THE QUENCHING TECHNIQUE IN NON-QUENCHABLE SYSTEMS: A DISCUSSION CONCERNING
THE ALLEGED THERMAL DECOMPOSITION OF PORTLANDITE AT HIGH PRESSURES*

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INTRODUCTION

Pistorius (1963) recently extended the earlier curve of Majumdar and Roy (1956) for the dissociation of portlandite from 3 kilobars to 20 kilobars. Prior to this, Wyllie and Tuttle (1960a) had presented evidence that at pressures greater than about 100 bars portlandite did not dissociate, but melted—incongruently at low pressures, but congruently at a pressure not much above 100 bars. In view of the care we took to describe in detail the several lines of evidence which led to our conclusion (Wyllie and Tuttle, 1960a, p. 4 to 8), we were somewhat surprised when Pistorius (1963) summarily dismissed our results as “anomalous” because they were at variance with his interpretation of his own quenched high pressure runs. His interpretation was based on identification of the products after a quench “by means of X-ray powder patterns, usually supplemented by microscopic observations”. In many systems containing non-quenchable phases such evidence can be inadequate and ambiguous, as indicated by some of the examples outlined below. We feel that the combination of techniques we employed for investigation of the solid-liquid-vapor phase relationships in the system CaO–CO₂–H₂O opens up a new area of high pressure studies in non-quenchable systems containing volatile components under pressure. Since Pistorius has dismissed our results so lightly, apparently ignoring the evidence we presented, we feel it is necessary to emphasize the validity of the method.

THE QUENCHING TECHNIQUE

The quenching technique was developed at the Geophysical Laboratory for investigation of the phase relationships in silicate systems at high temperatures. The kinetics of sluggish silicate systems are such that liquids can be quenched to glasses, and the equilibrium assemblages of phases at the high temperatures can be frozen in and preserved for later examination. Devitrification occurs in some silicate systems, even with a very rapid quench, but the phenomenon can usually be recognized by microscopic study, and the high temperature assemblages can be deduced from textural evidence. Few systems present serious problems of interpretation.

With the development of pressure vessels permitting the investigation of silicate, hydrate, and carbonate systems at high temperatures in the presence of volatile components under pressure, the problems of preserving the high temperature, high pressure assemblage of phases during a quench became more acute. Volatile components are far more reactive than most silicates, and it is

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usual for some degree of reaction to proceed during the quench. For example, the products of a dehydration or decarbonation reaction normally undergo at least partial rehydration or recarbonation when quenched in the presence of water vapor or of carbon dioxide. There are more variables to consider during a quench, and various procedures have been adopted. The temperature may be reduced first, with a subsequent pressure quench; the pressure may be reduced first, with a subsequent temperature quench; or the pressure and temperature may be reduced simultaneously. The procedure depends upon the nature of the reactions being studied and upon the particular experimental technique being employed. For example, if the sealed capsule method is used then the temperature must be reduced first, otherwise the capsules would burst open during the pressure quench.

In some systems, there may be serious problems of interpretation, leading to various estimates for the position of a particular reaction curve by different research groups. This is well illustrated by the growing literature on the apparently simple reaction:

\[ \text{Mg(OH)}_2 \rightleftharpoons \text{MgO} + \text{H}_2\text{O}. \]

This was first located by Bowen and Tuttle (1949) as part of their study of the system MgO–SiO$_2$–H$_2$O. Its position on a pressure–temperature diagram has been relocated many times since then by investigators using various techniques. Reviews of the several techniques used, and the results obtained, can be found in papers by Roy and Roy (1957), by Meyer and Yang (1962), and by Barnes and Ernst (1963). There is complete accord about the nature of the reaction in this system: it is a dehydration reaction. Much of the disagreement arises from interpretation of the significance of the crystalline phases present after the quench. Identification of the phases alone is not sufficient to locate the position of the reaction, even in this simple reaction.

In systems where a liquid phase appears, additional problems of interpretation arise because many liquids cannot be quenched to a glass in the presence of volatile components. Furthermore, during a quench the liquid crystallizes not to a mineral assemblage with the bulk composition of the original liquid, but to a mineral assemblage with the composition of the original liquid plus the volatile components from the vapor phase which react with the liquid during the quench and which sometimes continue to react even after the quench. Several examples of such systems could be quoted. Yoder and Tilley (1962, p. 445) found that a basaltic liquid in the presence of water vapor under high pressures cannot be quenched to a glass: the quenched product is an aggregate of amphibole. However, the quench amphibole can be distinguished from primary amphibole in equilibrium with the liquid at high temperatures and pressures by its microscopic texture. Again, we see that identification of phases is insufficient, and for interpretation of the high temperature phase assemblage study of the texture is necessary.

The presence of a liquid adds complexity to the quenching process, but it also adds one more parameter which can be of great help in identifying the phases present before the quench. This parameter is a function of the physical properties of a liquid phase. If liquid and vapor coexist at the pressure and temperature of a run there will either be a meniscus between them or the vapor
phase will occur as small bubbles within the liquid. These physical characteristics are preserved during a rapid quench, and their recognition can be regarded as incontrovertible evidence for the former coexistence of liquid and vapor phases.

In order to interpret the phase assemblage present before the quench in their study of the system CaO–CO$_2$–H$_2$O, Wyllie and Tuttle (1960a) combined all of these techniques. The phases present after a quench were identified by optical and X-ray methods, the textures were studied microscopically, and the physical nature of each change after a quench was carefully noted. The interpretations so obtained combined to provide consistent phase diagrams. The sealed capsule quenching technique at high pressures and temperatures is perfectly applicable for many non-quenchable systems, so long as it is used with care and discretion. Strangely enough, the more complex quenching processes involving a liquid phase are more easily interpreted than the solid-vapor reactions.

**THE MELTING OF PORTLANDITE**

Returning to the specific item under discussion, namely the question of whether portlandite melts or dissociates at high pressures, it is perhaps relevant to mention that Majumdar and Roy (1956) worked in this laboratory and that we had the advantage of building upon their earlier work and experience in the system CaO–H$_2$O when we revised their interpretations. When we started work in the system CaO–CO$_2$–H$_2$O, we expected to find CaO, not portlandite, as the stable phase on the liquidus. According to the available evidence, portlandite dissociated at temperatures below the solidus in the ternary system. Therefore, when we found portlandite in the quenched liquids, we tried to interpret this as CaO which had rehydrated during the quench. However, when we followed the ternary liquidus field boundaries towards the side CaO–H$_2$O we found they were not consistent with this interpretation. We then realized we would have to restudy the binary join CaO–H$_2$O. This we did, using the various methods described above, and once we recognized the fact that portlandite melted and did not dissociate, the results from the ternary system provided a consistent pattern.

It is significant that the results obtained in several other, more complex systems are all consistent with our interpretation. These systems include CaO–SiO$_2$–H$_2$O (Harker, Roy, and Tuttle, 1962), CaO–CaF$_2$–P$_2$O$_5$–CO$_2$–H$_2$O (Biggar and Wyllie, 1962), CaO–SiO$_2$–CO$_2$–H$_2$O (Haas and Wyllie, 1963), and CaO–Na$_2$O–CO$_2$–H$_2$O (Gittins and Tuttle, unpublished information). Internal consistency within each system, and among systems, we regard as strong evidence for the interpretive method. The same methods were used in the system CaO–CO$_2$ (Wyllie and Tuttle, 1960a), and our rather meagre data are in agreement with extrapolations from results obtained by Smyth and Adams (1923) and Baker (1961), using heating curves and differential thermal analysis at pressures up to 300 bars. Further proof of the validity of the quenching technique is provided by results obtained in the system CaF$_2$–BaSO$_4$–CaCO$_3$–Ca(OH)$_2$. Here, in compositions near the quaternary eutectic, the liquids quench to a glass, and all gradations between glass and the usual crystalline
quench product can be observed by changing the bulk composition slightly (Kuillmer, Visocky, and Tuttle, unpublished information).

Finally, we may add that we were not the first to recognize that portlandite melted, rather than dissociated, at moderate pressures. Unknown to us, Syromyatnikov (1958) in U.S.S.R. had described melting in the system CaCO$_3$–Ca(OH)$_2$ and specifically the melting of portlandite at pressures between 500 bars and 1 kilobar. We had cause to disagree with some of his temperatures and interpretations (Wyllie and Tuttle, 1960b), and he in turn challenged some of our statements (Syromyatnikov, 1960), concluding that “the method of quenching miniature metal capsules so widely used in the U.S.A. is unsatisfactory for the study of phases with strong capacity for crystallization”. Our reasons for being satisfied with this technique are outlined above and in several published papers (e.g. Wyllie and Tuttle, 1960a). We wish to stress here simply the fact our contention that portlandite melts rather than dissociates is supported by Syromyatnikov’s results, obtained independently of ours, and obtained with a different technique.

In view of the evidence outlined above, we have no doubt at all that portlandite melts at pressures above about 100 bars. It melts incongruently at low pressures, but at some pressure only slightly in excess of 100 bars the melting becomes congruent.

A POSSIBLE RE-INTERPRETATION OF THE RESULTS OBTAINED BY PISTORIUS (1963)

This brings us to the interpretation of the results obtained by Pistorius (1963). Pistorius suggested that our results were anomalous because “it seems that a sufficient amount of water vapor could have been present in their containers to rehydrate their samples fully upon quenching”. In our table 2A, it can be seen that some of our runs contained an excess of water and that others contained a deficiency of water compared to the composition Ca(OH)$_2$. Now, all of Pistorius’ runs contained an excess of water and he used the same quenching technique which we used, namely, the temperature was quenched while the pressure was maintained constant. The excess of water in his runs should therefore have been just as efficient in fully rehydrating his samples as he suggests that it was in our samples. This, then, is no explanation for the different results obtained in the two studies.

The consistency of Pistorius’ results confirms that he is measuring a reaction of some kind. His description of an experiment designed to test reversibility suggests to us that the reaction is accompanied by loss of water from the sample, with consequent change in bulk composition. He says that “the boundary curve is very easily reversible”, and after holding a sample at a temperature where Ca(OH)$_2$ is allegedly converted to CaO, he lowered the temperature to a position below the measured reaction curve, quenched the run, and found that “the products contained an appreciable amount of Ca(OH)$_2$”. If the bulk composition of his charge remained the same as it had been at the beginning of the run, it is difficult to understand why such a readily reversible reaction did not result in complete rehydration of CaO to Ca(OH)$_2$. If water had been lost from the sample, however, the extent of rehydration would be limited by
the amount of water remaining in the sample. What kind of reaction would be likely to permit loss of water from the sample contained within a simple squeezer apparatus? It is not commonly lost during solid-vapor reactions, but it seems quite possible that if the charge melted completely, the physical nature of the charge could conceivably be changed sufficiently for some water to leak out. The only explanation we can think of to account for the anomalous results obtained by Pistorius is that he was locating a curve not for the reaction:

\[ \text{Ca(OH)}_2 \rightleftharpoons \text{CaO} + \text{H}_2\text{O}. \]

but for the reaction:

\[ \text{Ca(OH)}_2 + \text{H}_2\text{O} \rightleftharpoons \text{liquid}, \]

and that when the charge melted, water leaked from the sample. This could account for the preservation of CaO in quenched samples which originally contained more than enough water to rehydrate the lime. Pistorius chose to draw a curve with a small positive slope between his experimental points, and he connected this almost linear curve to the dissociation curve reported by Majumdar and Roy (1956) at lower pressures. It would be just as easy to draw a curve with a slight negative slope between his experimental points and to join this curve smoothly to our PT curve for the melting reaction in the presence of excess water. The fit is excellent, which suggests that our re-interpretation of the results obtained by Pistorius is a reasonable one.

**CONCLUSION**

We conclude by repeating an earlier statement: the sealed capsule quenching technique at high pressures and temperatures is perfectly valid for many non-quenchable systems as long as it is used with care and discretion. Interpretation of textures from petrographic studies is valid only if this is confirmed by study of the physical character of the charges, where applicable, and so long as the results combine to provide a consistent pattern of phase relationships for the system as a whole. We maintain that these conditions have been met in our studies of the systems CaO–H₂O and CaO–CO₂–H₂O, whereas Pistorius has used only one approach. His interpretations were based solely on identification of the phases present after a quench. Despite the details spelled out in our paper, Pistorius gave no indication of having recognized or even sought the textural characteristics of the liquid phase which we encountered in the system CaO–H₂O at all pressures above 100 bars.

**ACKNOWLEDGMENT**

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**REFERENCES**


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NOTE BY C. W. F. T. PISTORIUS

Recently, W. Sharp and A. Jayaraman (personal communication) showed that my curve is, in fact, the congruent melting curve of Ca(OH)₂. The above interpretation of my results by Drs. Wyllie and Tuttle must consequently be considered correct.