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EWALDITE, A POSSIBLE MEMBER OF THE WELOGANITE GROUP

and

UK62, A NEW SODIUM CALCIUM FLUOROCARBONATE

FROM MONT ST.-HILAIRE, QUEBEC

by

ANDREW MICHAEL MCDONALD, B.Sc. (Hons.)

A thesis submitted to the Faculty of Graduate Studies
and Research in partial fulfillment of the requirements
for the degree of Master of Science.

Department of Earth Sciences

The Ottawa-Carleton Geoscience Centre

Ottawa, Ontario

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"EWALDITE, A POSSIBLE MEMBER OF THE WELOGANITE GROUP AND
UK62, A NEW SODIUM CALCIUM FLUOROCARBONATE FROM
MONT ST.-HILAIRE, QUEBEC"

submitted by Andrew Michael McDonald, B.Sc.(Hons.)
in partial fulfillment of the requirements for
the degree of Master of Science

Thesis Supervisor

Chairman, Department of Earth Sciences

Carleton University
September, 1989

ABSTRACT

Ewaldite, ideally $\text{Ba,NaCaY}(\text{CO}_3)_{.3}\text{H}_2\text{O}$ and originally discovered at the Green River Formation, Wyoming, has been found in silicate cavities, carbonate cavities and pegmatite veins at Mont St.-Hilaire, Quebec. The mineral occurs both in a clear, yellow transparent variety and a mottled blue-green, translucent variety. Both occur in polycrystals composed of intimate intergrowths with, and syntactic overgrowths on, donnayite, mckelveyite and UK37a, a mineral believed to be the Sr-analogue of ewaldite. Originally assigned to the space group $P6_3mc$, Mont St.-Hilaire ewaldite may be indexed on a hexagonal cell, $a = 5.284$ and $c = 12.74$ Å. Optically, the presence of a biaxial indicatrix ($2V = 5^\circ$) and deviation of the acute bisectrix by more than 6° from the normal to the basal cleavage, combine to suggest that the true symmetry of ewaldite is lower than hexagonal or trigonal. Infrared spectroscopy shows a significant amount of water in ewaldite. Microprobe data indicate very similar cationic contents for ewaldite and mckelveyite, and both may be recalculated to the same ideal formula, suggesting they are dimorphous. Based on similar chemistries, weloganite, donnayite, mckelveyite, ewaldite and UK37a, are proposed to belong to one group. X-ray diffraction data suggest this group be divided into two subgroups: the weloganite subgroup, composed of pseudo-trigonal weloganite, mckelveyite and donnayite and the ewaldite subgroup, consisting of ewaldite and UK37a, whose true symmetry is unknown.

UK62, ideally $\text{Na,Ca}(\text{CO}_3)_2\text{F}$, is a new mineral from Mont St.-Hilaire, Quebec. The tan to colourless mineral was found in a sodalite xenolith associated with villiaumite and aegirine. It is transparent to translucent and occurs in crystalline masses up to 3 mm and euhedral crystals less than 1 mm in length. Two varieties, distinguishable by their termination faces, are observed. UK62 is monoclinic, $C2/c$ or Cc , $a = 8.043$ $b = 15.812$, $c = 7.030$ Å and $\beta = 101.16^\circ$. Good $\{001\}$ and imperfect $\{010\}$ cleavages are present. Optically biaxial negative, $\alpha = 1.472$, $\beta = 1.561$ $\gamma = 1.569$, $2V(\text{meas.}) = 25^\circ$, $2V(\text{calc.}) = 31.9^\circ$, $b = Y$, $c \wedge X = 6^\circ$. Infrared spectroscopy suggests the presence of hydroxyl. Substitutions $\text{Mn} \rightleftharpoons \text{Ca}$ and $\text{F} \rightleftharpoons \text{OH}$ are both believed to occur. It has been hydrothermally synthesized at 700°C and 1.5 kbars.

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TABLE OF CONTENTS

ABSTRACT.....	iii
ACKNOWLEDGEMENTS.....	v
TABLE OF CONTENTS.....	vii
LIST OF FIGURES.....	viii
LIST OF PLATES.....	ix
LIST OF TABLES.....	x
1 EWALDITE, A POSSIBLE MEMBER OF THE WELOGANITE GROUP...1	
Introduction.....	1
Occurrence.....	2
Crystallography.....	6
Optical and Physical Properties.....	12
Infrared Spectrum.....	15
Electron Microprobe Analysis.....	23
The Refinement of the Structure of Ewaldite.....	35
Related Minerals.....	41
2 UK62, A NEW SODIUM CALCIUM FLUOROCARBONATE FROM	
MONT ST.HILAIRE, QUEBEC.....	48
Introduction.....	48
Occurrence and Associations.....	48
Crystallography.....	50
Physical Properties.....	54
Electron Microprobe Analyses	
and the chemical formula of UK62.....	57
Infrared Spectrum.....	61
Thermogravimetric Gravimetric	
and Evolved Gas Analysis.....	64
Discussion of TGA-EGA results.....	66
UK62 Synthesis.....	68
Appendix.....	73
References.....	74

LIST OF FIGURES

	Page
Figure 1. The infrared spectrum of ewaldite.....	16
Figure 2. The infrared spectrum of $Y_2(CO_3)_3 \cdot 2H_2O$. After Caro et al. (1971).....	20
Figure 3. The infrared spectrum of weloganite.....	21
Figure 4. The infrared spectrum of donnayite.....	22
Figure 5. The structure of weloganite. After Grice and Perrault (1975).....	44
Figure 6. The optical orientation of UK62.....	56
Figure 7. The infrared spectrum of UK62.....	62
Figure 8. TGA, P_{total} , and EGA of UK62.....	65

LIST OF PLATES

	Page
Plate 1. Hemimorphic polycrystals of type I ewaldite and donnayite.....	3
Plate 2. Euhedral crystals of type II ewaldite.....	4
Plate 3. A polycrystal composed of type II ewaldite, donnayite, mckelveyite and UK37a.....	5
Plate 4. 0-level $\bar{c}$ -axis precession photograph of Mont St.-Hilaire ewaldite.....	9
Plate 5. 0-level $\bar{c}$ -axis precession photograph of Mont St.-Hilaire ewaldite.....	46
Plate 6. 0-level $\bar{c}$ -axis precession photograph of triclinic welcganite.....	47
Plate 7. A euhedral crystal of type 1 UK62.....	51
Plate 8. A euhedral crystal of type 2 UK62.....	52

LIST OF TABLES

	Page
Table 1. Gandolfi X-ray diffraction data for ewaldite...	11
Table 2. A comparison of the optical and physical properties of Mont St.-Hilaire and Green River Formation ewaldite.....	14
Table 3. The band assignments for the infrared spectrum of ewaldite.....	17
Table 4. A description of Fujita et al. (1962) carbonate group notation.....	18
Table 5. Cambridge Microscan 5 and standard data.....	24
Table 6. JEOL Superprobe 733 and standard data.....	25
Table 7a. Electron microprobe analyses of ewaldite.....	27
Table 7b. Electron microprobe analyses of ewaldite.....	28
Table 8. Electron microprobe analyses of mckelveyite....	29
Table 9a. The chemical formula of ewaldite based on six oxygens.....	31
Table 9b. The chemical formula of ewaldite based on six oxygens.....	32
Table 10. The chemical formula of mckelveyite based on six oxygens.....	33
Table 11. Final atomic parameters for ewaldite.....	39
Table 12. Bond distances and angles for ewaldite.....	40
Table 13. The cell parameters of ewaldite and and related minerals.....	42
Table 14. The cell parameters of the ewaldite subgroup...	43
Table 15. Minerals associated with UK62.....	49
Table 16. Gandolfi X-ray diffraction data for UK62.....	53
Table 17. Cambridge Microscan 5 electron microprobe and standard data.....	58

Table 18a.	Electron microprobe analyses of UK62 and number of ions based on three oxygens.....	59
Table 18b.	Electron microprobe analyses of UK62 and number of ions based on three oxygens.....	60
Table 19.	Band assignments for the infrared spectrum of UK62.....	63
Table 20.	Hydrothermal synthesis of UK62.....	69
Table 21.	A comparison of the refined cell parameters for natural and synthetic UK62.....	71

EWALDITE, A POSSIBLE MEMBER OF THE WELOGANITE GROUP

INTRODUCTION

Ewaldite, originally given the formula $\text{BaCa}(\text{CO}_3)_2$, was first discovered in 1965 from a drill core in the highly sodic, lacustrine sediments of the Green River Formation, Sweetwater Co., Wyoming (Donnay and Donnay, 1971). Here it was found as a syntactic overgrowth on mckelveyite, $\text{Ba}_3\text{NaCaY}(\text{CO}_3)_6 \cdot 3\text{H}_2\text{O}$, in association with another rare carbonate, burbankite, $(\text{Na,Ca})_3(\text{Sr,Ba,Ce})_3(\text{CO}_3)_5$. The mineral was believed to be hexagonal, $\text{P6}_3\text{mc}$ (#186) and more ordered than the associated mckelveyite. The chemical, physical and structural characteristics of ewaldite were sufficient for species designation.

About five years later, ewaldite was encountered at Mont St.-Hilaire, Rouville Co., Quebec. Here it commonly occurs in polycrystals composed of intimate intergrowths with, and syntactic overgrowths on, mckelveyite, donnayite ($\text{Sr}_3\text{NaCaY}(\text{CO}_3)_6 \cdot 3\text{H}_2\text{O}$) and occasionally, an unidentified mineral tentatively designated UK37a (Chao et al., 1978). A re-evaluation of the original work on ewaldite, together with results from analyses of Mont St.-Hilaire material, revealed a number of serious problems as outlined below:

1. A discrepancy between the measured density, $D_{\text{meas}} = 3.25 \text{ g/cm}^3$ and the calculated density, $D_{\text{calc}} = 3.37 \text{ g/cm}^3$. Donnay and Donnay (1971) attributed the difference to the presence of lighter, Na-rich and carbonaceous inclusions.
2. An attempt by Donnay and Preston (1971) to solve the structure of ewaldite assuming a hexagonal cell was inconclusive, as only one of the two carbonate groups, believed to be occupying different crystallographic sites, could be located.

3. Chemical precipitation methods did not provide a CO_2 or water content for ewaldite.
4. The presence of an optically biaxial indicatrix ($2V = 5^\circ$) and a deviation of the acute bisectrix by more than 6° from the normal to the basal plane, suggest that the symmetry of ewaldite may not be higher than monoclinic.

The purpose of the present investigation was to resolve some of these problems through a complete re-study of ewaldite, using material from both the type locality and the new occurrence at Mont St.-Hilaire.

OCCURRENCE

Ewaldite occurs predominantly in two environments at Mont St.-Hilaire. First, it is found in silicate and carbonate vugs as 0.5 - 1 mm, clear, yellow crystals in parallel growths (termed type I; see Plate 1). The crystals retain a roughly hexagonal outline, and are most commonly terminated by a pedion. They appear to be hemimorphic, developing outwards from a relatively small base, and are commonly intergrown with donnayite (Plate 1). Associated minerals include analcime, aegirine, calcite, natrolite, sphalerite and ilmenite. It should be noted that mckelveyite has not been detected as a phase intergrown with ewaldite in this particular environment.

Ewaldite also occurs in pegmatite dikes, where, in addition to the type I material, a mottled pastel blue-green variety is also found (termed type II). The type II crystals range in size from 0.5 - 2 mm, with a barrel- or pagoda-shaped morphology. The crystals have a step-like or layered appearance, and may be terminated by a shallow, tapered pyramid or a pedion (Plate 2). Polycrystals of the

Plate 1. Hemimorphic polycrystals composed of ewaldite (dark bands) and donnayite (light bands), with caps of donnayite (from Chao et al., 1978).

Plate 2. Ewaldite crystals demonstrating the common pedial termination and their characteristic layered appearance.

Plate 3. A polycrystal composed of (a)ewaldite, (b)UK37a, (c)donnayite and (d)mckelveyite (from Chao et al., 1978).

type II ewaldite may contain up to three additional phases: donnayite, mckelveyite and UK37a, a mineral believed to be the Sr-analogue of ewaldite (Plate 3; Chao et al., 1978). Associated minerals include quartz, labuntsovite, pyrite, millerite and aegirine.

Regardless of the type of ewaldite being examined, their gross morphological features (layering or step-like growth, large pedial termination, etc.) are very much like those of weloganite, $\text{Sr}_3\text{Na}_2\text{Zr}(\text{CO}_3)_6 \cdot 3\text{H}_2\text{O}$, from the Francon Quarry, Montreal, Quebec (Sabina et al., 1968).

THE CRYSTALLOGRAPHY OF EWALDITE

In their original description, Donnay and Donnay (1971) analyzed a crystal of what they believed to be nearly pure ewaldite, purity determined by the absence of mckelveyite layer lines on 100-hour cone-axis photographs. Using a combination of precession ($\text{MoK}\alpha$ radiation) and back-reflection Weissenberg (Ni -filtered $\text{CuK}\alpha$ radiation) methods, the authors were able to ascertain that ewaldite possessed the diffraction aspect $\text{P6}/**c$, suggesting space group $\text{P6}2c$ (#190), P6_3mc (#186) or $\text{P6}/mmc$ (#194). In light of the hemimorphic morphology exhibited by euhedral crystals, they concluded that the correct space group for ewaldite must be P6_3mc . None of the diffuse streaking parallel to c^* observed in mckelveyite was noted in ewaldite. Although no X-ray powder diffraction pattern was given, the authors did provide the least-squares refined cell parameters of $a = 5.284(7) \text{ \AA}$ and $c = 12.78(1) \text{ \AA}$. Donnay and Donnay explained the syntactic relationship exhibited by ewaldite and mckelveyite as the sharing of a common c -direction, with the two sets of a -axes rotated 30° with respect to each other about the c -axis. This generated the observed

syntactic relationship: $a_{\text{ewald}} \approx a_{\text{mckelvey}}/\sqrt{3}$ and $c_{\text{ewald}} = 2 \times c_{\text{mckelvey}}/3$. The authors state that a crystal identified by X-ray diffraction to be predominantly ewaldite, exhibited the forms: $c\{0002\}$, $c'\{000\bar{2}\}$, $e\{11\bar{2}4\}$ and $r\{11\bar{2}2\}$, the latter two of which are not predicted by the first generalization of the law of Bravais (Donnay and Harker, 1937). Except for $r\{11\bar{2}2\}$, all the observed forms are characteristic of mckelveyite, and on this basis, they concluded that this particular crystal of ewaldite must be bounded by the forms of mckelveyite, indicating that mckelveyite was genetically first, later replaced by ewaldite. Further evidence to support this hypothesis was indicated by the fact that pure crystals of mckelveyite were known to occur, but that all nearly pure ewaldite crystals contained some residual mckelveyite. The transformation of mckelveyite to ewaldite is believed to be due to disorder, based on the smaller unit cell and higher symmetry of ewaldite, and is believed to be in the direction $\text{mckelveyite} \rightarrow \text{ewaldite}$, since no composition surface could be discerned between the two phases in the polycrystals (Donnay and Donnay, 1971).

Prior to single-crystal X-ray studies, all Mont St.-Hilaire (MSH) ewaldite was first verified on a 114.6 mm Gandolfi camera, using Ni-filtered $\text{CuK}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). At the same time, the powder diffraction patterns were examined for the presence of other phases. Potential crystals were then optically examined for sharpness of extinction and content of included material. As type II ewaldite is extremely translucent, no optical investigation could be performed on it, and so, it was deleted from subsequent single-crystal work. Suitable type I crystals were mounted on lead-free glass capillaries using nail polish. These crystals were placed on a Supper spindle stage and examined under a polarizing microscope at 500x magnification. Of the eight fragments selected, two had to be eliminated due to high

amounts (30-40%) of included material. The remainder contained less than 5% included material. The crystals were next examined using orientation photographs obtained with unfiltered $\text{MoK}\alpha$ ($\lambda = .7107 \text{ \AA}$) radiation. Of the six remaining fragments, three had to be eliminated because of the presence of split X-ray diffraction streaks. The separation of these streaks may be attributed to twinning or multiple crystals, but at this point the true cause is unknown. One ewaldite crystal from the type locality (Smithsonian catalogue # 121683) was also examined in this fashion, although it had to be deleted from subsequent analyses, as it too exhibited splitting of X-ray diffraction streaks. 24-hour precession photographs of MSH ewaldite were taken about the $\underline{a}$ - and $\underline{c}$ -axes using Zr-filtered $\text{MoK}\alpha$ radiation ($\lambda = .7107 \text{ \AA}$) up to the third level. Measurements from these photographs gave $\underline{a} = 5.312 \text{ \AA}$ and $\underline{c} = 12.69 \text{ \AA}$, in good agreement with the refined values given by Donnay and Donnay (1971). The systematic extinction, $hh\ell$, $\ell \neq 2n$, observed by Donnay and Donnay (1971) is confirmed here. On $\underline{a}$ cone-axis photographs, weak layer lines at values of $1/3$ and $2/3$ between each layer line were noted. This suggests the presence of a supercell with $a' = 3a$. It was found that the structural extinction (Donnay and Donnay, 1971), reflections with $h-k = 3n$ weak or absent when $\ell \neq 2n$, would be correct for MSH ewaldite only if the reflections were indexed on the basis of the supercell. A 72-hour precession photograph of the innermost superlattice layer line showed a number of dense streaks running parallel to c^* . No discernible individual reflections were noted within these streaks. The symmetry and space group of the supercell are therefore indeterminate. However, this superlattice does suggest ordering, yet the dense streaking suggests disorder within these superlattice layers along $\underline{c}$. The fact that Donnay and Donnay (1971) observed the above structural extinction on their ewaldite photographs suggests that superlattice

Plate 4. 0-level c -axis precession photograph of MSH ewaldite showing the curious inner reflections ($\mu = 30^\circ$; Zr-filtered $\text{MoK}\alpha$ radiation).

reflections were present. Therefore, the ewaldite from the Green River Formation (GRF) is apparently more ordered than that from MSH.

The streaking of reflections parallel to c^* noted on some crystals from MSH may indicate stacking disorder in these crystals (Gait and Grice, 1971). Alternatively, it could be caused by twinning on a submicroscopic scale, with adjacent twin members acting as antiphase domains (Chen and Chao, 1975).

Curious inner reflections noted on ewaldite 0-level c -axis precession photographs were found on both MSH and the GRF ewaldite (see Plate 4). These reflections are not indexable on the hexagonal cell adopted for ewaldite, suggesting that another phase may be present. They appear as compressed "x"s, and are significantly different from those reflections attributable to ewaldite, which occur as dots. The appearance of these non-indexable reflections suggests that the phase responsible for them is not oriented with the ewaldite cell. However, given that all of the ewaldite fragments from MSH and the one from the GRF show these same inner reflections, it is unlikely that they may be attributed simply to an additional phase.

The powder diffraction patterns of type I and II ewaldite from MSH are identical, although the patterns of the type II material tend to be slightly more diffuse with a darker background. It was also noted that ewaldite from the GRF gave an identical diffraction pattern to that of the MSH material. The ewaldite X-ray diffraction pattern could be indexed on a hexagonal cell with $a = 5.312 \text{ \AA}$ and $c = 12.69 \text{ \AA}$. Using the least-squares refinement program of Appleman et al. (1973) and ten lines between $d = 6.37 \text{ \AA}$ and $d = 2.25 \text{ \AA}$, for which unambiguous indexing was possible, the refined cell parameters $a = 5.284 (1) \text{ \AA}$ and $c = 12.74 (1) \text{ \AA}$ were

TABLE 1. GANDOLFI X-RAY DIFFRACTION DATA FOR EWALDITE

<u>hkl</u>	<u>dcalcÅ</u>	<u>dobsÅ</u>	<u>I</u>
002	6.368	6.366	3
100	4.576	4.575	4
101	4.306	4.305	9.5
004	3.179	3.179	1
103	3.112	3.112	10
110	2.642	2.640	5
104	2.614	2.610	3
112	2.440	2.438	3
200	2.288	2.288	1
201	2.252	2.250	4
106	1.926	1.925	1
204	1.858	1.859	<1
210	1.729	1.727	<1
211	1.714	1.714	1
107	1.691	1.691	1.5
116	1.655	1.656	1
213	1.602	1.602	3.5
300	1.525	1.524	1.5
304	1.376	1.378	1
220	1.321	1.322	<1
217	1.254	1.254	1
306	1.239	1.239	<1

Plus additional lines

Visual intensities, 114.6 mm Gandolfi camera, Ni-filtered CuK α radiation ($\lambda = 1.5418 \text{ \AA}$).

obtained, in excellent agreement with those given by Donnay and Donnay (1971). The indexed diffraction pattern, assuming a hexagonal cell, is presented in Table 1.

OPTICAL AND PHYSICAL PROPERTIES

The colour of ewaldite varies from amber to yellow for the type I variety, to a mottled pastel blue-green for the type II variety. The streak is white. No external evidence of zonation is present. Type I ewaldite has a vitreous lustre, but type II appears quite dull and earthy. A poor basal cleavage is present on type I ewaldite, but not on the type II material, which does not possess any discernible cleavage. Hardness could only be determined on type I ewaldite, and was found to be approximately 3 on Moh's hardness scale.

The density of ewaldite could not be determined by flotation method, as the type I material was found to be denser than methylene iodide ($D_{\text{meas}} = 3.27 \text{ g/cm}^3$) and the type II material, too porous for an accurate measurement. Berman balance and pycnometer methods were not suitable due to the small amount of sample available. As we can state that ewaldite's measured density must exceed 3.27 g/cm^3 , the value of $D_{\text{meas.}} = 3.25 \text{ g/cm}^3$ quoted by Donnay and Donnay (1971), appears to be too low. As GRF ewaldite is similar in appearance to type II MSH material, it is possible that the type material studied by Donnay and Donnay (1971) was porous. As well, these authors indicated that this type material was contaminated with Na- and carbonaceous material. Therefore, the $D_{\text{meas.}}$ given for the type material is most likely incorrect due to the high porosity and contamination of the analyzed material.

Optically, only the type I variety could be analyzed, due to the translucent nature of the type II variety. Using a Supper spindle stage and immersion mounts,

the type I variety exhibits a sharp extinction when viewed with the basal cleavage vertical, but a patchy or absence of extinction with the basal cleavage horizontal. The interference figures were all found to be reasonably sharp. Ewaldite is biaxial negative, with a very small $2V$ ($\sim 5^\circ$). The acute bisectrix was observed to be inclined $\sim 6.5^\circ$ from the "hexagonal" ϵ -axis. Pleochroism was not observed. The refractive indices of ewaldite were determined at room temperature (25°C) using Cargille immersion oils, a Na-lamp ($\lambda = 589\text{ nm}$) and a crystal previously oriented by the X-ray precession method. The indices of the oils were verified using a Bausch and Lomb Abbe-3L refractometer. The measured values are: $\alpha = 1.572$ (2) and $\beta \approx \gamma = 1.646$ (1), very close to those determined by Donnay and Donnay (1971) for ϵ and ω respectively. The optical and physical properties of ewaldite from MSH are summarized and compared with those given by Donnay and Donnay (1971) for GRF ewaldite in Table 2.

The observed biaxial character and extinction behaviour exhibited by ewaldite are very interesting. The deviation of the acute bisectrix from the "hexagonal" ϵ -axis, strongly suggests that the symmetry of ewaldite is lower than trigonal or hexagonal. In this regard, it is very similar to the observations documented for weloganite and donnayite (Sabina et al., 1968; Chen and Chao, 1975; Chao et al., 1978). Both weloganite and donnayite are triclinic, pseudo-trigonal. The concept of ewaldite having lower symmetry is further supported by the fact that no uniaxial interference figures were noted for any of the ewaldite analyzed in this study. The patchy or absence of extinction noted when ewaldite is viewed with the basal cleavage horizontal has also been observed in weloganite (Chen and Chao, 1975) and donnayite (Chao et al., 1978), and could be caused by the stacking of crystals.

TABLE 2. PHYSICAL PROPERTIES OF EWALDITE

<u>PROPERTY</u>	<u>GREEN RIVER FORMATION</u> <u>(DONNAY AND DONNAY, 1971)</u>	<u>MONT ST.-HILAIRE</u> <u>(THIS STUDY)</u>
Size	0.25 mm across base along <u>a</u> direction	0.05 - 1 mm in length, average of 0.15 mm across base along <u>a</u> direction
Forms	hexagonal pyramid	hexagonal pyramid hexagonal prism
Colour	bluish-green	bluish-green to yellow
Lustre	dull	dull, earthy to vitreous
Streak	not noted	white to pale greenish-white
Cleavage	not noted	poor basal
Fracture	not noted	conchoidal to irregular
Tenacity	not noted	powdery to brittle
Hardness	not noted	< 3 on Moh's scale
Reaction with HCl	not noted	soluble in 1:1 HCl with strong effervescence
Density (g/cm ³)	3.25 (5) (meas.) 3.37 (calc.)	>3.27 (2) (meas.)
Transparency	opaque	translucent to transparent
Refractive Indices	$\epsilon \leq 1.572$ $\omega = 1.646$ (3) (Na light)	$\alpha = 1.572$ (1) $\beta \approx \gamma = 1.646$ (2) (Na light)
Optic Sign	Uniaxial negative	biaxial negative 2V = 5°

The orientation of the optic plane was not found to deviate in a random scan across the grain, unlike the observations made for donnayite (Chao et al., 1978).

INFRARED SPECTRUM

The infrared spectrum of ewaldite shown in Figure 1 was obtained using 3 mg of type II ewaldite. The material was powdered and mixed with 400 mg of KBr (previously kept heated at 140°C) and shaken for two minutes. The mixture was then compressed into a 1.5 cm diameter disk. This disk was then placed in a Perkin-Elmer 1600 series FTIR infrared spectrometer (4 cm⁻¹ resolution capability) employing a neon laser. Background atmospheric conditions were determined and subtracted prior to data collection. The ewaldite spectrum was produced from ten scans of the disk performed over 39 seconds at a threshold of 2% transmission. Band assignments are listed in Table 3, with possible carbonate groups assigned according to the notation of Fujita et al. (1962; see Table 4 for an explanation of this notation).

The spectrum is characterized by strong bands in the region 1600-1200 cm⁻¹, attributable to carbonate group groups and a strong band in the region 3400 - 2600 cm⁻¹ attributed to H₂O. The majority of the remaining bands in the spectrum are attributable to carbonate group overtones.

The most significant observations made from the ewaldite infrared spectrum are the broad band at 3250 cm⁻¹ and the small shoulder at 1650 cm⁻¹. These bands are consistent with those assigned to H₂O or OH⁻ in a number of hydrous rare earth carbonates (Caro et al., 1972) and hydrous carbonates (White et al., 1971). According to Caro et al. (1972), the broad nature of the strong band in the region

Figure 1. The infrared spectrum of ewaldite

**TABLE 3. BAND ASSIGNMENTS FOR THE INFRARED SPECTRUM
OF EWALDITE (in cm^{-1})**

3255	O - H stretching
1600	H - O - H bending
1484	ν_5 carbonate mode
1393	ν_1 carbonate mode
1071 976	ν_2 carbonate mode
862	ν_8 carbonate mode
722	ν_3 carbonate mode
695	ν_6 carbonate mode

TABLE 4. BAND ASSIGNMENTS FOR CARBONATE IONS
USING FUJITA ET AL. (1962) NOTATION

- v_1 - $\text{CO}_{(11)2}$ symmetrical stretching,
oxygen ($\text{O}_{(1)}$) not coordinated by a metal
ion, i.e. CO bonds not involved in metal
bonding.
- v_2 - $\text{C-O}_{(1)}$ symmetrical stretching, oxygen ($\text{O}_{(1)}$)
coordinated by a metal ion, CO bonds
involved in metal bonding.
- v_3 - $\text{CO}_{(11)2}$ bending
- v_4 - metal- $\text{O}_{(1)}$ asymmetrical stretching
- v_5 - $\text{C-O}_{(11)}$ planar rocking
- v_6 - $\text{O}_{(11)}\text{-C-O}_{(11)}$ non-planar rocking
- v_7 - metal- $\text{O}_{(1)}\text{-C-O}_{(1)}$ bending
- v_8 - out of plane bending or out of plane
deformation

3600-2600 cm^{-1} is particularly characteristic of H_2O (see Figure 2) in contrast to OH^- , which is noted by sharp bands in the same region. The presence of water in ewaldite is also strongly supported by the infrared spectra of weloganite (Figure 3) and donnayite (Figure 4), which show H_2O bands in regions similiar to that of ewaldite.

The bands assigned to carbonate groups in the ewaldite infrared spectrum are all reasonably sharp and distinct. Multiple bands, often interpreted as being indicative of the presence of more than one crystallographically distinct carbonate group, are observed only for the ν_2 vibration. The presence of a ν_5 doublet, suggested by some authors to be the strongest evidence of more than one crystallographically distinct CO_3 group (Caro et al., 1972), is not evident on our spectrum. However it is not valid to conclude that it is absent, as our present resolution may be insufficient to detect it. Furthermore, Turcotte et al. (1969) indicate that the peak of the ν_5 band in many compounds with only one type of carbonate group, falls at $1450 \pm 10 \text{ cm}^{-1}$. In ewaldite, the ν_5 peak position is at 1480 cm^{-1} , possibly reflecting the presence of more than one distinct carbonate group. Donnay and Donnay (1971) also discussed the infrared spectrum of ewaldite, although the spectrum itself was not presented. These authors concluded that the appearance of a the ν_3 doublet (band believed assigned according the Herzberg (1945) notation; equivalent to the ν_5 and ν_1 modes of Fujita et al.'s (1962) notation), was due to crystallographically distinct carbonate groups, one group with $3m$ point group symmetry, and the other with m or 1 point group symmetry.

Figure 2. The infrared spectrum of $\text{Y}_2(\text{CO}_3) \cdot 2\text{H}_2\text{O}$ (after Caro et al., 1972)

Figure 3. The infrared spectrum of weloganite

Figure 4. The infrared spectrum of donnayite

The small separations of the $\nu_5 - \nu_1$ (101 cm^{-1}) and the $\nu_6 - \nu_3$ absorption bands seem to be consistent with a uni- or monodentate carbonate group(s) in ewaldite (Gatehouse et al., 1958; Fujita et al., 1962).

ELECTRON MICROPROBE ANALYSIS

The original chemical formula of ewaldite, $\text{BaCa}(\text{CO}_3)_2$, was based on analyses from a combination of electron microprobe (Ba,Ca,Na,Y), spectrographic (rare earth elements), and chemical precipitation methods (CO_2), supplemented by a crystal structure determination (site occupations). As the type material used by Donnay and Donnay (1971) was believed to be highly contaminated with sodium- and carbonaceous-rich inclusions, the analytical results were deemed unreliable and an electron microprobe study was undertaken to establish the chemical composition of ewaldite.

Ewaldite was analyzed by wavelength dispersive spectroscopy (WDS) using both a Cambridge Microscan 5 (MK 5) and a JEOL Superprobe 733 electron microprobes. In both cases, mckelveyite from the GRF and/or MSH were used as internal standards, as earlier results suggested ewaldite and mckelveyite possessed similar major-element concentrations (Donnay and Donnay, 1971). Pertinent information with regards to operating conditions and standards is listed in Tables 5 and 6. Prior to analyses, the ewaldite and mckelveyite material was qualitatively analyzed using a Tracor Northern 5500 energy dispersive spectrometer (EDS) to determine the elements present.

For the JEOL Superprobe 733 microprobe, the MSH type I ewaldite and mckelveyite grains used were both clear, yellow, and relatively inclusion-free (<5%).

TABLE 5. CAMBRIDGE MICROSCAN 5 (MK5) DATA

Operating conditions: 15 kV, 75° fixed take-off angle,
26 nA beam current measured on barite

<u>ELEMENT</u>	<u>STANDARD</u>	<u>ANALYZING CRYSTAL</u>	<u>X-RAY LINE USED</u>
Na	tugtupite	TAP (2d = 25.7 Å)	K α
Ca	dolomite	Quartz (2d = 6.687 Å)	K α
Sr	celestite	TAP	L α
Ba	barite	QUARTZ	L α
Y	REE3 glass	Mica (2d = 19.84 Å)	L α
La	REE3 glass	LiF (2d = 4.028 Å)	L α
Ce	REE3 glass	LiF	L β
Nd	REE2 glass	QUARTZ	L β
Sm	REE2 glass	QUARTZ	L α
U	brannerite	QUARTZ	M α
Th	thorite	QUARTZ	M α

NOTE: TAP = Thallium Acid Phthalate

TABLE 6. JEOL SUPERPROBE 733

Operating conditions: 15 kV, 40° fixed take-off angle,
20 nA beam current measured at the
Faraday cup.

<u>ELEMENT</u>	<u>STANDARD</u>	<u>ANALYZING CRYSTAL</u>	<u>X-RAY LINE USED</u>
Na	albite	TAP	K α
Al	albite	LiF	K α
Ca	gehlenite	PET	K α
Sr	celestite	TAP	L α
Ba	sanbornite	PET	L α
Y	YAG	TAP	L α
La	monazite	PET	L α
Ce	monazite	PET	L α
Pr	monazite	PET	L α
Nd	monazite	LiF	L α
Sm	REE glass	LiF	L α
Eu	REE glass	LiF	L α
Gd	REE glass	LiF	L α
Dy	REE glass	LiF	L α
U	brannerite	PET	M α
Th	monazite	PET	M α

NOTE: YAG = Yttrium Aluminum Garnet; TAP = Thallium Acid Phthalate; PET = Pentaerythritol.

The identity of the grains used had been previously verified by Gandolfi X-ray diffraction method. Regions for background measurement were determined to be as free of line overlaps and as flat as possible. An empirical factor was introduced to correct the X-ray counts due to the $\text{CeL}\alpha_1$ - $\text{BaL}\beta$, overlap. This factor, assuming identical collection times is:

$$\text{Ce}_{\text{true counts}} = \text{Ce}_{\text{apparent counts}} - 0.284 \times \text{Ba}_{\text{true counts}}$$

The type I ewaldite grain was analyzed using defocussed beams of diameters 30 and 40 μm , to prevent cratering and to minimize the vapourization of Na. Using the same operating voltages and beam currents, the 30 μm beam generated a sample current variation of up to 20% (due to specimen burn-up), whereas the 40 μm beam showed less than a 1% variation. As such, the 40 μm beam was chosen to analyze both the ewaldite and mckelveyite crystals. The secondary electron image of the ewaldite grain indicated it to be homogeneous, but the mckelveyite grain showed a small number of sub-parallel bands running throughout. These bands were analyzed using the available EDS system which indicated a major peak attributable to Sr and smaller peaks due to Ba, Y, Ca and Na. These bands may be donnayite or UK37a. Using the WDS system, elemental X-ray counting time were for 15 seconds or the time required to attain a relative precession of 0.5% on the standard, whichever was achieved first. Raw X-ray data were reduced using the Tracor Northern ZAF routine. Errors on the resulting weight per cent values at the 2σ level are: BaO(.58 wt. %), SrO(.18 wt. %), Y_2O_3 (.21 wt. %), CaO(.15 wt. %), Na_2O (.46 wt. %), ThO_2 , REE_2O_3 (.46 wt. %).

For the Cambridge Microscan 5 electron microprobe, a crystal of clear, yellow type I ewaldite from MSH and an ewaldite grain from the GRF were used. In addition, a clear yellow crystal of mckelveyite from MSH and a number of black,

TABLE 7a. ELECTON MICROPROBE ANALYSES FOR EWALDITE (wt. %)

OXIDE	1	2	3	4	5	6	7
Na ₂ O	5.60	2.71	3.38	3.48	3.27	3.64	3.46
K ₂ O	1.40	-	-	-	-	-	-
CaO	7.60	5.51	4.25	4.59	4.69	3.68	4.65
Fe ₂ O ₃	2.00	-	-	-	-	-	-
SrO	0.80	2.35	0.99	0.83	0.79	0.93	1.10
BaO	45.00	40.27	41.99	41.44	41.60	41.78	42.31
Y ₂ O ₃	4.76	5.80	6.31	6.28	6.27	5.21	6.42
La ₂ O ₃	0.05	-	0.05	0.06	0.01	-	0.12
Nd ₂ O ₃	-	1.24	0.44	0.15	0.15	0.54	0.37
Sm ₂ O ₃	0.03	1.18	0.09	0.17	0.13	0.18	0.20
Eu ₂ O ₃	0.07	-	-	-	-	-	-
Gd ₂ O ₃	0.65	-	-	-	-	-	-
DY ₂ O ₃	0.50	-	-	-	-	-	-
Ho ₂ O ₃	0.12	-	-	-	-	-	-
Er ₂ O ₃	0.81	-	-	-	-	-	-
Yb ₂ O ₃	0.65	-	-	-	-	-	-
Lu ₂ O ₃	0.05	-	-	-	-	-	-
ThO ₂	-	0.60	1.06	1.63	1.66	1.29	1.34
UO ₂	0.80*	-	5.14	3.09	2.66	7.95	4.78
CO ₂	-	(29.42)	(28.81)	(29.02)	(29.03)	(26.78)	(28.56)
H ₂ O	-	(6.02)	(5.89)	(5.94)	(5.94)	(6.02)	(5.84)
SUM	70.89	95.10	98.40	96.68	96.20	98.04	99.15

NOTE: () = determined by stoichiometry, i.e. 6CO₂ and 3H₂O;
 * Given as UO₃ by Donnay and Donnay (1971).

1. GRF, Donnay and Donnay, 1971
2. MSH, Jeol Superprobe
3. GRF, spot 1, MK5 probe
4. " , spot 2, "
5. " , spot 3, "
6. " , spot 4, "
7. " , spot 5, "

TABLE 7b. ELECTRON MICROPROBE ANALYSES OF EWALDITE (wt. %)

OXIDE	<u>8</u>	<u>9</u>	<u>10</u>	<u>11</u>	<u>12</u>	<u>13</u>
Na ₂ O	3.26	3.42	3.30	3.13	3.45	3.28
CaO	5.45	5.04	5.17	5.46	4.37	5.28
SrO	2.45	2.46	2.36	2.39	0.93	2.42
BaO	40.29	39.51	39.69	40.56	41.82	40.01
Y ₂ O ₃	6.66	6.56	6.59	6.63	6.10	6.61
La ₂ O ₃	0.19	0.25	0.32	0.25	0.05	0.25
Ce ₂ O ₃	0.66	0.74	0.78	0.63	-	0.70
Nd ₂ O ₃	1.98	1.37	1.70	1.93	0.33	1.74
Sm ₂ O ₃	0.79	0.67	0.67	0.77	0.15	0.72
ThO ₂	0.69	0.58	0.62	0.75	1.40	0.66
UO ₂	-	-	0.05	-	4.72	0.01
CO ₂	(29.68)	(29.68)	(29.80)	(29.24)	(28.44)	(31.61)
H ₂ O	(6.07)	(6.07)	(6.09)	(5.98)	(5.82)	(6.46)
SUM	98.17	96.35	97.14	97.72	97.58	99.75

NOTE: () = determined by stoichiometry, i.e. 6CO₂ and 3H₂O.

- 8. MSH, spot 1, MK5 probe
- 9. " , spot 2, " "
- 10. " , spot 3, " "
- 11. " , spot 4, " "
- 12. GRF avg. with MK5 probe
- 13. MSH avg. with MK5 probe

TABLE 8. ELECTRON MICROPROBE ANALYSES OF MCKELVEYITE (wt. %)

OXIDE	1	2	3	4	5	6	7
Na ₂ O	3.90	3.30	3.68	3.29	3.14	3.21	3.33
K ₂ O	0.1	-	-	-	-	-	-
CaO	4.0	6.17	5.84	6.33	5.63	5.72	5.88
Fe ₂ O ₃	-	-	-	-	-	-	-
SrO	1.7	8.41	13.98	10.11	5.65	6.30	9.01
BaO	40.6	33.92	23.88	31.40	36.85	36.18	32.08
Y ₂ O ₃	7.7	7.37	10.55	9.12	8.86	8.76	9.32
La ₂ O ₃	0.09	-	0.85	0.05	0.04	0.07	0.25
Ce ₂ O ₃	0.16	-	0.71	-	-	-	0.18
Pr ₂ O ₃	0.05	-	-	-	-	-	-
Nd ₂ O ₃	0.26	-	-	-	-	-	-
Sm ₂ O ₃	0.34	-	-	-	-	-	-
Eu ₂ O ₃	0.19	-	-	-	-	-	-
Gd ₂ O ₃	1.18	-	-	-	-	-	-
Tb ₂ O ₃	0.38	-	-	-	-	-	-
Dy ₂ O ₃	1.00	-	-	-	-	-	-
Ho ₂ O ₃	0.28	-	-	-	-	-	-
Er ₂ O ₃	0.95	-	-	-	-	-	-
Tm ₂ O ₃	0.12	-	-	-	-	-	-
Yb ₂ O ₃	0.61	-	-	-	-	-	-
Lu ₂ O ₃	0.08	-	-	-	-	-	-
ThO ₂	0.1	-	1.23	0.28	0.19	-	0.57
UO ₂	4.6	-	-	-	-	-	-
CO ₂	(25.70)	(30.92)	(32.29)	(31.63)	(30.62)	(30.75)	(31.38)
H ₂ O	(6.10)	(6.32)	(6.60)	(6.47)	(6.26)	(6.29)	(6.42)
SUM	100.2	96.41	99.61	98.68	97.24	97.28	98.42

NOTE: () = determined by stoichiometry, i.e. 6CO₂ and 3H₂O molecules.

1. GRF, data from Milton et al. (1965)
2. MSH, Jeol Superprobe
3. MSH, spot 1, MK5 probe
4. " , spot 3, "
5. " , spot 4, "
6. " , spot 5, "
7. " , average of MK5 results

translucent mckelveyite crystals from the GRF were analyzed. All specimens were verified by Gandolfi X-ray diffraction prior to data collection. A defocussed 30 μm beam was employed in the study. The mckelveyite crystals from the GRF gave consistently low oxide totals, presumably owing to the high concentration (40-50%) of hydrocarbon inclusions. Therefore, they had to be eliminated from the final analyses. L_{β} lines were used to analyze Ce and Nd because of the overlap of $BaL_{\beta 1}$ on CeL_{α} and CeL_{β} on NdL_{α} . Sm and La were analyzed using the $L_{\alpha 1}$ lines despite the overlap of the $CeL_{\beta 2}$ line, as the Ce contents of most specimens fell below the detection limit. Counting times varied from 4-5 seconds for Ca, Ba, Sr and Na on each spot, to 20 seconds for Y, the rare-earths, U and Th. Raw X-ray data were processed using a modified version of the ZAF correction procedure of EMPADR VII (Rucklidge and Gasparinni, 1969). Error on the resulting weight per cent values is estimated at the 2σ level to be: BaO(.35 wt. %), Ca(0.9 wt. %), Na₂O(0.5 wt. %), Y₂O₃(.06 wt. %), SrO(0.3 wt. %), UO₂, ThO₂ and REE₂O₃(0.2 wt. %).

The results of the present analyses of ewaldite are compared with the original chemical data given by Donnay and Donnay (1971) in Tables 7a and 7b. Similarly, the present analyses for mckelveyite are given with that obtained from the GRF type material (Milton et al., 1965) in Table 8. For both minerals, the following elements were looked for but not detected: Al, K, Fe, Zr, Eu, Gd, Dy, Ho, Er, Yb, Lu and F. The number of cations calculated on the basis of six oxygens for both ewaldite and mckelveyite are presented in Tables 9a, 9b and 10 respectively. The total weight percentages for both ewaldite and mckelveyite are slightly short of 100%, which may be attributed to the decomposition of the minerals under the electron beam.

In this study, the electron microprobe analyses of ewaldite from both localities

TABLE 9a. CHEMICAL FORMULA OF EWALDITE PER 6 OXYGEN ATOMS

FORMULA DESIGNATION	CATION	1	2	3	4	5	6	7
A	Ba	2.97	3.00	3.00	3.00	2.97	3.00	2.81
	Sr	0.14	-	-	-	0.03	0.01	0.19
Σ A		<u>3.11</u>	<u>3.00</u>	<u>3.00</u>	<u>3.00</u>	<u>3.00</u>	<u>3.01</u>	<u>3.00</u>
B	Na	0.99	1.00	1.16	1.13	1.00	1.11	1.12
		<u>0.99</u>	<u>1.00</u>	<u>1.16</u>	<u>1.13</u>	<u>1.00</u>	<u>1.11</u>	<u>1.12</u>
Σ B								
C	Na	-	0.16	0.09	0.06	0.28	0.10	-
	Ca	1.00	0.83	0.91	0.94	0.72	0.90	1.04
Σ C		<u>1.00</u>	<u>0.99</u>	<u>1.00</u>	<u>1.00</u>	<u>1.00</u>	<u>1.00</u>	<u>1.04</u>
D	Ba	-	-	0.01	0.05	-	-	-
	Sr	0.12	0.10	0.09	0.08	0.07	0.11	0.06
	Ca	0.11	-	-	-	-	-	-
	Y	0.58	0.61	0.62	0.62	0.50	0.62	0.63
	La	-	-	-	-	-	0.01	0.01
	Ce	-	-	-	-	-	-	0.04
	Nd	0.08	0.03	0.01	0.01	0.03	-	0.13
	Sm	0.08	-	0.01	0.01	0.01	0.01	0.05
	Th	0.03	0.04	0.07	0.07	0.05	0.06	0.03
	U	-	0.21	0.13	0.11	0.32	0.19	-
Σ D		<u>1.00</u>	<u>0.99</u>	<u>0.94</u>	<u>0.95</u>	<u>0.98</u>	<u>1.00</u>	<u>0.99</u>

1. MSH, JEOL Superprobe
2. GRF, MK5 probe, spot 1
3. " , " , spot 2
4. " , " , spot 3
5. " , " , spot 4
6. " , " , spot 5
7. MSH, MK5 probe, spot 1

TABLE 9b. CHEMICAL FORMULA OF EWALDITE PER 6 OXYGEN ATOMS

<u>FORMULA DESIGNATION</u>	<u>CATION</u>	<u>8</u>	<u>9</u>	<u>10</u>	<u>11</u>	<u>12</u>
A	Ba	2.84	2.83	2.86	3.04	2.82
	Sr	0.16	0.17	0.22	-	0.18
ΣA		<u>3.00</u>	<u>3.00</u>	<u>3.08</u>	<u>3.04</u>	<u>3.00</u>
B	Na	1.22	1.16	1.09	1.11	1.14
ΣB		<u>1.22</u>	<u>1.16</u>	<u>1.09</u>	<u>1.11</u>	<u>1.14</u>
C	Na	-	-	-	0.13	-
	Ca	0.99	1.00	1.00	0.87	1.00
ΣC		<u>0.99</u>	<u>1.00</u>	<u>1.00</u>	<u>1.00</u>	<u>1.00</u>
D	Ba	-	-	-	0.01	-
	Sr	0.10	0.08	0.05	0.10	0.07
	Ca	-	0.01	0.05	-	0.02
	Y	0.65	0.64	0.63	0.60	0.63
	La	0.02	-	0.02	-	-
	Ce	0.05	0.05	0.04	-	0.04
	Nd	0.09	0.11	0.12	0.02	0.11
	Sm	0.04	0.04	0.05	0.01	0.04
	Th	0.02	0.02	0.06	0.06	0.05
	U	-	-	-	0.20	-
ΣD		<u>0.97</u>	<u>0.95</u>	<u>1.00</u>	<u>1.00</u>	<u>0.96</u>

8. MSH, MK5 probe, spot 2

9. " , " , spot 3

10. " , " , spot 4

11. GRF average with MK5 probe

12. MSH average with MK5 probe

TABLE 10. CHEMICAL FORMULA OF MCKELVEYITE PER 6 OXYGENS

FORMULA DESIGNATION	CATION	1	2	3	4	5	6	7
A	Ba	2.65	2.33	1.50	2.07	2.55	2.49	3.14
	Sr	0.16	0.74	1.30	0.96	0.48	0.55	0.86
	Ca	-	-	0.05	-	-	-	-
	Y	-	-	0.08	-	-	-	-
ΣA		<u>2.81</u>	<u>3.07</u>	<u>2.93</u>	<u>3.03</u>	<u>3.03</u>	<u>3.04</u>	<u>3.00</u>
B	Na	1.26	1.12	1.14	1.08	1.08	1.09	1.10
	K	0.02	-	-	-	-	-	-
ΣB		<u>1.28</u>	<u>1.12</u>	<u>1.14</u>	<u>1.08</u>	<u>1.08</u>	<u>1.09</u>	<u>1.10</u>
C	Ca	0.73	1.00	1.00	1.00	1.00	1.00	1.00
	U	0.15	-	-	-	-	-	-
ΣC		<u>0.88</u>	<u>1.00</u>	<u>1.00</u>	<u>1.00</u>	<u>1.00</u>	<u>1.00</u>	<u>1.00</u>
D	Sr	0.11	0.11	-	0.03	0.10	0.09	0.03
	Ca	-	0.16	-	0.14	0.06	0.08	0.07
	Y	0.68	0.69	0.82	0.82	0.83	0.82	0.84
	La	0.15*	-	0.05	-	-	0.01	0.02
	Ce	-	0.04	0.04	-	-	-	0.01
	Th	-	0.04	0.09	0.01	0.01	-	0.02
ΣD		<u>1.00</u>	<u>1.00</u>	<u>1.00</u>	<u>1.00</u>	<u>1.00</u>	<u>1.00</u>	<u>0.99</u>

* La represents the total rare earth element sum.

1. Results from Milton et al. (1965) for GRF mckelveyite.
2. MSH, JEOL Superprobe
3. " , MK5 probe, spot 1
4. " , " , spot 3
5. " , " , spot 4
6. " , " , spot 5
7. Average of MSH results on MK5 probe

are reasonably consistent, with deviations from the mean being less than 2% for the major elements. Differences are noted when these are compared with the original analysis given by Donnay and Donnay (1971). The sodium content indicated by these authors is almost double that obtained from this study. Donnay and Donnay (1971) pointed out that the material used for the chemical analyses was recovered from the waste of a soda-manufacturing process and on this basis, they have significantly reduced the analytical value of sodium to accommodate their proposed formula. Even so, the Na_2O content for ewaldite quoted by Donnay and Donnay (1971) is still considerably higher than values obtained in this study (Tables 7a,7b). Donnay and Donnay (1971) reported 2.0% Fe_2O_3 in their analyses, whereas Fe was not found in the EDS spectra in this study. The Fe content observed by Donnay and Donnay could be due to the contamination of hematite inclusions reported by these authors. Electron microprobe analyses of ewaldite from the GRF and MSH show very minor concentrations of rare-earth elements, although Donnay and Donnay (1971) stated that a spectrographic analysis indicated the presence of all the Ce-earths except for Ce and Pr. Only Ce, La, Nd and Sm were detected in this study. Y_2O_3 is a major constituent of ewaldite from both localities, and the Y_2O_3 weight percentages appear reasonably constant in the analyses determined in this study. Therefore, it is probably essential to ewaldite.

The electron microprobe analyses and calculated cationic contents show a marked similarity between ewaldite and mckelveyite, strongly suggesting that these two minerals are polymorphs. The possibility of such a relationship was first pointed out by Donnay and Donnay (1971), who stated that the two minerals could be dimorphous, except for water contents. It should be noted however, that the

presence of water in ewaldite has been verified in this study by infrared spectroscopy.

Considering the possibility of these two minerals being polymorphs, it was found that both minerals could be accommodated quite well in the formula, $\text{Ba}_3\text{NaCaY}(\text{CO}_3)_6 \cdot 3\text{H}_2\text{O}$, recently proposed for mckelveyite (Chao et al., 1978). The empirical formulas obtained from analyses in this study are:

$(\text{Ba}_{2.14} \text{Sr}_{.86})_{\Sigma=3.00} \text{Na}_{1.10} \text{Ca} (\text{Y}_{.84} \text{Ca}_{.07} \text{Sr}_{.03} \text{La}_{.02} \text{Th}_{.02} \text{Ce}_{.01})_{\Sigma=.96} (\text{CO}_3)_6 \cdot 3\text{H}_2\text{O}$,
for mckelveyite and,

$(\text{Ba}_{2.92} \text{Sr}_{.17})_{\Sigma=3.09} \text{Na}_{1.18} \text{Ca}_{.93} (\text{Y}_{.61} \text{U}_{.11} \text{Nd}_{.06} \text{Th}_{.04} \text{Sm}_{.03} \text{Ce}_{.02} \text{La}_{.01})_{\Sigma=.88} (\text{CO}_3)_6 \cdot 3\text{H}_2\text{O}$
for ewaldite, both of which are close to the ideal formula $\text{Ba}_3\text{NaCaY}(\text{CO}_3)_6 \cdot 3\text{H}_2\text{O}$.

A comparison of the electron microprobe results for ewaldite from the GRF and MSH indicate that the Ba-site in MSH ewaldite has a greater Ba:Sr ratio than in its GRF counterpart. The only other noteworthy difference is in the site assigned to Y. Although the site is predominantly occupied by Y in ewaldite from both localities, the unfilled portion of this site is predominantly assigned to U in GRF ewaldite and rare earth elements in MSH ewaldite.

THE REFINEMENT OF THE CRYSTAL STRUCTURE OF EWALDITE

In their attempt to solve the structure of ewaldite, Donnay and Preston (1971) employed a three-dimensional Patterson synthesis with which they were able to determine the atomic coordinates for the Ba and Ca atoms, and one of the two carbonate groups. Although two carbonate groups were suggested by infrared spectroscopy, the second carbonate group failed to show up. A subsequent difference-electron density map showed possible positions for the second carbonate

atom. However, least squares refinement produced unacceptably high temperature factors for the carbon atom when it was placed in any of these possible special positions. It was noted that oxygen-oxygen distances in the plane $z = 0.665$ seemed quite reasonable (2.1 - 2.3 Å). As such, an attempt was made to move the second carbon atom to a general position instead, but this produced large standard deviations (0.25 Å) on the oxygen atoms presumably bonded to this atom. Although the location of the second carbonate group could not be pin-pointed, the authors felt confident that it must lie in the plane $z = 0.665$, owing to the reasonable oxygen-oxygen distances. Donnay and Preston (1971) go on to explain that the apparent absence of this second group might possibly be due to a low occupancy factor. The final R-value given by the authors for their proposed structure was 6.5%.

The attempt by Donnay and Preston (1971) failed to solve the structure of ewaldite. Its chemistry is highly suspect owing to contamination of the type material by Na and other included phases (Donnay and Donnay, 1971) and its CO_2 and H_2O contents were not determined. Mckelveyite, which has been documented to be genetically and structurally related to ewaldite (Donnay and Donnay, 1971), has recently been found to be triclinic, pseudo-trigonal and a new formula, $\text{Ba}_3\text{NaCaY}(\text{CO}_3)_6 \cdot 3\text{H}_2\text{O}$, has been proposed for it (Chao et al., 1978). As such, it was decided to try and determine the structure of ewaldite, in the hopes that it would resolve: 1. the true symmetry of ewaldite, 2. its actual chemical formula and 3. its structural relationship with mckelveyite.

One crystal of type I ewaldite from MSH was selected for data collection. It was verified by X-ray Gandolfi diffraction, and the obtained pattern was found to be contamination-free. In addition, the crystal was analyzed in cross-polars and a

strong, sharp extinction was observed parallel to the direction of elongation. The crystal was then spherized, to minimize any X-ray absorption effects during intensity collection.

The crystal, ground to a 0.18 mm sphere, was mounted on an ENRAF-NONIUS CAD-4 single crystal diffractometer. The operating conditions were 50 kV and 20 mA, employing graphite-crystal monochromatized $\text{MoK}\alpha$ radiation ($\lambda = .7107$ Å). All intensities in one octant of the sphere of reflection out to $2\theta = 70^\circ$ were collected. A $\theta/2\theta$ scan was used, with a scan rate of $1^\circ/\text{min}$ and a base-peak width of 1.6° . Background counts of 20 seconds were made on either side of each peak. Three strong reflections were chosen as standards to monitor crystal alignment and instrument stability, and these were measured every three hours. Data were collected in point group 6/mmm, in accordance with the previously determined space group for ewaldite of $\text{P6}_3\text{mc}$ (Donnay and Donnay, 1971).

The collected data were then averaged and reduced to structural amplitudes using the Crystal Structure Reduction programs of Gabe et al. (1985). Lorentz, polarization and absorption ($\mu = 83.10 \text{ cm}^{-1}$) corrections were applied. The absorption coefficient was calculated based on the formula presented by Donnay and Donnay (1971). Variation in intensity of standard reflections (relative to mean values) was found to be less than 2% over the entire collection period, indicating the absence of any systematic variation in the intensity data. In the volume of the given sphere of reflection, there were 580 reflections collected, 549 of which were considered observed ($I \geq 2.5\sigma$).

The structure amplitudes were then analyzed using the Shelex-76 program (Sheldrick, 1976) available in the Crysruler set of programs (Rizzoli et al., 1986). Least-squares refinement (available in the Shelex-76 program) was performed on the

structure proposed by Donnay and Preston (1971), using the newly collected data. This gave $R = 9.4\%$ and confirms the atomic coordinates given by Donnay and Preston (1971) for Ba, Ca, C(1) and O(1). In order to be consistent with the formula proposed for the mineral in this study, a complete solution to the structure of ewaldite requires as a minimum, locating another carbonate group, a Na atom and a water molecule, in addition to those atoms already defined.

A difference Fourier map was generated after the least-squares refinement of the atoms given by Donnay and Preston (1971). Only three peaks worthy of attention were noted on the map. Least-squares refinement was performed assuming all the peaks to be oxygen atoms, and this reduced R to 3.6%. The final atomic parameters and bond lengths are presented in Tables 11 and 12 respectively.

Despite the low R -value, the newly located X atoms all have low site occupancy factors (Table 11), corresponding to three electrons for X(2), two electrons for X(3) and one electron for X(4). In addition, some of the bond lengths involving these X atoms are quite unreasonable (Table 12), and no sensible interpretation of them is possible. These are therefore considered to be spurious peaks.

In summary, this attempt at solving the structure has been unsuccessful. Although it did verify the atoms and their atomic coordinates given by Donnay and Preston (1971), the locations of the missing carbonate group, water molecule and Na atom were not found.

TABLE 11. FINAL ATOMIC POSITIONS AND THERMAL PARAMETERS* FOR
EWALDITE (standard deviations in parentheses)

Atom	X/A	Y/B	Z/C	S.O.F	U ₁₁	U ₂₂	U ₃₃	U ₁₂
Ba	1/3	2/3	0	1/6	0.0138(4)	0.0138(4)	0.0218(5)	0.0069(2)
Ca	1/3	2/3	0.3044(3)	0.06(1)	0.01(1)	0.01(1)	0.02(2)	0.01(1)
Y	1/3	2/3	0.3044(3)	0.11(1)	0.025(4)	0.025(4)	0.021(5)	0.012(2)
C(1)	0	0	0.428(1)	0.20(2)	0.020(6)	0.020(6)	0.026(8)	0.010(1)
O(1)	0.141(1)	0.281(2)	0.431(1)	0.61(3)	0.019(2)	0.019(2)	0.050(1)	0.009(1)
X(2)	0.071(5)	0.304(6)	0.174(2)	0.38(4)	0.033(8)	0.033(8)	0.01(1)	0.016(4)
X(3)	0.55(1)	0.062(9)	0.172(2)	0.28(5)	0.05(1)	0.05(1)	0.04(1)	0.026(8)
X(4)	0.26(2)	0.47(1)	0.709(2)	0.17(2)	0.04(2)	0.04(2)	0.02(2)	0.02(2)

*Anisotropic thermal parameters refer to the expression:

$$\bar{T} = \exp -2\pi^2 (U_{11}h^2a^2 + \dots + U_{12}hka^*b^* + \dots)$$

Note: S.O.F. = Site Occupancy Factor

TABLE 12. AVERAGE BOND DISTANCES AND BOND ANGLES FOR EWALDITE
(standard deviations in parentheses)

DONNAY AND PRESTON (1971)
 (GRF ewaldite)

Ba polyhedron
 distances(Å)

Ba - O(1) 2.82(2)
 bond angles(°)
 45.4(4)
 66.8(4)

Ca polyhedron
 distances(Å)

Ca - O(1) 2.36(2)

Carbonate group
 distances(Å)

C(1) - O(1) 1.26(3)
 O(1) - O(1) 2.25-2.97
 bond angles(°)
 O(1) - C(1) - O(1) 119.7(3)

THIS STUDY
 (MSH ewaldite)

Ba polyhedron
 distances(Å)

Ba - O(1) 2.79(1)
 bond angles(°)
 52.7(2)
 8.4(3)

Ca polyhedron
 distances(Å)

Ca - O(1) 2.38(1)

Carbonate group
 distances(Å)

C(1) - O(1) 1.28(1)
 O(1) - O(1) 2.22(1)
 bond angles(°)
 O(1) - C(1) - O(1) 119.1(1)

X(2)
 distances(Å)

X(2) - Ba 2.79(2)
 X(2) - Ca 2.38(2)
 X(2) - O(1) 2.61(2)

X(3)
 distances(Å)

X(3) - Ba 2.84(3)
 X(3) - Ca 2.47(3)
 X(3) - O(1) 1.58(2)

X(4)
 distances(Å)

X(4) - Ba 3.69(2)
 X(4) - Ca 3.10(2)
 X(4) - O(1) 3.52(2)

RELATED MINERALS

Ewaldite, which is here redefined as $\text{Ba}_3\text{NaCaY}(\text{CO}_3)_6 \cdot 3\text{H}_2\text{O}$, is chemically similar to weloganite, donnayite and mckelveyite (Table 13). A comparison of the geometry of the structural cells of these minerals with those of ewaldite, indicates they all have the same a -axes, with different, but rationally related, c -axes (Table 13). In addition, they all share a strong morphological resemblance, which is highlighted by their apparent trigonal or hexagonal symmetry (Table 13), oscillatory or layer-like growth, and occurrence in hemimorphic sub- to euhedral crystals, which are commonly terminated by a pedion. Optically, they possess a weak biaxial character ($2V$ commonly $< 10^\circ$), and a small deviation of the acute bisectrix from the normal to the basal cleavage.

From the close chemical relationship illustrated in Table 13, these minerals may be considered members of one group, with the general formula $\text{A}_3\text{BCD}(\text{CO}_3)_6 \cdot 3\text{H}_2\text{O}$, where $\text{A} = \text{Ba}, \text{Sr}$, or REE, $\text{B} = \text{Na}$, $\text{C} = \text{Na}$ or Ca and $\text{D} = \text{Zr}, \text{Y}$, or REE, with the sum of the cationic charges for the C and D sites totalling five. Rare-earths in the A and D sites is supported by analyses of a donnayite-like mineral from MSH which contains 16.83 wt. % total rare earth oxides, in addition to 8.02 wt. % of Y_2O_3 (Chao, pers. comm.).

X-ray diffraction data suggests that this chemical group may be divided into two structural subgroups: the weloganite subgroup and the ewaldite subgroup. The weloganite subgroup consists of weloganite, mckelveyite and donnayite, which are isomorphous as demonstrated by Chao et al. (1978). These minerals are characterized by a triclinic, pseudo-trigonal cell (Table 13). The ewaldite subgroup consists of ewaldite and the mineral UK37a, whose true symmetry is uncertain.

TABLE 13. CELL PARAMETERS OF EWALDITE AND RELATED MINERALS

	<u>WELOGANITE</u>		<u>DONNAYITE</u>		<u>MCKELVEYITE</u>		<u>EWALDITE</u>
	$\text{Sr}_3\text{Na}_2\text{Zr}(\text{CO}_3)_6 \cdot 3\text{H}_2\text{O}$		$\text{Sr}_3\text{NaCaY}(\text{CO}_3)_6 \cdot 3\text{H}_2\text{O}$		$\text{Ba}_3\text{NaCaY}(\text{CO}_3)_6 \cdot 3\text{H}_2\text{O}$		$\text{Ba}_3\text{NaCaY}(\text{CO}_3)_6 \cdot 3\text{H}_2\text{O}$
	<u>TRUE CELL</u> (Grice + Perrault, al., 1968) 1975)		<u>TRUE CELL</u> (Chao et al., 1978) comm.)		<u>TRUE CELL</u> (Chao et al., 1978) al., 1965)		<u>ADOPTED CELL</u> (MSH; This study)
	<u>TWINNED CELL</u> (Sabina et al., 1968)		<u>TWINNED CELL</u> (Chao et al., 1978) comm.)		<u>TWINNED CELL</u> (Milton et al., 1965)		<u>ADOPTED CELL</u> (GRF; Donnay & Donnay, 1971)
SYMMETRY	P1	P3 _{1,2}	P1	P $\bar{3}$	P1	P $\bar{3}$	P6 ₃ mc
a (Å)	8.966(1)	8.96	9.000(1)	9.000	9.170(3)	9.174(2)	5.284(1) or 9.152(1)
b	8.980(2)		8.999(1)		9.169(3)		
c	6.730(1)	18.06	6.793(1)	18.605	7.075(2)	19.154(7)	12.78(1)
$\alpha(^{\circ})$	102.72(1)		102.77(1)		102.50(3)		
β	116.65(1)		116.28(1)		115.63(3)		
γ	60.06(1)		59.99(1)		59.99(3)		

TABLE 14. CELL PARAMETERS OF THE EWALDITE SUBGROUP

	<u>EWALDITE</u>	<u>UK37a</u>
	Ba ₃ NaCaY(CO ₃) ₆ ·3H ₂ O	Sr ₃ NaCaY(CO ₃) ₆ ·3H ₂ O
	<u>ADOPTED CELL</u>	<u>ADOPTED CELL</u>
	(MSH; This Study)	(Chao, pers. comm.)
SYMMETRY	P6 ₃ mc	P6 ₃ mc
<u>a</u> (Å)	5.284(1) or 9.152(1)	5.193(1) or 8.994(1)
<u>c</u>	12.78(1)	12.25(1)

Figure 5. The structure of weloganite projected down c^* : elevations of each atom above the base (001) in fractional coordinates $\times 100$ (after Grice and Perrault, 1975).

UK37a, an unnamed mineral from MSH, is believed to be isomorphous with ewaldite, based on X-ray single-crystal and Gandolfi diffraction work (Chao, pers. comm.; Table 14). Preliminary probe analyses indicate the mineral to have a much greater Sr content than Ba content, suggesting that UK37a is the Sr-analogue of ewaldite (Chao, pers. comm.). Since ewaldite is dimorphous with mckelveyite, then by analogy, UK37a is dimorphous with donnayite.

Despite the fact that the true symmetry of the ewaldite is uncertain, its structure must be closely related to that of the weloganite (Figure 5), owing to the similarity in their 0-level $\underline{c}$ -axis precession photographs (as shown in Plates 5 and 6). These photographs show they possess very similar subcells, but different supercells. Grice and Perrault (1975) note that by taking three consecutive triclinic cells along the c' direction, an apparently trigonal cell may be obtained for weloganite. Table 13 shows that the $\underline{c}$ -axis of the ewaldite subgroup is two-thirds that of the $\underline{c}$ -axis of the trigonal cell of weloganite. Thus suggestion the structural differences between the two subgroups may be a result of stacking.

The extra reflections observed on 0-level $\underline{c}$ -axis precession photographs of ewaldite, are also found on the same 0-level photographs of twinned members of the weloganite subgroup. However, they are absent on those photographs of untwinned members. This suggests that these reflections may be the product of twinning, although their true origin is still not known.

Plate 5. 0-level c-axis precession photograph of MSH ewaldite.

Plate 6. 0-level c-axis precession photograph of weloganite from the Francon Quarry, Montreal, Quebec.

UK62, A NEW SODIUM CALCIUM FLUOROCARBONATE FROM MONT ST.-HILAIRE, QUEBEC

INTRODUCTION

A sodium calcium fluorocarbonate was found in the fall of 1988 within a sodalite xenolith, 0.5 m in diameter, at the Poudrette Quarry, Mont St.-Hilaire, Rouville Co., Quebec. As the X-ray Gandolfi diffraction pattern and qualitative EDS analyses indicated the mineral to be a new species, it has been designated UK62.

OCCURRENCE AND ASSOCIATIONS

UK62 is moderately abundant in this sodalite xenolith, occurring most commonly as irregular crystalline masses up to 3 mm, and rarely as well-formed crystals up to 1 mm within cavities. The xenolith consists predominantly of sodalite with <5% villiaumite (NaF) and aegirine. It was found in situ heavily encrusted with a white effervescence, presumably thermonatrite, $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$. Associated minerals are listed in Table 15. UK62 resembles cancrinite and serandite, both of which also occur in clear, colorless euhedral crystals in open vugs.

Free-growing crystals of UK62 are often associated with villiaumite. It is also infrequently found as <0.5 mm crystals within the villiaumite. This suggests crystallization of the mineral prior to villiaumite. Kupletskite, $\text{K}_3\text{Mn}_7\text{Ti}_2\text{Si}_8\text{O}_{24}(\text{O},\text{OH})_{12}$, commonly occurs as bladed inclusions within UK62. Another unusual association is pyrophanite, MnTiO_3 , which develops as blood-red hexagonal plates.

TABLE 15. MINERALS ASSOCIATED WITH UK62

aegirine	kupletskite	thermonatrite
analcime	lorenzenite	villiaumite
burbankite	microcline	vinogradovite
cancrinite	molybdenite(2H)	vitusite
catapleiite	natrolite	vuommenite
clinoamphibole	pectolite	UK66
cryolite	pyrophanite	a metamict
eudialyte	serandite	mineral
fluorite	shortite	
galena	sphalerite	
kogarkoite	sodalite	

CRYSTALLOGRAPHY

Although not abundant, euhedral crystals of UK62 have been found. They are prismatic, elongate along c and commonly less than 1 mm in length. The crystals are observed to occur in two distinct varieties: type 1, bounded by the forms $b\{010\}$, $m\{110\}$, $a\{100\}$, $d\{101\}$, $w'\{023\}$ and $w'\{0\bar{3}2\}$ (Plate 7) and type 2, bounded by the forms $b\{010\}$, $m\{110\}$, $a\{100\}$ and $c\{001\}$ (Plate 8). Most of the euhedral crystals found thus far possess the type 1 morphology.

Prior to X-ray precession investigation, all potential study material was verified with a 114.6 mm Gandolfi camera using Ni-filtered $\text{CuK}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). Suitable crystals were then mounted on a goniometer head and studied on a spindle stage for quality of extinction and included material.

Precession photographs were taken about the a (0-2 levels), b (0-3 levels) and c (0-2 levels) axes using Zr-filtered $\text{MoK}\alpha$ radiation ($\lambda = .7107 \text{ \AA}$) and indicate that UK62 is monoclinic. The systematic extinctions $h + k \neq 2n$ for reflections $hk\ell$ and $h0\ell$, $\ell \neq 2n$ for $h0\ell$ reflections, are consistent with space groups Cc (#9) and $C2/c$ (#15) or $C2$, although $C2$ is eliminated based on morphological considerations. The cell parameters obtained from single-crystal photographs were refined by the least-squares program CELREF (Appleman and Evans, 1973) using X-ray Gandolfi diffraction data. The refined values are: $a = 8.043(4) \text{ \AA}$, $b = 15.812(5) \text{ \AA}$, $c = 7.030(3) \text{ \AA}$, $\beta = 101.16(3)^\circ$ which give $V = 877.1(4) \text{ \AA}^3$. The Gandolfi diffraction pattern (Table 16) was indexed using the intensity of reflections on the precession photographs as a guide. Both type 1 and 2 crystals have identical Gandolfi diffraction and single-crystal precession photographs.

Plate 7. A typical type 1 UK62 crystal showing development of the forms $b\{010\}$, $m\{110\}$, $a\{100\}$, $d\{10\bar{1}\}$, $w'\{023\}$ and $w\{0\bar{3}2\}$.

Plate 8. A typical type 2 UK62 crystal showing development of the forms $b\{010\}$, $m\{110\}$, $a\{100\}$ and $c\{001\}$.

TABLE 16. GANDOLFI X-RAY DIFFRACTION DATA FOR UK62

<u>hkl</u>	<u>dcalcÅ</u>	<u>dobsÅ</u>	<u>I</u>
110	7.060	7.081	7
11 $\bar{1}$	5.425	5.433	4
021	5.197	5.194	4
111	4.555	4.538	2
130	4.383	4.387	<1
040	3.953	3.952	1
131	3.531	3.524	2
220	3.530		
$\bar{1}$ 12	3.334	3.326	1
150	2.935	2.937	5
20 $\bar{2}$	2.888	2.895	10
240	2.792	2.791	5
22 $\bar{2}$	2.713	2.711	8
060	2.635	2.637	6
132	2.579	2.580	5
202	2.378	2.377	2
15 $\bar{2}$	2.319	2.321	3
222	2.278	2.277	2
260	2.191	2.241	<1
170	2.172	2.169	3
331	2.118	2.118	<1
062	2.094	2.096	3.5
242	2.038	2.039	6
$\bar{2}$ 62	1.947	1.946	1
312	1.906	1.906	2
35 $\bar{2}$	1.870	1.869	6
$\bar{4}$ 22	1.825	1.825	2
332	1.804	1.805	3
280	1.767	1.767	5
$\bar{1}$ 14	1.746	1.746	5
190	1.715	1.716	4
082	1.715		
460	1.579	1.580	1
24 $\bar{4}$	1.566	1.566	1
$\bar{4}$ 04	1.444	1.444	1

Plus additional lines

Visual intensities, 114.6 mm Gandolfi camera,
Ni-filtered CuK α radiation ($\lambda = 1.5418$ Å).

The morphology of the type 1 crystals is interesting in that the morphological symmetry is not consistent with the space groups Cc or C2/c derived from X-ray precession work. This morphological inconsistency is reflected in the termination faces which do not appear to be symmetrically related. For discussion purposes, the larger termination face will be referred to as Y and the smaller one as Z. One type 1 crystal, approximately 0.04 mm in length was selected for optical goniometric analyses. The crystal was mounted to rotate about the zone axis of the termination faces and the large prismatic faces (verified by X-ray goniometry to be {010}). Although the signals from the faces were weak, the interfacial angles for the Y and Z faces and {010} were found to be: $(010) \wedge Y = 58(2)^\circ$ and $(010) \wedge Z = 70(2)^\circ$, verifying that these faces are not symmetrically equivalent. From precession photographs, these measured angles correspond closely to $(010) \wedge (0\bar{3}2)$ (measured angle = 57°) and $(010) \wedge (023)$ (measured angle = 71°). Calculated values for the angles are $(010) \wedge (0\bar{3}2) = 56^\circ$ and $(010) \wedge (023) = 71^\circ$. This suggests that faces Y and Z are indexable as $(0\bar{3}2)$ and (023) respectively. Thus far, 2 of the type 1 crystals have been observed to possess these non-symmetrically equivalent faces and the angular relationship of these faces does not appear to vary. It is unclear whether this morphological enigma may be attributed to the presence of twinning or to multiple crystals.

PHYSICAL PROPERTIES

Pure UK62 is pale tan to colourless, but often appears reddish-brown due to kupletskite inclusions. The mineral possesses a white streak and a vitreous to slightly waxy lustre. A good {001} and imperfect {010} cleavage are observed. It displays an uneven fracture and is quite brittle. Inclusion-free UK62 is transparent,

but it becomes slightly translucent as the amount of included material increases. It has a hardness of about 3 on Moh's hardness scale and does not fluoresce in short-wave or long-wave radiation. A strong effervescence is noted when UK62 is placed in 1:1 HCl at room temperature. The mineral is not soluble in water.

The measured density was determined by weighing a heavy liquid in a 25 mL pycnometer of known weight. All mass measurements were made at room temperature using a Mettler H2O balance. A cleavage fragment of dimensions 1 x 0.5 x 0.25 mm and previously verified by X-ray diffraction, was placed in a 40 mL beaker with approximately 10 mL of bromoform. The bromoform was diluted with methyl alcohol until the grain remained in suspension. The measured density was found to be 2.67 (2) g/cm³, quite close to the value of 2.68 g/cm³ calculated from the empirical formula and refined cell dimensions.

An optical investigation of UK62 was carried out at room temperature using a spindle stage and a 1 x 1 x 0.3 mm cleavage fragment. The fragment was oriented by X-ray precession method to rotate about the b-axis, which was previously shown to correspond to the optic normal. The pale brown fragment demonstrated both the {001} and {010} cleavages and was not found to be pleochroic. Under crossed-polars, it showed sharp extinctions. The mineral is optically negative and gives a sharp, well-defined biaxial interference figure with a moderately high birefringence. It shows a weak dispersion with $r > v$. Refractive indices, determined using a sodium vapour lamp ($\lambda = 589.3$ nm), Cargille immersion liquids and a Bausch and Lomb Abbe-3L refractometer are: $\alpha = 1.472$ (1), $\beta = 1.561$ (1) and $\gamma = 1.569$ (1). The 2V, measured by direct observation of the optic axes is 25 (1)°, whereas the calculated 2V is 31.9 (1)°. The optical orientation (shown in Figure 6), is b = Y, c $\wedge$ X = 6° in the acute angle of β .

Figure 6. The optical orientation of UK62.

ELECTRON MICROPROBE ANALYSES AND THE CHEMICAL FORMULA OF UK62

UK62 was first qualitatively analyzed using the energy dispersive spectrometry (EDS) system on a Cambridge Microscan (MK) 5 electron microprobe. These results indicated major Na, Ca and F with minor Mn, Fe and Mg. Li was analyzed by the atomic absorption method but not detected. The strong effervescence in 1:1 HCl exhibited by this mineral suggested it to be a carbonate (later confirmed by TGA-EGA). Quantitative analyses for the elements were then carried out using wavelength dispersive spectroscopy (WDS) on the same microprobe. The operating conditions, standards used and other analytical details for the WDS analyses are presented in Table 17. Most samples were analyzed with a defocussed 10 μm beam to minimize the loss of Na and to maximize the X-ray counts. Total X-ray counts for all elements but Na were obtained by averaging several sets of 20-second counts. Na was determined from an average of six 2-second counts, counting times shortened to minimize Na loss. F counts were maximized by using a collecting period of 20 seconds, twice as long as is usually done. Analytical results are presented in Tables 18a and 18b. Sample UK62-2, analyzed with a 40 μm beam to determine if specimen instability was affecting elemental contents, shows only a slightly higher Na₂O content (analyses #5 and #6), indicating that specimen volatilization is not a serious source of error. Errors on the weight per cent values at the 2 σ level are: Na₂O(.21 wt. %), CaO(.23 wt. %), MnO(.18 wt. %), FeO(.12 wt. %), MgO(0.1 wt. %), F(.39 wt. %).

The cation and F content within a unit cell of UK62, obtained using the density-mass-volume relationship from the average of the microprobe analyses, refined cell parameters and measured density is: $4 \times [(\text{Na}_{2.98}\text{Ca}_{1.66}\text{Mn}_{.33}\text{Fe}_{.03})\text{F}]$.

**TABLE 17. CAMBRIDGE MICROSCAN 5 (MK5) ELECTRON MICROPROBE
AND STANDARD DATA**

OPERATING CONDITIONS: 15kV, 75° fixed take-off angle,
25nA beam current (estimated).

<u>ELEMENT</u>	<u>STANDARD</u>	<u>DETECTING CRYSTAL</u>	<u>X-RAY LINE ANALYZED</u>
Na	tugtupite	TAP (2d = 25.7 Å)	Kα
Ca	dolomite	Quartz (2d = 6.687 Å)	Kα
Mn	MnCO ₃	Quartz	Kα
Fe	KAKHB	Quartz	Kα
Mg	KAKHB	Quartz	Kα
F	LiF	TAP	Kα

NOTE: KAKHB = Kakanui hornblende; TAP = Thallium Acid Phthalate

**TABLE 18a. ELECTRON MICROPROBE ANALYSES OF UK62
FROM MONT ST.-HILAIRE, QUEBEC (wt.%)**

<u>OXIDE</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>
Na ₂ O	25.50	25.66	25.38	25.59	26.50
CaO	25.12	26.02	26.80	26.01	26.32
MnO	7.13	6.35	6.59	6.01	6.00
FeO	0.31	0.31	0.28	0.27	0.65
MgO	0.03	0.03	0.02	0.04	-
CO ₂	(36.22)	(36.37)	(37.06)	(36.04)	(37.19)
F	5.39	5.55	5.41	5.60	5.42
Sum	99.70	100.29	101.54	99.56	102.08
O=F	-2.27	-2.34	-2.28	-2.36	-2.28
Corr. Sum	97.43	97.95	99.26	97.20	99.80

NUMBER OF IONS ON THE BASIS OF 3 OXYGENS

Na	3.00	3.00	2.92	3.02	3.04
Ca	1.63	1.68	1.40	1.70	1.66
Mn	0.36	0.32	0.33	0.31	0.30
Fe	0.02	0.02	0.01	0.01	0.03
Sum	2.01	2.02	2.04	2.02	1.99
F	1.03	1.06	1.01	1.08	1.01

NOTE: () = calculated by stoichiometry.

1. UK62-1, spot 1, Mont St.-Hilaire.
2. UK62-1, spot 2, "
3. UK62-1, spot 3, "
4. UK62-1, spot 4, "
5. UK62-2, spot 2, "

**TABLE 18b. ELECTRON MICROPROBE ANALYSE OF UK62
FROM MONT ST.-HILAIRE, QUEBEC (wt.%)**

<u>OXIDE</u>	<u>6</u>	<u>7</u>	<u>2</u>	<u>9</u>	<u>10</u>
Na ₂ O	26.68	25.38	26.06	25.84	26.72
CaO	26.67	28.17	25.65	26.34	32.23
MnO	5.70	6.70	9.56	6.76	-
FeO	0.61	0.65	0.63	0.46	-
MgO	-	-	-	0.02	-
CO ₂	(36.96)	(37.56)	(37.75)	(37.02)	37.94
F	5.38	6.03	6.11	5.61	5.46
Sum	102.00	104.49	105.76	102.25	102.35
O=F	-2.26	-2.54	-2.57	-2.36	-2.30
Corr. Sum	99.74	101.95	103.19	99.89	100.05

NUMBER OF IONS ON THE BASIS OF 3 OXYGENS

Na	3.08	2.88	2.94	2.97	3.00
Ca	1.65	1.75	1.59	1.68	2.00
Mn	0.29	0.33	0.47	0.34	-
Fe	0.03	0.03	0.03	0.02	-
Sum	1.97	2.11	2.09	2.04	2.00
F	1.01	1.12	1.12	1.05	1

NOTE: () = calculated by stoichiometry.

6. UK62-2, spot 3, Mont St.-Hilaire.
7. UK62-3, spot 1, "
8. UK62-3, spot 2, "
9. Average of microprobe results from this study.
10. Calculated components of the ideal formula,
Na,Ca₂(CO₃)₂F

The number of carbonate ions required for charge balance is very close to one, two or three within 1/4 of a cell, suggesting the ideal formula $\text{Na}_3\text{X}_2(\text{CO}_3)_3\text{F}$, where $\text{X} = \Sigma \text{Ca} + \text{Mn} + \text{Fe} + \text{Mg}$. The probe analyses, presented in Tables 18a and 18b, were therefore recalculated on the basis of three oxygens per formula.

INFRARED SPECTRUM

The infrared spectrum of UK62 shown in Figure 7, was obtained from a KBr pellet composed of 3.5 mg of UK62 and 400 mg of KBr (previously kept heated at 140°C). The spectrum was produced on a Perkin-Elmer 1600 series FTIR infrared spectrometer (4 cm^{-1} resolution capability), with the background subtracted prior to data collection. Wavenumber values for bands obtained from the spectrum are listed in Table 19, with the carbonate bands assigned according to the notation of Fujita et al. (1967).

The spectrum is characterized by a major band in the region 1600 - 1250 cm^{-1} , attributable to a carbonate group. There is also a less pronounced band in the region 3600 - 3100 cm^{-1} , possibly due to H_2O or OH^- . As the background atmosphere was subtracted from the spectrum, this band must be due to hydroxyl. The presence of hydroxyl in UK62 is also supported by the fact that UK62 is a F-bearing mineral and that in many F-bearing minerals such as topaz, the humite group etc., hydroxyl is a common substitute for F. The fact that the O-H stretching band is broad and diffuse suggests that short, strong hydrogen bonds are present (White, 1971).

The pronounced ν_5 doublet and weakly split ν_2 band, strongly suggest the presence of at least two non-equivalent carbonate groups in the UK62 structure

Figure 7. The infrared spectrum of UK62.

**TABLE 19. BAND ASSIGNMENTS FOR THE INFRARED SPECTRUM
OF UK62 (in cm⁻¹) ***

3537	O - H stretching
3420	
3027	Hydrogen bonding
2923	phenomena
2855	
1497	ν_s carbonate mode
1457	
1376	ν_1 carbonate mode
1071	ν_2 carbonate mode
867	ν_8 carbonate mode
756	ν_3 carbonate mode
722	ν_6 carbonate mode
699	

*Carbonate bands have been assigned according to the notation of Fujita et al. (1962).

(Adler & Kerr, 1962; Caro et al., 1972; Turcotte et al., 1969). The maximum separations of the $\nu_5 - \nu_1$ (120 cm^{-1}) and $\nu_3 - \nu_6$ (57 cm^{-1}) bands combine to suggest that the carbonate groups in UK62 are all monodentate (Fujita et al., 1968).

THERMOGRAVIMETRIC AND EVOLVED GAS ANALYSIS

Simultaneous thermogravimetric analysis (TGA) and evolved gas analysis (EGA) were performed on 8.293(6) mg of crushed and purified UK62, using a Mettler TA-1 thermoanalyzer in conjunction with an Inficon IQ 200 Quadrupole mass spectrometer. The starting material was visually estimated to be 98-99% pure and no extra lines were observed in the X-ray Gandolfi diffraction pattern.

Preliminary high-vacuum treatment resulted in a loss of 0.124 mg or 1.5(5) weight percent (wt. %). Following this, the sample was heated at a constant rate of $10^\circ\text{C}/\text{min}$ to 1400°C .

The TGA-EGA curves (Figure 8) show five exothermic peaks. The first occurs between 150 and 280°C , peaking at 265°C . This represents a weight loss of 0.027 mg or 0.3(1) wt. %. The remaining four peaks occur at 525, 715, 910 and 1195°C , and represent a combined weight loss (after pressure correction) of 5.15 mg or 61.8 wt. %, bringing the total weight loss of UK62 to 5.301 mg or 63.6 wt. %. The significance of the peak occurring at 1195°C (representing $<7\%$ of the total weight loss) may be exaggerated, since the nitrogen traps used in the TGA system may have begun to heat up at this point. This may have caused an overestimation of the weight loss corresponding to this peak (R. Ramik, pers. comm.). The residue of the run appears heterogeneous, suggesting the presence of immiscible melts or that incongruent crystallization had occurred. The residue is composed of three

Figure 8. The P_{total} (A), TGA (B) and EGA (C) curves for UK62.

phases: 1. a thin, white layer which formed on the walls of the crucible, 2. a light grey-brown powdery material with surficial black splotches and 3. a darker grey-brown glass which was enclosed by phase number #2. An X-ray diffraction investigation was carried out only on a mixture of residue phases #1 and #2, as phase #3 could not be removed from the crucible in which it formed. This analysis revealed the presence of lime, CaO , and portlandite, Ca(OH)_2 , plus weak lines attributable to an unidentified phase. Quantitative analyses of the residue indicate that it is composed essentially of Mn and Ca, with no detectable F or Na.

DISCUSSION OF TGA-EGA RESULTS

The water lost during the preliminary high-vacuum step of this analysis can be treated as adsorbed water. The peak occurring between 150 and 280°C, is interpreted as the loss of OH^- , which is consistent with the interpretations drawn from the infrared spectrum of the mineral. The remaining four peaks are attributed to the loss of compounds or atoms with atomic or molecular weights of 32 and 44, based on mass spectrometry. The latter is apparently CO_2 , and the former could be S or O_2 . However, as S was not detected by microprobe, this substance must be O_2 . The EGA portion of this study indicates that O_2 and CO_2 were given off contemporaneously, and the relative sizes of the peaks for these compounds suggest that CO_2 is more than twice as abundant as O_2 (Figure 8).

As the starting material used in the TGA-EGA study was believed to be very pure, contamination cannot be called upon to explain the significant amount of O_2 that was evolved. One possibility is that this O_2 is the dissociation product of one

of the oxides produced during heating. Na_2O is strongly suspected as the most probable source of the O_2 for the following reasons:

1. Na is an extremely volatile element.
2. X-ray Gandolfi diffraction analyses of the residue did not detect the presence of any Na compounds.
3. Wavelength dispersive microprobe analyses showed no detectable Na in the residue.
4. The sum of the Na_2O (≈ 26 wt. %) and CO_2 (≈ 37 wt. %) estimated from microprobe analyses, is very close to the total weight loss of ≈ 64 wt. % recorded by the TGA-EGA analysis.
5. The TGA curve shows areas where the rates of loss are relatively constant, but which are marked on the pressure chart by a decrease in pressure (e.g. 1010°C), suggesting that an element or compound with a low atomic weight was given off. Furthermore, due to the low vapour pressure of Na, the mass spectrometer employed by the EGA system is unable to detect it.
6. Na_2O vapourizes by decomposition into its gaseous elements, i.e. $2\text{Na} + 1/2\text{O}_2$ (Brewer and Margrave, 1955). The melting point of Na_2O has been experimentally established to be 1190 K or 917°C , determined at what is believed to be ambient pressure (Brewer and Margrave, 1955). It is conceivable therefore, that the melting point and hence, decomposition temperature of Na_2O , could be much lower in a vacuum as the TGA-EGA was carried out in.

It is interesting to note in the TGA-EGA run that F was not detected, and neither was it detected in the wavelength dispersive microprobe analyses of the TGA-EGA residue material. It is possible that F was released from the mineral in the form of NaF, by combining with the Na liberated through the decomposition of Na_2O . NaF is not detectable by the mass spectrometer used (R. Ramik, pers. comm.).

UK62 SYNTHESIS

To determine if Mn is essential to UK62, a number of attempts were made to synthesize both Mn-bearing and Mn-free UK62. Syntheses runs were carried out in 5mm diameter gold capsules (≈ 4 cm in length), which were placed in a cold seal cylindrical pressure vessel (≈ 20 cm long), and by means of a thermocouple, heated isothermally. Temperatures were monitored on a 24-hour basis using the computer program "OVENS" (D. Marshall, 1987). Temperature error, estimated to be $< \pm 10^\circ\text{C}$, is attributed mainly to temperature gradients, controller variation and thermocouple error. Hydrostatic pressure, monitored daily with Heise bourdon tube guages, is estimated to be within ± 5 bars of the quoted pressures. Most runs were allowed to cool gradually within the oven, except for runs #5 and #6, which were air-quenched.

Starting mixes were prepared from stoichiometric concentrations of reagent-grade Na_2CO_3 , CaCO_3 , MnCO_3 and NaF or LiF. All runs were composed of approximately 70 mg of starting mixture and 20 mL of doubly-distilled, de-ionized H_2O . The mixtures were placed in the gold tubes, and physically shaken to ensure through mixing. The tubes were crimped and welded at both ends. The sealed tubes were weighed before and after the runs to ensure that no mass was lost. The compositions of the starting mixes are given in Table 20. A very small amount of natural UK62 was introduced to runs #5 and #6 to facilitate nucleation.

Immediately after the runs had cooled, the tubes were opened and their contents examined. The products were initially found to be wet and soft, almost gelatinous, but exposure to air for approximately 1 hour caused them to dry and harden. The products were identified by a combination of microscopic and X-ray

TABLE 20. HYDROTHERMAL SYNTHESIS OF UK62

Starting Composition
(Number of moles)

<u>Run</u>	<u>NaCO₃</u>	<u>CaCO₃</u>	<u>MnCO₃</u>	<u>LiF</u>	<u>NaF</u>	<u>Products</u>
1. ^a	1.5	1.8	0.2	1	-	UK62+Tr+Cc+Gr
2. ^b	1.5	2.0	-	1	-	UK62+Tr+Cc+Gr
3. ^c	1.0	1.8	0.2	-	1	Cc
4. ^d	1.0	2.0	-	-	1	Cc+Fl+Th
5. ^e	1.0	1.8	0.2	-	1	UK62+Tr+Cc
6. ^f	1.0	2.0	-	-	1	UK62+Tr+Cc+Nah

Tr = trona; Cc = calcite; Gr = griceite; Fl = fluorite;
Th = thermonatrite; Nah = nahcolite.

- a. 700(5) °C, 1.50(2) kb, 4 days.
- b. 700(5) °C, 1.50(2) kb, 4 days.
- c. 700(5) °C, 1.50(2) kb, 4 days.
- d. 700(5) °C, 1.50(2) kb, 4 days.
- e. 680(5) °C, 1.50(2) kb, 11 days.
- f. 680(5) °C, 1.50(2) kb, 11 days.

Gandolfi diffraction techniques. UK62 was identified in runs #1, #2, #5 and #6. The X-ray diffraction patterns indicated it to be the predominant phase, with additional, less abundant phases also present (Table 20). The lines on the diffraction films of synthesized UK62 were found to be diffuse for runs #1 and #2, but significantly sharper for runs #5 and #6, suggesting that crystallinity increased with run duration. The only euhedral crystals noted in any of the runs, was in run #6 where clear crystals of nahcolite, NaHCO_3 , with distinct crystal faces, were observed. These crystals were not found in contact with the bulk of the product material.

Under the polarizing microscope at 500x magnification, all products were found to be extremely fine-grained and consisted of clear crystalline material with cloudy, yellowish cores. Much of the clear material was identified by X-ray Gandolfi diffraction to be trona and calcite, suggesting that UK62 had been enveloped by these phases. Due to the fine-grained nature of the products, UK62 could not be separated out for optical analyses.

These experiments demonstrated that Mn is not essential to UK62. This conclusion is based on the successful production of UK62 in runs #2 and #6, which were carried out in the absence of Mn. Although UK62 was also produced in the absence of Mn (runs #1 and #2), the Mn-content of the synthetic products could not be determined, as no pure UK62 was found.

The solubility of LiF, used in runs #1 and #2, is quite low at moderate temperatures (375°C, solubility = 0.0222 g/100g H_2O ; Booth and Bidwell, 1950). Although its solubility under the experimental conditions is not known, F may not have participated in the chemical reactions in these runs. Thus, the possibility exists

**TABLE 21. A COMPARISON OF REFINED CELL PARAMETERS
FOR NATURAL AND SYNTHETIC UK62**

<u>Parameter</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>
<u>a</u> (Å)	8.043(4)	8.113(5)	8.105(6)	8.087(9)	8.140(5)
<u>b</u> (Å)	15.812(5)	15.921(7)	15.909(7)	15.885(8)	15.917(7)
<u>c</u> (Å)	7.030(3)	7.059(4)	7.056(4)	7.058(5)	7.051(4)
β (°)	101.16(3)	101.62(4)	101.57(4)	101.44(5)	101.66(4)
<u>V</u> (Å ³)	877.1(4)	893.2(6)	891.3(6)	885.0(8)	894.8(6)

1. Natural UK62, Mont St.-Hilaire
2. Synthetic Mn-bearing UK62, product of synthesis run 1, LiF used.
3. Synthetic Mn-free UK62, product of synthesis run 2, LiF used.
4. Synthetic Mn-bearing UK62, product of synthesis run 5, NaF used.
5. Synthetic Mn-free UK62, product of synthesis run 6, NaF used.

that an hydroxyl-analogue of UK62 was synthesized in runs #1 and #2. However, as optical and X-ray Gandolfi diffraction methods have been unsuccessful in determining the amount of unreacted LiF in the products, the extent of $\text{OH}^- \leftrightarrow \text{F}^-$ substitution could not be estimated. The fact that although subjected to the same P-T conditions and run durations, UK62 was successfully synthesized in runs #1 and #2, and not in runs #3 and #4 (which used NaF in lieu of LiF), may indicate that LiF possibly acted as a catalyst.

The X-ray Gandolfi diffraction patterns of the synthetic UK62 produced in these experiments were readily indexed based on that of the natural UK62. The cell parameters of the synthetic UK62 were derived from least-squares refinement, and are listed in Table 21 along with those of the natural material.

The cell parameters and cell volume of UK62 are theoretically dependent on both the ratio of Mn:Ca and F^-/OH^- . However, as no estimate of the Mn : Ca or F^-/OH^- substitutions is available for the synthetic material, no relationship can be made between chemical composition and cell size for UK62. It can only be stated that the smaller cell parameters and cell volume of the natural UK62 relative to that of the synthetic material, must indicate a greater ratio of Mn:Ca and/or F^-/OH^- .

APPENDIX 1. GANDOLFI X-RAY DIFFRACTION DATA FOR UK37a

<u>hkl</u>	<u>dcalcÅ</u>	<u>dobsÅ</u>	<u>I</u>
002	6.123	6.123	4
100	4.497	4.498	6
101	4.222	4.227	8
103	3.023	3.023	10
110	2.596	2.596	7
104	2.531	2.530	4
112	2.390	2.391	5
200	2.248	2.249	2
201	2.212	2.211	5
105	2.151	2.152	<1
006	2.041	2.038	<1
106	1.859	1.860	1
210	1.700	1.697	2
211	1.684	1.683	2.5
107	1.630	1.632	1.5
116	1.605	1.604	2
213	1.569	1.569	3
304	1.346	1.348	<1
109	1.302	1.301	1
220	1.298		
310	1.247	1.243	<1
311	1.241		
312	1.222	1.220	1
217	1.219		
306	1.208	1.195	1
224	1.195		

Plus additional lines

Visual intensities, 114.6 mm Gandolfi camera,
Ni- filtered CuK α radiation ($\lambda = 1.5418$ Å).

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