

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

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INTRODUCTION

Gittins et al. (1990) offered a critical reappraisal of the importance of F in carbonatite petrogenesis, primarily by attempting to rebut the inference that a unique carbonatite from the Oka complex, Quebec, was in equilibrium with H₂O-rich fluid (Treiman and Essene, 1984). We are pleased that our paper can still generate spirited discussion eight years after publication. However, we do not agree with the criticisms of Gittins et al. and believe that their arguments are flawed.

It was clear from the early part of this century that carbonatite magmas could not exist without some mineralizing fluid because dry calcite and dolomite do not melt at geologically reasonable temperatures. Wyllie and Tuttle (1960) showed that H₂O alone could lower the melting point of calcite to easily attained temperatures. From this and other works by Wyllie and colleagues, it became clear that H₂O alone was sufficient to explain much of the apparent phase equilibria and origins of carbonatite magmas. But it had never been demonstrated that natural carbonatites contained significant H₂O. Thus, it was a significant confirmation of experimental results when we were able to infer that the volatile phase of a natural carbonatite was rich in H₂O (Treiman and Essene, 1984). Our method was thermodynamic calculation based on tabulated values and on electron microprobe analyses of magmatic phases. We assumed that the carbonatite magma was vapor saturated and that we could infer which mineral compositions had been in equilibrium with magma and vapor. Upon calculation, the pressures of CO₂, O₂, CO, S₂, etc., summed to a tenth of the inferred load pressure, so we further assumed that H₂O was an essential constituent of that fluid. We were then able to calculate fugacities and partial pressures of H- and F-bearing species, and thus of all gas species in the system C-O-H-S-F. We concluded that this particular carbonatite equilibrated with H₂O-rich vapor, which contained very little HF or F₂. If the carbonatite crystallized without a free vapor phase, the calculated fugacities and pressures of all H-bearing species would be upper limits. Thus a decrease in $P_{\text{H}_2\text{O}}$ would also diminish P_{HF} . Our result for this carbonatite, the Husereau dike, is not necessarily relevant to

other carbonatites because the Husereau carbonatite is unlike any other in the world.

Our comments on the paper by Gittins et al. (1990) are of three types: general remarks on their assumptions; further constraints on the abundance of F in the vapor phase of the Husereau carbonatite; and comments on the consistency of experimental results.

GENERAL COMMENTS

Is it a dike?

Gittins et al. suggest that the Husereau body may not be a dike, as we originally inferred from field observations. The actual form of the body is irrelevant to the inferences of Treiman and Essene (1984); we merely needed to establish that the body is magmatic. Gittins et al. apparently agree that it is.

Is it a eutectic mineral assemblage?

The conclusions of Treiman and Essene (1984) depend on the inference that the carbonatite magma and its vapor were in equilibrium with seven minerals in the rock: calcite, dolomite, periclase, apatite, forsterite, magnesioferrite, and pyrrhotite. By analogy with the experimental results of Fanelli et al. (1981), expanded on by Wyllie (1989), we inferred that this assemblage represented a eutectic. On textural grounds, we also inferred that alabandite was a eutectic mineral, although it did not enter into our calculations.

Gittins et al. (1990) assert that a eutectic with so many solid phases is unlikely. But this putative eutectic is entirely consistent with the phase rule. Ignoring for the moment the accessory phases, the Husereau body is well represented by the system CaO-MgO-SiO₂-CO₂-H₂O and the phases calcite + dolomite + periclase + forsterite + liquid. In terms of this system, there is 1 degree of thermochemical freedom; if a vapor phase were present, the system would be invariant, just as a eutectic should be. The full mineral assemblage includes ten phases (eight solids plus melt and vapor), which represent 11 components (Ca, Mg, Fe, Mn, Si, P, C, H, O, S, and F). The degrees of freedom are thus 2, and the phase rule has not been violated.

Whether or not the full assemblage represents a eutectic is completely irrelevant to the calculations. It is merely necessary to infer that these solid phases equilibrated last

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at the solidus, estimated by Treiman and Essene (1984) to be 640 °C and 1 kbar. This is eminently reasonable, as no reaction textures were observed, and because equilibrium should be rapidly attained down to the solidus because of the high fluidity (Treiman and Schedl, 1983) and reactivity of carbonatitic magma.

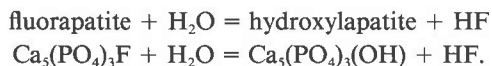
Abundance of magmatic periclase

Gittins et al. assert that if the Husereau carbonatite had been rich in H₂O, all magmatic periclase would have been converted to brucite during subsolidus cooling. In fact, we did ascribe the brucite present to just such conversion. However, the inferred solidus temperature, 640 °C, is well above the dehydration temperature for brucite (Wyllie and Tuttle, 1960; Treiman and Essene, 1984, Fig. 3). Most of the H₂O 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.

CONSTRAINTS ON F ABUNDANCE

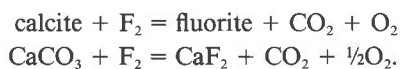
Gittins et al. (1990) suggested that F may have been important in the genesis of the Husereau dike, so it is important to quantify the permissible abundances of F as F₂ and HF in the dike's fluid phase. Two constraints are available: the F and OH contents of the apatite in the Husereau dike and the absence of fluorite from the dike.

In Treiman and Essene (1984), the fugacities of F-bearing gas species were calculated from the inferred $f_{\text{H}_2\text{O}}$ and the composition of apatite. To look at that calculation another way, the composition of the Husereau dike apatite monitors the ratio $f_{\text{H}_2\text{O}}/f_{\text{HF}}$ by the exchange reaction



At 640 °C and 1 kbar the apatite composition implies that the f_{HF} was approximately $10^{-5.6}$ times the $f_{\text{H}_2\text{O}}$. Reducing the $f_{\text{H}_2\text{O}}$ reduces the f_{HF} . Following the calculations of Treiman and Essene (1984), the f_{F_2} must be equal to or less than approximately $10^{-43.5}$ bars. Clearly, this is not very much F.

The f_{F_2} in carbonatites is restricted in the presence of calcite alone by the following reaction, in which calcite is consumed to form fluorite:



If the f_{F_2} were higher than that buffered by this reaction, no solid calcite could form, and the resultant rock could hardly be called a carbonatite. If f_{O_2} is constant, the ratio $f_{\text{CO}_2}/f_{\text{F}_2}$ must be constant in rocks with calcite and fluorite. From thermochemical data of Robie et al. (1979), this fugacity ratio is approximately 10^{38} for 640 °C at 1 kbar and at an f_{O_2} at QFM. So in a dry carbonatite with fluorite and calcite at 1-kbar fluid pressure, f_{F_2} is approximately 10^{-35} bars. This value is approximately 10^9 greater than that calculated from the composition of the Husereau apatite (above, and Treiman and Essene, 1984)

and is consistent with the lack of fluorite in the Husereau dike.

We note that a low abundance of F in a carbonatite's fluid phase does not necessarily imply that the carbonatite magma itself is poor in F. Na-bearing carbonatite magma in equilibrium with calcite and fluorite may contain approximately 10 wt% F (Jago and Gittins, 1991), while still being in equilibrium with a vapor of $f_{\text{F}_2} =$ approximately 10^{-35} bars (see above). Thus, it is very important to distinguish between F abundances in the vapor phase and in the melt phase. For the Husereau dike, the calculated f_{F_2} is orders of magnitude below that of fluorite saturation, suggesting that the magma also had F abundances orders of magnitude below that of fluorite saturation.

CRITIQUE OF EXPERIMENTS

The case Gittins et al. (1990) make for the importance of F in carbonatite petrogenesis rests heavily on their experimental data, particularly the rock + water experiments of their Table 1. Their experimental results are interpreted to show that H₂O alone cannot induce melting of the Husereau dike rock at geologically reasonable temperatures. However, their results are inconsistent with a large literature on carbonate + H₂O phase equilibria.

Gittins et al. find no firm evidence for melting of Husereau dike rock with 7–20 wt% added H₂O at 1 kbar of pressure and temperatures up to 932 °C. These results are inconsistent with other experimental studies on the melting of carbonate + H₂O. Specifically, the assemblage dolomite + calcite + periclase + H₂O (a subset of the Husereau dike assemblage) melts at a eutectic at 650 °C, 2 kbar (Fanelli et al., 1981; Wyllie, 1989). In addition, the experiments of Gittins et al. are inconsistent with the mass of experimental data on carbonate melting, including those of Wyllie and Tuttle (1960): at 1 kbar (the same pressure inferred for the Husereau dike), “. . . addition of H₂O extends the liquidus field for calcite down to about 650 °C . . .” (Wyllie, 1989). This melting temperature is consistent with the results of all subsequent experimental studies of carbonatite petrogenesis (e.g., Gittins and Tuttle, 1964; Wyllie and Raynor, 1965; Wyllie and Boettcher, 1969; Helz and Wyllie, 1979; Boettcher et al., 1980; Jones and Wyllie, 1986).

To be consistent with previous experimental studies, the rock + water experiments of Gittins et al. (1990) ought to have yielded significant quantities of melt. The lack of recognized melt in their experiments is troubling, but there are at present insufficient data to resolve the inconsistency between the results of Gittins et al. (1990) and the extensive literature cited above. We note that no vapor phase was reported in the rock + water experiments, which contained 10–20 wt% H₂; the lack of a vapor phase may provide a clue to the inconsistency among experimental results. The experimental results of Fanelli et al. (1981), expanded on by Wyllie (1989), are still a reasonable basis for inferring that a magma like the

Husereau carbonatite would have been in equilibrium with H₂O-rich fluid near 650 °C and 1 kbar.

CONCLUSIONS

The conclusions of Treiman and Essene (1984) about the vapor phase of the Husereau dike carbonatite are consistent with available data; the criticisms of Gittins et al. (1990) are flawed. The critical issues here are three: there is no basis for inferring that the minerals of the Husereau dike were not in chemical equilibrium with carbonatite magma and vapor (fluid); the composition of the Husereau apatite and the absence of fluorite restrict f_{HF} and f_{F_2} to low levels; and the experiments of Gittins et al. are inconsistent with the extensive literature on carbonatite melting relations. We maintain that the unique magnesian Husereau carbonatite dike was fluxed by H₂O rather than by HF or F₂.

The conclusions of Treiman and Essene (1984) are applicable only to the Husereau dike. The importance of other fluxes, such as NaHCO₃, Na₂CO₃, and NaF, for the much more common sodic carbonatites remains to be evaluated thermodynamically and experimentally. These carbonatites, which contain sodic pyroxenes, sodic melilites, or both (e.g., Treiman and Essene, 1985), may have equilibrated with rather different fluxes than did the Husereau dike. The widespread sodic metasomatism (finitization) associated with most intrusive carbonatites clearly indicates the importance of sodic fluxes. None of these features, however, is associated with the magnesian Husereau dike, and (contrary to Gittins et al., 1990), such occult fluxes should not be postulated for the Husereau dike.

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REFERENCES CITED

- Boettcher, A.L., Robertson, J.K., and Wyllie, P.J. (1980) Studies in synthetic carbonatite systems: Solidus relationships for CaO-MgO-CO₂-H₂O to 40 kbar and CaO-MgO-SiO₂-CO₂-H₂O to 10 kbar. *Journal of Geophysical Research*, 85, 6937–6943.
- Fanelli, M.F., Cava, N., and Wyllie, P.J. (1981) Co-precipitation of calcite and portlandite in CaO-MgO-CO₂-H₂O at 2 kbar illustrates carbonatite petrogenesis. *Eos*, 62, 413.
- Gittins, J., and Tuttle, O.F. (1964) The system CaF₂-Ca(OH)₂-CaCO₃. *American Journal of Science*, 262, 66–75.
- 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.
- Helz, G.R., and Wyllie, P.J. (1979) Liquidus relationships in the system CaCO₃-Ca(OH)₂-CaS and the solubility of sulfur in carbonatite magmas. *Geochimica et Cosmochimica Acta*, 43, 259–265.
- Jago, B.C., and Gittins, J. (1991) The role of fluorine in carbonatite magma evolution. *Nature*, 349, 56–58.
- Jones, A.P., and Wyllie, P.J. (1986) Solubility of rare earth elements in carbonatite magmas, as indicated by the liquidus surface in CaCO₃-Ca(OH)₂-La(OH)₃. *Applied Geochemistry*, 1, 95–102.
- 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 (10⁵ Pascals) pressure and at higher temperatures (revised). *U.S. 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.
- (1985) The Oka carbonatite complex, Quebec: Geology and evidence for silicate-carbonate liquid immiscibility. *American Mineralogist*, 70, 1101–1113.
- Treiman, A.H., and Schedl, A. (1983) Properties of carbonatite magma and processes in carbonatite magma chambers. *Journal of Geology*, 91, 437–447.
- Wyllie, P.J. (1989) Origin of carbonatites: Evidence from phase equilibrium studies. In K. Bell, Ed., *Carbonatites: Genesis and evolution*, p. 500–545. Unwin-Hyman, London.
- Wyllie, P.J., and Boettcher, A.L. (1969) Liquidus phase relationships in the system CaO-CO₂-H₂O to 40 kilobars pressure with petrologic applications. *American Journal of Science*, 267-A, 489–508.
- Wyllie, P.J., and Raynor, E.J. (1965) D.T.A. and quenching methods in the system CaO-CO₂-H₂O. *American Mineralogist*, 50, 2077–2082.
- Wyllie, P.J., and Tuttle, O.F. (1960) The system CaO-CO₂-H₂O and the origin of carbonatites. *Journal of Petrology*, 1, 1–46.

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