

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

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### ABSTRACT

Uncertainty exists about the composition of fluids in equilibrium with carbonatite magma. Such fluids will reflect both the identity of components that are responsible for maintaining carbonates in a liquid state at petrologically reasonable temperature and pressure and the composition of metasomatizing fluids that separate from carbonatite magmas to fenitize the surrounding country rocks. In much of the literature on carbonatite H<sub>2</sub>O has come to be accepted as the most likely principal constituent, a view that derives from studies of synthetic carbonate systems. Further support was offered in a study of a carbonatite specimen from Oka, Quebec, by Treiman and Essene (1984), who calculated the composition of the fluid assumed to have been in equilibrium with the magma from which this rock crystallized and deduced it to be "a water-rich H<sub>2</sub>O-CO<sub>2</sub> fluid with  $X(\text{H}_2\text{O}) + X(\text{CO}_2) > 0.99$  and  $X(\text{CO}_2)$  near 0.1." Central to their argument is the concept that the rock represents a eutectic assemblage. We argue that this interpretation is untenable and that if the rock were a eutectic assemblage with H<sub>2</sub>O as the principal fluid, it ought to melt with an excess of H<sub>2</sub>O at an acceptable temperature and over a very small temperature range. We were unable to melt the rock dry or with excess H<sub>2</sub>O up to 930 °C. In a test of the possible role of other likely constituents of a carbonatite fluid phase, we determined the melting characteristics of the rock in the presence of Na<sub>2</sub>CO<sub>3</sub> and F, separately and in combination, but without H<sub>2</sub>O. The rock melts to varying degrees between 750 °C and 915 °C with up to 90% melting at the higher temperature and is not, therefore, a eutectic mineral assemblage. Consequently, a fluid composition cannot be calculated by assuming that it is. The experiments establish that H<sub>2</sub>O alone was not the principal fluid phase in equilibrium with the magma from which the dike crystallized. They do not prove that alkalis and F are the dominant constituents of the fluid or that H<sub>2</sub>O is not present but do offer confirmation of the effect of these components. Furthermore, carbonatite mineral and rock chemistry offer abundant evidence of the importance of alkalis and F in carbonatite magmas. Hence, it is highly likely that both will find their way into a fluid phase that separates from a carbonatite magma and is in equilibrium with it. We caution that the role of H<sub>2</sub>O in carbonatite magma evolution has probably been exaggerated.

### INTRODUCTION

Carbonatite studies contain much speculation about the nature and composition of any fluid phase that might accompany carbonatite magma. Suggestions of excess CO<sub>2</sub> were implicit in Eckermann's classic account of Alnö (1948). Wyllie (1966) introduced the concept of a CO<sub>2</sub>-H<sub>2</sub>O fluid, referred to as a "carbothermal solution," and considered that a carbonatite magma might exhibit a continuous transition into such a solution. Others have considered the compositions of fluids that might be responsible for fenitization (McKie, 1966; Verwoerd, 1967; LeBas, 1977; Woolley, 1982). These discussions introduce a secondary concept in that the fluid acting upon the rocks surrounding a carbonatite intrusion may, and probably does, undergo considerable chemical changes as the metasomatic processes evolve and the fluid progresses farther from its parental magma. Therefore, fenitiza-

tion bears only indirectly on the composition of fluid that might be in equilibrium with carbonatite magma during crystallization.

An H<sub>2</sub>O-rich fluid has dominated these discussions as a result of experimental studies by Wyllie and Tuttle (1960), followed by Wyllie (1966) and Watkinson and Wyllie (1971), which demonstrated the effect of H<sub>2</sub>O in lowering the liquidus of calcite-bearing systems to petrologically reasonable temperatures and pressures. However, this does not necessarily mean that it is the component most commonly present in naturally occurring carbonatite magmas.

In 1984 Treiman and Essene published a study of a carbonatite in the Oka complex in which they concluded that the fluid phase accompanying the carbonatite was essentially H<sub>2</sub>O-rich. The approach was a very thorough investigation that involved chemical analysis of the con-

stituent minerals, deductions based on petrographic study, and a thermodynamic analysis of the mineral assemblage.

Because we doubted the validity of the deductions, we tested experimentally whether the fluid is essentially H<sub>2</sub>O and concluded that it is not. We first of all offer a critique of the Treiman and Essene (1984) study.

### CRITIQUE

The rock on which this study is based occurs as "a possible dike" on Husereau Hill in the Oka carbonatite complex. It contains the assemblage calcite + dolomite + periclase + apatite + forsterite + pyrrhotite + magnesioferrite + alabandite, and the authors present chemical analyses of the major mineral phases. The assemblage "is interpreted as a eutectic assemblage based on analogy with the experiments of Fanelli et al. (1981) and absence of reaction textures." They use the compositions of coexisting calcite and dolomite and a series of compensating adjustments to refine the crystallization temperature to 640 °C. Load pressure is estimated at 1 kbar from stratigraphic reconstruction, and then a composition is calculated for the vapor phase that would be in equilibrium with the solid phases by making a series of assumptions about the effect of various mineral buffers. It is concluded that "the eutectic vapor phase of the Husereau dike was essentially a water-rich H<sub>2</sub>O-CO<sub>2</sub> fluid with  $X(\text{H}_2\text{O}) + X(\text{CO}_2) > 0.99$  and  $X(\text{CO}_2)$  near 0.1. Methane, carbon monoxide and hydrogen had low but significant partial pressures, and partial pressures of the other gas species were negligible." It is an approach that deserves examination in greater detail.

One cannot say with any certainty that the rock is a dike; there is no outcrop, and so the implied intrusive relationship cannot be established. Angular fragments of the rock form a roughly linear pattern in a ploughed field, but the nearest outcrops are a considerable distance away.

The description states (p. 149) that the rock is fine-grained, holocrystalline, and "traversed by anastomosing gray zones of alteration" and that along these zones the periclase is completely replaced by brucite. Our own observation is that the rock has a strongly developed planar fissility along which it breaks into flat slabs. Rather than being anastomosing these gray zones are subparallel; it is along them that the rock is most altered and the calcite at least partly recrystallized. Elsewhere periclase is fresh with very little brucite. We conclude, therefore, that hydration to brucite is a localized and secondary phenomenon. In contrast, the authors refer to the "ubiquitous alteration of periclase to brucite" (p. 151), and so conclude that "it seems reasonable that the dike was saturated with a water-bearing fluid." It is upon this assumption of the rock being saturated with H<sub>2</sub>O at the time of final crystallization that an estimation of the composition of the fluid phase is largely based, and the authors "have calculated  $P_{(\text{H}_2\text{O})}$  as the difference between load pressure and the sum of the pressures of the other gases in C-O-H-S-F," each of which is separately estimated. Our con-

cern with this approach is that the solution may follow from the assumptions.

The amount of periclase in the rock is important. If the magma had been H<sub>2</sub>O-saturated at the time of crystallization, periclase would have hydrated to brucite during subsolidus cooling. That it did not weigh heavily against there having been any significant amount of H<sub>2</sub>O present.

The evidence presented for the mineral assemblage constituting a eutectic is not strong. It consists largely of an assertion that three of the minerals are analogous to a eutectic found experimentally by Fanelli et al. (1981), and to "the absence of reaction textures." It is weakened further by the large number of solid phases (eight) presumed to have crystallized at the eutectic. A eutectic with eight solid phases seems unlikely even in a carbonatite magma. It is more likely that the assemblage is the result of the sequential crystallization of a series of minerals.

Even more pertinent in assessing whether the rock is a eutectic assemblage is its melting characteristics. If the rock is indeed a eutectic mineral assemblage, it ought to be possible to melt it at a single temperature that is within the range considered petrologically reasonable for carbonatites. Even if the assemblage is a eutectic, but not in the appropriate proportions (i.e., the rock contains one or two minerals that were crystallizing before the eutectic temperature was reached), it should still be possible at a single temperature to produce largely melt with only one or two minerals remaining unmelted. Furthermore, since Treiman and Essene assert that the fluid was essentially H<sub>2</sub>O it is reasonable to attempt to melt it under an excess of H<sub>2</sub>O.

All attempts to melt the rock dry or water-saturated failed. Melting was achieved only by adding other components that might originally have been present in the magma from which the rock crystallized. These results eliminate the possibility of the rock being a eutectic mineral assemblage and are described below.

### EXPERIMENTAL STUDY

The study employed standard cold-seal pressure vessels and hydrothermal experimental techniques. All experiments were conducted using Au tubes of 3-mm diameter, previously degreased with alcohol, cleaned with hydrochloric acid, and annealed. Chromel-alumel thermocouples were regularly standardized and temperature measurements are accurate to within  $\pm 3$  °C with a precision of 0.5 °C. The design of the pressure vessels permits insertion of a thermocouple through the pressure line so that it is adjacent to and touching the Au tube during the experiment, thereby achieving a more accurate temperature measurement than is obtained in the older design. All experiments were brought to temperature at a constant pressure of 1 kbar and, at the end of the experiment, quenched with an air and H<sub>2</sub>O jet to a subsolidus temperature in less than 30 s.

Rock powder was prepared from coarsely crushed rock after rejecting any with surficial alteration, and crushing

TABLE 1. Results of experiments

T (°C)	Dura- tion	Wt% H <sub>2</sub> O	Experimental products
<b>Rock with no additional components</b>			
600	80 min	0	unrecrystallized
700	80 min	0	unrecrystallized
750	80 min	0	unrecrystallized
802	65 min	0	unrecrystallized
852	70 min	0	unrecrystallized
910	20 min	0	unrecrystallized
<b>Rock plus approx. 10 wt% H<sub>2</sub>O</b>			
648	26.0 h	6.9	poorly recrystallized
700	26.7 h	9.8	poorly recrystallized
749	26.5 h	9.7	poorly recrystallized
802	26.6 h	9.6	poorly recrystallized
875	26.5 h	10.5	well recrystallized: cc + per + ap + mf + Q(tr?)
906	2.1 h	9.4	well recrystallized: cc + per + ap + mf + Q(tr?)
932	2.2 h	9.4	well recrystallized: cc + per + ap + mf + Q(tr?)
<b>Rock plus approx. 20 wt% H<sub>2</sub>O</b>			
700	24.2 h	18.6	poorly recrystallized: cc + dmt + per + ap + mf
749	24.1 h	18.4	weakly recrystallized: cc + dmt + per + ap + mf
804	24.3 h	17.7	well recrystallized: cc + dmt + per + ap + mf + Q(tr?)
876	24.7 h	19.8	well recrystallized: cc + per + ap + mf + Q(tr?)
906	0.5 h	20.1	well recrystallized: cc + per + ap + mf + Q(tr?)
932	0.5 h	16.9	well recrystallized: cc + per + ap + mf + Q(tr?)
<b>Rock plus 10 wt% Na<sub>2</sub>CO<sub>3</sub></b>			
751	3.0 h	10.0	cc + per + ap + mf + Q(tr)
800	75.0 h	10.0	cc + per + ap + mf + Q(~5%)
850	0.5 h	10.0	cc + per + ap + mf + Q(~10%)
901	0.5 h	10.0	cc + per + (ap) + mf + Q(~85%)
<b>Rock plus 20 wt% Na<sub>2</sub>CO<sub>3</sub></b>			
774	20.0 h	20.0	cc + mf + mt + (ap) + Q(~50%)
799	3.0 h	20.0	cc + mf + mt + (ap) + per + Q(~75%)
854	0.5 h	20.0	mt + (mf + ap) + per + Q(~90%)
899	0.5 h	20.0	mt + (mf + ap) + Q(>90%)
<b>Rock plus approx. 3 wt% F</b>			
602	20.1 h	3.5	poorly recrystallized: cc + per + ap + mf + cf + v
700	19.9 h	3.2	poorly recrystallized: cc + per + ap + mf + cf + v
754	25.8 h	2.7	cc + per + ap + mf + v + Q(tr)
799	20.0 h	2.9	cc + per + ap + mf + v + Q(~15%)
915	20 min	3.1	cc + per + mf + ap + v + Q(~75%)
<b>Rock plus approx. 5 wt% F</b>			
602	19.9 h	5.9	poorly recrystallized: cc + per + ap + mf + cf + v
701	3.1 h	5.4	cc + per + ap + mf + v + Q(tr)
799	19.8 h	4.3	cc + per + (ap) + mf + v + Q(~60%)
915	20 min	5.0	cc + per + (ap) + mf + v + Q(~80%)
<b>Rock plus 10 wt% Na<sub>2</sub>CO<sub>3</sub> and approx. 3 wt% F</b>			
798	23.5 h	2.8	cc + mf + mt + per + ap + v + Q(~50%)
850	23.5 h	3.2	cc + mf + mt + per + (ap) + v + Q(~80%)

Note: ap = apatite, cc = calcite, cf = fluorite, dmt = dolomite, mf = magnesioferrite, mt = magnetite, per = periclase, Q = quenched liquid, Q(tr) = trace of quenched liquid, Q(tr?) = possible but unlikely that a trace of quenched liquid is present, v = vapor (represented by bubbles), h = hours, min = minutes.

Five groups of the experiments were carried out in which attempts were made to melt the rock powder dry, oversaturated with H<sub>2</sub>O, dry with F, dry with Na<sub>2</sub>CO<sub>3</sub>, and dry with both Na<sub>2</sub>CO<sub>3</sub> and F. Critical experimental data are in Table 1.

### Dry experiments

It was not possible to melt the rock dry at any temperature up to 900 °C with durations of 20 min to 80 min. Because of the stress imposed on pressure vessels at 900 °C, it is not practical to exceed 20 min, but it is the common experience of petrologists working with carbonate systems that melting always occurs within this time period. We are, therefore, confident that equilibrium was achieved, but we recognize that the absence of reaction does not prove the stability of the solid assemblage.

### Water-saturated experiments

With 10 wt% and 20 wt% H<sub>2</sub>O no melting at all occurs up to 800 °C. A mere trace of brown discoloration occurs at 875, 905, and 930 °C, but we do doubt that it is quench because the amount remains constant from 875 to 930 °C; such a result would be most unusual if melting had begun. We conclude, therefore, that no melting occurs up to 930 °C. Furthermore, dolomite has dissociated to periclase + calcite + CO<sub>2</sub> in the three higher temperature experiments. Because the rock contains abundant dolomite that crystallized from a magma, it follows that the magma temperature must have been less than that of the dissociation temperature of dolomite during crystallization, either 835 °C (Harker and Tuttle, 1955) or 805 °C (Beckett, 1987). It is possible that the rock might melt at a temperature above 930 °C, but that would be very high for a subvolcanic dike and almost 300 °C above the temperature estimated by Treiman and Essene (1984). It would also be at least 100 °C too high for dolomite to crystallize.

The conclusion seems inescapable that some other component of the magma, no longer present, must have reduced the magma temperature to a more realistic value. In view of the importance that has regularly been attached to alkalis in discussions of carbonatite magma evolution, and in particular the importance that we now attach to F (Twyman and Gittins, 1987; Gittins, 1989) we examined the effect of both on the rock from Huse-reau.

### Experiments with Na<sub>2</sub>CO<sub>3</sub> but no H<sub>2</sub>O

Samples composed of rock plus 10 wt% Na<sub>2</sub>CO<sub>3</sub> were held at four temperatures between 750 °C and 900 °C. They showed a progressive increase in degree of melting from a trace to at least 80%. Samples composed of rock plus 20 wt% Na<sub>2</sub>CO<sub>3</sub> held at temperatures between 775 °C and 900 °C showed from 50% to greater than 90% melting. The amounts of Na<sub>2</sub>CO<sub>3</sub> used are large, but they do demonstrate the capability of alkalis to induce considerable melting.

the remainder to a mean grain size of -200 mesh in a mechanical shaker mill. The resulting powder was stored in glass at 110 °C. H<sub>2</sub>O was distilled and deionized, F was added by the use of AgF as described by Jago and Gittins (1989), and Na<sub>2</sub>CO<sub>3</sub> used was Baker Analyzed.

### Experiments with F but no H<sub>2</sub>O

Samples composed of rock powder plus approximately 3 wt% F showed a trace of melting at 755 °C and about 75% melting at 915 °C. With approximately 5 wt% F, there was a trace of melting at 700 °C and 75–80% melting at 915 °C. F is not only enormously effective in inducing melting in carbonate compositions, but it is also vastly more effective than H<sub>2</sub>O.

### Experiments with F and Na<sub>2</sub>CO<sub>3</sub> but no H<sub>2</sub>O

A sample consisting of rock powder with 10 wt% Na<sub>2</sub>CO<sub>3</sub> and approximately 3 wt% F was held at 800 °C and 850 °C. At the lower temperature it was approximately 50% melted and at the higher temperature about 80% melted.

## DISCUSSION

H<sub>2</sub>O alone does not induce melting at a temperature permissible by any reasonable geological constraints. The components Na<sub>2</sub>CO<sub>3</sub> or F, which can be expected in most carbonatite magmas, do cause the rock to melt at acceptable magmatic temperatures but not at a single temperature, or even over a very narrow temperature interval, as is required of a eutectic mineral assemblage. The rock is not, therefore, a eutectic assemblage, and a fluid composition cannot be calculated from it by assuming that it is. There is now general acceptance, summarized by Gittins (1989), that carbonatite magmas have lost components during crystallization. Hence, the fluid in equilibrium with the magma from which the Oka rock crystallized probably did not have "X(H<sub>2</sub>O) + X(CO<sub>2</sub>) > 0.99 and X(CO<sub>2</sub>) near 0.1," as asserted by Treiman and Essene (1984).

Our intention is not to maintain that alkalis and F necessarily were responsible for the once magmatic state of the Oka rock but merely to suggest the possibility. It is, of course, possible that an aqueous fluid containing small amounts of F and alkalis could have separated from the carbonatite magma; a logical extension of these experiments would be to test the combined effect of H<sub>2</sub>O, F, and Na<sub>2</sub>CO<sub>3</sub>, but this is a technique that we have not developed to an adequate degree of confidence, and therefore the possibility cannot yet be tested.

We caution against assuming that fluids in equilibrium with carbonatite magmas are primarily H<sub>2</sub>O and, hence, that H<sub>2</sub>O plays the dominant role in carbonatite magma evolution. Studies in progress at the University of Toronto (Jago, 1990), and partly reported here, show that F lowers the liquidus of carbonate systems even more dramatically than does H<sub>2</sub>O. F is, of course, very abundant in the alkalic carbonatite lava of Oldoinyo Lengai volcano in Tanzania (at least 8% F and 4.5% Cl; Gittins and McKie, 1980; Jago, 1990). Further support for the importance of F in carbonatite magmas is to be found in the high F content of most carbonatite micas, amphi-

boles, and pyrochlore. A fluid composed almost entirely of water is far too simple.

## ACKNOWLEDGMENTS

The carbonatite research of J.G. has been supported by the Ministry of Energy Mines and Resources (Geological Survey of Canada); by the Natural Sciences and Engineering Research Council of Canada; its support has varied widely, and his gratitude is in proportion to these variations. Both M.B. and B.C.J. are grateful to the NSERC and the University of Toronto for scholarship support. J.G. wishes to express his appreciation to the Warden and Fellows of Robinson College, University of Cambridge, for the tenure of a Bye-Fellowship in 1989–90, and to Professor I.N. McCave of the Department of Earth Sciences, University of Cambridge, for sabbatical leave facilities.

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MANUSCRIPT RECEIVED NOVEMBER 14, 1989

MANUSCRIPT ACCEPTED JUNE 13, 1990