MICROCRYSTALLINE QUARTZ, UNDULATORY EXTINCTION & THE ALKALI-SILICA REACTION

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Microcrystalline quartz, with a mean diameter of <100 µm, is shown to be the probable reactive component in novaculite and mylonitic gneiss. Evidence was found indicating that microcrystalline quartz from gneisses may be more reactive than that found in sedimentary rocks such as novaculites. The size of the undulatory extinction angle may not be used to determine the potential reactivity of quartz, due to the complexities of the physical processes causing undulatory extinction.

INTRODUCTION

In laboratory tests some correlation has been shown to exist between the amount of microcrystalline quartz, in a variety of aggregates, and expansion of mortar bars or concrete prisms, due to alkali-silica reaction, Grattan-Bellew (1). This correlation strongly suggests that microcrystalline quartz is the reactive component in these aggregates. During the past 15 years a number of authors have suggested that strained quartz, indicated by high undulatory extinction (UE) angles, is responsible for expansion, due to alkali-silica reaction in mortar or concrete, Gogte, (2), Dolar-Mantuani, (3), and Mullick (4). However, no rigorous proof that quartz grains showing high UE angles are reactive has been demonstrated, and in fact, it can be shown that large quartz grains showing high UE angles are invariably accompanied by microcrystalline quartz, Grattan-Bellew (5).

The purpose of this review is to examine the common mechanisms that lead to the development of microcrystalline quartz, and of undulatory extinction, and to attempt to correlate both with alkali-silica reactivity in cherts, novaculite, and deformed quartz-rich metamorphic rocks.

Microcrystalline quartz has been described as consisting of equant polyhedral grains, randomly oriented with a quoted grain size varying from 2.5 μm to <20 μm, Keller (6), Goldman & Klein (7), Sathyandarayan & Muller (8), and Gao & Land (9). In the context of alkali-reactivity, enhanced solubility of quartz occurs when the mean grain size is < 100 μm, and therefore such material is classed as microcrystalline and potentially reactive. When considering reactivity, the texture and origin of the quartz may however be as important as the grain size.

MICROCRYSTALLINE QUARTZ

Overview

The solubility of quartz is related to it's free energy. In small grains, much of the free energy may be concentrated at grain boundaries. Accordingly, in quartz bearing rocks, in which the grain size is small (<100 μm), the grain boundary area per unit volume of rock is high, and solubility is enhanced, Mather (10).

Microcrystalline quartz may be formed in two ways:

 i. By crystallization and grain growth from precursor amorphous material, e.g. opal.
 ii. By recrystallization from highly strained and deformed quartz under conditions of stress metamorphism.

Examination of microcrystalline quartz, formed by either process, shows remarkably similar surface features although the quartz formed under metamorphic conditions is frequently coarser. Despite apparent similarities, microcrystalline quartz formed under metamorphic conditions often shows undulatory extinction, indicating the presence of numerous lattice mismatches or dislocations. Lattice mismatches, and dislocations contain energy which would enhance reactivity. The nature of the crystallographic defects, and the reactivity of microcrystalline quartz is discussed below.

Effect of Crystallinity on Reactivity of Microcrystalline Quartz

Reactivity of silica appears to increase with decreasing

crystallinity, Figure 1. The solubility of silica minerals in NaOH in the chemical test, ASTM C289 (11), is generally used as an indicator of reactivity. Opal is usually a mixture of amorphous material and cristobalite, and or tridymite, and is generally the most reactive form of silica. Chert consists of a mixture of microcrystalline quartz and chalcedony. The composition of cherts vary considerably, as do their reactivities. Arkose is essentially a quartz-rich sandstone.

The apparent increase in solubility of crushed quartz with decreasing grain size, in Figure 3, is due to the increased surface area. The surface area plotted in Figure **3** was calculated assuming spherical quartz particles with a density of 2.65. The solubility of silica in a fragment, composed of an agglomerate of microcrystalline quartz grains, e.g. a fragment of novaculite, with a mean grain size of 5- 10μm, Figure **4,** would be expected to be lower than in the same weight of crushed material of the same grain size.

An index of crystallinity (I_c) of quartz may be determined from x-ray diffractograms, by measuring the intensity of the (21$\bar{3}$0) reflection in the quintuplet which occurs between 67° and 69° 2θ, with Cu K$^\alpha$ radiation, Murata & Norman (12). Diffractograms of quartz from a large single crystal, novaculite, microcrystalline quartz from mylonitic gneiss, and chert are shown in Figure **2**. The values of I_c for crystal quartz, novaculite, and microcrystalline quartz from mylonitic gneiss are 10.0, 9.65, and 8.16 respectively. Chert produces only a broad diffraction maximum in the region from 67° to 69° 2θ. The poor crystallinity of chert implies a high grain boundary/unit area, and therefore a higher free energy than well crystalline quartz. This leads to chert being more reactive. Surprisingly, I_c for microcrystalline quartz is lower than for novaculite. This indicates that microcrystalline quartz, in the gneiss, may be more reactive than that occurring in novaculite. The value of I_c determined for novaculite is essentially the same as that of quartz crystal, indicating that it is well crystalline, and hence should be non reactive. This however is not the case, as mortar bars containing novaculite expanded by almost 0.6% Mielenz et al (13). There are obviously other factors, in addition to the crystallinity index, contributing to the reactivity of novaculite. Recent work by Thomson (personal communication) suggests that novaculite is composed of several textural types of quartz, and may include precursor opal, which considering the pessimum effect where an amount of 1 to 5% could cause significant expansion in mortar bars, or solubility in alkaline solution, could be the reactive component.

Expansion Mechanism of Microcrystalline Quartz Formed from Precursor Opal

Novaculite has no measurable porosity, down to 300 nm pores, as measured by mercury porosimetry. Hence, in a fragment of novaculite, initially, the alkali would only have access to the outer surface of the fragment. How then can the alkali gain access to the surfaces of the grains in the interior of the fragment, and how can the reactivity of novaculite to be explained? Recently, Lee at al (14) noted that on fractured surfaces of novaculite, "triple junctions appear to form an interconnected network of very fine tubules." The diameter of the tubules is estimated to be in the range of 0.03 μm, which is too small to permit measurement using the mercury porosimeter Figure **5.** The fine tubules would provide channels for the alkali to penetrate the aggregate particles. Initially the alkali would attack exposed grain boundaries, but would gradually penetrate along the tubules and dissolve silica from the high energy grain boundary areas in the interior of the particle, and form a layer of gel around the grain boundaries. This would be aided by the presence of isolated water filled pores, commonly observed at the grain boundaries Brenan, (15). The formation and subsequent swelling of the gel layer around the grains of microcrystalline quartz is illustrated diagrammatically in Figure **6.** Uptake of water by the gel layer would cause it to swell and push the grains apart. Struble (16) showed that under a confining pressure of 2 MPa, swelling of more than 100%, by synthetic gels, was possible. If a particle of novaculite 10 mm in diameter, has a mean grain size of 10 μm, it would have 1,000 grains across it's diameter. Assuming that the energy associated with grain boundaries would lead to 0.1 μm of silica being dissolved from the two grains either side of the boundary and converted to a 0.1 μm wide layer of gel between the grains, the sum of the widths of the initially formed gel layers across the diameter would be 100 μm. If this gel increases in volume by 100% it would lead to a 1% increase in the diameter of the 10 mm grain, which is in the order of the expansions measured in mortar bars with very reactive aggregates (13).

Expansion Mechanism of Microcrystalline Quartz Formed Under Metamorphic Conditions

Some familiarity with the mechanism of formation of microcrystalline quartz, from coarse grained quartz under conditions of

stress metamorphism, is needed to understand the factors which contribute to it's reactivity. The stages in the development of microcrystalline quartz from unstrained, coarse grained, quartz under stress metamorphism are outlined schematically in Figure **7.** Dislocations are created in the quartz grains in response to the applied stress. The work done in creating the dislocations is incorporated as free energy of the grain. Movement of the dislocations also requires work; this further enhances the free energy and hence the solubility and reactivity of the grains. Once a critical dislocation density is reached, dislocations tend to migrate to form sub-grain boundary walls which give rise to the optical phenomenon of undulatory extinction. The build up of dislocations at sub-grain boundary walls increases the grain boundary energy of the crystals and enhances grain boundary solubility Zhang et al (17). With increasing stress, the sub-grain boundaries gradually change to 'low angle grain boundaries' which are misaligned to the original crystal by, typically, <1.° The misalignment of sub-grains is most readily observed in electron diffraction patterns, in which the single spots in the pattern from well crystalline quartz are split into a number of sub-spots Balakirev (18). The formation of low angle boundaries is a recovery process, which results in dislocations being concentrated at the grain boundaries, leaving the center of the grains relatively free of dislocations. White (19) noted that grains containing low angle grain boundaries will be in a lower energy state than those containing randomly distributed tangles of dislocations.

If dislocations, are concentrated at grain boundaries, which would thus be areas of high free energy, then it may be expected that a zone, approximately the width of the low-angle boundary, i.e. 0.3 μm would be soluble in alkali, Balakirev, (18). As in the case of microcrystalline quartz formed from opal, isolated bubbles commonly occur along sub-grain boundaries, Figure 4. These bubbles contain water, and in some instances alkali ions, Folk & Weaver (20). If the zone of solubility at grain boundaries in metamorphic microcrystalline quartz is wider than in microcrystalline quartz formed from opal, the former should be more reactive than material of similar grain size developed by crystallization of precursor opal. Some evidence to support this hypothesis comes from the limited number of measurements made on the reactivity of a series of samples of highly deformed gneiss, containing microcrystalline quartz derived from one quarry, Figure **8.** The gneiss appears to be more reactive than other rock types with the same content of microcrystalline quartz. This conclusion is supported by the observation that microcrystalline quartz from gneiss has a lower index of crystallinity than that from novaculite, however, more research is needed to confirm this.

UNDULATORY EXTINCTION AND REACTIVITY OF QUARTZ

Conflicting results are reported in the literature concerning correlation between the undulatory extinction angles in quartz, and reactivity of quartz bearing aggregates, Gogte (2), Dolar-Mantuani (3), Mullick (4), and Cortelezzi et al (22). Gogte reported that the degree of deformation observed in thin sections of granites correlated with the 6-month expansion, of these rocks, in mortar bars stored at 60°C
Figure **9**. Subsequently, K. Mather (10) concluded that 'there is no association or correlation between undulatory extinction angle and dissolved silica in mM/l (i.e. potential reactivity) in these rocks. She concluded that 'the amount of dissolved silica (*and hence reactivity*)[*] is higher in rocks with more grain boundary per area', i.e. in microcrystalline quartz. White (21) studying the dislocation structures responsible for UE in deformed quartzes concluded, that 'optical strain features *(UE)*[*] cannot be used as strain or stress gauges' to evaluate the amount of deformation that has occurred in metamorphic rocks. If this is correct, it is obvious that the size of the UE angle likewise cannot be used to measure the potential reactivity of strained quartz. Mullick (4) attempted to find a correlation between the average UE angle and expansion in mortar bars stored at 60°C for 180 days. Mullick's results show no such correlation Figure **10**. However his measurements did show that there was some correlation between the percentage strained quartz and expansion in mortar bars. Examination of Mullick's photographs of thin sections shows that microcrystalline quartz is ubiquitous in the reactive rocks. Although Mullick notes the presence of 'fractured and granulated quartz', he does not appear to have considered it as a potentially reactive component in the rocks. There is thus some doubt whether the reactivity is due to the presence of quartz showing undulatory extinction, or to the presence of microcrystalline quartz.

In analyzing the possible correlation between undulatory extinction and the presence of microcrystalline quartz in aggregates, it is important to realize that the development of UE and microcrystalline quartz are part of the same process, which is a response of a crystal to applied stress, as shown in Figure 7. The development of UE is thus a step in the process which, if the stress is high enough, will ultimately lead to the conversion of a single quartz grain to an agglomerate of microcrystalline quartz. In

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[*] material in parenthesis added by author

a very simple case, where the applied stress is small, the UE angle may give some indication of the applied stress, but when the stress level is high enough to create marked strain effects, such as are typically observed in alkali silica reactive metamorphic rocks, the complexity of the deformation, e.g. the density and location of dislocations, the formation of extinction lamellae, sub grain boundaries, the movement of grain boundaries into adjacent grains which gives rise to sutured grain boundaries, and the development of low, and high angle boundaries, all complicate determination of the stress levels in the rock. The problem is further complicated by the common occurrence, in highly metamorphosed terrains, of several generations of stress metamorphism superimposed on each other. Even if determination of UE angles could provide a measure of the reactivity of the quartz, there are several additional problems which limit the accuracy with which UE angles can be measured:

    i. the size of the measured angle is dependent on the grain size of the fragment being measured.
    ii. The orientation of the grain effects the measured UE angle.

There is little doubt that the presence of stress related features, such as undulatory extinction and the formation of sub-grain boundaries in large quartz grains enhance the solubility and hence reactivity of these grains. However, the large size, and hence low grain boundary surface area limits the amount of silica which could react, and cause expansion.

CONCLUDING REMARKS

It is evident from the above discussions that microcrystalline quartz is most probably the reactive component in novaculites and in metamorphic quartz bearing rocks, such as quartzites, granites, and mylonitic gneisses, and greywackes. Examination of microcrystalline quartz from novaculites and mylonitic gneisses, in the SEM, shows that the grains in both exhibit the same physical features, despite differences in the modes of formation.

Microcrystalline quartz from gneisses may, due to higher dislocation densities, be more reactive than that derived by crystallization from opal, as in novaculites. However, definitive experiments demonstrating the reactivity of microcrystalline quartz in novaculite and in mylonitic gneiss still remain to be performed.

Although measurement of undulatory extinction angles of quartz can not be used to measure potential reactivity, the presence of quartz, showing UE, in rocks which have been subjected to regional stress

metamorphism, is an indication that they may be reactive, as marked UE is invariably associated with the presence of microcrystalline quartz. It has been demonstrated that there is reasonable correlation between the content of microcrystalline quartz in rocks, and their expansivity in mortar bars.

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REFERENCES

1. Grattan-Bellew, P.E., 1990, Canadian Developments in Testing Concrete Aggregates for Alkali-Aggregate Reactivity, Report EM-92, Ministry of Transportation of Ontario, 17-34.

2. Gogte, B.S., 1973. Engineering Geology, 7, 135-153.

3. Dolar-Mantuani, L.M.M., 1981, Proc. of 5th International Conference on Alkali-Aggregate Reaction, Cape Town, S252/36.

4. Mullick, A.K., 1987. NCB Quest, August, 35-46.

5. Grattan-Bellew, P.E., 1987. Concrete Alkali-Aggregate Reactions, Proc. 7th Internat. Conference on Alkali-Aggregate Reaction, Ottawa, Noyes Publications New Jersey, 434-439

6. Keller, W.D., 1941. Bull. Geol. Soc. America, 52, 1271-1298

7. Goldman, H.B., & Klein, I.E.,1959, Special Report 55, California Division of Mines, San Francisco, 28.

8. Sathyandarayan, S., & Muller, G.,1980, Sedimentary Geology, 25, 209-221.

9. Gao, G., & Land, L.S., 1991, Sedimentology, 38, 857-870.

10. Mather, K. 1976, Alkali Reactive Quartz at Normal Temperature. Transcript of Oral Presentation, TRB, Washington DC.

11. ASTM C289-87. Potential Reactivity of Aggregates, (Chemical Method).1990 Book of ASTM Standards. V. 4.02, 159-165, ASTM Philadelphia.

12. Murata, K.J., & Norman, M.B., 1976, American J. of Science, 276, 1120-1130.

13. Mielenz, R.C., Greene, K. T., & Benton, E.J., 1947, J. American Concrete Institute, 19, 193-221.

14. Zhang, X., Blackwell, B.Q., and Groves, G.W. 1990, Br. Ceram. Trans. J. , 89, 89-92.

15. Lee, V.W., Mackwell, S.J., & Brantley, S.L., 1991, J. Geophysical Res., 96, 10,023-10,037.

16. Brenan, J. M., 1991, Chapter 6, Reviews in Mineralogy, V. 26, Contact metamorphism, Editor D.M. Kerrick. Min. Soc. America, Washington D.C.

17. Struble, L.J., 1979, Swell and Other Properties of Synthetic Silica Gels, Ph.D. Thesis, Purdue University, Lafayette, Indiana.

18. Balakirev, V.G., 1981, Phys Chem Minerals, 7, 5-9.

19. White,S., 1976, The Physics & Chemistry of Minerals & Rocks, Editor R.G.J. Strens, John Wiley & Sons, 75-91.

20. Folk, R.L., Weaver, C.E., 1952, American J. of Science, 250, 498-510.

21 White, S., 1973, J. of Materials Science, 8, 490-499.

22. Cortelezzi, C.R., Maiza, P., and Pavicevic, E. Petrography Applied to Concrete and Concrete Aggregates, ASTM STP 1061, Editors. B. Erlin and D. Stark, American Society for Testing and Materials, Philadelphia, 1990, pp.145-158.

23. ASTM C-9 proposal P 214. Accelerated Detection of Potentially Deleterious Expansion of Mortar Bars Due to Alkali-Silica Reaction. 1990 Book of ASTM Standards. V. 4.02, 739-742. ASTM Philadelphia.
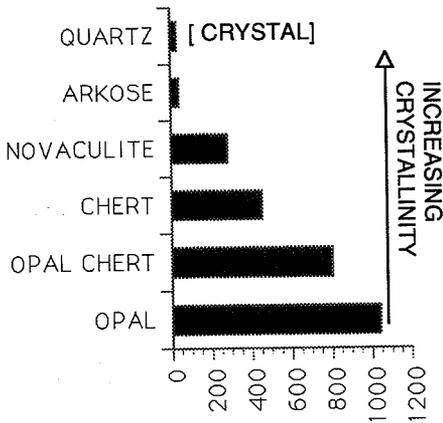
Figure 1. Chart showing amount of dissolved silica (Sc) in the chemical test, i.e., the solubility of various types of siliceous rocks versus crystallinity. After Mielenz et al (13).
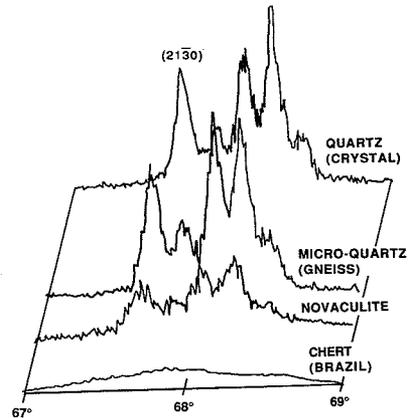

Figure 2. X-ray diffractograms illustrating differences in crystallinity of crystal quartz, novaculite, microcrystalline quartz from mylonitic gneiss, and chert. The region shown is from 67° to 69° 2 Θ (Cu Kα)
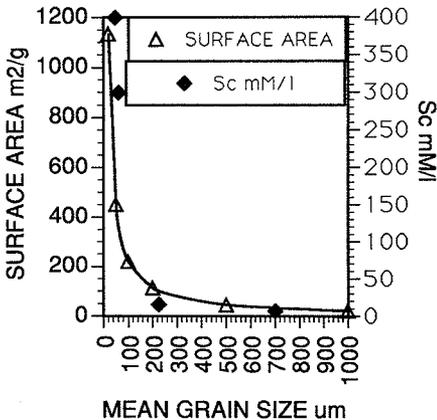

Figure 3. Correlation between calculated surface area and solubility of quartz versus grain size. The surface area was calculated assuming spherical particles. The solubility Sc was measured in ASTM C289.
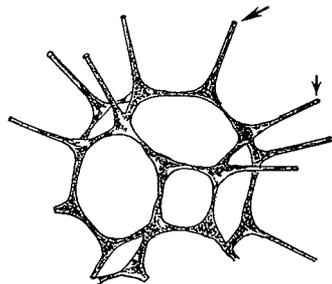
Figure 5. Sketch showing interconnecting pores at triple junctions of a number of grains in novaculite. The diameter of the small tubules, indicated by arrows is about 30 nm. (Adapted after Lee et al (15))
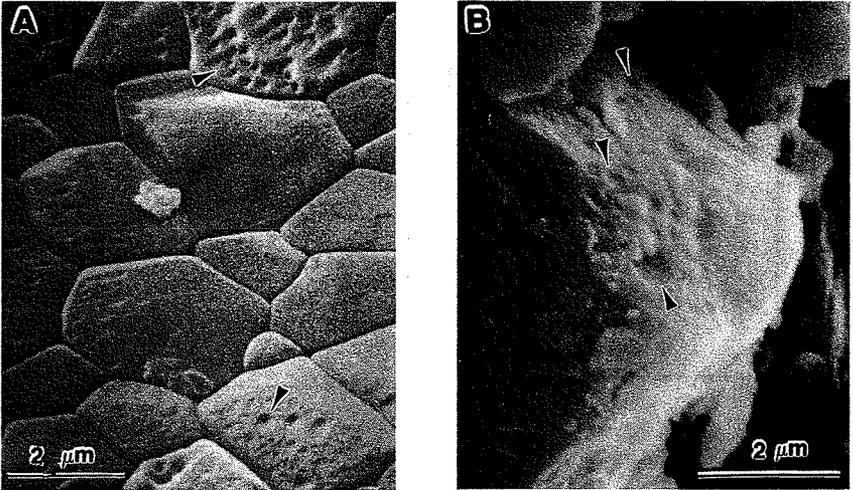
Figure 4. SEM micrographs of (A)- novaculite, showing grain size, presence of pores at triple junctions, and presence of bubbles, indicated by arrows on the grain boundaries. (B)- Larger grain of microcrystalline quartz from a mylonitic gneiss showing bubbles on grain boundaries, similar to those in, novaculite.
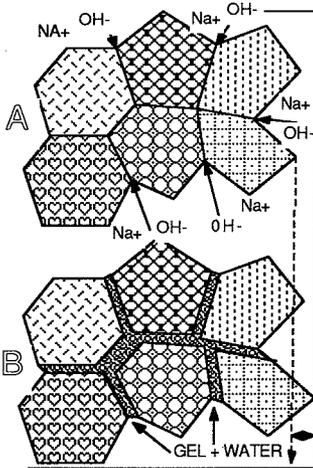

Figure 6. Alkali-silica reaction:
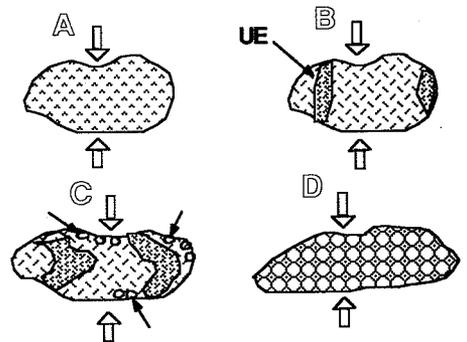A Attack by OH- ions along grain boundaries. B Grains pushed apart by formation and swelling of gel due to uptake of water.

Figure 7. Development of UE and sub grain boundaries in response to stress: A- few or minimal dislocations. B- increased dislocations and development of sub-grain boundaries. C- recrystallization (shown by arrows). D- grain recrystallized to micro-quartz.
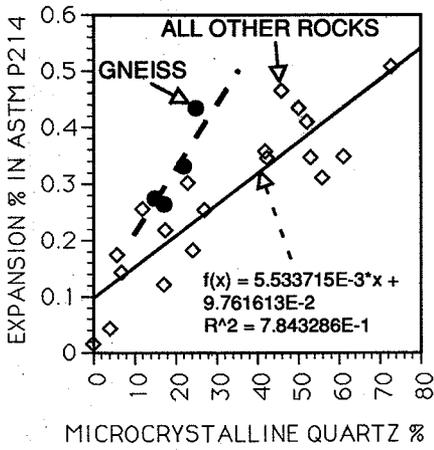
Figure 8. Correlation of expansion in mortar bars with microcrystalline quartz content of mylonitic gneisses and other rocks.
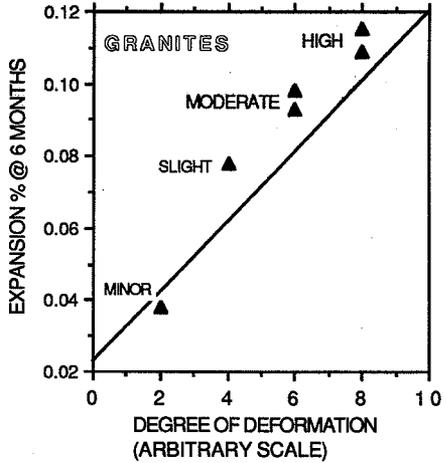

Figure 9. Comparison of degree of deformation, on an arbitrary scale, with expansion of mortar bars stored at 60°C for 6 months. After Mullick (4).
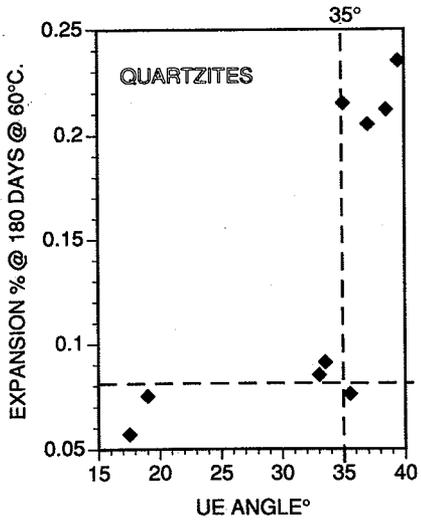

Figure 10. Variation of expansion in mortar bars, stored at 60°C for 6 months, with UE angle. After Mullick (4)