The strongly superlinear dose dependence of thermoluminescence in synthetic quartz

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Abstract. The 110 °C thermoluminescence (TL) peak of unfired, synthetic quartz (Sawyer Research Products) has been found to be strongly superlinear with the dose of excitation. Quadratic and nearly cubic dependences have been observed with both β- and γ-irradiation. Firing the samples at 300 °C or higher increased the sensitivity substantially and removed the superlinearity. The fired samples have been found to have a pre-dose (sensitisation) effect similar to natural quartz, however, the pre-dose effect is weaker than in many of the other types of quartz. A model of competition during the heating phase, previously suggested to explain a quadratic dose dependence, is now shown to be capable of explaining the very strong superlinearity observed with the unfired sample. Furthermore, the model can also be used to account for the observed shifts in the temperature of the TL peak, the linearity and sublinearity of the fired samples, and their higher sensitivity.

1. Introduction

The 110 °C TL peak in fired quartz has been used for dating despite it being rather close to room temperature and therefore prone to thermal fading. This is done by using the 'pre-dose' (sensitisation) property of this peak (the so-called 'pre-dose effect'; see Zimmerman 1971, Bailiff 1983, McKeever 1984, 1985, Aitken 1985). The manifestation of this effect is the change in the sensitivity of the 110 °C peak by the combined effect of a relatively high dose of irradiation followed by heating the sample to a temperature around 500 °C. A subsequent irradiation by a 'test dose' results in an appreciably higher 110 °C glow peak than is observed prior to the high-dose-plus-heating treatment. These results have been obtained in archaeological quartz, presumably fired in antiquity to ~900 °C, as well as in geological quartz fired to ~900 °C in the laboratory for periods of time in excess of one hour.

Zimmerman (1971) suggested a model to account for the pre-dose effect. In this model the increase in TL output following pre-dose sensitization is believed to be due to an enhanced probability of radiative recombination at the luminescence site. Recent ESR data lend support to this notion (McKeever *et al* 1985) although the precise mechanism by which this enhanced recom-

bination takes place is not yet confirmed. Nevertheless, no matter what the mechanism of pre-dose sensitisation, Chen (1979) has pointed out that in order to understand the linear dependence of the TL peak on the size of the test dose on the one hand, and on the amount of the sensitising dose on the other, the existence of another (i.e. competing) trapping state has to be postulated.

A similar postulate, involving competition during the heating stage of a TL experiment, was advanced by Rodine and Land (1971) in order to explain quadratic TL superlinearity in ThO_2 samples. Kristianpoller *et al* (1974) developed this model further and showed that quadratic and even stronger superlinearity can be explained by this model. Numerical calculations by these latter authors have also shown an unusual dependence of the maximum temperature of the glow peaks upon dose, over a certain range of doses. Here, an increase in the dose results, initially in an increase in the maximum temperature, followed then by a decrease.

It is to be noted that a slight superlinearity in the 110 °C peak in fired quartz has already been reported by Zimmerman (1971) as well as by other researchers. Also, stronger superlinearity has been reported by Ichikawa (1968) for a peak at about 200 °C in natural quartz. In the present paper, however, some new results are reported on β- and γ-irradiated synthetic quartz. In our work the 110 °C peak in *unfired* quartz has been found to be strongly superlinear with the dose of excitation. Firing at different temperatures increased the sensitivity

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substantially and caused the dose dependence to become linear at low doses and sublinear at higher doses. Although this peak is usually referred to as the '110 °C peak', it actually occurred at ~140 °C in the unfired sample. Firing above 300 °C, however, shifted the peak which then appeared at 110–120 °C.

The model by Rodine and Land (1971), further developed by Kristianpoller *et al* (1974), is now extended to account for the superlinearity, the sensitisation effects and the temperature shift of the 110 °C peak. Since, as noted above, the presence of competitors is an essential feature of the pre-dose effect (Chen 1979) we discuss the relevance of the present data to a description of a model for the pre-dose mechanism.

2. Experimental details

Two types of synthetic quartz, both produced by Sawyer Research Products, have been used in this work— namely, 'Premium Q' and 'Electronic Grade'. Each consisted of two sub-types; the x-growth zone, which is relatively rich in impurities (notably Al), and the z-growth zone which is 'cleaner'. The measurements were performed on the x- and z-growth zones separately.

The quartz samples were crushed, ground and sieved, grain sizes of 110–250 μm (140–60 mesh) being used in our measurements. Four to eight milligrams of powder were placed in a stainless steel dish which, in turn, was placed on a nichrome heating strip. A heating rate of 6.0 °C s^{-1} was used in these measurements. The emitted light was detected by a 9558QB (S-20) photomultiplier tube cooled to −10 °C using a FACT 50 Mk III Thorn EMI Gencom Cooler. The temperature of the TL oven was controlled, via a chromel–alumel thermocouple, by a Daybreak 520 controller. The oven was evacuated first to ~10^{-1} Torr, then back-filled with nitrogen gas to a pressure of ~600 Torr.

For high-temperature firing, the samples were annealed in air in a tube furnace and held at the desired temperature for one hour, and subsequently allowed to cool to room temperature over a period of several hours.

Most of the irradiations were carried out using a ^{90}Sr beta-source. Different doses were achieved using both different irradiation times and by placing the sample at different distances from the source. Some measurements were also made following irradiation with a ^{60}Co gamma-source. The results were found to be basically the same, independent of the method of irradiation.

3. Theoretical background

Since the work by Kristianpoller *et al* (1974) gives the basis for understanding the strong superlinearity observed in this work, we would like to repeat briefly the main points of the analysis.

The model of Kristianpoller *et al*, and now being used by us, is illustrated in figure 1. We postulate the existence of N_1 trapping centres per unit volume (of
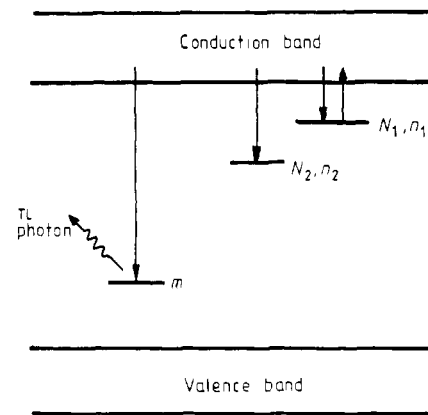

Figure 1. An energy level diagram for the competition model used to describe the experimental results. For a definition of terms, see text.

which n_1 are occupied) and m trapped holes per unit volume acting as recombination centres. Additionally, we consider there to be N_2 competing traps per unit volume, of which n_2 are occupied.

Electron spin resonance studies by Yang and McKeever (1988) and McKeever *et al* (1985) have pointed to the possibility that $(GeO_4)^-$ centres may be acting as the electron traps, of concentration n_1. The recombination site may in fact be two different defects, namely a $(AlO_4)^0$ centre and an, as yet, unidentified hole site, but which may be related to hydrogen (Yang and McKeever 1988, Jani *et al* 1984). More than one emission component has been observed in emission spectra studies of the 110 °C TL peak (Zimmerman 1971, Akber *et al* 1988) consistent with the proposal that more than one luminescent site is involved. However, this does not alter the main thrust of the model being discussed. We discuss a possible identity for the competitor later in the paper (§ 5).

Concentrations n_1, n_2 and m, as well as n_c, the instantaneous concentration of electrons in the conduction band, are time dependent. Since the sample is heated at a known rate during TL readout, $T = T(t)$, the time-dependent functions $n_1(t)$, $n_2(t)$, $m(t)$ and $n_c(t)$ can also be considered to be temperature dependent. We assume in the model that the trap, of filled concentration $n_1(t)$, is shallow enough for thermal release of electrons to the conduction band to take place. However, thermal release of electrons from the competitor to the conduction band is not allowed. We further allow retrapping of electrons at the unstable trap to take place, but, as described below, we shall assume that the probability of electron localisation at the competitor is relatively strong. The four simultaneous, differential equations governing the trapping process are then:

$$\mathrm{d}n_1(t)/\mathrm{d}t = -\gamma(t)n_1(t) + A_1 n_c(t)(N_1 - n_1(t)) \qquad (3.1)$$

$$\mathrm{d}n_2(t)/\mathrm{d}t = A_2(N_2 - n_2(t))n_c(t) \qquad (3.2)$$

$$I(t) = -\mathrm{d}m(t)/\mathrm{d}t = A_m m(t)n_c(t) \qquad (3.3)$$

$$\mathrm{d}m(t)/\mathrm{d}t = \mathrm{d}n_1(t)/\mathrm{d}t + \mathrm{d}n_2(t)/\mathrm{d}t + \mathrm{d}n_c(t)/\mathrm{d}t. \qquad (3.4)$$

Here, $\gamma(t) = s \exp(-E/kT(t))$, where E is the activation energy for the release of electrons from the trap, s is the frequency factor and $T(t)$ is the temperature. In the above equations A_1 is the probability of retrapping into the unstable trap, A_2 is the probability of trapping by the competitors and A_m is the recombination probability. $I(t)$ is the TL intensity.

By using the usual assumption that $\mathrm{d}n_c(t)/\mathrm{d}t \ll \mathrm{d}m(t)/\mathrm{d}t$, Kristianpoller *et al* (1974) reached a single differential equation in $m(t)$, namely

$$I(t) = -\mathrm{d}m(t)/\mathrm{d}t = \gamma(t)A_m m(t)F(t) \qquad (3.5)$$

where

$$\begin{aligned} F(t) = & [(n_{1_0} + n_{2_0} - m_0 - N_2) + m(t) \\ & + (N_2 - n_{2_0})(m(t)/m_0)^{A_2/A_m}] \\ & \times [A_1(N_1 + N_2 - n_{1_0} + m_0) + (A_2 - A_1)m(t) \\ & + (A_2 - A_1)(N_2 - n_{2_0})(m(t)/m_0)^{A_1/A_m}]^{-1}. \end{aligned}$$

For a given set of initial parameters (n_{1_0}, n_{2_0}, m_0) this equation can be solved numerically and the maximum intensity, as well as the temperature at the maximum, can be evaluated. Once we assume a certain dependence of n_{1_0}, n_{2_0} and m_0 on absorbed dose, then one can repeat the calculation and monitor the variations of the maximum TL intensity I_m, the area under the TL curve S and the temperature of the maximum T_m, as functions of dose.

It can be shown that strong superlinearity occurs when retrapping into N_2 is relatively strong (Kristianpoller *et al* 1974). By assuming linear dose D dependences for n_{1_0}, n_{2_0} and m_0, the analysis results in $I_m \propto D^2$. In some of these cases, the peak temperature

decreases with the dose. However, in cases where a saturating exponential growth of the type $n_{2_0}(D) = N_2[1 - \exp(-\alpha D)]$ is assumed ($\alpha =$ a constant) a rather special behaviour is noted (see figure 5 of Kristianpoller *et al* 1974). At low doses the values of I_m increase like D^2, while at higher doses stronger superlinearity is found. Once saturation is reached ($n_{2_0} = N_2$), the dependence becomes linear. Also, the peak temperature increases somewhat anomalously with the dose initially, but, at about the dose of transition from strong superlinearity to linearity, it starts to move back to lower temperatures.

In addition to the numerical solutions of equation (3.5), Kristianpoller *et al* (1974) also showed analytically that if one assumes strong competitor retrapping, namely

$$A_2(N_2 - n_2(t)) \gg A_1(N_1 - n_1(t)) + A_m m(t) \quad (3.6)$$

and weak retrapping, namely

$$\gamma(t)n_1(t) \gg A_1(N_1 - n_1(t)) \qquad (3.7)$$

and a small initial filling of the trap, i.e. $n_{1_0} \ll N_2$ and N_1, then one can arrive at

$$S \simeq [A_m/A_2(N_2 - n_{2_0})]m_0 n_{1_0}. \qquad (3.8)$$

From this equation we see that if both m_0 and n_{1_0} are linearly dependent on the dose, and $n_{2_0} \ll N_2$, then the area under the TL curve S (and, to a very good approximation, I_m as well) depends quadratically on the dose. However, if n_{2_0} is not negligible compared to N_2, then the dose dependence is expected to be more quadratic—i.e. $S \propto D^\nu$, where $2 < \nu \leqslant 3$.

4. Results

Typical TL glow curves from specimens of Premium Q x-growth quartz are shown in figure 2. These have been obtained after test doses of 1.47 Gy and show the TL peak of interest from an unfired (figure 2(A)) and a fired (figure 2(B)) sample. The firing temperature was 950 °C, maintained for 1 hour.

Representative results of TL intensity versus dose are shown in figures 3 and 4. All data are plotted on a log–log scale, thus a linear growth is revealed as a slope of one, and a slope of ν means a D^ν function. The TL data are normalised to the weight of the samples.

Figure 3 (curve A) depicts the strongest superlinearity observed. This is for the unfired Premium Q x-growth sample. The very strong superlinearity, i.e. a slope of almost 3, is readily seen. Curve B in figure 3 shows the dose dependence for a fired Premium Q x-growth sample. It is immediately seen that the TL intensity of the fired sample is much stronger than that of the unfired specimen—especially at low doses—and that the dose dependence after firing is nearly linear, with just a very slight superlinearity remaining. Also to be noted is the fact that whereas in the unfired samples the peak temperature varied between 130 and 150 °C,
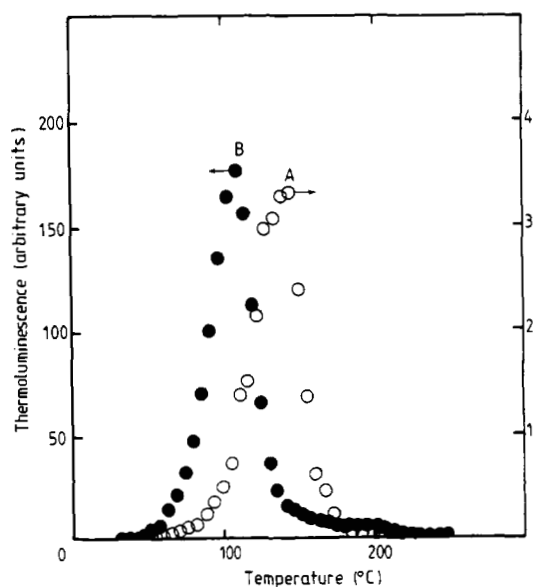

Figure 2. Thermoluminescence glow curves from two samples of Premium Q x-growth quartz. Figure 2(A) shows the TL peak of interest from an unfired sample following a β-dose of 1.47 Gy at room temperature. Figure 2(B) is the same, except that it is from a fired (950 °C for 1 hour) sample.

depending on dose (averaging at 140°C) in the fired sample the peak appeared between 110 and 118 °C (averaging at 113 °C). This general behaviour can be observed in figure 2 wherein the unfired sample reveals a peak at a higher temperature than the fired sample.

Firing fresh specimens to different temperatures and repeating the dose dependence measurements revealed that the transition from highly superlinear to nearly linear behaviour occurs near 300 °C. Curve C in figure 3 represents the dose dependence of the TL from a sample fired to only 300 °C. The dependence is linear at low doses with a sublinear-to-superlinear transition at higher doses. The peak in this ca ∶ appears at about 120 °C. Curve D in figure 3 gives the dose dependence of the sample fired to 250 °C. Strong superlinearity is still retained, though some tendency towards transition is seen at lower doses. The temperature of the peak in this case averages at 128 °C.

The same measurements were repeated for the z-growth Premium Q sample, as well as for the x- and z-growth Electronic Grade specimens. In general, the results show a distinct superlinearity for the unfired specimens with a slope on a log–log scale of up to 2, and a nearly linear behaviour for the samples fired at high temperature. As an example, figure 4 shows the results for the Premium Q z-growth sample. For the unfired sample (figure 4, curve A) the slope is approximately 1.7. For the fired sample (figure 4, curve B) the dependence is nearly linear with sublinearity at high doses and a very slight superlinearity at low doses. The temperature of the TL maximum for these samples was 121 °C (average) for the unfired specimen and 120 °C (average) for the fired sample. In the Electronic Grade
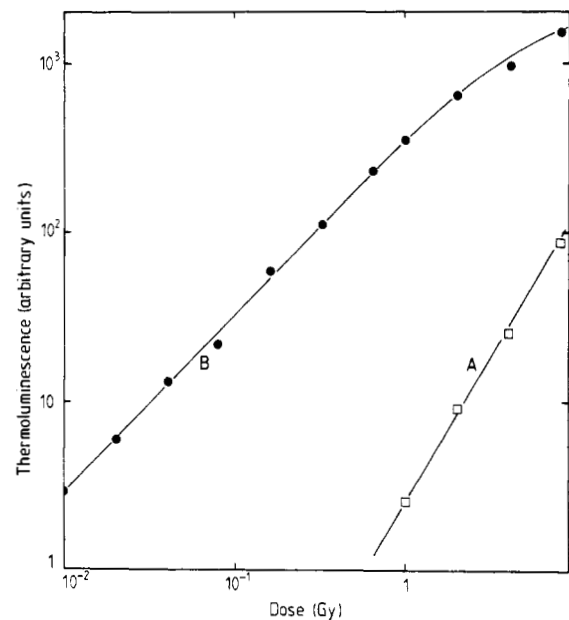
Figure 4. Growth curves for samples of Premium Q z-growth quartz: A, unfired; B, fired at 950 °C for 1 hour in air.

x- and z-growth unfired samples, which generally speaking behaved similarly to the Premium Q z-growth sample, the peak temperatures were 133 and 137 °C, respectively. Both of these temperatures are significantly higher than in the fired samples.

Finally, we would like to mention that the pre-dose sensitisation effect was still seen in the samples fired to 950 °C, although to a smaller extent than is usually reported for geological quartz.

5. Discussion

The primary motivation behind this investigation is the fact that the 110 °C TL peak in quartz exhibits the well known effect of sensitisation by a combination of an irradiation and a subsequent heating—namely, the pre-dose effect. The utilisation of this effect for dating and dosimetry purposes occasionally runs into difficulties (see, e.g., Bailiff 1983) some of which may be attributed to the effects discussed here. An important point in using synthetic quartz rather than geological or archaeological samples lies in the fact that in the present case we monitor the 'virgin' form of quartz, whereas in the geological and archaeological specimens the samples have a history of irradiations and heatings about which we usually know nothing.

Aitken (1985) and others mention, for example, that in some samples irradiation alone can sensitise the quartz samples. The present results of superlinearity can be described in the same way. Superlinearity means, for example, that if the dependence is quadratic and if two units of dose are given sequentially, then the sensitivity for the second unit is three times greater than that for the first unit. Although in geological and archaeological quartz the effect is smaller, probably due
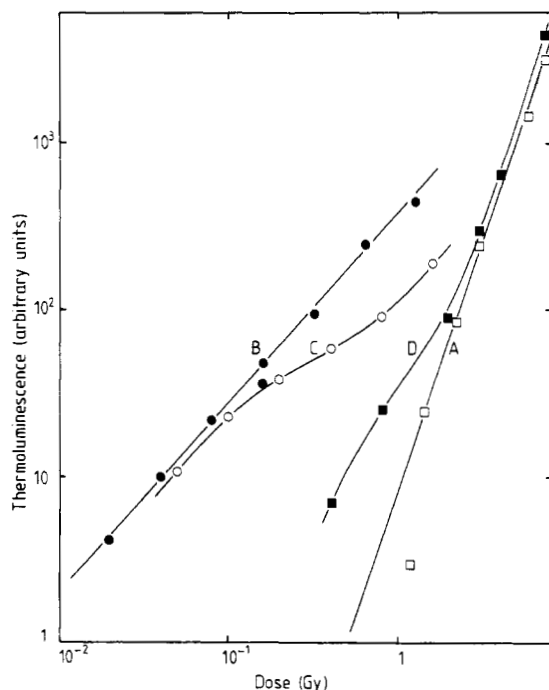

Figure 3. Growth curves for various samples of Premium Q x-growth quartz. The samples have been heat treated thus: A, as received (i.e. unfired); B, fired at 950 °C for 1 hour in air; C, fired at 300 °C; D, fired at 250 °C.

to a previous firing of the sample, a remainder of the effect may still be there.

Also the very strong sensitisation by firing alone merits some consideration (see also McKeever *et al* 1983). This very strong effect found here in the synthetic samples has actually been reported by David (1981) in geological quartz although in his case the effect was much smaller and the temperature of activation significantly higher. The important point of this observation is that if, for example, a sample fired in antiquity has relaxed partially towards its original state (presumably similar to a synthetic sample) then firing at 500 °C would reveal a change of sensitivity which may be only partly related to the archaeological dose and partly to mere firing sensitisation. If ignored, this would result in an overestimate of the archaeological dose and, therefore, of the archaeological age.

There is a number of ways to explain a superlinear dependence on the dose. Quadratic and even cubic dependences of the TL upon the dose have been reported in semiconducting diamonds by Halperin and Chen (1966). In this material, however, the superlinearity was observed only while exciting by UV light having energies appreciably below that of the band gap. The data were subsequently interpreted as being due to multistage transitions. It is obvious that with the range of energies used for the excitation of quartz in this work, the multistage transitions cannot explain the results.

Since, as we mentioned earlier, the presence of a competitor is actually *required* in order to explain the pre-dose properties observed in quartz, we have used a model involving competing traps. One possible way to include such traps in a model for superlinearity is to allow for competition during *irradiation* (see Chen and Kirsh 1981, pp 181, 361). The prediction of this model, when applicable, is that at low doses a linear dependence is expected, followed by a superlinear range which, in turn, is followed by another linear range and, finally, a tendency towards saturation. In the present case, however, the primary linear region is never seen. Furthermore, studies of the growth of the various ESR signals in quartz as a function of dose (Mondragon *et al* 1988) have revealed simple, saturating exponential growth curves, not the superlinear curves as would be expected from a model involving competition during irradiation. As a result we prefer a model involving competition during *heating*, as described in § 3.

The conversion from superlinear behaviour to linear behaviour, following high-temperature firing follows naturally from the competition-during-heating model. If firing to high temperatures removes the competitor (i.e. reduces the value of $N_2 - n_{2_0}$) then competition is no longer an important factor to consider and a linear dose response should result. The linear behaviour is reached, however, before $N_2 - n_{2_0}$ is nil. The remainder is sufficient to act as the competitor for the pre-dose effect.

Furthermore, the shift of the TL peak to lower temperature following firing can also be explained using the model. It is observed that the firing brings the sample

to a state where its dependence on dose is linear. From the analysis of Kristianpoller *et al* (1974; see figure 5 of their paper in particular) a decrease in the peak temperature is seen to be predicted theoretically in this region. In more intuitive terms, the partial removal of the competitor yields a larger, effective radiative transition probability which results in the luminescence being seen sooner (i.e. at lower temperatures).

One can also explain in a straightforward manner the increase in sensitivity following firing to high temperatures. Once the competitor has been made ineffective, or removed, all charges released from traps will find their way to luminescence sites with a result that the TL/unit dose (i.e. the sensitivity) will increase. In a recent study (Yang and McKeever 1988) we examined the ESR signals from samples of fired and unfired Premium Q and Electronic Grade quartz. We were looking for a defect centre that increased its concentration following firing and which we could then correlate with the increased TL sensitivity. However, none of the defect centres which we believed to be involved in the TL production process (i.e. $(GeO_4)^-$, $(AlO_4)^0$ and possibly $(H_3O_4)^0$) increased their concentrations in an appreciable manner after the firing treatment. (The last-named centre was not examined in the work of Yang and McKeever but recent results from our laboratory have demonstrated that it displays only minor increases following high-temperature firing.) These data are consistent with the present proposition that the increased sensitivity is due to the removal of competitors rather than an increase in the number of one of the above-named defects. It is interesting to note that a *decrease* (by factors varying from 2 to 4) in the concentration of E_1' centres was observed following firing. These are electron traps which have been shown to anneal between 300 and 400 °C (Jani *et al* 1983). Since this temperature range coincides with that over which the strong superlinearity is removed (see figure 3) then one might speculate that these centres fill the role of the competitors in the present model.

To summarise, we have reported new results of a strong superlinearity of the 110 °C TL peak in unfired, synthetic quartz. The dependence has been observed to be quadratic (D^2) with the z-growth Premium Q and z- and x-growth Electronic Grade samples, and close to cubic (D^3) with the x-growth Premium Q specimen. A previously suggested model including the involvement of a strong competitor during the heating stage has been used successfully to explain the results. The model can be used to explain the enhanced sensitivity, the conversion to linear growth and the shift of the peak to lower temperature, all following firing at high temperatures.

The existence of a competitor is required to explain certain aspects of the pre-dose effect (Chen 1979). It is to be emphasised that firing at a relatively low temperature ($\geqslant 300$ °C) removes the superlinearity without reaching the maximum sensitivity. This may be related to a partial removal of the competitors. In fact, as argued earlier, even firing at 950 °C appears to not totally remove the

competitors, but merely reduce their relative abundance. The remaining competitors can still explain the pre-dose properties of fired quartz.

Acknowledgments

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