

Apparent effects of molecular water on the lattice geometry of cordierite: a reply

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I would like to preface my reply to Langer and Schreyer's discussion (1976) of the lattice geometry of cordierite by emphasizing two fundamental facts which must underlie any explanation of the distortion index. First, as Stout (1975, p. 230) has shown, the distortion index is a direct measure *only* of the shape of the cordierite lattice. As such, variations in the index depend only on the relative values of measured lattice parameters, and are therefore independent of point-group symmetry. It follows that any variable, whether structural or compositional, that is capable of changing the axial ratios of cordierite may be expressed as a change in the distortion index. In the event that two or more variables simultaneously operate, a single-valued index will result, and any examination of that index alone will not permit distinction between the variables or even recognition of their number.

The second fact is that the state of Al-Si order in cordierite can only be known through additional data. Specifically, the tetrahedral site occupancies must be determined by structural refinement. Any statement regarding Al-Si order based on the cordierite distortion index in the absence of site-occupancy information must be considered interpretation rather than fact. To my knowledge, such information is known only for the Guilford cordierite (Gibbs, 1966), the Haddam cordierite and two other cordierites studied by Meagher (1967), and an Australian cordierite described by Cohen *et al.* (1975). These studies not only confirm the suggestion made by Zolnai (1960) that cordierite be considered a tetrahedral framework silicate, but also demonstrate that the problem of its variable lattice geometry is far from solved. Given hopeful agreement on these two facts, I believe it will become clear in the following reply that the number of disregarded "facts" referred to by Langer and Schreyer (1976) in their introductory remarks are based on their interpretation of the significance of the distortion index.

To begin, it should be clarified that Stout's first "argument" is defined as such by Langer and Schrey-

er and then neatly rejected by them. The statement was not intended as an argument in support of the effect of molecular water on the lattice, but as a statement of observation that molecular water is incorporated into the structure. The Gladstone-Dale relationship is well known, but there is another fundamental concept that is perhaps more relevant to this discussion. That is the important distinction between the *structure* of cordierite and its *lattice*. The issue addressed in Stout's (1975) model deals primarily with the apparent effect of channel constituents on the cordierite lattice, and consequently is concerned only with translational symmetry.

Regarding the effects of Be (Langer and Schreyer argument 2) on the lattice geometry of cordierite, a ". . . number of facts previously determined through synthesis experiments . . ." were taken into account in Stout's (1975) model. This is apparent from Stout's (1975) text and extended footnote (p. 231). It is true, as Langer and Schreyer point out, that the Haddam cordierite contains 0.52 percent Be (Iiyama, 1960; Newton, 1966), but it does not follow that its low distortion index ($\Delta = 0.12$) relative to the Guilford cordierite ($\Delta = 0.24$) may "easily be explained" on this basis alone. The formula unit of the Haddam cordierite recalculated on the basis of 18 oxygens excluding H₂O is:



where *M* is the sum of Fe²⁺, Mn²⁺, Mg²⁺, and Ca²⁺ in octahedral coordination. This corresponds to 4.1 mole percent beryl on an ideal $\text{M}_2\text{Al}_4\text{Si}_5\text{O}_{18}$ - $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$ binary and 13 mole percent $\text{NaMg}_2\text{Al}_3\text{BeSi}_5\text{O}_{18}$ based on the substitution of Na + Be for Al suggested by Povondra and Langer (1971a, b). If it is assumed that this substitution is valid for the Haddam cordierite as Langer and Schreyer (1976) suggest, then according to Povondra and Langer's (1971a, Fig. 2) data, the distortion index of the Be-free phase would increase from 0.12 to 0.16, thus accounting for only one-third of the observed difference between the Haddam and the Guilford cordierites.

Even if this substitution were to be proven valid, the specific role of Be in distorting the cordierite lattice is still open to question. If all of the Be in the Haddam cordierite were distributed equally on tetrahedral sites, this would amount to replacing 3.1 atom percent of the total Al with Be. Because the ionic radii of Be^{2+} (0.35 Å) and Si^{4+} (0.34 Å; Whittaker and Muntus, 1970) in tetrahedral coordination are so similar, the Be substitution for Al ($r = 0.47$ Å) should have about the same shortening effect on $\text{T}_5\text{-O}_4$ and $\text{T}_5\text{-O}_5$ bond lengths (Stout, 1975, Fig. 3) as would a 3 percent disordering of an Al-filled T_5 site. As this has a very small effect on mean $\text{T}_5\text{-O}$ bond lengths (Gibbs, 1966; Meagher, 1967), the distortion index may not be measurably changed.

Stout's (1975) model offers an alternative explanation for Langer and Povondra's (1971a) data. The substitution of $\text{Na} + \text{Be}$ for Al requires that Na ions occupy sites within the open channels. As Stout (1975, p. 232) emphasizes, "the presence of other channel constituents, such as Na^+ and K^+ , in positions where coordination with O_4 is likely could have the same distorting effect as molecular water." It therefore seems likely that in conjunction with a small shortening of mean T-O bond lengths due to Be substitution for tetrahedral Al, there may be an additional effective shortening due to coordination with channel constituents.

Another set of observations on which Stout's model is based is Harwood and Larson's (1969) study of 52 cordierites from a contact aureole. Their data argue strongly in favor of variables other than Be as having measurable effect on the lattice geometry. They found that a systematic decrease of Be from 15 to 7 ppm toward the contact correlates with an increase of the distortion index from 0.23 to 0.29. The substitution of such trace amounts of Be for Al cannot represent a significant contribution to mean T-O bond lengths, and therefore the distortion index would not be expected to change on that account. It also is questionable that the increase of the distortion index toward the igneous contact is due solely to increased Al-Si ordering. On the basis of previous studies (Steiger and Hart, 1967; Wright 1967) on Al-Si disordering in K-feldspars around igneous stocks, the degree of ordering should decrease near the contact, rather than increase as Harwood and Larson's study would suggest. Other parameters are obviously more important. One which has yet to be tested is the likely variation in H_2O contents of the cordierite.

The problem of hydrogen bonding (Langer and

Schreyer argument 3) in cordierite was first suggested by Farrell and Newnham (1967) on the basis of polarized infrared studies. Their data, in combination with the anomalously low rms amplitude of vibration of O_4 in the ordered Guilford cordierite (Gibbs, 1966 and Stout, 1975, Table 2), are further evidence for Stout's (1975) model. Since then, many additional data have accumulated (Lungren and Olovsson, 1975; Falk and Knop, 1972) that indicate it would be premature for Langer and Schreyer (1976) to eliminate the possibility of substantial energies associated with possible O_4 -water hydrogen bonds based only on comparisons with the fundamental absorption bands of liquid and vapor H_2O alone. The concern here is not for water-molecules hydrogen bonded with each other, but rather for the energy of interaction between the water-molecule dipole and the surrounding ions. Newton (1972) estimates this interaction in the case of cordierite with 0.7 moles of H_2O to be -2.5 kcal/mole of H_2O at 830°C in order to account for the discrepancy of 3-4 kbar between the breakdown pressures of cordierite in wet and dry systems. In these experiments, the state of Al-Si order in the synthetic cordierites is not known.

It is important to note in this connection that the comparisons made by Langer and Schreyer based on the properties of molecular water in beryl ($\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$) are not totally appropriate. A fundamental part of Stout's (1975) model is the dependent relationship between the state of Al-Si order and the effect of channel constituents on the lattice distortion. In the case of beryl, all six tetrahedra of the ring surrounding the open channels are occupied by Si and are symmetrically equivalent. Unlike cordierite, there are no bridging oxygens between Si and Al in the six-membered rings and consequently no local charge imbalance. It therefore seems unlikely that the interaction energy between channel constituents and surrounding ions in beryl will be the same as in cordierite.

Turning now to the interpretation of Chernosky's (1974) data, it is difficult to accept Langer and Schreyer's (1976) proposal that two separate cordierites with different structural states exist in Chernosky's experimental runs rather than the single phase reported. Chernosky's high-temperature assemblage (forsterite + cordierite + spinel) was synthesized from an anhydrous oxide mix at high temperature. The measured distortion index of the resultant cordierite was 0.28. The observed effect of prolonged hydrothermal treatment (an average of 422 hours for the 19 reported runs) at temperatures ranging from

576°C to 766°C was to decrease the distortion index to "very small or unmeasurable value ($\Delta < 0.10$)" (Chernosky, 1974, p. 501).

In view of the demonstrated reversibility of Chernosky's data, the possibility of the disequilibrium implied by Langer and Schreyer's proposal is minimized. Reversibility in this case requires that cordierite be consumed on the low-temperature side of the reaction curve and generated on the high temperature side. A careful inspection of Chernosky's Table 2 (p. 501) will show that all of the experiments in which the clinocllore stability is established on the low-temperature side of the reaction curve show incomplete reaction. That is, the starting amount of cordierite decreases but the remainder must be preserved *metastably* in the clinocllore stability field, contrary to Langer and Schreyer's statement. It is difficult to conceive how two cordierites could be present in these cases.

It is important to note that a single metastable cordierite within the clinocllore stability field may be fully equilibrated with respect to equality of pressure, temperature, and the chemical potential of H_2O . It differs from stable cordierite only in that the full phase assemblage has not achieved a state of minimum free energy under the specified water pressure and temperature.

Finally, Langer and Schreyer suggest (argument 5) that the observed increase of the distortion index during Iiyama's (1960), Meagher's (1967), and Stout's (1975) heating experiments is due to additional Al-Si ordering. If this is true, it requires that the correlation of the observed increase of the index with dehydration be accepted as a coincidence. Stout's (1975) dehydration experiments with the Guilford cordierite extended over a period of 2 hours and were carried out in a carbon crucible in an attempt to minimize oxidation. The experiment was designed to liberate molecular water at temperatures below that believed necessary to break significant numbers of Si-O and Al-O bonds. The only cordierite proven to have experimentally-induced disorder of Al and Si is the Guilford material which was heated by Meagher (1967) at 1400°C and then refined. Even after this treatment, only partial disordering was achieved, and the distortion index decreased by only 0.04 (Stout, 1975, Fig. 4 and Table 3). In contrast, the increase of the distortion index by 0.03 to 0.09 in Iiyama's (1960) and Stout's (1975) dehydration experiments was achieved at much lower temperatures (900°C), where the kinetics of Al-Si ordering is less favorable. It therefore seems likely that natural cordierites, such as

from Guilford and Haddam, are as difficult to order at 900°C and 1 atm pressure as pure anhydrous Mg-cordierite (Schreyer and Schairer, 1961).

In closing this reply, it is important to realize that Stout's (1975) hypothesis, like all new models, was conceived in the face of a large number of observations that were left unexplained by previous models. But like all models, this one is designed to be tested, confirmed, or refuted in the light of new data. Until those data appear, I trust that mineralogists and petrologists will proceed with an open mind and with the realization that the case is far from closed on the water problem in cordierite.

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*Manuscript received, January 20, 1976; accepted
for publication, May 12, 1976.*