Zeitschrift für Kristallographie, Bd. 145, S. 73—95 (1977)

Nyerereite: a new volcanic carbonate mineral from Oldoinyo Lengai, Tanzania

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(Received 23 July 1976)

Auszug

Nyerereit, $(Na_{0,82}K_{0,18})_2Ca(CO_3)_2$ mit geringem Ersatz von CO_3^{2-} durch SO_4^{2-}, PO_4^{3-} und F^-, hat die Dichte 2,541, die Brechungsindizes $n_\alpha = 1{,}5112$, $n_\beta = 1{,}5333$, $n_\gamma = 1{,}5345$, den optischen Achsenwinkel $2V_\alpha = 29°$. Neben Interferenzen mit ganzzahligen Indizes treten auch solche mit $h = n + m\delta$ auf, worin m und n wie k und l ganze Zahlen sind, aber $\delta = 0{,}383$ ist. Aus den ganzzahligen Interferenzen wurde eine gemittelte Tieftemperaturstruktur mit $a = 5{,}044$, $b = 8{,}809$, $c = 12{,}743$ Å, $Z = 4$ und der Raumgruppe $Cmc2_1$ gefunden. Die Hochtemperaturstruktur ist hexagonal, in der Raumgruppe $P6_3mc$; die Gitterkonstanten sind $a = 5{,}05$, $c = 12{,}85$ Å. Die Tieftemperaturstruktur wird diskutiert und aus ihr die Hochtemperaturstruktur abgeleitet, die als Prototyp für alle Glieder des Systems $Na_2Ca(CO_3)_2$—$K_2Ca(CO_3)_2$ angesehen wird.

Abstract

Nyerereite has the idealized composition $(Na_{0.82}K_{0.18})_2Ca(CO_3)_2$ with significant minor substitution of SO_4^{2-}, PO_4^{3-}, F^- for CO_3^{2-}, optical properties $\alpha = 1.5112$, $\beta = 1.5333$, $\gamma = 1.5345$, $2V_\alpha = 29°$, and density 2.541 g cm^{-3}. The average unit cell has space group $Cmc2_1$, dimensions $a = 5.044$, $b = 8.809$, $c = 12.743$ Å and contains four formula units. Non-Bragg reflexions have $h = n + m\delta$ where n and m are integers and $\delta = 0.383$ and indicate a structural modulation. The natural mineral is an inversion product from a high-temperature hexagonal polymorph, high nyerereite with $a = 5.05$, $c = 12.85$ Å and space group $P6_3mc$. The average structure of the natural mineral (low nyerereite) is discussed and the structure of high nyerereite is inferred. The high-nyerereite structure is the aristotype for all phases except buetschliite in the system $Na_2Ca(CO_3)_2$—$K_2Ca(CO_3)_2$. Mineralogical nomenclature in this system is discussed.

I. Introduction

Nyerereite, an orthorhombic carbonate mineral of composition approximating to $(Na,K)_2Ca(CO_3)_2$, was discovered by J. B. DAWSON (DAWSON, 1962a, 1962b; DUBOIS *et al.*, 1963; GUEST, 1963) in the remarkable carbonate lavas (lengaite) erupted by the volcano Oldoinyo Lengai, Tanzania between March 1960 and September 1965. Nyerereite was established as a new mineral by the senior author of this paper and by Dr. C. MILTON (then of the U.S. Geological Survey, Washington, D.C.) working independently on material supplied by DAWSON. The mineral name nyerereite was approved by the Commission on New Minerals and Mineral Names of the International Mineralogical Association in 1963 on the evidence of preliminary data submitted by MILTON and INGRAM of the U.S. Geological Survey. The present paper corrects and adds substantially to the preliminary description of MILTON and INGRAM and constitutes the first published account of the mineralogy and crystallography of nyerereite. The stability of nyerereite has been discussed in advance of a published description of the mineral by FRANKIS and MCKIE (1973) and by COOPER, GITTINS, and TUTTLE (1975).

II. Description of nyerereite

Unit-cell dimensions

In its natural occurrence in lengaite nyerereite is invariably twinned. With care such a twinned crystal can be dissected under a binocular microscope so as to yield a grain in which one individual is clearly dominant. The data reported in this and the next section were obtained from such single or nearly single crystal grains.

Accurate dimensions of the orthorhombic unit-cell of natural nyerereite were obtained by two methods. By utilizing the back-reflexion oscillation method described by MCKIE (1965) with an internal silicon standard the dimensions of the unit-cell were determined as $a = 5.042 \pm 0.002$, $b = 8.806 \pm 0.005$, $c = 12.744 \pm 0.002$ Å. By using travelling microscope measurements of $\alpha_1\alpha_2$ splitting at high θ on zero and upper-layer Weissenberg photographs, as described by ALCOCK and SHELDRICK (1967) the dimensions of the unit-cell were determined as $a = 5.050 \pm 0.005$, $b = 8.816 \pm 0.012$, $c = 12.7 \pm 0.3$ Å. We acknowledge our indebtedness to Dr. G. M. SHELDRICK for processing our measurements of $\alpha_1\alpha_2$ splitting on 84 (23 independent) reflexions on the University of Cambrige TITAN computer;

the standard deviation reported for c is high because the reflexions measured all had $l \leq 5$. Critical comparison of the cell dimensions obtained by the two methods yields preferred dimensions for the orthorhombic unit-cell: $a = 5.044 \pm 0.003$, $b = 8.809 \pm 0.007$, $c = 12.743 \pm 0.003$ Å.

Non-Bragg reflexions

At first sight the x-ray diffraction pattern of natural nyerereite exhibits a fivefold superlattice parallel to the x axis; but careful measurement of precession photographs reveals that the superlattice reflexions have non-integral h indices. The non-Bragg nature of the superlattice reflexions in natural nyerereite was noticed by EVANS and MILTON (1973). The complete diffraction pattern of natural nyerereite referred to the unit-cell whose dimensions are given in the preceding paragraph is such that for a sharp reflexion hkl, k and l are always integral and $h = n \pm m\delta$, where n and m are integers. For the Bragg reflexions $m = 0$ and for the non-Bragg reflexions $m = 1$ usually (some of these reflexions are of the same order of intensity as neighbouring Bragg reflexions and may be quite strong), but less commonly $m = 2$ (usually relatively weak). The magnitude of δ has been determined as 0.383 ± 0.001 by travelling microscope measurements of $h0l$, $h1l$ and $h2l$ precession photographs taken with Cu$K\alpha$ radiation. EVANS and MILTON (1973) found $\delta = 0.38$ by measurement of precession photographs taken with Mo$K\alpha$ radiation.

Diffuse streaks

Quite weak streaks of diffuse intensity are observed on Weissenberg photographs $h0l$ to $h6l$ running parallel to a^* at integral values of l. The streaks do not display any diffuse intensity maxima between adjacent sharp reflexions and they do not extend to high values of h. Generally the diffuse streaks weaken with increasing k and l.

Space group

Inspection of $hk0$, $hk1$, $hk2$, $hk3$, $hk4$, $hk5$ and $h0l$, $h1l$, $h2l$, $h3l$ Weissenberg photographs of an untwinned crystal of nyerereite established the symmetry of the diffraction pattern unambiguously as mmm and the systematic absences on these photographs enabled the diffraction symbol to be determined as $mmm\ C\text{-}c\text{-}$; the non-Bragg reflexions are satellites about permitted Bragg reflexions. The possible space groups for the orthorhombic C cell are $Cmc2_1$, $C2cm$, or $Cmcm$.

The structural study of natural nyerereite (FRANKIS and MCKIE, in preparation) has shown, by use of intensity statistics, that the probable space group is $Cmc2_1$.

The axes of the orthorhombic unit-cell of nyerereite have been labelled so as to be consistent with the conventions adopted in *International tables for x-ray crystallography*, vol. 1 (1969). The choice is at variance with the convention of *Crystal data* (1973) for orthorhombic substances, namely $c < a < b$; but it is considered more useful for the space group to be in the standard orientation. Moreover the unit-cell dimensions quoted above are such that $b \simeq a\sqrt{3}$, so that the orthorhombic C cell is pseudohexagonal with $a \simeq 5.04$ Å and $c = 12.743$ Å. The observed systematic absences are consistent with the diffraction symbol $6/mmm\ P{-}{-}c$ for the pseudohexagonal unit cell.

Twinning

In its natural occurrence in lengaite, nyerereite is invariably twinned, the twin operator being a triad parallel to [001] of the orthorhombic unit cell. The x-ray diffraction patterns of nyerereite crystals yield clear evidence of such twinning both by the disposition of non-Bragg reflexions and by splitting of reflexions at high Bragg angle due to the small difference in magnitude between a^* and $b^*\sqrt{3}$. Equally clear evidence of the ubiquity of triad twinning in natural nyerereite crystals is provided by optical studies, which will be detailed later.

Twinning in natural nyerereite has been examined by travelling microscope measurement of splitting at high Bragg angle of reflexions recorded on an $hk0$ Weissenberg photograph: the value of $a^{*2}-3b^{*2}$ derived from such measurements is 0.00059 ± 0.00001 Å^{-1}, in satisfactory agreement with the value derived from the preferred unit-cell dimensions 0.00064 ± 0.00008 Å^{-1}. Moreover the $h0l$ Weissenberg photograph shows twin splitting at high θ only for l even and the magnitude of the splitting corresponds to $a^{*2}-3b^{*2} = 0.00063 \pm 0.00004$ Å^{-1}. Further, observations on twin splitting of reflexions at high θ on [001] oscillation photographs yields a value of $a^{*2}-3b^{*2} = 0.00063 \pm 0.00002$ Å^{-1}, again in very good agreement with the value calculated from the preferred unit-cell dimensions derived from studies of the diffraction pattern of untwinned crystals.

X-ray powder diffraction pattern

The description of the powder pattern of nyerereite is complicated by the fact that lines due to non-Bragg reflexions cannot be ignored. Table 1 records spacings, d, and relative intensities of all lines observed on powder photographs and powder diffractometer traces of natural nyerereite. The powder lines were indexed using a table of sorted spacings calculated from the preferred orthorhombic unit-cell dimensions given above and having regard to the single-crystal intensity data collected in the course of the structure determination. Indices of non-Bragg lines are shown in the form $h \pm \delta, k, l$ where $\delta = 0.383$. Indexing was not attempted for lines with $d < 1.80$ Å.

Table 1. *X-ray powder pattern of nyerereite*

d	I	Indices	d	I	Indices
6.377 Å	vs	002	2.001 Å	vw	$2-\delta$, 2,4; $1-\delta$, 1,6
5.769	vvw	δ02	1.989	vw	134
4.385	vs	110; 020	1.956	s	043
4.165	vw	021	1.951	w	223
3.608	vw	112	1.933	vvw	δ43
3.471	vw	$1-\delta$, 1,3; δ22	1.858	vvw	$1+\delta$, 3,4
3.261	vw	$1+\delta$, 1,1	1.812	s	044
3.181	ms	004	1.805	s	224
3.090	vvw	δ04	1.765	vvw	
3.046	vvs	113; 023	1.680	w	
2.983	vvw	δ23	1.647	vw	
2.735	vvw	$1-\delta$, 3,1	1.627	w	
2.582	s	114; 024	1.600	vvw	
2.536	vs	130	1.547	vvw	
2.523	w	200	1.524	vvw	
2.491	w	131	1.471	vw B	
2.349	vw	132; $1-\delta$, 1,5	1.458	vw B	
2.327	vvw	$1+\delta$, 1,4	1.401	vvw	
2.199	s	040; 115	1.348	vw	
2.161	ms	221	1.270	vvw	
2.122	s	006	1.263	vvw	
2.097	m	δ06	1.229	vvw	
2.081	s	042	1.175	vvw	
2.071	vs	222	1.138	vw	

Radiation: Cu$K\alpha$.
B: broad line.

Optics

Nyerereite is biaxial negative with $2V = 29°$. The limiting refractive indices, determined by the immersion method, are $\alpha = 1.5112 \pm 0.0005$ and $\gamma = 1.5345 \pm 0.0005$. The intermediate principal refractive index β has been evaluated as 1.5333 ± 0.0005 by measurement of the birefringence $\gamma - \beta$ in sections of known thickness (*i.e.* ground to the same thickness as prismatic sections of quartz mounted on either side of it and showing first order sensitive tint) exhibiting a centred acute bisectrix figure; the same technique confirmed the maximum birefringence $\gamma - \alpha$ as 0.0232 ± 0.0002.

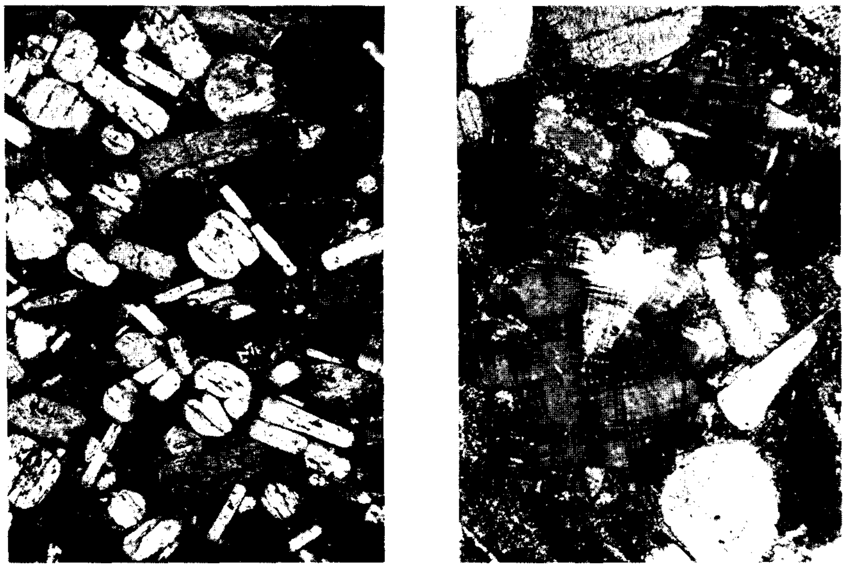
The orientation of the indicatrix has been determined by observation of the diffraction pattern of a grain to which glass fibres had been attached to mark the principal vibration directions. This orientation of the indicatrix is $\alpha \| z$, $\beta \| x$, $\gamma \| y$.

Habit

In lengaite the nyerereite crystals are tabular with {001} faces well developed and no proper faces in the [001] zone. The smallest dimension is typically in the [001] direction. Sections parallel or sub-parallel to [001] are thus length slow and, at standard thickness, display interference colours ranging up to second order blue; such sections yield no evidence of twinning. But sections more or less parallel to (001) display first order greys and characteristic cross-hatched twinning (Fig. 1) such that the twin individuals extinguish at 60° to one another. Such triad twins do not have composition planes.

Chemical composition

Nyerereite was separated by crushing a sample of the host rock to pass a 90 mesh sieve, stirring with cold distilled water to convert the other principal mineral phases to aggregates of calcite, cleaning on the Franz isodynamic separator, and finally by successive centrifugal sinking and floating in CH_2I_2-CCl_4 mixtures. The resultant sample, which appeared optically to be a better than 99% concentrate of nyerereite, was subjected to wet chemical analysis by Mr. J. H. SCOON. This analysis, which is set down in column 1 of Table 2, presented some difficulty of interpretation in crystal-chemical terms, suggesting that the sample presented for analysis may have been more impure than routine optical examination could reveal. Optical examination at high magnification of thin-sections of the host rock revealed sporadic



(a) (b)

Fig. 1. Microphotographs of lengaite between crossed polars: (a) general view showing plates of nyerereite *N*, rounded grains of the unnamed carbonate mineral *G* in a dark matrix of devitrified carbonate glass, magnification × 23, (b) nyerereite twin, magnification × 60. Specimen numbers, Mineralogical Museum, Cambridge: (a) 102265, (b) 120108

clusters of inclusions within nyerereite crystals and a tendency for small grains of accessory minerals to be concentrated along the boundaries of nyerereite grains. Such inclusions and adherent impurities would inevitably have been present in the analysed sample.

Electron microprobe analysis, kindly performed for us by Dr. J. V. P. Long on the GEOSCAN, has made possible some degree of correction for inclusions and adherent impurities. Clear areas of nyerereite crystals were found to have Fe $< 0.02\%$, Si $< 0.2\%$, and Al $< 0.05\%$; the content of these three elements in nyerereite is thus insignificant. The concentrations of certain other elements in such inclusion-free areas of nyerereite crystals are shown, together with the major elements, in column 2 of Table 2.

In the course of the electron probe microanalysis decarbonation was observed; but it was found that stability could be maintained by use of a low probe current and an enlarged probe. In the conditions

Table 2. *Chemical composition of nyerereite*

	1	2	3	4		5
MnO	0.07	0.1	0.07	Mn^{2+}	0.01	0.01
MgO	0.12	n.d.	0.12	Mg^{2+}	0.03	0.03
CaO	24.95	24.47	24.47	Ca^{2+}	3.78	3.73
SrO	1.70	2.20	2.20	Sr^{2+}	0.18	0.18
BaO.	1.10	0.59	0.59	Ba^{2+}	0.03	0.03
Na_2O	23.94	24.1	23.94	Na^+	6.69	6.60
K_2O	7.90	8.4	7.90	K^+	1.45	1.43
CO_2	38.10	n.d.	38.10	CO_3^{2-}	7.50	7.39
SO_3	1.45	1.50	1.50	SO_4^{2-}	0.16	0.16
P_2O_5	n.d.	0.36	0.36	PO_4^{3-}	0.04	0.04
F	0.51	n.d.	0.51	F^-	0.23	0.22
Cl	0.50	0.26	0.26	Cl^-	0.06	0.06
H_2O^+	0.26	n.d.	0.26	OH^-	0.25	0.25
				O^{2-}	0.10	0.10
SiO_2	0.20	< 0.2	nil			
TiO_2	nil	nil	nil			
Al_2O_3	0.26	< 0.05	nil			
Fe_2O_3	0.05	< 0.02	nil			
FeO	n.d.					
H_2O^-	0.06	n.d.				
	101.17		100.28			
less O ≡ F	0.22		0.22			
less O ≡ Cl	0.11		0.56			
	100.84		100.00			

1. Wet chemical analysis: analyst J. H. SCOON.
2. Electron microprobe partial analysis of the same specimen.
3. Preferred analysis from columns 1 and 2.
4. Unit-cell contents calculated from column 3, determined density, and unit-cell dimensions.
5. Unit-cell contents assuming that all twelve cation sites are filled.

under which all the data recorded in column 2 were obtained the counts of Na$K\alpha$, K$K\alpha$, and Ca$K\alpha$ showed no discernible drift attributable to decomposition of the specimen.

Preferred values selected from the wet chemical and electron microprobe analyses are shown in column 3 of Table 2. Some of the criteria on which the selection was based have been mentioned above.

Other criteria are (*i*) that the electron microprobe determination of Ca is to be preferred because of the difficulty of separating Ca and Sr completely by oxalate precipitation and (*ii*) that the flame photometric determinations of Na and K, shown in column 1, are likely to be more precise than the electron microprobe determinations of these elements and are unlikely, being determinations of principal constituent elements, to be significantly affected by minor impurities.

Unit-cell contents

The density of a sample of nyerereite has been determined by adjusting the dilution of Clerici's solution so that grains of nyerereite neither sink nor float during the course of centrifuging for 10 minutes at 5000 rpm. The density of the resultant solution was then measured by the loss in weight of a totally immersed mercury-in-glass mass. Determinations on two separately prepared samples gave a density of 2.541 ± 0.002 g · cm^{-3}.

Column 4 of Table 2 shows the atomic contents of the Bragg unit-cell of volume 566.2 Å^3 and density 2.541 g · cm^{-3}. It is assumed that all the H_2O^+ determined in the wet chemical analysis is present as hydroxyl anions in the nyerereite structure; but the possibility that a significant proportion of the determined H_2O^+ content may be attributable to a small percentage of highly hydrated impurities must be borne in mind. But whether one chooses to ignore the H_2O^+ determination shown in column 1 or to interpret it as OH^- in the nyerereite structure, there remains an excess of positive charge in the unit-cell contents unless balancing O^{2-} is introduced, as it is in column 4 of Table 2.

The substitution of SO_4^{2-} for CO_3^{2-} without change of structure, but with considerable structural distortion, is well known in the Na_2SO_4—Na_2CO_3 system (FISCHMEISTER, 1962). The PO_4^{3-} anion is, like SO_4^{2-}, tetrahedral and of similar size so that it too should be able to substitute for CO_3^{2-} to a limited extent without intolerable structural distortion.

The discrepancy between the chlorine determinations by wet chemical analysis of a bulk sample and electron microprobe analysis of inclusion-free areas of nyerereite grains is taken as confirmation of the presence of (?) halite inclusions within and especially on the margins of nyerereite grains. The hypothesis that the significant fluorine content found by wet chemical analysis represents fluorine within the nyerereite structure, rather than fluorine confined to inclusion material and to impurities in the separation, is supported by the evidence of single-crystal heating experiments to be described below. The chlorine, fluorine, hydroxyl, and excess oxygen anions, which must apparently be attributed to the nyerereite structure, are inadequate to occupy a separate structural site but must be assigned as random occupants of carbonate sites; their presence can be expected to give rise to significant local distortion of the nyerereite structure. This conclusion is supported by our structural studies which will be reported separately. In contrast hanksite $Na_{22}K(CO_3)_2(SO_4)_9Cl$, the structure of which has been determined by KATO and SAALFELD (1972), has its chlorine content on distinct structural sites and moreover the disposition of carbonate and sulphate groups is fully ordered.

III. Thermal stability

The response of natural nyerereite to elevated temperatures has been studied with the aid of a high-temperature x-ray oscillation camera of the type described by RICKSON, HALL, and MCCONNELL (1963). X-ray diffraction patterns were obtained at regular temperature intervals from single (untwinned) crystals with the x axis of natural nyerereite parallel to the oscillation axis of the camera and from twinned crystals with variously the y axis and the z axis parallel to the oscillation axis. Temperatures, measured with a Pt—Pt/13 % Rh thermocouple situated 5 mm above the crystal, are considered to be reproducible to within 5 °C. The thermocouple was calibrated by optical observation of the melting of benzoic acid, silver nitrate and potassium nitrate. Crystals were mounted either in dental cement or in MgO-waterglass paste; the nature of the mounting medium had no effect on the diffraction patterns obtained at high temperature.

The nyerereite diffraction pattern persists unchanged up to 292 ± 3 °C. At this temperature the diffraction pattern changes suddenly: the non-Bragg reflexions disappear, the Bragg reflexions persist, and additional reflexions, which can only be indexed on an hexagonal unit cell with $a = 10.1$ Å, appear. In the experiments with twinned crystals, it was not possible to determine whether this intermediate-temperature polymorph was hexagonal or was an orthorhombic twin with unit-cell dimensions corresponding to those of synthetic $Na_2Ca(CO_3)_2$ (FRANKIS and MCKIE, 1973). However the study of an initially untwinned crystal of nyerereite demonstrates conclusively that the intermediate-temperature polymorph is hexagonal. The data obtainable from the oscillation photographs are inadequate for determination of the diffraction symbol of the intermediate-temperature polymorph.

On further heating the additional reflexions characteristic of the intermediate unit cell steadily weaken above 322 °C and are only just visible on a photograph taken at 336 °C. A photograph taken at 356 °C shows only reflexions which can be indexed on an hexagonal unit cell with $a = 5.05\,^\circ\mathrm{C}$; that is to say only the Bragg reflexions of the original natural nyerereite diffraction pattern persist. Detailed exploration of the temperature range 322—356 °C enables the temperature of the transformation from the intermediate to the high-temperature structure to be specified as 340 ± 10 °C.

On cooling from 356 °C the diffraction pattern of the intermediate temperature polymorph is recovered at least by 321 °C, the additional 10 Å reflexions becoming steadily stronger until they disappear suddenly when the temperature falls below 292 °C. In the initially untwinned crystal the low-temperature polymorph produced by cooling is quite clearly triad-twinned about its c axis.

There is a clear distinction in type between the transformations at 292 °C and at 340 °C. The former is relatively rapid in that there is no obvious forewarning at lower temperatures and the non-Bragg reflexions are eliminated within the duration of the normal 24 hour exposure of an oscillation photograph. In contrast the latter transformation exhibits forewarning for at least 20° below the transformation temperature.

After successive heating and cooling through the transformation at 340 °C nyerereite crystals exhibit arcuate diffuse reflexions on the low-θ side of each strong reflexion. The resultant diffraction pattern bears some resemblance to the remarkable diffuse diffraction pattern of the other principal phenocryst mineral (as yet unnamed) which accompanies nyerereite in the lengaite lavas and will be the subject of a subsequent communication. The diffraction patterns of successively heated and cooled crystals also exhibit increasingly strong powder rings attributable to fluorite. These experimental observations remain unexplained at the present time.

The thermal behaviour of nyerereite has also been studied optically with a high-temperature stage mounted on a polarizing microscope in the conoscopic mode. Biaxial natural nyerereite is found to become uniaxial at high temperature. The temperature at which the change in symmetry of the indicatrix occurs could not be determined precisely with the experimental arrangement employed; it appears to correspond to the low → intermediate transformation at 292 °C.

For most, if not all, of the temperature range over which it exists the low-temperature polymorph of nyerereite is metastable. The synthetic data presented for the composition $Na_2Ca(CO_3)_2$ by FRANKIS and MCKIE (1973) show that the minimum stability limit of the nyerereite structure at 1 kbar in the presence of water vapour is 313 °C and the data of COOPER, GITTINS and TUTTLE (1975) for the same composition at the same pressure under dry conditions indicate a minimum stability limit of 335 °C. The P, T data of FRANKIS and MCKIE (1973) permit extrapolation of the equilibrium nyerereite $=$ shortite $+$ Na_2CO_3 to 1 bar at 284 °C. Information is not yet available about the effect of potassium and other substituents in the nyerereite structure on this equilibrium; but we consider it unlikely that the minimum stability limit of the natural mineral differs from that of $Na_2Ca(CO_3)_2$ by more than 20 °C. So it would appear that the transformation from the low to the intermediate temperature polymorph of natural nyerereite coincides approximately at atmospheric pressure with the minimum stability limit of the nyerereite structure at that composition. Thus the intermediate-temperature polymorph, at least for most of its temperature range, and the high-temperature polymorph, throughout its temperature range, occur within the stability field of the nyerereite structure.

IV. The nyerereite structures

Polymorphism

All compositions between $Na_2Ca(CO_3)_2$ and $K_2Ca(CO_3)_2$ have structures which can be described as thermal or compositional modifications of what is evidently an important carbonate aristotype, hexagonal with $a \simeq 5$ Å, $c \simeq 13$ Å. This type is exemplified by the mineral fairchildite $K_2Ca(CO_3)_2$ which is stable at 1 kbar above 547 °C (COOPER, GITTINS and TUTTLE, 1975) and can persist metastably for long periods of time at room temperature in a dry atmosphere. The type is also exemplified by the high-temperature polymorph of nyerereite $(Na_{0.82}K_{0.18})_2Ca(CO_3)_2$, which cannot be quenched. Synthetic studies, which will be reported in a subsequent communication, indicate that there is solid solution over the whole range between $Na_2Ca(CO_3)_2$ and $K_2Ca(CO_3)_2$ in the type structure immediately below the solidus at 1 kbar and that only the most potassium-rich compositions can be quenched without undergoing modification. It would be appropriate to designate the type as either the high-nyerereite structure or as the fairchildite structure; we prefer the former designation because our structural study of nyerereite under atmospheric conditions, although as yet incomplete, enables us to infer with presumed reliability the structure of high-nyerereite whereas fairchildite has, surprisingly, not yet been the subject of structural investigation. In conformity we designate the structure of the natural mineral nyerereite as the low-nyerereite structure and that of the polymorph which appears to be stable between 292 °C and 340 °C at 1 bar as the intermediate-nyerereite structure.

The average structure of low-nyerereite

Intensity data were collected from a single crystal of natural nyerereite by means of Weissenberg photographs taken with Cu$K\alpha$ radiation. Reflexions were recorded on multiple-film packs for the layers $hk0$ to $hk9$, $h0l$ to $h6l$, and $0kl$. In all, the intensities of 858 reflections were measured by visual comparison with a calibrated intensity scale. After absorption, Lorentz and polarization corrections had been made to the raw data, statistical study of the reduced data indicated that the space group of low nyerereite must be $Cmc2_1$.

When the contents of the unit cell are simplified to $(Na,K)_8Ca_4(CO_3)_8$ by neglecting minor constituents, the assignment of the space group as $Cmc2_1$ requires the Ca atoms to be on mirror plane sites, $0yz$, etc., z can arbitrarily be set at zero. Utilizing the information provided about the average structure by the 338 measured Bragg reflexions in a Patterson synthesis approximate coordinates were obtained for Na,K on two sets of mirror-plane sites, for one set of carbon atoms on mirror-plane sites, for one set of oxygen atoms on mirror-plane sites, and for one set of oxygen atoms in general equivalent positions. The set of four carbonate groups thus located is disposed so that each has one C—O bond on a mirror plane and the other two oxygen atoms are related by the mirror plane. The space group requires that the remaining four carbonate groups should have their carbon atoms on one set of mirror-plane sites and their oxygen atoms on one set of mirror-plane sites and one set of general sites; the situation of these atoms was not apparent in the Patterson synthesis. Refinement of this partial structure failed to locate the second set of carbonate groups in the average structure suggesting that the non-Bragg reflexions, so far ignored, may be due to a modulation in the position or orientation of this set of carbonate groups.

The problem posed by the non-Bragg reflexions in low nyerereite will be the subject of a subsequent communication. It can however be said at this stage that preliminary study of the modulated structure has served to locate the missing carbon atoms and to indicate that the associated oxygen atoms may occupy alternative positions according to whether the adjacent alkali-cation site is occupied by Na^+ or by the larger K^+ cation. It is already apparent that the planes of the second set of carbonate groups are not parallel to the plane of the first set; this conclusion is supported by the low maximum optical birefringence of nyerereite, $\gamma - \alpha = 0.0233$, compared with that of aragonite 0.155 or calcite 0.172, where all the carbonate groups have their planes aligned parallel. It is found also that potassium atoms are confined to sites derivative from one set of alkali atom sites in the average structure.

Table 3. *Atomic coordinates (approximate) in low nyerereite*, origin on $mc2_1$

	x	y	z
Ca	0	0.98	0
(Na,K)(1)	0	0.32	0.82
Na(2)	0	0.32	0.12
C(1)	0	0.35	0.51
O(1)	0.22	0.28	0.52
O(2)	0	0.49	0.49
C(2)	0	0.99	0.23
O(3) O(4)	uncertain		

The average structure of low-nyerereite, so fas as it is known, is summarized in Table 3. It would be pointless to explore the average structure further; it is introduced here as a stage in the argument leading to the inferred structure of high nyerereite.

Inter-relationship of the nyerereite polymorphs

The space group and unit-cell dimensions of low nyerereite have been determined as $Cmc2_1$, $a = 5.044$ Å, $b = 8.809$ Å, $c = 12.743$ Å. Measurement and indexing of three a-axis 15°-oscillation photographs taken at 356 °C with the incident x-ray beam (*i*) parallel to c, (*ii*) in-

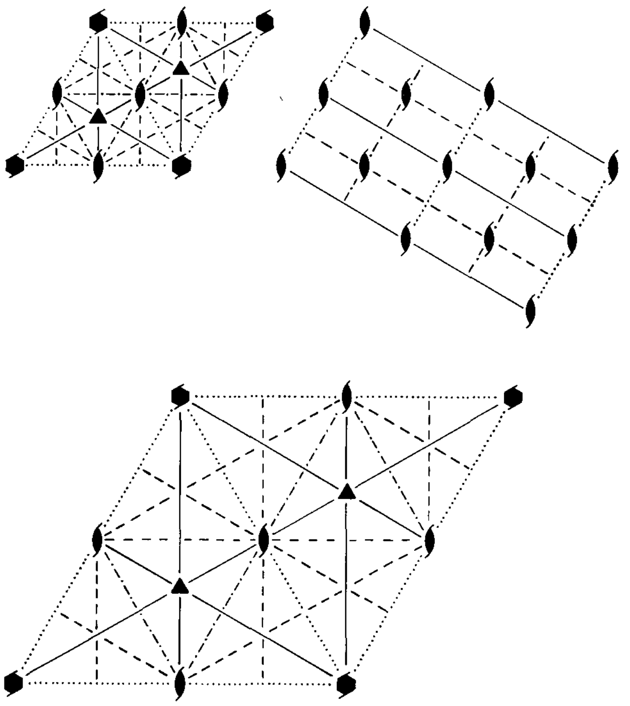


Fig. 2. Inter-relationship of the nyerereite polymorphs. The space group diagrams are drawn to scale and mutually orientated

clined at 15° to c, (*iii*) inclined at 30° to c yielded the dimensions $a = 5.05$ Å, $c = 12.85$ Å for the hexagonal unit cell of high nyerereite and systematic absences indicative of the diffraction symbol $6/mmmP{-}{-}c$. There is thus an increase of about 1 % in the c dimension, which may be attributed in part to normal thermal expansion and in part to an increase in molar volume at one or both of the polymorphic transformations. Of the three space groups consistent with the observed diffraction symbol $P\bar{6}2c$ is excluded by the principle of derivative symmetry while $P6_3mc$ and $P6_3/mmc$ are supergroups of the space group of low nyerereite, $Cmc2_1$. The necessity for a simple structural relationship between the high and low polymorphs then indicates $P6_3mc$. In the transformation from high to low nyerereite the triads are lost (including those inherent in the 6_3 axes) and two orientations of interleaved mirror planes and $\langle 12 \cdot 0 \rangle$ glides are lost as are two orientations of interleaved c glides and n glides; all other symmetry elements persist (Fig. 2.).

The dimensions of the hexagonal unit cell of intermediate-nyerereite have been determined as $a = 10.10$ Å, $c = 12.75$ Å. Not enough reflexions were observable on the oscillation photographs taken at 298 °C to enable the diffraction symbol to be determined unambiguously; but the data obtained are consistent with $6/mmmP\text{-}\text{-}c$. Application of the principle of derivative symmetry leads to the assignment of the space group of intermediate nyerereite as $P6_3mc$. However in the transformation from the high to the intermediate polymorph the doubling of the a axis requires not only the suppression or degradation of some symmetry elements but the change in character of others as indicated in Fig. 2. Thus alternate $\{11\bar{2}0\}$ mirror planes become $\langle 12 \cdot 0\rangle$ glides and alternate c glides become n glides. In the transformation from the intermediate to the low-temperature polymorph some of the suppressed symmetry elements reappear in consequence of the halving of the a axis so at temperatures both above and below the apparent stability range of the intermediate polymorph nyerereite has a higher density of symmetry elements.

It will be shown in the next section that the transformation from low to high nyerereite must involve reorientation of the second set of carbonate groups and adjustment in cation positions. In order to explain the status of the intermediate polymorph it is postulated that these two processes occur separately. A relatively rapid process, almost certainly the reorientation of carbonate groups, occurs at 292 °C and leads to the intermediate structure. A slower process, presumably cation movement, begins below 322 °C and reaches completion at 340 °C to yield the high-nyerereite structure. Such precursor structures, either with reduced symmetry or enlarged unit-cells, have been observed in several systems. In general terms the intermediate structure appears to play a similar rôle in the nyerereite system to that of Phase R in the $NaNbO_3$ system (MEGAW, 1973).

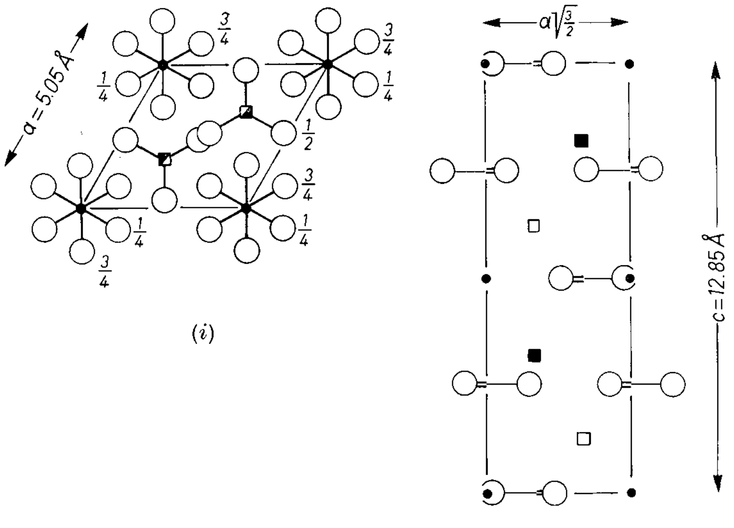
The structure of high nyerereite

Before proceeding to structural argument it is necessary to dismiss the possibility of free rotation of carbonate groups in nyerereite at temperatures just above 340 °C. At atmospheric pressure free planar rotation of carbonate groups has been demonstrated in calcite above 975 °C and in $BaCO_3$ above 803 °C by LANDER (1949). No information is available for Na_2CO_3 or any other alkali carbonate. It therefore seems reasonable to suppose that free rotation is improbable in nyerereite at a temperature as low as 340 °C, the minimum stability limit of high nyerereite.

The unit cell of high nyerereite contains two formula units of $(Na,K)_2CO_3 \cdot CaCO_3$. There are thus only two Ca atoms in the unit cell and they must be situated on $3m$ sites, which can be selected arbitrarily as 000 and $00\frac{1}{2}$. The four carbonate groups must be present as two sets of two equivalent carbonate groups with the carbon atoms on $3m$ sites. By analogy with the average structure of low nyerereite (Table 3) one pair of carbon atoms, C(1), will be at $\frac{1}{3}\,\frac{2}{3}\,\frac{1}{2}$ and $\frac{2}{3}\,\frac{1}{3}\,0$ and the other pair, C(2), will be at $00\frac{1}{4}$ and $00\,\frac{3}{4}$. The twelve oxygen atoms in the unit-cell must be situated on two sets of sixfold m sites such that all four carbonate groups have their planes parallel to (0001) and all C—O distances are equal to 1.294 Å (Sass, Vidale and Donohue, 1957, in calcite). This can be achieved for the six oxygen atoms, O(1), bonded to the two C(1) carbon atoms by fixing the parameters of the $6c$ sites of $P6_3mc$ as 0.48, 0.52, $\frac{1}{2}$ and this assignment is consistent with what is known of the low-nyerereite structure. For the determination of the coordinates of the six oxygen atoms, O(2), bonded to the two C(2) carbon atoms the guidance obtainable from the low-nyerereite average structure is less certain; but the O(2) sites must again be $6c$ positions and coordinates 0.15, 0.85, $\frac{1}{4}$ etc. would be consistent with the known C—O bond length in carbonates and with what has been inferred about the probable orientation of these carbonate groups in low nyerereite. The four alkali metal atoms must be situated on two pairs of $3m$ sites. One such pair of sites (Na, K)(1) is occupied, if the analogy with low nyerereite is valid, by 1.3 sodium atoms and 0.7 potassium atoms and these sites have coordinates $\frac{1}{3}, \frac{2}{3}, 0.825$ and $\frac{2}{3}, \frac{1}{3}, 0.325$. The other pair of sites Na(2), by analogy also, is exclusively occupied by sodium atoms and the coordinates of these sites are $\frac{1}{3}, \frac{2}{3}, 0.125$ and $\frac{2}{3}, \frac{1}{3}, 0.625$. In both cases the z parameter of the $2b$ position has been selected so as to be generally consistent with what is known of the average structure of low nyerereite and to place the cations as symmetrically as possible between nearest-neighbour oxygen atoms.

Projections of the proposed high-nyerereite structure on (0001) and on $(2\bar{1}\bar{1}0)$ are shown in Fig. 3 and atomic coordinates are listed in Table 4.

The coordination polyhedron of oxygen atoms about calcium is unusual in being a plane irregular hexagon, with all Ca—O distances equal to 2.531 Å and O—Ca—O bond angles alternately equal to 52.1°



(*i*) (*ii*)

Fig. 3. The high-nyerereite structure in projection (*i*) down z on to (0001) and (*ii*) down x on to (2$\bar{1}\bar{1}$0). Calcium atoms are shown as small solid circles and oxygen atoms as large open circles. Only oxygen atoms coordinated to carbon atoms within the unit-cell are shown. Alkali metal atoms are shown as squares: solid for (Na,K)(1), open for Na(2) and, in the (0001) projection, half-solid for superimposed (Na,K)(1) and Na(2). Carbon atoms are not shown explicitly. In the (2$\bar{1}\bar{1}$0) projection C—O bonds parallel to the plane of projection are shown as single strong lines; double strong lines represent C—O bonds inclined symmetrically on either side of the plane of projection

and 67.9°. The next-nearest-neighbour oxygen atoms are $\frac{c}{4}$ above and below the Ca atoms and very much further away at 3.445 Å. The disposition of the two shells of oxygen atoms about calcium bears a gen-

Table 4. *Atomic coordinates in high nyerereite*, origin on $6_3(3m)$

	x	y	z
Ca	0	0	0
(Na,K)(1)	$\frac{1}{3}$	$\frac{2}{3}$	0.825
Na(2)	$\frac{1}{3}$	$\frac{2}{3}$	0.125
C(1)	$\frac{1}{3}$	$\frac{2}{3}$	0.50
C(2)	0	0	0.25
O(1)	0.48	0.52	0.50
O(2)	0.15	0.85	0.25

eral geometrical resemblance to the pinwheel bracelets used by Moore (1973) to describe certain calcium orthosilicate and alkali sulphate structures.

The (Na, K)(1) cations (at $z = 0.825$) are coordinated to six O(2) oxygen atoms (at $z = \frac{3}{4}$) and the three O(1) oxygen atoms (at $z = 1$) so that there are six (Na, K)—O bond lengths of 2.779 Å and three of 2.763 Å. Such bond lengths are adequate for random disposition of Na^+ and K^+ on the (Na, K)(1) sites.

The Na(2) cations are coordinated to six oxygen atoms [three O(2) distant 2.260 Å and three O(1) distant 2.281 Å] disposed at the corners of a nearly regular octahedron such that O(1)—Na(2)—O(2) is 90.9°. Such bond lengths are too short for any K^+ to be accommodated on these cation sites.

Thus the inferred structure of high nyerereite is physically acceptable and it is consistent with what is known as yet about the more complicated structure of low nyerereite. It is instructive to compare sequences parallel to z with those in the structure Na_2CO_3-*I* proposed by Fischmeister (1954). In high nyerereite the sequence along $0, 0, z$ is Ca-CO_3-Ca-CO_3 whereas that along $\frac{2}{3}, \frac{1}{3}, z$ is CO_3-(Na, K)(1)-Na(2). The corresponding sequences in Na_3CO_3-*I* are Na—Na along $00z$ and CO_3—Na along $\frac{2}{3}, \frac{1}{3}, z$ with a c repeat approximately one half that in high nyerereite. The change in sequence is required by the change in stoichiometry, the cation/anion ratio being 1.5 in nyerereite and 2 in Na_2CO_3. Since the carbonate anions are parallel to (0001) in both structures the magnitude of a is similar.

If all compositions between $Na_2Ca(CO_3)_2$ and $K_2Ca(CO_3)_2$ have essentially the same structure at high temperatures, the proposed high-nyerereite structure poses no crystal chemical problems for $0 \leq K/Na \lesssim 1$. But for $1 < K/Na \leq 2$ potassium must enter Na(2) sites and be in sixfold coordination to oxygen with rather short alkali-oxygen bond lengths. The determination of the structure of fairchildite, $K_2Ca(CO_3)_2$, currently in progress in this laboratory, may be expected to resolve this problem.

V. Nomenclature

Four names have been given to minerals in the compositional range between $K_2Ca(CO_3)_2$ and $Na_2Ca(CO_3)_2$. The names fairchildite and buetschliite were given by Milton and Axelrod (1947) to minerals with compositions close to $K_2Ca(CO_3)_2$, the compositional error in the original description of buetschliite being corrected by Mrose, Rose and MARINENKO (1966): these minerals have been shown to correspond to the high- and low-temperature polymorphs of $K_2Ca(CO_3)_2$ in the synthetic system K_2CO_3—$CaCO_3$ by MROSE *et al.* and that has subsequently been confirmed by COOPER, GITTINS and TUTTLE (1975). Fairchildite is hexagonal with $a = 5.294$ Å, $c = 13.355$ Å and space group $P6_3/mmc$ (National Bureau of Standards, 1970); in spite of the difference in space group it is clearly related to the aristotype with which we are dealing. Buetschliite is trigonal with $a = 5.38$ Å, $c = 18.12$ Å and space group $R\bar{3}m$ (PABST, 1974); the structure has been shown by PABST to be related to that of eitelite $Na_2Mg(CO_3)_2$ and so need concern us no further. The name natrofairchildite was proposed by KAPUSTIN (1971) for a mineral of composition approximating to $(Na_{0.97}K_{0.03})_2Ca(CO_3)_2$ occurring in burbankite-calcite veins in the Vuorijärvi carbonatite (see GITTINS in TUTTLE and GITTINS, 1966). The brief description of natrofairchildite is rather puzzling in that the mineral is stated to be uniaxial (sometimes biaxial) and commonly polysynthetically twinned: our experience of natural and synthetic phases in the system $Na_2Ca(CO_3)$—$K_2Ca(CO_3)_2$ is that only the hexagonal phases, necessarily restricted to compositions close to fairchildite under atmospheric conditions, are uniaxial and that phases which exhibit polysynthetic twinning are always orthorhombic and quite obviously biaxial. KAPUSTIN gives a powder pattern of 25 lines for natrofairchildite which shows no more than general correspondence with the more detailed powder data available for fairchildite (PDF-21-1287) and nyerereite (Table 1) and does not closely resemble in detail, as one might expect, the powder pattern of the synthetic orthorhombic $Na_2Ca(CO_3)_2$ noted by FRANKIS and McKIE (1973). In short it is impossible to discern from the meagre published data just how KAPUSTIN's natrofairchildite fits into the structural family with which we are concerned; a thorough single-crystal study of this most interesting Russian material would be welcome.

Nomenclature poses the problem, familiar in solid solutions, of whether to name only the end-members or to give separate names to each compositional range as in plagioclase and olivine. COOPER, GITTINS and TUTTLE (1975) have proposed that the names nyerereite and fairchildite should be applied strictly to the end-members $Na_2Ca(CO_3)_2$ and $K_2Ca(CO_3)_2$ and loosely to relatively sodic and relatively potassic compositions of the structural family. We find some difficulty in accepting this proposal because it is evident from our synthetic experiments that the stoichiometric end-members and compositions close to them display polymorphic sequences quite distinct from that common to most of the compositional range. We prefer to restrict the mineral name nyerereite to orthorhombic phases with the appropriate unit-cell dimensions displaying non-Bragg reflexions and to restrict the mineral name fairchildite to hexagonal phases with appropriate unit-cell dimensions. We have named the aristotype structure high nyerereite rather than fairchildite simply because more is presently known about the former. In a structural context we see no inconsistency in describing the structure of the mineral nyerereite as low nyerereite. We reserve judgement on the usefulness of the name natrofairchildite until more data become available.

EVANS and MILTON (1973) have proposed a nomenclature for the polymorphs of the dehydration product, $Na_2Ca(CO_3)_2$, of gaylussite and pirssonite: eugsterite, α-N, β-N and γ-N. BILLHARDT (1969) has used the terms DC_T, DC_M and DC_H for the synthetic polymorphs of $Na_2Ca(CO_3)_2$. FRANKIS and MCKIE (1973) have proposed the term "synthetic nyerereite" for the 10 Å orthorhombic polymorph of $Na_2Ca(CO_3)_2$ which is evidently a structural modification produced by quenching from a high-temperature hexagonal structure. All studies of $Na_2Ca(CO_3)_2$, except for that of FRANKIS and MCKIE, have been by x-ray powder methods or DTA (WILBURN, METCALFE and WARBURTON, 1965); rationalization of the nomenclature of the $Na_2Ca(CO_{32})$ polymorphs must await further single-crystal study and in particular the structure determination of the 10 Å orthorhombic polymorph currently in progress in this laboratory. What information is now available however suggests that all the $Na_2Ca(CO_3)_2$ polymorphs are derivative from the high-nyerereite aristotype.

Acknowledgements

We are indebted to Dr. C. H. MCKIE for help with computing generally and for critical discussion of this paper, to Dr. G. M. SHELDRICK for the use of his crystallographic programs, to Mr. K. O. RICKSON for invaluable technical help with the x-ray work and to Dr. CHARLES MILTON for his most generous gift of specimens of lengaite and especially for his sustained interest in the problems of the mineralogy of the Na_2CO_3—K_2CO_3—$CaCO_3$ system. One of us (E.J.F.) has to acknowledge the grant of a Natural Environment Research Council Studentship during the tenure of which his contribution to this work was performed.

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