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**CANADA**

**DEPARTMENT OF MINES AND TECHNICAL SURVEYS**

**OTTAWA**

**MINES BRANCH INVESTIGATION REPORT IR 62-80**

**THE STUDY OF CARBONATE MINERALS  
FROM THE WABUSH LAKE AREA, LABRADOR**

by

**N. F. H. BRIGHT & R. H. LAKE**

**MINERAL SCIENCES DIVISION**

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by

Norman F. H. Bright\* and Richard H. Lake\*\*

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SUMMARY OF RESULTS

A study of a group of seven carbonate mineral samples from the Wabush Lake area of Labrador has been conducted using differential thermal analysis, thermogravimetric analysis, X-ray diffraction and petrographic microscopical procedures. It has been found possible to determine the proportions of calcium, magnesium, iron and manganese carbonates present and to deduce a consistent assessment of their combination to form the various possible carbonate minerals. Certain accessory minerals, principally a varying amount of quartz, were also identified as being present. This work was done on behalf of a Post-doctorate Fellow attached to the Geological Survey of Canada.

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## INTRODUCTION

At the end of 1961, a request was received from the Geological Survey of Canada for an examination in the Mineral Sciences Division, Mines Branch, of a group of carbonate minerals from the Wabush Lake area of Labrador. The scientists concerned with this work were Dr. K.L. Chakraborty, an N.R.C. Post-doctorate Research Fellow from India, and Dr. G.A. Gross of the Economic Geology Division. This request is given as Appendix I to this report (see page 29). In January, 1962 it was agreed to undertake this work (see Appendix II, page 30).

Insofar as the Mineral Sciences Division of the Mines Branch was concerned, the larger part of the work, involving differential thermal analysis, thermogravimetric analysis and X-ray diffraction examination of the materials, was undertaken in the Physical Chemistry Section. Semi-quantitative emission spectrographic results were produced in the Spectrographic Laboratory, Analytical Chemistry Subdivision. Dr. Chakraborty himself supplied the results of a petrographic microscope study of the minerals concerned.

This report contains details of the results obtained in these various locations by the above-mentioned techniques. Although the original request mentioned ten samples, only seven were, in fact, supplied and examined.

## EXPERIMENTAL TECHNIQUES

The techniques employed in the Physical Chemistry Section in this investigation were three-fold, namely; differential thermal analysis (DTA), thermogravimetric analysis (TGA), and X-ray diffraction examination (XRD). Brief details concerning these three techniques, which are all standardized procedures, are given below.

### (a) Differential Thermal Analysis

The technique of DTA is well-known and need not be described in detail here. In the current tests, the heating rate was 12 deg C per min. The samples were heated in a palladium sample holder, against alumina as the standard reference material. Pt to Pt:13% Rh thermocouples were used to measure the sample and differential temperatures. Experiments

were made in air and in flushing CO<sub>2</sub> atmospheres from room temperature up to 1100°C-1200°C.

(b) Thermogravimetric Analysis

The thermogravimetric analyses were conducted in a Stanton Recording Thermobalance. The heating rate was approximately 385 deg C per hr and the tests were made in CO<sub>2</sub>, and occasionally in air, from room temperature up to 1000°C-1100°C. The sample weights were determined directly on an analytical balance, both before and after the experiments, as a check on the thermobalance readings.

(c) X-ray Diffraction

The samples, as received, were submitted to the standard procedures of X-ray diffraction examination. Solid rollings of the powders were examined using filtered CuK radiation in 57.3 mm Debye-Scherrer powder cameras. The resulting patterns were measured and identified, as far as possible, by comparison with the data published in the X-ray Powder Data File issued by the American Society for Testing and Materials, or with standard patterns in the possession of the Physical Chemistry Section.

In interpreting X-ray diffraction patterns, the following limitations of the technique must be borne in mind. Crystalline constituents that are present in quantity less than about 5% of the total will probably not be detected, and those less than about 2% will almost certainly not be detected. Any amorphous material present cannot be identified, and even its presence can be detected only when a substantial amount occurs. In this investigation, the relative abundance of the constituents present was assessed merely on the basis of the relative strengths of their diffraction patterns and, hence, this information should be considered as an approximation only. The strength of the diffraction pattern is, in fact, dependent not only on the abundance of the material giving rise to it, but also on the crystalline symmetry of the materials, their degree of crystallinity, and the chemical nature of the atoms present. Compounds of high symmetry give patterns containing relatively few, but intense, diffractions, while those of low symmetry give numerous weaker diffractions. Patterns of well-crystallized materials consist of sharp, well-defined lines, while those of poorly-crystallized materials consist of broad, diffuse lines. Compounds of heavy atoms tend to give stronger patterns, other things being equal, than do compounds of lighter elements.

In the problem that forms the subject of the present report, there is, in addition, another factor that must be borne in mind in interpreting the X-ray diffraction patterns. In the case of the various mineral carbonates that could occur in the present samples, widespread solid solubility can occur between certain of the various possible end-members, giving X-ray diffraction patterns that cannot be specifically and exactly identified. The carbonates involved are calcite ( $\text{CaCO}_3$ ), magnesite ( $\text{MgCO}_3$ ), siderite ( $\text{FeCO}_3$ ) and rhodocrosite ( $\text{MnCO}_3$ ). Certain more or less stoichiometric compounds are known, involving two or more of these carbonates, e.g., dolomite [ $\text{CaMg}(\text{CO}_3)_2$ ], and ankerite [ $\text{CaFe}(\text{CO}_3)_2$ ].

These single carbonates, the stoichiometric double carbonate compounds, and solid solutions between two or more of the single carbonates, where such are possible, all give somewhat similar X-ray diffraction patterns. Hence, the interpretation may be difficult and some of the results open to ambiguity. However, comparison with patterns from known materials was of considerable assistance in identifying the present materials.

#### (d) Spectrographic Analysis

The samples were examined by semi-quantitative emission spectrography for the commoner cations and silicon. This work was conducted in the Spectrographic Section, Analytical Chemistry Subdivision, Mineral Sciences Division, Mines Branch.

#### (e) Microscope Study

This was made by Dr. K.L. Chakraborty in the laboratories of the Geological Survey. He used thin sections of the various minerals concerned and also crushed material of various particle sizes. The thin sections were examined for colour and the presence of inclusions. The optic sign and refractive indices of the main carbonate minerals were determined and comments made on the various subsidiary minerals associated with the carbonates. The results of this study have been included in this report for the sake of completeness, although the authors had no part in the production of them. The findings were accepted exactly as supplied by Dr. Chakraborty. Their significance in relation to the findings by the other techniques is, however, considered in the section dealing with the discussion of the results (see pages 21 to 28).

## EXPERIMENTAL RESULTS

The results of the optical examination of the minerals by Dr. K.L. Chakraborty are given in Table 1.

The results of the semi-quantitative emission spectrographic examination of the samples are given in Table 2.

The results of the X-ray diffraction examination of the samples are given in Table 3.

The results of the analysis of the thermogravimetric traces of the samples, when examined in a flushing  $\text{CO}_2$  atmosphere, are given in Table 4. Sample W 5 was the only sample examined in air by this technique; no additional information was obtainable from this examination; hence, the results reported are exclusively those obtained in carbon dioxide. Attention is drawn to the footnote to Table 4, which explains the basis on which the various weight losses due to  $\text{CO}_2$  evolution have been converted into carbonate contents in the sample, as received. A typical thermogram is shown in Figure 1 to indicate the type of result obtained by this technique. The thermograms of all the other samples exhibited the same types of characteristic weight changes, varying in magnitude according to the amounts of the individual carbonates present.

TABLE 1

Optical Examination of Wabush Lake Carbonate Minerals

(Results of tests made by Dr. K.L. Chakraborty, G.S.C.).

Sample No.	Colour in Thin Section	Inclusions	Refractive Index at 25°C (Along ordinary ray)	Optic Sign	Mineral Association
W 5	Colourless. Transparent.	Few grains have dusty inclusions of iron oxide.	$N_o = 1.795$	Uniaxial negative	Quartz.
W 6	Colourless. Transparent.	Nil	$N_o = 1.710$	Uniaxial negative	Quartz.
60-GF-55	Colourless. Transparent.	Grains frequently have dusty inclusions of magnetite.	$N_o = 1.755$	Uniaxial negative	Quartz.
60-GF-62	Colourless. Transparent.	Nil	$N_o > 1.80 (?)$	Uniaxial negative	Quartz. Amphibole (?). Chlorite (?).
60-GF-65	Colourless. Transparent.	Nil	$N_o = 1.676$	Uniaxial negative	Quartz. Second variety of transparent carbonate with R.I. less than that of bulk. Few grains of tremolite (?).
60-GF-66A	Colourless. Transparent.	Nil	$N_o = 1.715$	Uniaxial negative	Quartz. Chlorite (?).
60-GF-66B	Greyish. Transparent. Absorption pleochroism visible in thick grains.	Grains sometimes have dusty inclusions of fine grains of magnetite.	$N_o > 1.80$	Uniaxial negative	Quartz. Second variety of transparent carbonate with R.I. < 1.70. Chlorite (?).



TABLE 2

Semi-Quantitative Spectrographic Analyses of Wabush  
Lake Carbonate Minerals\*

(Figures are in weight per cent)

Sample No.	Spec. Lab. No.	Elements										
		Si	Mn	Fe	Mg	Al	Ca	Cu	Ti	Ni	Be	Co
W 5	S 83	10	0.7	9	3	0.03	3	0.003	0.003	0.005	Tr	N.D.
W 6	S 84	6	0.7	8	4	0.004	9	0.002	N.D.	Tr	N.D.	N.D.
60-GF-55	S 85	3	2	9	8	0.01	6	0.003	Tr	N.D.	N.D.	Tr
60-GF-62	S 86	3	1	P.C.	4	0.08	0.6	0.003	Tr	Tr	N.D.	N.D.
60-GF-65	S 87	3	0.4	0.6	7	0.01	P.C.	0.002	N.D.	N.D.	N.D.	N.D.
60-GF-66A	S 88	9	2	2	3	0.07	5	0.003	Tr	Tr	N.D.	N.D.
60-GF-66B	S 89	P.C.	0.4	0.8	1	0.2	3	0.002	N.D.	0.008	0.01	N.D.

\* Information taken from Mineral Sciences Divisional Report MS-AC-62-176, incorporating Spectrographic Laboratory Report SL-62-029 by Miss E.M. Kranck.

The following abbreviations are used in the above table:

Tr = trace, P.C. = principal constituent, N.D. = none detectable.

TABLE 3

Results of X-ray Diffraction Examination\* of  
Wabush Lake Carbonate Minerals

Sample No.	Mesh (as supplied)	Constituents Identified			
		Major	Minor	Trace	Small Trace
W 5	-	Siderite ( $\text{FeCO}_3$ ) Quartz ( $\text{SiO}_2$ )	Dolomite [ $\text{CaMg}(\text{CO}_3)_2$ ]	-	-
W 6	-80+100	Dolomite	Quartz	Siderite	-
60-GF-55	-80+100	Dolomite Siderite	Quartz (small minor)	-	-
60-GF-62	-80+100	Siderite	-	Quartz	-
60-GF-65	-80+100	Dolomite Calcite ( $\text{CaCO}_3$ )	Quartz (small minor)	-	-
60-GF-66A	-100+150	Quartz	Dolomite	-	Siderite
60-GF-66B	-100+150	Quartz	-	Dolomite	-

\* Examinations made by Mr. J.F. Rowland and Mr. E.J. Murray, Physical Chemistry Section.

TABLE 4

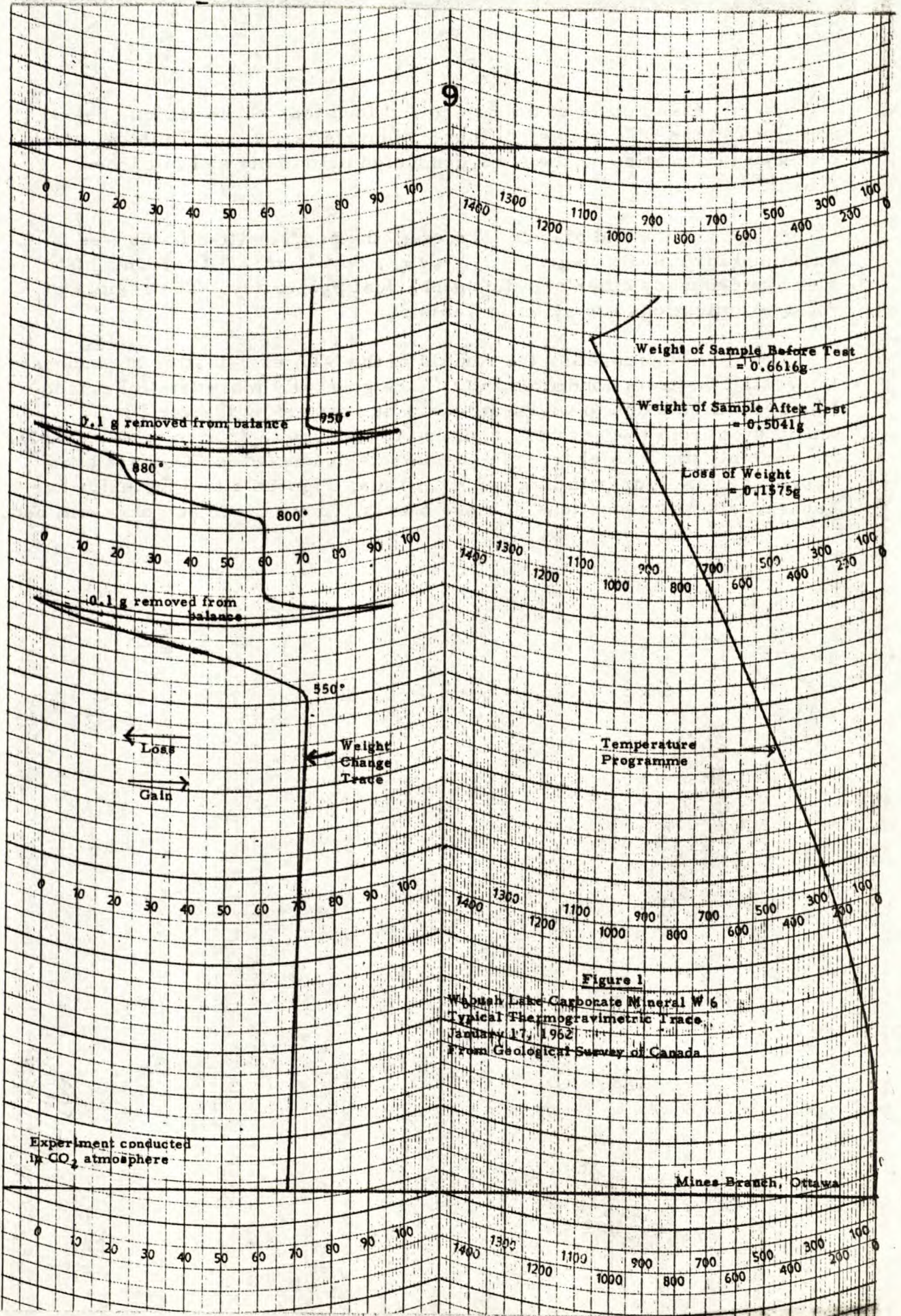
Analysis of Thermogravimetric Results on  
Wabush Lake Carbonates

(Samples examined in flushing CO<sub>2</sub> atmosphere).

Sample No.	Temperature Range (°C)	% Change in Weight (- = loss; + = gain)	Total % Weight Change to Maximum Temp.	% Mineral Carbonate Causing Losses*	Total Percentage Carbonate in Sample*
W 5	RT-540	-0.2	-19.1	} (Fe, Mn)CO <sub>3</sub> = 41.0 } MgCO <sub>3</sub> = 4.2 } CaCO <sub>3</sub> = 3.2	48.4
	540-675	-15.4			
	675-805	-0.1			
	805-861	-2.1			
	861-885	0			
	885-940	-1.4			
	940-1150	+0.1			
W 6	RT-550	+0.1	-30.6	} (Fe, Mn)CO <sub>3</sub> = 45.0 } MgCO <sub>3</sub> = 11.3 } CaCO <sub>3</sub> = 17.5	73.8
	550-700	-17.2			
	700-800	0			
	800-880	-5.9			
	880-950	-7.7			
	950-1070	+0.1			
60-GF-55	RT-515	0	-37.6	} (Fe, Mn)CO <sub>3</sub> = 79.4 } MgCO <sub>3</sub> = 5.4 } CaCO <sub>3</sub> = 10.9	95.7
	515-720	-30.2			
	720-820	0			
	820-885	-2.8			
	885-955	-4.8			
	955-1050	+0.2			
60-GF-62	RT-491	0	-31.9	} (Fe, Mn)CO <sub>3</sub> = 84.1	84.1
	491-645	-32.0			
	645-930	+0.1			
60-GF-65	RT-630	-0.1	-39.3	} (Fe, Mn)CO <sub>3</sub> = 0.3 } MgCO <sub>3</sub> = 21.1 } CaCO <sub>3</sub> = 64.1	85.5
	630-800	-10.0			
	800-880	-1.0			
	880-994	-28.1			
	994-1055	-0.1			
	1055-1140	0			
60-GF-66A	RT-590	0	-13.5	} (Fe, Mn)CO <sub>3</sub> = 19.7 } MgCO <sub>3</sub> = 2.7 } CaCO <sub>3</sub> = 10.2	32.6
	590-740	-7.5			
	740-825	-0.1			
	825-880	-1.4			
	880-923	-4.5			
	923-1000	0			
60-GF-66B	RT-655	-0.1	- 5.0	} (Fe, Mn)CO <sub>3</sub> = 6.8 } MgCO <sub>3</sub> = 1.7 } CaCO <sub>3</sub> = 3.4	11.9
	655-720	-2.5			
	720-810	0			
	810-870	-0.9			
	870-940	-1.5			
	940-1025	0			

Notes:- RT = Room temperature

\* In calculating the percentages of FeCO<sub>3</sub>, MnCO<sub>3</sub> and total carbonates, the FeCO<sub>3</sub> and MnCO<sub>3</sub> have been combined since they cannot be resolved thermogravimetrically. It has also been assumed that the Fe:Mn ratio is 5:1 on an atomic basis. This figure will not be strictly true in any individual case, but no serious error will have been introduced since the molecular weights of FeCO<sub>3</sub> and MnCO<sub>3</sub> are extremely close, 115.86 and 114.95 respectively. The figures given for the individual carbonates carry no implication as to how the carbonates may be combined crystallographically into such minerals as dolomite, ankerite, etc.



A summary of the nature and locations of the various peaks observed in the DTA studies of these minerals is given in Table 5, which includes information on the tests conducted both in air and in carbon dioxide.

At the end of each DTA test, the product after firing was examined for colour, degree of sintering, development of ferromagnetic behaviour and any other significant physical properties. The results of these examinations are given in Table 6.

In interpreting the results of the DTA examination of carbonate minerals, the tests conducted in  $\text{CO}_2$  are generally more fruitful since this procedure tends to segregate the peaks caused by the various carbonates from one another, and also to sharpen their form considerably. Hence, only the DTA charts of experiments conducted in  $\text{CO}_2$  have been reproduced as figures in this report. Thus, Figures 2 to 8 inclusive are reduced-size reproductions of these charts, one for each sample examined.

TABLE 5

DTA Observations with Wabush Lake Carbonate Minerals

(+ = exothermic peak; - = endothermic peak).

Sample No.	Atmosphere Unit	Peak Observations			Comments		
		Temperature (°C)		Size		Thermal Sign	
		Test 1	Test 2				
W 5	Air	572	573	Moderate	-	Very sharp.	
		599	613	Small	+		
		621	635	Large	-		
		650	657	Very large	+		Very sharp.
		865	809	Moderate	-		
		876	859	Fairly large	-		
	CO <sub>2</sub>	573-9	Small	-	Very sharp.		
	630	Large	-				
	675	Moderate	-				
	853	Moderate	-	Shoulder at 861°C. Very sharp.			
	920	Large	-				
	962	Small	+				
	W 6	Air	573-574			Small	-
			660-673		Small	-	
691-710				Small	+		
799-806				Large	-		
810-821				Moderate	+		
842-858				Moderate	-		
900-934			Very large	-			
CO <sub>2</sub>		578	Small	-	Very sharp. Shoulder at 620°C.		
608		Moderate	-				
692		Large	-				
760		Very small	-				
859		Large	-				
935		Very large	-				
970		Small	+				
60-GF-55	Air	575		Very small		-	Sharp.
		635		Very small	-		
		672		Large	-		
		709		Moderate	-		
		733		Moderate	+		
		808		Moderate	-		
	903		Very large	-			
	CO <sub>2</sub>	576	Very small	-	Sharp. Broad. Sharp, with small shoulder at 907°C.		
	667	Very large	-				
	853	Moderate	-				
	926	Very large	-				
	990	Moderate	+				
	60-GF-62	Air	537			Small	-
			637		Very large	-	
701				Very large	+		
841				Very small	+		
898				Small	+		
CO <sub>2</sub>			507	Small	-	Sharp.	
637		Extremely large	-				
830		Very small	-				
858		Very small	-				
907		Small	-				

(Continued)

TABLE 5 (Concluded)

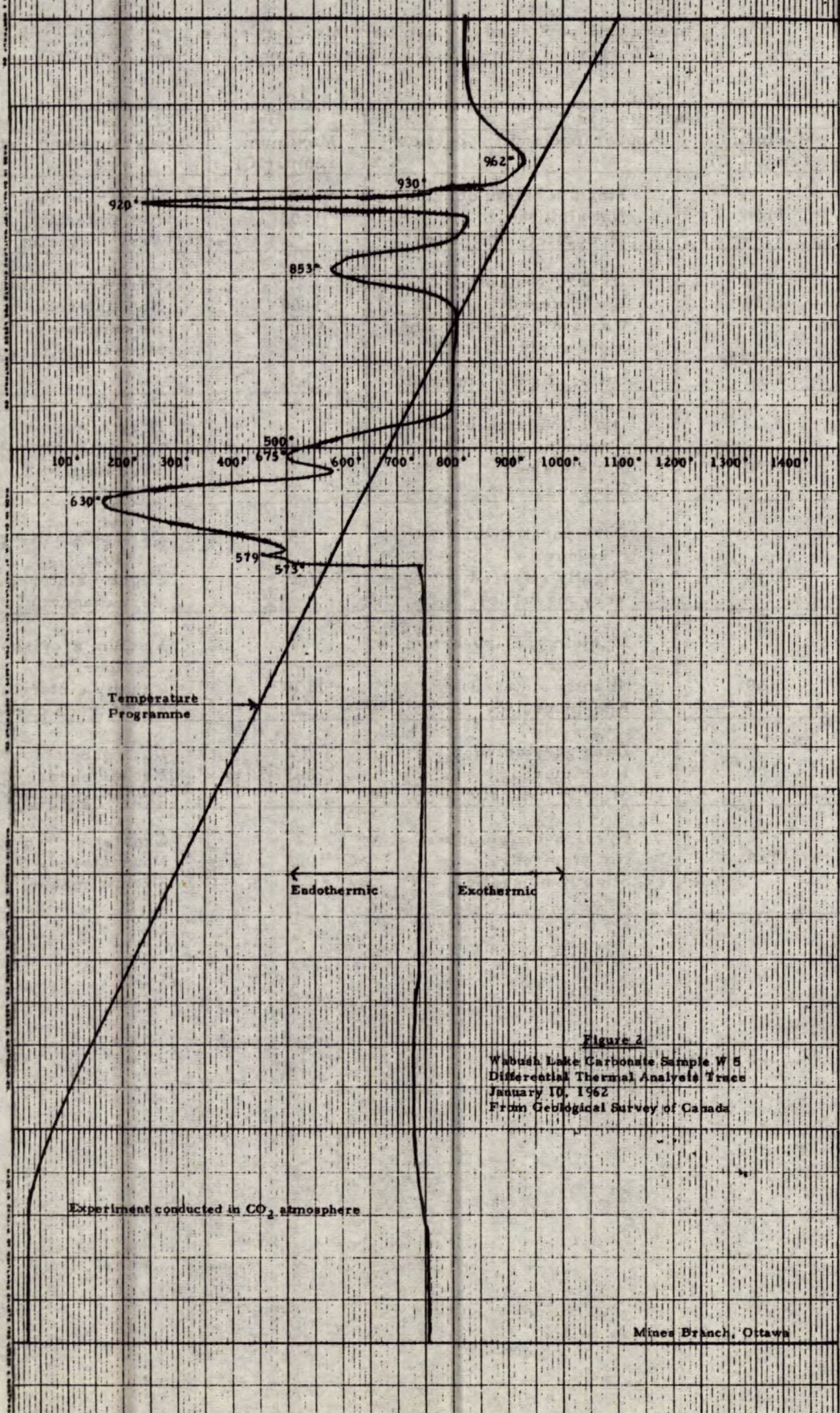
Sample No.	Atmosphere Unit.	Peak Observations			Comments
		Temperature (°C)	Size	Thermal Sign	
60-GF-65	Air	573 780 967	Very small Large Extremely large	- - -	Sharp.
	CO <sub>2</sub>	580 773-793 994	Very small Large Extremely large	- - -	Sharp. Broad.
60-GF-66A	Air	574 680 709 773 791 880	Moderate Very small Very small Large Moderate Large	- - + - - -	Very sharp. Broad. Broad. Very sharp.  Shoulder at 912°C.
	CO <sub>2</sub>	576 679 740 799 844-860 942	Moderate Small Large Small Small Large	- - - + - -	Very sharp.  Shoulder at 718°C.  Double-headed peak. Very sharp, with shoulder at 923°C.
60-GF-66B	Air	577 801 848	Moderate Large Moderate	- - -	Very sharp. Extremely sharp. Shoulders at 858°C and 881°C.
	CO <sub>2</sub>	576 754 773 838 934	Moderate Large Small Small Large	- - + - -	Very sharp.  Sharp. Broad. Sharp.

TABLE 6

Physical Properties of Wabush Lake Minerals after Thermal Treatment in DTA Examination

Sample No.	Heated in Air		Heated in CO <sub>2</sub> Atmosphere	
	Maximum Temp. (°C)	Appearance and Properties	Maximum Temp. (°C)	Appearance and Properties
W 5	1100	Medium brown colour. Not sintered. Moderately magnetic.	1105	Medium brown colour. Not sintered. Very magnetic.
W 6	1030	Dark brown colour. Not sintered. Considerable expansion. Moderately magnetic.	1100	Dark brown colour. Not sintered. No expansion. Moderately magnetic.
	1165	Ditto; slightly sintered.		
60-GF-55	1130	Dark brownish-black colour. Not sintered. Very magnetic.	1180	Dark brownish-black colour. Not sintered. Very magnetic.
60-GF-62	1115	Dark purplish-brown colour. Slightly sintered. Very magnetic.	1085	Dark purplish-brown colour. Slightly sintered. Very magnetic.
60-GF-65	1150	Medium greyish-brown colour. Slightly sintered. Non-magnetic.	1130	Medium greyish-brown colour. Slightly sintered. Slight trace of magnetism.
60-GF-66A	1100	Dark grey colour. Not sintered. Slightly magnetic.	1065	Dark grey colour. Not sintered. Slightly magnetic.
60-GF-66B	1110	Greyish-brown colour. Not sintered. Slightly magnetic.	1065	Greyish-brown colour. Not sintered. Slightly magnetic.





**Figure 2**  
Wabush Lake Carbonate Sample W 5  
Differential Thermal Analysis Trace  
January 10, 1962  
From Geological Survey of Canada

Experiment conducted in CO<sub>2</sub> atmosphere

Mines Branch, Ottawa

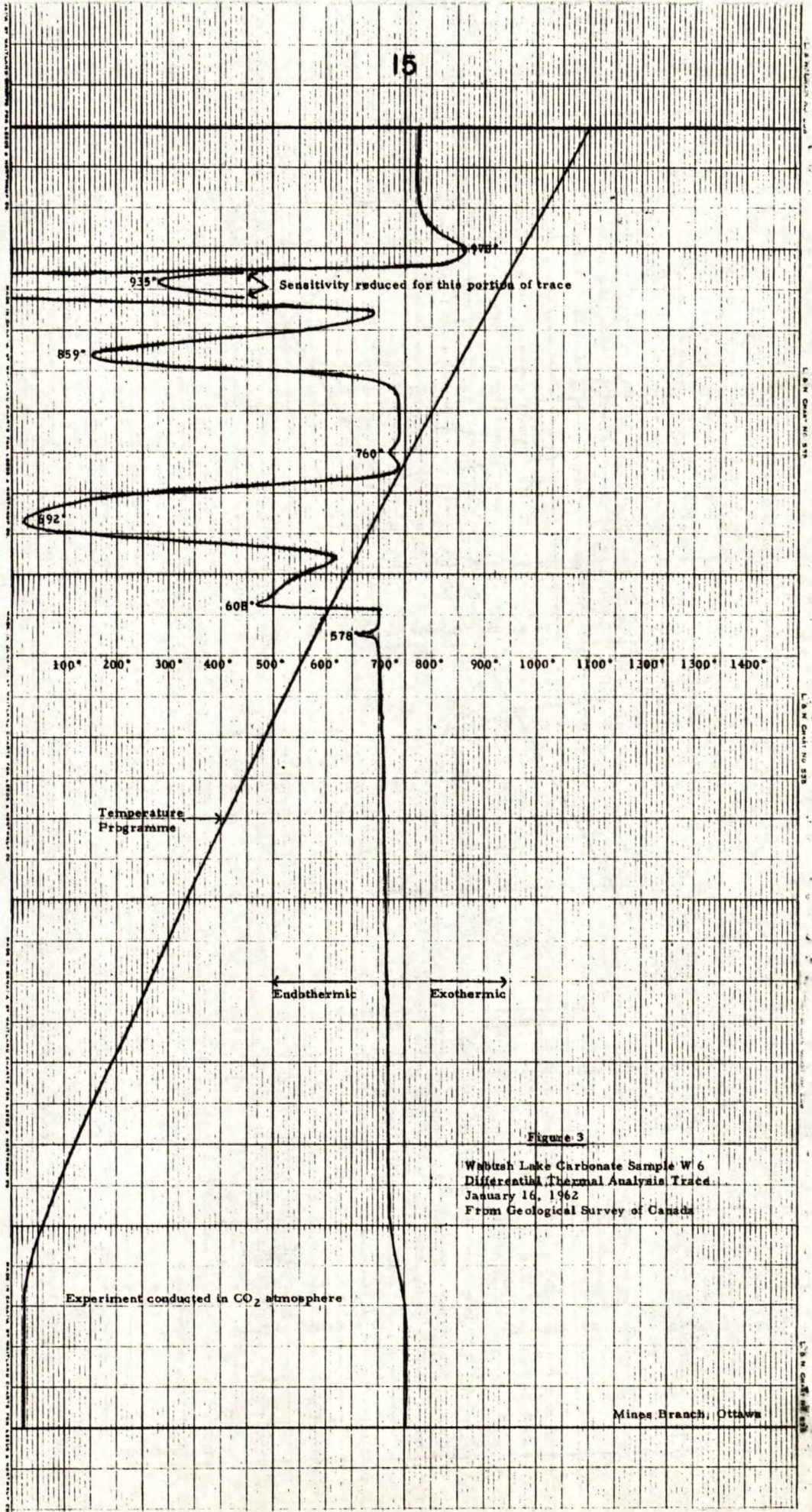


Figure 3  
White Lake Carbonate Sample W 6  
Differential Thermal Analysis Trace  
January 16, 1962  
From Geological Survey of Canada

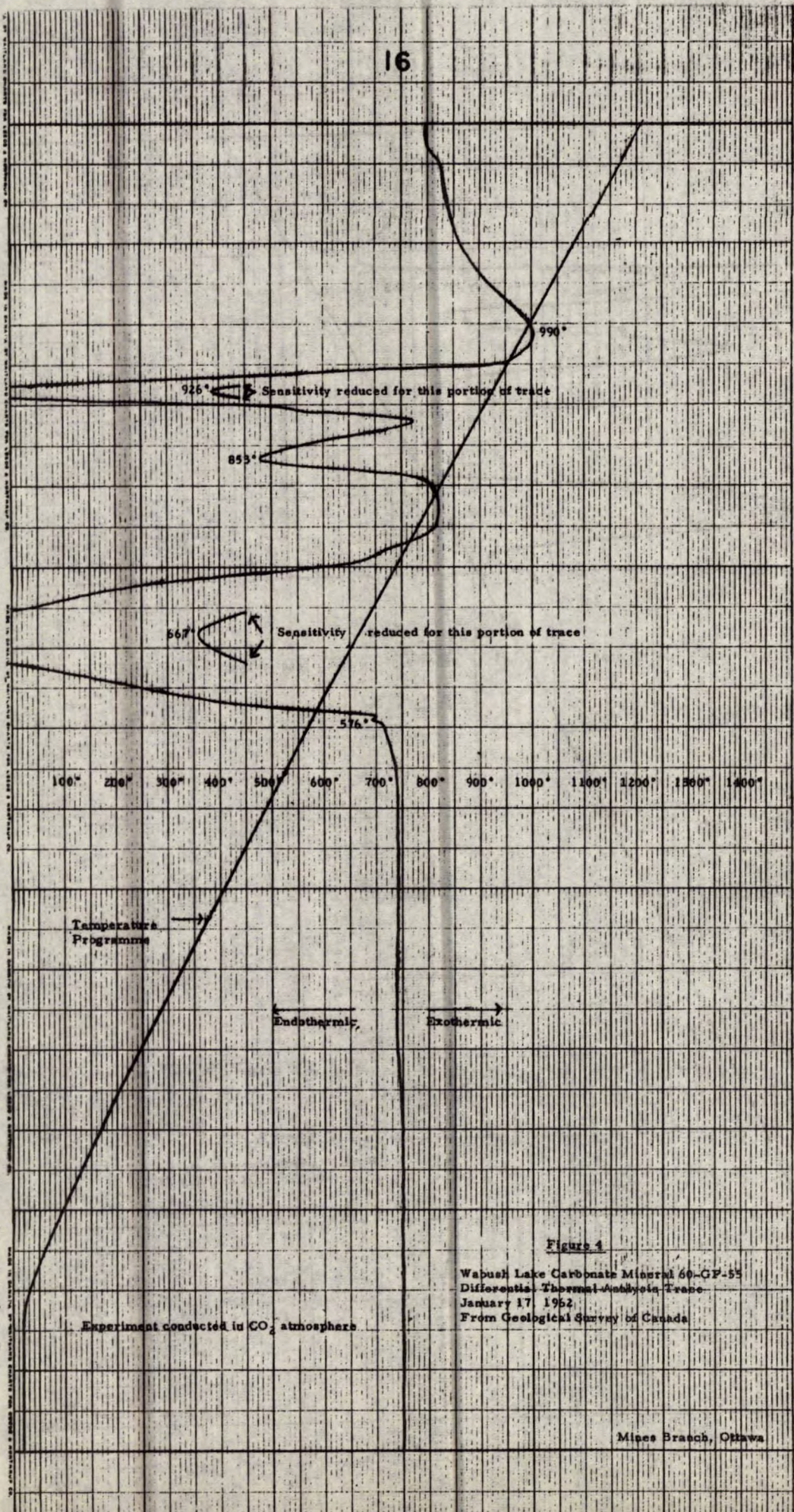
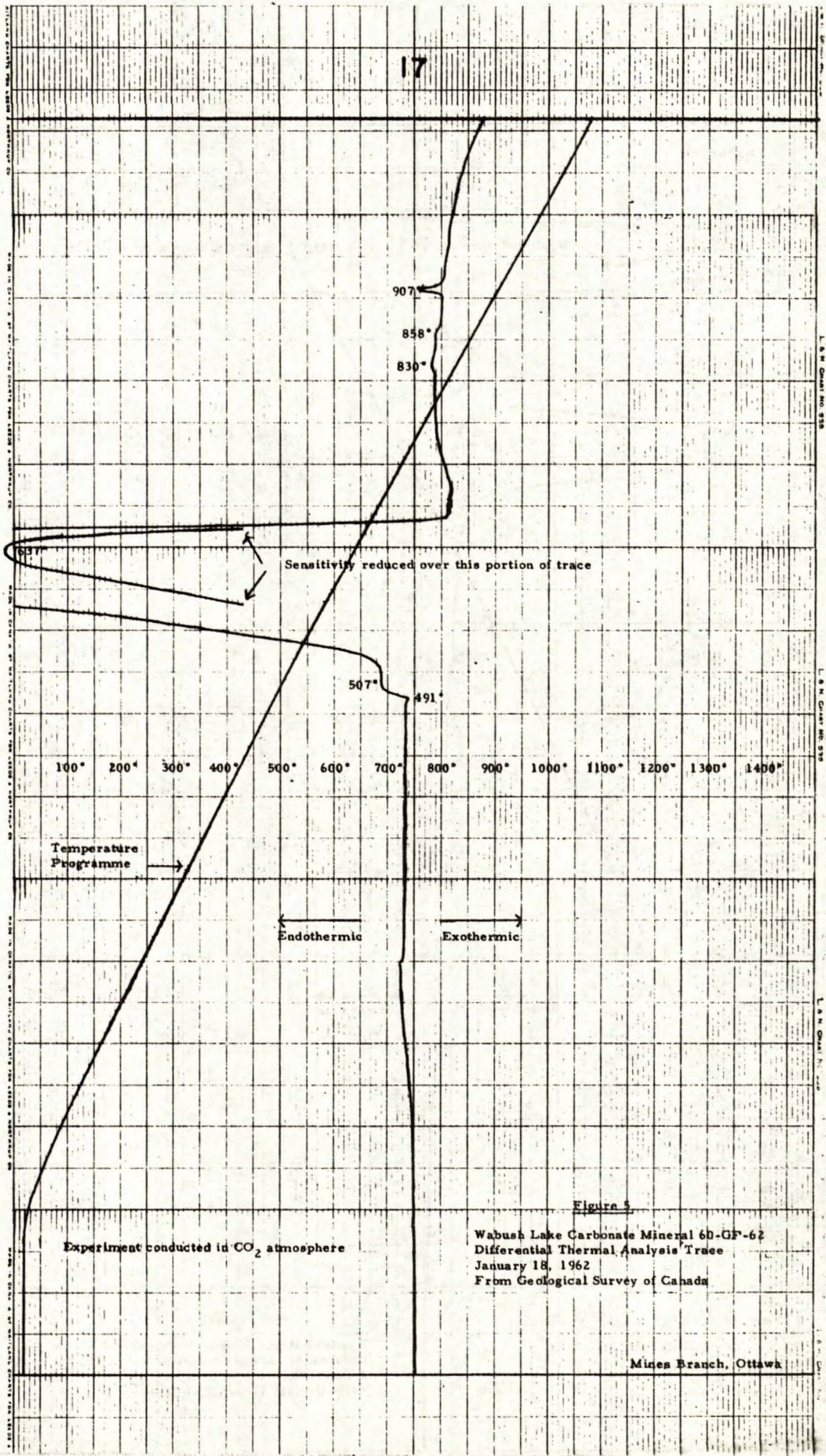


Figure 4

Wabush Lake Carbonate Mineral 60-GF-55  
 Differential Thermal Analysis Trace  
 January 17, 1962  
 From Geological Survey of Canada

Experiment conducted in CO<sub>2</sub> atmosphere



Temperature Programme

Endothermic

Exothermic

Sensitivity reduced over this portion of trace

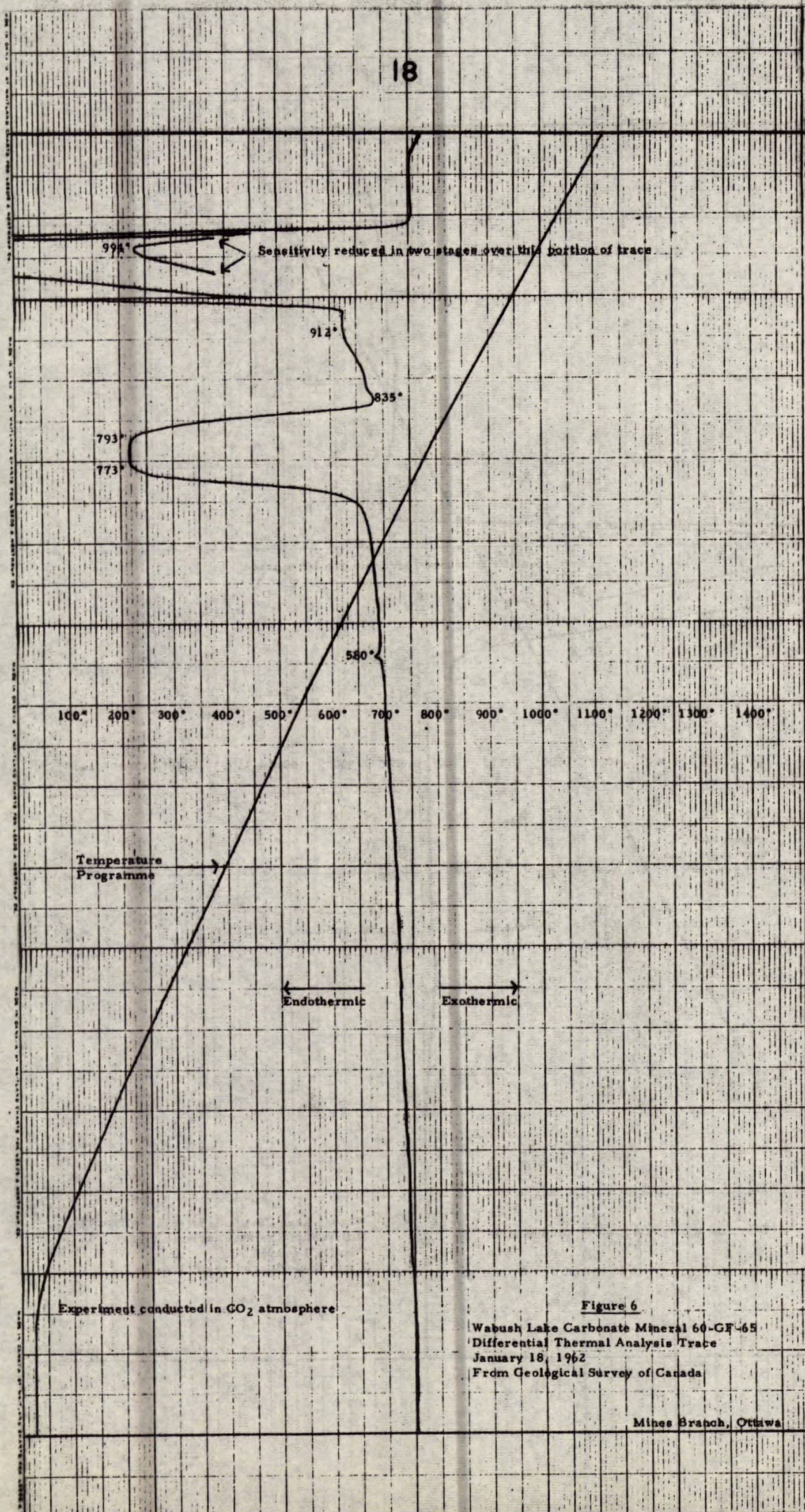
Experiment conducted in CO<sub>2</sub> atmosphere

Figure 5

Wabush Lake Carbonate Mineral 60-GP-62  
Differential Thermal Analysis Trace  
January 18, 1962  
From Geological Survey of Canada

Mines Branch, Ottawa

18

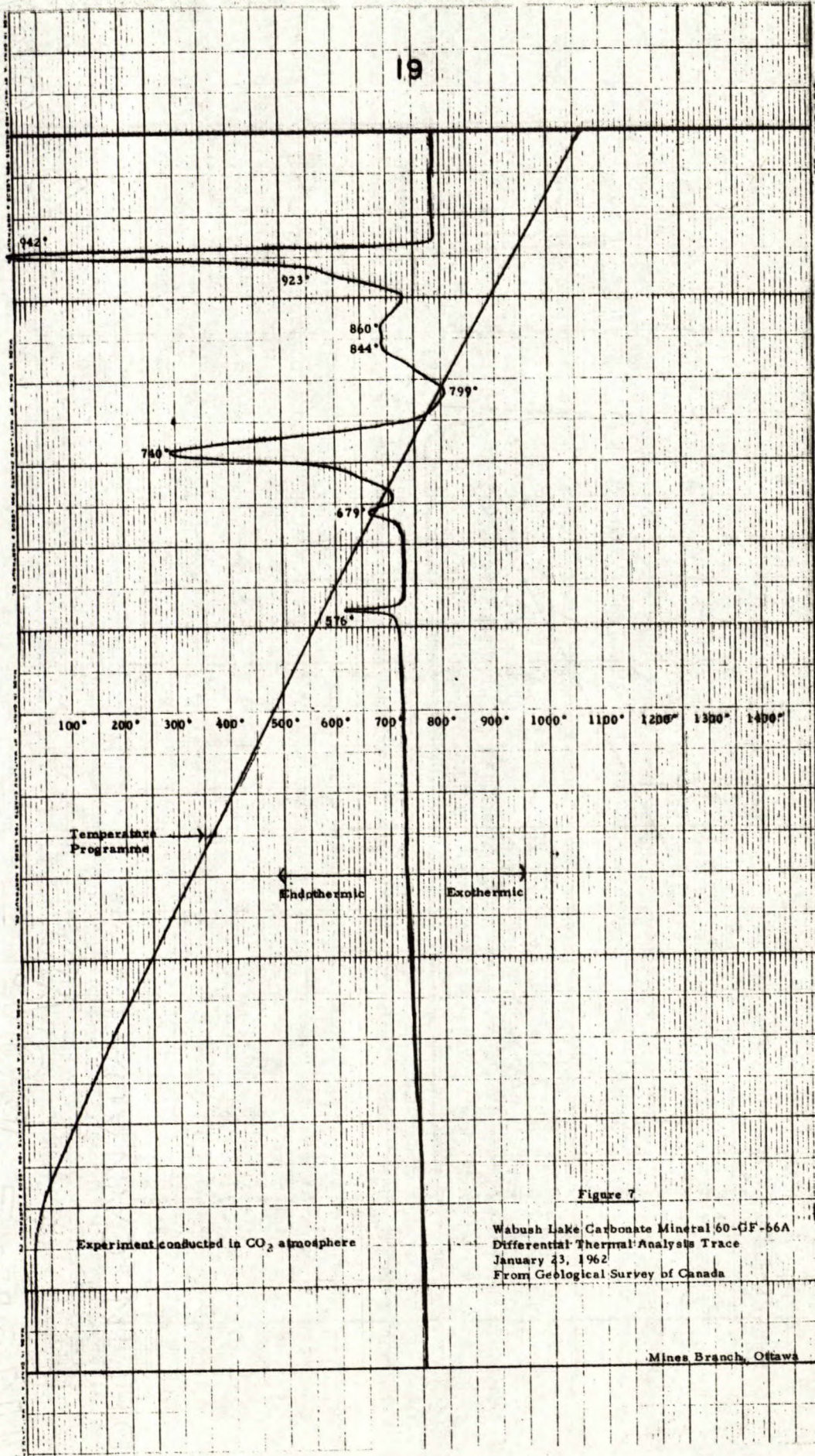


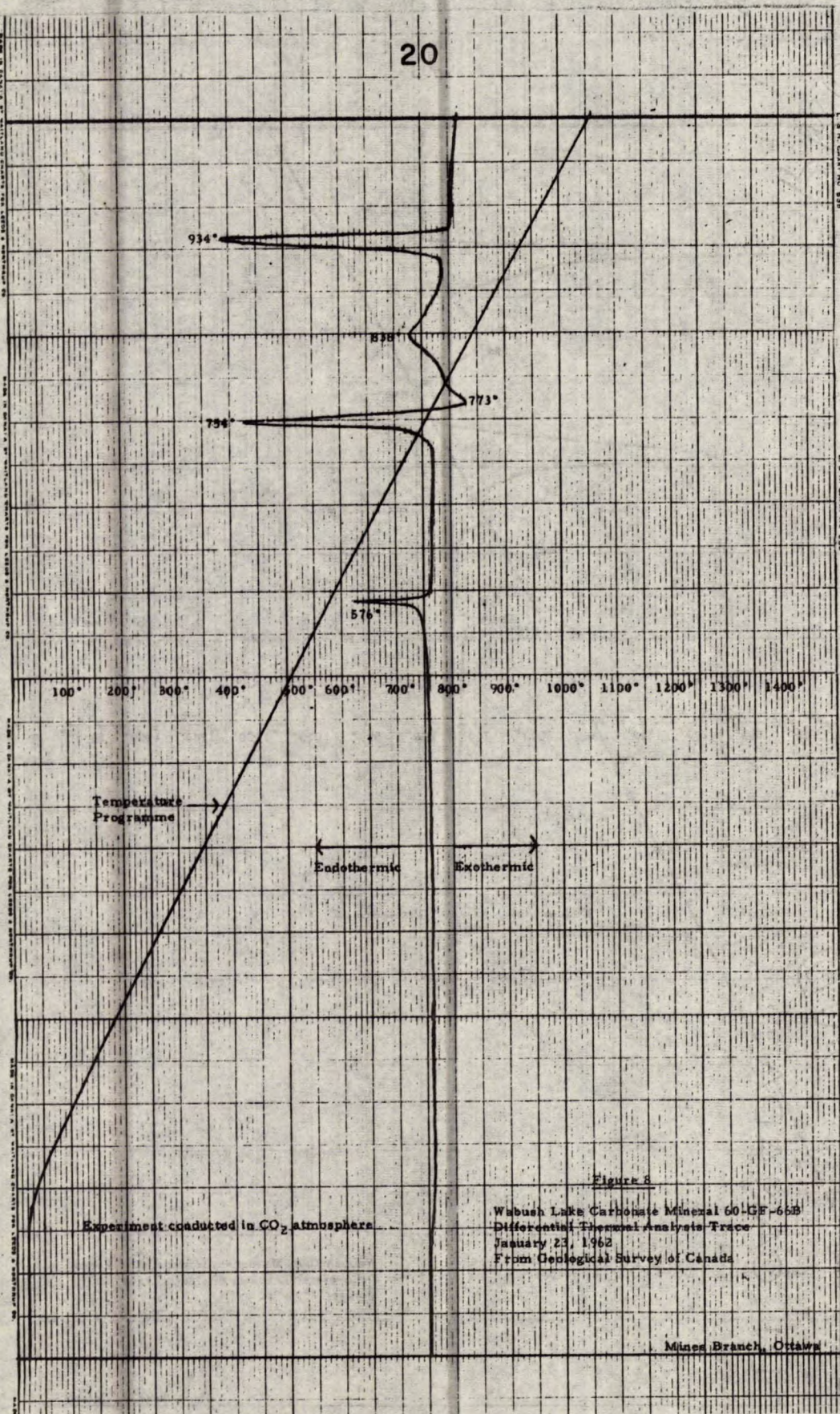
Experiment conducted in CO<sub>2</sub> atmosphere

Figure 6

Wabush Lake Carbonate Mineral 60-GF-65  
Differential Thermal Analysis Trace  
January 18, 1962  
From Geological Survey of Canada

Mines Branch, Ottawa





Temperature Programme

Endothermic

Exothermic

Experiment conducted in CO<sub>2</sub> atmosphere

Figure 8  
 Wabush Lake Carbonate Mineral 60-GE-65B  
 Differential Thermal Analysis Trace  
 January 23, 1962  
 From Geological Survey of Canada

Mines Branch, Ottawa

## DISCUSSION OF RESULTS

The purpose of this discussion will be to correlate the experimental results obtained by the various techniques and reported in Tables 1 to 6 inclusive, in an attempt to arrive at a mineralogical composition of the various samples submitted, at least on a semi-quantitative basis, but preferably on a fully quantitative basis.

The thermogravimetric results reported in Table 4 give a reasonably quantitative estimate of the amounts of  $\text{CaCO}_3$ ,  $\text{MgCO}_3$  and  $(\text{Fe, Mn})\text{CO}_3$  present in the various samples, since the weight losses occurring in the temperature range  $870^\circ\text{C}$  and upwards will be due to the presence of  $\text{CaCO}_3$ , those in the range  $630^\circ\text{C}$  to  $880^\circ\text{C}$  will be due to the presence of  $\text{MgCO}_3$  and those in the range  $490^\circ\text{C}$  to  $740^\circ\text{C}$  will be due to the presence of  $(\text{Fe, Mn})\text{CO}_3$ . It will be observed that there is a certain amount of overlap in the temperature ranges quoted. This is caused by the wide variations in relative amounts of the carbonates present from sample to sample and, perhaps more important, by a variation in the way the various carbonates can occur, e.g.,  $\text{MgCO}_3$  can be present as free magnesite, as dolomite, or as a magnesitic ankerite;  $\text{FeCO}_3$  can be present as siderite, or as ankerite, and so on. The nature of the occurrence controls the temperature of the liberation of the  $\text{CO}_2$ . Thus the thermogravimetric results, while giving valid information on the gross amounts of the various carbonates present, do not solve the problem of their mineralogical distribution.

Similarly, a study of the refractive indices reported in Table 1 may, in some instances, give an indication of the nature of the main carbonate mineral in each sample. The figures given in this Table are the values of one of the two refractive indices of the predominant carbonate material present. All the possible carbonate minerals have the same general optical properties, and the refractive indices will vary continuously as one goes from any one end-member to any other, across a solid-solution series. In the case of a binary solid-solution series, the value of the refractive index would be sufficient data to enable the precise composition of the material concerned to be deduced. If, however, as is the case with most of the present materials, three or more carbonates may be involved in any one mineral species, then the refractive index data alone do not permit an unequivocal identification of the mineral, since the problem of identification is mathematically indeterminate. However, in those cases where the index is near the extreme end of the possible range for carbonate minerals, a reasonably certain identification becomes possible. Similarly, if one takes into account information obtainable from any other source that yields an additional parameter whereby the material may be assessed, then the refractive index data do become useful as a means of identification.

Table 7 gives the refractive indices of certain typical carbonate minerals, as taken from a standard reference.



TABLE 7

Refractive Indices of Carbonate Minerals

(Data taken from "The Microscopic Determination of the Non-Opaque Minerals", U.S. Geological Survey Bulletin # 848, published in 1934, by E.S. Larsen and H. Berman).

Composition in mol. per cent				Refractive Index N <sub>o</sub>	Name
CaCO <sub>3</sub>	MgCO <sub>3</sub>	FeCO <sub>3</sub>	MnCO <sub>3</sub>		
100	-	-	-	1.658	Calcite
50	50	-	-	1.681	Dolomite
53	37	10	-	1.698	Ankerite
52	26	22	-	1.716	"
48	11	38	3	1.749	"
-	100	-	-	1.700	Magnesite
-	85	15	-	1.726	"
58	-	-	42	1.721	"
-	-	-	100	1.817	Rhodocrosite
1	-	20	79	1.826	"
2	23	73	2	1.830	Siderite
-	7	77	16	1.849	"
5	5	90	-	1.855	"
-	-	100	-	1.875	"

Note: Smithsonite, the natural form of zinc carbonate has a refractive index (N<sub>o</sub>) of 1.849; however, the spectrographic analyses given in Table 2 do not indicate the presence of any significant amount of Zn; hence this mineral will be ignored in further discussion of the present samples.

By comparing the data in Table 7 with those given in Table 1, one can readily see in what range of composition the minerals giving the figures of Table 1 may lie in most instances. As mentioned above, however, the answer may be far from unequivocal. For example, a siderite with significant Ca or Mg substitution could readily have the same refractive index as a rhodocrosite ( $\text{MnCO}_3$ ); similarly, if magnesite ( $\text{MgCO}_3$ ) will tolerate a small degree of lime substitution, the resultant material could readily be confused with an ankerite (essentially  $\text{CaCO}_3 \cdot \text{FeCO}_3$ ) insofar as refractive index data are concerned. Nevertheless, one can hazard a reasonable suggestion as to the main carbonate mineral in each specimen from these refractive index figures thus:

Sample W 5:	Probably siderite
Sample W 6:	Probably ankerite
Sample 60-GF-55:	Probably ankerite and/or siderite
Sample 60-GF-62:	Siderite
Sample 60-GF-65:	Dolomite
Sample 60-GF-66A:	Probably ankerite
Sample 60-GF-66B:	Probably siderite

A study of the results obtained by semi-quantitative spectrographic analysis, as reported in Table 2, yields further information. In particular, there is a good indication from the percentage of Si of the amount of quartz present in each sample. This is supported strongly by

- (a) the X-ray diffraction results given in Table 3, and
- (b) the magnitude of the endothermic  $\alpha \rightarrow \beta$  quartz inversion DTA peak for the various samples, as reported in Table 5; this peak is recorded at temperatures in the range  $572^\circ - 580^\circ \text{C}$ .

From these considerations it would appear that Samples 66B, 66A and W 5 contain more quartz than the remaining materials, with 66B having the largest amount of all.

A consideration of the X-ray diffraction results reported in Table 3 also gives a qualitative guide as to the nature and abundances of the various minerals present. Again, as already pointed out on pages 2-3, it is not possible to be certain that the indication is absolutely correct, either as to relative abundance or even as to chemical identity. This is particularly true in the case of the minerals dolomite and ankerite, which are virtually indistinguishable by X-ray means.

It is from the DTA results that one gets the most useful information as to the actual nature of the minerals present and, when combined with the data from the TGA work, the true composition of the minerals can be deduced.

As already mentioned, the endothermic peak at about 573°C is due to the  $\alpha \rightarrow \beta$  inversion occurring in free quartz. The magnitude of this peak parallels closely the percentage of Si, as indicated by the spectrographic results.

The thermal decomposition of carbonate minerals has been studied extensively through use of the DTA technique by J. Lawrence Kulp, Paul F. Kerr and their co-workers at Columbia University, New York (1, 2, 3). From their work, it can be seen that the approximate temperatures associated with the endothermic loss of  $\text{CO}_2$  from the various single mineral carbonates encountered in the present samples are as follows:

Calcite ( $\text{CaCO}_3$ ),	980°C;
Magnesite ( $\text{MgCO}_3$ ),	685°C;
Dolomite [ $\text{CaMg}(\text{CO}_3)_2$ ],	two peaks at 790°C and 940°C;
Siderite ( $\text{FeCO}_3$ ),	580°C, followed by an exothermic peak when examined under oxidizing conditions;
Rhodocrosite ( $\text{MnCO}_3$ ),	630°C, followed by an exothermic peak when examined under oxidizing conditions;
Ankerite [ $\text{CaFe}(\text{CO}_3)_2$ ],	three peaks at 700°C, 840°C, and 910°C to 950°C.

The positions of these DTA peaks are, however, affected to a considerable extent by a) the presence of impurities, inert or otherwise, b) the state of division of the mineral, c) the precise experimental conditions of examination, d) the nature of the atmosphere under which the test is conducted, whether in air or in carbon dioxide, and e), of course, the extent of mutual substitution of the various metal ions involved. According to Kulp et al., complete ionic substitution appears to occur between the pairs Ca-Mn and Fe-Mg, whereas between Ca-Mg and Ca-Fe, however, the amount of substitution in a calcite-type lattice is very limited. Complete substitution between Fe and Mn, and between Mg and Mn appears possible, but is not completely represented in naturally-occurring carbonate minerals.

In addition to the complexities arising from the presence of several mineral species, and from the possibility of extensive inter-ionic substitution, one has also to allow for the interaction of the products of decomposition of the various species. For example, under oxidizing conditions, the iron carbonates can be expected to yield hematite,  $\text{Fe}_2\text{O}_3$ , and/or magnetite, depending upon the oxygen partial pressure and the temperature. The magnesium carbonate would yield  $\text{MgO}$ . Interaction

might then occur between MgO and  $\text{Fe}_2\text{O}_3$  to form  $\text{MgO}\cdot\text{Fe}_2\text{O}_3$ , magnesio-ferrite; this, in turn, could go into solid solution in the magnetite to give a complex spinel solid-solution product. In addition, manganese, which is present in some samples in reasonably significant quantity, can also enter this spinel phase. Again, a further complication that has to be taken into account is the possibility of the formation of  $\gamma$ -hematite or maghemite. It has recently been shown by G.H. Hickie (4) that when ferrous oxalate dihydrate is heated in air, the intermediate product of the decomposition is  $\gamma$ -hematite and that, on further heating, an exothermic reaction occurs, which is the conversion of  $\gamma$ -hematite to  $\alpha$ -hematite. It is not at all unreasonable to expect that the ferrous carbonate (or siderite) decomposition would follow a similar pattern under oxidizing conditions. The temperatures of the reactions, however, would probably be markedly higher since the endothermic loss of  $\text{CO}_2$  from  $\text{FeCO}_3$  occurs at approximately  $600^\circ\text{C}$ , whereas the endothermic loss of  $\text{CO}$  and  $\text{CO}_2$  from the oxalate occurs in the region of  $400^\circ\text{C}$ . If  $\gamma$ -hematite is formed, it, too, can enter into the complex spinel phase since it has a defect spinel structure. This, however, may be only a temporary state of affairs since, at higher temperatures, it might revert to the  $\alpha$ -form, which is hexagonal and could not form part of the spinel phase.

Another observation made by Kulp, Kerr, et al., which may well be relevant to the present problem concerns the decomposition of ankerite. Ankerite is essentially a calcium-ferrous iron carbonate in which the ferrous iron is generally substituted by a certain amount of magnesium in such a way that the number of magnesium ions plus the number of ferrous ions is equal to the number of calcium ions. The decomposition of ankerite shows three endothermic stages. The first of these peaks is due to the decomposition of the carbonate ions most closely associated with the magnesium and iron positions. The products after this first stage are calcite ( $\text{CaCO}_3$ ), MgO, and maghemite, the last being formed from FeO under oxidizing conditions. The magnitude of the second endothermic stage has been found to increase with the degree of iron substitution in the magnesium positions. It might be expected that this second endothermic peak was due to the formation of magnesio-ferrite,  $\text{MgO}\cdot\text{Fe}_2\text{O}_3$ , from the constituent oxides. A consultation of tables of thermodynamic data will show that the formation of a double oxide, such as a spinel, from its constituent oxides is usually accompanied by a small thermal effect, which can be either exothermic or endothermic, though more usually the former. However, in this case, the peak does not appear to be associated with magnesio-ferrite formation but rather, this second endothermic peak seems, according to Kulp, Kerr et al., to be due to the formation of a compound  $\text{CaCO}_3\cdot\text{Fe}_2\text{O}_3$ . Experiments in our own laboratories have shown that a mixture of finely ground hematite and calcite in 1:1 molar ratio produced the same peak as is observed with ankerite, and the product, when examined by X-ray diffraction, showed the presence of a material for which no published data are available, in addition

to residual hematite and calcite. No concomitant weight change occurs during this reaction.

Having now discussed the various possible reactions that could occur in such an assemblage of natural mineral carbonates, we have made an attempt to assess, from the results quoted earlier in this report, the actual nature of the minerals present in the current samples.

The results obtained from these various considerations, incorporating the knowledge obtained by each of the techniques employed, are given in Table 8.

TABLE 8

Approximate Mineralogical Composition of  
Wabush Lake Carbonate Samples

Sample No.	Constituents Present	Approximate amounts (wt. %)
W 5	<u>Major</u> : Quartz, $\text{SiO}_2$ .	50
	Siderite, $(\text{Fe}, \text{Mn})\text{CO}_3$ , with Mn content, probably quite low.	40
	<u>Minor</u> : Dolomite, $[\text{CaMg}(\text{CO}_3)_2]$ .	10
W 6	<u>Major</u> : Ankerite, $[\text{CaFe}(\text{CO}_3)_2]$ .	35
	Siderite, $(\text{Fe}, \text{Mn})\text{CO}_3$ , with Mn content quite low.	25
	<u>Moderate</u> : Quartz, $\text{SiO}_2$ .	20
	<u>Minor</u> : Magnesite, $\text{MgCO}_3$ .	10
60-GF-55	<u>Major</u> : Siderite $(\text{Fe}, \text{Mn})\text{CO}_3$ with a significant amount of Mn substitution.	60
	Ankeritic Dolomite, $[\text{Ca}(\text{Mg}, \text{Fe})(\text{CO}_3)_2]$ .	35
	<u>Small Minor</u> : Quartz, $\text{SiO}_2$ .	5

(Continued)

TABLE 8 (Concluded)

Sample No.	Constituents Present	Approximate amounts (wt. %)
60-GF-62	<p><u>Major:</u> Siderite, <math>(\text{Fe}, \text{Mn})\text{CO}_3</math> with some Mn substitution.</p> <p><u>Small Minor:</u> Quartz, <math>\text{SiO}_2</math>.</p>	<p>85</p> <p>5 (?)</p>
60-GF-65	<p><u>Major:</u> Calcite, <math>\text{CaCO}_3</math>.</p> <p>Dolomite, <math>[\text{CaMg}(\text{CO}_3)_2]</math> with a small degree of Fe and Mn substitution.</p> <p><u>Minor:</u> Quartz, <math>\text{SiO}_2</math>.</p>	<p>45</p> <p>40</p> <p>5</p>
60-GF-66A	<p><u>Major:</u> Quartz, <math>\text{SiO}_2</math>.</p> <p><u>Minor:</u> Ankerite, <math>[\text{CaFe}(\text{CO}_3)_2]</math>.</p> <p>Dolomite, <math>[\text{CaMg}(\text{CO}_3)_2]</math>.</p> <p>Siderite, <math>(\text{Fe}, \text{Mn})\text{CO}_3</math> with quite considerable Mn substitution.</p>	<p>50+</p> <p>20</p> <p>10</p> <p>5</p>
60-GF-66B	<p><u>Predominant Major:</u> Quartz, <math>\text{SiO}_2</math>.</p> <p><u>Small Minor:</u> Ankerite, <math>[\text{CaFe}(\text{CO}_3)_2]</math>.</p> <p>Dolomite, <math>[\text{CaMg}(\text{CO}_3)_2]</math>.</p>	<p>80-90</p> <p>} 10 (in total)</p>

It will be observed that, in some instances, the approximate amounts given do not total to 100%. This is entirely reasonable since, as indicated from the microscope observations recorded in Table 1, there are small quantities of various accessory minerals present whose amount is insufficient to be recorded by X-ray diffraction and whose DTA and TGA indications are either too small to be observed or are unequivocal in interpretation.

It will be seen by a comparison of the results quoted in Table 8 with the appearance and other physical properties of the fired materials, as listed in Table 6, that the extent of development of ferromagnetism and the colour of the product are both in good accord with the amounts of Fe present in the various samples. There is also general, though not perfect, agreement between the refractive index indications, as listed on page 5, and the results quoted in Table 8.

In general, it can be stated that the results indicated from the findings by the various techniques employed in this investigation are reasonably self-consistent and that the mineralogical composition of the various samples is essentially as reported in Table 8.

#### REFERENCES

1. P.F. Kerr and J.L. Kulp. "Differential Thermal Analysis of Siderite". American Mineralogist, Vol. 32, Nos. 11 and 12, pp. 678-680 (1947).
2. J.L. Kulp, H.D. Wright and R.J. Holmes. "Thermal Study of Rhodocrosite". American Mineralogist, Vol. 34, Nos. 3 and 4, pp. 195-219 (1949).
3. J.L. Kulp, P. Kent and P.F. Kerr. "Thermal Study of the Ca-Mg-Fe Carbonate Minerals". American Mineralogist, Vol. 36, Nos. 9 and 10, pp. 643-670 (1951).
4. G.H. Hickie. "The Thermal Decomposition of Ferrous Oxalate Dihydrate and the Preparation of Forsterite-Fayalite Olivines". Internal Report MS-60-86, September 14, 1960, of the Mineral Sciences Division, Mines Branch, Ottawa.

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(Appendices I and II  
follow on pages 29 and 30.)

APPENDIX I

MEMORANDUM. GOVERNMENT OF CANADA

TO: Dr. John Convey,  
Director, Mines Branch.

DATE: Dec. 20, 1961

Dr. K.L. Chakraborty, who is presently working in this Branch, has submitted 10 samples for differential thermal analyses of carbonate minerals. It would be very much appreciated if this work could be done in your Mineral Sciences Division. Dr. Chakraborty has been in touch with Dr. Bright and he is willing to do the work. He agreed to advise Dr. Chakraborty when they are ready so that he, Dr. Chakraborty, can observe the methods used for this work.

The samples are from the Wabush Lake area, Labrador.

(sgd.) J.M. Harrison,  
Director.



APPENDIX II

Dr. J.M. Harrison,  
Director, Geological Survey of Canada.

Dr. John Convey,  
Director, Mines Branch.

Examination of Wabush Lake Carbonate Minerals

8 Jan. 1962

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In reply to your memorandum dated December 20, 1961, requesting differential thermal analyses of a group of Wabush Lake carbonate minerals on behalf of Dr. K.L. Chakraborty, I would state that we are willing to undertake this work.

Dr. K.L. Chakraborty and Dr. G.A. Gross recently had a discussion concerning these samples with Dr. N.F.H. Bright, Head, Physical Chemistry Section, Mineral Sciences Division, who would be responsible for this work. They agreed that Dr. Bright's group would conduct X-ray diffraction examinations, differential thermal and thermogravimetric analyses on the seven samples provided, and that Dr. Chakraborty would conduct mineralogical and optical examinations of the materials. The results obtained in the two locations will then be correlated by discussions between the various parties concerned.

(sgd.) John Convey,  
Director, Mines Branch.