

TEMPERATURE INVESTIGATION OF COEXISTING DOLOMITE AND
CALCITE IN MARBLE FROM GATINEAU PARK AND
SURROUNDING AREA, QUEBEC.

by

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ABSTRACT

The Mg content of calcite, in calcite - dolomite pairs, suggests temperatures of equilibration in the system $\text{CaCO}_3 - \text{CaMg}(\text{CO}_3)_2$. Out of a total of 140 samples collected, only 21 contained calcite - dolomite pairs and were suitable for this study.

X-ray diffraction techniques indicate the calcites have MgCO_3 [$\Delta d_{(104)}$] contents up to 7.1 mol % which provided that equilibrium was attained, the crystallization temperature was 600°C or greater. The corresponding pressure, deduced from the mineral assemblage of the neighboring pelitic gneisses, is in the range of 4.2 - 6.3 Kb.

Low MgCO_3 in the high temperature calcites may be a consequence of such factors as a) magnesium exsolved as dolomite during a period of cooling, b) retrograde metamorphism caused by a later thermal episode and c) leaching of magnesium by permeating solutions.

Partial chemical analyses of purified calcite for Ca, Mg, Mn, Sr and Fe were made with a Techtron AA-4 atomic absorption spectrophotometer. The MgCO_3 contents were consistently higher as compared with the results obtained by X-ray diffraction methods. A range of 4.19 - 10.73 mol per cent of MgCO_3 was determined, corresponding to a minimum equilibrium temperature of $409^\circ - 700^\circ\text{C}$.

Some samples of calcite, separated from primary dolomite, were rehomogenized in a hydrothermal bomb at 2 Kb. pressure

and a temperature of approximately 700°C. After this treatment, the calcite X-ray diffraction patterns showed smaller spacings indicating that additional Mg (or Mn, Fe) from secondary dolomite has been resubstituted in the calcite structure.

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CHAPTER I

INTRODUCTIONSample locations and purpose of the investigation.

The thesis area (about 15 square miles) is located in the Gatineau Park extending northwestward from about one mile north of Hull. Four different areas have been chosen for study. Individually, these divisions do not indicate any special geological significance but are selected more for easy access. In these studies, only the carbonate rocks with the pair, calcite-dolomite are considered.

The object of this work was to obtain an estimate of the temperature of formation of calcite, using the magnesium content of calcite as a geothermometer. Compositions of calcite were determined by three separate methods:

- 1) X-ray diffraction (X-ray powder photograph and X-ray diffractometer).
- 2) Chemical analysis for Ca, Mg, Mn, Sr and Fe by atomic absorption spectrophotometry.
- 3) Rehomogenization of exsolved dolomite and subsequent determination of Mg by X-ray diffraction.

Another aspect of the study was the comparison of the temperatures determined by the calcite - dolomite geothermometer with those deduced by other means. Finally accurate cell parameters of individual specimens were determined by a computer program and the d-spacings of calcite were recalculated,

based on the refined cell parameters.

Previous work.

Owing to the abundance of calcite and dolomite in the earth's crust, a knowledge of their limits of stability would throw much light on the conditions of pressure and temperature prevailing during the formation of igneous and sedimentary rock and their metamorphic derivatives. Work has been done in the past on the dissociation of calcite, dolomite and magnesite including studies of the mechanism and products of dissociation and the rates of dissociation under varying conditions.

Mitchell (1923) attempted to determine the equilibrium thermal decomposition curve of dolomite at rather low pressures by heating dolomite and measuring the CO_2 pressure developed.

Chave (1952) used the X-ray diffraction method to correlate the magnesium content of calcite with the d-value of the strongest X-ray reflection from the shells of modern and fossil organisms. He established a curve relating the weight per cent MgCO_3 and the d-value of (100).

Graf and Goldsmith (1955, 1958) and Goldsmith, Graf and Joensuu (1955) using the X-ray diffraction method to determine the MgCO_3 content in the natural and synthetic samples, established the phase relationships in the system $\text{CaO} - \text{MgO} - \text{CO}_2$ from the concentration of 0 to 15 mol % of MgCO_3 .

The variation in the cell parameters of calcite with substitution of bivalent ions was investigated by Krieger (1930), Goldsmith, Graf, Witter and Northrop (1962) for manganese; by

Froese (1967), Froese and Winkler (1966) for strontium and Graf and Goldsmith (1955, 1958), Goldsmith, Graf and Joensuu (1955), Harker and Tuttle (1955) and Rosenberg (1959, 1960 and 1963) for magnesium.

Phase relations in the system of $\text{CaCO}_3 - \text{MgCO}_3$ were investigated by Graf and Goldsmith (1955, 1958), Goldsmith and Heard (1961), Harker and Tuttle (1955), and Goldsmith and Newton (1969). The phase boundary of dolomite - calcite was determined from 500° to 800°C and 0.001 to 1.4 Kb. (Graf and Goldsmith, 1955); 500° to 900°C and 1.4 to 3.1 Kb. (Harker and Tuttle, 1955); 700° to $1,200^\circ\text{C}$ and 2 to 8 Kb. (Goldsmith and Heard, 1961) and 400° to 800°C and 1 to 25 Kb. (Goldsmith and Newton, 1969). The calcite - dolomite solvus curves determined by different investigators are in good agreement with each other. As a result of its reliability, the calcite - dolomite solvus should be a very useful geothermometer for metamorphic calcite.

Sheppard (1966) studied calcite from central Vermont and the Grenville province (thesis area 100 x 160 miles). He used the X-ray diffraction technique described by Graf and Goldsmith (1955, 1958) and Goldsmith, Graf and Joensuu (1955) and determined T_{sx} (solvus temperatures from X-ray data) in the range 415° to 485°C . Höy (1970) used calcite from brucitic marble from near Wakefield, Quebec and, with the same X-ray technique, determined the equilibrium temperature of a single specimen at more than 600°C .

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CHAPTER II

THE PRECAMBRIAN GEOLOGY OF GATINEAU PARK.Rock types.

Although good exposures of Precambrian rocks crop out in the Gatineau Park, the geology of this area has been discussed by few people. The first work in this area was by Ellis (1901). The geology of the Wakefield area, which includes Meach Lake, was described by Baland (1955). Hogarth (1959) mapped the Meach Lake - Camp Fortune area in detail. MacDonald (1968) published a geological map (1 inch to 4 miles) which covered a large area surrounding Ottawa. The occurrence of brucitic marble was described by Goudge (1939) and the genesis of brucitic marble from Wakefield area by Hoy (1970). The area was mapped on a scale of 1 inch to 1,500 feet by Hogarth (1970).

All the metamorphic rocks of the area are Precambrian, and comprise several lithological units such as gneisses, marbles, quartzites and calc-silicate rocks. Most of the rocks were metamorphosed during the Grenville orogeny, 900 - 1,100 million years ago (Hogarth, 1970). Hogarth (1970) has subdivided the gneisses, quartzites and calc-silicate rocks on the basis of mineral assemblages.

Most marble is calcitic. Large bodies crop out north of Old Chelsea, south of Kingsmere Lake and near Pinks Lake. Hogarth (1970) subdivided the marble into seven types,

according to differences in mineralogy: diopsidic marble, actinolitic marble, phlogopitic marble, serpentine marble, graphitic marble, brucitic marble and chondrodite marble. Phlogopite, diopside, actinolite and serpentine are locally present. Dolomite and dolomitic marble are found in Dawson Field and along the northwest shore of Meach Lake. Small deposits of brucitic marble are present in a few localities.

Igneous and meta-igneous rocks form another important lithological group in the study area. Hogarth (1970) classified these rocks into seven units comprising syenite, granitoid rocks, pegmatites, potassic aplite, intrusive carbonate, peridotite, diorite and diabase. The intrusive carbonate rock occurs south of Meach Lake. It is made up of several types of small bodies such as the dolomite - calcite bodies, calcite veins, and breccias with phlogopite - apatite - carbonate matrix. They are found both within the aplite and in surrounding syenite (Plate 4). Hogarth (1966, pp. 48) has pointed out that "the dolomitic calcite is often distinctly foliated" and "the foliation is in part, caused by alternating layers of dolomite and calcite and in part, by a dimensional orientation of inequant grains of dolomite".

All of these rocks appear to be younger than the marble and all except the diabase were affected by Grenville metamorphism Hogarth(1970). Grenville ages (900 - 1,100 million years) have been determined by the potassium - argon method for syenite, aplite, intrusive carbonate, peridotite and diorite (Hogarth, personal communication, 1970).

Metamorphic conditions.

In McCloskey's Field (or the Champlain Lookout area), the intrusive carbonate postdates the Wakefield syenite (indicated by field and geochronological data), and hence the syenite did not have any effect on the equilibrium in the carbonate rocks. Therefore, the temperature of equilibration of the carbonate rocks in and around the syenite complex has probably remained largely unchanged since emplacement.

The approximate temperature of recrystallization of the carbonate rock in this region can be deduced from the mineral assemblages of the surrounding rocks e.g. quartz - plagioclase (An₃₀₋₄₅) - microcline - garnet - sillimanite, quartz - orthoclase - mesoperthite - biotite - garnet - sillimanite (Hogarth, personal communication, 1970). All indicate an uppermost almandine amphibolite facies or perhaps hornblende granulite subfacies of the granulite facies with a temperature condition of about 550° to 750°C (Turner and Verhoogen, 1960, pp. 553). Very locally a quartz - plagioclase (An₅₅₋₆₅) - hypersthene - garnet - orthoclase assemblage has been observed (Hogarth, personal communication, 1970). Although this may indicate a locally high temperature condition, the assemblage can also be explained by local anhydrous rocks and it does not change the general metamorphic condition, as described above. As a matter of fact, the equilibration temperature of carbonates for this region may be still lower than expected due to slight retrograde effects as indicated by minor alterations in the rocks. The

final temperature condition of the carbonate now observed in this region is therefore very likely to be lower than the original equilibrium temperature.

Towards the east (near Notch Road), about 5 miles away from the Wakefield Syenite Complex (Champlain Lookout), the grade of metamorphism appears to be somewhat lower according to the mineral assemblage: quartz - muscovite - biotite - garnet - sillimanite - orthoclase. These rocks belong to the sillimanite - almandine - muscovite subfacies of the almandine - amphibolite facies. Taking into consideration the slight degree of retrograde metamorphism, the equilibration temperature of carbonates might be below the equilibrium temperature of upper almandine amphibolite facies' assemblages.

Still eastward (Dawson Field) about 7 miles away from Champlain Lookout, orthopyroxene appears in the surrounding gneiss and mineral assemblages such as quartz - plagioclase - biotite - garnet, quartz - plagioclase - biotite - garnet - sillimanite, quartz - plagioclase - biotite - garnet - orthopyroxene and, very rarely, plagioclase - augite - orthopyroxene have been reported (Hogarth, personal communication, 1970). However, these rocks have been subjected to intense secondary hydrothermal alteration as evidenced by an intense sericitization of plagioclase and biotitization of orthopyroxene in the gneisses and serpentinization of diopside and forsterite in the marbles. It is therefore not surprising that carbonate rocks in this part of the Gatineau Park suggest a temperature no higher than 600°C.

The marbles (O-1) near Otter Lake village, which is about 40 miles northwest of Gatineau Park, are associated with Precambrian metamorphic rocks such as hornblende - plagioclase gneiss (pyroxene or garnet may be present) and pyroxenite (Kretz, 1957). These mineral assemblages are consistent with the uppermost amphibolite facies or the lowermost granulite facies with the same temperature conditions as discussed previously.

CHAPTER III

PETROLOGY OF MARBLE

In this study five types of marbles are considered: calcite - dolomite - serpentine marble, calcite - (dolomite) - quartz marble, calcite - dolomite - brucite marble, calcite - dolomite - apatite marble and calcite - dolomite marble.

The marble is generally medium to coarse grained and equigranular to subequigranular. The colour on a fresh surface varies from pure white, pale yellowish to dark grey. Minerals were identified mainly by optical properties and partly by X-ray diffraction. The approximate volumetric compositions are listed in Table 1.

Calcite - dolomite - serpentine marble.

The marble is the predominant rock type occurring in the Dawson Field. Individual, dome-shape outcrops varied from 3 to 10 feet in height. The contacts with other marble types are sharp or gradational.

This marble is generally fine to medium grained with grain size $< 0.5 - 2$ mm. diameter. The colour varies from light yellow-green to dark grey-green on fresh surfaces. The serpentine (X-rayed as antigorite) is the most predominant mineral (Plates 6 and 7). Concentric and elliptical forms of serpentine (+ talc) were observed (Plate 5). A 3 to 5 cm. - thick ring of serpentine (+ talc) is concentrated at the rim

Table 1.

Approximate modes of specimens studied.

Sample	Minerals %													
	Calcite	Dolomite	Antigorite	Quartz	Apatite	Brucite	Graphite	Talc	Diopside	Plagioclase	Magnetite	Pyrite	Chondrodite	Tremolite
358	>75	20	--	--	--	--	--	--	--	--	--	>1	--	--
O-1	85	<10	--	--	tr*	--	--	5	--	<1	--	--	tr	--
H-4	50	45	--	--	>1	--	--	<1	--	1	--	tr	--	--
350	>55	20	--	--	tr	1	--	--	--	--	--	--	20	--
P-730	65	>30	--	--	>1	--	--	--	--	--	--	tr	--	--
H-1	75	20	--	--	<5	--	tr	--	--	--	--	1	--	--
H-2C	10	80	--	--	10	--	--	--	--	--	--	--	--	--
H-3	50	>45	--	--	1	--	--	--	--	--	--	tr	--	--
M-118	65	25	5	--	--	--	1	>1	--	--	tr	--	1	--
H-2A	50	<50	--	--	1	--	tr	--	--	--	--	--	--	--
E-1	45	<10	45	--	--	--	--	1	--	--	--	--	--	--
C-1	40	25	35	--	--	--	tr	--	--	--	--	--	--	--
M-58	30	35	--	--	--	--	--	--	--	--	--	--	--	35
E-2	>35	>20	40	--	--	tr	--	1	--	--	--	--	--	--
M-5	<45	50	--	>1	--	--	>1	--	--	--	tr	--	--	--
M-14	35	25	40	--	--	--	tr	--	--	--	--	--	--	--
A-1	<60	--	--	<40	--	--	1	--	--	--	--	1	--	--
A-4	<60	--	--	30	5	--	--	--	1	--	--	tr	--	1
C-6	20	<10	70	--	--	--	tr	--	--	--	--	--	--	--
M-135	80	tr	--	<10	--	--	>1	--	10	--	--	--	--	--
H-2B	5	85	--	--	10	--	--	--	--	--	--	--	--	--
224S-2	60	20	--	--	1	<10	--	--	--	--	--	--	<10	--

* trace amount.

of the structure surrounding a marble core. The serpentine and talc are dark-green. The dolomite appears only when the marble is stained. Grains are normally less than 0.1 mm. diameter. Some graphite was identified and chondrodite was observed only in sample M-118.

Calcite - (dolomite) - quartz marble.

The marble described here was mainly collected about one mile south of Old Chelsea (A-1 and A-4). One sample (M-5) (Plate 13) was collected from Dawson Field. Quartz marble is named because of the presence of quartz in essential amounts. The quartz marble is generally medium to coarse grained (<2 mm.) and equigranular to subequigranular. The colour varies from white to grey.

Calcite is the major mineral and is generally coarse grained (>2 mm.). Dolomite occurs in minor amounts. Phlogopite and diopside have been observed in the sample A-4 (Plate 14).

Calcite - dolomite - brucite marble.

Only two rock specimens were observed to contain brucite (350 and 224S-2). These were collected from near Meach Lake. The rock is slightly pale grey to brownish with a distinct yellowish brown powder (pigmented by iron oxide). Grains are normally greater than 1 mm. diameter. Some brucite nodules show an "onion-skinned" texture (Plate 9). The mineral assemblage is simple: brucite, chondrodite (Plate 8), apatite, calcite, dolomite and secondary magnesium carbonates.

Calcite - dolomite - apatite marble.

These marbles were collected from McCloskey's field. They are pale yellowish to grey. The coarse-grained dolomite crystals (>3 mm.) have a euhedral outline. The marble occurs as veins surrounded by aplite fenitized with phlogopite and eckermannite. The mineral assemblage is different from the marble which has been previously discussed. Calcite and dolomite generally make up the bulk of the rock which varies from pure dolomite to pure calcite. The calcite grain size varies from medium to coarse grained (2 to 3 mm.) and generally contains tiny "bleb-like" dolomite crystals. This "bleb-like" dolomite (Plates 11 and 15) suggests that it is formed during the cooling stage of metamorphism, the magnesian component exsolving from calcite as dolomite. Apatite (~1 mm. diameter) is abundant (Plate 12); phlogopite, pyrite and magnetite are less common. Hogarth (1966) reported that the carbonate formed through the filling of the fractures by a high temperature, carbonate-rich fluid.

Calcite - dolomite marble.

Calcite - dolomite marble is classified as a distinct unit because calcite and dolomite are predominant, but no apatite, quartz, brucite or serpentine are present. It is commonly massive and may have either sharp or gradational contacts with other marble types. The dolomite grain size varies from sample to sample. Specimen 358 (Plate 15) is especially coarse grained, being formed of large crystals of dolomite (>3 mm.). The calcite is medium to coarse grained, white to grey in colour.

CHAPTER IV

CHOICE OF SPECIMENS

All the samples were collected from Gatineau Park area, Quebec, except one sample O-1 (see Figure 1b) which was collected from near Otter Lake village, Quebec. A total of 140 samples were collected. The thesis areas are located on Figure 1a and sample location of specimens studied in this thesis are listed in Table 2. The location of all the samples are marked on Figure 1. Four different locations can be distinguished:

- a) Otter Lake village, Figure 1b, (one sample, O-1).
- b) Old Chelsea area, about one mile south of Old Chelsea village, Figure 1c, (five samples, E-1, E-2, B-2, A-1 and A-4).
- c) Dawson Field, Figure 1c, (eight samples, M-14, M-5, M-58, M-118, M-129, M-135, C-1 and C-6).
- d) McCloskey's Field and Meach Lake area, Figure 1c, (ten samples, 350, 358, P-730, 224S-2, H-1, H-2A, H-2B, H-2C, H-3 and H-4).

Staining.

All samples were stained by the Alizarin Red S method described by Friedman (1959) and Ellingboe and Wilson (1964). This method was found to be thoroughly reliable for distinguishing calcite from dolomite in the specimens collected. Thin sections were stained without etching while all the polished surfaces of rock specimens were etched with 10 % HCl for 2 minutes before staining. The stain forms a strongly coloured complex with

Table 2.

Location and description of specimens.

Sample	Description	Location
358	Calcite - dolomite marble.	South of McCloskey's Field, near Meach Lake.
O-1	Calcite - dolomite marble.	4 miles east of Otter Lake village. Lat. 45° 50' north, Long. 76° 21' east.
H-4	Calcite - dolomite - apatite marble.	West of McCloskey's Field, near Meach Lake.
224S-2	Calcite - dolomite - brucite marble.	Southwest of Meach Lake.
350	Calcite - dolomite - brucite marble.	Southwest of Meach Lake.
P-730	Calcite - dolomite marble.	Southwest of McCloskey's Field, near Meach Lake.
H-1	Calcite - dolomite - apatite marble	East of McCloskey's Field.
H-2C	Calcite - dolomite - apatite marble.	South of McCloskey's Field.
H-3	Calcite - dolomite - apatite marble.	West of McCloskey's Field.
M-118	Calcite - dolomite - serpentine marble.	Dawson Field, north of Gatineau Parkway.
H-2A	Calcite - dolomite marble.	South of McCloskey's Field.
E-1	Calcite - dolomite - serpentine marble.	Near Old Chelsea village.
C-1	Calcite - dolomite - serpentine marble.	Dawson Field, north of Gatineau Parkway.
M-58	Calcite - dolomite marble.	Dawson Field, south of Gatineau Parkway.
M-129	Calcite - dolomite - quartz marble.	Dawson Field, north of Gatineau Parkway.
B-2	Calcite - dolomite - serpentine marble.	3/4 mile south of Old Chelsea.
E-2	Calcite - dolomite - serpentine marble.	Near Old Chelsea village.
M-5	Calcite - dolomite - quartz marble.	East of Dawson Field, south of Gatineau Parkway.
M-14	Calcite - dolomite - serpentine marble.	Dawson Field, south of Gatineau Parkway.
A-1	Calcite - quartz marble.	One mile south of Old Chelsea village.
A-4	Calcite - quartz marble	One mile south of Old Chelsea village.
C-6	Calcite - dolomite - serpentine marble.	North of Gatineau Parkway, near Pinks Lake.
M-135	Calcite - quartz marble.	Dawson Field, north of Gatineau Parkway.
H-2B	Calcite - dolomite - apatite marble	South of McCloskey's Field.

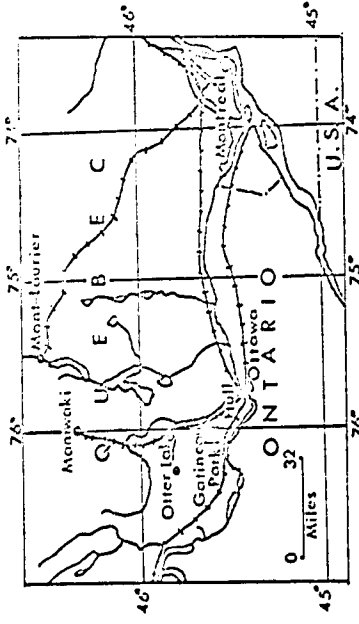


Figure 1a. Map showing areas of sampling.

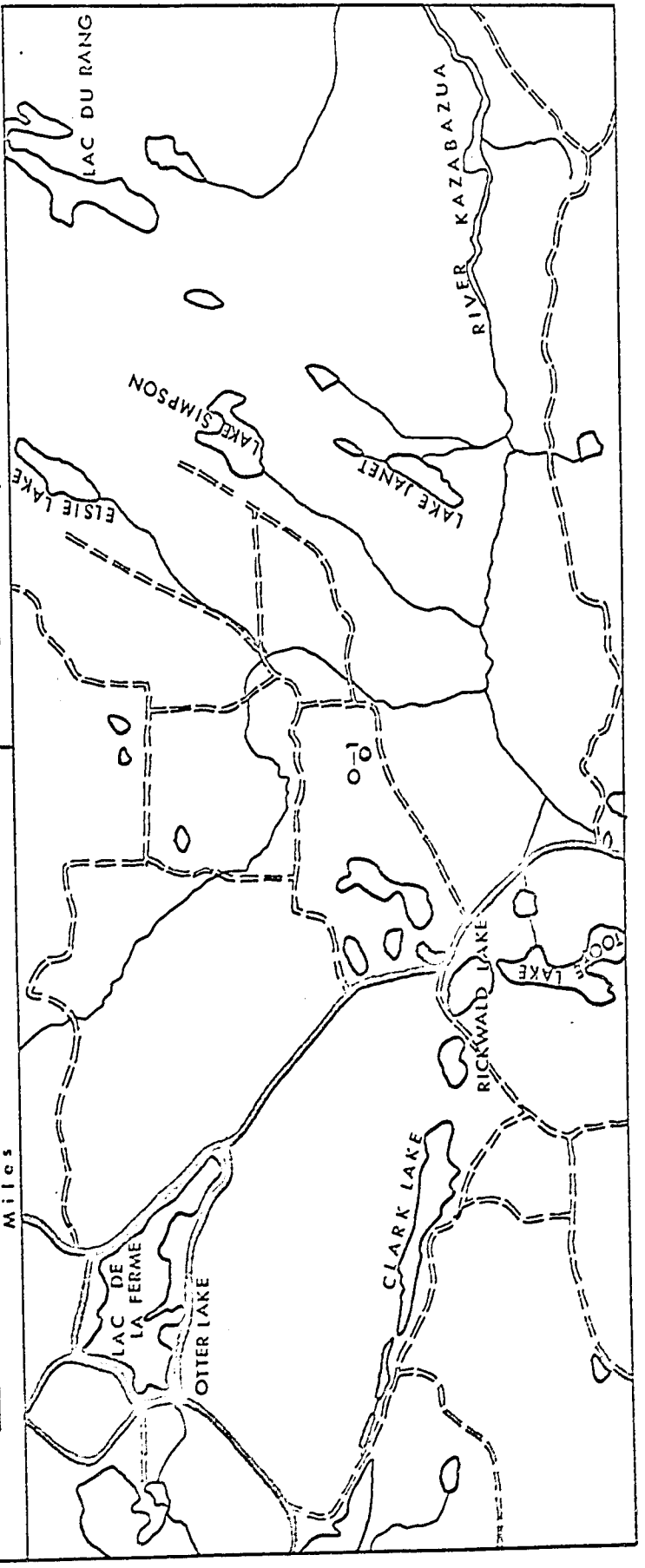
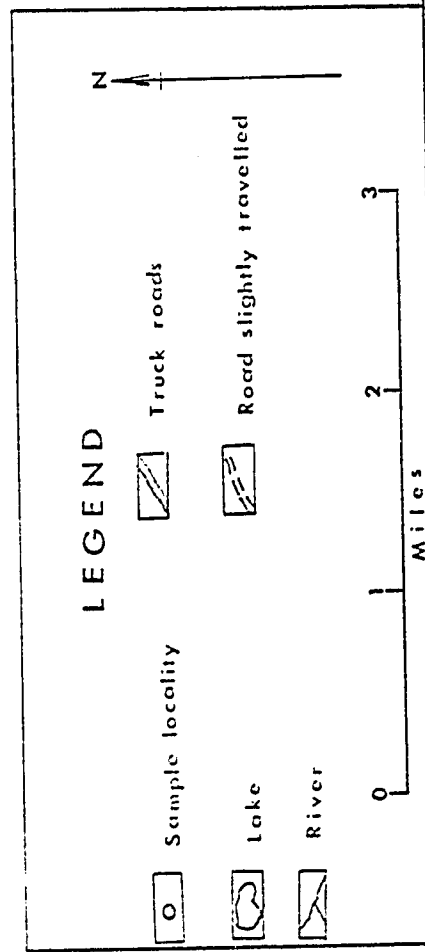
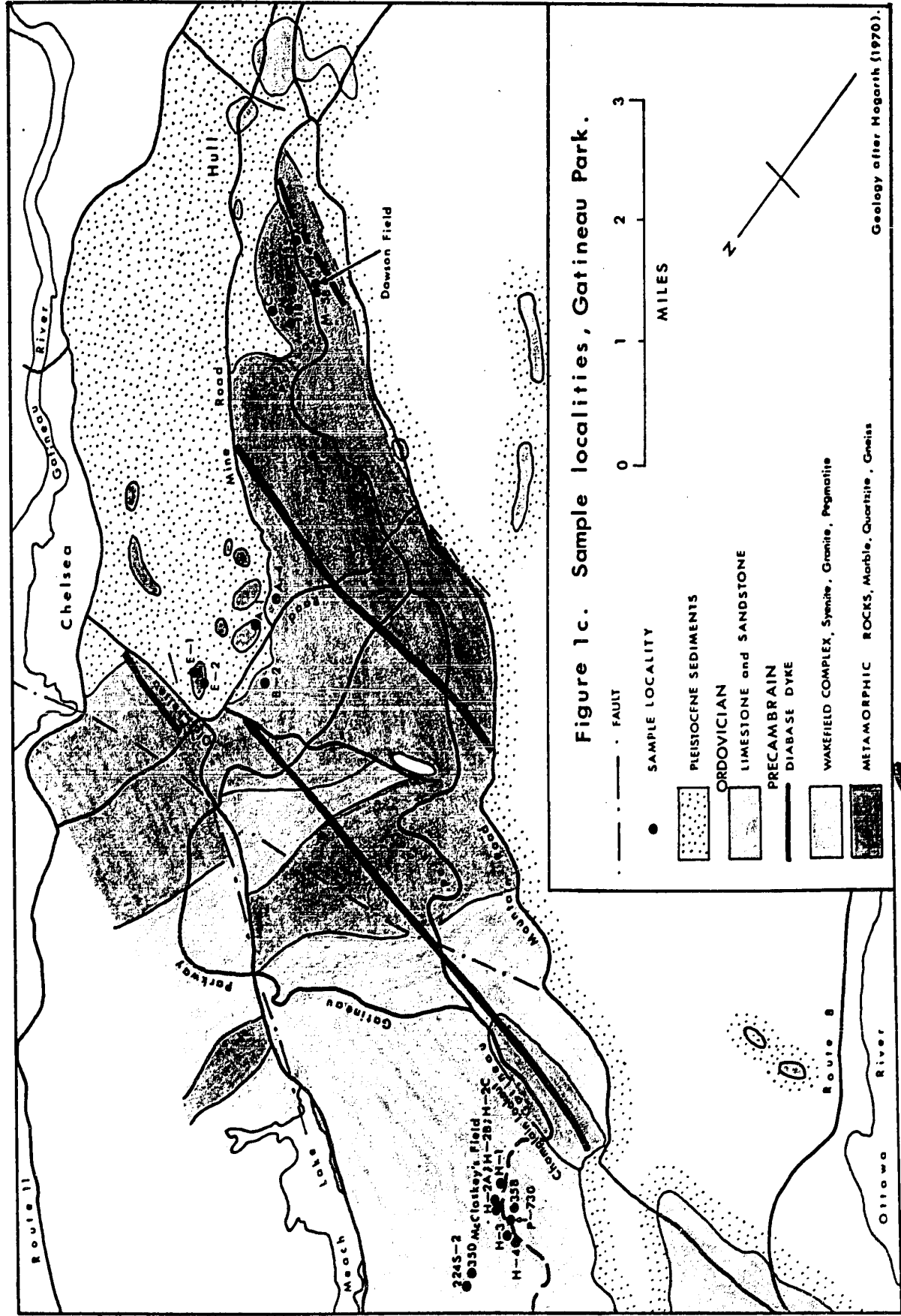


Figure 1b. Sample locality, Otter Lake area.



calcium ions in weakly acidic solutions. The rate of reaction with dolomite is very much slower. Therefore removal of excess solution after two or three minutes prevents the staining of dolomite. In a stained thin section a few per cent of either phase can usually be detected. Samples were chosen where calcite and dolomite co-existed. As a result, out of 140 samples, only 21 were chosen.

Treatment of the specimens.

Wherever possible, dolomite and calcite were separated by physical means, using heavy liquids and a Frantz-Isodynamic separator with samples crushed and sieved at -80/+100 mesh. This method was found to be only partly satisfactory because fine-grained "bleb-like" dolomite, observed in stained sections, could not be effectively separated. On the other hand, coarse-grained rhombohedral dolomite no doubt can be separated by means of heavy liquids, e.g. specific gravity = 2.80. X-ray diffraction was used extensively to check the quality of physical separations of dolomite and calcite. The method was repeated for all stages of separation and proved to be rapid and reliable.

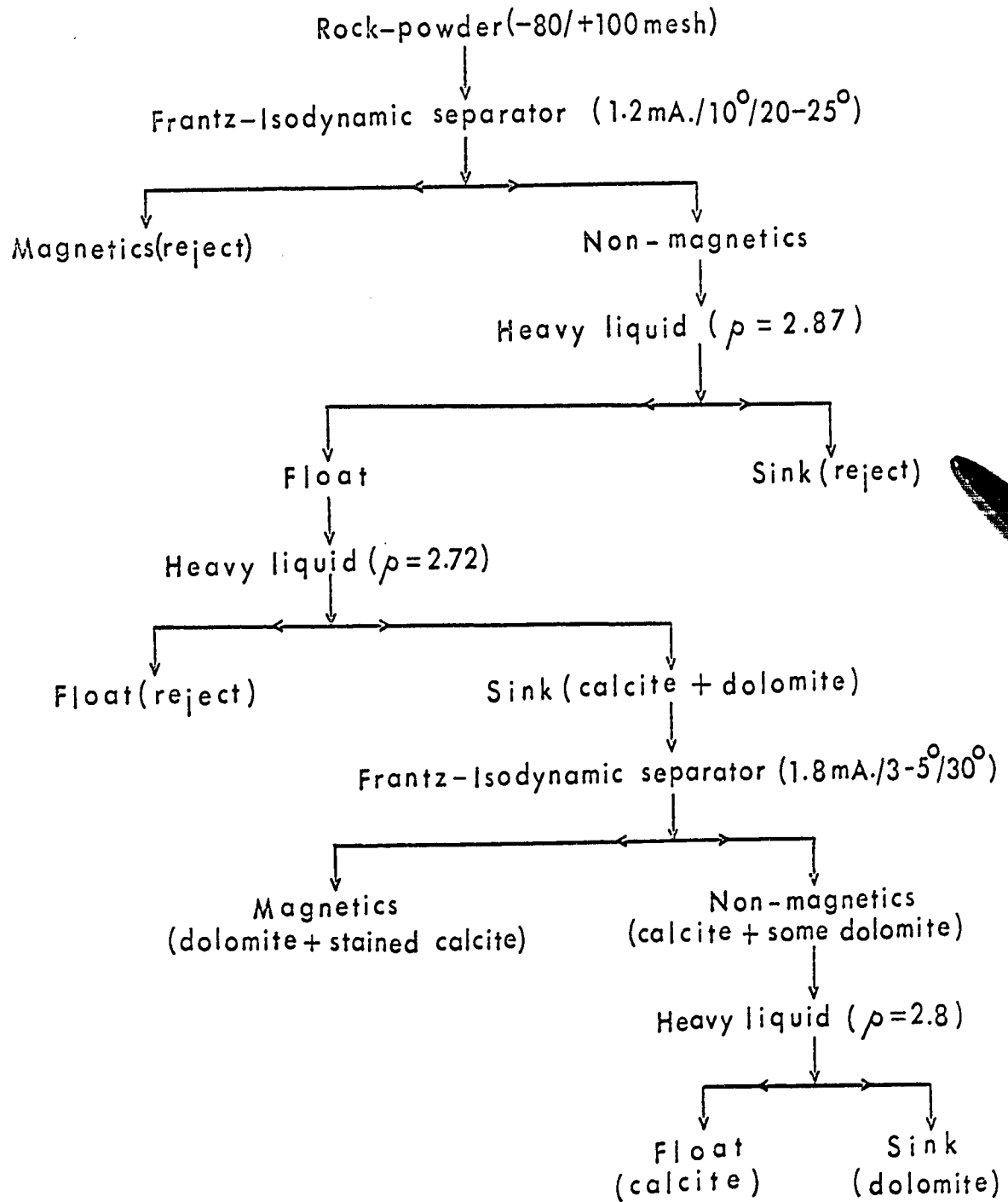
Crushed and ground samples were sieved to pass through a 200 mesh screen for X-ray diffractometry. To purify the sample of -80/+100 mesh size, a general scheme was followed.

- 1) Rock powdered to -80/+100 mesh.
- 2) Removal of any possible strongly magnetic mineral by a hand magnet.
- 3) Removal of magnetic minerals by a Frantz-Isodynamic separator.

- 4) Removal of minerals that have specific gravity greater than 2.87, e.g. apatite, by a heavy liquid. (Specific gravities of the heavy liquids were carefully standardized with a Westphal balance.)
- 5) Removal of minerals that have specific gravity less than 2.72, e.g. serpentine and graphite, by a heavy liquid.
- 6) Removal of weakly magnetic minerals with a Frantz-Isodynamic separator, e.g. calcite stained by iron oxide.
- 7) Calcite (+ "bleb-like" dolomite) was separated as a float product from dolomite by a heavy liquid with specific gravity = 2.80.
- 8) The above procedure (7) may be repeated.

A general flow chart for mineral separation is given in Figure 2. One part of -80/+100 mesh fraction was used for chemical analyses for Ca, Mg, Mn, Sr and Fe and the other part was used for rehomogenization of calcite.

Figure 2. Flow sheet showing the mineral-separation procedure.



CHAPTER V

TEMPERATURE DETERMINATION

In order to estimate the temperature of formation of the calcite, its content of magnesium should be obtained. There are several ways by which $MgCO_3$ may be determined in magnesian calcite. One of the quickest ways is by chemical analysis. The samples which are used for the temperature estimation have coexisting dolomite and calcite.

Some difficulties will be encountered in using calcite as a geothermometer. With almost the same chemical and physical properties, it is very difficult to separate calcite from dolomite and there is no reliable way to test the purity of the separated calcite

Jennings and Mitchell (1969), used the different rates of solution of calcite and dolomite to separate one mineral from the other in the carbonatite from Fen, southern Norway. Samples were brought into solution by treating with 6N HCl, filtered through a sintered glass Gooch crucible, and analysed for Mg and Ca by atomic absorption. They concluded that it is a successful method of testing calcite from dolomitic marble of known temperature formation.

X-ray diffraction methods.

The relation between the magnesium content of calcite and its X-ray spacings has been described by Goldsmith, Graf and Joensuu (1955). The method for determining the magnesium

content is discussed below:

Goldsmith (personal communication, 1969) pointed out that, for MgCO_3 determination of magnesian calcite, there is no method as accurate as X-ray diffraction. Because of this, the author used the X-ray diffraction method to determine the MgCO_3 content in calcite. As a test of reliability of results, the X-ray powder diffractometer data were compared with X-ray powder photographs (Plate 1). In the X-ray photographic method, silicon was employed as an internal standard and as a result, an accurate value was obtained. There are some photographs which were obtained from the double exposure method. This will be discussed later. Samples were mixed with silicon in 1:1 proportion and X-rayed using filtered copper and iron radiation (Plates 1-B, 1-C, 1-D). The distance between the two strongest peaks, i.e. the $d_{(111)}$ of the silicon and the $d_{(104)}$ of the calcite, was measured. The $d_{(111)}$ of silicon was calculated by IBM 360/65 digital computer. Thus the position of the 111 peak was fixed at $2\theta = 28.47^\circ$ for copper radiation, $d = 3.1350\text{\AA}$.

The Δd_1 value of the sample to be tested was obtained by subtracting the silicon $d_{(111)}$ from the calcite $d_{(104)}$. In the same way, Johnson-Matthey's "Specpure" CaCO_3 was mixed with silicon and an X-ray photograph was taken (Plate 1-A). The Δd_2 or $d_{(111)} - d_{(104)}$, fixed at 0.0951\AA was obtained for "Specpure" CaCO_3 . The difference [$\Delta d_{(104)}$] was then obtained from $\Delta d_1 - \Delta d_2$ (see Table 5). The departure of Δd_1 from 0.0951\AA in the tested calcite is considered as shifting due to magnesium (or Fe^{+2} , Mn^{+2} , Sr^{+2}) substituting in the calcite structure.

* Using $a_0 = 5.430\text{\AA}$ from ASTM card, card no. 5-0565.

The X-ray powder diffractometer method is similar to the above method. Sample powder (grains passing through 200 mesh) is mixed with silicon powder in 1:1 proportion and using a chart scale of four inches per degree, the specimens were run between $2\theta = 31^\circ$ to 28° . The $d_{(104)}$ of calcite and $d_{(111)}$ of silicon peaks were recorded. By measuring the distance between the peaks, Δd_1 was obtained. Again $\Delta d_2 = 0.0951\text{\AA}$ and $\Delta d_{(104)} = \Delta d_1 - \Delta d_2$. Data are recorded in Tables 8 and 9.

Double exposure method.

This method was carried out by employing the North American Philips 114.6 mm. diameter cameras using filtered copper radiation. The principle is similar to that of the Guinier camera, except for a double exposure. For the double exposure method, two sample rods are necessary (one calcite powder rod and one internal standard silicon rod). The procedure is the same as that of a normal exposure except that when the calcite powder rod is installed and film is loaded, a piece of 356 x 18 mm. Mo + Rh alloy plate covers about half the width of the X-ray film so that the portion covered by the alloy plate will be shielded from reflections. The silicon powder rod is changed in a dark room and centred by a very small beam of light. The alloy plate is carefully transferred to the position which has been exposed. Then the unexposed portion is used for receiving the silicon pattern. The patterns are illustrated on Plates 1-E and 1-F. The measurements of the double exposure films were standardized by the 111 reflection of silicon.

All reflection lines of calcite were converted to d-spacing values. These values were refined by computer and d-spacings were recalculated. Two computer programs were used: first using the d-spacing of the lines (the hkl, d-spacing values and intensities of the reflection lines) from the X-ray powder photographs as the input. Cell parameters of the calcite were refined by a least squares method by the GE 400 digital computer, Carleton University. The cell parameters were refined to a standard deviation of an individual parameter of $\pm 0.002\text{\AA}^{\circ}$ * (see Table 3). Secondly, using the cell parameter obtained from the least squares program (see Table 3), the spacings of all the reflections of calcite up to $h^2 + k^2 + l^2 = 264$; $h = 2$, $k = 2$, $l = 16$ were calculated (see Appendix 1) by the IBM 360/65 digital computer, University of Ottawa. The hkl indices were re-indexed to fulfill the condition $-h + k + l = 3n$ (see Appendix 2).

MgCO₃ determination.

MgCO₃ determinations are based on the Goldsmith, Graf and Joensuu (1955) curves (Figures 3 and 4). The mol % MgCO₃ was obtained indirectly (Tables 5, 6, 7, 8 and 9). The author considered the d-spacing shifting as due to magnesium substitution only, but other divalent ions such as iron,

* This standard deviation only applies for the a-axis. The c-axis standard deviation is always greater than 0.002\AA . Thus by using reflections of planes parallel to a₁ and a₂ for generating the Δd value as from $d(0.0.12)$, one might obtain lower MgCO₃ contents.

Table 3.
Cell parameters of calcite.

Sample	a_0	c_0	c_0/a_0
Spc.* CaCO_3	4.998 \pm 0.001	17.083 \pm 0.0051	3.418
358	4.970 \pm 0.002	16.992 \pm 0.0083	3.419
O-1	4.963 \pm 0.001	16.976 \pm 0.0124	3.421
H-4	4.974 \pm 0.002	16.999 \pm 0.0069	3.418
350	4.971 \pm 0.003	16.996 \pm 0.0146	3.419
P-730	4.982 \pm 0.002	17.034 \pm 0.0081	3.419
H-1	4.980 \pm 0.001	16.991 \pm 0.0108	3.419
H-2C	4.979 \pm 0.003	17.049 \pm 0.0095	3.424
H-3	4.969 \pm 0.002	17.016 \pm 0.0162	3.424
M-118	4.987 \pm 0.004	16.948 \pm 0.0220	3.398
H-2A	4.981 \pm 0.002	17.013 \pm 0.0084	3.416
E-1	4.979 \pm 0.001	17.020 \pm 0.0040	3.419
C-1	4.981 \pm 0.004	17.013 \pm 0.0099	3.416
M-58	4.983 \pm 0.002	17.032 \pm 0.0070	3.418
M-129	4.972 \pm 0.002	16.966 \pm 0.0128	3.412
B-2	4.975 \pm 0.002	17.002 \pm 0.0086	3.417
E-2	4.987 \pm 0.003	17.038 \pm 0.0092	3.416
M-5	4.971 \pm 0.001	16.986 \pm 0.0046	3.417
CaCO_3 (20°C)	4.990**	17.061**	3.419
CaCO_3 (26°C)	4.990**	17.064**	3.420

* "Specpure" CaCO_3 .

** Data from Graf, 1961. pp. 1285.

Table 4.

Spacings $d_{(104)}$, $d_{(318)}$ and $d_{(3.0.12)}$ of calcite obtained through a computer program.

Sample	$d_{(104)} (\text{\AA})$	$d_{(318)} (\text{\AA})$	$d_{(3.0.12)} (\text{\AA})$
Spc. * CaCO_3	3.0399	1.0464	1.0133
358	3.0225**	1.0404**	1.0075**
O-1	3.0200	1.0394	1.0067
H-4	3.0253	1.0414	1.0084
350	3.0241	1.0409	1.0080
P-730	3.0309	1.0432	1.0103
H-1	3.0263**	1.0422**	1.0088**
H-2C	3.0313	1.0430	1.0104
H-3	3.0253	1.0408	1.0084
M-118	3.0245	1.0427	1.0081
H-2A	3.0285	1.0426	1.0095
E-1	3.0286	1.0425	1.0095
C-1	3.0286	1.0427	1.0096
M-58	3.0310	1.0434	1.0103
M-129	3.0218	1.0407	1.0073
B-2	3.0259	1.0416	1.0087
E-2	3.0328	1.0441	1.0109
M-5	3.0231	1.0407	1.0077

* "Specpure" CaCO_3 .

** Values from X-ray photographs using Fe radiation; without (**), indicating values derived from X-ray photographs with Cu radiation.

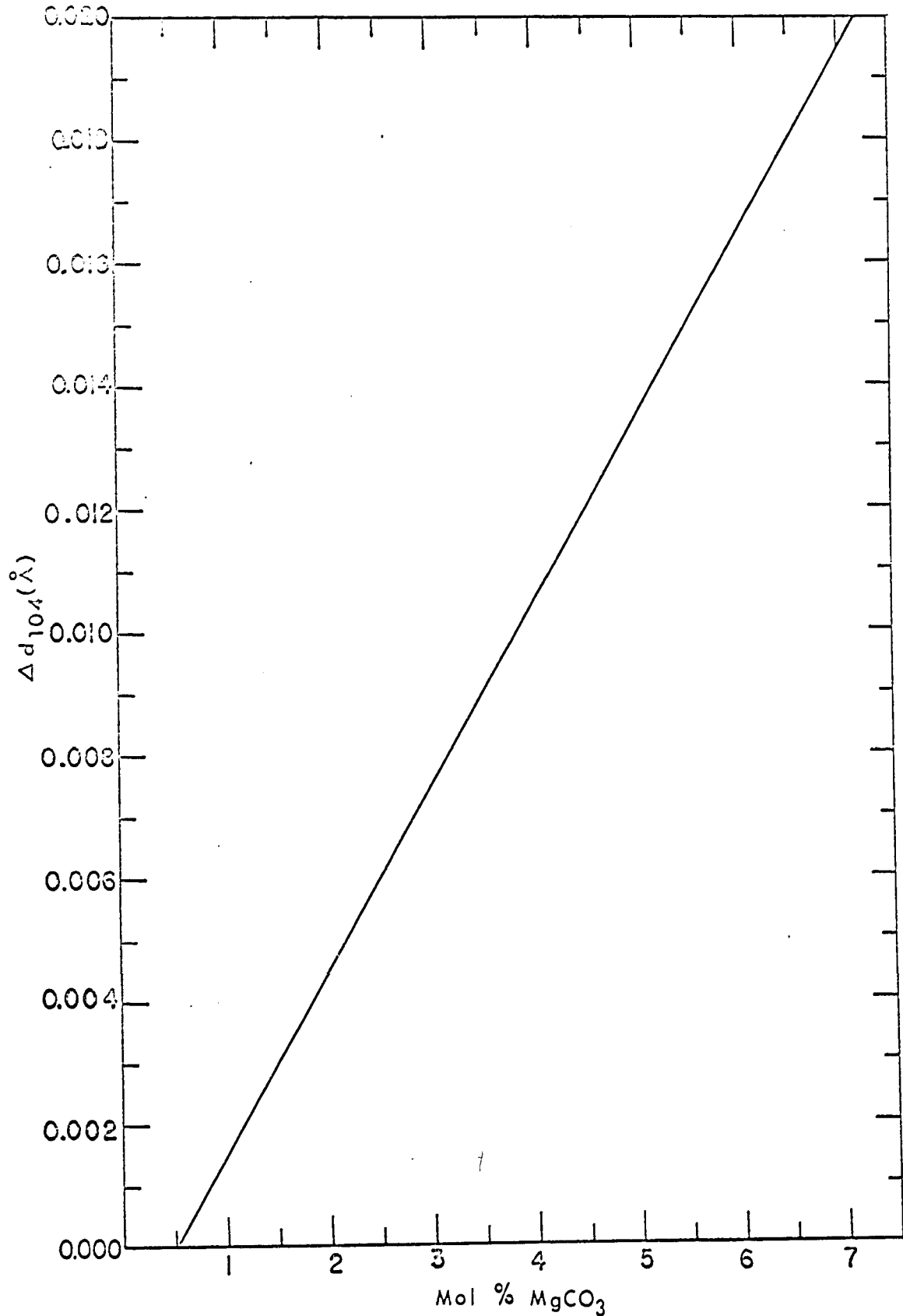


Figure 3. Variation of d(104) spacing of natural calcites with increasing substitution of Mg, referred to "Specpure" CaCO₃ as standard. After Goldsmith, Graf and Joensuu (1955).

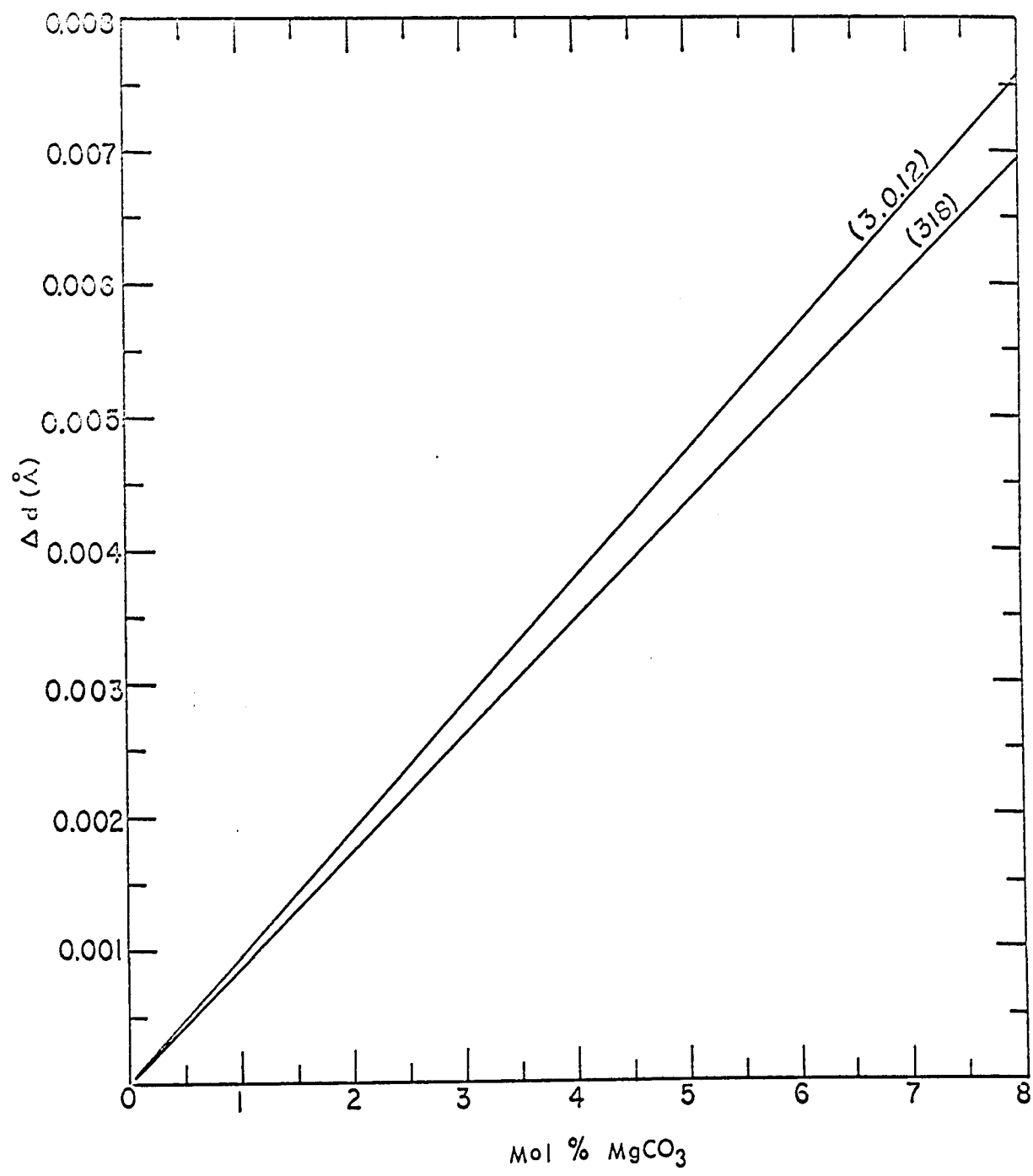


Figure 4. Variation of $d_{(3.0.12)}$ and $d_{(318)}$ spacings of natural calcites with increasing substitution of Mg, referred to "Specpure" CaCO₃ as standard. After Goldsmith, Graf and Joensuu (1955).

Table 5.

The mol % [$\Delta d_{(104)}$, X-ray powder photograph] of MgCO_3 in, and temperature of formation of, calcite.

Sample	$\Delta d_{(104)}$ (\AA)	Mol % MgCO_3	Temp. ($^{\circ}\text{C}$)* determination
358	0.016**	5.82	558
O-1	0.020	7.10	603
H-4	0.015	5.35	538
350	0.016	5.82	558
P-730	0.009	3.50	460
H-1	0.014**	5.15	525
H-2C	0.009	3.50	460
H-3	0.015	5.50	545
M-118	0.016	5.82	558
H-2A	0.011	4.30	495
E-1	0.011	4.30	495
C-1	0.011	4.30	495
M-58	0.009	3.50	460
M-129	0.018	6.50	583
B-2	0.014	5.15	530
E-2	0.007	2.83	429
M-5	0.017	6.16	570

* Based on the curve of Goldsmith and Newton (1969).

** Values from X-ray photographs, using Fe radiation, sample numbers without (**), indicate values derived from X-ray photographs with Cu radiation.

Table 6.

The mol % [$\Delta d_{(318)}$, X-ray powder photograph] of MgCO_3 in, and temperature of formation of, calcite.

Sample	$\Delta d_{(318)} (\text{\AA})$	Mol % MgCO_3	Temp. ($^{\circ}\text{C}$)* determination
358	0.0057**	6.55	584
O-1	0.0070	8.00	630
H-4	0.0050	5.75	555
350	0.0055	6.30	575
P-730	0.0032	3.65	466
H-1	0.0042**	4.80	517
H-2C	0.0034	3.90	477
H-3	0.0056	6.42	580
M-118	0.0037	4.25	492
H-2A	0.0038	4.35	497
E-1	0.0039	4.45	501
C-1	0.0037	4.25	493
M-58	0.0030	3.45	458
M-129	0.0058	6.65	588
B-2	0.0048	5.50	545
E-2	0.0023	2.65	420
M-5	0.0058	6.65	588

* Based on the curve of Goldsmith and Newton (1969).

** Values from X-ray photographs, using Fe radiation, sample numbers without (**), indicate values derived from X-ray photographs with Cu radiation.

Table 7.

The mol % [$\Delta d(3.0.12)$, X-ray powder photograph] of $MgCO_3$ in, and temperature of formation of, calcite.

Sample	$\Delta d(3.0.12)$	Mol % $MgCO_3$	Temp. ($^{\circ}C$)* determination
358	0.0060**	6.30	575
O-1	0.0066	6.95	595
H-4	0.0049	5.75	555
350	0.0053	5.58	548
P-730	0.0030	3.17	444
H-1	0.0045**	5.75	555
H-2C	0.0029	3.05	438
H-3	0.0049	5.17	531
M-118	0.0052	5.48	544
H-2A	0.0038	4.02	482
E-1	0.0038	4.02	482
C-1	0.0038	4.02	482
M-58	0.0030	3.17	444
M-129	0.0061	6.45	581
B-2	0.0047	4.95	523
E-2	0.0024	2.52	414
M-5	0.0056	5.91	560

* Based on the curve of Goldsmith and Newton (1969).

** Values from X-ray photographs, using Fe radiation, sample numbers without (**), indicate values derived from X-ray photographs with Cu radiation.

Table 8.

The mol % [$\Delta d_{(104)}$, X-ray diffractometer] of $MgCO_3$ in, and temperature of formation of, calcite.

Sample	$\Delta d_{(104)} (\text{\AA})^*$	Mol % $MgCO_3$	Temp. ($^{\circ}C$)** determination
358	0.015	5.20	546
O-1	0.018	6.50	583
H-4	0.012	4.50	504
350	0.014	5.15	530
P-730	0.010	3.85	452
H-1	0.016	5.82	558
H-2C	0.011	4.15	488
H-3	0.012	4.50	504
M-118	0.013	4.85	518
H-2A	0.013	4.82	517
E-1	0.006	2.50	414
C-1	0.010	3.82	474
M-58	0.011	4.20	490
M-129	0.008	3.20	445
B-2	0.008	3.20	445
E-2	0.009	3.50	460
M-5	0.012	4.50	504
M-14	0.005	2.15	<400***
M-135	0.010	3.82	474
224S-2	0.011	4.20	490

* $\Delta d_{(104)}$ was obtained by X-ray diffractometer unit at the University of Ottawa. Cu/Ni. Chart speed = 4"/2 θ .

** Based on the curve of Goldsmith and Newton (1969).

*** Value beyond the range of the curve of Goldsmith and Newton (1969).

Table 9.

The mol % [$\Delta d_{(104)}$, X-ray diffractometer] of $MgCO_3$ in, and temperature of formation of, calcite.

Sample	$\Delta d_{(104)}$ (Å)*	Mol % $MgCO_3$	Temp. (°C)** determination
O-1	0.017	6.16	570
H-4	0.012	4.50	504
350	0.013	4.85	518
H-1	0.016	5.82	558
M-118	0.011	4.15	488
E-1	0.013	4.85	518
M-129	0.011	4.15	488
B-2	0.012	4.50	504
E-2	0.011	4.15	488
M-5	0.010	3.82	474
M-14	0.007	2.83	429

* $\Delta d_{(104)}$ was obtained by X-ray diffractometer unit at the Soil Research Institute, Department of Agriculture of Canada. Co/Fe. Chart speed = 8 cm./2θ.

** Based on the curve of Goldsmith and Newton.

manganese and strontium may be substituted for calcium in the calcite structure. These will be discussed later. It appears that the X-ray powder diffractometer method generally gives lower $MgCO_3$ contents than those from the X-ray powder photograph method. Some possible explanations are as follows:

i) The author is confident that the $MgCO_3$ contents obtained from the X-ray powder diffractometer method should be more accurate than those from the X-ray powder photograph method. With the X-ray diffractometer, the scale is equivalent to four inches per one degree (2θ), whereas with the X-ray photograph (camera diameter = 114.6 mm.) the scale is equivalent to one millimeter per one degree (2θ). It is possible that the X-ray diffractometer at the University of Ottawa is not reliable and as a result, is not sufficiently sensitive for this purpose. In order to test these possibilities, samples were run in a different diffractometer unit from the Soil Research Institute, Department of Agriculture of Canada, using Co radiation, chart speed 16 cm. per degree (2θ)(Plate 2). The results are listed in Table 9.

ii) This discrepancy may also be attributed to personal errors, such as the misjudgment of the correct position of the reflection lines in the photograph method.

iii) Variation in the amount of Mg in solid solution within the same hand specimen.

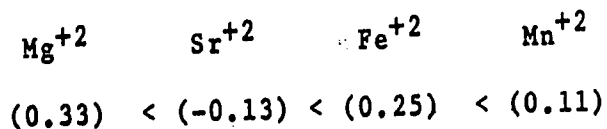
Relation between magnesium content in calcite from different localities.

The dolomitic marble specimens gave a range of $MgCO_3$ contents. Most of the specimens contain considerable amounts of $MgCO_3$ (Tables 5, 6, 7, 8 and 9). From the compositional point of view, specimens from Dawson Field (along the Gatineau Parkway with sample number M- and C-, but with the exception of samples M-118 and M-5, Table 8) gave lower contents of $MgCO_3$ than samples from McCloskey's Field and the Meach Lake area (this is true of the results obtained by X-ray diffractometer, Table 8). This reflects the mineralogical content of the samples. The mineral assemblages are different at different locations. Samples from Dawson Field are composed mainly of calcite, dolomite, antigorite (X-rayed) and graphite or talc in some specimens. Samples from McCloskey's Field are composed of apatite, pyrite, in addition to the carbonates. Samples from Meach Lake area are brucitic marbles. The sample from Otter Lake village (O-1) is mainly of calcite and dolomite but contains the highest $MgCO_3$ content among the tested calcite. The calcite of calcite - dolomite - quartz marble (samples M-5 and M-129, see Chapter III) has a high $MgCO_3$ content.

Effects of Fe, Mn and Sr on X-ray spacings.

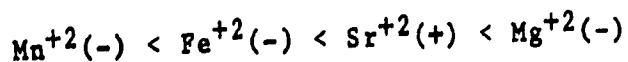
Divalent ions, notably Fe, Mn and Sr may be substituted for Ca and Mg in the calcite structure. The studies of Goldsmith and Graf (1960), Goldsmith et al. (1962) indicate that the maximum solubility of these ions in calcite at a given

temperature increases in the order:



The figure in parentheses is the ionic radius of Ca^{+2} (0.99) minus that of the cation with data taken from Ahrens (1952, pp. 168). This order of increasing solubility is, perhaps significantly, one of decreasing difference in ionic radius from that of Ca^{+2} with the exception of the switching of positions of Sr^{+2} and Fe^{+2} .

Substitution of divalent ions may influence the cell parameters. Substitution of Sr^{+2} increases the lattice constants, a_0 and c_0 , whilst substitution of Mn^{+2} , Fe^{+2} and Mg^{+2} decreases them (Goldsmith and Graf, 1958 and Goldsmith et al., 1960, 1962). For a given concentration the relative magnitude of the change is in the order:



where the (+) refers to an increase and the (-) to a decrease of the cell parameters. Calcite with 20 mol % of MgCO_3 has, $a_0 = 1.82\%$ smaller than pure calcite while c_0 is 2.54% smaller. (Goldsmith and Graf, 1958). The Mg-calcite from the Gatineau Park area, has $a_0 = 0.42\%$ smaller (average of 17 values) than "specpure" CaCO_3 , while c_0 is 0.46%* smaller (see Table 10). The partial chemical analyses of calcite from Gatineau Park (Table 13) show Mn only occurred in those samples from

* These percentages were obtained from the average values of all calcite in this study.

Table 10.

The reducing of a_0 and c_0 axes of calcite due to Mg + (Fe, Mn) substitution.

Sample	Δa_0 %*	Δc_0 %**
358	0.55	0.53
O-1	0.70	0.62
H-4	0.48	0.48
350	0.53	0.51
P-730	0.31	0.29
H-1	0.35	0.54
H-2C	0.37	0.20
H-3	0.58	0.39
M-118	0.22	0.79
H-2A	0.34	0.41
E-1	0.38	0.37
C-1	0.33	0.41
M-58	0.29	0.30
M-129	0.51	0.68
B-2	0.45	0.47
E-2	0.21	0.26
M-5	0.54	0.56
Average	0.42	0.46

$$* \Delta a_0 \% = \frac{a_0 \text{ of "Specpure" CaCO}_3 - a_0 \text{ of sample}}{a_0 \text{ of "Specpure" CaCO}_3} \times 100$$

$$** \Delta c_0 \% = \frac{c_0 \text{ of "Specpure" CaCO}_3 - c_0 \text{ of sample}}{c_0 \text{ of "Specpure" CaCO}_3} \times 100$$

McCloskey's Field, MnO does not exceed 0.04 %, (samples 358, P-730 and H-2A) whilst Sr is rather high from McCloskey's Field, SrO = 0.95 to 1.09 % (samples 358, P-730 and H-2A). Froese (1967) and Froese and Winkler (1966) pointed out that the substitution of Sr in carbonate is less influenced by temperature than by pressure. Pouliot (1970) reported that the Sr (0.013 to 2.01 %) is a principal substituting element in calcite from Oka, Quebec, but it bears no relationship to other substituting elements such as Mn, Fe and Mg. In Gatineau Park, other than Mg, Fe is the most abundant of the ions (FeO = 0.01 to 1.14 %) having a marked effect on the lattice parameter of calcite. The relative effect on the cell parameters of calcite when Fe⁺² is substituted has been discussed by Goldsmith, Graf, Witter and Northrop (1962) and Rosenberg (1963). Sheppard (1966) concluded that the Fe⁺² ion can be neglected when less than 2 mol % is present.

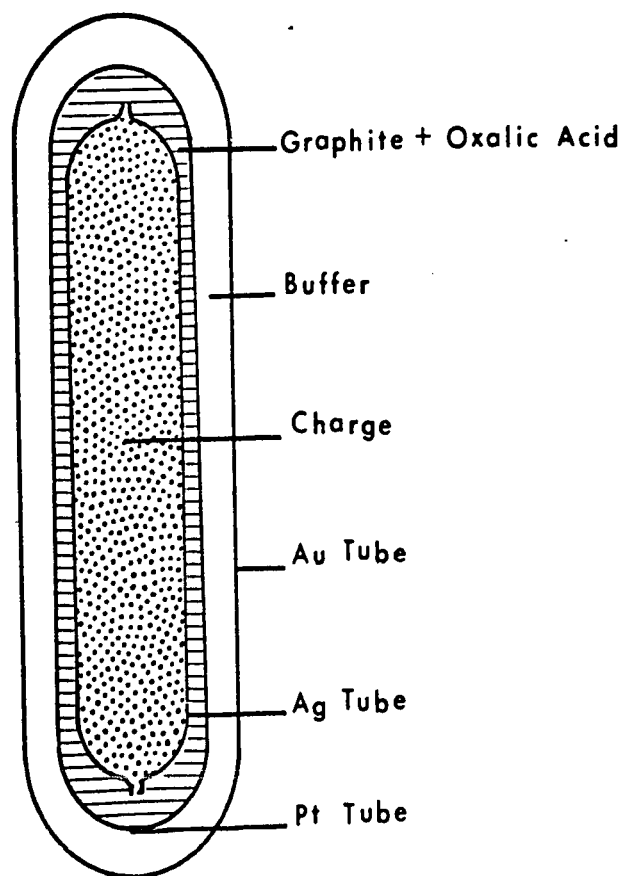
Rehomogenization study.

The MgCO₃ contents obtained from the natural calcite are believed to be at a lower concentration than when formed. As a result, the metamorphic temperature obtained from the concentration of MgCO₃ is misleadingly low. In the studies of both thin and polished sections, two generations of dolomite have been observed. That, corresponding to large crystals (2 to 4 mm.) with rhombohedral form, may be the primary mineral. During metamorphism calcite dissolved magnesium, the maximum amount being at the highest temperature. On cooling, magnesium

exsolved from the calcite solid solution, thus "bleb-like" dolomite is formed. These textures are noticed only in stained calcite (Plates 11 and 15). The calcite in these cases contains a low amount of magnesium in its structure. Therefore, the temperature determination gives a low value.

Skippen (1970, personal communication) suggested that it is necessary to rehomogenize the calcite in order to resubstitute the correct amount of magnesium in the calcite structure, so that an accurate temperature may be obtained.

The experimental procedures were carried out at the Experimental Petrology Laboratory in Carleton University under the direction of Dr. Skippen. Six samples were examined. The calcite powder for this treatment was thoroughly purified by all means available (see Chapter IV). The experimental set-up is illustrated in Figure 5. It consists of an inner or charge system which is contained in a welded Pt or AgPd membrane and is surrounded by the outer or buffer system, which in turn is sealed in an Au tube. The charge is contained in a crimped Ag tube and is surrounded by graphite. Oxalic acid, benzoic acid, and water are used as a source of the C-O-H gas. The proportions are chosen to approximate the equilibrium composition of the gas. The buffer system consists of any assemblage of solid and gas with a fixed fugacity of hydrogen for a given pressure and temperature. For this purpose, the standard oxygen buffer + water as well as the assemblage oxygen buffer + graphite + C-O-H gas were used. The powders were heated to 666° to 778°C with constant pressure of 2 Kb. Samples were heated in the



System C-O-H

Figure 5. Buffering for C-O-H gases. The portion with horizontal lining indicates a sealed Pt or AgPd tube acting as hydrogen membrane; the speckling indicates a crimped tube which allows free exchange of the gas. After Eugster and Skippen (1967). Scale: about 4X natural size.

furnance (hydrothermal bomb) for twelve to fifteen days. The products were quenched with cool air which brought the temperature of the bomb to room temperature in about one minute.

All samples were examined by means of X-ray powder photographs (Plate 3) as described in the last chapter. The results are recorded in Table 11.

Table 11.
Temperatures of rehomogenized calcite.

Sample	Maximum furnace temperature (°C).*	Duration (days).	Temperature (°C)** from rehomogenized calcite.
358	778	12	560
H-1	727	15	529
M-116	771	14	529
H-2A	684	15	610
M-14	778	12	550
224S-2	666	15	509

* The maximum temperature which samples have been treated in the hydrothermal bomb.

** Temperatures obtained from X-ray powder photographs with internal standard (using the $d_{(104)}$ of calcite and $d_{(111)}$ of silicon).

Chemical analysis.

Calcite was purified by all available processes in preparation for chemical analysis (see Chapter IV). X-ray diffraction was used for checking the impurities in this calcite. The powdered samples were dissolved in 10 ml. of 10 % of hydrochloric acid and allowed to stand in the reagent for 10 - 12 hours to make sure that all the calcite was brought into solution. The solutions were made up to 100 ml. and Mg, Ca, Sr, Mn and Fe were determined by using a Techton AA-4 atomic absorption spectrophotometer. The procedure used to obtain suitable dilutions and overcome interferences is briefly outlined in Table 12, while representative calibration curves are shown in Figure 6. Samples were analysed in duplicate.

The analytical results are listed in Table 13. The elements were converted to oxides and carbonates. The mol per cent (or mole fraction) of $MgCO_3$ was calculated.

The chemical composition of calcites are very similar to the results reported by Goldsmith, Graf and Joensuu (1955), and Sheppard (1966). The $MgCO_3$ contents of calcite are slightly higher than those obtained from X-ray diffraction (see Table 15). It is interesting that samples from McCloskey's Field contained high amounts of SrO , (0.95 - 1.09 %) and whenever strontium was present, almost equal amounts of FeO and small amounts of MnO were determined. This is rather unusual composition in calcite and as Sr isotopes have not been investigated in this area, little is known concerning the origin of this rock. Recently,

Table 12.

Scheme for chemical analysis of calcite by atomic absorption spectrometry.

Sample solution	Aliquot	Element determined	Flame
100 mg. sample dissolved in 10 ml. of 10 % HCl for 10-12 hours, made up to 100 ml.	10 ml.	Mn, Sr, and Fe.	Acetylene-air.
	2 ml. diluted to 100 ml.	Ca.	Acetylene-air.
	1 ml. diluted 50 or 25 ml.	Mg.	Acetylene-air.

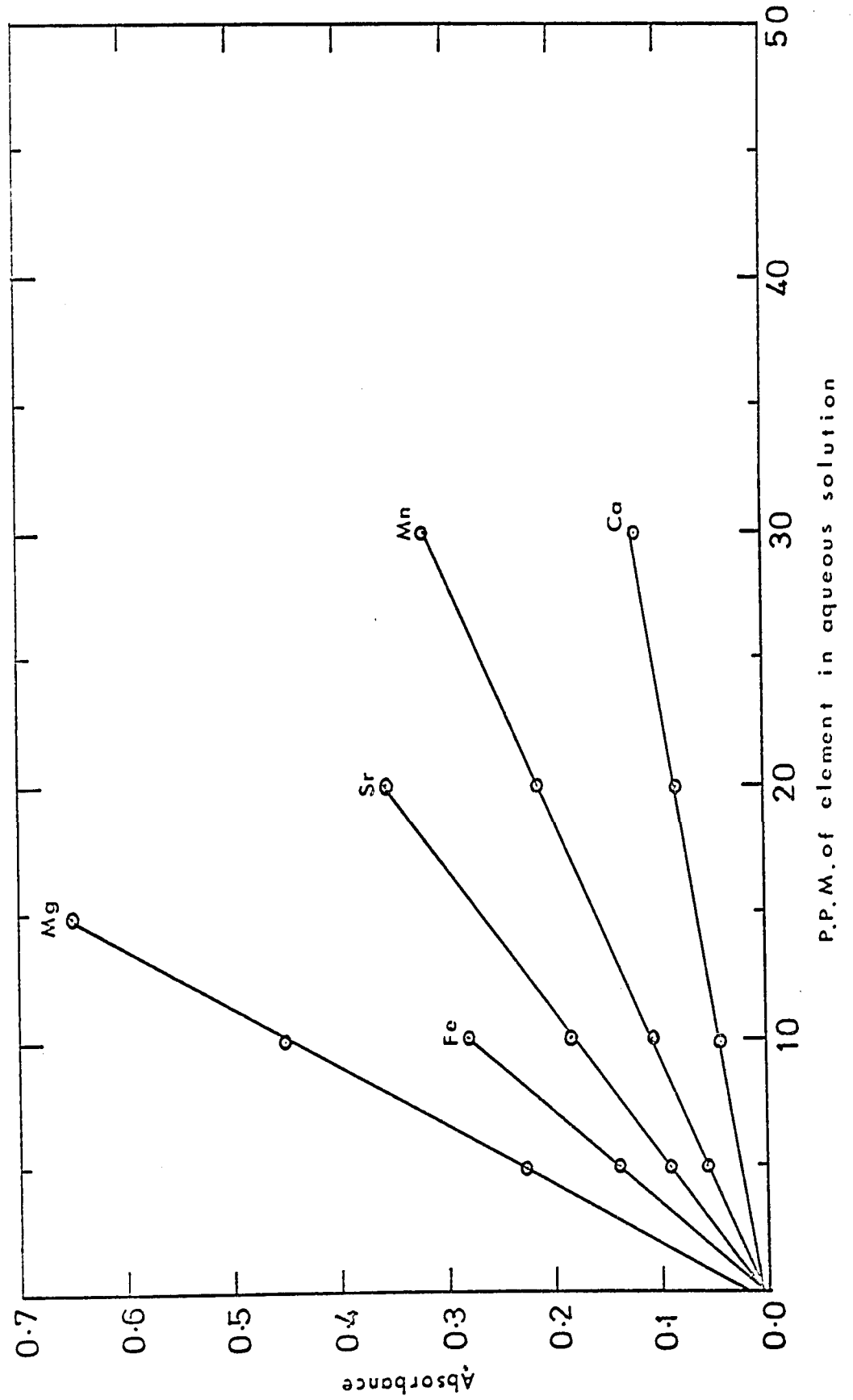


Figure 6. Calibration curves for chemical analysis.

Table 13. Partial chemical analyses of calcites.

Sample	Weight %							Weight % as carbonate						Mol % MgCO ₃ *
	CaO	MgO	MnO	SrO	FeO	CaCO ₃	MgCO ₃	MnCO ₃	SrCO ₃	FeCO ₃				
358	51.14	4.32	0.04	0.95	0.96	91.26	9.03	0.06	1.35	1.55	10.53			
P-730	54.87	3.10	0.03	1.06	0.93	97.92	6.48	0.05	1.51	1.50	7.59			
H-2A	54.71	1.70	0.03	1.09	1.14	97.63	3.56	0.05	1.55	1.84	4.19			
E-1	50.32	4.40	n.d.**	n.d.	n.d.	89.80	9.20	--	--	--	10.73			
C-1	53.03	2.49	n.d.	n.d.	0.57	94.63	5.21	--	--	0.92	6.11			
M-58	53.73	2.91	n.d.	0.14	0.21	95.88	6.09	--	0.20	0.34	7.14			
B-2	52.26	3.17	n.d.	0.14	n.d.	93.26	6.63	--	0.20	--	7.77			
224S-2	50.37	2.98	n.d.	n.d.	n.d.	89.89	6.23	--	--	--	7.29			

$$\begin{aligned}
 \star \text{ Mol \% MgCO}_3 = & \frac{\text{MgCO}_3 \text{ (true weight)}}{\text{Molecular weight of MgCO}_3} \times 100 \\
 & \frac{\text{CaCO}_3 \text{ (recalculated to 100)}}{\text{Molecular weight of CaCO}_3} + \frac{\text{MgCO}_3 \text{ (recalculated to 100)}}{\text{Molecular weight of MgCO}_3} \times 100
 \end{aligned}$$

** n.d. : not detectable (less than 0.01 %).

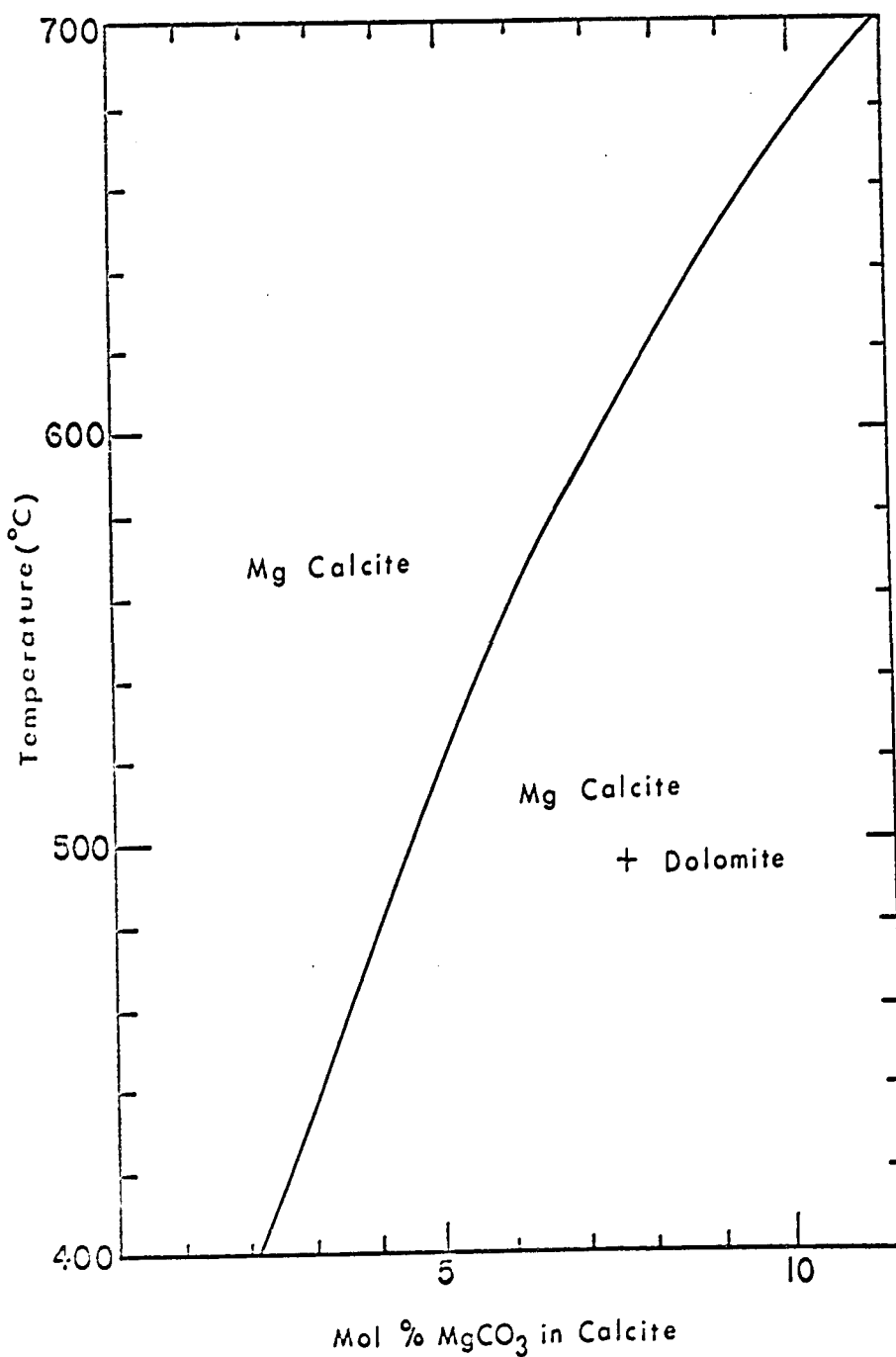
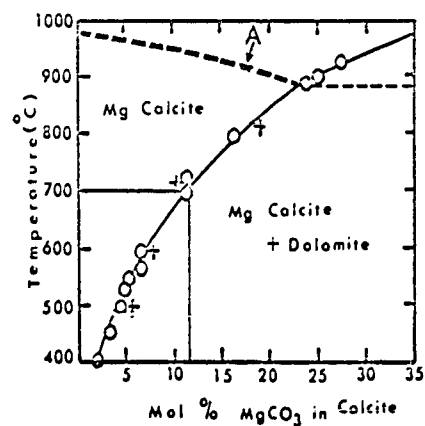
Pouliot (1970) has shown that Sr substitutes for Ca in the carbonatitic calcites from Oka, Quebec. Before concluding this aspect it could be stated that it is not unusual or impossible for Sr to substitute for Ca, when it is originally present in the system. Moreover the energetics of Ca and Sr are almost identical, at least in certain structures such as plagioclase, aragonite and probably calcite (Virgo, 1969), Froese and Winkler (1966) and Froese (1967).

Strontianite has been observed locally in McCloskey's Field (Hogarth, personal communication, 1970). After long exposure, X-ray diffraction photograph of samples from this area show a faint line of the strongest reflection (111) of strontianite. This suggests that there might be a tiny amount of strontianite coexisting with calcite.

Results of temperature determinations.

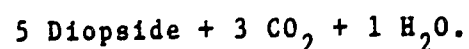
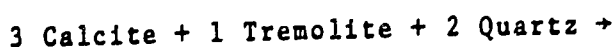
The $MgCO_3$ contents of the calcite coexisting with dolomite were determined by means of X-ray diffraction. Curves of mol % $MgCO_3$ vs temperatures were established by Harker and Tuttle (1955), Graf and Goldsmith (1955, 1958), and Goldsmith and Newton (1969). All the temperatures discussed in this thesis were obtained directly from the curve given by Goldsmith and Newton (1969) (see Figure 7). Tables 5 to 9 present the temperatures derived from natural calcite; Tables 5, 6 and 7 from interpretation of X-ray photographs and Tables 8 and 9 from X-ray diffractometer. The metamorphic grade was inferred from the mineral assemblages of nearby pelitic rocks which

Figure 7. Unique polybaric calcite - dolomite solvus. Circles denote data of Goldsmith & Newton (1969). Crosses are data of Harker & Tuttle (1955). The dashed lines represent the narrow (postulated) two-phase field (A) of calcite I and Calcite II and the estimated temperature of the calcite I-II inversion of the solvus. Figure below is the inset portion of the above figure.



suggest upper amphibolite or granulite facies (see Chapter II). Of all the temperatures determined from calcite, no sample gave a temperature sufficiently high to be correlated with the metamorphic grade.

The coexisting calcite - dolomite pairs were from Gatineau Park region (except one sample, O-1 which was collected near Otter Lake village) and were samples that Hogarth (1970) classified as marble and intrusive metamorphosed carbonate (McCloskey's Field). The sample from Otter Lake village gave the highest temperature (577° - 583°C by X-ray diffractometer; 595° - 603°C by X-ray powder photograph). The marble with brucite indicated a temperature range of 490° - 530°C from X-ray diffractometer (samples 224S-2 and 350). The marble with serpentine generally gave a rather low temperature (less than 500°C). The calcite - apatite marble normally gives a temperature in the range 490° - 558°C (from Table 6). One calcite - quartz marble (M-5) indicates a temperature of 504°C by X-ray diffractometer (University of Ottawa unit) and those samples from Old Chelsea area are without any temperature indication [i.e. their $d_{(104)}$ peak has exactly the same position as the "Specpure" CaCO_3] and have not been included in the tables. From thin section studies, A-4 (Plate 14) shows the mineral assemblage: calcite + quartz + tremolite + diopside, which indicates the following reaction:



If this reaction took place, a rather high metamorphic temperature is suggested. Winkler (1965, pp. 25-27) notes that the formation

of diopside according to reaction above indicates that the temperature of 530°C has been exceeded. This is a maximum temperature for a total pressure of 2 Kb.

Previously, some investigators using the same X-ray diffraction technique, determined MgCO₃ in calcite and corresponding equilibration temperatures of Grenville marble. Sheppard (1966) obtained T_{sx} (solvus temperature from X-ray data) from Grenville calcite in the range 415° to 485°C. Höy (1970) estimated a temperature of 600°C by using the calcite from brucitic marble.

The rehomogenized calcite yielded higher MgCO₃ contents and therefore a slightly higher temperature can be obtained by this technique as compared to temperatures obtained from natural samples (see Table 11). The samples (H-2A and 358) show some exsolved dolomite in calcite. Thus rather high temperatures (610° and 560°C, Table 11) were obtained. However, these are still low compared to the temperatures of almandine - amphibolite facies or even granulite facies to which the mineral assemblages of the pelitic gneisses of this area belong. These lower values are considered to be due to complete exsolution of dolomite from the calcite grain while the rock was still hot in its natural environment.

MgCO₃ contents derived from slightly different X-ray diffraction techniques are compared in Table 14. The corresponding temperatures are also listed. Columns 1, 2 and 3 suggest that the amount of exsolving dolomite may be different

Table 14.
Comparison of the temperatures determined by different X-ray methods.

Method	1	2	3	4	5
Sample	Temp. (°C) from X-ray photograph	Temp. (°C) from X-ray photograph	Temp. (°C) from X-ray photograph	Temp. (°C) from X-ray diffractometer	Temp. (°C) from X-ray diffractometer
358	550	558	560	546	--
H-1	462	525	529	558	558
M-118	462	558	529	518	488
H-2A	530	495	610	517	--
M-14	462	--	550	400	429
224S-2		--	509	490	--

1: X-ray photographs taken using filtered Cu radiation and internal standard (Si).

2: X-ray photographs taken without internal standard (Si) but shrinkage corrections have been made (Table 5).

3: Temperatures from rehomogenized calcite which mixed with internal standard (Si) (Table 11)

4: X-ray diffractometer work carried out with the University of Ottawa unit, using

filtered Cu radiation, internal standard (Si) and chart speed of 4 inches/2θ (Table 8).

5: X-ray diffractometer work carried out with the Soil Research Institute unit, using

filtered Co radiation, internal standard (Si) and chart speed 8 cm./2θ (Table 9).

even within the same specimen (Plate 15).

The chemical analyses for $MgCO_3$ from a few selected calcites are compared in Table 15 with the X-ray determinations for $MgCO_3$. The chemical analyses are consistently higher. Exsolved dolomite is possibly responsible, in part.

Guilloux (1969) reported from his studies at the Forsyth ore-body (about one mile northwest of Dawson Field) the P-T condition: $P = 7 - 8$ Kb. from mineral assemblage in pelitic gneisses and $T = 700 \pm 20^\circ C$ by the distribution of Mg in coexisting almandine and biotite.

Engel and Engel (1953) utilizing the magnetite - ilmenite and calcite - dolomite systems, indicated that the probable maximum temperature of metamorphism in the area near Balmat, New York was $550^\circ C$.

Doe (1962) using the sphalerite - pyrrhotite geothermometer, estimated the temperature of metamorphism in Balmat, New York to be $510 \pm 50^\circ C$ (with a total pressure of 3 ± 1 Kb.).

Lessing and Grout (1971), determined the temperature of formation of dolomitic marble from Edwards, New York to be $450^\circ C$. The Balmat-Edwards district is about 90 miles south-southeast of thesis area. Marble in this region has undergone metamorphism during the Grenville orogeny.

Table 15.

Comparison of the temperatures determined by X-ray diffraction with those determined by chemical analysis.

Sample	Temperature (°C)* from X-ray photograph.	Temperature (°C)** from chemical analysis.
358	558	700
P-730	460	618
H-2A	495	490
E-1	495	700
C-1	495	569
M-58	460	605
B-2	530	624
224S-2	--	609

* Temperatures from X-ray powder photographs (Table 5).

** Temperatures from chemical analyses (only MgCO_3 were considered), (Table 13).

CHAPTER VI

PRESSURE ESTIMATION

The latest experimental results for the univariant kyanite - sillimanite phase boundary in the Al_2SiO_5 system are geologically more satisfactory than earlier results. Richardson, Gilbert and Bell (1969) reported that the triple point of the three Al_2SiO_5 polymorphs kyanite, sillimanite and andalusite is 5.5 Kb. in pressure and 622°C in temperature (Figure 8). In the Grenville Province knowledge of pressure is uncertain. Evans (1964) reported that in the Denbigh area, sillimanite together with rare kyanite are ubiquitous in pelitic schists. The temperature in this area was probably in the range of 500° to 700°C (Sheppard, 1966), indicating a pressure of 4 to 7 Kb. (Newton, 1966).

In Gatineau Park, sillimanite is the common Al_2SiO_5 polymorph occurring in biotite gneiss (Hogarth, 1970). Rarely, as north of Pinks Lake, andalusite coexists with sillimanite (Hogarth, personal communication, 1970). The minimum metamorphic temperatures in this area are believed to be in the range of 500° to 700°C. Thus a pressure range of 4.2 to 6.3 Kb. can be suggested (those results referred to the curve of Richardson, Gilbert and Bell, 1966).

Peach (1950) estimated the pressure of the MacDonald pegmatite (Bancroft, Ontario) on the basis of fluid inclusions in quartz. He estimated a pressure of 3 Kb. at 530°C and 650°C (temperatures from fluid inclusions and pyrite respectively).

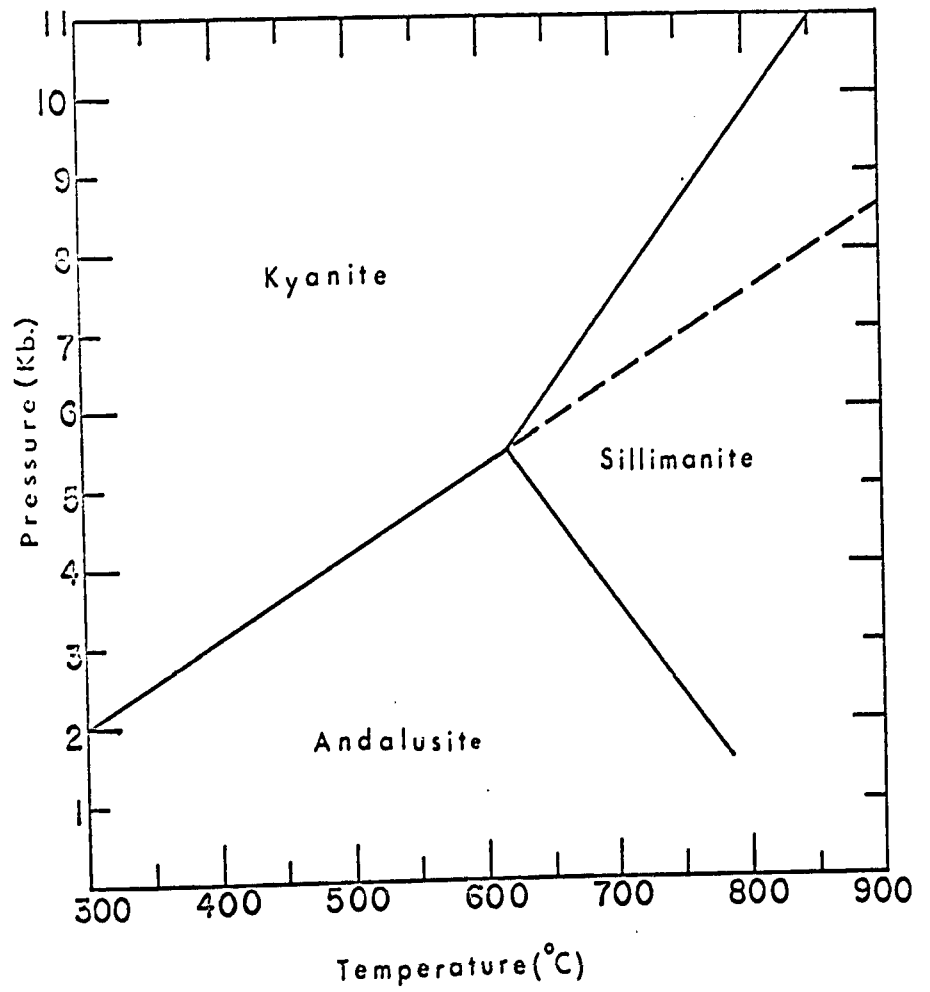


Figure 8. Phase diagram showing stability field of the polymorphs of Al_2SiO_5 . After Richardson, Gilbert and Bell (1969).

Engel and Engel (1953) reported that the thickness of meta-sedimentary rocks of the Grenville series in southeastern Ontario and northwest Adirondacks totals 20,000 feet (equivalent to 7 Km.). If we considered the marble was formed at a depth of 7 Km. and if the pressure gradient was as low as 1 atm./3 m. an upper limit of about 2.3 Kb. is given.

In conclusion comparison with adjoining areas and independent considerations suggest that calcite in Gatineau Park was formed in the range of 4.2 to 6.3 Kb. pressure.

CHAPTER VII
GENERAL CONSIDERATIONS

Discussion.

The present work is concerned with the possibility of using the Mg content of calcite in coexistence with dolomite to indicate the temperature of crystallization of marble. Using the calibration curve given by Goldsmith and Newton (1969), temperatures were obtained for different Mg contents in calcites from the Gatineau Park. The following results were obtained:

- 1) A sample near Otter Lake village gave the highest temperature ($T_{xp}^* = 603^{\circ}\text{C}$; $T_{xdCu}^{**} = 583^{\circ}\text{C}$).
- 2) Marble with brucite (+ chondrodite) indicated temperatures $T_{xp} = 558^{\circ}\text{C}$; $T_{xdCu} = 530^{\circ}\text{C}$ from sample 350 and $T_{xdCu} = 490^{\circ}\text{C}$ from sample 224S-2.
- 3) Marble with apatite gave temperatures normally in the range 490° to 558°C .
- 4) Marble with serpentine (\pm graphite) indicated a fairly low temperature generally less than 500°C .
- 5) One sample (M-5) with quartz has an indication of temperature at $T_{xp} = 570^{\circ}\text{C}$; $T_{xdCu} = 504^{\circ}\text{C}$.

The above results indicate a rather wide range of temperatures derived from Mg calcite. All these temperatures are considerably

* Temperature derived from X-ray powder photographs (Table 5).

** Temperature derived from X-ray diffractometer, using filtered copper radiation (Table 8).

lower than the temperatures obtained by Guilloux (1969) for Mg distribution in coexisting biotite - garnet in gneiss from the area which the samples in the present study were taken. The highest temperature determined by the method of $\Delta d_{(104)}$ (Tables 5, 8 and 9), corresponds to 558°C for samples of calcite - apatite marble from Meach Lake.

The temperatures obtained using the $MgCO_3$ content of calcite tend to be lower than the temperatures deduced by other methods (Guilloux, 1969) for the same metamorphic grade, because at present, the amount of $MgCO_3$ preserved in the calcite structure, is believed to be less than at the time of formation of the calcite. This is because of exsolution of Mg (as "bleb-like" dolomite) from calcite during retrograde conditions.

In this thesis, all samples contained both calcite and dolomite. Petrographic study of dolomite indicated two grain sizes (Plates 11 and 15). The coarse-grained fraction is believed to be primary dolomite equilibrated with calcite during prograde metamorphism. The magnesium substituted at maximum amounts when the highest metamorphic temperature was reached. On cooling, dolomite exsolved from calcite. This exsolved dolomite is the finer grained fraction and appears as a "bleb-like" texture. The reaction can be represented as:



For this reason, the $MgCO_3$ contents pertain to low-magnesium calcite and the derived temperatures will be below the maximum

temperature of prograde metamorphism. A brief flow sheet (Figure 9) illustrates the inter-reaction of calcite and dolomite.

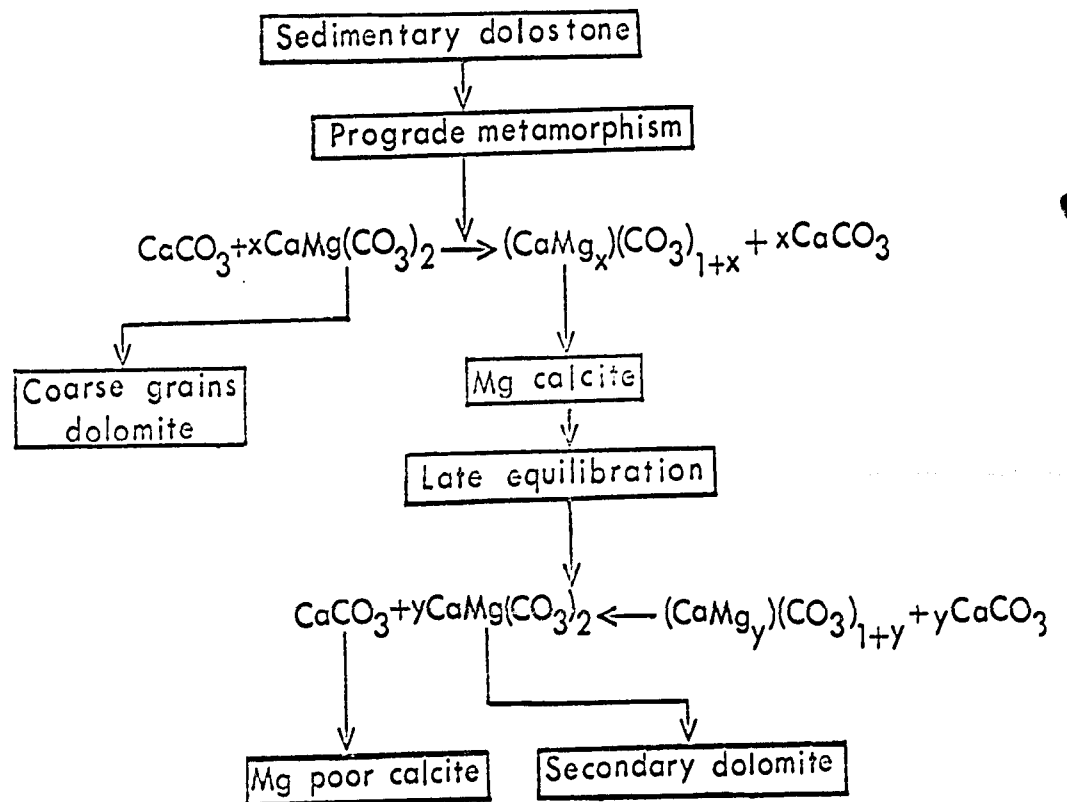
Exsolution textures are clearly indicated in some samples. Optical study of the stained calcite separates revealed up to 2 % of dolomite. This is probably insufficient dolomite to be detected by the X-ray diffraction methods. However, many of the more magnesium-rich calcite separates ($\text{MgCO}_3 > 3 \text{ mol } \%$) gave a weak dolomite $d_{(104)}$ reflection after a long (18-20 hours) exposure. Exsolved "bleb-like" dolomites were observed in some thin sections, and most of calcite from the high grade rocks are cloudy, possibly due to the presence of very fine exsolved dolomite. These features are indicative of slow cooling which makes temperatures of formation difficult to assess.

Rehomogenization of some purified calcites under the hydrothermal bomb was successful in that the X-ray data led to higher temperatures. These rehomogenized calcites yield a rather high MgCO_3 content (see Table 11) as compared to the natural sample. The temperature obtained by this method indicates the temperature at which rehomogenized calcites are in equilibrium with dolomite and is low compared to the probable temperature of formation of marble and its associated rocks. Some possible explanations are:

- 1) There is insufficient Mg resubstituted in the calcite structure because part of the exsolved dolomite (secondary dolomite) in the calcite may be partially separated during the processes of separation of dolomite from calcite.

Figure 9.

The relationship of the inter-reaction of calcite and dolomite.



- 2) An incomplete rehomogenized reaction occurs due to short duration.
- 3) Slow quenching of the hydrothermal bomb might cause back reaction.

Nevertheless this method shows promise in indicating more exact temperatures of formation of calcites.

Origin of carbonate rocks.

Carbonate rocks may be classified into two extreme types in this thesis area. The carbonate bodies located at Dawson Field and near Old Chelsea village are clearly derived from the sedimentary limestones by metamorphism whereas the carbonate bodies at McCloskey's Field are products of intrusive carbonate (Hogarth, 1966).

The intrusive nature is supported by several lines of evidence:

- a) tongues of carbonate cut through aplite,
- b) brecciation,
- c) carbonate veins and dykes transect the foliation of syenite.

An affiliation with carbonatites is suggested by the mineralogy and geochemistry of these rocks:

- a) presence of apatite,
- b) high concentration of Sr (up to 1.09 % SrO) occurred in all analysed calcite samples from this area,
- c) presence of unusual radioactive minerals such as pyrochlore - betafite (Hogarth, 1959).

Future work.

The carbonate rocks merit further work along at least three lines:

- a) The true substitution of divalent ions for Ca in calcite should be tested by such methods as electron spin resonance and electron microprobe.
- b) Isotope study on $\text{Sr}^{87}/\text{Sr}^{86}$ ratios.
- c) The relationship between temperature determined from rehomogenized calcite and the thermal and geological history of the samples. More work on rehomogenization of calcite under a long duration in the hydrothermal bomb say, two months and a more advanced quenching techniques should be developed.

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Appendix 1.

Comparison of calculated and observed d-spacings of "Specpure" CaCO_3 with those of calcite separated from a representative sample (M-5). X-ray powdered photographs. Cu/Ni. Camera diameter = 114.6 mm.

h k l	"Specpure" CaCO_3		I/I ₀	M-5		I/I ₀
	d calc.	d obs.		d calc.	d obs.	
0 1 2	3.8608	3.863	20	3.8396	3.840	15
1 0 4	3.0399	3.048	100	3.0231	3.023	100
0 0 6	2.8471	2.849	15	2.8310	2.834	8
1 1 0	2.4989	2.501	50	2.4853	2.484	40
1 1 3	2.2882	2.289	60	2.2757	2.274	40
2 0 2	2.0978	2.0995	50	2.0863	2.085	40
0 1 8	1.9149	1.9188	65	1.9042	1.9048	45
1 1 6	1.8781	1.8771	60	1.8677	1.8673	45
2 1 1	1.6284	1.6298	10	1.6196	1.6190	10
1 2 2	1.6067	1.6071	30	1.5979	1.5972	25
1 0 10	1.5890	1.5926	<5	1.5801	--	--
2 1 4	1.5277	1.5275	30	1.5193	1.5191	25
2 0 8	1.5199	1.5124	20	1.5115	1.5051	<5
1 2 5	1.4755	1.4751	15	1.4674	1.4670	10
0 3 0	1.4427	1.4427	40	1.4348	1.4347	20
0 0 12	1.4235	1.4234	40	1.4155	1.4152	20
2 1 7	1.3588	1.3584	10	1.3514	1.3513	5
0 2 10	1.3409	1.3407	20	1.3334	1.3344	10
1 2 8	1.2986	1.2983	25	1.2914	1.2924	10
3 0 6	1.2869	1.2881	8	1.2799	--	--
2 2 0	1.2494	1.2487	8	1.2426	1.2429	<5
1 1 12	1.2369	1.2363	25	1.2300	1.2289	8
2 1 10	1.1815	1.1816	25	1.1750	1.1755	8
1 3 4	1.1556	1.1551	30	1.1493	--	--
2 2 6	1.1441	1.1437	10	1.1378	--	--

Appendix 2.

Reindexed "Specpure" CaCO₃.

d(Å)	h k l*	d(Å)	h k l*
3.8545	0 1 2	1.2966	1 2 8
3.0355	1 0 4	1.2848	3 0 6
2.8437	0 0 6	1.2473	2 2 0
2.4945	1 1 0	1.2353	1 1 12
2.2844	1 1 3	1.2798	2 1 10
2.0942	2 0 2	1.1537	1 3 4
1.9272	0 2 4	1.1422	2 2 6
1.9124	0 1 8	1.1246	1 2 11
1.8753	1 1 6	1.0615	2 0 14
1.6256	2 1 1	1.0471	0-4 4
1.6039	1 2 2	1.0447	3 1 8
1.5869	1 0 10	1.0353	1 0 16
1.5251	2 1 4	1.0350	1 1 15
1.5177	2 0 8	1.0230	2 1 13
1.5094	1 1 9	1.0118	3 0 12
1.4731	1 2 5	0.9896	3 2 1
1.4402	0 3 0	0.9846	2 3 2
1.4218	0 0 12	0.9767	1 2 14
1.3567	2 1 7	0.9655	3 2 4
1.3409	0 2 10		

* Rhombohedral lattice indexed on hexagonal reference system:

$$-h + k + l = 3n.$$

Plate 1. Selected X-ray diffraction Photographs. Cu/Ni.

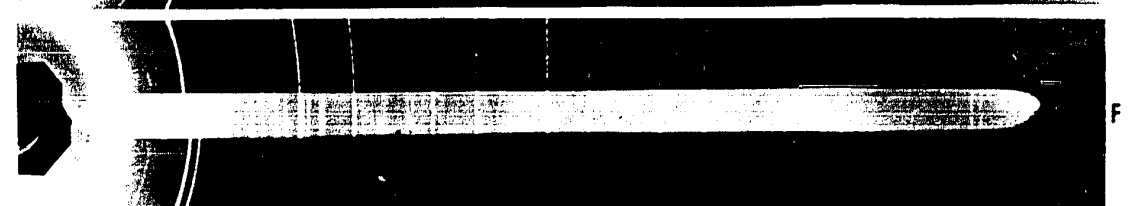
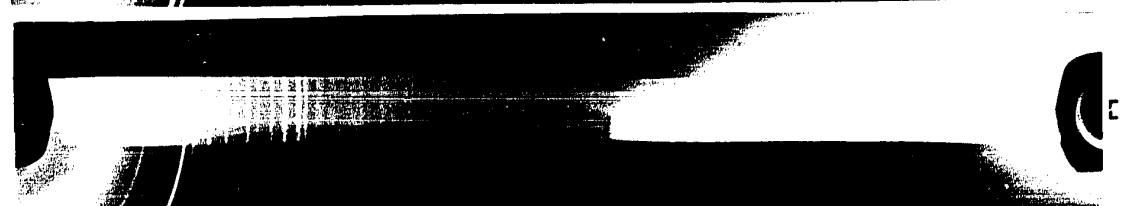
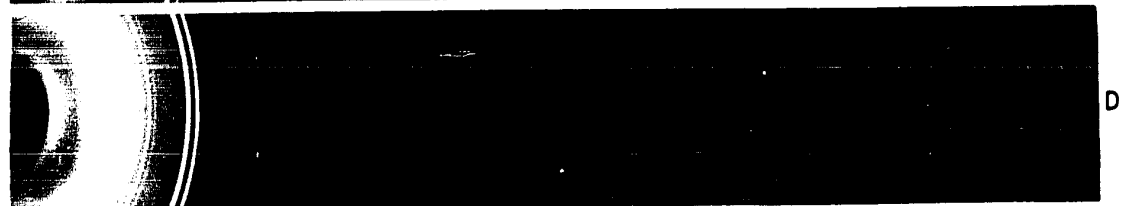
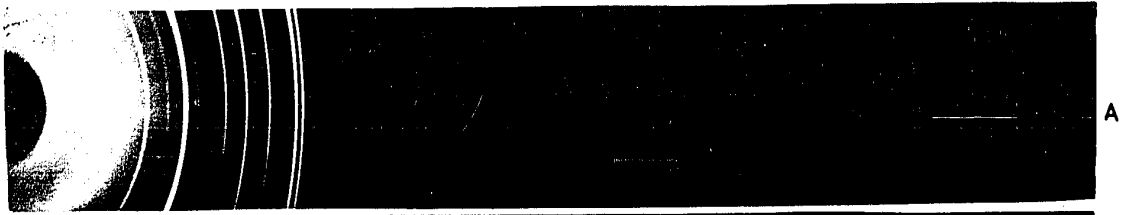
Camera diameter = 114.6 mm. Contact print.

- A: "Specpure" CaCO_3 , standard (Johnson, Matthey and Company Ltd.).
- B: Sample H-2A, calcite and dolomite from McCloskey's Field.
- C: Sample P-730, calcite and dolomite from McCloskey's Field.
- D: Sample 350, calcite and dolomite from southwest of Meach Lake.
- E: Sample O-1, calcite and dolomite from Otter Lake. The patterns were obtained by double exposure method. The upper portion is the silicon pattern.
- F: Sample B-2, calcite and dolomite from Old Chelsea, Gatineau Park. The patterns were obtained by double exposure method. The upper portion is the silicon pattern.

Key to X-ray lines.

- 1: The strongest reflection line, 111 of silicon.
- 2: The strongest reflection line, 104 of calcite.
- 3: The strongest reflection line, 104 of dolomite.

2
↓



↑↑
123

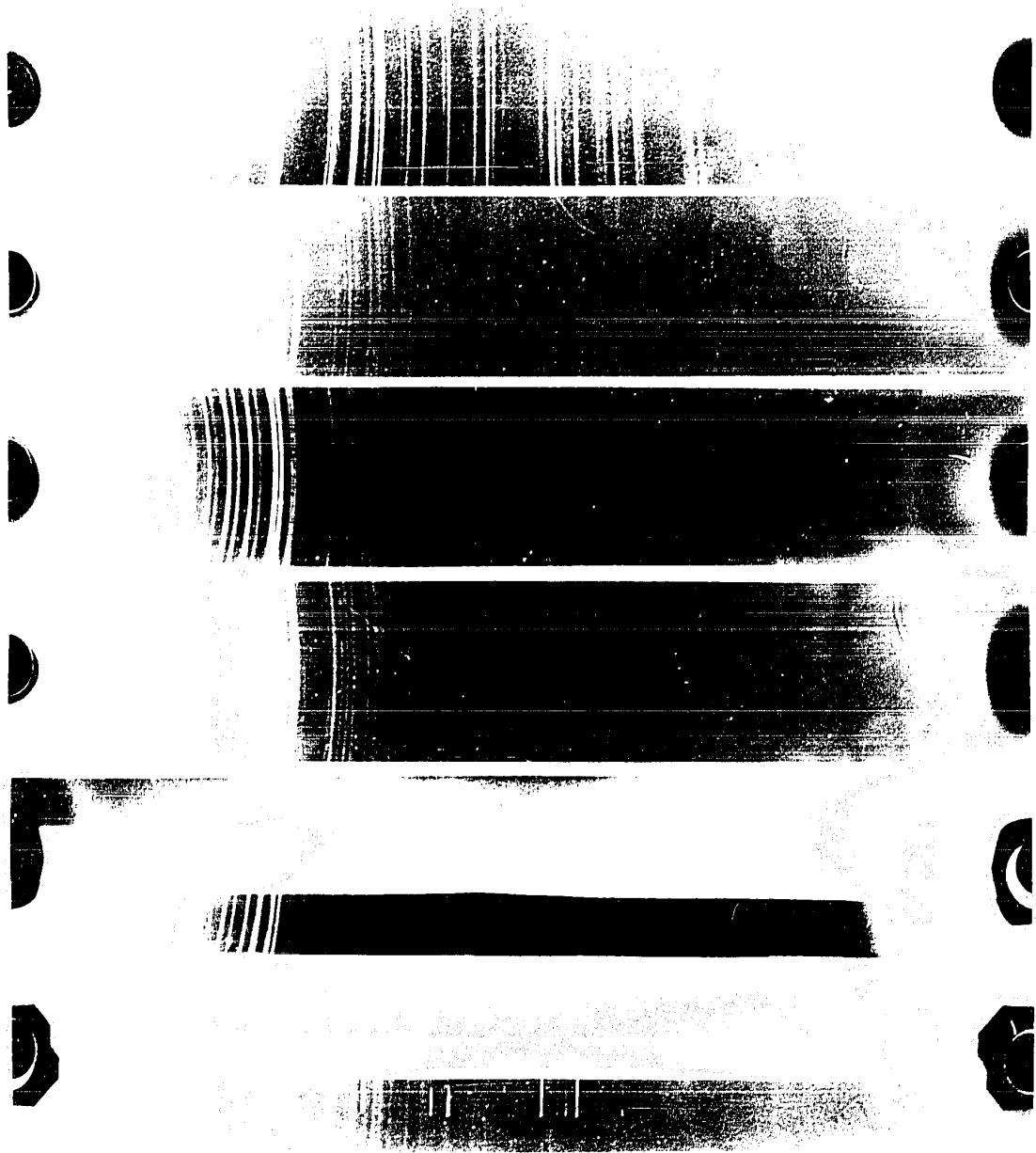


Plate 2. Typical X-ray diffractometer chart for $2\theta = 32.5 - 34.5^\circ$. Co/Fe. Chart speed = 16 cm./degree (2θ). In all runs sample powder (<200 mesh) was mixed with standard silicon.

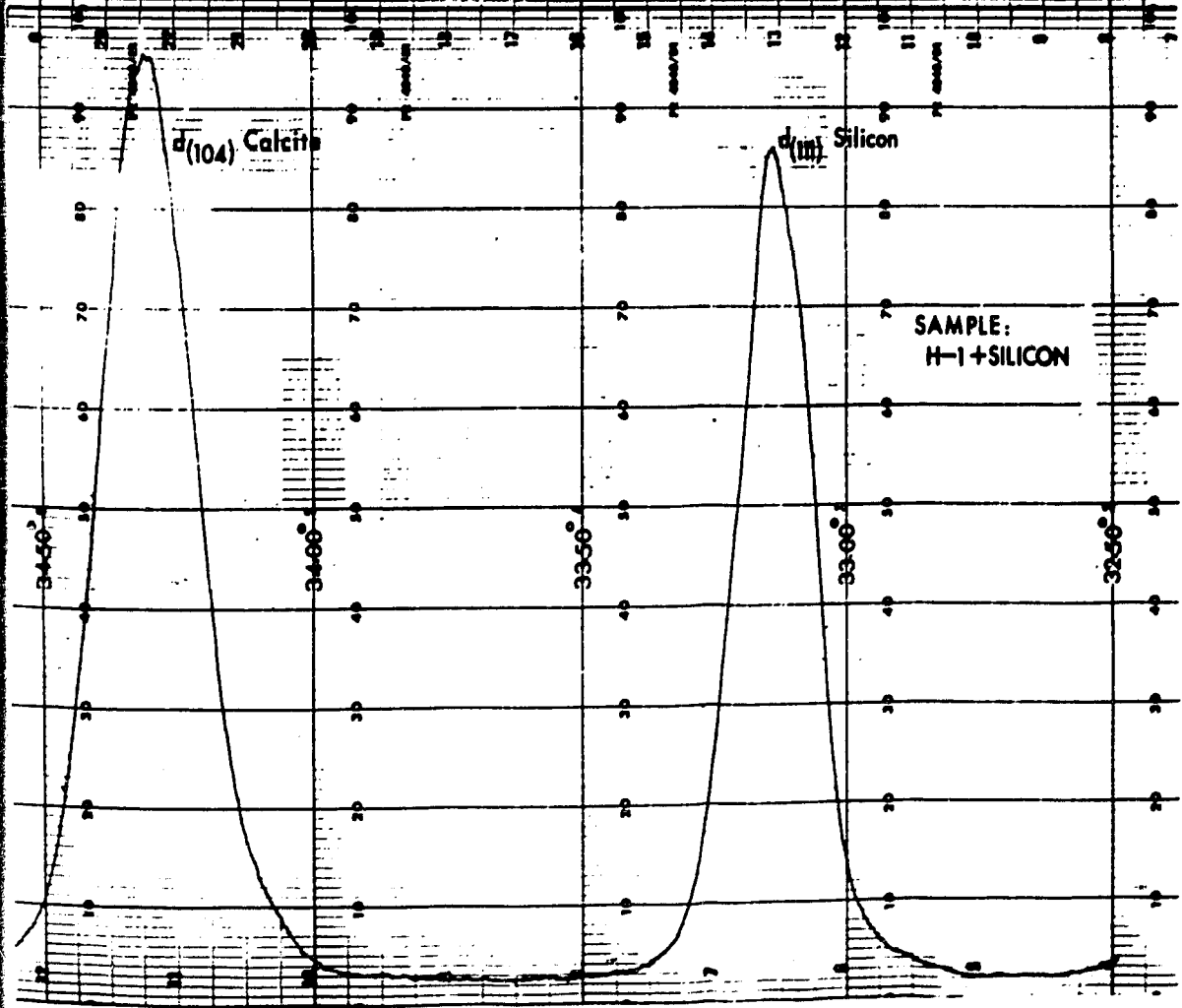
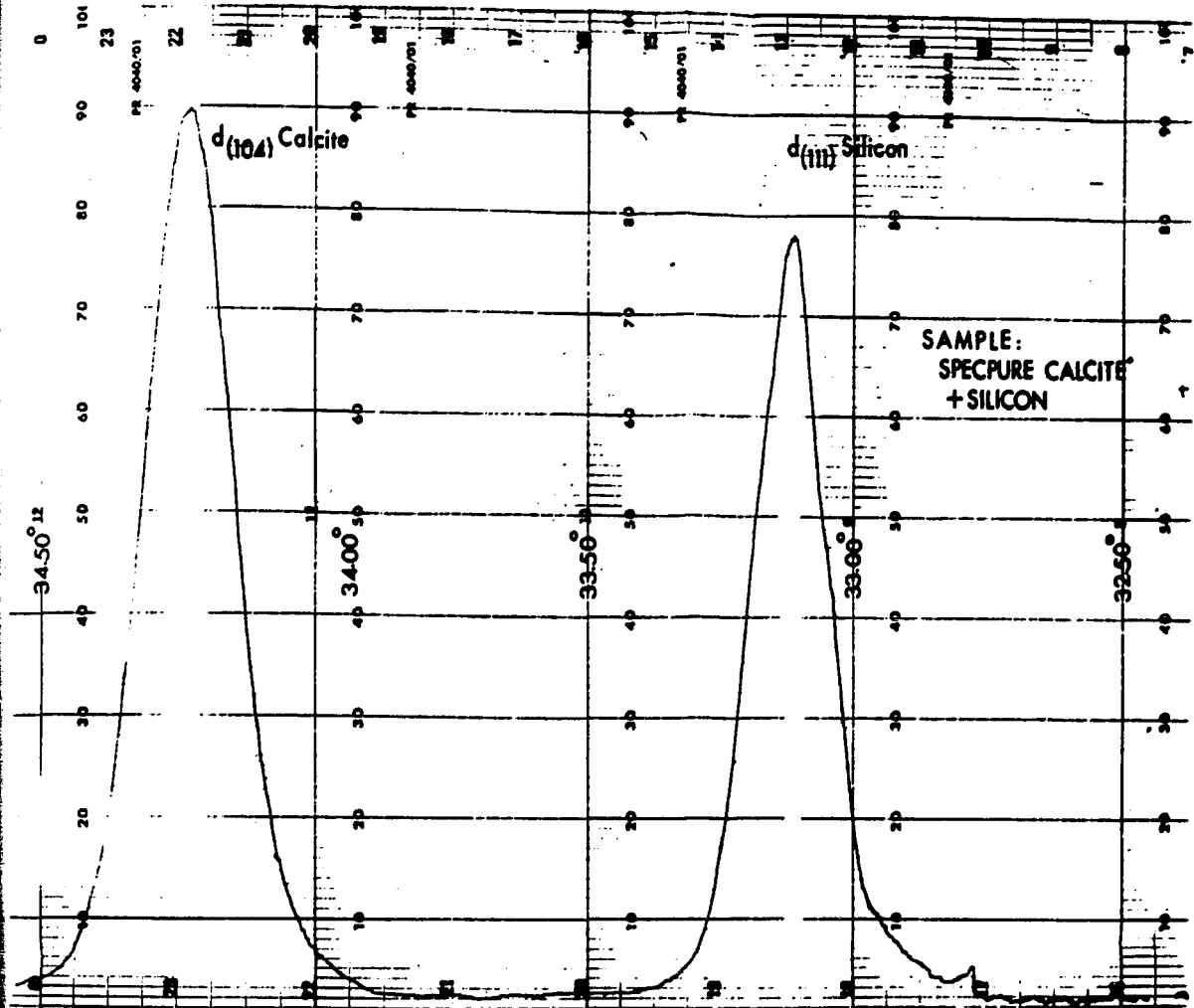


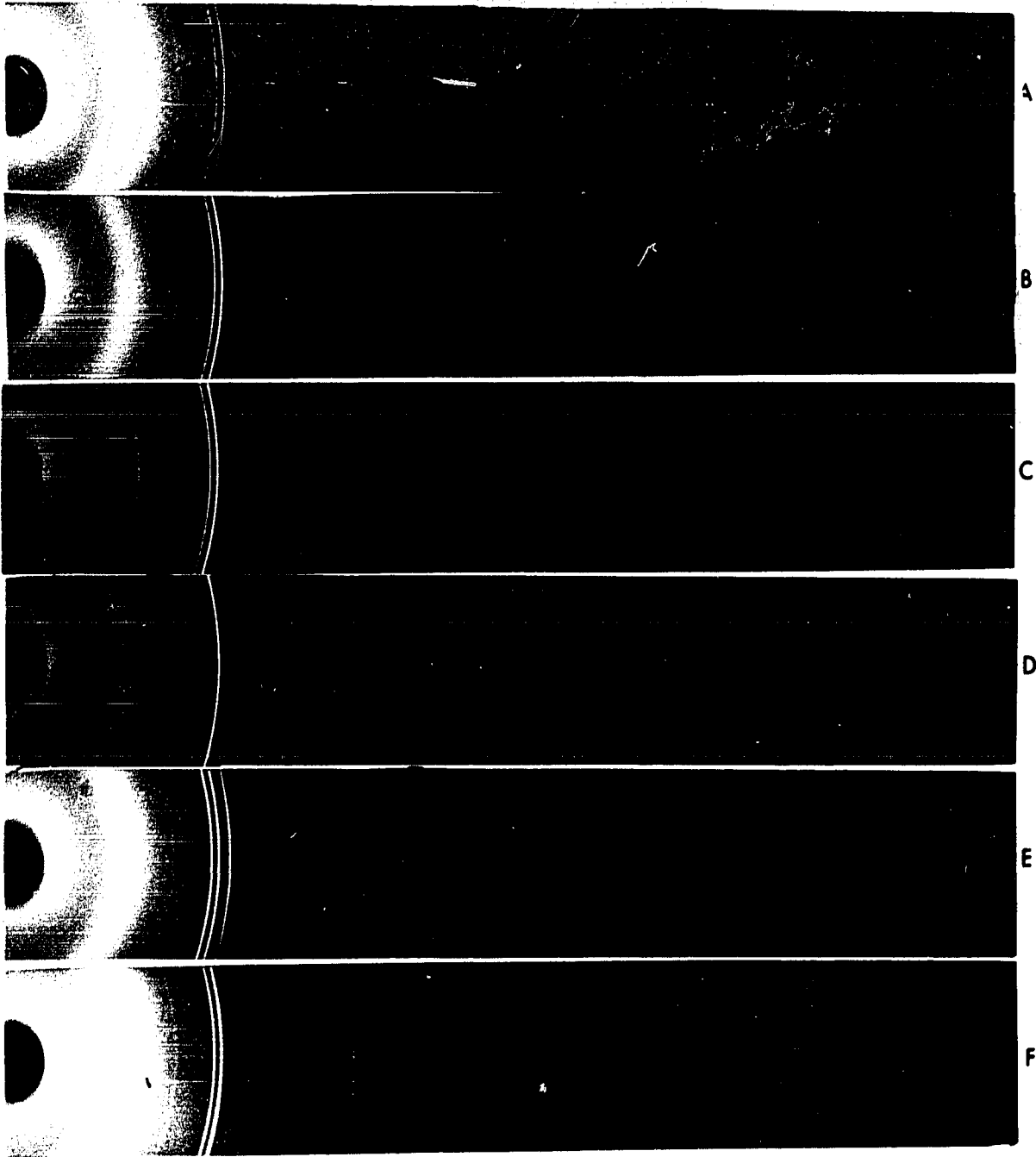
Plate 3. Selected X-ray diffraction photographs. Fe/Mn.

Camera diameter = 114.6 mm. Contact print.

- A: Mixture of calcite and silicon patterns. The calcite is the purified natural sample (H-2A).
- B: Mixture of calcite and silicon patterns. The calcite is the rehomogenized product from sample (H-2A).
- C: Mixture of calcite and silicon patterns. The calcite is the purified natural sample (224S-2).
- D: Mixture of calcite and silicon patterns. The calcite is the rehomogenized product from sample (224S-2).
- E: Mixture of calcite, dolomite and silicon patterns. The calcite is the natural sample (M-118).
- F: Mixture of calcite and silicon patterns. The calcite is the rehomogenized product from sample (M-118).

Key to X-ray lines.

- 1: The strongest reflection line, 111 of silicon.
- 2: The strongest reflection line, 104 of calcite.



↑↑
12

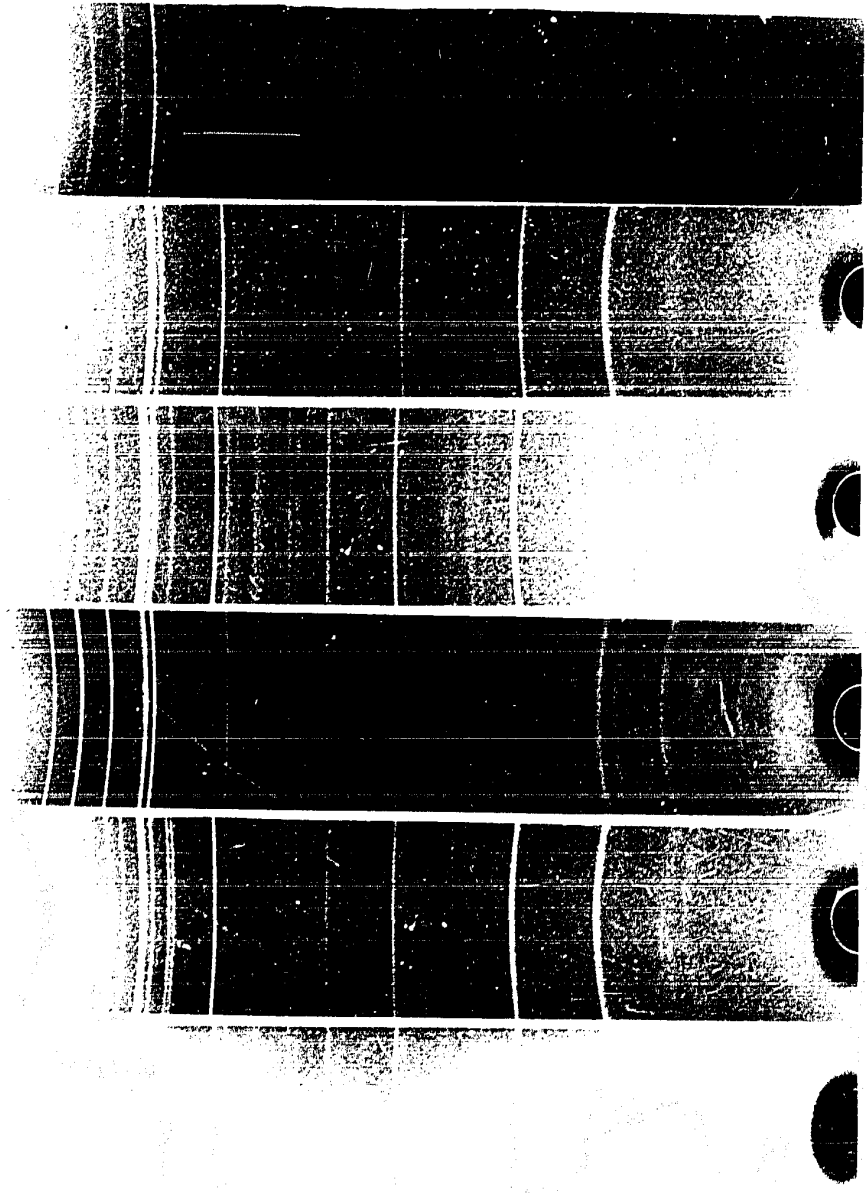


Plate 4. Outcrops showing calcite (Ca) vein surrounded by fenitized rock (FR) from McCloskey's Field. The fenitized rock is composed of eckermannite, phlogopite and very small quantities of acmite.

Plate 5. Outcrops of calcite - dolomite - serpentine marble from Dawson Field with an elliptical rim of serpentine (+ talc) enclosing more calcite - dolomite - serpentine marble.



1 foot



1 foot



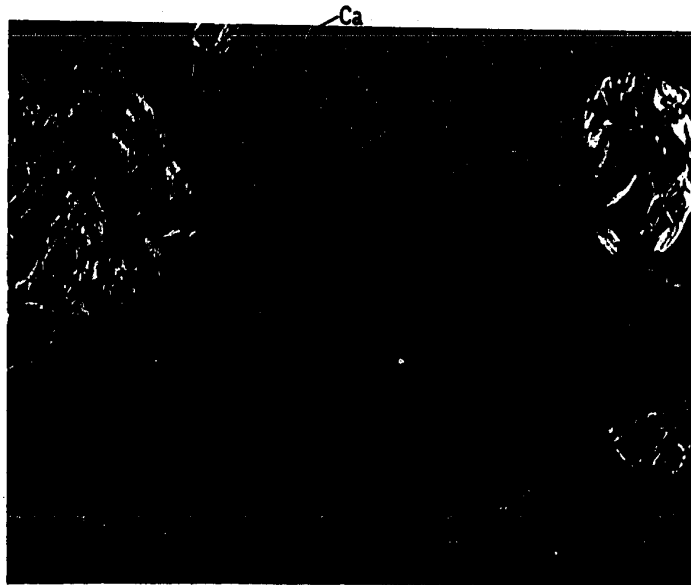
1 foot



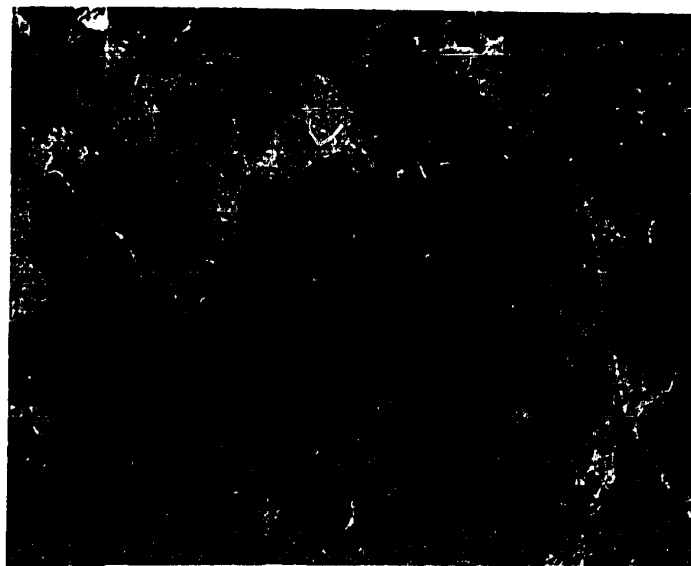
1 foot

Plate 6. Photomicrograph (E-1) showing the calcite - dolomite - serpentine marble from Old Chelsea. The surface was stained with Alizarin Red S solution for 2-3 minutes. Crossed nicols. Ca = calcite; Do = dolomite; Sp = serpentine.

Plate 7. Polished surface (E-1) in reflected (plane) light showing the calcite - dolomite - serpentine marble after etching by 10 % HCl for 2 minutes and stained with Alizarin Red S solution for 2-3 minutes. Ca = calcite; Do = dolomite; Sp = serpentine.



1 mm.



Ca

1mm.



100 μm

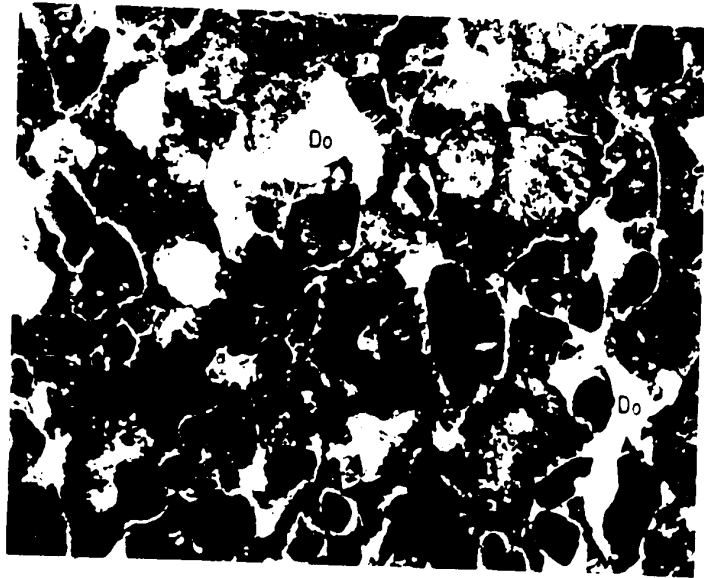
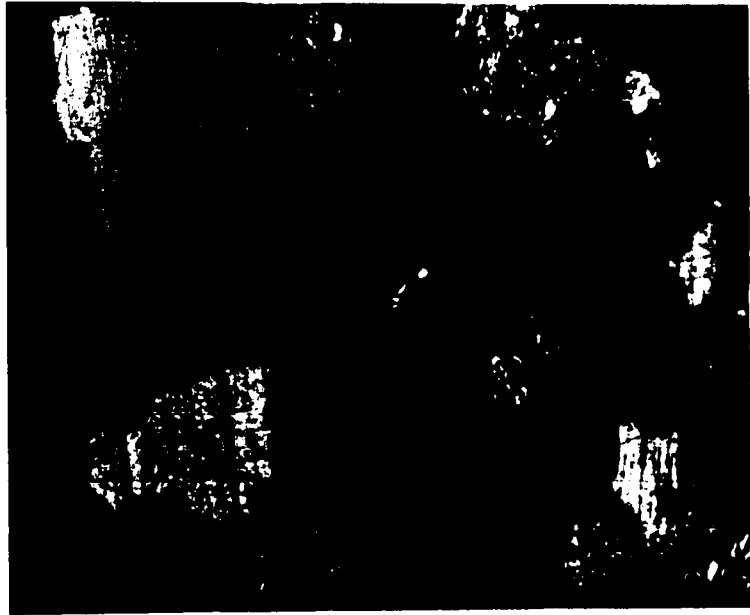
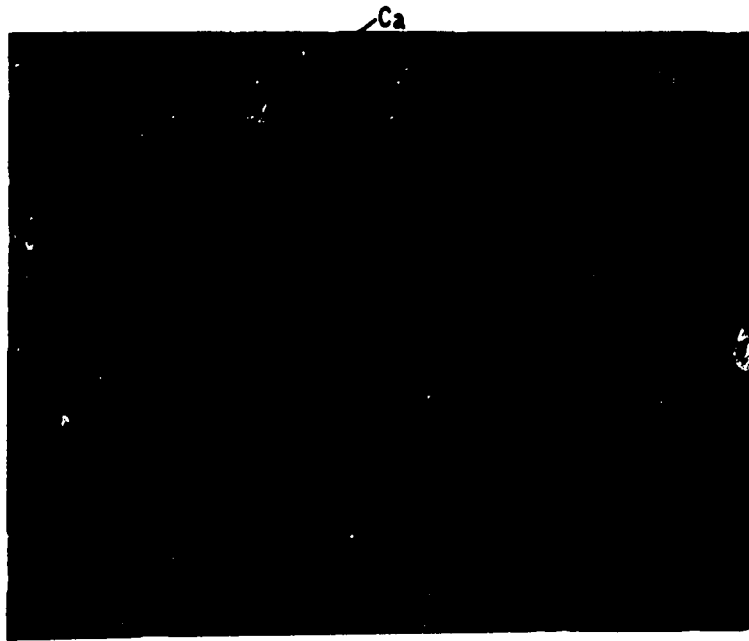


Plate 8. Photomicrograph (224S-2) showing the calcite - dolomite - brucite marble from southwest of Meach Lake. The surface was stained with Alizarin Red S solution for 2-3 minutes. Crossed nicols. Ca = calcite; Do = dolomite; Ch = chondrodite.

Plate 9. Polished surface (224S-2) in reflected (plane) light showing the "onion-skinned" texture of brucite after etching by 10 % HCl for 2 minutes and staining with Alizarin Red S solution for 2-3 minutes. Ca = calcite; Do = dolomite; Br = brucite.



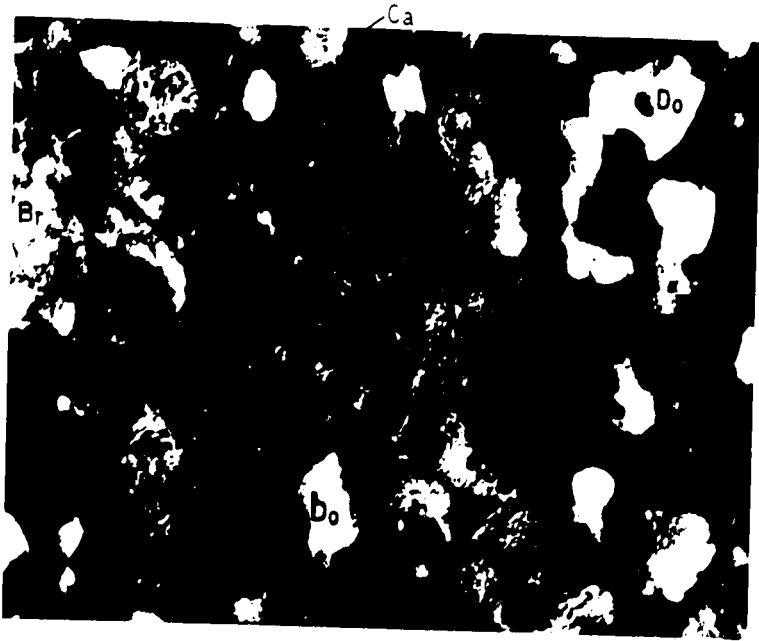
1 mm.



1 mm.



100



100

Plate 10. Photomicrograph (358) showing the calcite - dolomite marble from McCloskey's Field. Crossed nicols. The surface was stained with Alizarin Red S solution for 2-3 minutes. The opaque crystal is pyrite (Py). Ca = calcite; Do = dolomite.



Plate 11. Polished surface (H-2A) in reflected (plane) light showing the coarse crystals of dolomite in a stained surface of calcite. The section was stained with Alizarin Red S solution for 2-3 minutes. The dolomite crystals are apparent as the light portion of the "speckled" pattern of calcite. Ca = calcite (dark); Do = dolomite (light).



1 mm.



1 mm.



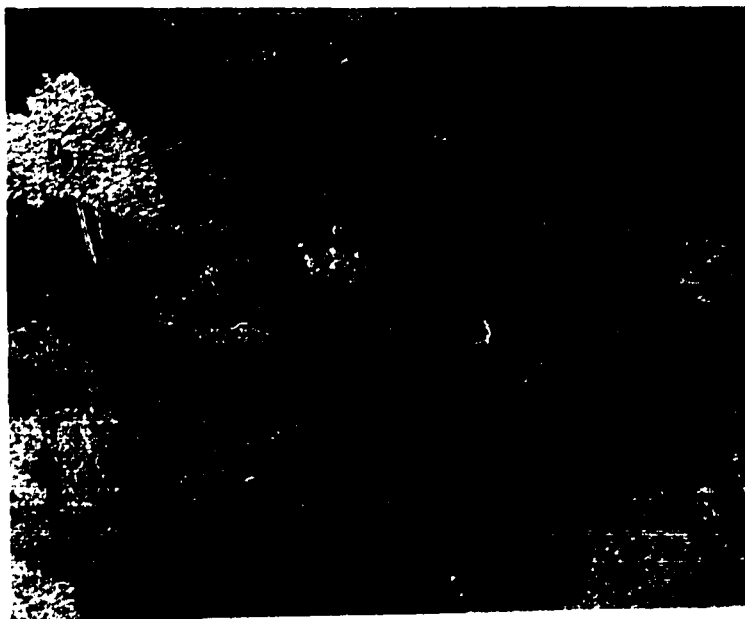
1 mm.



1 mm.

Plate 12. Photomicrograph (H-2C) showing the calcite -
dolomite - apatite marble from McCloskey's
Field. Crossed nicols. The surface was stained
with Alizarin Red S solution for 2-3 minutes.
Ap = apatite; Ca = calcite; Do = dolomite

Plate 13. Photomicrograph (M-5) showing the complex
intergrowth of dolomite and calcite in the
calcite - dolomite - quartz marble on the
stained section. Crossed nicols.
Ca = calcite; Do = dolomite; Qt = quartz.



1 mm.



1 mm.



1 μm



1 μm

Plate 14. Photomicrograph (A-4) showing the quartzitic marble with mineral assemblage of calcite, quartz and diopside. Unstained surface. Crossed nicols. X125. Ca = calcite; Qt = quartz; Di = diopside.

Plate 15. Polished surface (358) in reflected (plane) light showing the coarse crystals of dolomite in the stained surface of calcite. The dolomite crystals are apparent as the light portion of the "speckled" pattern of calcite. Ca = calcite; Do = dolomite.



0.1 mm.



1mm.

