan *et al.*, 1988; Ghio *et al.*, 1990). This scarring can permit entry of the opportunistic infections and carcinogens which cause most of the problems, often leading to death, associated with silicosis. Pneumoconiosis, irritant bronchitis, focal emphysema, broncogenic carcinoma, mesothelioma, tuberculosis and metal-fume fever are related lung diseases with links to respirable dusts (Ghio *et al.*, 1990).

Silicosis is usually attributed to quartz, although cristobalite, tridymite and coesite have also been implicated (Bye *et al.*, 1984). Recent work by Vallyathan *et al.* (1988) has illustrated the surprisingly high reactivity of sheared or fractured "silica", one of the major factors in silicosis. These workers note that the freshly broken surfaces of the silica (exact species unspecified, presumably quartz) have a high surface reactivity due to

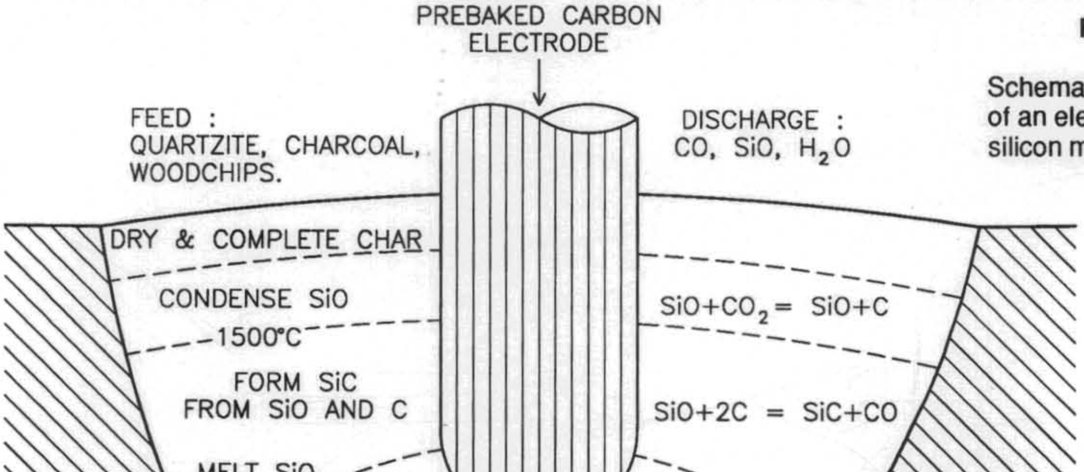


Figure 2

Schematic cross section of an electric furnace for silicon metal production.

the formation of free radicals. These free radicals are metastable molecules with unpaired electrons or unbalanced electron pairs, such as single oxygen or silicon monoxide. They are highly oxidizing, illustrated by the formation of hydrogen peroxide from the reaction of freshly-ground silica with water (Vallyathan *et al.*, 1988). Freshly pulverised quartz also reacts vigorously with hydrogen peroxide, probably forming oxygen molecules (unpublished data). These peroxides and other oxidizing molecules cause scarring of the lung tissues.

The reactivity of sheared or crushed silica was stated by Vallyathan *et al.* (1988) to have a "half-life" of about 20–30 hours in air, indicating that freshly-ground silica presents a greater hazard than "aged" ground silica. This is not a strict half-life as the reactivity decreases rapidly after a few minutes, and remains at about 20% after four weeks, suggesting two or more modes of decay (Vallyathan *et al.*, 1988).

It seems rather odd that quartz, one of the most abundant minerals on the Earth's surface, should seem so abnormally dangerous to our lungs, but this may reflect a lack of research into similar effects with less common minerals. The strong covalent bonding, and lack of small, mobile cations to neutralise charge misbalances on broken surfaces, would also be important in the ready formation of free radicals.

Ghio *et al.* (1990) noted that many lung diseases are reported to be caused by silica and a number of silicates, including asbestos, clays, talc, mica and zeolites. They hypothesised that silicate dusts may cause these lung diseases through surface co-ordination of iron, causing oxidant generation. Silica and silicates readily absorb ferric iron on their surfaces, under physiological conditions, and this can mediate electron exchange, reacting with chemicals in the body to form free radicals in a similar manner to the model of Vallyathan *et al.* (1988). Ghio *et al.* (1990) referred to reports that mineral dusts in the lungs of workers remove the body's iron, resulting in low serum iron and a high content of iron in the lungs. In addition, they noted other supporting factors, including the fact that iron in the lungs, not the dusts themselves, is responsible for the radiological appearance of pneumoconioses. This important hypothesis suggests that further research is needed into comparative health effects of silica and other silicate minerals, plus the synergistic effects of iron and other respirable substances in the working environment.

The health effects related to silica fume exposure are the subject of a current epidemiological study, funded by government and industry. Results to date suggest, however, that in lungs silica fume behaves quite differently to crystalline silica.

One great problem with epidemiological studies of silica fume is the difficulty in isolating the health effects of silica fume itself from that of the many other phases contributing to respirable dust in the workplace, particularly quartz and other forms of crystalline silica (Jahr, 1981). Asbestos is another serious health hazard which would be present with most furnaces, and would complicate health studies.

DUST COLLECTION AND FILTER TESTING

Silica fume and other forms of dust can be collected by a number of methods: bulk dust, high volume filter sampling and personal monitoring. The bulk dust can be collected manually from the baghouse or other areas where dust accumulates.

High volume samplers are suction pumps which draw air through a large filter paper (approximately 0.1 m^2), with a relatively large pore size (about 5 μm), and usually operate outdoors. The dust samples on these filters are usually relatively small, and may be concentrated by ashing the filter.

Personal monitoring uses small, rechargeable, battery-operated pumps with a filter holder and a small cyclone to collect respirable-size fractions of atmospheric dust, intended to closely reflect what the wearer would breathe. The pumps operate at 1.9 L/min, equivalent to about 0.9 m^3/shift. The filters recommended for respirable dust collection in personal monitors are of the membrane type, made of mixed esters, PVC, polycarbonate or similar material, usually about 0.8 μm in pore size, and 25, 37 or 45 mm in diameter. These filters can be weighed to give the weight of respirable-sized dust, and analysed for various components. Humidity and static effects can give weighing problems, although a static eliminator (an ionising radiation source) should remove most static effects.

Several different types of membrane filter have been tested by this department, particularly the mixed ester (Millipore AA), PVC (Nucleopore PVC and Gelman GLA5000), and polycarbonate (Nucleopore PC). Static effects were found to produce serious weighing errors with the PVC filters, but these were much less serious with the mixed ester filters. X-ray powder diffraction (XRD) analysis of the filters indicated that they all showed undesirable broad peaks (fig. 3, 4 and 5), with PVC being best, polycarbonate unacceptable, and mixed ester intermediate. Figure 6 shows an XRD pattern for quartz.

IR pattern for quartz

Figures 7, 8 and 9 show Infrared Absorption Spectrophotometry (IR) traces of the three types of filter, and again the PVC would be best for resolving the silica peaks (fig. 10 and 11), with mixed ester filters unacceptable, and polycarbonate intermediate. This is discussed further below.

4/16

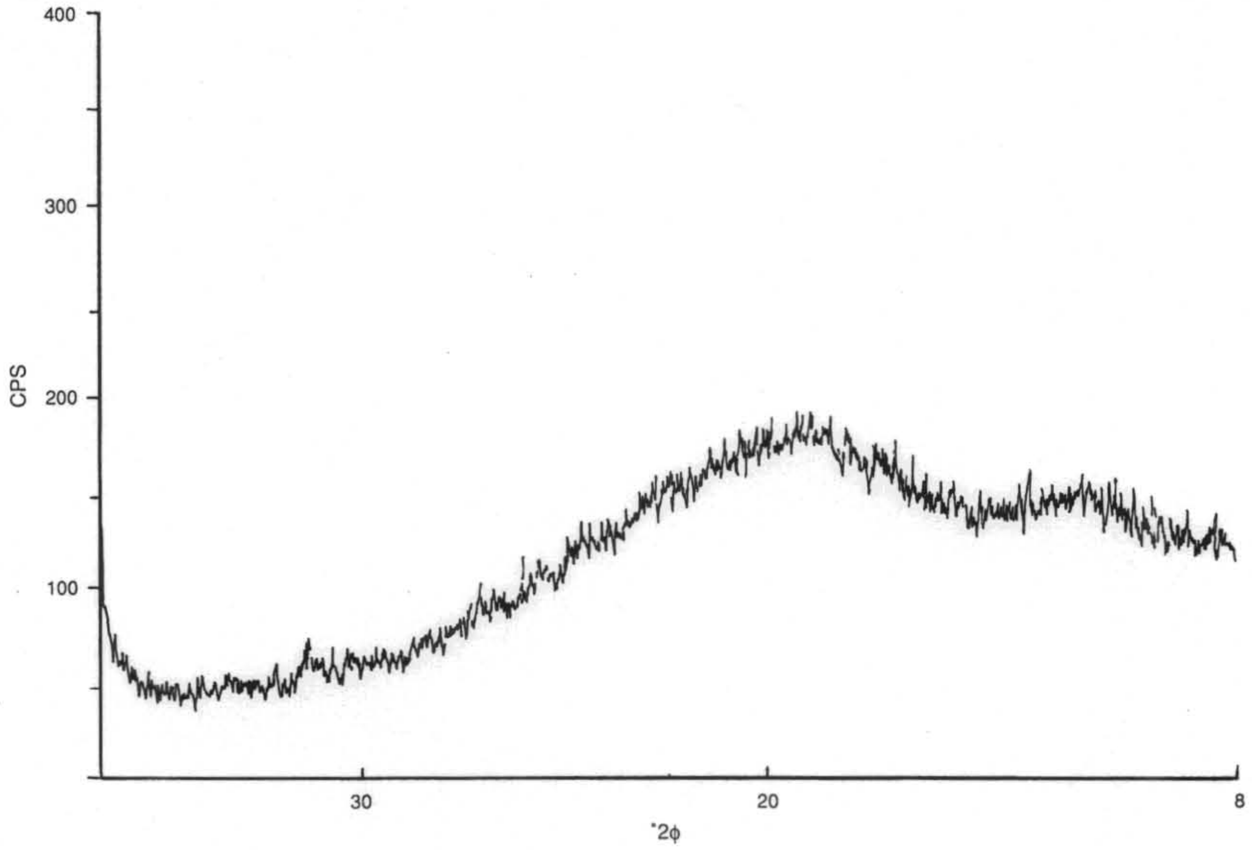


Figure 3

X-ray diffraction pattern of a blank Millipore AA filter (mixed ester).
Settings: Ni - filtered Cu radiation, 500 cps, 40 kV, 30 mA.

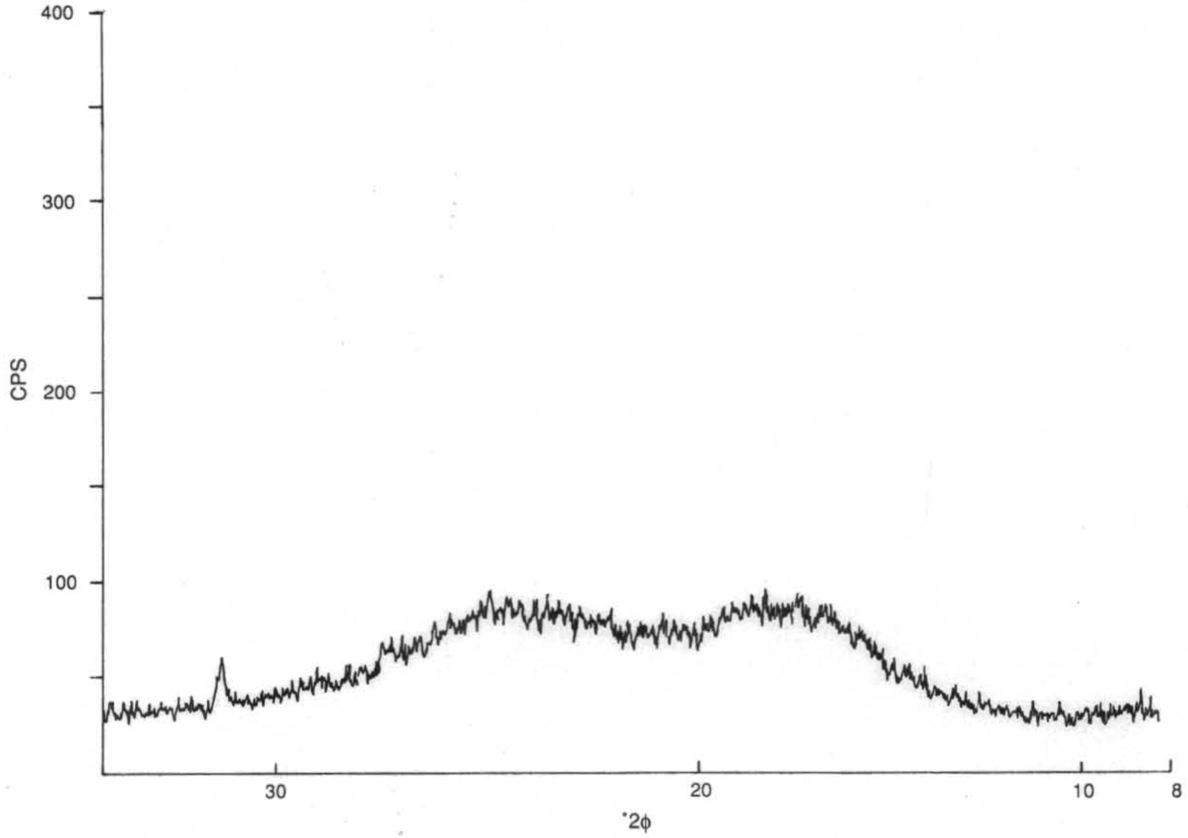


Figure 4

X-ray diffraction pattern of a blank Nucleopore PVC filter (Polyvinyl Chloride).
Settings: Ni - filtered Cu radiation, 500 cps, 40 kV, 30 mA.

5 cm

5/16

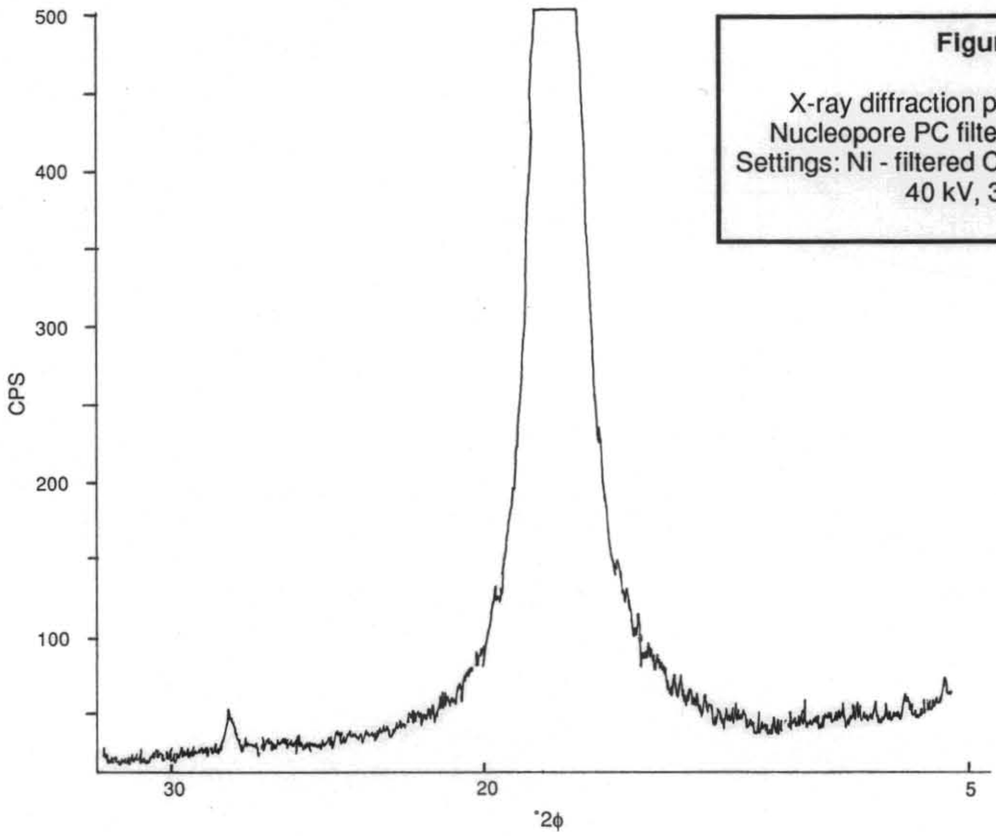


Figure 5

X-ray diffraction pattern of a blank Nucleopore PC filter (polycarbonate). Settings: Ni - filtered Cu radiation, 500 cps, 40 kV, 30 mA.

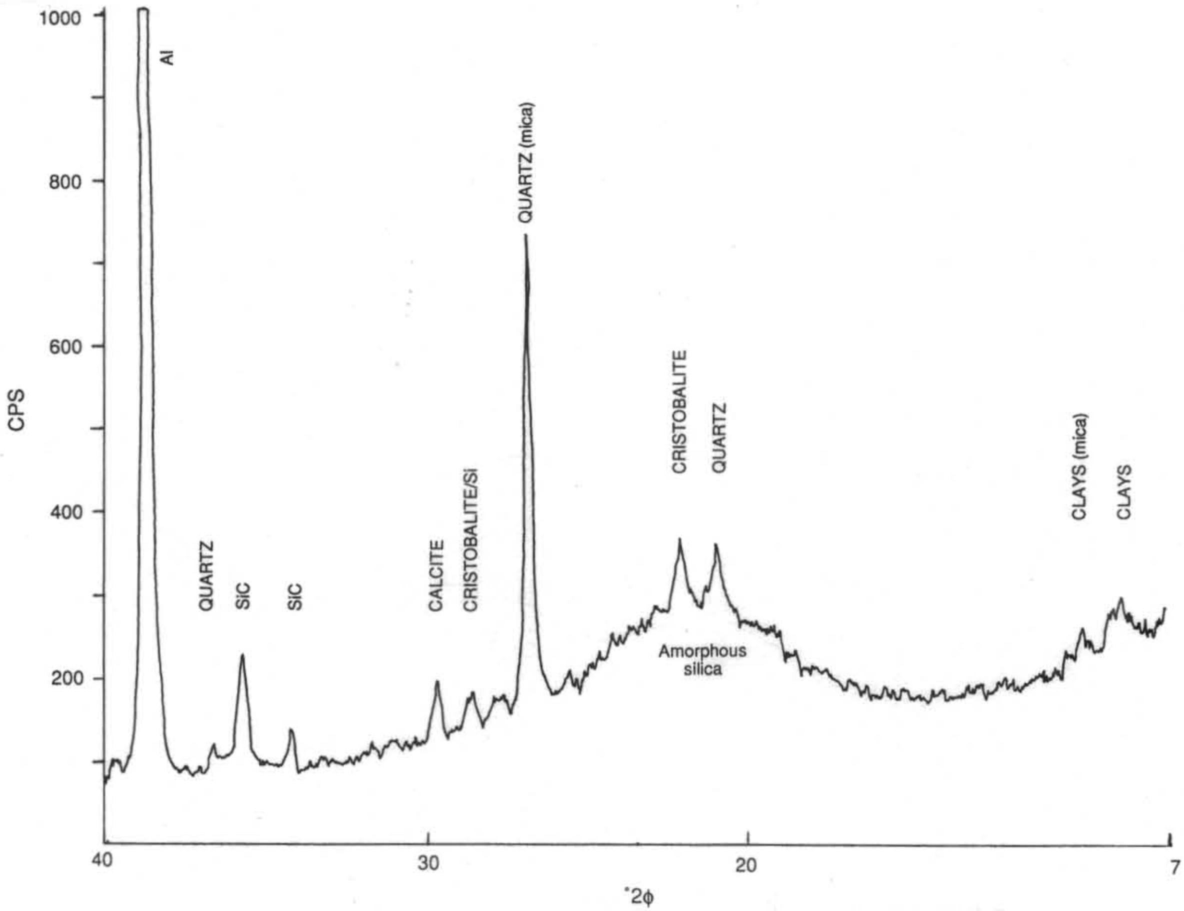


Figure 6

X-ray diffraction pattern of a silica fume sample, containing amorphous silica, quartz, cristobalite and other phases. Settings: Ni - filtered Cu radiation, 1000 cps, 40 kV, 30 mA.

6/16

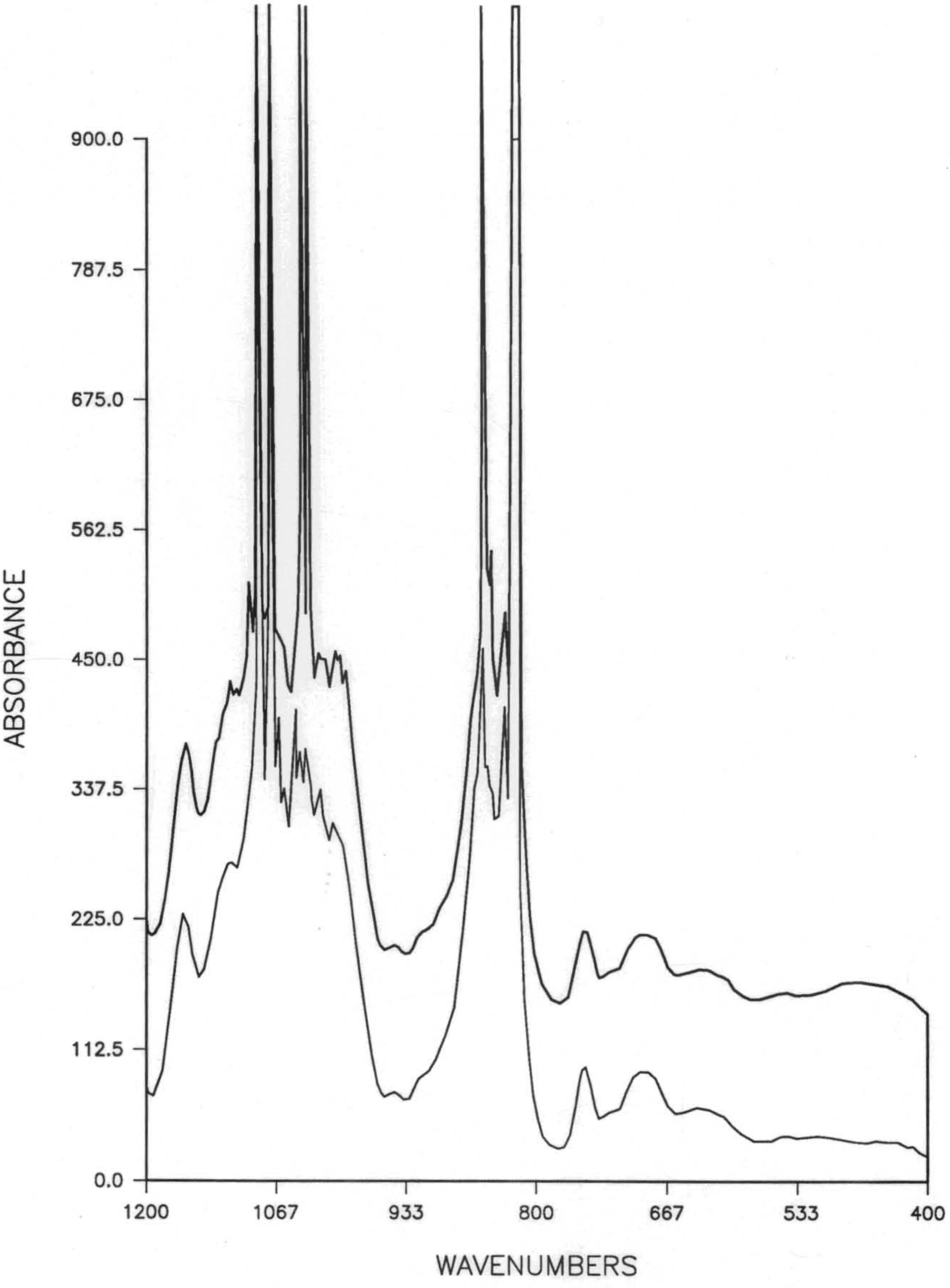


Figure 7

Fourier Transform Infra Red absorption spectrometry trace for a blank Millipore AA filter (mixed ester)

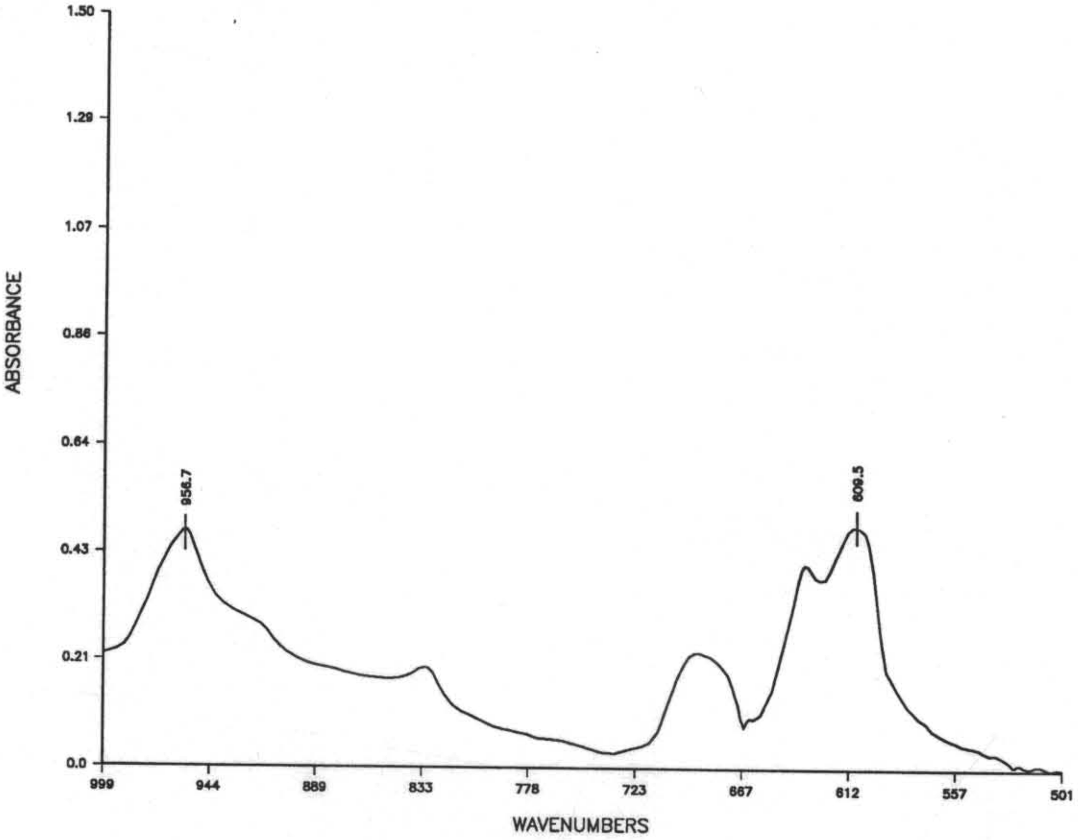


Figure 8

Fourier Transform Infra Red absorption spectrometry trace for a blank Nucleopore PVC filter (Polyvinyl Chloride)

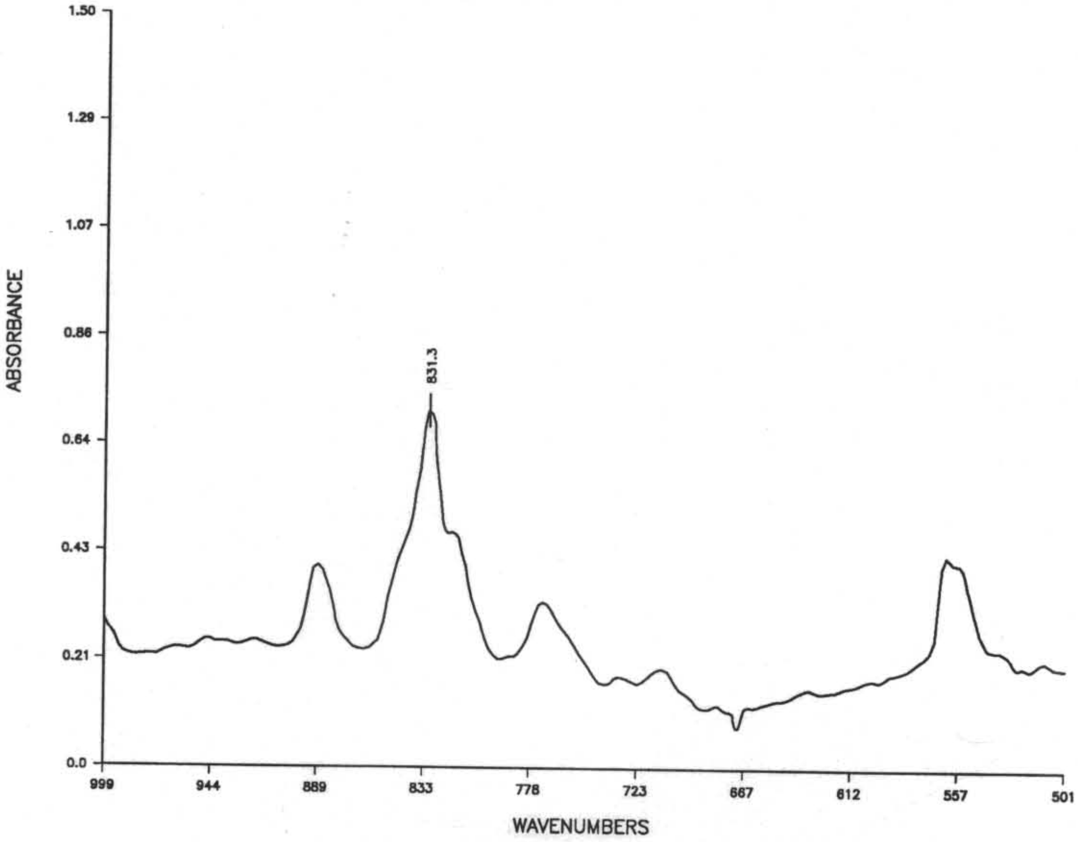


Figure 9

Fourier Transform Infra Red absorption spectrometry trace for a blank Nucleopore PC filter (Polycarbonate)

8/16

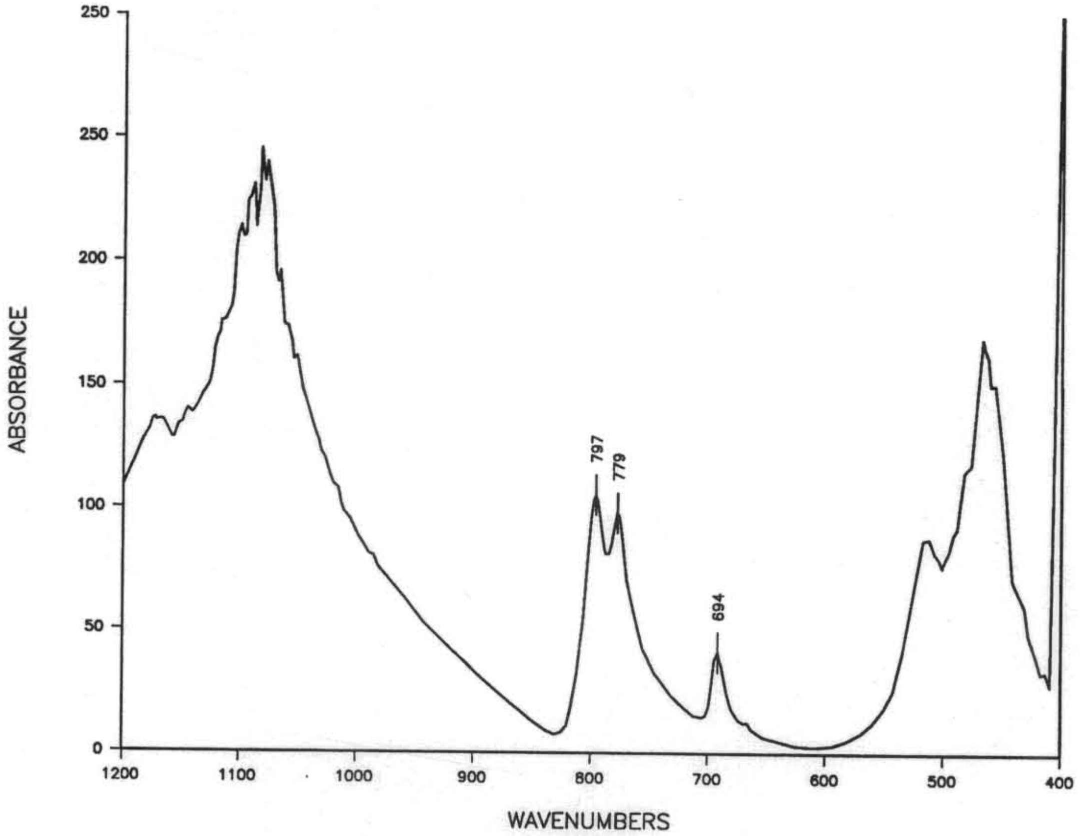


Figure 10

Fourier Transform Infra Red absorption spectrometry trace for alpha quartz in a KBR disk

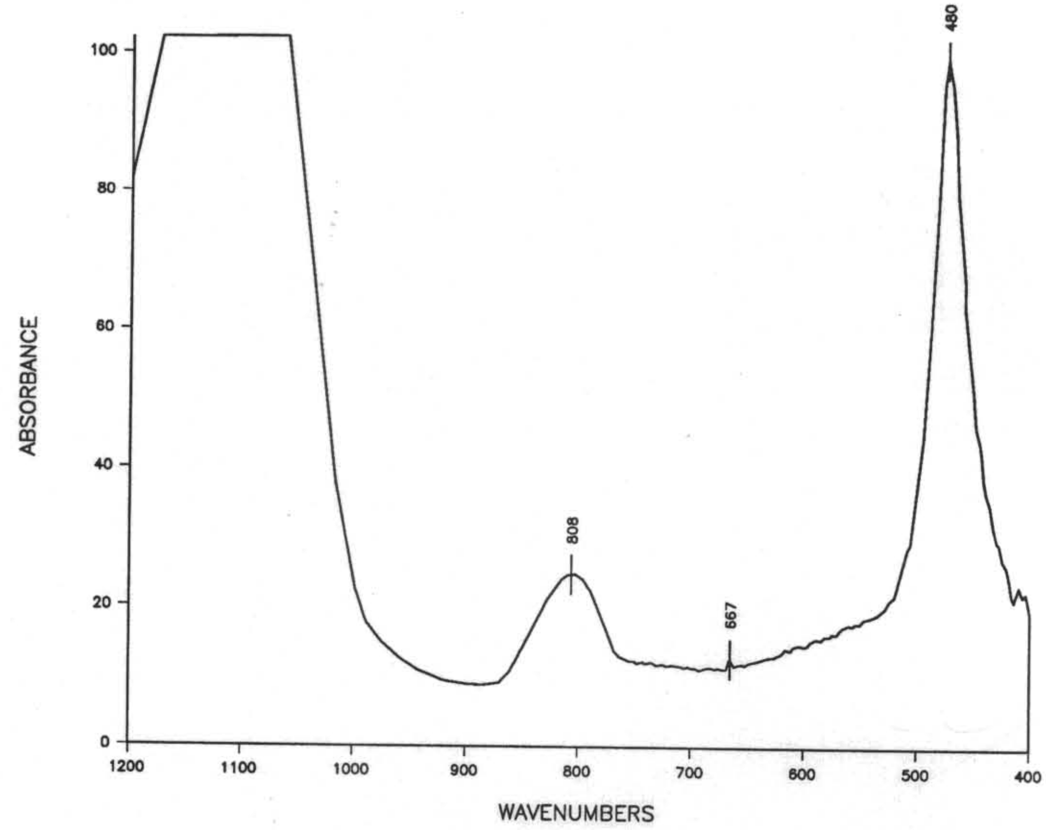


Figure 11

Fourier Transform Infra Red absorption spectrometry trace for amorphous silica fume

5 cm

SILICA FUME IN TASMANIA

Two ESA furnaces currently operate in Tasmania: the Pioneer Silicon Industries (PSI) plant at Electrona, south of Hobart, and the TEMCO ferrosilicon refinery at Bell Bay, north of Launceston. The PSI plant was converted in 1986 from a relatively old Calcium Carbide-producing works, dormant for about six years, and now produces silicon metal. The Temco plant produces mainly "ferrosilicon", a mixture of silicon and iron silicides, and has been operating since about 1974. Both plants produce by-product silica fume, most of which is collected in large filters in baghouses. The PSI smelter has sparked particular controversy as it is situated in an otherwise non-industrial area favoured by city workers desiring a semi-rural or seaside lifestyle.

Table 1 identifies the mineralogical composition of feed material at the two sites, and Tables 2 and 3 identify the mineralogical composition of typical baghouse products (mostly silica fume).

Results of testing various dust samples (unpublished data, using X-ray diffraction and polarised light microscopy), mostly collected on filters from within the PSI plant, indicate great complexity, with up to 100% amorphous silica, 95% silicon metal, 55% quartz, 40% cristobalite, 30% silicon carbide, 25% coke, 5% silicon carbide, 7% corundum (Al_2O_3), and traces (probably <2%) of tridymite, zincite (ZnO), calcite, halite ($NaCl$), aluminium (± silicon) carbides, ammonium phosphates and wood fibre. Outside of the plant, local dusts and sea spray contribute salts, quartz, pyroxenes, plagioclase, iron oxides, soot, organic material, clay minerals and probably many other materials. Some of these are difficult to interpret as filter-collected samples are often ashed, producing various reaction and recrystallisation products (e.g. halite ($NaCl$), thenardite (Na_2SO_4), aphthitalite ($K_3Na(SO_4)_2$), combeite ($Na_4(Ca,Al,Fe)_3Si_6O_{16}(OH,F)_2$), $Na_4Al_2Si_2O_9$, and some unidentified phases.

Simple sedimentation in water is very effective at separating silica fume from quartz and most other

TABLE 1

XRD analyses of feed material — PSI and TEMCO

Sample No.	Date/ID	Approximate %								
		Amorphous Carbon	Quartz	Hematite	Magnetite	Kaolinite	Si	$FeSi_2$	SiC	Other
L300408	Temco remelt	-	-	-	-	-	major	minor	-	?
L300409	Coal, Temco	major	trace	trace	-	minor	-	-	-	-
L300410	Iron ore, Temco	-	-	major	trace	-	-	-	-	-
L300411	Coke, Temco	major	trace	trace	-	-	-	-	trace	-
L300412	Ferrosilicon, Temco	-	-	-	-	-	major	minor	-	-
L300413	Quartzite feed, Temco	-	major	-	-	-	-	-	-	-
L300419	Quartzite feed — PSI	-	major	-	-	-	-	-	-	-

- not detected ? unknowns, probably minor

TABLE 2

Fume XRD analyses — PSI

Sample No.	Date	Approximate %					
		Amorphous Silica	Quartz	Cristobalite	Silicon	Silicon Carbide	Other*
L300414	12-Nov-89	90	5.5	2	0.5	2	-
L300415	14-Dec-89	89	6.5	2.5	0.5	2.5	-
L300416	18-Dec-89	89	6	2.5	0.5	2.5	-
L300417	19-Dec-89	90	6.5	1.5	0.5	1.5	-
L300418	20-Dec-89	90	6.5	1.5	0.5	1.5	

contaminants, because of the very fine grainsize of the fume.

Baghouse dusts from the Barrack Silicon Plant in Bunbury, W.A. and the Zimbabwe Alloys Plant in Harare, Zimbabwe are shown in Table 4 for comparison.

METHODS OF ANALYSIS

Silica in environmental samples can be determined by a number of methods, but the ideal method should necessitate a minimum of handling (to prevent sample loss, as sample sizes are typically only about 0.1–1 mg), and should readily differentiate the different crystalline forms of silica, and determine amorphous silica as well. The detection limits should be about 0.05 mg or less, with reasonable accuracy and reproducibility, and little interference.

Silica in these samples can be determined quantitatively by a number of methods, including XRD, IR, visible absorption spectrophotometry (VAS; spectrophotometry or colorimetry), X-ray fluorescence (XRF), and atomic absorption spectroscopy (AAS).

AAS and VAS can determine the total silica content in aqueous solution quite accurately, but there are problems in the removal of quartz from other silicates (Eller *et al.*, 1984; Leinen, 1977), and it destroys the sample. It is also impossible to differentiate the different crystalline forms of silica (e.g. by selective dissolution).

XRF can determine total silicon, non-destructively on a filter, but has a relatively low precision and high detection limits, and is also non-specific for the chemical or crystalline form of silicon.

IR can determine the total free silica, but has difficulty resolving the different silica polymorphs, or even differentiating crystalline from amorphous silica (Bye *et al.*, 1980; Eller *et al.*, 1984). It can be used directly on filter (NHMRC, 1984) but filters usually produce undesirable

TABLE 3

Fume XRD analyses — TEMCO

Sample No.	Date	Approximate %					
		Amorphous Silica	Quartz	Cristobalite	Silicon	Silicon Carbide	Other
L300403	23-Nov-89	99	0.5	-	0.5	?	*
L300404	24-Nov-89	98	1	-	0.5	0.5	-
L300405	25-Nov-89	98	0.5	-	0.5	1	-
L300406	26-Nov-89	98	0.5	-	0.5	1	-
L300407	28-Nov-89	96	3	?	0.5	0.5	-

- not detected * Hematite (iron oxide) in 300403

TABLE 4

Fume XRD analyses — Samples from Simcoa, Bunbury , WA, and Zimbabwe Alloys, Harare

Sample No.	Identification	Approximate %					
		Amorphous Silica	Quartz	Cristobalite*	Silicon	Silicon Carbide	Other
Zimbabwe:							
L300492	$FeSi_{75}$	?	minor	major	-	-	U
L300493	FeSiCr	major	minor	minor	-	-	U, S
Simcoa (wt. %):							
L300497	Densified + C	97	1.5	-	-	-	-
L300498	Standard	98	1	-	-	-	-

- not detected U unknown phases S spinel type phases?
* Cristobalite of low to moderate crystallinity.

11/16

interference, and lower detection limits are obtained by ashing the filter and preparing a KBr pellet (Eller *et al.*, 1984).

XRD is one of the most useful methods for determining the presence of major amounts (usually > about 1%) of different crystalline compounds. It can also be used, with some difficulty, for the detection of some amorphous compounds. It is most frequently used for semi-quantitative analysis of geological and pedological samples, but with appropriate techniques can produce quantitative analyses of a wide range of materials with quite satisfactory accuracy and precision (Snyder and Bish, 1989).

XRD methods to quantitatively determine the proportions of several different silica polymorphs have been developed by several workers, including Altree-Williams *et al.*, 1977; Bye *et al.*, 1983; Eller *et al.* (1984); and NHMRC (1984). These methods appear quite adequate for quartz, but there are some doubts about cristobalite, as there are variations in crystallinity when it is formed metastably (Foster *et al.*, 1966).

The detection limit for silica fume is very high (~10–40%, depending upon the sample size and matrix) because of the very broad, weak peak (fig. 6). Eller *et al.* (1984) have suggested a method for silica fume by thermal conversion of the amorphous silica to cristobalite. This method has some drawbacks in that sample loss could be quite significant at levels near the proposed TLV, and there may be considerable variation in the crystallinity of cristobalite (mentioned above), which would also decrease the accuracy. Thermal experiments, described below, have been conducted with silica fume to partially test the procedure and crystallinity variations.

Bye *et al.* (1980) have devised a method for the determination of both amorphous and crystalline silica by a combination of XRD and IR techniques. Errors are again introduced by the need to ash and refilter samples. A modification of this technique, to analyse samples directly on filter, was under investigation but found unworkable. Fanke (1991) found the method unsatisfactory for samples with large amorphous silica/quartz ratios, as found in most dust samples from ESA furnaces.

Heggestad *et al.* (1984) indicated the value of thermosonimetry in determining the presence of small amounts of cristobalite in amorphous silica. The method measures mechanical vibrations relating to volume changes with temperature, and can detect about 0.3 wt.% or more cristobalite in amorphous silica. This could be a very useful tool, but the effect of other contaminating compounds is unquantified and probably serious, and the method appears to use a moderate sample size. The method probably could not readily analyse dusts on filters.

SYNTHESIS EXPERIMENTS

The stability of silica fume has been examined in a series of heating experiments, carried out by this department, PSI and TEMCO. The products were analysed by XRD and the results are shown in Tables 5, 6 and 7, and Figure 12. Table 8 and Figure 13 indicate the relative crystallinity of different cristobalites. The "crystallinity index" (I(3.15)/I(4.05)) used ranges from 0.061 to 0.083, compared with 0.036 to 0.073 for Foster (1966), indicating that these samples show a relationship between crystallinity and temperature, but not as extreme as for Foster's samples. These results suggest that heating at 1000°C for about one hour produces cristobalite of adequate and reproducible crystallinity. Prolonged heating between 1000 and 1500°C initiates tridymite formation (fig. 14).

The results of heating tests on natural amorphous silica (opal-A) are shown in Table 9 and Figure 15 for comparison (Jones and Segnit, 1971). Opal-A obviously behaves somewhat differently to silica fume, and other forms of amorphous silica apparently also vary in this regard: Jahr (1981) noted that precipitated amorphous silica recrystallises to cristobalite at 500°C, but the time taken was not stated. Wahl *et al.* (1961) described a grainsize dependence for the inversion temperatures for silica polymorphs.

Alkaline solutions promote recrystallisation (Campbell and Fyfe, 1960), and this is probably the cause of cristobalite formation on ashed filters containing silica fume, environmental dusts and mixed salts (unpublished data). Campbell and Fyfe (1960) noted that amorphous silica recrystallises to minor cristobalite in 20 hours, to cristobalite + minor quartz in 80–90 hours, and to pure quartz in about 100 hours, in alkaline solutions at 245°C.

DISCUSSION AND CONCLUSIONS

The physical and toxicological properties of quartz are relatively well established, but there is much less certainty regarding the properties and behaviour of silica fume and other forms of amorphous silica. The physical properties of the different crystalline and amorphous forms of silica depend on the grainsize, chemistry and method of formation, and probably other factors.

Testing methods indicate some difficulties in the determination of silica fume, but XRD appears to be adequate for quartz and other crystalline materials. XRD is also adequate for amorphous silica, where present in major amounts in bulk samples, but not for samples on filters or where present in small amounts. IR appears adequate for crystalline materials, but has difficulty with amorphous silica. XRD of heated samples shows potential for quantitatively determining the different forms of silica, but other possible methods should be investigated. Thermosonimetry, in particular, could prove to be a useful analytical technique for bulk samples.

TABLE 5

Heating tests on amorphous silica, Departmental studies

Temperature(°C)	Time (hours)	Approximate %		
		Amorphous Silica	Cristobalite	Tridymite
800	12	100	0	0
938	2	99	1	0
973	6	0	100	0
973	1	0	100	0
1000	12	0	94	6
1078	24	0	100	0
1078	2	0	100	0
1200	15	0	85	15
1200	12	0	94	6
1200	36	0	88	12
1200	52	0	71	29
1400	1	0	99	1

TABLE 6a

Sample details — PSI fume treatment products

Sample No.	*Identification*
L300422	A: Fume, heated to 500°C for 21 hours
L300423	B: Fume, heated to 500°C for 21 hours and 900°C for 4 hours
L300424	C: Fume + CaO, heated to 800°C
L300425	D: Fume + CaO, slurried and heated to 800°C
L300426	E: Fume & Ca $(NO_3)_2$, heated to 800°C
L300427	F: Fume & Ca (CO_3), heated to 800°C
L300428	G: Fume, heated to 900°C O/N, & 1200°C 3 hours
L300429	H: Fume, heated to 900°C O/N
L300430	I: Fume, untreated
L300672	17 hours at 900°C
L300673	24 hours at 900°C
L300674	26 hours at 900°C
L300675	45 hours at 900°C

TABLE 6b

Sample No.	Approximate %						
	Amorphous Silica	Quartz	Cristobalite	Silicon	$Ca(OH)_2$ Portlandite	CaSiO3 Wollastonite	Other (trace) *
L300422	99.5	0.5	-	-	-	-	-
L300423	99	0.5	-	-	-	-	-
L300424	minor	-	-	-	major	-	lime, ?larnite
L300425	35	-	-	-	-	65	-
L300426	96	2	0.5	1.5	-	-	-
L300427	minor	-	-	-	-	-	calcite, ?larnite
L300428	-	trace	>90?	-	-	-	??
L300429	99.5	-	-	0.5	-	-	-
L300430	99	0.5	-	0.5	-	-	lime, ?larnite
L300672	99	1	-	-	-	-	-
L300673	99	1	<1	-	-	-	-
L300674	99	<1	-	-	-	-	-
L300675	99	<1	-	-	-	-	-

TABLE 7a

XRD analyses — Temco

Sample No.	*Identification*
L300420	A: Fume, filtered and heated to 1200°C for 12 hours
L300421	B: Fume, filtered and unheated
L300438	C: Fume, unfiltered and heated to 1200°C for 12 hours
L300465	SF-A
L300466	SF-B
L300467	800°C, 12 hours
L300468	1000°C, 12 hours
L300469	1400°C, 1 hour
L300611	1200°C, 36 hours
L300612	1200°C, 52 hours
L300613	1400°C, 4 hours
L300614	1400°C, 2 hours

TABLE 7b

Sample No.	Approximate %							
	Amorphous Silica	Quartz	Cristobalite	Tridymite	Silicon	Silicon Carbide	Temperarture (°C)	Time (hours)
L300420	-	-	85	15	-	-	1200	12
L300421	100	-	-	-	-	-	0	
L300438	-	1	93	6	-	-	1200	12
L300465	98.5	-	-	-	0.5	1	0	
L300466	98	0.5	-	-	0.5	1	0	
L300467	99.5	0.5	-	-	-	-	800	12
L300468	-	1	93	6	-	-	1000	12
L300469	-	trace	99	1	-	-	1400	1
L300611	-	1	87	12	-	-	1200	36
L300612	-	1	70	29	-	-	1200	52
L300613	-	1	98	1	-	-	1400	4
L300614	-	1	98	1	-	-	1400	2

TABLE 8

Cristobalite crystallinity (as used by Foster, 1966)

Temp. °C	*Run (hours)*	*I(3.14)/I(4.05)*
980	1	0.064
980	6	0.061
1000	12	0.063
1080	2	0.062
1080	24	0.066
1200	3	0.062
1200	36	0.082
1400	1	0.079
1400	2	0.083

TABLE 9

Heating tests on amorphous silica (from Jones and Segnit, 1971)

Temp. (°C)	Run (Days)		
	Amorphous silica	Amorphous silica + cristobalite	Cristobalite
900	58	76	
900		97	
950			21
1000	2		8
1050			2
1100			3
1300			0.05

14/16

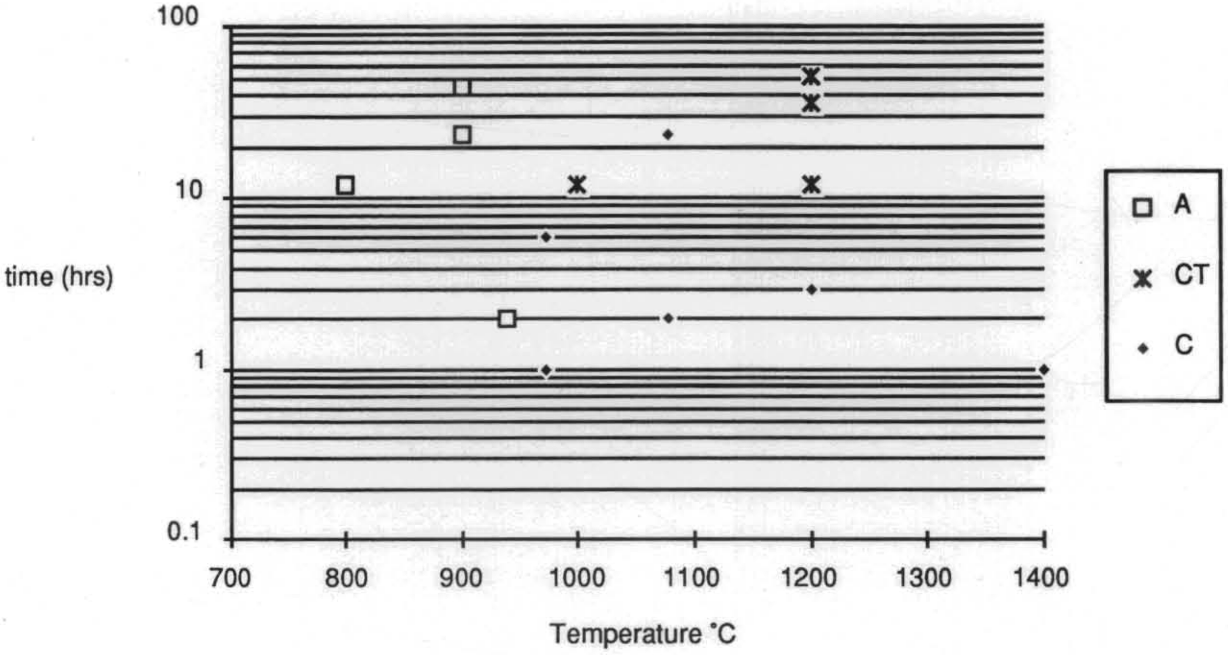
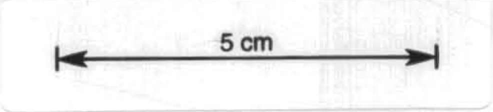


Figure 12

Results of heating tests on amorphous silica
(maximum temperature reached versus time at that temperature).
Products: A = amorphous silica; C = cristobalite only; CT = mixtures of cristobalite and tridymite.



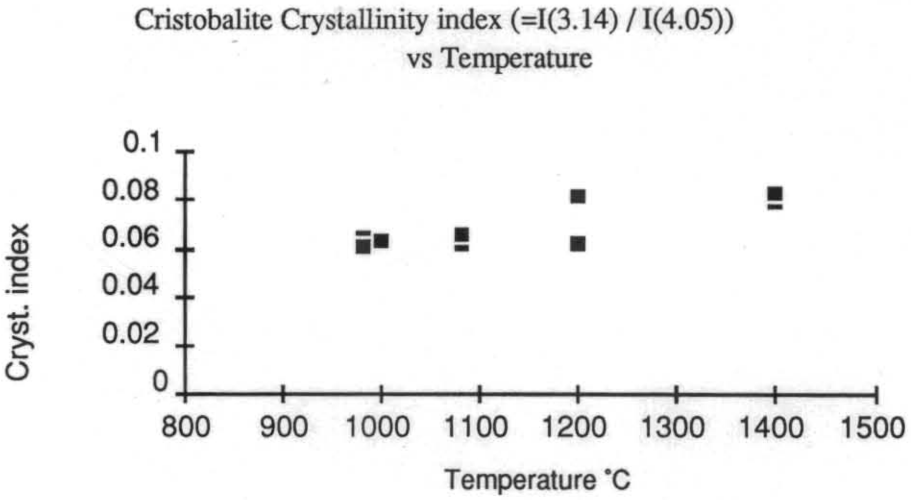


Figure 13

Crystallinity of cristobalite in heated amorphous silica samples, by the method of Foster (1966).

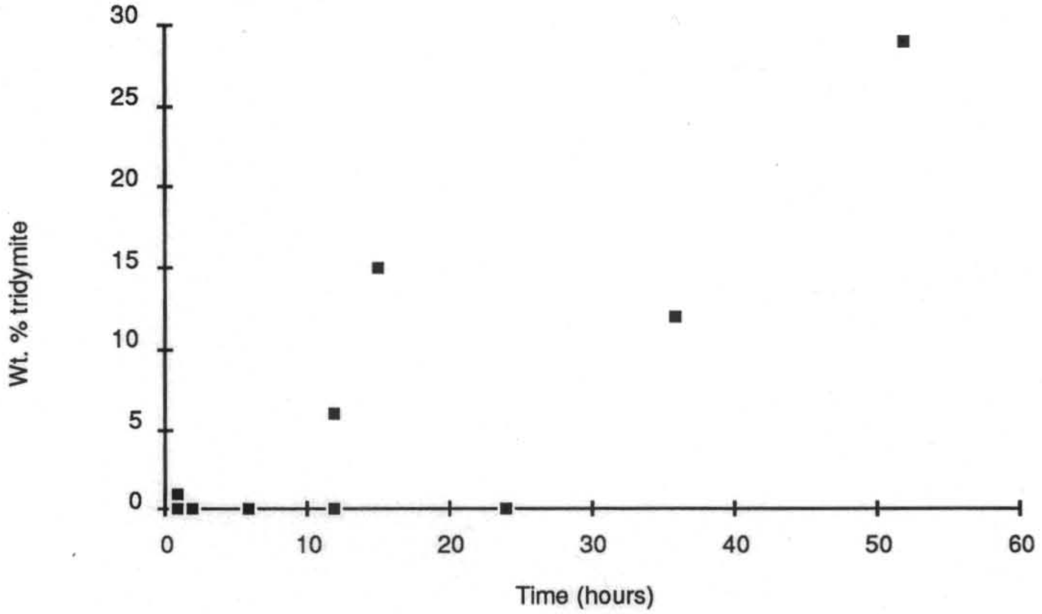


Figure 14

Weight percentage of tridymite in heated fume, as determined by X-ray diffraction, related to the heating period at maximum temperature

5 cm

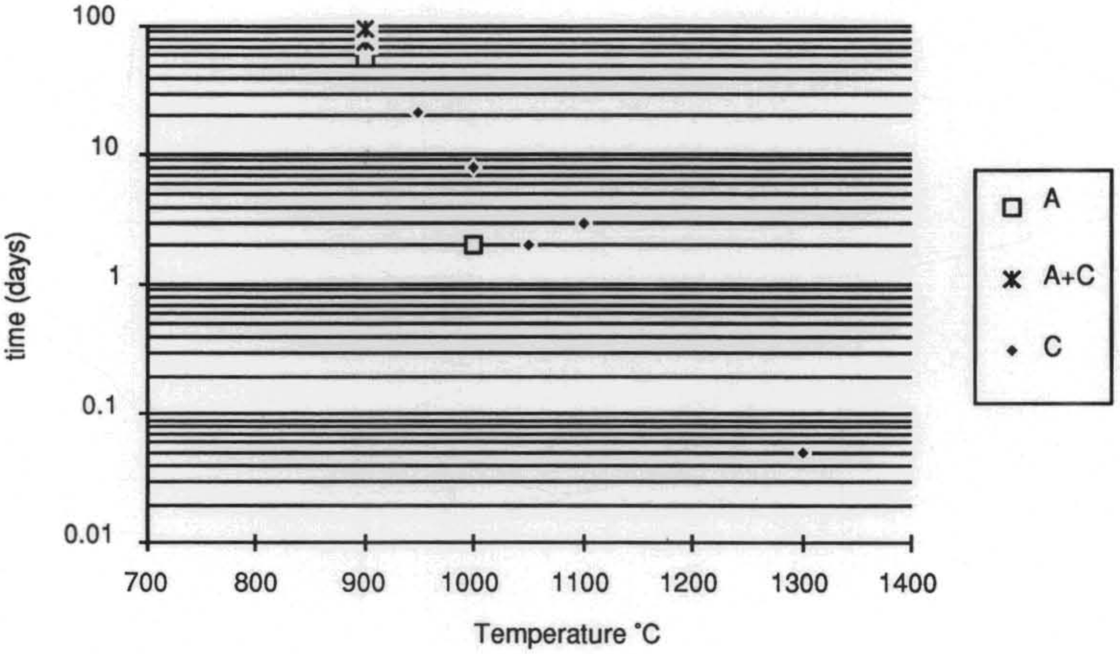


Figure 15

Results of heating tests on natural amorphous silicas ("opals") (maximum temperature reached versus time at that temperature). Products: A = amorphous silica; C = cristobalite only; A + C = mixtures of cristobalite and amorphous silica. Data from Jones and Segnit (1971)

BIBLIOGRAPHY

ACGIH, 1989. ACGIH threshold limit values committee (chemical substances). *Appl. Ind. Hygiene* 4 (2):R10–R12.

Altree-Williams, S.; Lee, J.; Mezin, N. V. 1977. Quantitative X-ray diffractometry on respirable dust collected on Nucleopore filters. *Ann. Occ. Hygiene* 20:109–126.

Bye, E.; Edholm, G.; Gylseth, B.; Nicholson, D.G. 1980. On the determination of crystalline silica in the presence of amorphous silica. *Ann. Occup. Hyg.* 23:329–334.

Bye, E.; Davies, R.; Griffiths, D. M.; Gylseth, B.; Moncrieff, C. B. 1984. In vitro cytotoxicity and quantitative analysis of diatomaceous earth products. *British J. Ind. Medicine* 41:228–234.

Campbell, A. S.; Fyfe, W. S. 1960. Hydroxyl ion catalysis of the hydrothermal crystallisation of amorphous silica; a possible high temperature pH indicator. *Amer. Mineral.* 45:464–468.

Eller, P. M. (ed.), 1984. *NIOSH manual of analytical methods, 3rd edition.*

Fenner, C. N. 1913. Stability relations of the silica minerals. *Amer. J. Sci.* 36:331–384.

Foster, P. K.; Hughes, I. R.; MacKenzie, K. J. D, 1966. X-ray diffraction and thermal properties of cristobalite-containing ceramics. *NZ J. Sci.* 9:249–260.

Franke, E. 1991. *Temco silica fume project: Investigation into a method for the quantitative determination of amorphous silica in the presence of crystalline silica.* BHP report (unpublished).

Ghio, A. J.; Kennedy, T. P.; Schapira, R. M.; Crumbliss, A. J.; Hoidal, J. R. 1990. Hypothesis: is lung disease after silicate inhalation caused by oxidant generation? *Lancet* 336:967–969.

Heggestad, K.; Holm, J. L.; Lonvik, K.; Sandberg, B. 1984. Investigations of Elkem Micro Silica by Thermosonimetry. *Thermochimica Acta* 72:205–212.

Jahr, J. 1981. Possible health hazards from different types of amorphous silicas, *in:* Dunnom, D. D. (ed.). *Health effects of synthetic silica particulates.* 199–213. American Society Testing Materials. ASTM STP 72.

Jones, J. B.; Segnit, E. R. 1971. The nature of opal. 1. Nomenclature and constituent phases. *J. geol. Soc. Aust,* 18:57–68.

Kastner, M.; Keene, J. B.; Gieskes, J. M. 1977. Diagenesis of siliceous oozes — 1. Chemical controls on the rate of opal-A to opal-CT transformation — an experimental study. *Geochim. Cosmochim. Acta.* 41:1041–1059.

Leinen, M. 1977. A normative calculation technique for determining opal in deep-sea sediments. *Geochim. Cosmochim. Acta.* 41:671–676.

NHMRC, 1984. *Methods for measurement of quartz in respirable airborne dust by Infrared Spectroscopy and X-ray diffraction.* NHMRC.

Snyder, R. L.; Bish, D. L.1989. Quantitative analysis. *in:* Modern Powder Diffraction. *Reviews in Mineralogy* 20:101–142, Mineral. Soc. Amer.

Vallyathan, V.; Shi, X.; Dalal, N. S.; Irr, W.; Castranova, V. 1988. Generation of free radicals from freshly fractured silica dust. *Am. Rev. Respir. Dis.* 138:1213–1219.

Vitums, V. C.; Edwards, M. J.; Niles, N. R.; Borman, J. O.; Lowry, R. D. 1977. Pulmonary fibrosis from amorphous silica dust, a product of silica vapour. *Archives Envir. Health* 32(2):62–68.

Wahl, F. M.; Grim, R. E.; Graf, R. B. 1961. Phase transformations in silica as examined by continuous X-ray diffraction. *Amer. Mineral.* 46:196–208.

[24 July 1991]