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# The Surface Chemistry of Crushed Quartz Dust in Relation to its Pathogenicity

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## Abstract

The surface chemistry of finely divided quartz dust has been investigated from the standpoint of its fibrogenicity by EPR and adsorption calorimetry. Even after grinding in the atmosphere, quartz bears surface radicals, originating from homolytic cleavage of Si–O–Si bonds and subsequent reaction with atmospheric components. These radical sites, which readily react with both $O_2$ and $H_2O$, can be regarded as possible initiators of the macrophage-mediated reaction resulting in lung fibrosis. The heat of adsorption of water indicates the presence of $\sim 3 \times 10^{17}$ very strong sites ($-\Delta H \geqslant 180$ kJ mol$^{-1}$) on all quartz samples, but these are totally absent in chemically prepared amorphous silicas. Mechanical cleavage of the covalent Si–O bond, more than crystallinity, is suggested as the primary cause of $SiO_2$ toxicity.

## Introduction

The biological mechanism through which the inhalation of quartz dusts starts a fibrogenic process resulting in silicosis, has not yet been fully understood at the molecular level. In spite of a large number of published papers on this subject there is a gap between medical and chemical work. Most biological tests *in vitro* or *in vivo* are not precise enough on crystallinity, particle size and origin of the surface (precipitation, ignition, grinding). On the other hand, in the few chemical studies, some confusion exists between cytotoxic action (caused by any silica and probably related to hydroxyl population) and fibrotic action, which occurs as a consequence of failed phagocytosis; this is due to a macrophage fibrogenic factor (MFF), revealed and characterized by Heppleston and coworkers [1–3]. Also the immunological theory recently revised by Pernis and Vigliani [4] requires a primary interaction between the cell and the $SiO_2$ particle – probably a selective oxidation – which has not yet been discussed on a chemical basis.

The MFF – a protein of molecular weight around 15 000 – only appears when quartz or other crystalline polymorphs have been phagocyted; its synthesis is probably catalyzed by quartz itself within the macrophage [5].

It is widely accepted that only crystalline polymorphs are dangerous in yielding pneumoconiosis, whereas amorphous silicas are mainly inactive [6]. We recall here that, with the exception of only stishovite, all crystalline polymorphs are made up of tetrahedral units variously linked together. Much attention has thus been given to the role of crystallinity, and the primary cause of the whole process has been sought in some particular surface states characteristic of crystalline materials. Some notable exceptions, however, should be considered. On the one hand, stishovite, the only octahedral polymorph (Si six-fold coordinated), is totally inactive [7, 8]; on the other hand, vitreous silica, *i.e.* the material obtained by rapid solidification of the melt, is somewhat silicotigenic [9]. It is our opinion that not only crystallinity but also the way in which the surface has been created (grinding, precipitation. pyrolysis) have to be considered. In fact all amorphous silicas – except the vitreous one – have been chemically prepared and their surface is largely covered by silanols and molecularly bonded water in equilibrium with atmospheric components. On the contrary, when dealing with quartz dusts or vitreous silicas the exposed surface is created by mechanical cleavage and this causes a particular reactivity towards atmospheric components: in fact, dangling bonds and strained siloxane bridges are formed upon grinding [10–13].

Criteria for ‘surface reconstruction’ usually invoked to explain the relationship between surface and bulk arrangements of atoms or ions in chemically prepared materials do not hold in such a case and the surface has to be considered as a non-equilibrium interphase, which is very reactive and likely to undergo slow subsequent modifications. The crucial role of the grinding process has been largely stressed, even in recent studies [14], but a clear relationship between the surface chemistry of mechanically ground silica and its toxicity has not yet been proposed.

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On the basis of the mentioned biological data and model proposed, it is clear that the clue for the molecular basis of silica pathogenicity will come from a detailed investigation of the surface chemistry of various silica samples, in order to clarify:

(i) the existence of differences in the nature of the surface and its activity due to crystallinity, *i.e.* comparison between amorphous and crystalline samples; and

(ii) evidence of particular sites on powdered samples obtained by grinding, which is the condition of the dusts inhaled by patients afflicted by silicosis.

Differences between the surface properties of quartz and amorphous silicas have already been found in our laboratory [15–17].

A particular reactivity of crushed quartz has been reported by several authors [10–13, 18, 19]. To our knowledge, however, no attempt has been made to relate these physicochemical properties to the specific biological activity of quartz.

Surface work on freshly ground specimens is obviously very difficult to perform because of the very poor surface area which can be attained. Surface radicals reported so far in the literature [11–13, 19] have never been related to quartz toxicity. The aim of our research is a general correlation between what is known of the basic surface chemistry of quartz dusts and its biological impact. The present paper reports some preliminary investigation on the free radicals created by grinding any quartz sample and on the energy of interaction of water vapour with crystalline and amorphous silicas.

## Experimental

Very pure crystalline quartz chips (99.999%, Atomergic Chemical Corp.), obtained by purification of the melt, natural Madagascar quartz, and pure silica glass crushed in an agate ball mill or in a mortar were used for EPR investigations.

Three crystalline powdered silicas (99.5% purity) of different origin, having the quartz structure as tested by XRD analysis, were used for water vapour adsorption (BET surface area 4.5–5 $m^2 g^{-1}$). An amorphous silica (Porasil Alltech) of surface area as close as possible to the crystalline silicas used for the adsorption work (BET surface area 16.1 $m^2 g^{-1}$) was used to compare amorphous to crystalline behaviour.

EPR spectra were performed on a Varian E 109 spectrometer operating in the X band mode (9.4 GHz). After grinding, the samples were introduced in an appropriate EPR cell which allowed evacuation and introduction of different gases without exposure to air.

The heats of adsorption of water were measured at 303 K by means of a Tian Calvet microcalorimeter connected to a volumetric apparatus, following the procedure previously described [20].

## Results and Discussion

### *Surface Radicals*

All our samples were free of paramagnetic signals before grinding. Upon grinding, all quartz samples gave rise to structured spectra, whereas no spectra at all could be detected with the chemically prepared amorphous samples, even after prolonged ball milling. Silica glass also gave rise to paramagnetic signals upon grinding but these were less intense than crystalline specimens. The EPR spectra recorded *in vacuo* at room temperature and at 77 K of freshly ground quartz chips are reported in Fig. 1. Spectra of the other crushed crystalline specimens were similar, differing in the mutual intensity of the various components but not in the *g* values. The spectrum of an industrially micronized quartz, already reported [16], is somehow different, and its comparison with the present ones will be discussed elsewhere. The spectra in Fig. 1 are due to several paramagnetic centres, whose origin has to be sought in the simultaneous action of grinding and interaction with the atmosphere. The component centered at $g = 2.0004$ is very easily saturated. When the same spectrum is recorded at a very low microwave power (0.5 mW) (Fig. 2), two components appear ($g_{\parallel} = 2.0017$, $g_{\perp} = 2.0004$) which are characteristic of the well known E′ centre ($Si^{\bullet}$), *i.e.* a dangling bond with the unpaired electron in the $sp^3$ orbital of the silicon atom [10, 11]. Such a spectrum has been reported to occur either in the bulk, as a consequence of artificial creation of defects, or at the surface of samples ground in vacuum [12] or in an inert atmosphere [13]. It is noteworthy that the same spectrum is visible also for a sample ground in air. The compo-

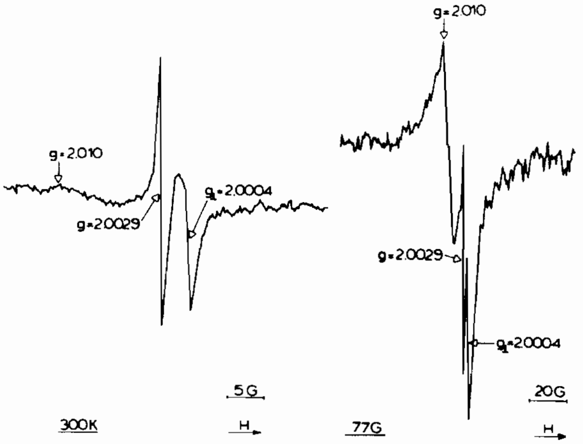

Fig. 1. EPR spectra recorded respectively at room temperature (a) and 77 K (b) on freshly crushed pure quartz (chips) (microwave power 10 mW).

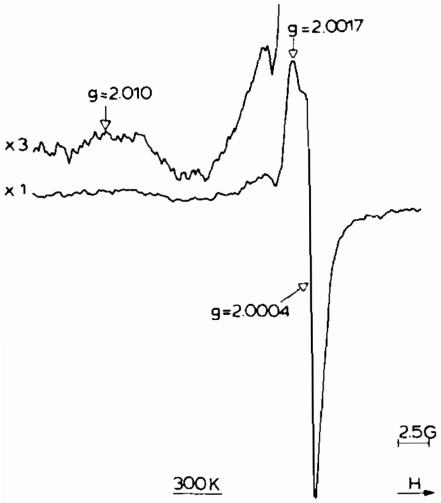

Fig. 2. EPR spectrum as in Fig. 1(a) recorded at low microwave power (0.5 mW).

nent indicated at $g = 2.010$, which is much enhanced at low temperature, is probably related to a $SiO_2^{\bullet}$ peroxy radical, originating from contact of oxygen with the surface $Si^{\bullet}$, according to the assignment given by Radtsig and Bystrikov [12]. The sharp component at $g = 2.0029$ is very unstable and reactive and disappears from the surface in a short period of time. It is seemingly related to some oxygenated radicals, since the signal is lowered or enhanced depending on the partial pressure of oxygen. Its reactivity as well as its origin are still under investigation.

It has already been proved that quartz, if crushed under vacuum, gives rise to $Si^{\bullet}$ and $SiO^{\bullet}$ radicals [10–13], formed as a consequence of homolytic cleavage of the Si–O–Si bonds which can react with several gases [21–24]. No data, however, are available so far on the reactivity and stability of these radicals upon exposure to atmosphere. The spectra recorded thus report the vestiges of these radicals not annealed by atmospheric components, and probably the product of the reaction of the surface radicals with the latter. The presence of the E′ centre in spite of exposure to the atmosphere has to be related to unreactive $Si^{\bullet}$, probably located in subsurface layers or in the bulk. The other signals arise mainly from the reaction of free radicals with $O_2$.

The presence of mechanically activated chemisorbed oxygen has been well established by several authors from the Russian school [12, 18, 19]. Three main forms have been identified, namely bridging structures (–Si–O–O–O–Si–), peroxide radicals ($-SiOO^{\bullet}$) and radical anions ($O_2^{-}$). Evidence of singlet oxygen emission from these species has also been recently put forward [19]. All these investigations have been carried out from the standpoint of a precise analysis of the reactivity of crushed $SiO_2$, giving particular care to the grinding process. In fact, the above papers quote a surface area of 10 $m^2\ g^{-1}$ for their crushed specimens. In our case, only a relatively coarse grinding was used in order to be as close as possible to the actual dusts inhaled, and the surface area attained was definitely below 0.5 $m^2\ g^{-1}$. It has been previously reported that the number of surface radicals is proportional to the surface area [11, 12] and the number of E′ centres is estimated to the $2 \times 10^{18}$ per square meter. It can thus be estimated that on the basis of surface area the spectra in Fig. 1 arise from some $10^{16}$ paramagnetic centres. The absence of several details in the spectra, which have been previously reported by other authors [11, 12], is justified by the much lower concentration of paramagnetic centres in the case examined. In any case it is clear from the analysis of the spectra that the surface radicals are created and somehow stabilized at the surface even when grinding is carried out in the atmosphere.

In the presence of oxygen the various species found by the Russian school [12, 18, 19] will probably be present both as active ESR centres, such as the one appearing at $g = 2.010$ ($SiO_2^{\bullet}$), and possibly as transient species, such as the $g = 2.0029$ one, which may evolve into the ESR inactive bridges reported by Berestetskaya *et al.* [18].

A possible scheme is reported in Fig. 3 following the reaction:

$$Si^{\bullet} + SiO^{\bullet} \xrightarrow{+O_2} SiO_2^{\bullet} + SiO^{\bullet} \longrightarrow Si{-}O{-}O{-}O{-}Si$$

A more clear-cut detection of these oxygen species is required and research is proceeding on these lines; this detection is obviously not as easy as in biological aqueous media, where specific scavengers may be used [25], or as in high surface area oxides [26]. On the basis of the present results it has, however, to be pointed out that oxygenated reactive species are present at the surface of crushed silica and these may be responsible for its fibrotic action, either by transforming the quartz surface into a very selective oxidating agent or as a possible initiator of a sequence of reactions. The toxicity and cancerogenicity of $O_2^{-}$ and similar compounds has in fact been well established in recent years [27].

The hypothesis that the toxicity of quartz might be related to its oxidative properties, and particularly to lipid peroxidation or oxidation, was put forward several years ago [28, 29]. In these cases, however, much attention was given to the membranolytic action of silica, caused by oxidation of phospholipids, and regarded as the primary step in silicosis. No connection has been made so far between: (i) the fibrogenicity of silica particles and the mechanically created surface; and (ii) the presence of oxygen active surface species and the synthesis of the MFF factor during the macrophage–particle interaction.

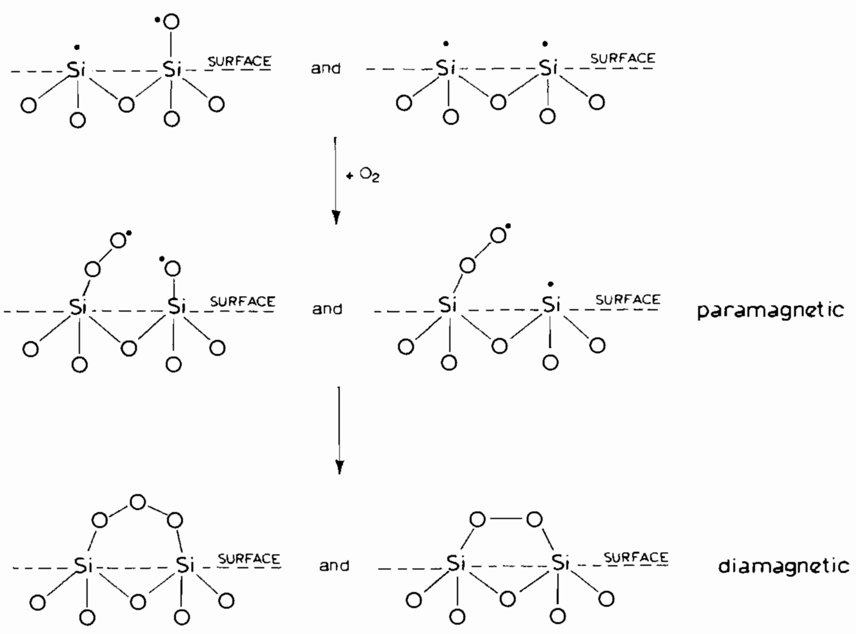

Fig. 3. Possible model of the reactivity of crushed quartz towards oxygen.

*Heat of Adsorption of Water*

The heats of adsorption of water on various quartz samples are reported in Fig. 4 as the differential heats of adsorption ($dQ^{int}/dn_a$, where $Q^{int}$ = integral heat and $n_a$ = number of adsorbed $H_2O$ moles) *versus* adsorbed amount ($n_a$). Figure 4 also reports data on an amorphous silica (Porasil) for comparison. Prior to adsorption, the samples were evacuated and outgassed at 423 K for two hours in order to eliminate molecularly adsorbed water without affecting the surface hydroxyl population [17].

It is noteworthy that in spite of different origins and morphologies, on the differential heat plot all curves merge together at coverages above 1 μmol $m^{-2}$, but all crystalline samples exhibit a very small fraction of sites ($3 \times 10^{17}$ $m^{-2}$) with an extremely high heat of adsorption (400 kJ $mol^{-1} \leqslant q^{diff} < 180$ kJ $mol^{-1}$) which are totally absent in the amorphous silica. The expected interaction of water with a silica surface, mildly outgassed as in the present case, is the coordination of the molecule via two H bonds to the surface silanols, followed by physical adsorption of water in multilayers. The former process, involving two H bonds, is expected to release a heat of interaction not higher than 120 kJ $mol^{-1}$, whereas that of the latter should be close to the latent heat of liquefaction (44 kJ $mol^{-1}$) [30, 31].

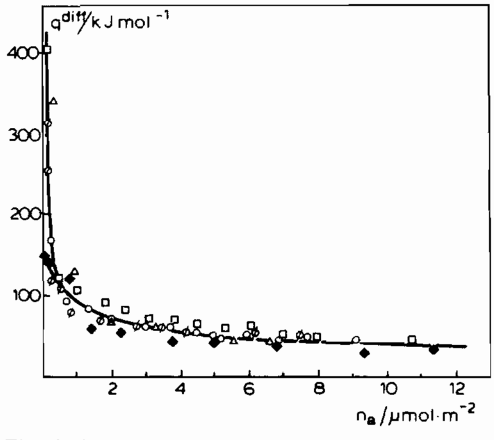

Fig. 4. Heat of adsorption of $H_2O$ onto various crystalline samples (○; ϕ, △, □) and amorphous silica (◆); differential heat ($q^{diff}$) *vs.* adsorbed amount ($n_a$).

This is completely in agreement with what happens both on quartz and on amorphous silicas at coverages higher than 0.5 mol $m^{-2}$, where the heat progressively decreases from 100 kJ $mol^{-1}$ to the heat of liquefaction of water, as expected. In contrast, the extremely high value recorded on quartz when the first 0.5 μmol $m^{-2}$ of water are adsorbed is rather exceptional and clearly indicates the occurrence of a surface reaction, probably involving the dissociation of water. Moreover, this value is even higher than that found for more ionic solids, such as $TiO_2$ and $Al_2O_3$, upon heterolytic dissociation of water on an anion–cation site [32, 33]. The corresponding dissociation of water on silica, via cleavage of a regular siloxane bridge, only occurs at high temperature and pressure because of the high stability of the Si–O–Si bond ($\pi$ bond from a p orbital of oxygen and a d orbital of Si) [30]. The sites dissociating water on quartz have thus to be sought in strained siloxane bridges caused by mechanical grinding, or in oxygen bridges and surface radicals which are present in very low concentration but are highly reactive on the outgassed surface. It is noteworthy that the concentration found for these strong sites ($3 \times 10^{17}$ sites $m^{-2}$) is close to that expected for a substantial fraction of the estimated bonds cleaved upon mechanical grinding [11, 12].

On the basis of the more recent findings by Kolbanev *et al.* [34], some possible mechanisms for the initial reaction of water are reported in Fig. 5.

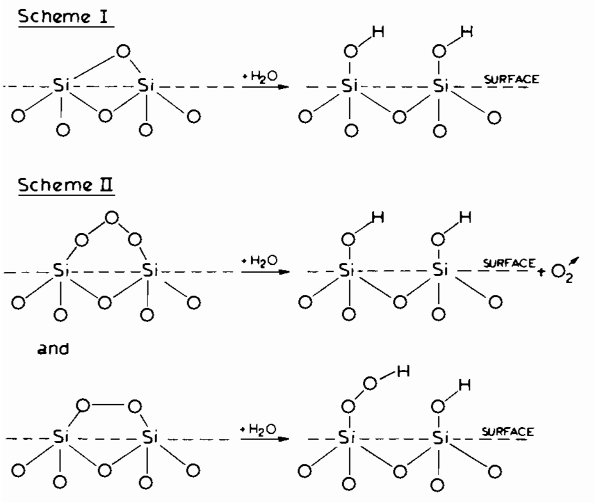

Fig. 5. Possible models for the reactivity towards water of quartz crushed in air.

## Conclusions

The surface of mechanically ground quartz exhibits some peculiar reactivity originating from the homolytic cleavage of Si–O–Si bonds, which can be related to its toxicity.

Surface radicals are formed, which upon contact with oxygen yield several partially reduced oxygen surface species of different stabilities, potentially dangerous to the organism. Strained bridges capable of dissociating water with an extremely high heat are also formed, which may also react with other biological molecules, causing structure modifications.

Both these findings can be regarded as a possible hypothesis for a molecular interpretation of the fibrogenicity of quartz dusts.

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