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Oxygen Fugacity Geothermometry of the Oka Carbonatite

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Abstract

In order to learn more about the petrogenesis of the carbonatite at Oka, Quebec, a solid electrolyte oxygen fugacity sensor was used to study coexisting olivine (Fo_{80}), magnetite, and niobian perovskite (latrappite). Plots of fO_2-T data obtained for each of these three minerals show a triple intersection at 710° ± 15°C and an fO_2 of $10^{-17.1 \pm 0.5}$ atm. The hypothesis is that this temperature and fO_2 represents the last solid-liquid-vapor equilibration among these three minerals. The temperature is in agreement with O^{18}/O^{16} work (Conway and Taylor, 1969), and the fO_2 value is consistent with standard solid and gaseous fO_2 buffer curves. Wyllie and Tuttle (1960) found the presence of a liquid phase at similar low temperatures throughout a wide range of synthetic carbonate systems at various total pressures. The temperature measured by this technique when compared with synthetic phase equilibria work supports a magmatic origin for the Oka carbonatite.

Introduction

The origin of carbonatites has long been a subject of controversy among petrologists, and it is hoped that a knowledge of the temperature of formation of one of these rock bodies may provide some insight into their petrogenesis. Work on synthetic systems has produced carbonate liquids over a wide range of temperatures, extending at least as low as 450°C (Gittens, 1963). It is, therefore, the purpose of this paper to attempt to determine the petrogenetic temperature of a lower Cretaceous carbonatite at Oka, Quebec, by measuring the oxygen fugacity *vs* temperature relationships of several minerals. The detailed regional mapping, petrography, and petrogenesis of the Oka area have been worked out from field evidence by Gold (1966), and Gold, Vallee, and Perrault (1967) who believe this carbonatite to be truly magmatic in origin. Minimum liquidus temperatures for simplified synthetic carbonatites like those reported by Wyllie (1966) can be compared with the temperature obtained in this current study to test the validity of a magmatic origin for the carbonatite core of the Oka complex.

Experimental Technique

This technique involves measuring the intrinsic oxygen fugacity (Sato, 1972) of several Oka minerals as a function of temperature. The intersection of these fO_2-T plots, at least theoretically, defines the temperature at which oxygen equilibration was last possible. The fO_2 was measured by means of a solid electrolyte fugacity sensor of the type discussed by Sato (1971). In this experiment zirconia (ZrO_2) stabilized with yttria (Y_2O_3) was used as the electrolyte in a double cell arrangement designed by Sato and utilized by Flynn (1972). The sample and cell were heated in a Pt20Rh resistance winding furnace with air used as the fugacity reference and a mixture of carbon dioxide and hydrogen as the furnace atmosphere. The furnace fO_2 was kept as near as possible to the fO_2 of the unknown sample by a servo-controlled hydrogen valve which has been described by Sato (1971).

The fO_2 as a function of temperature can be calculated from the relationship:

$$E = 0.04960T \log (fO_2 \text{ unknown}/fO_2 \text{ reference})$$

where E is in millivolts and T is in °K. Both E and T can be measured and the fO_2 of the reference is known. When air (21 percent oxygen) is used as a reference gas, a correction must be made for its e.m.f versus pure oxygen ($fO_2 = 1$) as follows:

$$\begin{aligned} E\,(\text{air : oxygen}) &= 0.04960T \log 0.21 \\ &= -0.0337T \end{aligned}$$

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A second correction, for the thermocouple effect caused by use of electrode and conducting wire and a silver-palladium inner electrode and conducting wire, is as follows (Sato, 1971):

$$E(Ag_{60}Pd_{40} - Pt) = -0.125 + 0.0108(t - 25) + 1.33 \times 10^{5}(t - 25)^{2}$$

where t is in degrees centigrade and E is in millivolts. While fugacity and partial pressure are very nearly the same at low pressures, it is actually the thermodynamic quantity, fugacity, that this technique measures.

Sample Preparation

The fO_2-T runs were made for three Oka minerals: magnetite, olivine (about Fo_{80}), and latrappite (a high niobium perovskite) (Nickel, 1964). The magnetite and latrappite were leached with 0.3N HCl and the olivine with glacial acetic acid to remove calcite. Each was then ground to about 100 microns and separated with a Frantz magnetic separator; a check of each sample under the petrographic microscope revealed no visible impurities. Latrappite was studied quantitatively with the electron microprobe at the Geophysical Laboratory of the Carnegie Institute of Washington utilizing the computer-interlock technique of Finger and Hadidiacos (1971). The latrappite crystals used were found to be homogeneous and contained 46 percent by weight Nb_2O_5. All of the material for these runs came from the D-pit (Bond zone) at Oka (Gold, Vallee, and Perrault, 1967).

Sample Description

The rock samples were a white to gray calcite-rich carbonatite of uniform texture. The three separated minerals were evenly dispersed throughout the calcite. Recovery of the minerals indicated that the amount of magnetite ≅ latrappite > olivine and that the total percentage of the three accessory minerals was always less than 5 wt percent of the total rock. The magnetite and latrappite were present as euhedral black crystals of an average size of 1 to 2 mm. The olivine was present as anhedral brown patches of about the same size.

Results

E.m.f. determinations were made from 600°–1000°C with equilibrium data obtained at each 50° increment. Each run was reproduced in both the up- and the down-temperature directions. The resultant fO_2-T curves (Fig. 1) are the least-squares-fit of the data points and show a triangle of uncertainty in the intersection of the three curves. The precision of these curves, which is affected by possible uncertainty in the measurement of temperature, is indicated by the length of the bars perpendicular to the curves, *i.e.,* the fO_2 and T intercepts of these bars give the range of uncertainty. This uncertainty decreases with increasing temperature. The measurement of fO_2 can have human or equilibration errors, but the precision of the electrometers is better than 1 mv, which corresponds to log fO_2 of about 0.01. The center of the triangle of intersection is 710°C and at an fO_2 of $10^{-17.1}$ atm, and it spans a temperature range of ±15°C and a log fO_2 range of ±0.5. This inter-

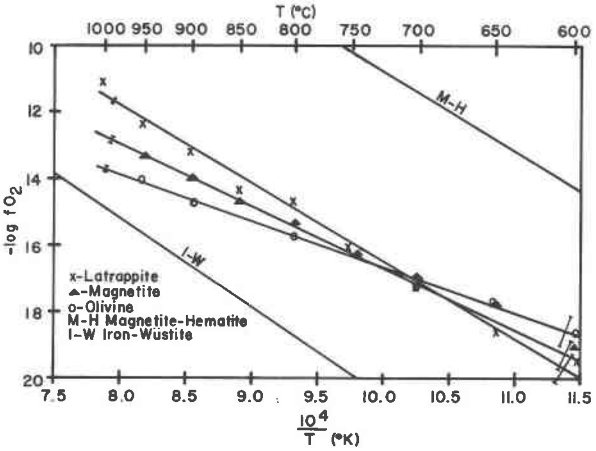

FIG. 1. Intrinsic oxygen fugacity *vs* temperature data for coexisitng latrappite, magnetite, and olivine from the Oka Carbonatite. Standard buffer curves (M-H, magnetite-hematite; and I-W, iron-wüstite) from Eugster and Wones (1962) are plotted for comparison.

TABLE 1. Experimental emf Data Recalculated as fO_2 Values in the Oka Minerals*

Temperature (°C)	-Log fO_2 Latrappite	Magnetite	Olivine
600 ± 12	19.5	--	18.5
650 ± 12	18.5	17.3	17.7
700 ± 12	17.2	17.0	17.2
750 ± 10	16.00	--	--
800 ± 8	14.6	15.3	15.7
850 ± 5	14.3	14.6	--
900 ± 5	13.1	14.0	14.6
950 ± 3	12.3	13.3	14.0
1000 ± 3	11.1	--	--

**All minerals from D-Pit at Oka.*

section theoretically can be interpreted as the fO_2-T conditions of last equilibration of these three minerals, each with each other.

Interpretation

The interpretation of the triple intersection in Figure 1 as the last equilibration for Oka needs to be examined in the light of work done by other authors by independent means. In the following paragraphs, available literature is reviewed to discuss whether the equilibration determined is a liquid-solid, a solid-vapor, or even a solid-liquid-vapor assemblage.

Comparison of the magnetite stability shown in Figure 1 to the various published versions of the iron-oxygen diagrams shows that the measured Oka magnetite curve will actually intersect the wüstite field of stability above 950°C. The authors interpret this to mean that, for the main Oka carbonatite, temperatures much greater than 950°C were never encountered in the crystallization of the magnetite.

A minimum for the fO_2-T conditions at Oka, where no graphite has been reported, would be the curve for the buffer: G(graphite)-CO_2-CO-O_2, or the buffer: QFM-OH-(GX-COH), *i.e.,* quartz, fayalite, magnetite, and water in an outer capsule with graphite, unknown, and a C-H-O source in the inner capsule as discussed by Skippen (1971). Plots of these buffers at various pressures can be found in Figure 2. The buffer G-CO_2-CO-O_2 is plotted at 1 atm and 10 kbar (French and Eugster, 1965), and the buffer QFM-OH-(GX-COH) is plotted at 500 bars and 2 kbar (Skippen, 1971). This figure also shows that the data from this study of Oka are above the wüstite-magnetite (WM) buffer and below the hematite-magnetite (HM) buffer (Eugster and Wones, 1962). Both the WM and HM buffers are reasonable geologic extremes of fO_2 and of temperature for Oka although these buffers do not fix the conditions very precisely. Even though the Oka olivine is not fayalite but Fo_{80}, the silica activity at Oka is very low; hence, the intersection data for the Oka minerals are very near the quartz-fayalite-magnetite buffer (Wones and Gilbert, 1969).

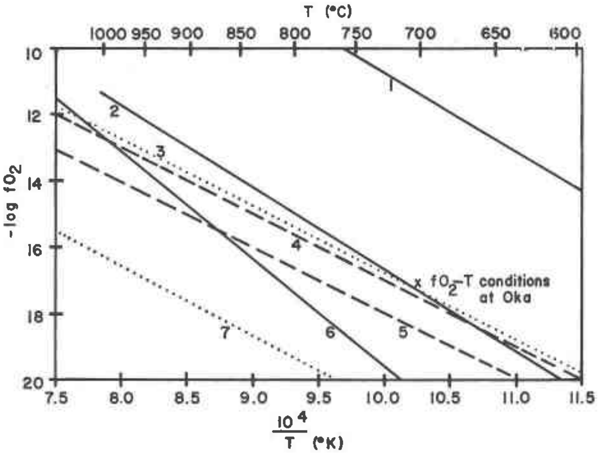

FIG. 2. A comparison of the fO_2-T relations determined for Oka (shown by an "X") with other known petrologic fO_2-T relationships. Plot 1: magnetite-hematite; Plot 6: magnetite-wüstite (Eugster and Wones, 1962); Plot 2: quartz-fayalite-magnetite (Wones and Gilbert, 1969); Plot 3: Graphite-CO_2-CO-O_2 at 10 kbar; and Plot 7: Graphite-CO_2-CO-O_2 at 1 atm (French and Eugster, 1965); Plots 4 and 5 are QFM-OH(GX,COH), as explained in the text, at 2 kbar and 500 bars respectively (Skippen, 1971).

Another line of interpretive evidence regarding the validity of the equilibrium suggested by the intersection in Figure 1 comes from the work of Conway and Taylor (1969) who studied the oxygen and carbon isotope ratios for the mineral pair, calcite-magnetite from Oka. From these isotopic ratios, they calculated temperatures of 720° and 730°C for the last isotopic equilibration within two Oka carbonatite samples. These two temperatures are probably analogous to those determined in this paper; that is, both techniques measure the temperature below which oxygen communication could no longer proceed. It is logical from the magnitude of the temperatures measured that deuteric alteration has not disturbed the record of the last thermal event at Oka.

The temperature measured here can also be compared with minimum liquidus temperatures for synthetic systems such as those studied by Wyllie and Tuttle (1960). The equilibria data for such synthetic phases suggest the presence of a liquid phase at this temperature. For example, in the system CaO-MgO-CO_2-H_2O, Wyllie found that liquids appear between about 650° and 750°C over a wide range of CO_2-H_2O ratios (about 20–80) at 500 bars pressure (Wyllie, 1966). Therefore, a small decrease in temperature in this range would dry up all liquid leaving only solid and vapor phases. Wyllie also shows that this reaction is affected only slightly by changes in total pressure. Furthermore, in the system CaO-CO_2-H_2O, they found that between 27 and 4000 bars the minimum liquidus temperature varies respectively between 685° and

640°C. Other systems investigated by Wyllie (1966) also show low temperature liquids over a wide range of pressures, even in systems containing SiO_2 and Na_2O. To maintain the low liquidus temperatures, the percentage of silica must be low, but this is still reasonable in the Oka complex, an area characterized by silica-undersaturated rocks. While it must be pointed out, as Wyllie (1966) does, that these systems are too simple to be true carbonatite magmas, they do inidcate that low temperature carbonatite liquids are at least possible, and the addition of more components would lower the minimum liquidus temperatures still further. Therefore, the temperature shown in Figure 1 would seem to be compatible with equilibria involving liquids, solids, and vapors.

When considering the value for the fO_2 obtained in this study, the value of $10^{-17.1}$ atm appears reasonable relative to the buffer curves previously discussed, but the fO_2 due to dissociation of CO_2 at this temperature is about 10^{-7} atm. With the preponderance of calcite in the carbonate, the ten-order-of-magnitude discrepancy between these two values must be explained. The most reasonable explanation is that the CO_2 vapor phase at Oka contained hydrogen to make it more reducing. For example, to have an fO_2 of $10^{-17.1}$ atm at 710°, the CO_2 would have to be diluted with only about 1 part by volume H_2 to about 80 parts CO_2 (Muan and Osborn, 1965). If dilution with CH_4 had occurred, the work of French (1966) and Skippen (1971) would then indicate that graphite would have been stable. As indicated earlier in reference to Figure 2, no graphite has yet been reported at Oka.

Summary

The cooling history of the main carbonatite body at Oka can therefore be envisaged as follows: A reactive carbonatite fluid containing solid, liquid, and vapor phases existed at temperatures above 700°C, and as it cooled to a temperature just above 700°, the solidus was reached, the liquid dried up, and therefore fO_2 equilibration could no longer proceed. Total pressure on the magma is unknown, but experimental studies on synthetic systems show that it should not greatly change the temperature measured at one atmosphere total pressure by this technique.

The entire history of Oka is complex, possibly involving multiple magma injection, vapor phase transport, and solid-state replacement. Much of this history has been worked out by Gold, Vallee, and Perrault (1967) from field evidence, and no attempt is made to discuss that work again in this paper. The final cooling history described above applies only to the main carbonatite core of the complex. The temperature of 710°C ±15° and fO_2 of $10^{-17.1\pm0.5}$ atm determined by this technique is corroborated by comparison with synthetic phase equilibrium studies and isotopic O^{18}/O^{16} data. The experimental equilibration data determined in this paper indicate an fO_2-T range comparable to that necessary to produce a liquid phase in synthetic carbonate systems. The measured temperature and the inferred presence of carbonate liquids at Oka therefore support Gold's interpretation of the field evidence, that is, a magmatic origin for the core of the Oka complex.

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