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The use of DTA/TGA to study the effects of ground quartz with different surface areas in autoclaved cement : quartz pastes. Use of the semi-isothermal thermogravimetric technique

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Abstract

Simultaneous DTA–TG and derivative thermogravimetry, DTG, have been employed to evaluate autoclaved cement : quartz pastes, before and after carbonation. DTG curves provided more detailed information about mass loss phenomena than the corresponding TG curves. Results indicated that the dynamic method did not allow sufficient time for reactions to be completed. Data obtained from dynamic methods can be used to carry out semi-isothermal thermogravimetry very successfully, the latter allowing separation of peaks due to overlapping decomposition phenomena. © 1997 Published by Elsevier Science B.V.

Keywords: Autoclaving; Carbonation; Cement : quartz; Semi-isothermal thermogravimetry; Quartz fineness

1. Introduction

Hydration products of both air-cured and autoclaved cement-based materials are known to react with atmospheric carbon dioxide, CO_2 [1]. Carbonation of air-cured products results in the destabilisation of the passive layer that usually covers and protects the reinforcing steel against corrosion [2]. The formation of carbonates from free lime, $Ca(OH)_2$, may cause swelling with subsequent cracking [3]. Durability of well-autoclaved products, made from cement and ground quartz, for example, can be lowered due to a combination of cracking and enhanced drying shrinkage as a result of carbonation [4,5]. Evaluation of cement-based materials by thermal analyses can be complex, due to simultaneous evolution of both H_2O and CO_2 over a wide temperature range, rendering distinction of different phenomena difficult. Additionally, carbonated phases can include both amorphous and crystalline polymorphs of calcium carbonate, $CaCO_3$, as well as calcium silicate carbonates and hydrocarbonates [6–8].

The present paper aims to illustrate how simultaneous DTA–TGA and derivative thermogravimetry, DTG, have been employed to evaluate autoclaved cement : quartz pastes before and after carbonation. Data obtained from dynamic methods was then used to carry out semi-isothermal thermogravimetry which enabled separation of peaks due to different decomposition phenomena.

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2. Experimental

Details of raw materials, mix proportions and curing regimes have been given elsewhere [9]. Briefly, autoclaved cement : quartz pastes were prepared using ordinary Portland cement (47.5%) and ground quartz (52.5%) of different grades, namely: 60G, 100G, 200G, 300G and 400G denoting increasing fineness. Water to total solids ratio was 0.35 for all mixes. Samples were autoclaved under saturated steam for 8 h at 177°C followed by oven drying. Disc milled, oven dried samples were analysed using a TA-instruments SDT 2960 simultaneous DTA/TGA analyser at a heating rate of 10°C/min to 1100°C under flowing nitrogen (100 ml/min). Sample sizes were between 40 to 50 mg and were packed into a Pt–Rh crucible with 20 taps. Additionally, autoclaved cement : quartz prisms were subjected to carbonation for 24 h, details of which are given elsewhere [4]. Oven dried, carbonated cement : quartz prisms were analysed as mentioned earlier.

3. Results and discussion

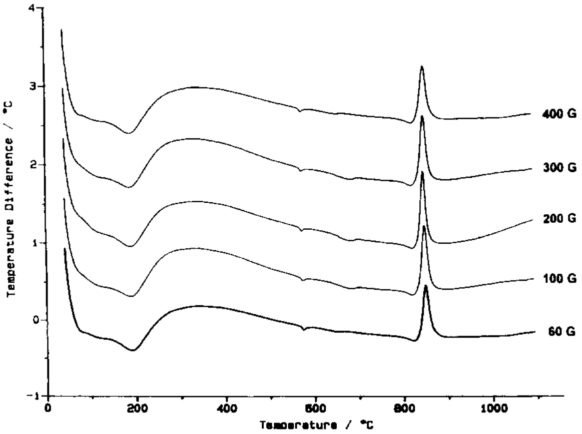

Fig. 1. DTA curves of autoclaved cement : quartz specimens before carbonation.

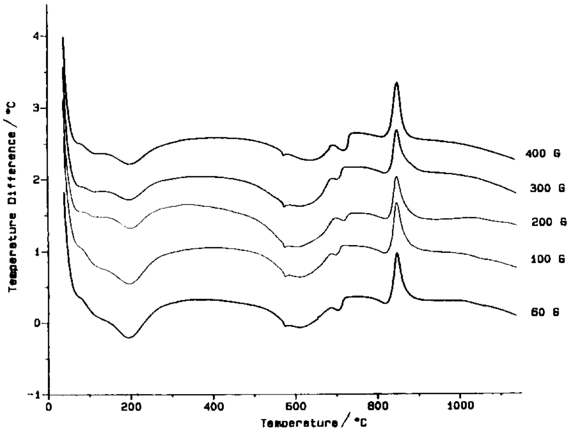

Fig. 2. DTA curves of autoclaved cement:quartz specimens after carbonation.

Figs. 1 and 2 are DTA traces of autoclaved cement : quartz samples before and after carbonation, respectively. Two point rotations were employed for all DTA curves as described previously [9]. From Fig. 2 it is evident that all carbonated samples display a similar pattern. The endotherm (~200°C), due to dehydration of calcium silicate hydrates, decreased slightly upon carbonation and with increasing quartz fineness. The broad endotherm ranging from ~500–750°C is the most prominent feature of carbonated samples, Fig. 2, and is absent for uncarbonated samples, Fig. 1. The small endotherm ~571–573°C, due to the crystalline inversion of unreacted quartz, is present in all samples. A smaller endotherm at ~680–750°C has increased in size when compared to uncarbonated samples. The endothermic dip at ~800°C, preceding the exotherm at ~840–850°C, has become slightly more accentuated when compared to uncarbonated specimens. The mass loss at ~800°C, due to well-crystallised calcite [10], is present in both carbonated and uncarbonated samples. The presence of CO_2-containing phases in autoclaved cement-based products is to be expected unless rigorous precautions are taken to eliminate atmospheric CO_2 during sample preparation and autoclaving [11,8]. Results from X-ray diffraction, XRD, of samples prior to carbonation revealed the presence of calcite and vaterite, and in some cases aragonite [4]. It is possible that scawtite, a calcium silicate carbonate, may have also been present, although its main X-ray reflections were not well resolved.

Peak temperatures of the exotherm in the 840–850°C region increased up to 7°C upon carbonation, the increase being greater the finer the quartz used.

Exotherm peak heights decreased while peak areas increased upon carbonation, the relative decrease/increase being greater the finer the quartz used. Goto et al. [12], investigated the effects of carbonation on 11 Å tobermorite samples and have shown, that the exotherm marked the crystallisation to wollastonite, β-CS, and to β-CS and/or pseudowollastonite, α-CS, for uncarbonated and carbonated specimens, respectively. α-CS was usually obtained when a mixture of silica and lime was heated to ~900°C. In carbonated 11 Å tobermorite, SiO_2–gel and $CaCO_3$ are present just as in a mixture of silica and lime [12]. The effect of carbonation on calcium silicate hydrates is decalcification, initially by lowering of their C/S ratio, and finally by converting into a highly porous, hydrous form of silica, SiO_2–gel, [13]. 11 Å tobermorite can decompose through the action of CO_2 into vaterite and SiO_2–gel, the former being transformed into the more stable calcite [14]. The calcium silicate hydrates, in this investigation, belonged to the tobermorite group exhibiting a decrease in crystallinity the finer the quartz used [15]. Additionally XRD and DRIFT, diffuse reflectance mid-infrared Fourier transform spectroscopy, analyses have shown that after carbonation the calcium silicate hydrate binder became more like SiO_2–gel in character the finer the quartz used [4]. The increasing diffuseness of peaks from DRIFT analysis suggested a poorer crystallinity. 11 Å tobermorite was detected in all samples, except the one made with the finest quartz [4]. The changes noted, in peak height and area of the exotherm in the 840–850°C region after carbonation, can thus be attributed to partial decalcification of calcium silicate hydrates. The difference in peak height and area of the exotherm, between uncarbonated and carbonated samples, became greater the finer the quartz used, presumably due to the decreased crystallinity of the binder before carbonation and the changes that occurred to the calcium silicate hydrates remaining after carbonation.

TG curves obtained with the dynamic method are shown in Figs. 3 and 4 for uncarbonated and carbonated samples, respectively. For all samples successive decomposition reactions or mass losses occur with increasing temperature. The mass losses do not occur at a particular temperature but over several ranges; consequently, some reactions may overlap and a constant-mass plateau does not occur between them, resulting in poorly resolved decomposition stages, particularly for temperatures below ~600°C.

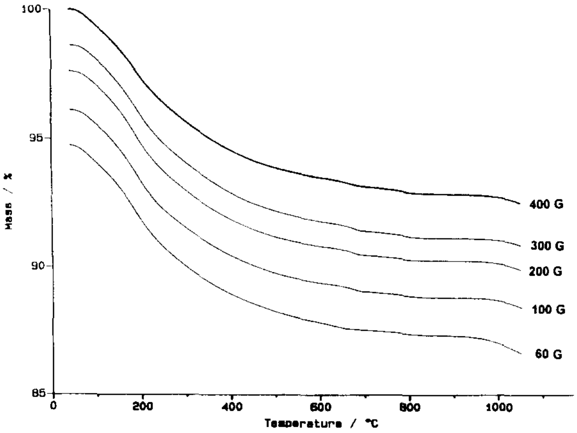

Fig. 3. TG curves of autoclaved cement : quartz specimens before carbonation using the dynamic method.

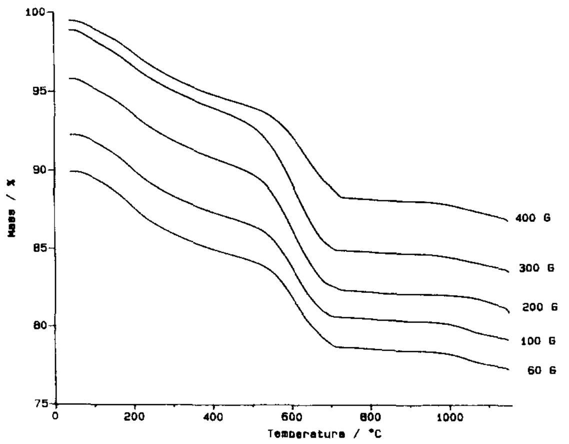

Fig. 4. TG curves of autoclaved cement : quartz specimens after carbonation using the dynamic method.

Improvement in resolution of complex or overlapping mass loss phenomena is facilitated by the corresponding DTG curve, Fig. 5. The DTG curve consists of a series of peaks corresponding to the various stages in the decompositions or mass losses, a peak maximum being equivalent to the point of inflection of the TG curve and corresponds to a maximum rate of mass change [16]. DTA curves are more easily compared with DTG curves than with TG curves, since both

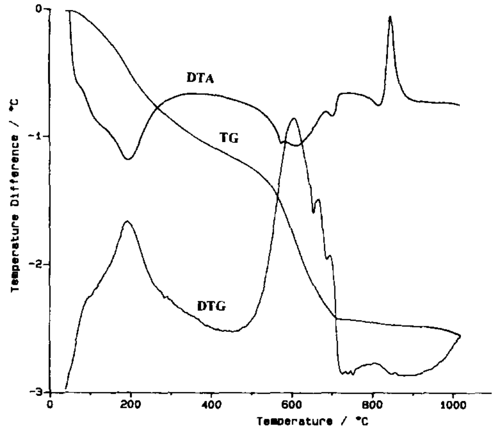

Fig. 5. Typical DTA curve for an autoclaved cement : quartz sample, prepared with 60G quartz, after carbonation, and corresponding TG and DTG curves using the dynamic method.

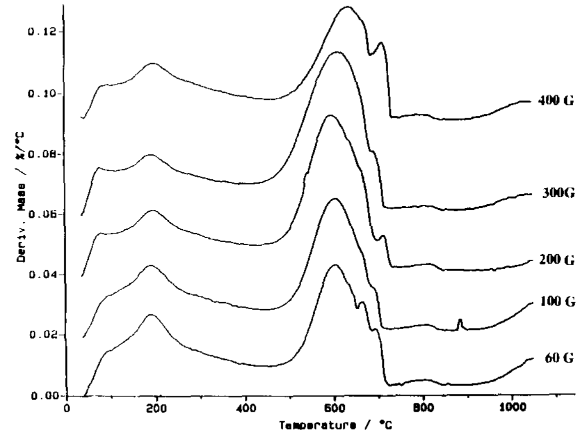

Fig. 7. DTG curves of autoclaved cement : quartz specimens after carbonation using the dynamic method.

DTA and DTG curves show a series of peaks, as illustrated in Fig. 5.

From the DTG curve, it is evident that the broad endotherm at ~500–750°C is due to three mass loss phenomena, which the corresponding TG curve fails to resolve. Also, the DTG curve shows the mass loss due to well-crystallised calcite at ~800°C more clearly than the TG curve.

Figs. 6 and 7 show DTG curves for samples before and after carbonation, respectively. Compared with the corresponding TG curves in Figs. 3 and 4, it is clear that DTG curves provide more detailed information about decomposition reactions in both uncarbonated and carbonated samples. From Fig. 7, however, it is apparent that carbonated specimens exhibit several mass losses in close succession, particularly in the 500–750°C region, signified by multiple peaks on the DTG curves. The troughs between the peaks are at considerable distance from the baseline, indicating a significant rate of mass loss at these points. The results thus show that, in this instance, the dynamic method does not allow sufficient time for the reactions to be completed, resulting in fairly broad DTG peaks with poor resolution of peaks in close succession.

Nevertheless, the results do demonstrate very clearly the effects of carbonation on autoclaved cement : quartz samples, particularly the increased and additional mass loss in the 500–750°C temperature region. Additionally, DTG curves revealed more detailed information about the mass loss phenomena than TG curves.

In the semi-isothermal thermogravimetric method, the sample is heated dynamically until the mass change reaches a maximum, at a DTG peak, and starts to decrease. The temperature programmer is then switched from dynamic heating to the isothermal condition for 30 min. At the end of the 30 min isotherm the temperature programmer is again switched to dynamic heating until it reaches the next peak.

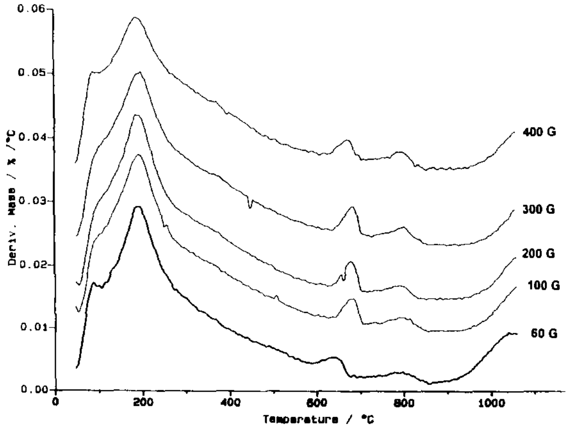

Fig. 6. DTG curves of autoclaved cement : quartz specimens before carbonation using the dynamic method.

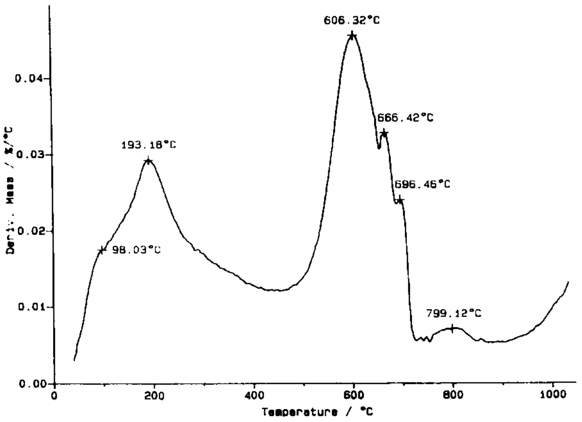

Fig. 8. DTG curve of carbonated, autoclaved cement : quartz sample, prepared with 60G quartz, using the dynamic method and showing DTG peak maxima.

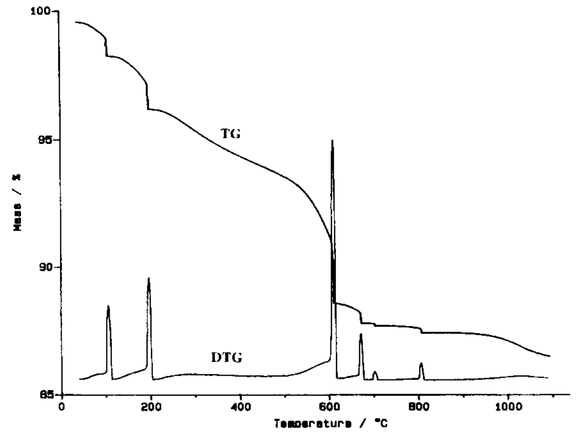

Fig. 9. Typical semi-isothermal TG/DTG curves for an autoclaved cement : quartz sample, prepared with 60G quartz, after carbonation.

It has been shown that decompositions reach completion so long as the isothermal period starts after the peak has been reached under dynamic conditions [17]. To obtain better peak resolution for carbonated and uncarbonated specimens, semi-isothermal thermogravimetry was employed very successfully as follows:

- DTG peak maxima, obtained with the dynamic method, were determined for uncarbonated and carbonated samples, this is illustrated in Fig. 8 showing a total of six peak maxima.
- Semi-isothermal thermogravimetry, was carried out for all samples, depending on the respective DTG peak temperatures.
- Samples were heated dynamically at a heating rate of 10°C/min up to 5–10°C past the DTG peak maximum at which point samples were heated isothermally for 30 min followed by dynamic heating until the next peak.

From Fig. 9 it is evident that the semi-isothermal TG–DTG method allows the separation of all peaks in both low- and high-temperature regions with constant-mass plateaus occurring between them.

Figs. 10 and 11 are DTG curves for autoclaved cement : quartz specimens before and after carbonation, respectively. Mass losses were determined from TG curves using the TA instruments DTA–TGA data analysis software as described previously [9]. In this instance, the '% mass loss' mode was selected for all analyses. The results are shown in Fig. 12 and reveal mass losses in three steps:

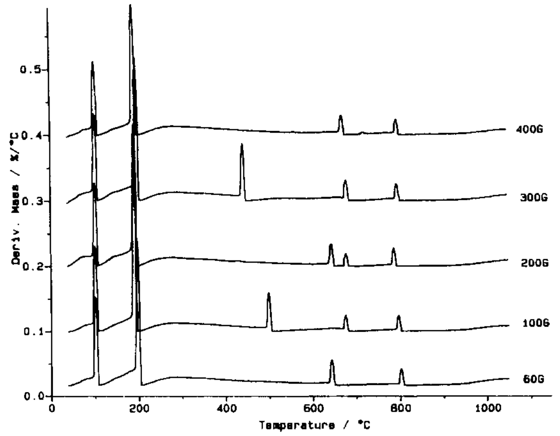

Fig. 10. Semi-isothermal DTG curves for autoclaved cement : - quartz specimens before carbonation.

TG1 Dehydration ~103–220°C.

TG2 Low-temperature decarbonation ~220–600°C.

TG3 High-temperature decarbonation ~600–1000°C.

Specimens were oven dried at 103°C followed by cooling in a desiccator over silica–gel and soda lime. Consequently, the mass loss below 103°C is most

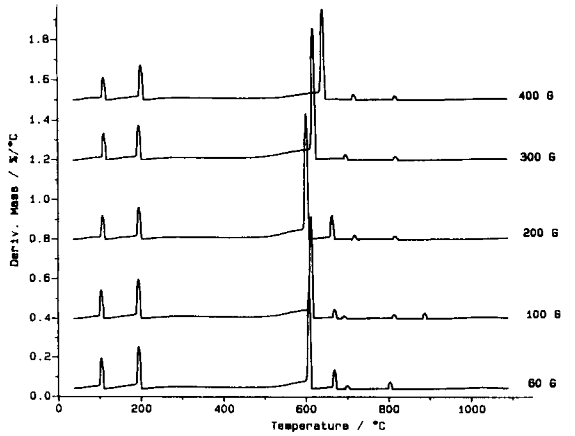

Fig. 11. Semi-isothermal DTG curves for autoclaved cement: quartz specimens after carbonation.

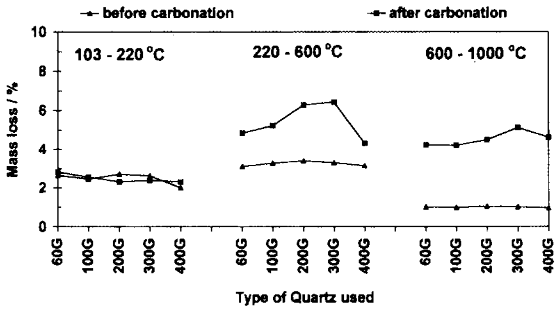

Fig. 12. Amount of mass loss of autoclaved cement : quartz specimens before and after carbonation.

likely due to moisture adsorption during sample preparation for thermal analysis. It is very likely that dehydration reactions contributed to the mass loss in the low-temperature decarbonation step; the larger mass loss for samples before carbonation, in the TG2 region compared to the TG3 region supports this notion. Dehydration of calcium silicate hydrates is known to occur over a wide temperature range extending well above ~300°C [18]. Ebert et al. [19] have reported mass losses, due to dehydration reactions, at ~200–250 and ~800°C for C–S–H (I), while for 11 Å tobermorite dehydrations were observed at ~120, ~300–400 and 500–600°C.

Samples prepared with 100G and 300G quartz, display DTG peaks at ~500 and 445°C, respectively. The fact that the corresponding DTA curves did not indicate any exothermic or endothermic deflections at these temperatures, Fig. 1, indicates that these effects are not due to phase changes. There is no obvious explanation for these observed peaks and more work is required to explain their origin. The identity of the various mass losses could best be confirmed by employing evolved gas analysis, EGA, using mass spectrometry.

From the mass loss results, Fig. 12, two further observations are made. First, the mass loss increased in magnitude after carbonation in both TG2 and TG3, with differences between samples being greater for TG2 than for TG3. The actual increase, however, was greater for TG3 than for TG2. Second, there appears to be a direct relationship between mass loss values and the fineness of quartz, with the exception of the sample made with the finest quartz, 400G. Evolution of CO_2 is complex. Most of the CO_2 comes from the decomposition of $CaCO_3$ but peaks associated with other processes are observed at temperatures lower than the $CaCO_3$ decomposition temperature. Cole and Kroone [7], for example, concluded that CO_2 is chemically bound as $CaCO_3$ largely in the form of poorly crystallised vaterite, aragonite and calcite, while Gaze and Robertson [20] suggested that CO_2 was absorbed into the two-dimensional lattice to give an interstitial compound which slowly released CO_2 on heating. Results from carbonation studies of calcium silicates, such as C_3S and C_2S, have suggested that an amorphous calcium silicate hydrocarbonate formed along with $CaCO_3$ [6]. The presence of such an amorphous species in the present samples is therefore a further possibility.

Butt et al. [21] have noted that less crystallised calcium silicate hydrates are characterised by forming a great number of loose calcium carbonates with small binding powers, while more crystallised calcium silicate hydrates are characterised by the formation of stable calcium carbonate crystal adhesions. Also, Hochstetter [22] reported that the type of carbonated product formed depended on the nature of calcium silicate hydrate present initially. The increased mass loss in the TG2 and TG3 regions upon carbonation, can in part, be explained by these observations and our previous findings of decreasing binder crystallinity with increased quartz fineness [15]. The reason for the anomalous behaviour in mass loss of samples made with the finest quartz remains unclear.

4. Conclusions

While it is apparent from the previous discussion that evaluation of cement-based materials after carbonation can be difficult, due to a multitude of factors involved, we conclude the following:

1. Simultaneous DTA–TG and DTG can be successfully employed in the evaluation of cement-based materials, both before and after carbonation.
2. The use of DTG improves resolution of complex or overlapping TG curves, thus providing additional information about decomposition or mass loss phenomena.
3. Data obtained from dynamic methods can be used to carry out semi-isothermal thermogravimetry, the latter enabling peak resolution, thus providing valuable information.
4. Results from semi-isothermal thermogravimetry of autoclaved cement : quartz samples, made with quartz of increasing fineness, revealed that the mass loss before and after carbonation consisted of three steps, namely: a dehydration step, a low- and a high-temperature decarbonation steps.
5. The mass loss for low- and high-temperature decarbonation steps increased upon carbonation and, generally, with quartz fineness.
6. DTG curves were found to be more useful than TG curves in identifying differences between samples after carbonation.
7. Autoclaved cement : quartz pastes, made with coarse quartz, were more resistant to the effects of carbonation than those made with finer quartz.

Acknowledgements

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