American Mineralogist, Volume 77, pages 666–667, 1992

Composition of the fluid phase accompanying carbonatite magma: A critical examination—Reply

John Gittins, Martyn F. Beckett, Bruce C. Jago
Department of Geology, University of Toronto, Toronto, Ontario M5S 3B1, Canada

The opening thrust of Treiman and Essene's reply suggests that the principal purpose of our 1990 paper was to offer "a critical reappraisal of F in carbonatite petrogenesis." This is not so. We simply emphasized that any fluid phase in equilibrium with carbonatite magma is not H_2O rich as Treiman and Essene (1984) had alleged. We raised the possibility of F or alkalis having played a role in the magma, but our conclusion was that "a fluid composed almost entirely of water is far too simple."

We are agreed that the rock at Husereau Hill is magmatic and that it matters little whether or not it is a dike.

We still feel that a ten-phase eutectic (eight solids plus melt plus vapor) is an unlikely occurrence, and that it is even more unlikely that a liquid of eutectic composition would exist in sufficient volume to be intruded as a magmatic body. The authors invoke ten phases and 11 components and state "the degrees of freedom are thus 2, and the phase rule has not been violated." We agree, but 2 degrees of freedom do not define a eutectic. Either the system is invariant or it is divariant. It cannot be both. However, Treiman and Essene now seem to feel that "whether or not the full assemblage represents a eutectic is, of course, irrelevant to the calculations" so perhaps we can pass on, although the eutectic claim was quite central to their argument in the original paper.

It is noteworthy that Treiman and Essene did not directly calculate that H_2O was the dominant component of the vapor phase; indeed, they said ". . . water fugacity cannot be calculated directly, and must be inferred from other constraints." What they did was to assume that H_2O played the dominant role because Wyllie and Tuttle (1960) had demonstrated how H_2O can drastically lower the melting temperature of calcite. They decided that ". . . it seems reasonable to infer that the dike was saturated with a water-bearing fluid," an inference based largely on the fact that they knew of nothing else likely to have been able to maintain a carbonatite magma liquid at acceptable temperature and pressure. Having estimated the load pressure at the time of crystallization, they obtained P_{H_2O} by subtracting from this load pressure the partial pressures of the various species that they calculated from the assumed eutectic mineral assemblage. Their method, given the eutectic assumption, allowed them to calculate the partial pressures of certain constituents of the vapor phase. The conclusion that the vapor was dominantly H_2O follows from the initial assumption that this was so. Indicative of this approach is the statement ". . . published phase equilibria (and geothermometry of the rock) are completely consistent with the presence of an H_2O-rich fluid." This is incorrect. They are consistent with the presence of H_2O in solution in the carbonatite magma, but that does not necessarily dictate that an H_2O-rich vapor phase will also be present. Furthermore, mere consistency with the presence of H_2O does not prove that H_2O was actually present.

In their comment the authors introduce the concept that, because the inferred solidus (640 °C) is above the temperature at which periclase hydrates to brucite, "most of the H_2O originally present in magma or vapor would have been able to migrate out of the solidified carbonatite before the stability limit for brucite was reached." Perhaps. But we remain skeptical that the rock would dehydrate to such an extent that there was too little H_2O left to hydrate the periclase.

The calculations and arguments about f_{F_2} are interesting but misleading. They are based on extrapolations from the data of Robie et al. (1979) but may be of limited value, given the lack of knowledge at that time about the solubility of F in carbonate liquids. In fairness it must be said that our data on this subject (Jago and Gittins, 1991) were not available to Treiman and Essene when they wrote the original paper, but that does not diminish their pertinence to the problem under discussion. The authors do now acknowledge that approximately 10 wt% F can dissolve in carbonate liquids before fluorite is stabilized as a liquidus phase, but they argue that, since their calculations indicate a vapor phase with a maximum $f_{F_2} = 10^{-35}$, there could have been little F in the Husereau magma. Perhaps that is so. We do not know how much F, if any, was present, and we must correct the impression of our having claimed that a fugitive F-rich fluid was required. We fully agree that "it is very important to distinguish between F abundances in the vapor phase and in the melt phase." That is precisely what we have done. But, if H_2O was not responsible for the liquid state of the Husereau magma something else clearly was. We merely offer F, dissolved in the carbonatite magma, as a viable possibility given its now generally accepted importance in carbonatite magma evolution.

Treiman and Essene say that our results are inconsistent with the mass of experimental data on carbonate melting and refer us to Wyllie and Tuttle (1960) who found that ". . . addition of H_2O extends the liquidus field for calcite down to about 650 °C. . . ." One of us (J.G.) was privileged to continue this work under the late Professor Tuttle's tutelage, and we must point out that Wyllie

0003–004X/92/0506–0666$02.00

and Tuttle also said (1960, p. 21), in referring to the beginning of melting of calcite at 740 °C, "only a trace of liquid is developed at this temperature, and for charges containing less than 30 weight per cent H_2O the presence of liquid was not established." In discussing the more complex ternary system $CaO-CO_2-H_2O$, in which $CaCO_3-H_2O$ is a pseudobinary join, they further emphasized the fact by stating, "At 750 °C . . . liquid was distinguished . . . only in charges containing more than 30 per cent water" (p. 26). In our reported data (Gittins et al., 1990, Table 1) we did employ the expression "Q(tr?)" which we defined as "possible but unlikely that a trace of quenched liquid is present," thus leaving the door ajar. We may well have seen quenched liquid, but in such small amount as to be entirely consistent with the results of Wyllie and Tuttle (1960) rather than inconsistent as Treiman and Essene purport. It is a misreading of Wyllie and Tuttle (1960) to say that "to be consistent with previous experimental studies, the rock + water experiments of Gittins et al. (1990) ought to have yielded significant quantities of melt." What is beyond dispute is that, at the upper temperature limit of our experiments (930 °C), any melting of the allegedly eutectic carbonatite from Husereau Hill was triflingly minor in the presence of 20 wt% H_2O.

Treiman and Essene make the further comment that ". . . no vapor phase was reported in the rock + water experiments, which contained 10–20 wt% H_2O; the lack of a vapor phase may provide a clue to the inconsistency among experimental results." We are afraid that no solace can be gleaned here. Calcitic and dolomitic liquids do not quench to a glass; they crystallize too rapidly during cooling. Thus, any H_2O dissolved in the liquid during the experiment is expelled during quench crystallization, condenses during cooling, and appears as liquid H_2O when the charge is examined; it is indistinguishable from any that might have existed as a vapor during the experiment and which has also condensed to liquid H_2O. These melting experiments do not involve decarbonation reactions that would produce CO_2; hence, there is no identifiable vapor when the capsule containing the experiment is opened. We have no way of knowing whether a vapor was present, and so no vapor is listed among the identified experimental products in Table 1. That is not to say that none was present.

We are grateful to Treiman and Essene for pointing out, in an earlier draft of this exchange, the apparent inconsistency in our experimental results where dolomite was reported as present to at least 804 °C. We have checked our laboratory records and find that dolomite (dmt) should not have been included in the assemblages for "rock plus approx. 20 wt% H_2O" at 700, 749, and 804 °C. This is a regrettable compiling error on our part, for which we apologize.

We do not accept that "the conclusions of Treiman and Essene (1984) about the vapor phase of the Husereau dike carbonatite are consistent with available data," or that "the criticisms of Gittins et al. (1990) are flawed." We do, however, note the hesitancy in Treiman and Essene's comment that "our result for this carbonatite . . . is not necessarily relevant to other carbonatites because the Husereau carbonatite is unlike any other in the world." We would not go so far as to say that it is unique [the carbonate of Kerimasi (Mariano and Roeder, 1983) has much in common with it], but we are inclined to return to our original suggestion that the deduction of H_2O-rich vapor is of dubious validity when applied even to the carbonatite of Husereau Hill.

Treiman and Essene close their discussion with a suggestion that ". . . the much more common sodic carbonatites . . . may have equilibrated with rather different fluxes than did the Husereau dike. The widespread . . . (fenitization) associated with most intrusive carbonatites clearly indicates the importance of sodic fluxes. None of these features, however, is associated with the magnesian Husereau dike. . . ." Possibly. But who knows what is present under the ploughed field that surrounds the (presumed) outcrops on Husereau Hill?

Treiman and Essene admonish us against postulating "occult fluxes." In our defense we must reiterate that, although we offered the role of alkalis or F as a more realistic possibility than that of H_2O alone, we were careful not to insist that they were the sole explanation of the liquid state of the Husereau magma at the time of its intrusion or that either constituted a vapor phase. We are reminded that more than a century ago Rossetti, in his appropriately titled poem "For Our Lady of the Rocks," warned of being caught "amid the bitterness of things occult." And who can forget Washington's anguished complaint of many years ago, "De profundis clamavi." Perhaps the time has come to leave this rather exhilarating debate to future research and (in the case of J.G.) to younger minds.

REFERENCES CITED

Gittins, J., Beckett, M.F., and Jago, B.C. (1990) Composition of the fluid phase accompanying carbonatite magma: A critical examination. American Mineralogist, 75, 1106–1109.

Jago, B.C., and Gittins, J. (1991) The role of fluorine in carbonatite magma evolution. Nature, 349, 56–58.

Mariano, A.N., and Roeder, P.L. (1983) Kerimasi: A neglected carbonatite volcano, Tanzania. Journal of Geology, 91, 449–455.

Robie, R.A., Hemingway, B.S., and Fisher, J.R. (1979) Thermodynamic properties of minerals and related substances at 298.15 K and 1 bar (10^5 pascals) pressure and at higher temperatures (revised). United States Geological Survey Bulletin 1452, 1–456.

Treiman, A.H., and Essene, E.J. (1984) A periclase-dolomite-calcite carbonatite from the Oka complex, Quebec, and its calculated volatile composition. Contributions to Mineralogy and Petrology, 85, 149–157.

Wyllie, P.J., and Tuttle, O.F. (1960) The system $CaO-CO_2-H_2O$ and the origin of carbonatites. Journal of Petrology, 1, 1–46.

MANUSCRIPT RECEIVED JULY 2, 1991
MANUSCRIPT ACCEPTED JANUARY 9, 1992