PETROGENETIC TEMPERATURE OF THE OKA CARBONATITE

A Thesis Submitted
to the Temple University Graduate Board

in Partial Fullfiment
of the Requirement for the Degree

MASTER OF ARTS

by

John J. Friel

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Approved : Gene C. Ulmer
Thesis Adviser

August 28, 1972
Date

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Abstract

The Oka complex is a carbonatite and feldspathoidal silicate complex belonging to the alkaline intrusive suite of the Monteregian petrographic province. In order to learn more about the petrogenesis of this carbonatite, a temperature of 710°C was determined from the intersection of the fO_2-T curves for the minerals: olivine, magnetite, latrappite. This is the temperature at which the minerals were last in oxygen equilibrium, and it is believed to be the original solidus.

This temperature is in agreement with O^{18}/O^{16} work (Conway and Taylor, 1969), and it is reasonable in light of Wyllie's work on synthetic systems (1966). Wyllie also found the presence of a liquid phase at these temperatures throughout a wide range of pressures, and therefore, the Oka carbonatite is believed to be of magmatic origin.

The mineralogy and phase equilibria of the mineral, latrappite, are also studied, and some possible explanations for the problems associated with its crystal chemistry are discussed.

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I INTRODUCTION

Carbonatites and the undersaturated-alkalic silicate rocks associated with them have been studied in great detail in the past and have caused serious problems to those desiring to interpret their petrogenesis. Although the total area of exposed carbonatite is probably no more than 0.03% of the area of igneous rocks in the world (Heinrich, 1966), the amount of attention given to them has been much greater. This is probably due to their unique mineralogy plus, of course, the economic deposits often associated with them. In addition, they are commonly associated with kimberlites which has led some investigators to at least consider an origin at great depth (Saether, 1958). Various hypotheses for carbonatite petrogenesis are discussed by Heinrich (1966), and in addition he describes many localities throughout the world.

One of the most informative factors in carbonatite petrogenesis would be a knowledge of the temperature of formation. Since workers in the past have determined temperatures from 450°C to 800°C from work on synthetic systems (Tuttle and Gittens, 1966), it is the purpose of this thesis to gather more information on this subject at least in one location, Oka, Quebec, and perhaps corroborate previous work or at least add another independent value to the list of temperatures already existing.

A. Specific Goals

To determine a temperature of formation for the Oka carbonatite, the mineral latrappite was chosen for study. This is a relatively new mineral, and not much work has been done on it to date (Nickel and McAdam, 1963). Also it appeared to have several problems associated with its stoichiometry, charge balance, and crystal chemistry. It was hoped that an understanding of the latrappite mineralogy would at least point to a direction for further investigation of the more general problem of formation temperature. This mineral is a high niobium perovskite named latrappite by Nickel (1964). It has a pseudo-cubic (orthorhombic?) structure of the ABO_3 type in which the cations in the A sites are in twelve-fold coordination with oxygen, and those in the B sites are in six-fold coordination. Many cations substitute in the structure, and the more common ones are as follows: $(Ca,Mg,Na,Ce)(Nb,Ti,Fe,Mn)O_3$.

It has been assumed that this was a simple solid solution of niobium and titanium; however, titanium is ordinarily found in the four-plus oxidation state while niobium is found in the five-plus oxidation state.

The possibilities to explain this solid solution are as follows: 1) Niobium in this mineral is in the four-plus oxidation state. 2) $Na^{+} + Nb^{5+} = Ca^{2+} + Ti^{4+}$. 3) $Fe^{3+} + Nb^{5+} = 2Ti^{4+}$. 4) $4Nb^{5+} = 5Ti^{4+}$ + defect. 5) The formula should be $CaNb_2O_6$ with a different structure. Whichever of these is actually the case, it should be obvious that there are many problems associated with stuffing niobium into the perovskite structure, and a study of the phase relationships of this mineral could well lead to a knowledge of the temperature of formation.

A paper by Nickel and McAdam, (1963) on the structure of the mineral was studied before determining the best direction for the present investigation. Some of their data are plotted on page 4 and show the relationship of each cell edge of an orthorhombic unit cell to composition. It can be seen that there is an apparant

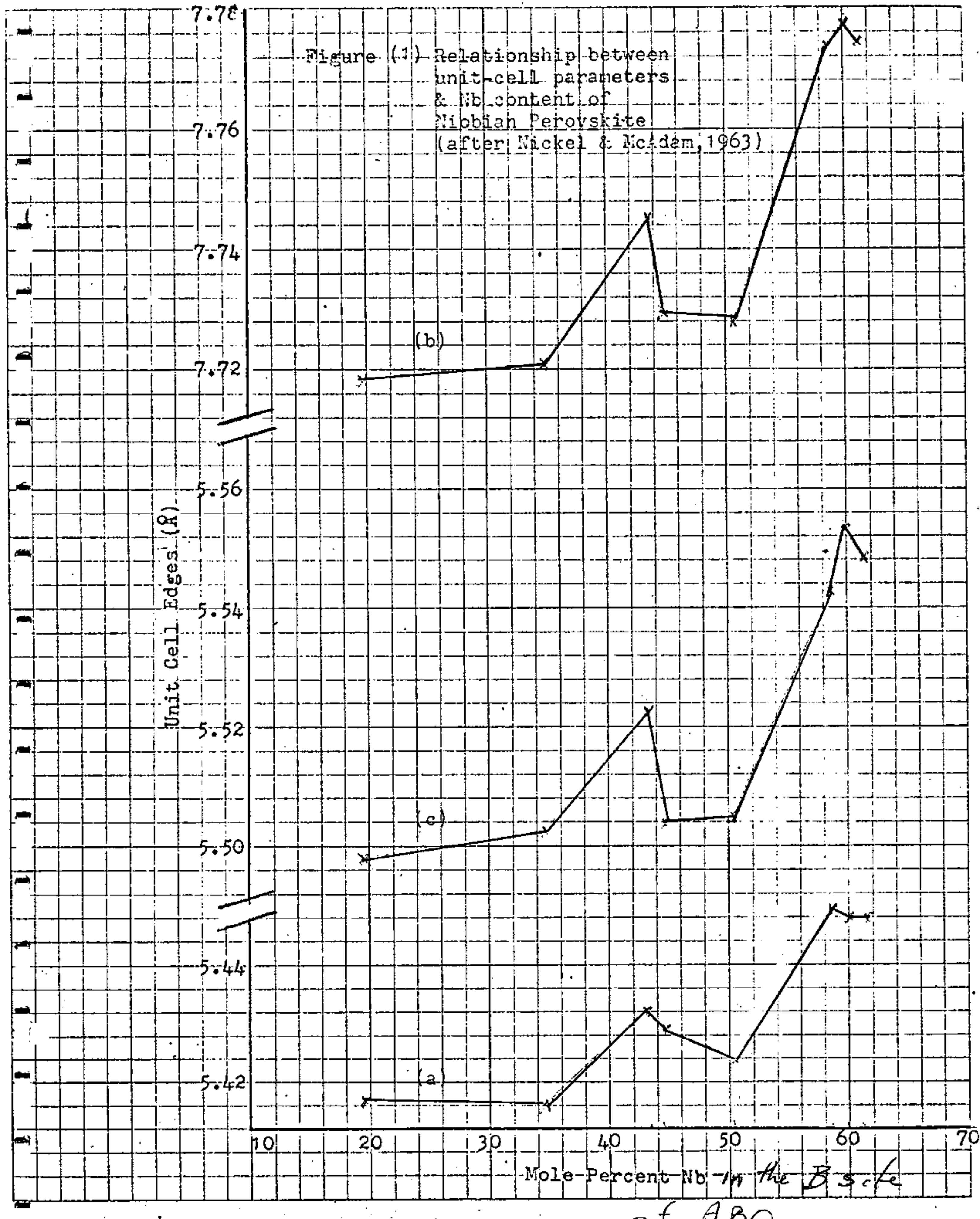


Figure (1) Relationship between unit-cell parameters & Nb content of Niobian Perovskite (after Nickel & McAdam, 1963)
7.78
7.76
7.74
7.72
5.56
5.54
5.52
5.50
5.44
5.42
(b)
(c)
(a)
Unit Cell Edges (Å)
10
20
30
40
50
60
70
Mole-Percent Nb in the B site of ABO3

break in slope on each of the three curves around 40 weight percent Nb_2O_5, which corresponds approximately to the following simplified formula: $Ca(Nb_{.55}Ti_{.45})O_3$. This could be interpreted as merely scatter of the data points since only eight analyses were used, or it could represent a real change in the crystal structure.

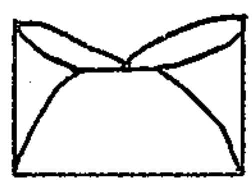
The concept of a perovskite tolerance factor was introduced by Goldschmidt in 1927. He postulated that in an ABO_3 type compound, the ratio $\frac{R_A+R_O}{2(R_B+R_O)}$ (where R is the ionic radius) must be between 0.80 and 1.00 for a perovskite-type structure to occur. While these numbers have been modified several times since, the concept of a tolerance factor is probably still valid, and perhaps this factor is being exceeded by the high niobium content perovskites examined by Nickel and McAdam.

Since we might expect, but do not find, exsolution producing two phases within the latrappite, it must be concluded that either A) the mineral crystallized higher in temperature and cooled quickly through any two phase region on a $CaTiO_3$-$CaNbO_3$ phase diagram, or that B) a true solid solution is possible; that is, that the tolerance factor has not been exceeded.

Possibility (A) above would involve the existence of phase relationships such as shown schematically in A or A' below and possibility (B) is shown in phase diagram geometry as B below. If then such a two phase region could be found experimentally in a phase diagram of the general form of type A or A' below, it could define a minimum temperature of formation for latrappite.

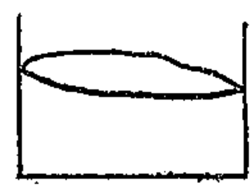
$CaTiO_3$ $CaNbO_3$

A



$CaTiO_3$ $CaNbO_3$

A'



$CaTiO_3$ $CaNbO_3$

B

Another approach would be to attempt to establish a temperature of equilibration of several minerals from the same rock or at least from the same area. Since latrappite is an oxide, moreover, an iron containing oxide, it would be worthwhile to determine its oxygen fugacity as a function of temperature at one atmosphere total pressure. If this were done with several coexisting minerals, a temperature could be found at which they were all in equilibrium with oxygen, and this temperature would define the petrogenetic formation of at least these minerals, if not of the whole rock body for one atmosphere pressure.

Data from either of these approaches should be interesting, although by no means complete due to the complexities of all variables. The most important of these is probably total pressure; however, any information about temperature would at least be another piece to be used in solving the carbonatite puzzle.

II GEOLOGY OF THE OKA COMPLEX

The rocks near Oka, Quebec, about 20 miles west of Montreal, Canada, comprise a carbonatite and feldspathoidal silicate complex, rich in exotic minerals and containing an economic deposit of niobium. Geologic field evidence can only date the complex as between middle Devonian and Tertiary (Rowe, 1955). However, radioisotope dates on the complex have been obtained as follows: 106 m.y. (Rb-Sr), 114 m.y. (K-Ar) (Fairbairn, 1962) and 95 m.y. (K-Ar) (Hurley, 1960). The complex intrudes the Precambrian rocks of the Beauharnois Arch which trends northwest-southeast from the Canadian shield to the Adirondacks. Anorthosites of the Morin Series underlie the northwestern part of the area and folded paragneisses underly the southeastern sector. The crystalline rocks of the Oka complex intrude these Precambrian rocks as a double ring structure with the long axis of the complex perpendicular to the regional structure, the Oka hills, and paralleling the axis of the arch. Parts of the area are overlain by as much as 400 feet of Pleistocene till (Gold et al., 1967).

There are two carbonatite cores; the one to the southeast is about 0.5 mi. in diameter and the one to the northwest is elongate and about 0.5 x 1.5 mi. Around these cores are ring dikes, arcuate dikes, and cone sheets, all of both silicates and carbonates and all complexly interleaved (Heinrich, 1966).

The rocks of the area have been divided into five different groups by Gold (1967). 1. The carbonatites underly more than half of the complex. They are coarse grained and mostly calcite with some dolomitic varieties. They have a banded appearance due to the presence of one or more of the following minerals: Aegirine-augite, biotite, magnetite, monticellite, pyrochlore, and perovskite. Of the sixty-six known minerals found here, most are alkalic varieties of more common minerals plus niobium and rare earth minerals.

2. The okaite-jacupirangite series consists of a gradational sequence from melilite-rich, through monticellite, nepheline, and hauyne bearing varieties to titanaugite-rich rocks. Okaite is a melilite-rich rock defined from Oka and containing some nepheline, perovskite, apatite, biotite, magnetite, and calcite. Monticellitic okaite contains monticellite phenocrysts

in a trachytic textured melilite matrix. Jacupirangite is a soda-pyroxenite sometimes containing titanium augite plus nepheline and accessories.

3. The ijolite series consists of urtite, which is essentially nepheline, grading through ijolite, which contains approximately equal amounts of nepheline and pyroxene, to melteigite, which is approximately 70% pyroxene and 30% nepheline with some wollastonite and melanite bearing varieties exposed to the south.

4. The replacement and alteration rocks occur in zones or discontinuous lenses and are formed by the hydrothermal biotization of silicate rocks. In sheared zones some of the silicates have been altered to chlorite. There are also vugs of pyrite, galena, and calcite. Also in the class of replacement rocks, fenites could be considered. These are country rocks which have been metasomatically replaced by the addition of Ca, Mg, and Na and the removal of Si, and K.

5. Last to be considered are the dike rocks. These are alnoite and basic lamprophyric rocks which intrude both the complex and the country rock, and

Table 1. Experimental emf data recalculated as fO_2 values for the Oka minerals*

	- LOG fO_2		
TEMPERATURE (°C)	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	16.0		
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.

some of which are similar to kimberlites both texturally and chemically.

Interpretation of petrogenesis from cross-cutting relationships here is complex; however, Gold (1967) envisions the sequence of events as follows: fenitization of the gneiss, emplacement of carbonatite dikes and ring dikes, ijolitization (pyroxenization) of the country rock and ultra-fenitization as indicated by relic cores of quartzo-feldspathic gneiss within the ijolite.

Secondly, occurred the intrusion of the okaite-jacupirangite series as crescent shaped masses and arcuate dikes. Thirdly, came the intrusion of the main pyrochlore carbonatite followed by the monticellite carbonatite. After this came the intrusion of the ijolite and microijolite dikes, followed by solid-state flow in the carbonatite to form boudins.

The next four steps may have been part of the same event according to Gold, and they are hydrothermal solutions causing biotization along fractures, late carbonatite dikes with pyrite, rare-earths and galena, late diabase and lamprophyre dikes, and finally emplacement of alnoite and alnoite breccia pipes and dikes.

Gold also mentions that the complex exhibits: 1) a positive magnetic anomaly conforming to its shape due to magnetite, 2) radioactivity due to U and Th principally in pyrochlore, and 3) a negative gravity anomaly consistent with an alkalic conduit of great vertical extent. The carbon, oxygen, strontium, and sulfur isotope ratios are similar to those of other carbonatite complexes and of kimberlites.

Figure 2: Geology of the Oka Complex

(See Gold, 1967, Fig. 1)

Figure 2

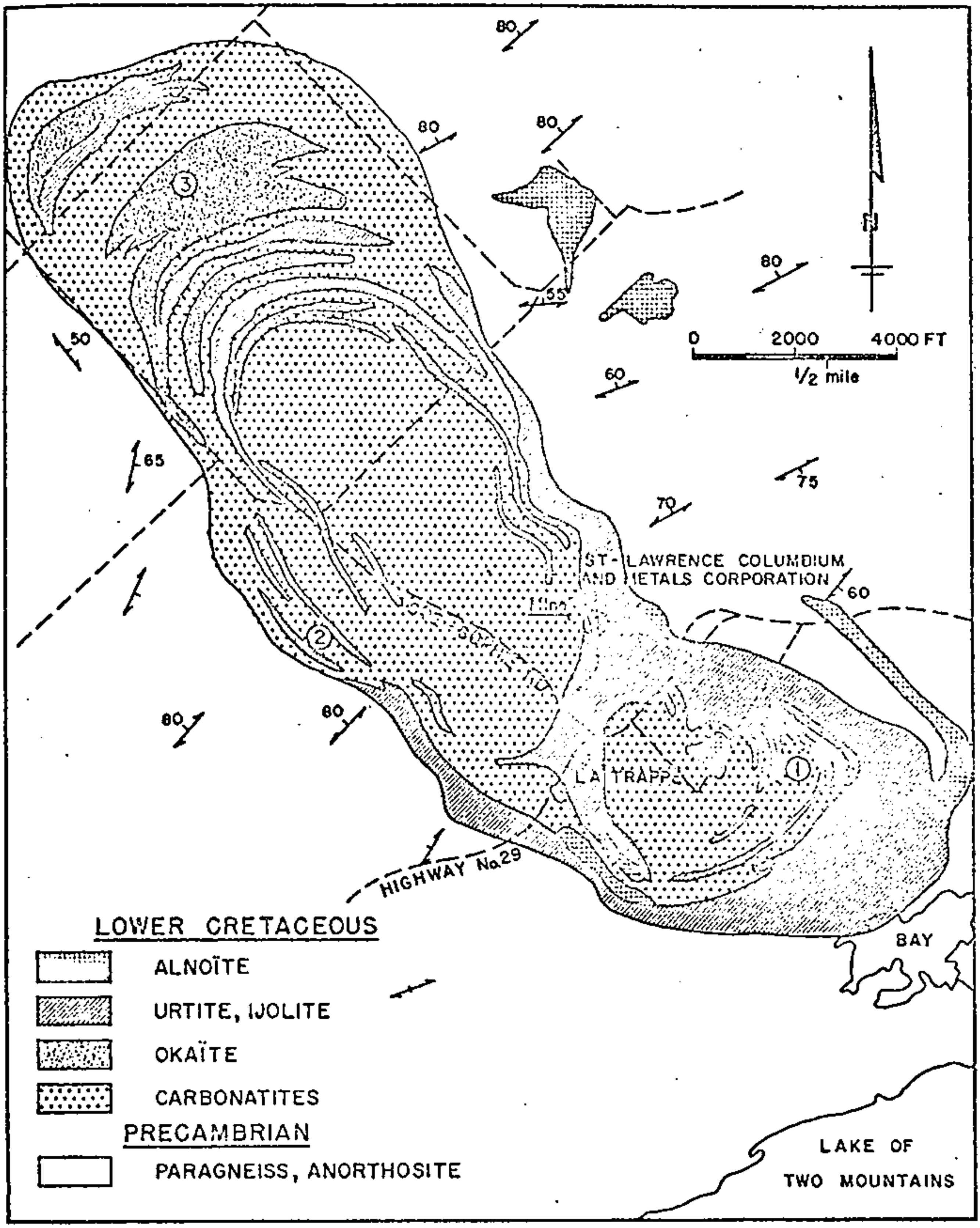

ST-LAWRENCE COLUMBIUM
AND METALS CORPORATION
LA TRAPPE
HIGHWAY No.29
0 2000 4000 FT
1/2 mile
N
BAY
LAKE OF
TWO MOUNTAINS
LOWER CRETACEOUS
ALNOÏTE
URTITE, IJOLITE
OKAÏTE
CARBONATITES
PRECAMBRIAN
PARAGNEISS, ANORTHOSITE

Figure 3: Photograph of countryside at Oka.

Hills in the background are carbonatite.

Figure 4: Photograph of boudinage structures at Oka. Ijolite is surrounded by layered carbonatite.

Figure 5: Photograph of banded rock from Oka showing layered ijolite (black) and carbonatite (white).

III SAMPLE COLLECTION AND PREPARATION

A. Collection

In order to collect rock samples and briefly observe the local geology, a trip was made to Oka, Quebec for two days, during which time all of the rocks for this thesis were collected. The St. Lawrence Columbium and Metals Corp. mines two large pits in the complex for pyrochlore, and some rock samples were collected from their number two pit; however, test pits have been dug on the southwestern side of the complex, and most of the samples used were collected from this area. Many of these pits are rich in perovskite, and while this mineral is not as rich an ore of niobium as pyrochlore, the substituted perovskite is more useful for the purposes of this thesis.

On page 20 is a detailed map of the area showing many of these pits. The pits labeled: C, D, and perovskite are of interest since they contain appreciable amounts of latrappite, and it is at these pits where samples were collected. Following the map are two photographs showing latrappite as it occurs in the rocks.

Large crystals (up to about 3 mm. on an edge) were broken out of the rocks and stored in separate vials for each pit. Smaller crystals, which are by far the most common, were left in the bulk rocks of which about 40 pounds were brought back for study.

B. Preparation

The minerals from Oka involved in these experiments were the following: latrappite (both high and low niobium varieties), calcite, magnetite, pyrochlore, and olivine. The phase equilibrium experiment used only latrappite from the various pits, and it was prepared by separating all magnetic material with a hand magnet and taking only those crystals which were cubes, thereby eliminating octahedral pyrochlore. Calcite attached to the cubes was then removed physically to the extent possible and then the crystals were leached in 20:1 HCl several times until no calcite remained (total time about one hour).

The material was then ground under acetone in a mullite mortar until the average fragment was about 10 microns, suitable for X-ray, and no birefringent material was present. The sample was then X-rayed and about 100 mg. were run in the furnace.

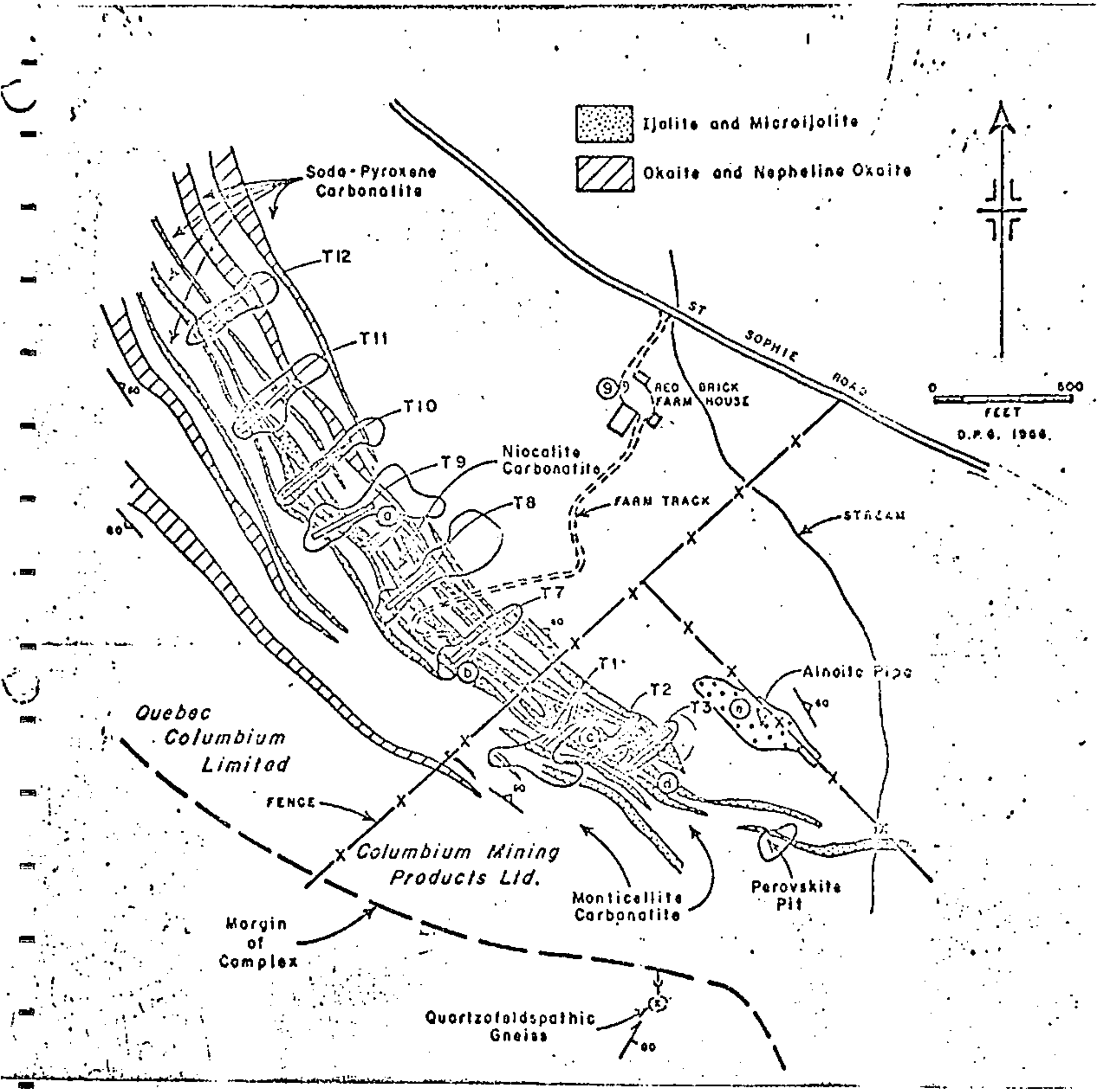


Figure 6: Detailed map of test pits at Oka (Gold, 1967).

Figure 7: Photograph of large latrappite crystal in carbonatite. Small divisions on scale = millimeters.

Figure 8: Photograph of small latrappite crystals in carbonatite. This is the most common occurrence.

The same procedures apply to latrappite for the oxygen e.m.f. cell except that it was only ground to about 100 microns for the average fragment. This seemed sufficient to expose any included calcite and provide sufficient surface area for oxygen equilibration.

Magnetite from the D-pit was separated for the oxygen cell with a hand magnet and then ground and separated with a Frantz isodynamic separator model L-1 run at minimum current and 40° forward, 20° side angles to remove any non-magnetic inclusions. No birefringent material was observed.

The olivine to be studied in the oxygen cell was hand separated and then ground to 10 microns and X-rayed in the diffractometer for identification. The diffractometer trace plus the following index of refraction: $\alpha = 1.660$, indicates that the olivine is probably about forsterite $_{80}$/fayalite$_{20}$. The material was then leached with acetic acid until no calcite was observed; 110 mg were then used for the run.

Pyrochlore was hand separated by taking only octahedral crystals and then removing magnetite with a hand magnet. It was then leached in 20:1 HCl, ground and separated as discussed above with the non-magnetic fraction from the Frantz separator. Part was then ground to X-ray size (less than 10 microns), and the X-ray pattern revealed no latrappite and the petrographic microscope showed no birefringent material.

Lastly, calcite was hand separated and observed under the petrographic microscope for impurities. All minerals were transferred directly from the mullite mortar to the Ag-Pd tubes for the runs.

IV PRELIMINARY WORK

Before proceeding with either of the two approaches previously mentioned; that is, phase relationships and fO_2-T relationships, more familiarity with the mineral latrappite was needed. Some of the knowledge which would be useful includes the X-ray diffraction pattern, information about the oxidation state of niobium in the mineral, and chemical analyses.

A. X-ray

One of the first things done was to X-ray material from each of the pits sampled at Oka and look for differences. After X-raying many different samples in a diffractometer under copper radiation, the only difference noted was that the pattern of all D-pit latrappite (niobium-rich variety, see Appendix A) was shifted about $0.08^{\circ}2\theta$ lower, which could possibly be explained by an increase in niobium, a larger cation than titanium.

B. Free Energy Calculations

To get some idea of the niobium oxidation state that would be expected in latrappite, that is 5+ or 4+, the free energy change of reaction was calculated for the following reaction at various temperatures from the free energies of formation of the oxides from Elliott and Gleiser (1960). The data are as follows:

$$Nb_2O_4 + CO_2 = Nb_2O_5 + CO \qquad (1)$$

T (°K)	ΔF_r (cal/mole)
298	-6948
700	-7430
1000	-8130
1500	-9760
2000	-15090
2500	-20990

Thus it can be seen that in a CO_2 environment, Nb 5+ should be stable relative to Nb 4+ over a wide range of temperature and that Nb 5+ is increasingly stable as temperature increases.

C. Thermogravimetric Analysis

To check the thermodynamic stability of Nb 5+, a thermogravimetric analysis (TGA) of Nb_2O_5 was generously performed at Bethlehem Steel Corp. Homer Research Lab. and the results appear in Appendix D. Niobium pentoxide (99.8% pure) was run in flowing air, CO_2 and H_2 up to 1000°C and no measurable weight loss was observed in air or carbon dioxide and no color change was observed. In hydrogen there was a 1.8% weight loss at 1000°C and the color became black apparantly due to the presence of Nb_2O_4. Thus even though the crystal field effects in latrappite may stabilize Nb 4+ to some extent, niobium 5+ is strongly indicated at the temperatures and conditions of oxidation assumed at Oka.

D. Chemical Analyses

Before beginning work chemical analyses of the mineral latrappite were desired to check for uniformity of composition from one pit to another and also to check uniformity within each pit and even within each crystal. To this goal an electron microprobe analysis was made through the kind cooperation and generous assistance of Dr. John Dickey of the Geophysical Lab. Two crystals were analyzed from each of the following pits: C-pit, D-pit, Perovskite-pit, and St. Lawrence Metals pit #2. These crystals had previously been examined in polished section, and while they appear somewhat mottled and replete with calcite, no evidence of two oxide phases could be found. A photomicrograph of one of these crystals in reflected light appears on page 30 and shows the uniformity of a latrappite crystal.

An average of five points per crystal were analyzed and the results are tabulated in Appendix A. The crystals were analyzed for: Na, Ca, Ti, Mn, Fe, and Nb on a Materials Analysis Corp. electron microprobe. The accelerating voltage was 15 kv, the beam current was 0.05 μa, and a broad 30 micron spot was analyzed for 20 sec. or 10K counts. The data was reduced through the computer program of Finger and Hadidiacos (1971). The analyses sum to slightly less than 90%, and the remainder is probably rare earth elements, or possibly magnesium, or vacancies.

The analyses agree with those of Gold (1966) done by standard wet chemical techniques and show remarkable consistency within each pit and within each crystal as indicated by the standard deviations. The difference between all D-pit analyses and all others, however, is quite substantial, showing a much higher Nb/Ti ratio in D-pit material while all other elements analyzed remain essentially constant. Stoichiometric formulas were then calculated for three of these analyses and six of Gold's and are listed in Appendix B.

E. Explanations

Five possible explanations for the $CaTiO_3$-$CaNbO_3$ solid solution series were given on page 3, but it can now be seen that several of these are unlikely if not impossible considering the data gathered here. Possibility (1) that niobium is in the 4+ oxidation state now seems unlikely considering free energy and TGA data. Possibilities (2) and (3) which allow sodium and iron plus niobium to substitute for titanium both seem unlikely since the amounts of sodium and iron together, from the formulas in Appendix B, are insufficient to account for the amount of niobium observed. Possibility (5) that the mineral is actually $CaNb_2O_6$ also seems impossible considering the formulas calculated from the observed analyses and also the X-ray diffraction pattern. Possibility (4), that of a defect structure, remains as the most likely explanation, but cannot be evaluated here due to the lack of a method available to check it.

With this work accomplished, some familiarity with the mineral had been gained and knowledge acquired, if only by elimination in some cases. Therefore, phase equilibrium studies by X-ray analysis and oxygen fugacity runs were indicated to gain further insight.

Figure 9: Photomicrograph of latrappite crystal (with irregular dark pits) in reflected light, 100X

Light gray = latrappite

Dark gray = calcite

V. DESCRIPTION OF TECHNIQUE

Two approaches to the problem of emplacement temperature of the Oka carbonatite have previously been mentioned and will now be discussed in more detail. It was decided to look at the temperature variable in terms of both the phase relationships of latrappite and also in terms of the oxygen fugacity of several minerals from the area.

A. Phase Equilibrium

To investigate the phase relationships, latrappite from each of the locations sampled was heated to varying temperatures in the hope of finding the appearance of two phases as could be expected considering the problems of stuffing 5+ niobium into the perovskite structure. The samples were held in silver-palladium (60-40) tubes which were then encapsulated in a silica glass capsule under vacuum. This was then heated in a Pt20Rh resistance furnace for varying durations. The shortest was 2 days and the longest was 52 days. The runs were held at 500, 600, 700, 800, 900, and 1000°C ±2° and then quenched into water. These runs in which the capsule did not shatter were checked for vacuum with a Tesla coil and were found to still have vacuum.

The samples were X-rayed both before the run and after quenching to check for differences. Most of the runs were checked with the diffractometer because of its ease of operation; however, several of the runs, including the longer duration ones were checked using the powder camera. The films before and after the run were then carefully compared for any changes. The powder camera allowed the less intense lines to be observed and also the high angle reflections, both of which were not possible with the diffractometer.

The Ag-Pd tubes were checked after each run for any evidence of oxidation or any darkening of the metal which would possibly indicate that it was taking up iron from the sample, and neither was found.

On the longer runs, two Ag-Pd tubes were run together in the same silica glass capsule. One tube contained D-pit material and the other, either C-pit or Perovskite-pit material, since the analysis of both of these is similar. It was thought that the higher niobium content material (D-pit) would be more likely to exsolve into two phases than either of the others. Therefore, the D-pit material could be compared with the lower niobium material under the same experimental conditions; this comparison would serve as control for a number of variables, such as an air leak in the capsule or iron mobility at high temperature in runs of long duration.

B. Oxygen Fugacity

The second approach involves measuring the oxygen fugacity of several of the Oka minerals as a function of temperature. The intersection of fO_2-T plots would define a temperature at which the last equilibration with oxygen took place; the interpretation of such a temperature will be discussed in detail later.

1) Theory

To measure oxygen fugacity, a solid electrolyte fugacity sensor was used similar to that used by Sato (1971). The theoretical background for this technique is as follows: In an electrochemical cell, an e.m.f. across a suitable electrolyte is generated which is proportional to the Gibbs free energy of reaction (ΔG_r) according to the Nernst equation,

$$E = -\Delta G_r/nF \tag{2}$$

where n is the number of electrons involved in the cell transfer ($O_2 + 4e^- = 2O^{2-}$) and F is the Faraday constant (96,484 abs. coulombs). ΔG is also defined as follows:

$$\Delta G = -RT \ln f/f' \qquad (3)$$

where R is the gas constant (8.314 abs. joules/degree-mole), T is the absolute temperature, f is the oxygen fugacity of the unknown and f' is the oxygen fugacity of the reference.

Combining (2) and (3) above and converting from natural logarithms to logarithms to the base 10, we have the following relationship:

$$E = 0.04960T \log(fO_2 \text{ unknown}/fO_2 \text{ reference}) \qquad (4)$$

This allows E to be measured (in millivolts), and T to be measured, which makes it possible to calculate the fO_2 of the unknown relative to some reference. It should also be noted that the fO_2 of a condensed phase is the same as that of the vapor phase in equilibrium above it. This fact, critical to the study of condensed phases is from the relationship:

$$\Delta G + RT \ln f/f' = 0 \text{ at equilibrium} \qquad (5)$$

Two other corrections need to be made in calculating the fO_2 of the unknown. The first of these arises from the fact that air is used as the reference, and while its fO_2 is relatively independent of temperature its e.m.f. versus pure oxygen (fO_2 = 1, for standard state calculation) can be calculated from equation (4) and is:

$$\begin{aligned} E(\text{air-oxygen}) &= 0.04960T \log .210 \\ &= -.0337T \text{ mv} \end{aligned} \quad (6)$$

The second correction arises from the use of dissimilar metals as electrodes. Platinum was used as the outer electrode, but an alloy of $\text{silver}_{60}\text{palladium}_{40}$ was used as the sample container and the inner electrode. These metals produce a thermocouple effect which displaces the zero e.m.f. reading of the cell. This effect has been calculated by Sato (1971) and is given as follows:

$$E(Ag_{60}Pd_{40}-Pt) = -.125 + .0108(t-25) + 1.33 \times 10^{5}(t-25)^{2} \text{mv} \quad (7)$$

where t is in degrees centigrade.

2) Electrolyte

The electrolyte used for this experiment was a zirconia (ZrO_2) tube stabilized with 7 weight percent yttria (Y_2O_3) and closed at one end. The yttria-stabilized zirconia was chosen for its specificity to O^{2-} anions, its high anionic conductivity even at relatively low temperatures (600°C - 1000°C), and its primarily anionic mechanism of conductivity throughout a wide range of oxygen fugacity.

3) Cell Design

The cell design was after Sato and modified by Flynn (1972), who previously set up the cell we used, and whose assistance is greatly appreciated. Flynn's diagram of the cell appears in figure 10. This cell is of the double-tube type design, in which two zirconia tubes with closed flat ends are installed with their closed ends adjacent in a Pt20Rh resistance winding furnace. The lower cell serves as the known cell, and the reference gas (in this case air) flows through the interior of it. The e.m.f. of air against the furnace atmosphere was measured using platinum electrodes, and the temperature of the lower cell was measured with a Pt-Pt10Rh thermocouple attached to the outer wall of the cell.

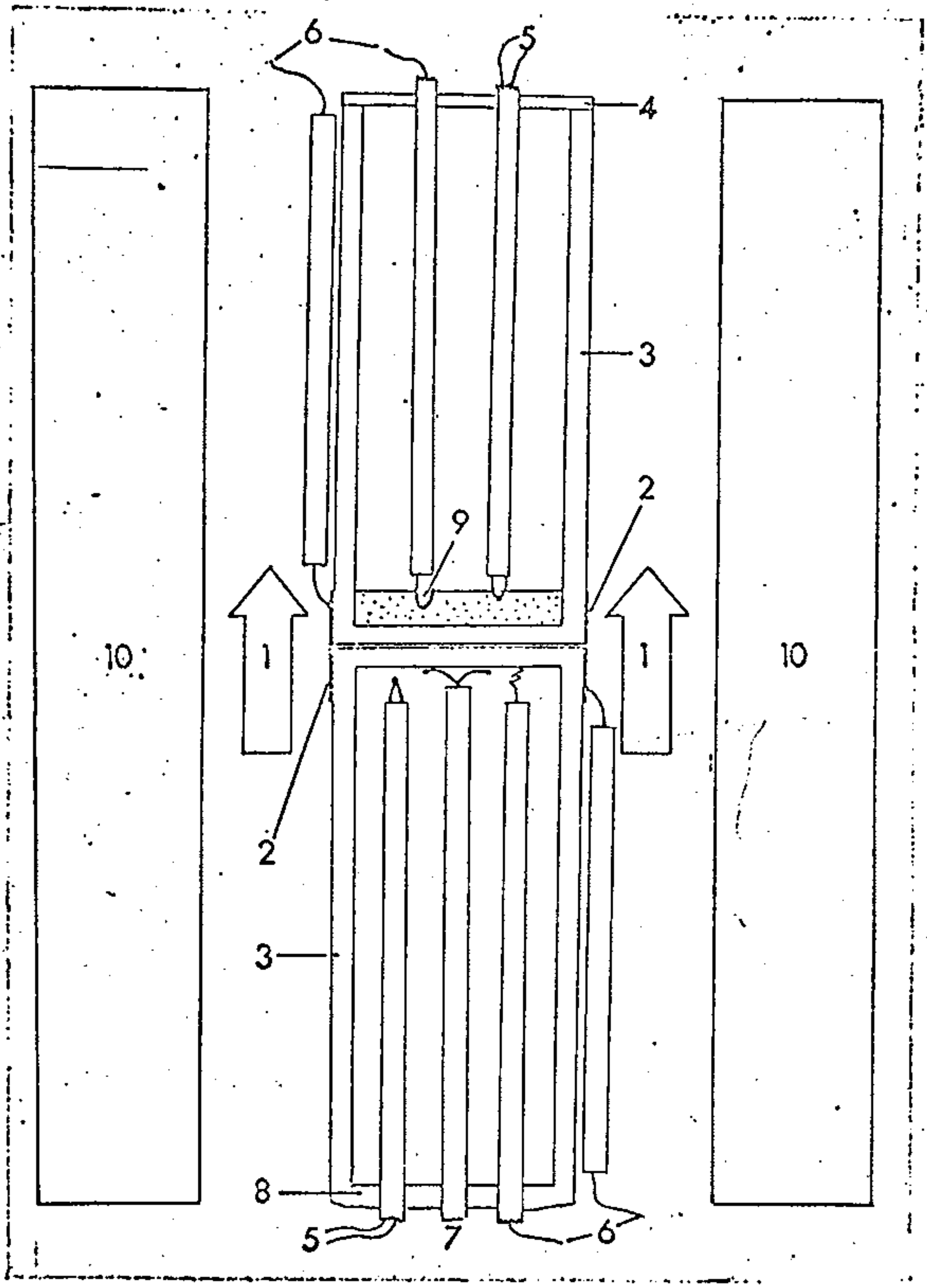
The atmosphere in the furnace was a mixture of carbon dioxide and hydrogen chosen to give a minimal e.m.f.

Figure 10: Schematic of Double Cell Design

(See Flynn, 1972, Fig. 5)

1. known fO_2 (furnace atmosphere)
2. outer electrodes
3. solid electrolyte
4. vacuum coupling
5. thermocouples
6. electrode leads
7. internal reference gas port
8. cement sealant
9. sample
10. furnace

Figure 10



(less than 50 mv) between it and the unknown sample in the top cell. The top or unknown cell was positioned several millimeters above the lower cell and with its closed end down. It contained a $Ag_{60}Pd_{40}$ tube with the bottom end welded closed and bent so that it made electrical contact with the bottom of the cell. This tube contained the sample and acted as one electrode. The top of the AgPd tube was left open to allow as rapid equilibration as possible, and the rest of the cell was filled with a vycor glass filler to occupy the rest of the space so the sample did not have to fill the entire cell with its oxygen.

A Beckman teflon compression fitting was used as the top connector on the unknown cell, and a silicone stopper sealed the top of the Beckman fitting. The cell was evacuated and then filled with 99.999% pure argon by means of a hypodermic needle which was inserted into the cell through the stopper with the electrode wire within the needle.

When the needle was removed the compression fitting caused the silicone stopper to seal around the electrode wire which was connected to one post of a compensated plug.

The other post of this plug was connected to the platinum outer electrode. This platinum electrode extended to the outside of the bottom of the cell through an alumina insulator tube along the side of the ZrO_2 tube. Also positioned along the side of the ZrO_2 cell was a Pt-Pt10Rh thermocouple, and these thermocouple leads were connected to another compensated plug.

The entire length of the cell and plumbing fittings were shrouded in the furnace atmosphere by a pyrex tube and connected to the top of the furnace with gooch tubing. The cell was positioned in the furnace and held by clamps. A schematic diagram of the set-up can be seen in figure 11.

4) Recorders

The e.m.f. from both cells were measured by Keithley electrometers, model 600C, capable of voltages to hundreths of a millivolt, and with an internal resistance of 10^{14} ohms. These electrometers allowed negligible current to flow across the cell. Since the sample stoichiometry is maintained only with zero current flow, a high internal circuitry resistance was absolutely necessary for this experiment.

Figure 11: Schematic Representation of Equipment Set-up (See Flynn, 1972, Fig. 18)

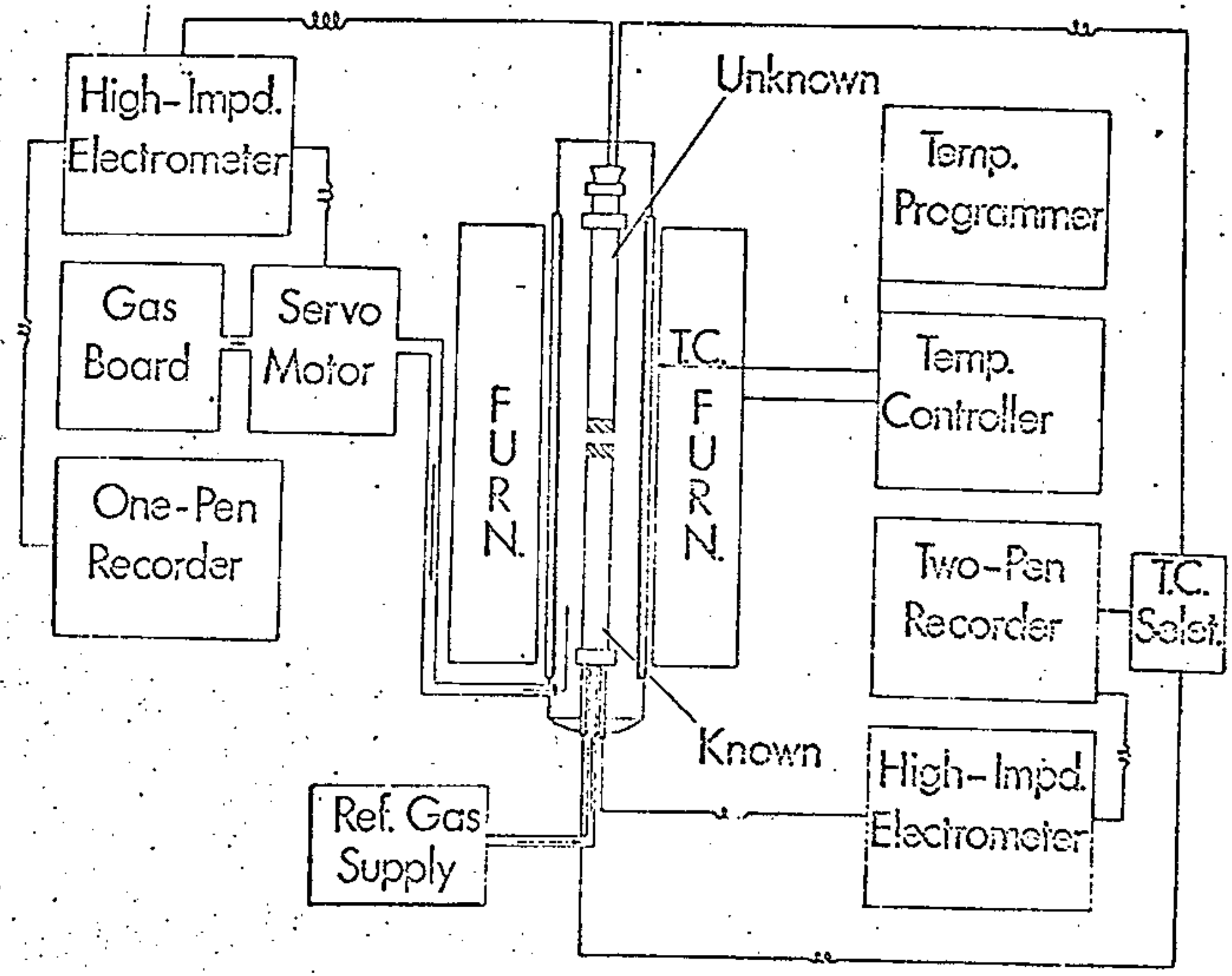

High-Impd. Electrometer
Gas Board
Servo Motor
One-Pen Recorder
FURN.
Unknown
T.C.
FURN.
Known
Temp. Programmer
Temp. Controller
Two-Pen Recorder
T.C. Selct.
High-Impd. Electrometer
Ref. Gas Supply

Figure 11

The e.m.f. from the unknown cell was fed from the electrometer into a Leeds & Northrup Speedomax single-pen recorder, which registered the unknown e.m.f. (always within the range +50 to -50 mv). The e.m.f. of the bottom, or known cell, was fed from the electrometer into an Esterline-Angus two-pen recorder model E1102E, which registered this e.m.f. from 0 to 1000 mv. The recorder also took the temperature information from the thermocouples through a thermocouple selector and registered the temperature alternately from the top and bottom cells so that both the cell temperatures and any possible divergence could be recorded.

The furnace temperature was controlled by a "Thermo-Electric Controller", Tem-Pres Research model 32422. This controller reads the signal from the furnace thermocouple, compares it to the desired set-point and adjusts the furnace power by means of a silicon controlled rectifier (SCR). This controller could be programmed for any temperature-time plot desired, but for this experiment, all readings were taken with the controller in the manual mode. This was done to allow time for equilibration at each temperature. The automatic feature, however, was sometimes used to bring the furnace up to the desired initial temperature.

5) Gas Mixing

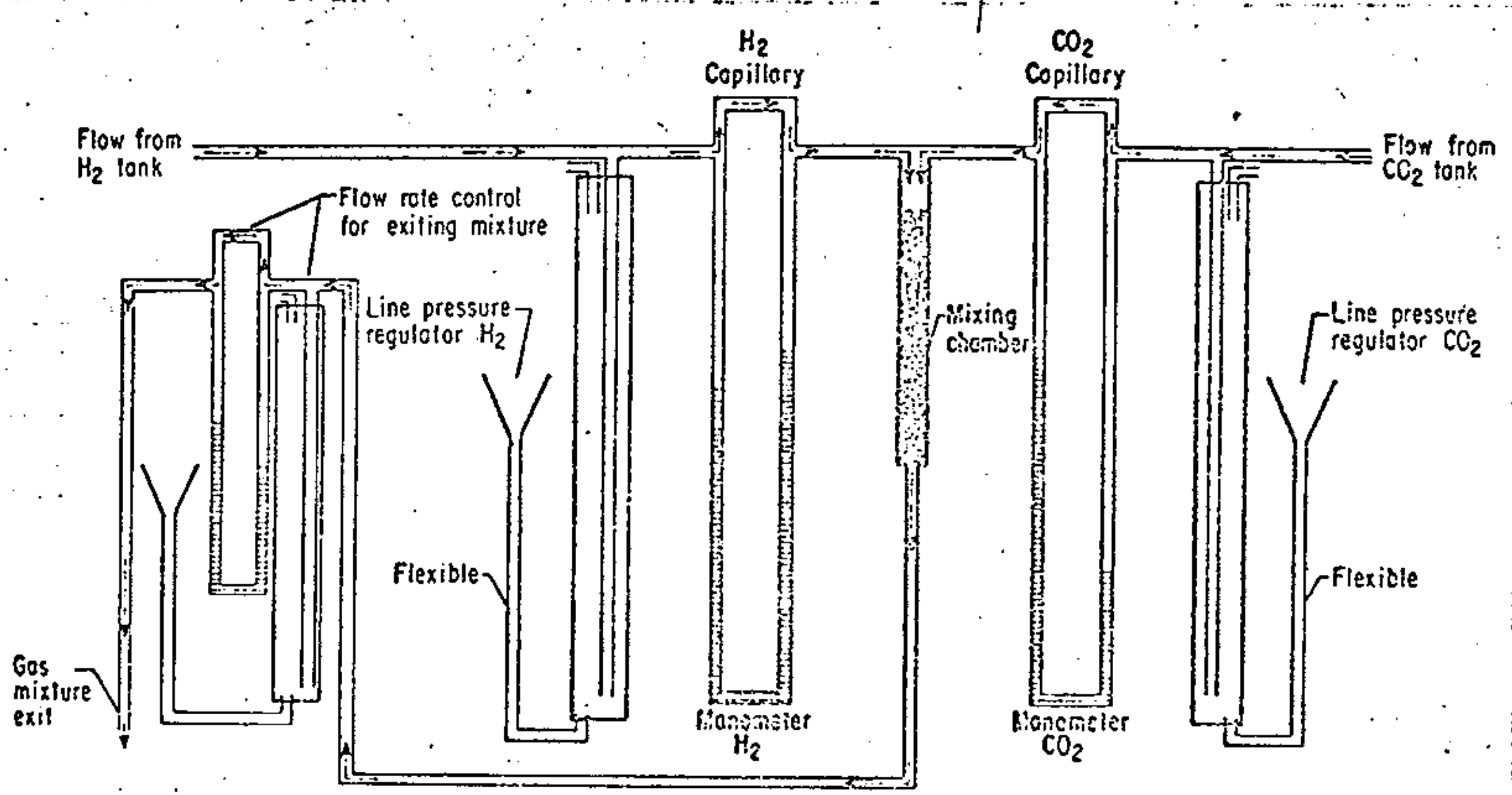
The CO_2/H_2 mixing was accomplished by a gas mixing board of the type discussed by Nafziger, Ulmer, and Woermann, (1971) and shown in figure 12. The mixing ratio was controlled by hand in an attempt to keep the fO_2 of the ambient atmosphere as close as possible to that of the unknown and thus avoid oxidizing or reducing the sample. A close match of oxygen fugacities is indicated by a minimal e.m.f. across the unknown cell (less than 50 mv). The average mixing ratio for this experiment, while it varied of course with temperature, was about 70/1 (CO_2/H_2). Extreme mixing ratios were avoided due to lack of complete mixing and resulting inhomogeneity of the gaseous buffer. Signals in excess of 50 mv on the top cell were tolerated for short periods of time in preference to large CO_2/H_2 ratios.

6) Runs

Once the cell had reached equilibrium at a given desired temperature, readings could be taken. The time to reach this equilibrium varied from about 2 mins. to 20 mins. and equilibrium could be determined by observing

Figure 12: Schematic of a Binary Gas Mixer.

(See Nafziger, Ulmer & Woermann, 1971, Fig. 1)



H_2 Capillary
CO_2 Capillary
Flow from H_2 tank
Flow from CO_2 tank
Flow rate control for exiting mixture
Line pressure regulator H_2
Mixing chamber
Line pressure regulator CO_2
Flexible
Flexible
Gas mixture exit
Manometer H_2
Manometer CO_2

Figure 12

a constancy of e.m.f. readings with time. The e.m.f. of the known cell is measured and algebraicly summed with the measured e.m.f. of the unknown cell. The air correction from equation (6) and the thermocouple correction from equation (7) are applied and this value is divided by 0.04960T (from equation (4)), which gives the log fO_2 of the unknown sample.

Runs were made from 600°C to 1000°C (with a few to 1200°C) with equilibration stops at each 50° increment to take data, and each run was read out in both the up and the down temperature mode. The technique is fairly simple and a direct method of measuring oxygen fugacity, and it should be remembered that while fugacity and partial pressure are very nearly the same at low pressures, it is actually the thermodynamic quantity, fugacity, that this technique measures. Presentation and interpretation of the fO_2 data are contained in the following sections.

VI RESULTS

A. Phase Equilibrium

Several preliminary runs were made by heating latrappite to temperatures from 500° to 900°C for up to 8 days and no changes in the mineral were observed by X-ray diffraction. It was then decided to look at the melting point with the hope that this would indicate which phase diagram geometry was probable of those shown on page 6. However, the melting point proved to be in excess of 1550°C, the practical upper limit of the furnace used. Subsequent runs were made at temperatures to 1000°C and durations to 52 days, but no exsolution or changes of any other kind were observed.

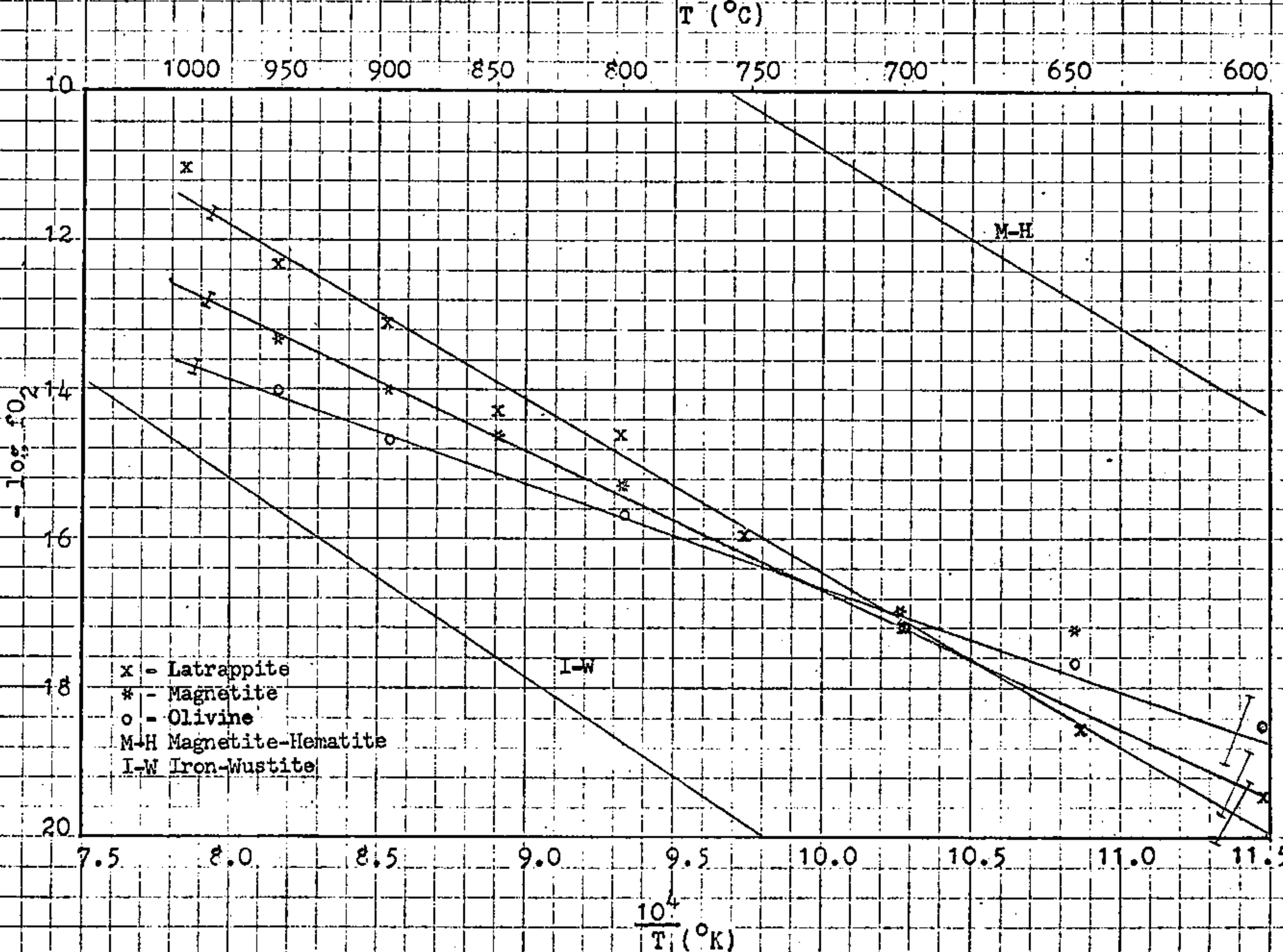
B. Oxygen Fugacity

Plots were made of fO_2-T data for the minerals: latrappite, magnetite, and olivine, and these curves are shown in figure 13. The data from which these curves were drawn is available in Appendix C. All of the material for these runs came from the D-pit at Oka and presumably were all in equilibrium with each other at least at the time of formation. Latrappite from the C and Perovskite-pits was also run and showed somewhat less oxidizing

Figure 13: fO_2-T plot of D-pit latrappite, magnetite, and olivine.

See text, p.51, for discussion of error bars.

Figure 13



T (°C)
1000
950
900
850
800
750
700
650
600
10
12
14
16
18
20
$-\log f_{O_2}$
7.5
8.0
8.5
9.0
9.5
10.0
10.5
11.0
11.5
$\frac{10^4}{T}$ (°K)
M-H
I-W
x - Latrappite
* - Magnetite
o - Olivine
M-H Magnetite-Hematite
I-W Iron-Wustite

conditions than the D-pit material. An attempt was made to run pyrochlore from the D-pit in addition, but this failed due to the very low buffering capacity of this mineral (see Sato, 1971). The results of the pyrochlore runs were unreproducable and unstable with time; at constant temperature the sample became increasingly oxidizing.

The curves in figure 13 are least-squares-fit to the data points in Appendix C and show a triangle of uncertainty in the intersection of the three curves. The center of this triangle is 710°C and this is taken as the temperature of last equilibration with oxygen. The significance of this temperature will be discussed in the following chapter.

C. Discussion of Error

The error in the data points in figure 13 as shown by the error bars is due mainly to possible error in the measurement of temperature. Both the known and unknown cells had their own thermocouples, and the temperature from each of them was read alternately. At low temperatures (about 600°C), the unknown and known cell had a difference of 25°C, whereas at higher temperatures, such as 1000°C, the difference was only 5°C, since the hot spot of the furnace becomes more broad and thermal expansion brings the cells closer together. In terms of log fO_2: ΔT of 25°C = ± 0.20, ΔT of 5°C = ± 0.05. Displacing the calculated curves to the maximum limits of temperature error in both the positive and negative direction forms two new triangles, the centers of which are 695° and 715°. Therefore, the uncertainty arising from error in the measurement of temperature can be considered as ±10°C.

Another source of error results from poor equilibration within the unknown cell. Small sample size and resulting kinetic problems, especially at low temperatures, sometimes produced a fluctuation of the electrometer reading the unknown cell. This fluctuation was rarely more than 10 mv, and this corresponds to an error of 0.20 log fO_2 at 750°C. This error was random, and in many cases non-existent. The electrometers used could be read to ±1 mv, and these instruments were a negligible source of error.

All of the runs for this experiment were made in both the up-and the down-temperature mode, and the differences were usually within 0.50 log units fO_2. However, the down-temperature runs tended to plot more exidizing than the up-temperature counterpart, and this was attributed to possible uneven contraction of the cell and plumbing fittings. The ZrO_2 cells were on the average 0.003 inches out of round, and it is possible that if the cell contracted faster than the Beckman fitting, a very small air leak would occur, resulting in a reading which would appear to be too oxidizing. This effect seemed to be most noticeable on the first couple of readings down temperature, and this is as expected since the furnace cooling rate is greatest at high temperature. Because of this effect only up temperature readings were used to calculate the curves rather than an average of up and down.

VII INTERPRETATION

It was the goal of this thesis to attempt to determine the temperature of formation of the carbonatite core of the rock complex at Oka, Quebec, and possibly from this temperature determine whether the complex is truly a magmatic intrusion or a result of solid-vapor reactions. It was also hoped that some knowledge could be gained about the mineralogy and chemistry of one of the unusual niobium minerals.

A. Phase Equilibrium

While the results of the phase equilibrium runs were negative in that no exsolution was observed at the various temperatures examined, some knowledge was still gained from the equilibration attempts. It is possible that the observed lack of exsolution is due to the sluggish kinetics of the dry reaction; that is, latrappite may exist metastably, but the barrier imposed by the energy of activation may be too great for the reaction to proceed, especially at the low temperatures concerned and without any fluids present in the experimental design.

It is also possible that a true solid solution exists between perovskite and latrappite, at least at the compositions of the natural material investigated. This would probably involve a defect structure as discussed previously, and while it was not the subject of this paper to look at the detailed structure of latrappite, further cooperative work is currently in progress on the crystal chemistry of latrappite by Dr. George Myer at Temple University, and Dr. P. Deines of Penn State University.

B. Oxygen Fugacity

Since the phase equilibrium work yielded no information about the temperature of formation of the Oka complex, this determination was left to the fO_2 work. A temperature of $710^{\circ}C \pm 10^{\circ}$ was determined as mentioned in the previous chapter, and while it was desired to have data from the phase equilibrium work corroborate this temperature, it will be seen that the temperature is reasonable in light of work done by other authors by different means.

A minimum for the fO_2-T conditions at Oka would be the curve for the buffer: graphite-CO_2-CO-O_2 since no graphite is observed at Oka. Plots for this buffer curve at 1 atm., 1 kb., and 10 kb. can be found in figure 14 (after French and Eugster, 1965). It can also be seen in this figure that the data from this study for temperature and fO_2 at Oka are above the wustite-magnetite (WM) buffer and below the hematite-magnetite (HM) buffer. Both the WM and HM buffers are reasonable geologic extremes of fO_2 and temperature for Oka although these buffers do not fix the conditions very precisely. The Oka data are, however, very near the quartz-fayalite-magnetite buffer, which again is geologically reasonable considering olivine and magnetite are two of the minerals used.

Another line of interpretation of the Oka fO_2-T data comes from Wyllie's work on the system, $CaO-MgO-CO_2-H_2O$, (1960A,B, 1966). In this system liquid first appears between about 650°C and 750°C over a wide range of CO_2/H_2O ratios (20-80) at 500 bars pressure. 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. In the system $CaO-CO_2-H_2O$ he found that between 27 and 4000 bars the minimum liquidus temperature varies

Figure 14: fO_2-T plot of standard buffer curves.

M-H Magnetite-Hematite (Eugster & Wones, 1962)

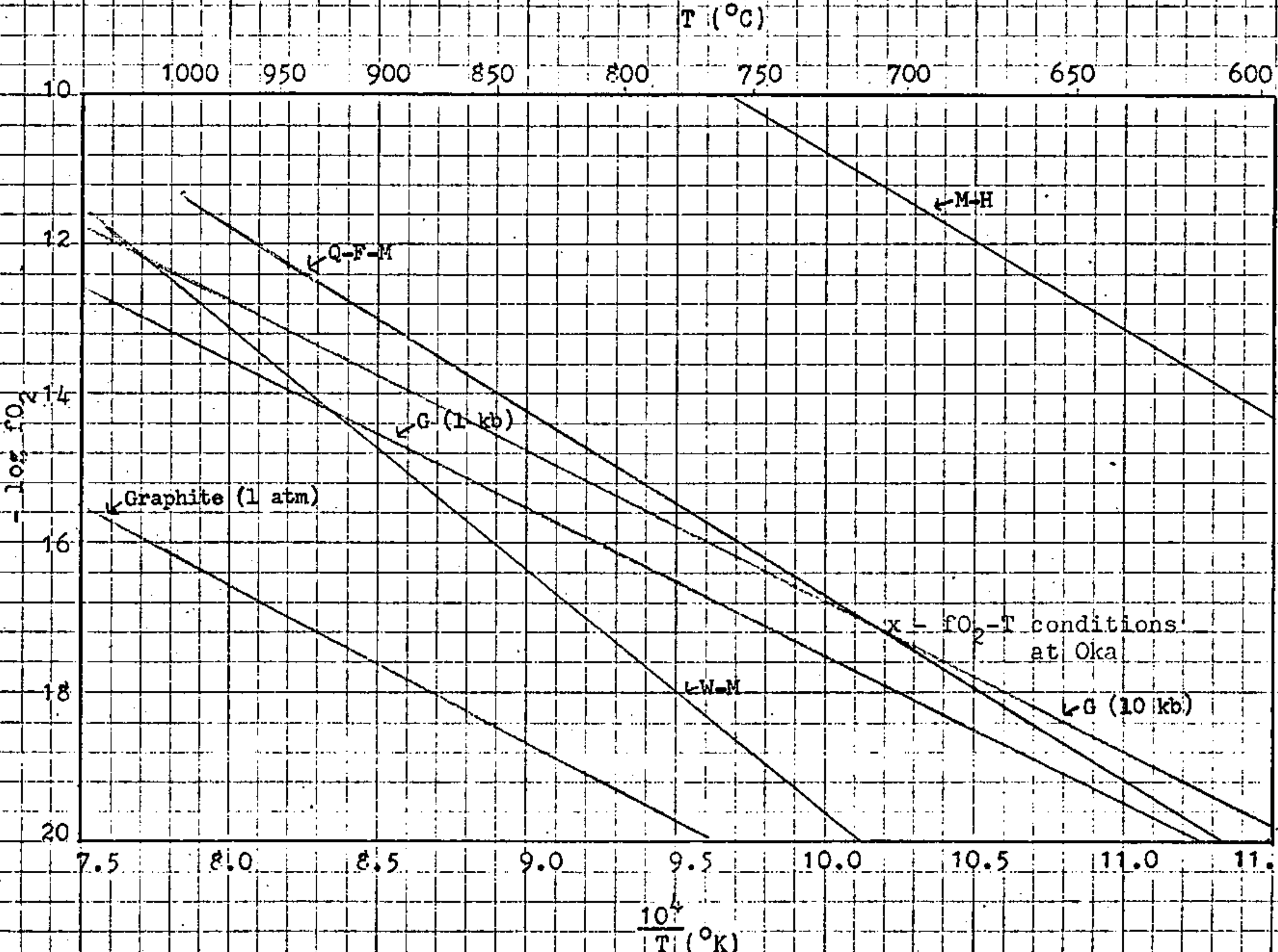
Q-F-M Quartz-Fayalite-Magnetite (Eugster & Wones, 1962)

W-M Wustite-Magnetite (Eugster & Wones, 1962)

Graphite (G) Graphite-CO_2-CO-O_2 (French & Eugster, 1965)

⊠ Conditions found at Oka (from fig. 13)

Figure 14


T (°C)
1000
950
900
850
800
750
700
650
600
10
12
14
16
18
20
- log fO_2
M-H
Q-F-M
G (1 kb)
Graphite (1 atm)
W-M
x - fO_2-T conditions at Oka
G (10 kb)
7.5
8.0
8.5
9.0
9.5
10.0
10.5
11.0
11.5
$\frac{10^4}{T}$ (°K)

between 685° and 640°C. Other systems investigated by Wyllie also show low temperature liquids over a wide range of pressures including systems containing SiO_2 and Na_2O. The percentage of silica, however, must be low, but this is still reasonable in an area characterized by silica-undersaturated rocks. While it must be pointed out, as Wyllie does, that these systems are too simple to be true carbonatite magmas, they do indicate that low temperature carbonatite liquids are at least possible, and the addition of more components would lower the minimum liquidus temperatures still further. While discussing calcite in ultramafic rocks, Wyllie states, "...it now appears possible for mineral assemblages involving olivine, pyroxene, monticellite, melilite, dolomite and calcite to be precipitated simultaneously from magmas at low to moderate temperatures (in the range 600° - 800°C)."

In considering the value for the fO_2 measured in this study it should be noticed that although it appears reasonable relative to the buffer curves previously discussed, the fO_2 of pure CO_2 at this temperature is about 10^{-7} atm. The discrepancy between this value and that measured for the minerals studied (about $10^{-17.2}$ atm) can only be explained by assuming CO_2 diluted with something to make it more reducing—possibly H_2. To have an fO_2 of $10^{-17.2}$atm., CO_2 would have to be diluted with 1 part H_2 to 80 parts CO_2. If dilution with CH_4 had occurred, the work of French (1966) would indicate graphite should be stable; as indicated earlier in reference to figure 14, no graphite has been found at Oka.

The partial pressure of CO_2 above calcite at 1 atm. total pressure is 26 mm Hg at 710°C (Smyth and Adams, 1923). This curve appears in figure 15, and it can be seen that this temperature occurs at the "knee" of the exponential curve. It is therefore possible that at this temperature there was insufficient CO_2 available to continue oxygen equilibration; that is, while cooling the Oka complex there may have been a statistically insufficient number of oxygen molecules available to redox react with the Oka minerals below a partial pressure of 10^{-2} atm. CO_2 (Muan, 1958).

Additional supporting evidence comes from the work of Conway and Taylor (1969) who studied the oxygen and carbon isotope ratios for the mineral pair, calcite-

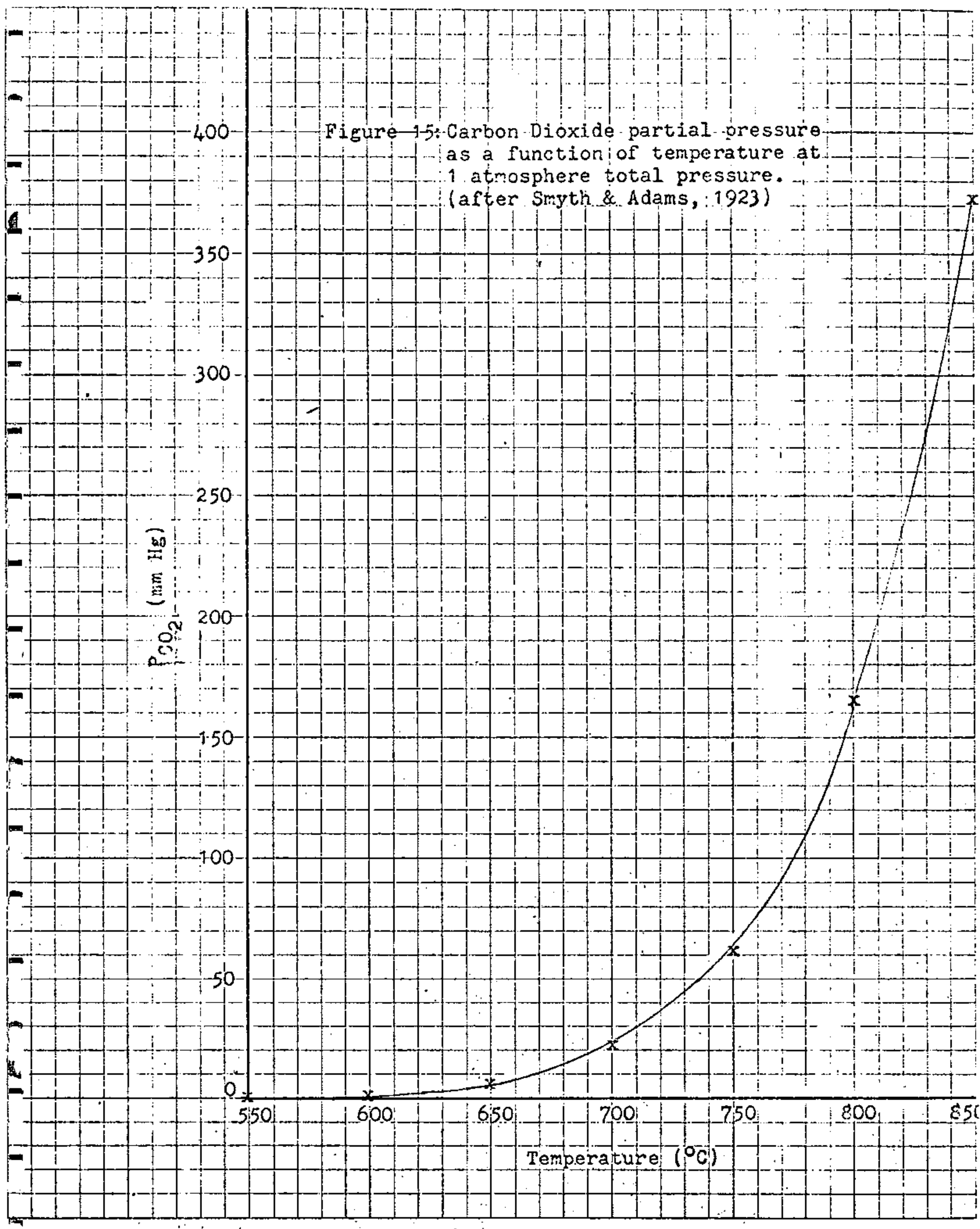


Figure 15: Carbon Dioxide partial pressure as a function of temperature at 1 atmosphere total pressure. (after Smyth & Adams, 1923)

magnetite from Oka. From these isotopic ratios, they calculated temperatures of 720° and 730°C for the last isotopic equilibration of two Oka carbonatites. These temperatures probably have the same meaning as those determined in this paper, since they both measure the temperature at which oxygen migration could no longer proceed, and they are certainly in agreement within the limits of experimental error.

C. Summary

The cooling history of the main carbonatite body at Oka is therefore envisioned 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 the vapor pressure was insufficient to continue oxygen equilibration. Total pressure on the magma is unknown, but experimental studies on synthetic systems show that it should not greatly change the temperature measured by this technique at 1 atmosphere total pressure.

The entire history of Oka is complex, probably involving multiple magma injection, vapor phase transport, and solid-state replacement. Much of this history has been worked out by Gold (1967) from field evidence, and no attempt is made to duplicate that work here. The cooling history described above applies only to the main carbonatite core of the complex. The temperature determined here is corroborated by comparison with synthetic systems and O^{18}/O^{16} data. Since field evidence for subsequent high temperature metamorphism or hydrothermal activity is lacking, the fO_2-T determination presented herein is probably the original solidus or liquidus minimum temperature for the carbonatite core at Oka. Thus, Gold's hypothesis of a magmatic origin for the Oka complex is supported.

VIII CONCLUSIONS

The following conclusions seem warranted:

(1) The mineral latrappite possesses a very complex crystal chemistry. Niobium is in the 5+ oxidation state, and thus latrappite is not a simple solid solution of Nb^{5+} for Ti^{4+} in perovskite.

(2) The lack of exsolution of latrappite into two phases upon annealing is probably due to sluggish kinetics.

(3) The main carbonatite body at Oka was last equilibrated at 710°C $\pm 10°$ and at an fO_2 of $10^{-17.2}$ atm.

(4) This temperature and fO_2 when compared with O^{18}/O^{16} work and simplified carbonatite synthetic systems can be interpreted as a solidus or liquidus invariant point.

(5) A magmatic origin for the carbonatite core at Oka is therefore substantiated.

*****

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PEROVSKITE AND LATRAPPITE ANALYSES

Sample #	TiO_2	CaO	Nb_2O_5	Na_2O	MgO	MnO	FeO*	Fe_2O_3*	Others	Total
1	51.20	38.20	.69	.31	.12	-		2.84	5.02	98.22
2	51.79	33.88	4.86	.67	-	-		5.85	2.76	99.81
3	38.63	33.16	15.80	1.22	-	-		8.31	2.74	99.86
4	25.00	28.70	27.60	3.75	-	.10		6.38	8.84	100.36
5	15.50	27.96	39.36	4.50	1.19	.18		7.18	2.22	98.08
6 (D-pit)	10.05	25.95	43.90	4.03	2.20	.77		8.74	4.06	99.70
D1 **	5.95	23.40	46.20	5.88		.39	6.24			88.06
S.D.	.45	2.55	2.80	1.16		.03	.53			
D2 **	7.15	23.82	46.80	6.06		.28	5.45			89.56
S.D.	.53	2.51	2.75	1.15		.02	.45			
C1 **	26.55	26.86	26.07	4.24		.09	5.71			89.54
S.D.	1.40	2.02	1.09	.57		.01	.33			
C2 **	28.03	27.50	24.19	4.08		.10	5.83			89.73
S.D.	1.44	2.01	.98	.54		.01	.33			
P1 **	20.75	30.14	27.62	2.16		.12	8.38			89.17
	1.16	2.39	1.21	.31		.01	.52			

Samples 1 through 6 are after GOLD (1966); samples D1 & D2 are from the D-pit, C1 & C2 are from the C-pit, and P1 is from the Perovskite pit.

* Total iron
S.D. - Standard Deviation
** See p. 28 for electron probe details

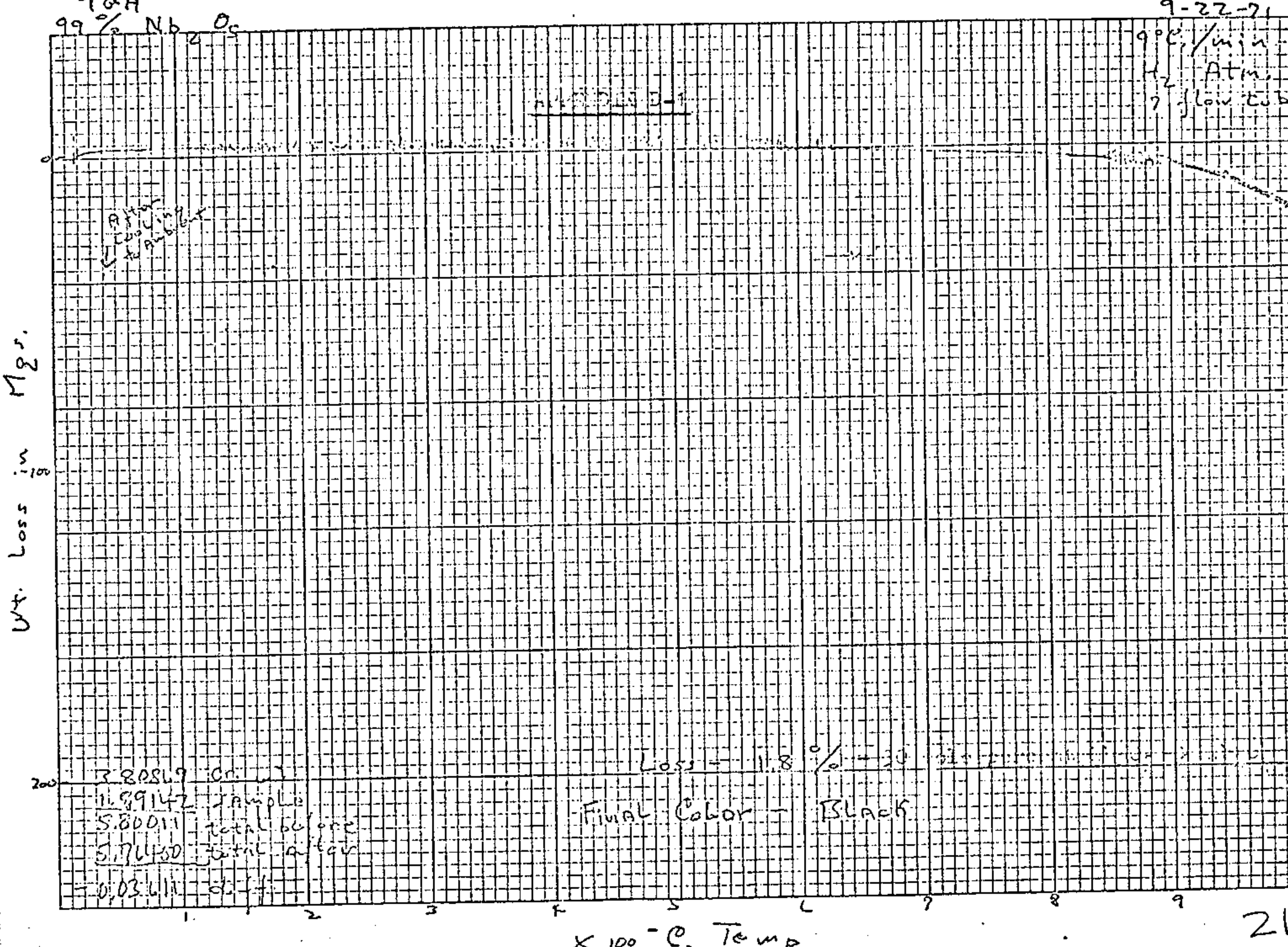
Appendix A

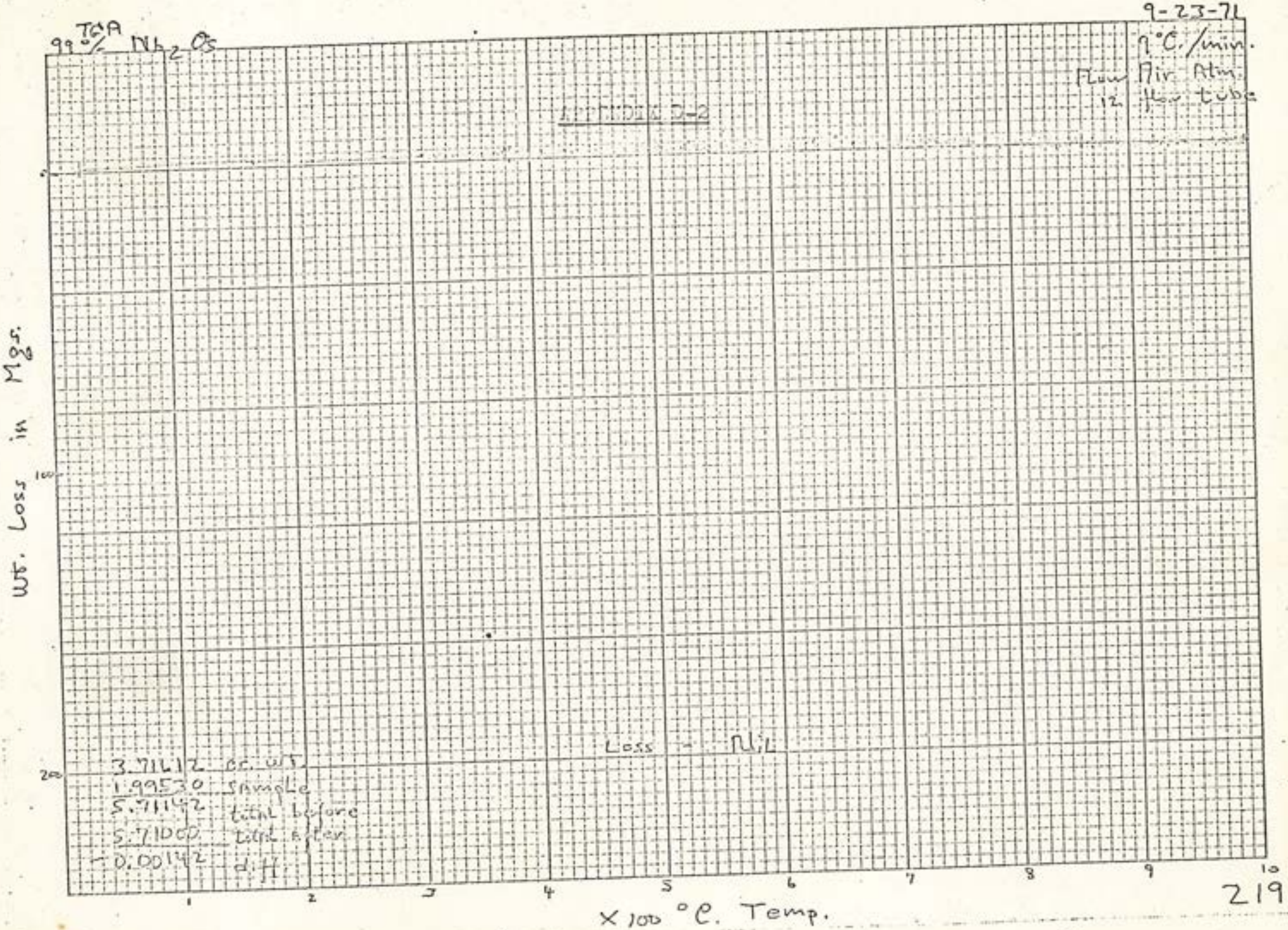
ANALYSIS (From Appendix A)	STOICHIOMETRIC FORMULA
1	$(Ca_{.96}Na_{.02}Ce_{.03})_{1.01}(Ti_{.94}Nb_{.01}Fe_{.05})_{1.00}O_3$
2	$(Ca_{.85}Na_{.04})_{.89}(Ti_{.91}Nb_{.05}Fe_{.12}Ta_{.01})_{1.09}O_3$
3	$(Ca_{.87}Na_{.05}Ce_{.01})_{.93}(Ti_{.71}Nb_{.17}Fe_{.16}Ta_{.01})_{1.06}O_3$
4	$(Ca_{.78}Na_{.19}Sr_{.01})_{.98}(Ti_{.48}Nb_{.32}Fe_{.12}Ta_{.02})_{.94}O_3$
5	$(Ca_{.80}Na_{.23}Mg_{.05})_{1.08}(Ti_{.31}Nb_{.48}Fe_{.14})_{.93}O_3$
6	$(Ca_{.75}Na_{.21}Ce_{.02}Mg_{.09})_{1.07}(Ti_{.20}Nb_{.53}Fe_{.18}Mn_{.02})_{.93}O_3$
D1	$(Ca_{.74}Na_{.37})_{1.11}(Ti_{.11}Nb_{.67}Fe_{.16}Mn_{.01})_{.95}O_3$
C1	$(Ca_{.80}Na_{.23})_{1.03}(Ti_{.56}Nb_{.33}Fe_{.13}Mn_{.01})_{1.03}O_3$
P1	$(Ca_{.93}Na_{.12})_{1.05}(Ti_{.45}Nb_{.36}Fe_{.20}Mn_{.01})_{1.02}O_3$

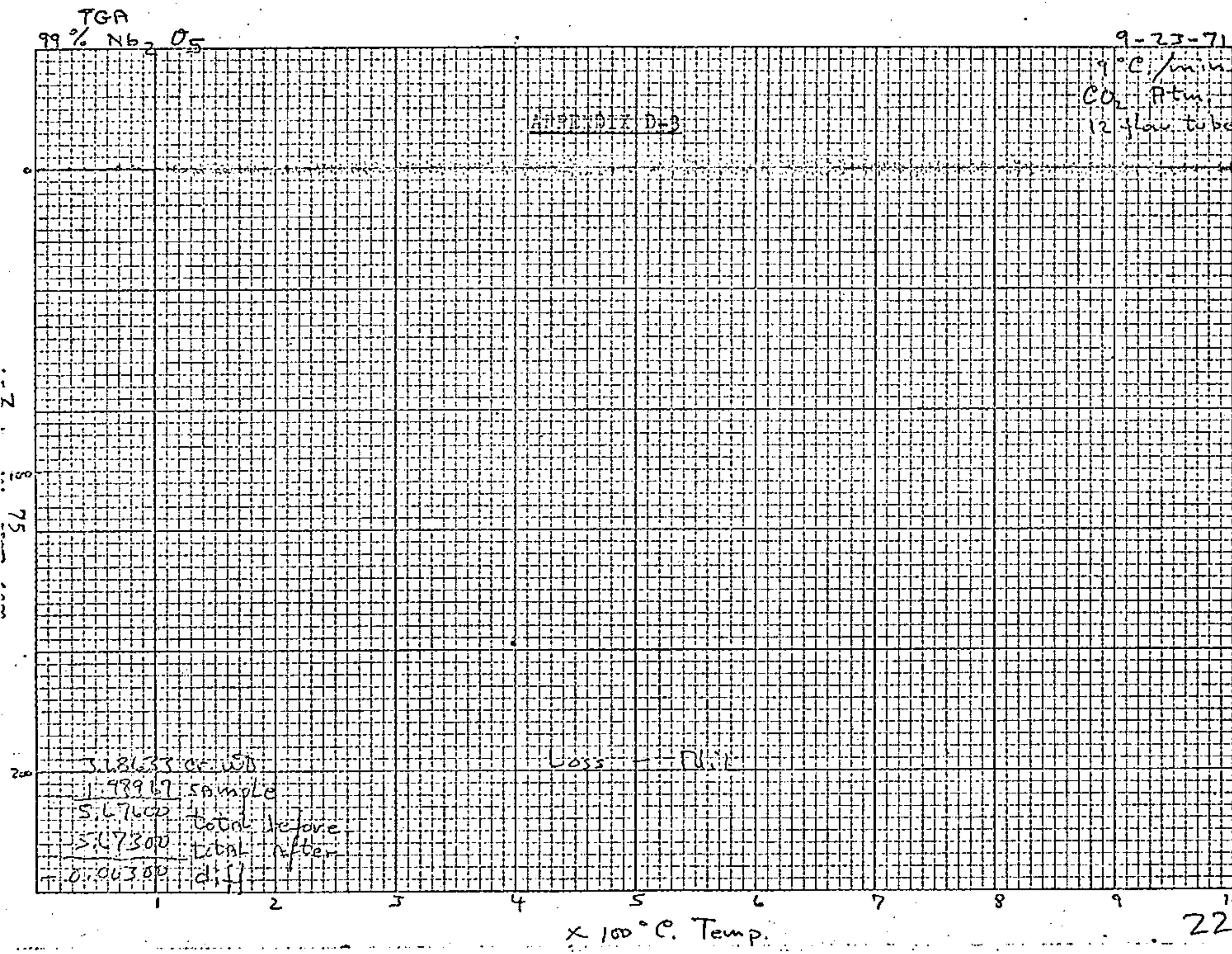
All formulas normalized to 3 oxygen atoms/molecule

Appendix B

APPENDIX D-1


TGA
99% Nb_2O_5
9-22-71
9°C/min
H_2 Atm.
7 flow tube
APPENDIX D-1
After cooling to ambient
0
100
200
Wt. Loss in Mgr.
3.80849 cr.
1.99142 sample
5.80011 total before
5.76450 total after
-0.03611 diff.
Loss - 1.8% - 20
Final Color - Black
1
2
3
4
5
6
7
8
9
X 100 - C. Temp.


TGA
99% Nb_2O_5
9-23-71
9°C./min.
Flow Air Atm.
12 flow tube
APPENDIX D-2
Loss - Nil
3.71612 cr. wt.
1.99530 sample
5.71142 total before
5.71000 total after
-0.00142 d.H
Wt. Loss in Mgs.
100
200
1
2
3
4
5
6
7
8
9
10
X 100 °C. Temp.
219


TGA
99% Nb_2O_5
9-23-71
9°C./min.
CO_2 Atm.
12 flow tube
APPENDIX D-3
0
100
75
200
Loss — Nil
3.18633 cr. wd
1.98967 sample
5.67600 total before
5.67300 total after
0.00300 diff
1
2
3
4
5
6
7
8
9
10
× 100 °C. Temp.