glacial times. Thus, McKeon's statement that for Grandfather Mountain to have been glaciated the necessary cooling would have been three times as great as those derived from other glacial studies must be regarded as not all-inclusive.

In conclusion, we wish to emphasize the reasonableness of Pleistocene glaciation in the southern Appalachian Mountains to at least some experienced Appalachian geologists. Wentworth (11) declared "The case against the hypothesis of local glaciation consists merely of lack of any other evidence than striated cobbles favoring it, and much detailed work with accurate maps is needed in the higher areas of the Southern Appalachians before this hypothesis can be discarded." Hack has studied the geology of the Appalachians more extensively than most workers. Yet Hack and Newell state (2) that they "were surprised" by the report of our discovery of evidence for Pleistocene glaciation south of the Laurentide ice sheet. The surprise could not have been of major proportions judging from a letter Hack wrote to us (12) prior to visiting the grooved outcrop on Grandfather Mountain. In the letter he stated: "We have known for some years through palynological evidence that the climate of the Appalachians was extremely poisonous as far south as Georgia . . . . Considering this fossil evidence, it is surprising that we haven't found evidence of glaciation in the southern Appalachians . . . it would not be surprising if some hollows were occupied by ice during the Pleistocene and glacial processes were active on a small scale."

In view of the reasonableness of the hypothesis of alpine glaciation in the southeastern mountains and for the sake of renewed interest in the subject by workers in many fields, we hope that this discussion will encourage open-mindedness on this issue. We also hope that we have demonstrated that a need does exist "for philosophical discussion of the possibility of alpine glaciation in the head of Boone Fork" (2).

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4 February 1974

Structure of Silica Glass

In their recent report Konnert *et al.* (1) purport to find "tridymite-like regions" in SiO_2 and GeO_2 glasses. I believe that they have gone somewhat too far in attempting to specify the structure of the "crystalline regions," as their own data will show. "Tridymite" and "cristobalite" are names which describe two families of SiO_2 phases. The relationship between these two structural groups, as first pointed out by Bragg (2) and elaborated on by Flörke (3) and Jagodzinski and Laves (4) is analogous to that between wurtzite and sphalerite, the two-layer hexagonal (2H) and three-layer cubic (3C) forms of ZnS, respectively. In fact [for details, see Hill and Roy (5)], as noted by Konnert *et al.*, there exist a variety of tridymites. Just how wide a variety, they possibly did not suspect. Furthermore, these tridymites undergo a wide variety of phase transitions in the range from 25° to 150°C. The actual pure 2H end-member tridymite has been reported in some high-temperature patterns (6). The complexity of nomenclature and structural identity is, however, increased still further in two dimensions. First, the probability of random stacking faults and ordered polytypes between 3C and 2H is very high, and, indeed, a mixture of such structures always exists in most samples (4). In fact, Konnert *et al.* used for the powder pattern a sample which was a 20-layer orthorhombic phase. [Buerger and Lukesh have reported on a 20H phase (7).] The ordered mixtures of cubic and hexagonal stacking are, of course, structurally intermediate between cristobalite and tridymite. Presumably a 4H phase would still be a "tridymite." But, is a 15-layer rhombohedral phase to be called tridymite or cristobalite? When one prepares or heat treats at a high temperature compositions which easily form polytypes, one usually obtains a distribution of polytypes. These observations are intended to demonstrate the meaninglessness of the concept that in a disordered glass at the highest temperature all the possibly "crystalline" units would ever have the same stacking to a degree that would justify a specific label.

Moreover, an enormous body of experimental evidence both on the difficulty of making "tridymite" at all and on the universality of cristobalite-like phases being formed from every type of noncrystalline SiO_2 renders the model proposed by Konnert *et al.* physically implausible.

An even more serious difficulty, however, is found in deciding the degree of perfection of stacking. Because of the enormous activation energy for the stacking changes compared to the kT (k is the Boltzmann constant and T is the absolute temperature) range of the α-β transition in cristobalites (50° to 300°C), it has been shown that it is possible to prepare cristobalites with a tremendous range of stacking fault order [Flörke (3) and Hill and Roy (8)]. The structural differences in the infinity of these individual phases (which can easily be prepared and preserved indefinitely at room temperatures) find a ready indicator in the tetragonal-cubic transition in cristobalite. This can vary from below room temperature to 268°C (8).

Let us return now to the limitations which must be placed on the conclusions of Konnert *et al.* The first limitation comes, as noted above, from the fuzziness in the meaning of the word "tridymite." The use of the term "tridymite" simply cannot be justified on such a minor coincidence. The second limitation exhibits sharply the deficiency of the radial distribution function (RDF) method for structure analysis; this deficiency is only partly acknowledged in the last paragraph of the report. The RDF approach makes it possible to compare only the experimentally computed RDF against that from a *possible* model.

The data of Konnert *et al.* in fact only show that the fit between experimental data and what they chose to call the "tridymite" model was better than the fit between experimental data and what they chose to call "cristobalite." Of course, Konnert *et al.* do not propose that their SiO_2 and GeO_2 glasses consisted of 100 percent microcrystalline "tridymite" with exactly the one structure they happened to choose. There is some "second phase." For noncrystalline phases in general, it is only our imagination that limits our models (beyond the first coordination sphere) of homogeneous and heterogeneous structures [see Roy (*9*)] that we may choose to examine. Among these models it is certainly a zeroth order guess to take the crystalline polymorphs of the same composition. When the known complexity of even the crystalline material (SiO_2) is already so enormous, I submit that it is at least necessary to cover all known crystalline phases for hints about the glass structure.

Indeed, Konnert *et al.* proceeded in precisely this fashion except that their universe of crystalline specimens was far too small. It may be that the 20-layer orthorhombic structure gives the best fit after being compared to the various polytypes at various temperatures and to the disordered 3C or $3C_{random}$ cristobalite-like phases below or above its transition. But it cannot be legitimate to tag the structure of the crystalline domains with a particular name on the basis of just a few comparisons. Conversely, on the basis of the crystallization behavior of SiO_2 one could with considerably more justification reverse the procedure and use a reasonable model to test the RDF method. The physical model for a SiO_2 melt based on the properties of SiO_2 glass and cristobalite and the well-studied crystallization behavior of SiO_2 glass certainly suggests that, in general, at equilibrium the glass structure will most resemble a disordered cristobalite. In hundreds of papers only cristobalite is observed on crystallizing SiO_2 glass at temperatures where tridymite has never been reported as converting to cristobalite. Thus, one could adjust the parameters of the RDF procedure and the relative amounts of crystallite and disordered "glue" until a match was achieved with a model of "20-Å" crystallites of pseudocubic $3C_{random}$ cristobalite held together with "monomeric" glue. I submit the proposition that the data of Konnert *et al.* could be shown to find an equally good match with the use of these adjustments only.

A final comment is needed with regard to the "second phase" which, of course, must also be present. I have recently (*9*) been engaged in attempting to establish the generality of the nonuniform (also variously called "microheterogeneous" or "two-phase") structure of glasses. The Zachariasen model of a uniform structure for glass is implicit in the vast majority of RDF papers. The data on the existence of nonuniformity of structure are now so overwhelming in so many glasses from elemental carbon or selenium to some complex silicates that it behooves us to be especially careful if we claim that there are indeed any glasses that are uniform on a 20- to 50-Å scale. Konnert *et al.* do in fact refer to the "differences in the inner regions of the RDF's" as being related to the junctures between the ordered regions; that is, they explicitly find that nonuniformity is consistent with their data. But how precisely can they know the percent volume fraction and the structure of the two "regions" (miscalled "phases")? Further, from what we know of surface disorder in oxides the "ordered" regions of 11-Å [sic] and 20-Å units will be largely disordered anyway. Perhaps the computer program could provide RDF's for a series of mixtures of different proportions and sizes and degrees of disorder of cristobalite-tridymite units as one region with a Zachariasen-Warren random network SiO_2 glass as the other region. Stated another way, I believe that the data of Konnert *et al.* are consistent with a model for the nonuniform structure of SiO_2 glass consisting of a good proportion (50 percent?) of relatively poorly ordered ("crystalline") material of the stacking-disordered cristobalite-tridymite family, in a matrix of random network material (*10*). In this respect it sounds not too different from its structural analog, liquid H_2O (*11*).

Note added in proof: Since this technical comment was written, Evans *et al.* (*12*) have also commented on this same report. One of the points raised by Evans *et al.* is a special case of one of the two main points raised herewith. They question whether Konnert *et al.* had examined the "keatite" structure as one of the other possible ordering models. Konnert *et al.*, in their reply (*13*), state that the RDF for keatite did not match that of the glass. This is, in my view, to be expected. Both keatite and silica-O (*14*), corresponding to the spodumene and eucryptite structures, respectively, are always metastable, relatively rare structures resembling quartz and (hence) are always obtained by low-temperature "annealing" procedures of various kinds. Disordered cristobalite, on the other hand, is the universally obtained first Ostwald step from SiO_2 glass at higher temperatures (1000° to 1700°C). The statement by Konnert *et al.* (*13*) in their reply to Evans *et al.* (*12*) is an accurate summary of their findings: "Our diffraction data, however, *are compatible with* a structure in which the atoms are ordered over distances up to about 20 Å in arrangements similar to those found in the crystalline polymorph tridymite" (italics mine). My point in this note is that, although this compatibility is a *necessary* condition for establishing "tridymite" as one possible candidate structure, it is far from *sufficient*, given the certain complexity of the presence of a variety of polytypes and the high probability of a nonuniform structure.

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In our recent investigations of glassy structures (*1, 2*), for example, silica glass, by means of diffraction techniques we had as our primary concern the optimization of the accuracy of the radial distribution function (RDF) so that reliable conclusions could be drawn with regard to the possibility of the presence of long-range order. In carrying out the analysis, important use was made of the mathematical and physical constraints on the system (*3*). For the silica glass, the resulting RDF's were shown by statistical analysis to contain significant features out to 15 to 20 Å. This implied the presence of considerably greater ordering in silica glass than had previously been reported.

As a secondary matter, it was of interest to determine whether the type of ordering displayed by the RDF's could be found in any of the more crystalline phases of SiO_2. Before discussing the results of this search, we would like to say a few words on the use of the term "ordering" when applied to crystalline materials and the physical meaning of the calculations that are carried out in the attempt to compare the RDF's of glassy and crystalline materials. These remarks will facilitate a response to the questions raised by Roy (*4*).

There are several types of order in a single crystal. There is the crystal symmetry which involves the symmetry elements associated with the packing of structural units in the unit cell and the translational symmetry which gives crystals their three-dimensional periodicity. In order to generate a crystal, the elements of the space group symmetry operate upon an arrangement of atoms called the asymmetric unit. The asymmetric units usually possess no elements of symmetry (although they may occasionally possess elements which are termed "noncrystallographic" symmetry). However, despite the absence of periodic order or other symmetry, the asymmetric unit or groupings of such units may very well possess atomic arrangements of high regularity. This could apply, for example, to the six-membered rings of silicate tetrahedra that occur in cristobalite and tridymite and the orderly fashion in which they may join or, in a different type of structure, to an α-helix in a protein crystal. The six-membered rings may be more highly ordered than the groupings of silicate tetrahedra which are connected together in a random fashion, subject only to the spatial constraints of neighboring tetrahedra and the limitations on the distribution of bond angles, as envisioned in the continuous random network model of silica glass. We thus have a type of structural ordering occurring in a crystal which exists independently of the crystallographic symmetry including periodicity that characterizes the crystallinity of a substance. We may term this type of order "structural" order as opposed to "crystallographic" order. In the case of silica glass and the comparison with crystalline materials, we are concerned with structural order. There is no clear indication of crystallographic order in the RDF's for silica glass, that is, no crystallographic symmetry.

The comparison calculations of the RDF's of crystalline materials are carried out in such a way as to sample only the structural order in these materials. The crystallographic order is suppressed. For example, for quartz, cristobalite, keatite, and the varieties of tridymite, the RDF's represent a weighted average of the distributions of distances found in spherical regions, sampled continuously throughout the crystal. The weightings were so adjusted that regions of larger diameter were given smaller weight and contributions from diameters greater than 20 Å were negligible, thus limiting the size of the regions sampled to the range found in silica glass. The RDF's are therefore composed of continuous samplings of the distance distributions comprising the structural order in regions not exceeding about 20 Å in diameter.

It is claimed by Roy (*4*) that various forms of tridymite have significantly different bonding topologies (stacking sequences consisting of layers of approximately hexagonal groups of silicate tetrahedra) within the domains that coherently scatter radiation. Crystallographic evidence to date refutes this. In three studies involving the 2-layer (*5*), 12-layer (*6*), and 20-layer (*7*) tridymites, the latter two not completely refined, the bonding topologies have been found to be quiet similar. They evidently differ primarily in terms of rotations about the silicon-oxygen bonds. The *R* factors range from 9 for the 2-layer to the low 20's for the 12- and 20-layer tridymites. If substances which are thought to be forms of tridymite are found to have a significant amount of bonding characteristic of alternative forms of silica, for example, cristobalite, it is evident that such substances should not be called tridymite.

We have calculated RDF's for the 20-layer (*1–3*) and the 2-layer tridymites. These RDF's are quite similar, another indication of a common bonding topology. The main question raised by Roy (*4*) concerns the description of the structure of silica glass as tridymite-like. Silica glass has been so described because the structural ordering in the various types of tridymite, for which RDF's were calculated, is sufficiently similar so that the RDF's compare well with each other and with the RDF for silica glass. This is the basis for calling silica glass tridymite-like. In contrast, it is not at all clear what basis Roy uses [see reference 10 in (*4*)] for specifying Raman spectra as belonging to cristobalite or tridymite. In fact, this terminology does not seem to be consistent with the main theme of his technical comment which characterizes cristobalite and tridymite as words with "fuzzy" meanings.

A structural model for a glass consists of a set of atomic coordinates or a recipe for generating the coordinates. We have not yet presented a model, although it is alleged (*4*) that we have done so. Also, we have not overlooked the possibility of the presence of some bonding topology characteristic of cristobalite (*2*). The significance of our results, in fact, is that they provide a detailed RDF that a model must obey and imply that the characteristic bonding topologies found in the tridymites, for example, the characteristic groupings of the six-membered rings of silicate tetrahedra, may well provide the structural units on which a useful trial model can be based. This approach contrasts with model building based on individual tetrahedra which are randomly connected. The latter mode of operation is unlikely to be successful.

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