

STUDY OF CARBONATITIC CALCITES FROM OKA, QUE.

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ABSTRACT

The purpose of this work has been to study the nature and variation in the chemistry of calcites within the Oka complex and to investigate the possible relationships between calcite chemistry and niobium mineralization. The effects of atomic substitution on the physical properties of carbonatitic calcites are also reported. Approximately 130 specimens of carbonatites from various occurrences in the complex and from drill holes across the ore zone at the St. Lawrence Columbium Mine were studied. The work involved the determination of Nb_2O_5 in the rocks by X-ray fluorescence methods and the determination of Ba, Sr, Mg, Mn and Fe in the calcites by atomic absorption methods. Physical properties studied include: lattice spacings (211) and (122), refractive index (ω) and axial angle (2V), fluorescence in U.V. and I.R. absorption spectra (ν_2 , ν_1 fundamentals).

The Nb_2O_5 content of the rocks studied varies from .08% to 1.50% and averages 0.39%. The chemistry of the calcites varies widely; the following ranges and average values were obtained: Sr (2.0—0.13; average 1.03%), Ba (0.92—0.01; average 0.216%), Mg (1.74—0.01; average 0.29%), Fe (0.25—0.002; average 0.067%), Mn (1.30—0.003; average 0.39%). Of these, only Mg, Fe and Mn show correlation with each other whereas no correlation exists between Sr and Ba and the other elements. Except for late calcites which show a marked decrease in Sr and Mn, the chemistry of carbonatitic calcite varies widely and sporadically. Similarly, no relationships could be established between calcite chemistry and the niobium content of carbonatites. Small scale cation substitution in the carbonate affects principally the lattice spacings whereas band position of the I.R. spectra are not significantly changed. Fluorescence in ultraviolet and the biaxial character of some calcites do not bear simple relationships to the chemistry of the mineral. These two properties may be related, in part at least, to the thermal and structural history of the mineral.

RÉSUMÉ

Le but de ce travail était d'étudier la distribution des oligo-éléments de la calcite à l'intérieur du complexe d'Oka et de vérifier leurs relations possibles avec la minéralisation du niobium. L'influence de la substitution atomique sur les propriétés physiques des calcites des carbonatites fut étudiée aussi. Sur environ 130 échantillons de carbonatites, nous avons déterminé la quantité de Nb_2O_5 par fluorescence X et de Ba, Sr, Mg, Mn, Fe par absorption atomique. Les propriétés physiques étudiées sont les espacements réticulaires (211) et (122), l'indice de réfraction (ω), l'angle axial (2V), la fluorescence dans l'ultra-violet et le spectre d'absorption infra-rouge (ν_2 , ν_1 , fondamentales).

Le contenu en Nb_2O_5 des roches étudiées varie de 0.08 à 1.50% et la teneur moyenne est de 0.39%. La quantité des éléments mineurs dans les calcites varie beaucoup, de la façon suivante: Sr (2.0—0.13%; moyenne 1.03%), Ba (0.92—0.01%; moyenne 0.216%), Mg (1.74—0.01%; moyenne 0.29%), Fe (0.25—0.002%; moyenne 0.067%), Mn (1.30—0.003%; moyenne 0.39%). La corrélation avec les autres éléments est notable pour Mg, Fe et Mn, mais inexistante pour Sr et Ba. La chimie des calcites des carbonatites varie

beaucoup et de façon sporadique, sauf pour les calcites tardives qui montrent une diminution marquée en Sr et Mn. De même, aucune relation n'apparaît entre la chimie des calcites et le contenu en niobium des carbonatites. La substitution de faibles quantités d'ions dans les carbonates affecte surtout l'espacement réticulaire, tandis que la position des bandes du spectre de l'infra-rouge ne varie pas de façon significative. La fluorescence sous illumination de l'ultra-violet et la biaxie de certaines calcites n'ont pas de relations simples avec la chimie du minéral. Ces deux propriétés sont apparentées, du moins en partie, à l'histoire thermique et structurale des calcites.

INTRODUCTION

Because of their important association with niobium and rare earths mineralization, carbonatites have been much studied in recent years. The results of these studies have fairly well defined the general petrography, chemistry and petrologic evolution of carbonatite rocks. However, comparatively little data exists on the systematic mineralogy and chemistry of their constituent minerals.

The carbonite at Oka has attracted several investigators. Gold (1963, 1966) has given chemical and physical data for some of the rock-forming silicate minerals and for the various niobium minerals, niocalite britholite, latrappite and pyrochlore. Similarly, Nickel (1956, 1964), Nickel & MacAdam (1963), Nickel *et al.* (1958) and Perrault (1959, 1968) have described and provided chemical and physical data for niocalite, perovskite, latrappite and the various pyrochlores. Apatites and their contained carbonate and liquid inclusions were studied by Girault (1966a, b). Except for Quon (1965) who determined the minor elements in five specimens of carbonatitic calcites from Oka, the work done on the carbonate minerals has been largely determinative. Carbonate minerals identified to date include: calcite, dolomite, magnesite, siderite, strontianite, ancylite, parisite and synchesite; details concerning the chemistry and paragenesis of most of these minerals are yet very imperfectly known.

Calcite is by far the principal carbonate mineral at Oka. As with carbonatitic calcite from other complexes, that from Oka has been known to contain varying proportions of Sr, Ba, Mn, Mg and Fe. Also, some varieties display a marked biaxial character whereas others fluoresce brilliantly under ultraviolet illumination. The present work investigated the chemistry and physical properties of a large number of calcites from Oka. The purpose of the work was twofold: (1) investigate the nature and variation in the chemistry of calcite and its possible relationships with rock types and niobium mineralization; (2) study the influence of combined atomic substitution of Ba, Sr, Mn, Fe and Mg on various physical properties of the mineral. The physical properties studied include: unit cell parameters by means of lattice spacings (211) and (122), refractive index (ω) and

character of the indicatrix, fluorescence under ultraviolet illumination and infrared absorption spectra (ν_2 , ν_4 fundamentals).

General geology of the Oka carbonatite

The Oka carbonatite complex is roughly oval shaped (Fig. 1) and measures approximately four miles in length and one mile in width (Gold 1963, 1969). It is made up of a southern and a northern ring structure that coalesce near La Trappe, giving rise to a pattern that resembles a distorted "Figure 8". The rock units within the complex are concentrically disposed relative to one another and represent either ring dykes or cone sheets. Approximately half of the complex is underlain by carbonatite rocks. These may be subdivided into at least nine types on the basis of mineralogy (Gold 1969). Arcuate masses, arcuate dykes and dykes of various alkaline silicate rocks make up the remainder of the complex.

The carbonatite rocks are commonly banded with layer-concentrations of ferromagnesian and/or magnetite minerals. The predominant type is a coarse-grained calcite carbonatite (sövite) layered with minor and accessory minerals such as sodian augite, biotite, apatite, nepheline, monticellite, melilite, pyrochlore, perovskite, niocalite, richterite, pyrite and pyrrhotite.

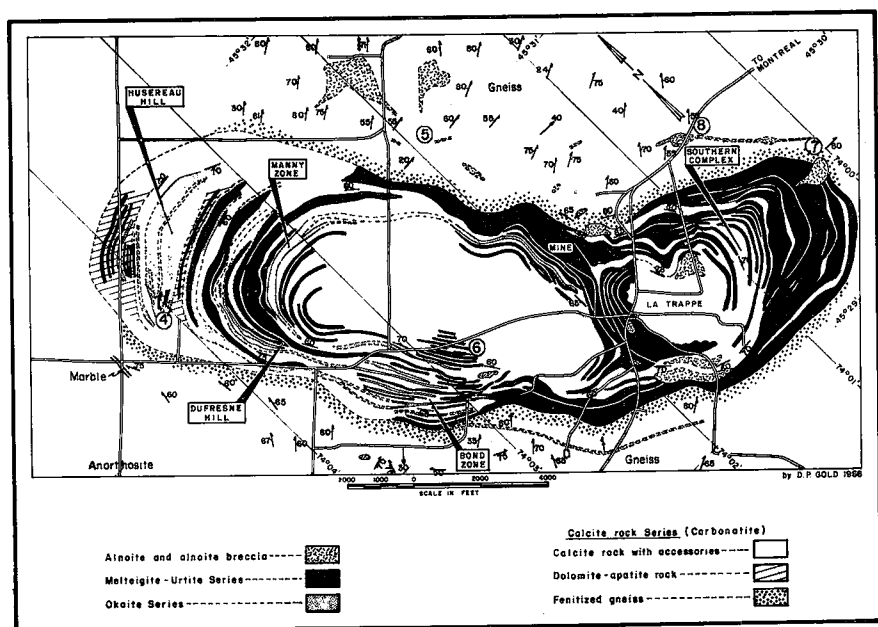


FIG. 1. Geology of the carbonatite complex at Oka, Que. (After Gold 1966).

Dolomite carbonatite (rauhaugite) occurs only in the northern part of the complex, around Husereau Hill.

Economic concentrations of pyrochlore occur in pyroxene-biotite-magnetite sovite, monticellite sovite, soda amphibole sovite and, locally, in rauhaugite. The niobium mineralization at the St. Lawrence Columbium and Metals' Mine, consists principally of pyrochlore disseminations in layers and/or irregular masses of biotite-pyroxene carbonatite, monticellite carbonatite and to a lesser extent in richterite carbonatite and perovskite-rich monticellite carbonatite (Gold *et al.* 1967). At the mine, the A-ore zones trend approximately 020° and dip steeply westward (Fig. 2). Gold *et al.* (1967) summarize the geological relationships as follows :

- (1) A first niobium-poor sovite was intruded by irregular bodies of urtite-ijolite series alkaline rocks and some nepheline okaite.
- (2) A main pyrochlore carbonatite was emplaced into the niobium-poor carbonatite and ijolite rocks.
- (3) Deuteric pyrochlore (higher in U and Th) was introduced along zones of alteration. This type of mineralization is of minor importance only.

Material used for study

The material studied comprises some twenty-five hand specimens from various localities in the complex, including the pit area at the St. Lawrence Mine, and over one hundred specimens obtained from drill holes across the A-ore zones at the mine. The drill holes sampled are in sections 6 + 00 and 11 + 00 (Fig. 2) and approximate a section from hanging wall to foot wall across the ore zones. Sampling interval varied considerably, depending on the mode of occurrence of the carbonatite. Thin bands of carbonatite in the ijolite foot wall were sampled wherever possible, whereas larger intersections of carbonate rocks were sampled at intervals varying from 40 to 80 feet. A suite of six specimens of very coarse, sometimes vuggy or stalactitic (the so-called late or "hydrothermally introduced") carbonate veins were also collected from the mine area. Dolomite carbonatites from the northern part of the complex are not included in the present study; these rocks could not be sampled in amounts and quality that could justify systematic investigations.

The carbonatite specimens used in the present work are generally medium to coarse-grained rocks composed of more than 60% calcite. Details concerning the preparation of the material for study and the various analytical methods used are given in Appendix I.

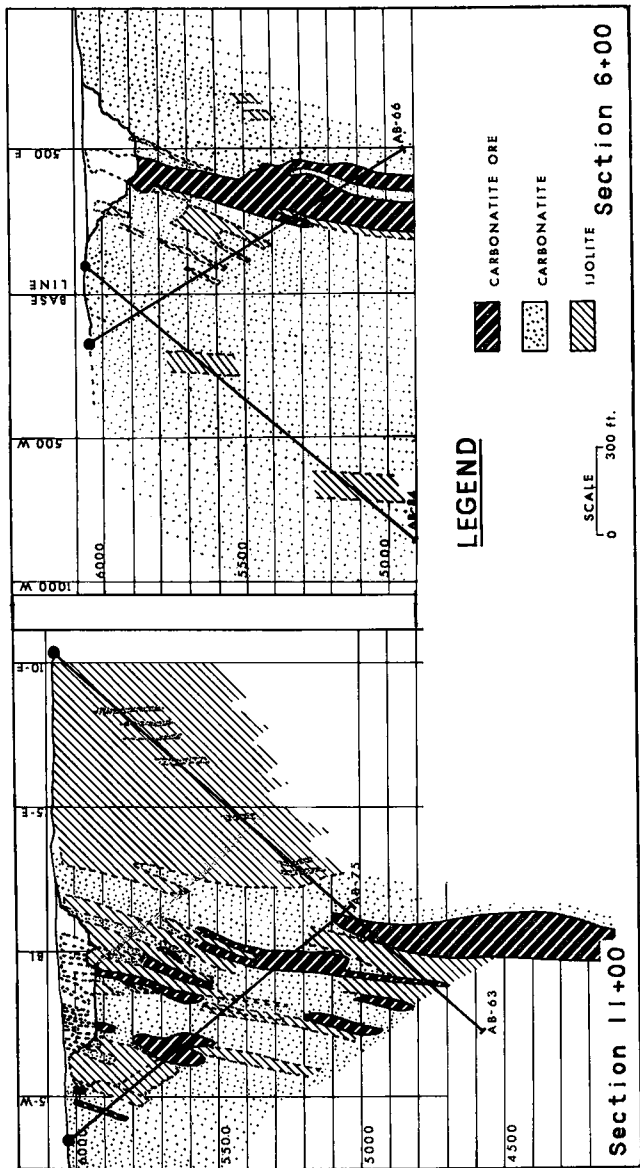


Fig. 2. Geological relationships in the A-ore zones; St. Lawrence Columbian and Metals Corp., sections 6 + 00 and 11 + 00 (modified from mine sections).

RESULTS

The data concerning chemical composition and physical properties of calcites from Oka, and the Nb_2O_5 content of the carbonatite samples from which the calcites were extracted are given in Table 1. The frequency distribution of the various elements determined is shown by histograms (a to f), Fig. 3. The chemical results will be discussed first.

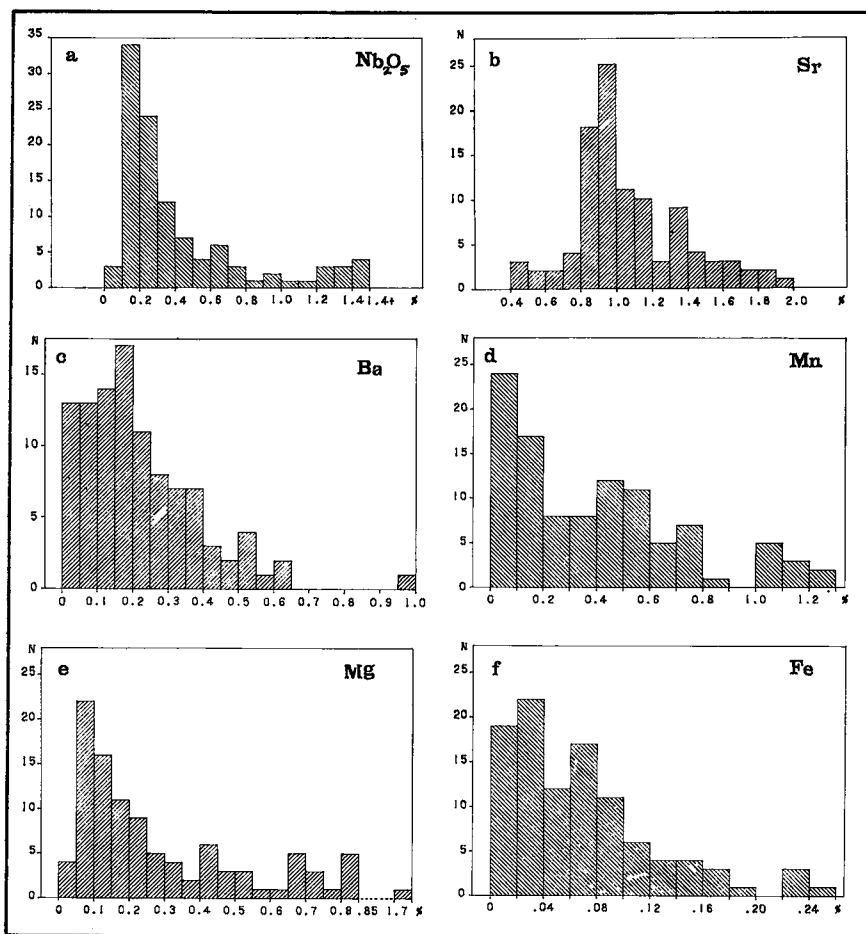


FIG. 3. Histograms showing the distribution of Nb_2O_5 in the carbonatite specimens studied (3a), and the Sr, Ba, Mn, Mg and Fe contents of associated calcites (3b—3f).

Whole rock Nb_2O_5 and its relationships with the carbonate minerals

The Nb_2O_5 content of the rocks studied range from .05 to 1.5% and the mean from all the determinations is 0.39%. However, this mean cannot be taken as representative for the carbonatite rocks as a whole, for it incorporates a large proportion of samples from ore zone carbonatite. The carbonatite away from the ore zones contains approximately .15 to .18% Nb_2O_5 . The distribution of Nb_2O_5 values is shown on Fig. 3a. When plotted on log-probability paper the distribution is not quite lognormal. However, a fairly good lognormal distribution is obtained when .06% Nb_2O_5 is subtracted from all the values. The exact physical significance of this is not known; one suspects that it may be related to the fact that the niobium is not uniformly distributed in the rocks. The metal is highly concentrated in accessory pyrochlore and is also present as trace amounts in other mineral phases.

The niobium content varies from one carbonatite specimen to another and sometimes, within adjacent portions of a single hand specimen; the cause for these variations is obviously the presence of mineralogical layering or banding in many of the rocks. The Nb_2O_5 content of series of specimens from a given carbonatite intersection in a drill hole was analyzed statistically and the values were found independent of each other. It is also most probable that layering is the principal factor responsible for this mode of variation. The spatial distribution of niobium content, and minor elements in associated calcites, is shown in Fig. 4 a, b. The two profiles shown approximate a section from foot wall to hanging wall across the A-ore zones (see also Fig. 2).

A first goal pursued in the present work was to study the possible correlation between the Nb_2O_5 content of carbonatite samples and the chemistry of the associated calcites. For this, several correlation diagrams were constructed using the data from Table 1; all attempts to find correlations between the Nb_2O_5 content and the various elements or combination of elements in associated calcites were unsuccessful. The diagrams obtained yielded typical "shot gun" distribution, indicating that the niobium bears no relationship to the chemistry of the calcite.

The erratic chemistry of the calcites within the complex does not appear particular to the Oka carbonatite; similar conclusions regarding the sporadic distribution of minor elements in carbonatites were reached, respectively by Davies (1956) and Johnson (1961) on the basis of geochemical studies of the Sukulu Hills and Tororo carbonatites in Uganda and of the Dorowa and Shawa carbonatites in Southern Rhodesia. Quon (1965, p. 132) concluded from his examination of the carbonate minerals from

TABLE 1. CHEMICAL AND PHYSICAL DATA ON CALCITES FROM OKA, QUÉ.

Sample	Nb ₂ O ₅ ¹	Sr	Ba	Mg	Fe	Mn	$d_{(122)}$	$d_{(211)}$	Fluorescence ²	RI ²	Indicatrix ⁴
P-1	1.34	1.145	0.127	0.810	0.096	0.709	1.5996	1.6214	M	—	—
P-2	0.12	0.013	0.075	0.091	0.002	0.010	1.6026	1.6240	N	1.6605	—
P-3	0.58	1.135	0.158	0.116	0.010	0.013	1.6032	1.6246	N	—	—
P-4B	0.20	0.915	0.152	0.097	0.010	0.092	1.6028	1.6246	N	—	—
P-5	0.13	0.709	0.253	0.056	0.011	0.034	1.6031	1.6235	N	—	16 B
P-6A	—	0.918	0.153	0.076	0.010	0.056	1.6034	1.6254	N	—	13 U-B
P-6B	0.54	0.487	0.335	0.065	0.022	0.108	1.6024	1.6242	M	—	14 B
P-7	0.10	1.114	0.363	0.829	0.137	1.295	1.6003	1.6213	S	1.6614	14 U-B
P-8	0.23	0.933	0.114	0.098	0.031	0.052	1.6029	1.6239	N	—	—
P-9	0.12	0.062	0.233	0.124	0.041	0.148	1.6011	1.6230	S	—	—
P-10A	0.24	0.160	0.235	0.074	0.012	0.031	1.6015	1.6234	N	—	20 U-B
P-10B	0.41	0.030	0.225	0.025	0.010	0.090	1.6015	1.6226	N	—	—
P-15B	0.10	0.100	0.916	1.266	1.233	0.433	—	—	N	—	—
P-16	0.13	0.068	0.312	0.011	0.023	0.032	1.6012	1.6224	N	1.6613	—

¹ Nb₂O₅ content of carbonatite specimen.² Fluorescence under short wavelength ultraviolet: S (strong), M (medium), N (weak to none).³ Average ω refractive index.⁴ Maximum 2V measured in thin section: B (biaxial crystals seem to predominate over uniaxial crystals); U-B (uniaxial crystals seem to predominate over biaxial crystals); U (largely uniaxial crystals).

TABLE 1 (continued).

Sample	Nb ₂ O ₆ ¹	Sr	Ba	Mg	Fe	Mn	d ₍₁₂₂₎	d ₍₂₁₁₎	Fluorescence ²	RI ³	Indicatrix ⁴
P-17	0.18	0.908	0.051	0.413	0.175	0.464	1.6016	1.6227	N	—	20 U-B
P-18	0.08	0.804	0.025	0.097	0.051	0.163	1.6030	1.6244	N	—	—
P-19	0.11	1.443	0.250	0.175	0.150	0.451	1.6031	1.6248	N	1.6599	—
P-21	0.22	0.910	0.200	0.800	0.230	0.600	—	—	S	1.6618	—
P-24	0.28	1.082	0.204	0.663	0.250	1.041	1.6004	1.6222	M	1.6613	—
P-25	0.46	1.345	0.513	0.693	0.180	1.150	1.5996	1.6210	N	—	—
P-26	0.21	0.865	0.254	0.737	0.081	0.783	1.5997	1.6206	M	—	26 B
P-27	0.13	0.880	0.414	0.248	0.083	0.466	1.6026	1.6246	M	—	—
P-28	0.94	1.087	0.212	0.170	0.074	0.424	1.6036	1.6248	N	—	—
P-29	0.70	1.450	0.369	0.137	0.053	0.316	1.6030	1.6250	M	—	—
P-30	0.44	0.903	0.239	0.186	0.085	0.212	1.6029	1.6242	N	—	20 U-B
P-31	0.31	1.338	0.306	0.092	0.041	0.168	1.6038	1.6252	N	—	—
P-32	0.28	1.297	0.102	0.112	0.051	0.198	1.6033	1.6250	N	—	—
P-33	0.18	1.182	0.079	0.126	0.073	0.173	1.6028	1.6246	N	—	13 B
P-34	0.21	1.716	0.264	0.079	0.032	1.206	1.6028	1.6252	N	—	—
P-35	0.12	2.010	0.958	0.311	0.062	1.161	1.6004	1.6223	S	1.6613	—
P-36	0.08	0.013	0.051	0.144	0.000	0.003	1.6033	1.6250	N	1.6608	25 B
P-37	0.40	0.867	0.108	0.108	0.011	0.087	1.6031	1.6246	N	—	—
P-38	0.76	1.327	0.478	0.292	0.117	0.425	—	—	N	—	—

TABLE 1 (continued).

Sample	Nb ₂ O ₆ ¹	Sr	Ba	Mg	Fe	Mn	$d_{(122)}$	$d_{(211)}$	Fluorescence ²	RI ³	Indicatrix ⁴
P-39	0.63	1.460	0.417	0.235	0.073	0.438	1.6028	1.6243	N	—	19 B
P-40	0.23	1.685	0.503	0.327	0.070	0.553	1.6012	1.6220	M	1.6604	—
P-41	0.29	1.899	0.369	0.221	0.074	0.548	1.6034	1.6250	M	—	—
P-42	0.33	1.353	0.162	0.243	0.049	0.400	1.6030	1.6250	N	—	20 B
P-43	0.39	1.264	0.103	0.155	0.051	0.144	1.6031	1.6250	N	—	—
P-44	0.81	1.309	0.160	0.080	0.027	0.214	1.6030	1.6245	N	—	—
P-45	0.38	1.169	0.305	0.132	0.071	0.203	1.6036	1.6254	N	1.6617	17 B
P-46	1.33	1.653	0.305	0.132	0.071	0.356	1.6034	1.6247	N	—	—
P-47	0.18	1.003	0.258	0.651	0.098	0.775	1.5988	1.6196	N	—	—
P-48	0.50	1.028	0.422	0.591	0.100	0.738	1.6001	1.6210	M	—	15 U-B
P-49	0.40	1.429	0.156	0.546	0.041	1.060	1.6006	1.6224	M	—	—
P-50	0.25	0.981	0.159	0.064	0.026	0.085	1.6036	1.6254	N	1.6617	—
P-51	0.44	0.916	0.052	0.167	0.031	1.050	1.6032	1.6244	N	—	21 U-B
P-52	0.16	1.042	0.631	0.431	0.100	0.547	1.6022	1.6236	N	—	—
P-54	0.22	0.858	0.483	0.815	0.188	1.202	1.6000	1.6210	M	—	—
P-56	0.22	0.908	0.155	0.648	0.041	0.778	1.5978	1.6193	M	1.6616	13 U-B
P-57	0.38	0.480	0.250	0.525	0.025	0.500	1.5940	1.6154	S	—	—
P-58	0.62	0.628	0.174	0.090	0.012	0.058	1.6026	1.6246	N	—	14 B
P-60	0.22	1.037	0.135	0.799	0.086	0.864	1.5993	1.6208	S	—	—

TABLE 1 (continued).

Sample	Nb ₂ O ₆ ¹	Sr	Ba	Mg	Fe	Mn	$d_{(122)}$	$d_{(211)}$	Fluorescence ²	RI ³	Indicatrix ⁴
P-61	0.64	1.651	0.305	0.356	0.112	1.036	1.6018	1.6228	S	—	—
P-62	0.60	1.150	0.175	0.350	0.040	0.370	1.6024	1.6237	M	1.6614	—
P-63	0.49	0.924	0.053	0.343	0.185	0.549	1.6007	1.6230	N	—	18 B
P-64	1.33	1.046	0.052	0.418	0.120	0.471	1.6026	1.6240	N	—	11 U-B
P-65	1.05	0.956	0.077	0.300	0.026	0.258	1.6026	1.6243	N	—	—
P-66	0.22	0.975	0.100	0.090	0.010	0.080	1.6260	1.6260	N	—	—
P-67	1.40	1.540	0.527	0.738	0.084	0.316	1.6239	1.6239	N	—	16 B
P-68	0.12	0.593	0.257	0.464	0.039	0.477	1.6190	1.6190	S	1.6616	—
P-71	0.74	1.531	0.332	0.485	0.163	0.765	1.6023	1.6235	M	1.6612	—
P-72	0.13	0.896	0.263	1.739	0.137	0.632	1.5982	1.6190	N	1.6613	—
P-73	0.20	0.861	0.279	0.658	0.030	0.679	1.6005	1.6222	M	—	18 U-B
P-75	0.18	0.875	0.400	0.450	0.040	0.700	1.6015	1.6234	M	—	—
P-76	0.64	1.225	0.150	0.450	0.010	0.075	1.6037	1.6250	N	—	14 B
P-77	0.21	1.134	0.206	0.180	0.062	0.227	1.6030	1.6250	N	—	—
P-79	0.19	0.892	0.561	0.280	0.071	0.561	1.6018	1.6236	S	—	13 U-B
P-80	0.22	1.900	0.550	0.225	0.025	0.550	1.6030	1.6248	N	—	—
P-82	0.23	0.855	0.352	0.513	0.030	0.553	1.6018	1.6236	N	—	—
P-83	0.20	0.924	0.359	0.421	0.031	0.565	1.6027	1.6239	N	1.6620	—
P-84	0.32	1.178	0.118	0.118	0.075	0.375	1.6037	1.6248	N	—	—

TABLE 1 (continued).

Sample	Nb ₂ O ₅ ¹	Sr	Ba	Mg	Fe	Mn	$d_{(122)}$	$d_{(211)}$	Fluorescence ²	RI ³	Indicatrix ⁴
P-85	0.14	0.700	0.190	0.030	0.025	0.055	1.6052	1.6273	N	—	—
P-89	0.14	0.794	0.026	0.102	0.020	0.123	1.6030	1.6247	N	—	14 U-B
P-90	0.35	0.825	0.000	0.140	0.050	0.200	1.6026	1.6239	N	—	—
P-91	0.18	0.975	0.162	0.240	0.130	0.141	1.6038	1.6254	N	—	—
P-92	0.16	0.950	0.026	0.231	0.072	0.100	1.6041	1.6251	N	—	—
P-93	0.29	1.075	0.190	0.175	0.075	0.160	1.6029	1.6246	N	—	17 B
P-94	0.24	0.825	0.075	0.140	0.150	0.350	1.6016	1.6226	N	—	—
P-95	0.14	0.946	0.223	0.239	0.234	0.446	1.6015	1.6235	N	1.6619	—
P-96	> 1.40	0.825	0.050	0.175	0.090	0.120	1.6030	1.6250	N	—	9 U
P-97	1.11	0.560	0.150	0.075	0.080	0.050	1.6024	1.6239	N	—	—
P-98	0.44	0.800	0.025	0.210	0.225	0.550	1.6029	1.6246	N	—	—
P-99	1.26	0.890	0.026	0.262	0.157	0.471	1.6034	1.6252	N	—	16 U-B
P-101	0.14	0.925	0.000	0.160	0.030	0.050	1.6029	1.6250	N	1.6611	—
C-27	0.10	0.781	0.243	0.125	0.042	0.260	1.6019	1.6236	S	—	—
C-28	0.20	1.010	0.000	0.125	0.025	0.120	1.6018	1.6235	M	—	—
C-45A	0.38	0.500	0.110	0.060	0.020	0.075	1.6039	1.6255	M	—	—
C-45B	0.29	1.160	0.110	0.100	0.030	0.135	1.6033	1.6253	N	—	—
C-59	1.00	0.975	0.210	0.075	0.010	0.060	1.6033	1.6248	N	—	—
C-69	0.16	0.937	0.000	0.031	0.010	0.052	1.6032	1.6246	N	—	—

TABLE 1 (continued)

Sample	Nb ₂ O ₅ ¹	Sr	Ba	Mg	Fe	Mn	$d_{(122)}$	$d_{(211)}$	Fluorescence ²	RI ³	Indicatrix ⁴
C-74	0.22	0.850	0.000	0.075	0.010	0.065	1.6040	1.6258	M	—	—
C-95	0.21	1.087	0.000	0.050	0.020	0.081	1.6043	1.6263	N	—	—
C-98	1.21	0.803	0.229	0.254	0.020	0.325	1.6013	1.6229	S	—	—
C-101	0.52	0.862	0.157	0.083	0.010	0.078	1.6030	1.6244	N	—	—
C-102B	0.26	1.080	0.609	0.842	0.011	1.163	1.6001	1.6211	S	—	—
C-103	0.39	0.978	0.163	0.152	0.081	0.543	1.6019	1.6235	S	—	—
C-108	>1.40	1.374	0.055	0.121	0.033	0.132	1.6022	1.6233	M	—	—
C-110	0.14	0.927	0.000	0.840	0.153	0.682	1.5993	1.6209	M	—	—
C-116	0.30	0.985	0.339	0.480	0.055	0.616	1.5991	1.6210	S	—	—
C-117	0.16	0.921	0.160	0.674	0.118	1.017	1.6001	1.6237	S	—	—
C-119	0.70	0.949	0.385	0.099	0.124	0.248	1.6016	1.6237	S	—	—
C-125	0.19	0.915	0.076	0.112	0.030	0.122	1.6037	1.6250	M	—	—
C-127	0.14	1.105	0.116	0.116	0.026	0.105	1.6036	1.6256	N	—	—
C-129A	1.40	1.532	0.118	0.064	0.011	0.086	1.6041	1.6254	N	—	—
C-129B	0.71	1.370	0.098	0.065	0.011	0.085	1.6036	1.6252	N	—	—
C-151	0.26	1.150	0.275	0.360	0.050	0.800	1.6016	1.6236	S	—	—
C-154	0.74	1.330	0.095	0.184	0.074	0.443	1.6026	1.6243	S	—	—
C-186	0.19	0.826	0.243	0.000	0.011	0.032	1.6035	1.6247	N	—	—
C-195	1.29	1.303	0.117	0.080	0.042	0.138	1.6044	1.6254	N	—	—

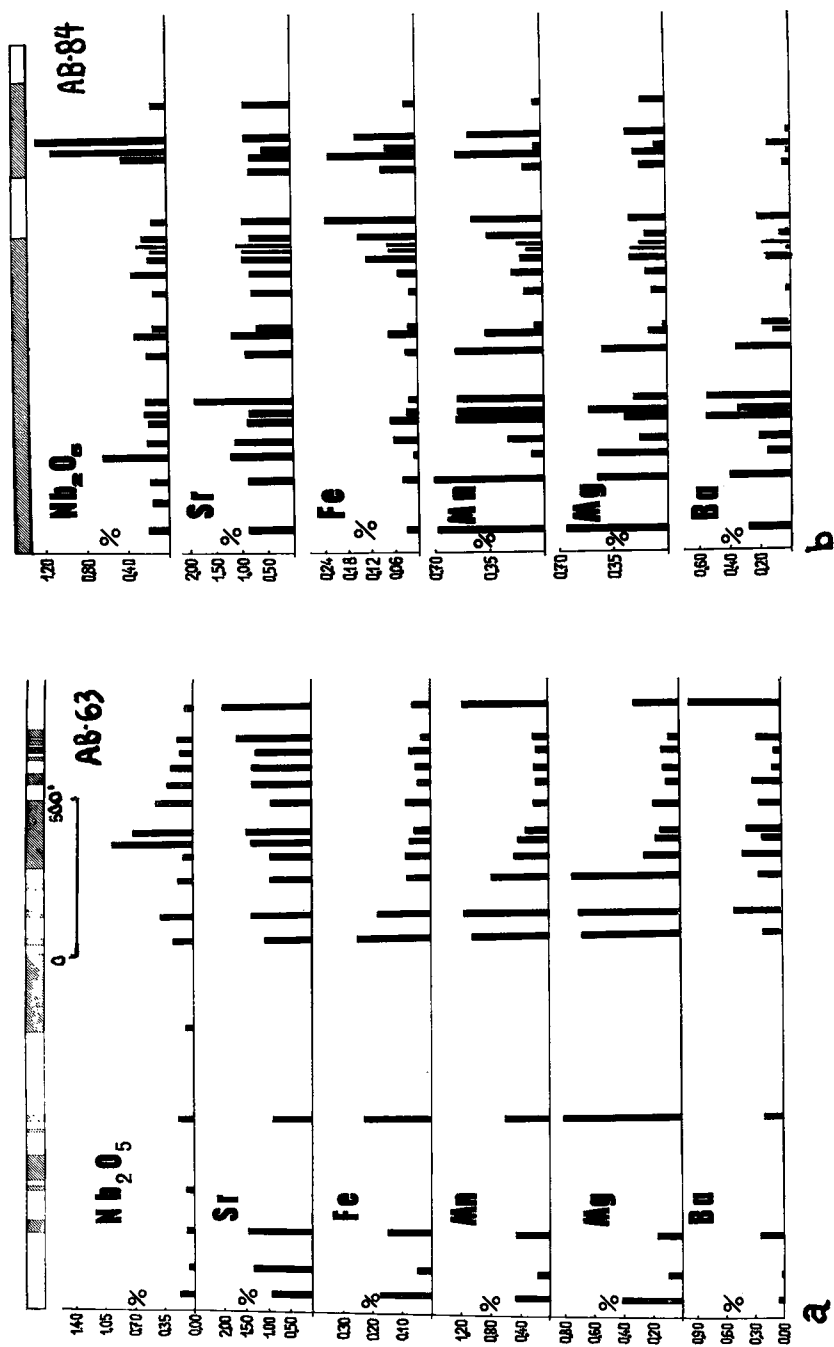


FIG. 4a, b. Profiles along drill holes AB-63 and AB-84 showing the distribution of Nb_2O_5 in carbonate and the minor elements in associated calcites.

several carbonatite complexes, that the minor elements in carbonate minerals show no systematic regularity with respect to closely related bodies, petrographic provinces or structural types of carbonatites.

Strontium in calcite

Strontium is a principal substituting element in calcites from Oka. The contents determined range from .013% to 2.0% ; the average content is 1.03%. The distribution of Sr values (Fig. 3b) approximates a normal rather than lognormal distribution ; also, the Sr content of calcite bears no relationship to other substituting elements such as Ba, Mn, Fe and Mg. The strontium appears entirely held in solid solution within the calcites. This is suggested by the fact that long exposure X-ray diffraction photographs of samples containing as much as 2% Sr, do not show any of the strong reflections of strontianite.

Minor elements in the calcites from the late or "hydrothermal" carbonate veins are presented in Table 2. Characteristically, these calcites contain the lowest concentrations of strontium. The occurrence of individual strontianite crystals with calcite in some of these veins suggests that low temperature physico-chemical conditions prevailed during the late stages and favoured the formation of individual strontium minerals rather than solid solution of strontium in calcite.

A low strontium content coupled with a low manganese content is characteristic of late calcites at Oka and provides a valid manner to differentiate these from coarse-grained carbonatitic calcites.

Barium in calcite

Barium (Fig. 3c) is very subordinate to strontium in calcites from Oka. The contents determined range from .01% to 0.92% ; the mean content is 0.216%. The barium distribution is fairly closely lognormal and the mean content reported here is slightly larger than the mean barium con-

TABLE 2. MINOR ELEMENTS IN LATE CALCITES FROM OKA.

Spec. No.	Sr	Ba	Mn	Fe	Mg
P-2	.013	.075	.010	.002	.091
P-9	.062	.233	.148	.041	.124
P-10A	.160	.235	.031	.012	.074
P-10B	.030	.225	.090	.010	.025
P-15B	.100	.916	.433	1.233	1.266
P-16	.068	.312	.032	.023	.011
P-36	.013	.051	.003	.000	.144

tent (0.106%) found by Quon (1965) for 47 calcites from various carbonatite complexes. The highest barium encountered is found in calcite from barite-bearing carbonate veins (No. 15B, Table 2); a slight contamination from barite cannot be entirely excluded for this sample. Although only a small number of late carbonate veins were studied, the barium content of calcites from these veins does not appear to differ from that of carbonatitic calcites. These relations suggest that barium may fractionate relative to strontium in late carbonate veins.

Manganese in calcite

Next to strontium, manganese is the second element in importance in calcites from Oka (Fig. 3d). The manganese content of carbonatitic calcites varies widely; the range determined is 0.003% to 1.30% and the mean content is 0.39%. As with strontium, the manganese content of calcites in late or "hydrothermal" veins is much lower than that in carbonatitic calcites.

The element shows a positive correlation with iron and magnesium in calcite (Fig. 5). This correlation is also readily noticed when examining the chemical profiles of calcites from the drill hole intersections (Fig. 4); in general, higher manganese contents of calcites are accompanied by higher magnesium and iron.

Iron and magnesium in calcite

The iron content of carbonatitic calcites from Oka is comparatively low (Fig. 3f). The range determined extends from 0.002% to 0.25%; the mean is 0.067%. Magnesium (Fig. 3e) in calcites ranges from 0.01% to 1.74%; the mean content is 0.29%.

It is interesting to note that magnesium has not remained entirely as a solid solution within the host calcite, some having unmixed to dolomite. Although microscopic examination of the samples could not identify the dolomite exsolution textures, long exposure X-ray diffraction photographs of calcites containing more than 0.50% Mg yield faint lines that correspond to the strongest lines of dolomite.

PHYSICAL PROPERTIES OF CALCITES

Various physical properties of carbonatitic calcites were investigated in order to study the effects of mixed atomic substitution in the calcite structure. Indirectly, it was hoped that this work should shed some light on the factors that cause certain calcites from Oka to fluoresce and some, to possess an optical indicatrix that is distinctly biaxial. The various properties

%Mn

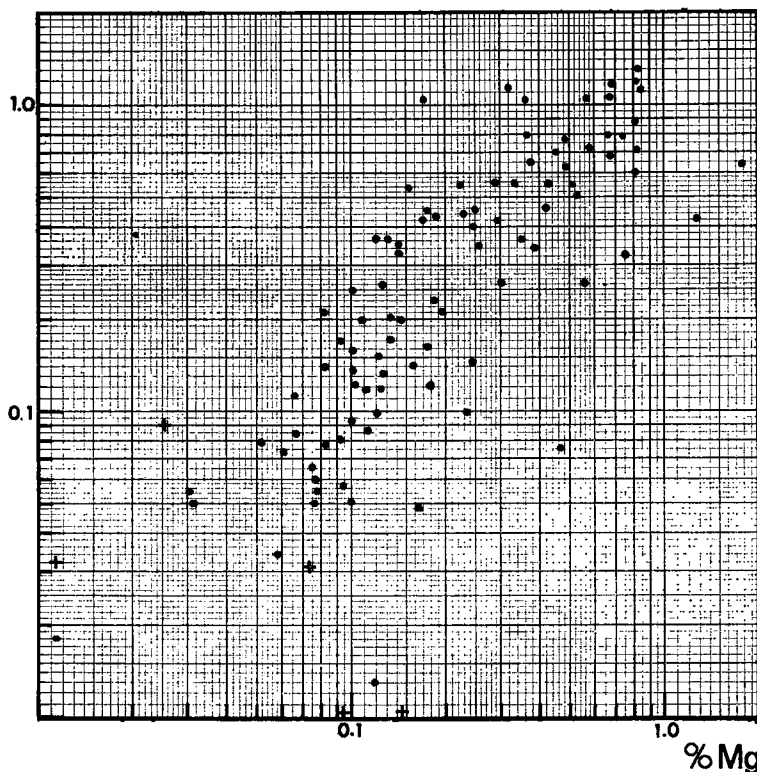


FIG. 5. Diagram correlating the Mn and Mg contents of carbonatitic calcites. Calcites from late carbonate veins are shown as crosses.

e.g., lattice dimensions, fluorescence and optics will be discussed in order. The results of infrared spectroscopy work on the calcites are described in Appendix 1 as being identical with one another and similar to that of pure calcite; these will not be commented on any further.

Lattice dimensions of carbonatitic calcites

The substitution for Ca^{2+} ($0.98\text{\AA}$) in calcite, of smaller cations such as Mg^{+2} ($0.68\text{\AA}$), Fe^{+2} ($0.74\text{\AA}$) and Mn^{2+} ($0.80\text{\AA}$) should decrease the axial parameters of the mineral, whereas the substitution of larger cations such as Ba^{+2} ($1.35\text{\AA}$), Sr^{+2} ($1.13\text{\AA}$) should increase the parameters. Such effects, deduced on the basis of the relative size of the cations

have been verified experimentally for the various solid solution series in rhombohedral carbonates by Goldsmith & Graf (1957), Goldsmith *et al.* (1958), Goldsmith, Graf & Heard (1961), Terada (1952), Rosenberg (1963), and Froese (1967).

Preliminary diagrams correlating lattice spacings d (122) and d (211) of carbonatitic calcites with the determined minor elements show that magnesium has the strongest influence in reducing the two spacings (Fig. 6); the combined Mg + Fe + Mn has a more subdued effect, largely because the trend is dictated by the more abundant and larger Mn ion. The combined Sr + Ba does not show any distinct effect. On Fig. 6, the Sr + Ba plot yields a cloud of points that trends subparallel to the abscissae and whose scatter is indicated by a vertical bar. The broad scatter of points and the lack of a distinct trend in the Ba + Sr plot is due largely to the highly variable Mg, Fe and Mn content of these same calcites.

The average a and c axial lengths calculated for all specimens from the data in Table 1 is: $a = 4.9828\text{\AA}$, $c = 17.086\text{\AA}$. The average a axis of carbonatitic calcite from Oka is thus significantly smaller than that of synthetic calcite as given in the Powder Diffraction File (No. 5-0586)¹ being $4.9828\text{\AA}$ vs. $4.990\text{\AA}$; the average c axis for the Oka material is, however, larger than that of synthetic calcite, being $17.086\text{\AA}$ vs. $16.946\text{\AA}$. Quon (1965) determined similar a and c values for two carbonatitic calcites from Oka. These findings are especially interesting if one considers

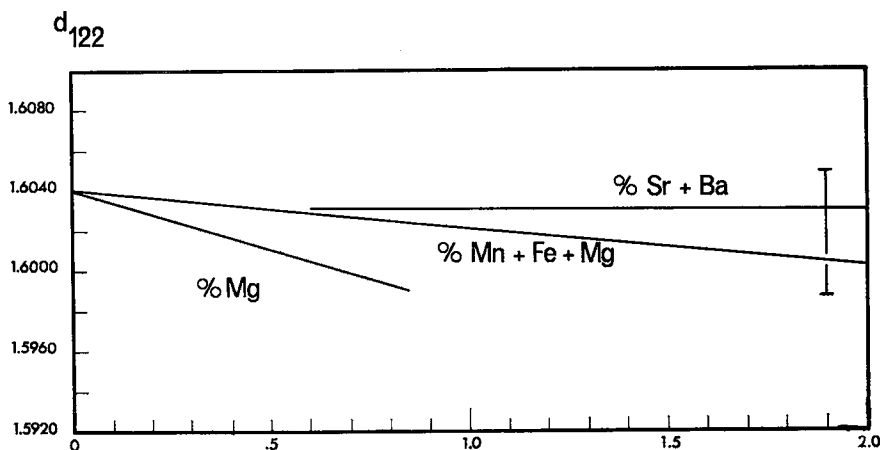


FIG. 6. Schematic diagram showing the variation of d (122) with minor element contents of carbonatitic calcites.

¹ Published by the Joint Committee on Powder Diffraction Standards, Philadelphia.

that more than 80% of the samples investigated have combined Ba + Sr contents larger than their combined Mg + Fe + Mn contents. Mixed substitution of Mg, Mn, Fe, Ba and Sr for calcium in carbonatitic calcite would thus appear to affect the a and c axial parameters in opposite fashion.

In order to study in greater detail the effects of combined atomic substitution, the ionic radius of the average cation in calcite was calculated by weighting the ionic radius of each substituting element according to its atomic proportion. The contributions from atoms smaller than calcium, (e.g., Fe, Mg, Mn) were considered negative whereas those from atoms larger than calcium (e.g., Ba, Sr) were given a positive sign. The weighted radii were added algebraically and the resultant was called P -factor (perturbation factor) and given the sign + or - depending on the sum. For instance, a P -factor of + .02 indicates that the average cation in calcite is larger than calcium by .02Å. A diagram that correlates P -factors with measured lattice spacings brings out several interesting features (Fig. 7) :

- (1) As expected, the trend of the plot is such that increasing positive values of P are accompanied by increased lattice spacings. A diagram identical to Fig. 7 is obtained when calculated a axes are plotted against P .

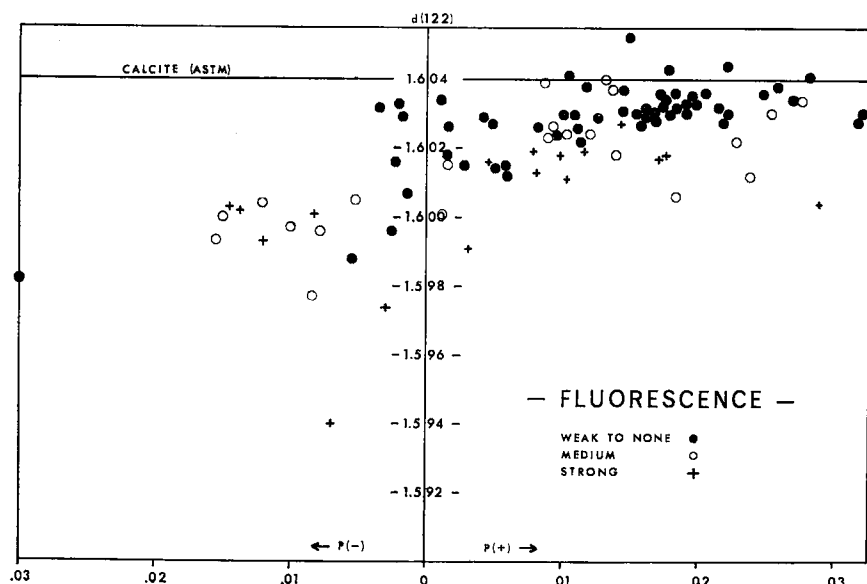


FIG. 7. Variation of $d(122)$ with calculated ionic radius for the average cation in carbonatitic calcites.

- (2) For a fixed value of P , there exists a range of lattice spacings; this range is significantly larger than the accuracy in the measurements of spacings ($\pm 0.0005\text{\AA}$).
- (3) Calcites that fluoresce strongly under ultraviolet illumination have spacings smaller than that of non-fluorescent samples and tend to occur in the lower part of the diagram (crosses).

Compared with pure or synthetic calcite, carbonatitic calcites from Oka have "shrunk" a axes in spite of the positive value of P . Quon (1965) noted briefly the unusual behavior of the a and c axes of barian and strontian calcites. The present study establishes and defines this anomaly conclusively.

Fluorescence of calcites

Spectacular specimens of fluorescent calcite may be collected at Oka. Not all calcites fluoresce; their occurrence appears quite irregular and their intensity of fluorescence, quite variable. Approximately 20% of the material studied fluoresce in shades of bright orange red, dull red or hot pink. This property is of interesting application for it often underlines unsuspected structures and/or heterogeneities in apparently homogeneous carbonite samples (Fig. 8).

The cation causing the fluorescence is very likely manganese. However, calcites with a wide range of Mn content fluoresce and there are no obvious ways of distinguishing fluorescent specimens from non-fluorescent ones on the basis of Mn content and/or combinations or ratios between Mn, Fe and Mg. The conditions propitious for fluorescence are suggested on the diagram of Fig. 7. Shrinkage of the calcite structure along the a axis and expansion along the c axis would deform the electronic structure of the Mn ions and render the calcite apt to fluoresce. The distribution of fluorescent specimens in Fig. 7 suggests that only those calcites in which sufficient deformation of the electronic structure of Mn has occurred can fluoresce. It is interesting to note that the intensity of fluorescence decreases gradually with increasing temperature; it ceases at approximately 275°C , and is reversible. Such a behavior may possibly be interpreted as due to the removal of strain on the Mn ions owing to the combined effects of thermal motion of atoms and the thermal expansion of the structure.

Optical properties of calcites

A suite of twenty calcite specimens was selected at random from the samples studied and the ω refractive index was accurately measured. The ω index given in Table 1 is a mean obtained from at least 10 determina-

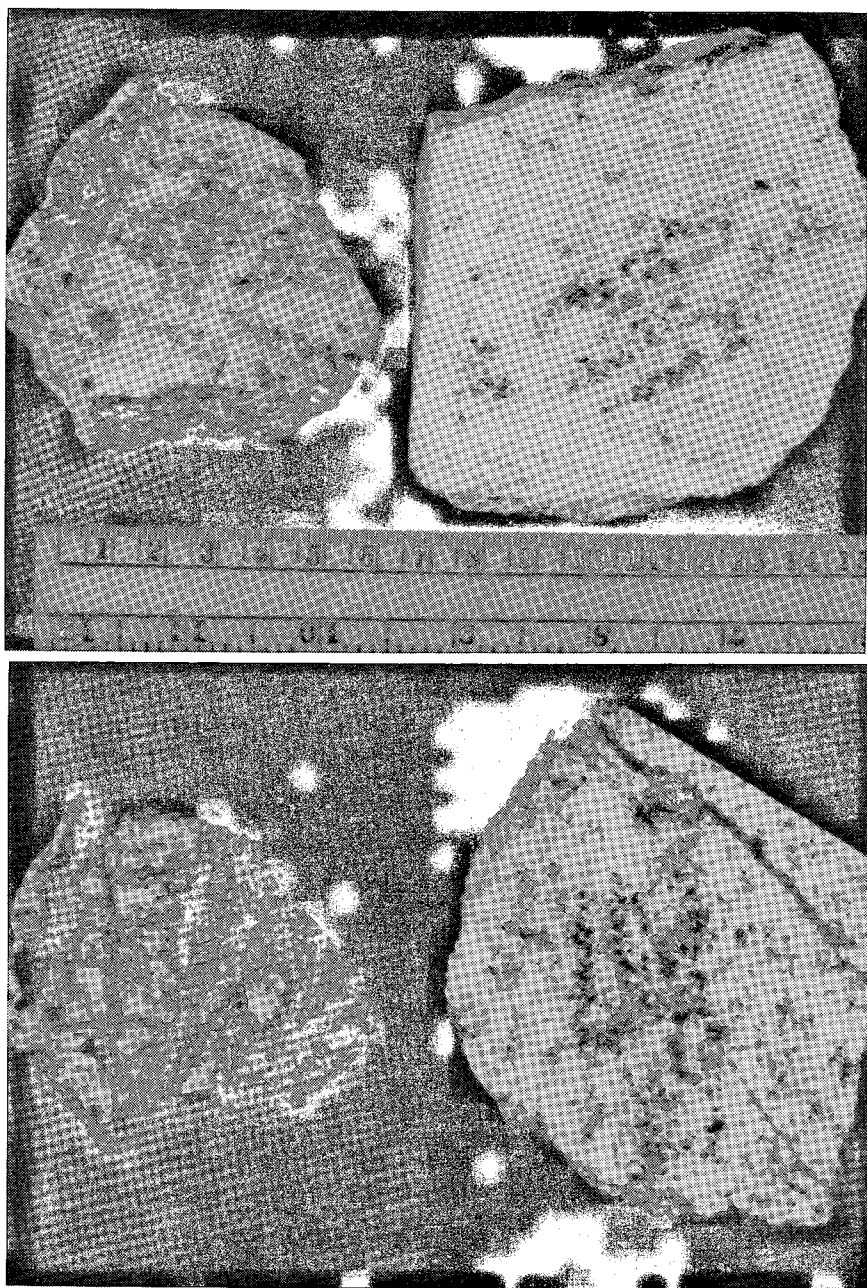


FIG. 8. Heterogeneities in carbonatite specimens. The upper photograph taken under ordinary illumination shows two apparently homogeneous specimens; ultraviolet illumination (lower photograph) brings out an important non-fluorescent vein network in the strongly fluorescent calcite matrix.

tions made within each concentrate. The range in refractive index observed in a concentrate generally deviates from the mean by $\pm .001$; however, deviations as high as $\pm .0015$ were measured in a few samples.

Attempts to correlate the ω index with the minor element content of the calcites did not yield definite conclusions. Doubtless, this results, at least in part, from the small number of samples studied and from the varied nature and small quantities of substituting elements, generally less than 3%. In general, carbonatitic calcites that contain less than 1.5% of combined minor elements have $\omega \approx 1.6609$ whereas calcites with a higher content of minor elements have $\omega \approx 1.6615$. Despite the limitations mentioned earlier, carbonatitic calcites appear to have ω indices significantly different from that of pure calcite ($\omega = 1.6584$, Winchell, 1951). This difference is no doubt largely due to the effects of the contained Ba, Sr, Mg, Fe and Mn. However, it is possible that this difference results partly from structural causes. The opposite effects of combined atomic substitution on the a and c axes of carbonatitic calcites, as described in previous paragraphs, may be analogous to the effect of strain on the structure of the mineral. Because calcite undergoes an increase in refractive indices with pressure (Davis & Vedom 1968) it may be possible that crystal-chemical strain in carbonatitic calcites causes a similar increase in refractive indices.

Certain calcites from Oka and from other carbonatite complexes are known to exhibit a biaxial indicatrix (Heinrich 1966, p. 170). The occurrence of biaxial calcite is briefly reviewed in Heinrich (1966) and more recently, by Boettcher & Wyllie (1967). The cause for biaxial optics in calcite has been attributed, to molecular rearrangements following crystallization at high temperatures (Walker & Parsons 1925), to postconsolidational deformation (Gillson 1927) and, perhaps most significant of all, to inversion from aragonite (Boettcher & Wyllie 1967). The distribution of biaxial calcite in carbonatite rocks and its exact petrologic significance are yet unknown. The present work investigated the distribution of biaxial calcite in the Oka rocks and, in the light of the accompanying chemical and physical data attempted to define the cause of this anomaly. The optic axial angle of calcites was systematically determined from thin sections, for 35 specimens selected at random from the material studied. It soon became evident during this investigation that a large number of the samples studied have a fabric, with the result that a statistical analysis of the data from thin sections cut at random would not be feasible. Indeed, for certain thin sections, examination of some sixty crystals often yielded only a small number of crystals for which $2V$ could be correctly measured. Despite these limitations, this work shows that the optic character of calcite varies from

sample to sample and within a same thin section. Biaxial calcites of varying $2V$ co-occur with uniaxial calcite in the same thin section; the proportion of uniaxial and biaxial crystals is such that a complete range, extending from specimens composed almost exclusively of uniaxial crystals to specimens containing a marked predominance of biaxial crystals, seems to exist. The largest $2V$ measured is 26° and the most common biaxial calcite has $2V$ approximating 12° .

Attempts to correlate or interpret the incidence of biaxial calcites in the specimens on the basis of the chemical and physical data for the calcites were not successful. It should be mentioned, however, that the lack of accurate statistical data on the distribution of biaxial calcites hinders considerably such a correlation. Although the calcites studied have good rhombohedral cleavages, this work attempted to detect by means of X-ray diffraction, the presence in the calcites of uninverted aragonite nuclei or domains. Specimens with a high incidence of biaxial crystals were studied by means of long exposure Guinier photographs but the strong reflections of aragonite that were sought were not found.

Considering the limitations imposed by the methods used in this investigation, further progress in the study of biaxial calcites will only be arrived at by detailed single crystal X-ray diffraction studies, coupled with microprobe analysis of the crystals investigated. The occurrence of biaxial calcite is perhaps significant. The presence of uniaxial, weakly biaxial and distinctly biaxial crystal in the same specimen suggests that this anomaly has a kinetic origin and results from atomic rearrangements in the crystals (order-disorder type) during the thermal history of carbonatitic calcites. This anomaly can possibly be grouped together with other cases of "hang-overs" in crystals (Goldsmith 1967).

SUMMARY AND DISCUSSION

Sr, Mn, Mg, Ba and Fe, in order of decreasing importance are the principal minor elements in carbonatitic calcites from Oka. The chemistry of the calcites varies widely and sporadically within the complex. Except for late or "hydrothermal" carbonate veins which characteristically contain calcites with low amounts of Sr and Mn, the chemistry of carbonatitic calcites bears no obvious relationships either to the mineralogical types of carbonatite or to the distribution of niobium in the rocks. The erratic minor element content of the mineral would indicate that calcite alone offers little or no help for unravelling sequences of carbonatite emplacement.

Factors that may be responsible directly or indirectly for the sporadic distribution of minor elements in carbonatitic calcites are numerous. Of particular significance for the Oka rocks are :

- (1) The difficulty in grouping and comparing carbonatite specimens from the same intrusive phase or age.
- (2) Modifications imposed on the parent material during emplacement of carbonatite rocks.
- (3) Fractionation of Ba, Sr, Mn, Mg and Fe in carbonatite systems.
- (4) Postconsolidational changes, in particular, recrystallization and deuteric alteration.

Whereas some of the factors mentioned are self-explanatory, others warrant brief details.

The evolution of carbonatite complexes is generally characterized by more than one generation of carbonate rocks ; these may form individual masses or occur as dykes, veins and irregular bodies intrusive into earlier carbonate rocks. Because availability of minor elements probably varies from one generation or phase to the other, a correct appraisal of the calcite chemistry requires that studies and comparisons be made only on specimens from the same phase. The field relationship of carbonatite rocks are generally complex, often contradictory and because rocks of identical mineralogy may be of different ages, it is almost impossible to group the rocks studied into their respective carbonatite phase. The rocks studied at Oka could only be grouped into mineralogical types. The interpretation of minor element data in calcite on the basis of mineralogical types of carbonatites thus most likely introduce additional heterogeneities in the results.

Modifications imposed on parent liquids affect both the mineralogy and minor element content of the rocks. The most evident modification imposed on the rocks at Oka is layering or mineralogical banding. Although the variations from layer to layer were not investigated in detail, the few analyses made indicate important variations in calcite chemistry and niobium content in adjacent layers.

Certain physical properties of carbonatitic calcite, such as lattice parameters, optical properties and, to a lesser extent, fluorescence under ultra-violet radiation, appear to differ from that of ordinary calcite. The cause of these differences is only partly attributable to the minor elements contained in the mineral. This feature indirectly suggests that the physical peculiarities of carbonatitic calcite result from atomic rearrangements during the thermal history of the mineral.

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APPENDIX I

*Laboratory methods of study**Preparation of material*

All specimens studied were processed according to the flow sheet outlined on Fig. 9, great care being taken to obtain carbonate concentrates as free as possible from impurities. The concentrates of calcite obtained after heavy liquid separation appeared *a priori* most satisfactory. However, in spite of the careful separation work, the presence of impurities in most concentrates was indicated by x-ray diffraction and oil immersion work as well as leaching experiments, where the concentrates were dissolved in cold, 5% acetic acid. The insoluble residue obtained vary from 0.1 to 8% by weight and consist principally of minute apatite inclusions and subordinate amounts of silicate minerals, largely biotite and pyroxene. Semi-quantitative x-ray fluorescence analysis of some of these residues indicates, in agreement with Girault (1966), that the apatites contain appreciable amounts Sr and rare earths and subordinate Ba, Mn, Fe and Nb.

These impurities in the concentrates rendered impracticable the determination of the minor elements chemistry of the calcites directly from the mineral powders; consequently, all concentrates were dissolved in cold, dilute (5%) acetic acid, the solution filtered and the residue weighed. A correction was subsequently applied to the chemical data determined on the acetate solutions.

Analytical methods

1. *Whole rock Nb_2O_5 content.* The Nb_2O_5 content of the carbonatite specimens studied was determined by an x-ray spectrographic method

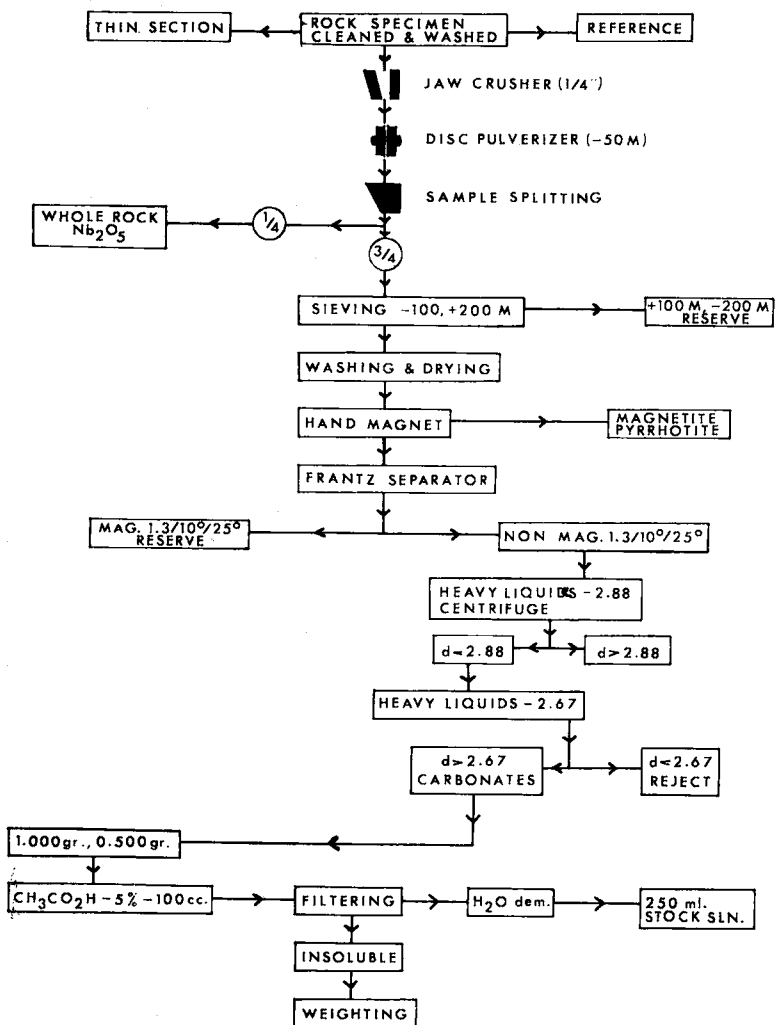


FIG. 9. Flow-sheet of rock preparation and mineral separation prior to chemical analysis.

using MoO_3 as an internal standard (Van Wambeke 1959). Standard carbonatite powders of Nb_2O_5 content ranging from .10 to 1.50% were made available by the assay laboratory at the St. Lawrence Mine; these were added 3% MoO_3 , mixed, and a working curve constructed. The relative accuracy of the determinations is $\pm 5\%$ Nb_2O_5 .

2. *Determination of Sr, Ba, Mn, Fe and Mg.* The minor elements of calcites were determined by atomic absorption spectroscopic methods using synthetically prepared carbonates of varying Ba, Sr, Mn, Mg and Fe contents. The standards were prepared from spectrographic grade CaCO_3 , BaCO_3 , SrCO_3 , MgCO_3 and Fe and Mn metals. Except for Si and Al which were not determined in the present work, the standards used, duplicate very closely those prepared by Quon (1965). The synthetic standards were made into standard solutions by dissolving the mixtures in 5% acetic acid, as was done for the calcite concentrates. Working curves were constructed for the various ranges of concentration encountered. Details concerning atomic absorption work are contained in Table 3. The procedure followed consisted in reading first the unknown solution on the working curve and follow by reading the two closest standards on either side of the unknown, and interpolating the results. The relative accuracy of the determinations is better than $\pm 10\%$.

3. *X-ray diffraction work.* Power patterns of calcite concentrates were obtained using a Guinier de Wolfe multiple powder camera, in order to detect impurities, possible unmixing and/or other carbonate phase that might be present in the concentrate. Similarly, a second series of patterns was obtained using fluorite as an internal standard. The two spacings of calcite which appeared to vary the most from one specimen to the other, d (122) and d (211), were measured against the (113) reflection of fluorite (2θ 55.79° $\text{Cu K}\alpha_1$). Measurements were made by two independent operators using a projector type film reader, and the results averaged. These

TABLE 3. ATOMIC ABSORPTION DETERMINATIONS OF MINOR ELEMENTS IN CALCITE.

Element	Anal. Line	Burner	Flame
Ba	553.6 m μ	Laminar	C_2H_2 , 1.5 psi — N_2O , 7 psi
Sr	460.7 m μ	Hetco	air, 20 psi — H_2 , 10 psi
Mg*	285.2 m μ	Hetco	" " " "
Mn*	279.5 m μ	Hetco	" " " "
Fe*	243.3 m μ	Hetco	" " " "

* Measured at the second order.

measurements were verified by careful fluorite controlled diffractometer scanning over the same reflections. Such work done on a suite of fifteen randomly selected samples shows that the two methods yield spacings that do not differ by more than $\pm 0.0005\text{\AA}$. A computer program was used to calculate a and c of calcites from the measured (122) and (211) reflections. The accuracy reported enables to calculate a to $\pm .001\text{\AA}$ whereas c is much less accurate (approx. $\pm .20\text{\AA}$).

4. *Infrared spectroscopy.* A suite of 30 specimens of calcite whose measured (122) and (211) reflections were spread over the entire range of values encountered were selected for study by infrared methods. The KBr pressed pellet technique was used and the spectra recorded using a Beckman IR-12 spectrophotometer. The absorption fundamentals ν_2 and ν_4 of calcites in the 715 and 878 wave number region were recorded and measured to the nearest wave number.

All spectra thus obtained were virtually alike to each others and similar to that of pure calcite ; band position did not shift significantly from their mean value (715 and 879 wave Nos.). In view of these results, the infra-red work was discontinued.

5. *Observations under ultraviolet illumination.* All carbonatite specimens and corresponding calcite concentrates were examined with a laboratory type ultraviolet lamp using both short wave and long wave radiation. These examinations often revealed unsuspected heterogeneities in the specimens, such as fracture network, gneissic structure, non-fluorescent carbonate veins, etc. The intensity of fluorescence was described as strong when brilliant orange red color was obtained ; medium, when dull red to pink colors were observed ; weak to none, from bluish to mauve colors.

6. *Optical work.* The ω refractive index of calcites from 20 concentrates was measured by oil immersion techniques using sodium light and a variable temperature stage (single variation method). A minimum of ten crystals were measured in each concentrate and the range and average ω index recorded. The accuracy in determining ω is better than $\pm .001$.

The optic axial angle ($2V$) of calcite was measured from thin section obtained from each carbonatite specimen, using a universal stage equipped for conoscopic orientation methods. The number of crystals investigated in a single thin section varied considerably. Often, the presence of a fabric in the specimen necessitated measurements of up to 60 crystals before an estimate of the average $2V$ and the proportion of biaxial and uniaxial crystals could be made.

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