

Crystal structure of natrite, $\gamma\text{-Na}_2\text{CO}_3$

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With 3 figures and 5 tables

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Abstract: A new occurrence of natrite, $\gamma\text{-Na}_2(\text{CO}_3)$, was discovered as monomineral lenses (more than 20 cm in size) in pegmatites of Mt. Koashva, Khibiny alkaline massif, Kola peninsula, Russia. Electron microprobe, XRD, IR and optical data for natrite of this new occurrence are given. A single-crystal fragment isolated from polysynthetic twinned material was used for collecting X-ray single-crystal data: $\lambda(\text{MoK}\alpha) = 0.71073 \text{ \AA}$, $C2/m$, $a = 8.905(4)$, $b = 5.237(3)$, $c = 6.045(2) \text{ \AA}$, $\beta = 101.32(3)^\circ$, 1290 reflections. Satellite reflections on oscillation photographs indicate the presence of modulation in the structure of natrite. The average structure converged to $R = 0.106$; models with (i) all atomic positions split and (ii) anharmonic thermal displacement parameters applied to unsplit atoms converged to $R = 0.036$ and 0.029 respectively. The structure of natrite contains [001] columns formed by face sharing Na octahedra and further 7-fold coordinated Na polyhedra; the columns are connected by CO_3 groups.

Key words: natrite, crystal structure, carbonate, modulated structure, Khibiny.

Introduction

Natrite, natural anhydrous sodium carbonate Na_2CO_3 , was discovered in Lovozero (Mt. Karnasurt) and Khibiny (Mt. Rasvumchorr) alkaline massifs, Kola Peninsula, Russia and described as a new mineral in 1982 by A. P. KHOMYAKOV. Later it was found also in the alkaline complex of Mont Saint-Hilaire, Quebec, Canada (HORVATH & GAULT 1990). In all these localities, natrite occurs in hyperagpaitic rocks and their pegmatites.

Natrite represents the most rare species in the group of six natural Na carbonates which are usually considered under the name “soda minerals”. The other five minerals of the group are nahcolite, NaHCO_3 , wegscheiderite, $\text{Na}_5\text{H}_3(\text{CO}_3)_4$, thermonatrite, $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$, natron, $\text{Na}_2\text{CO}_3 \cdot 10 \text{H}_2\text{O}$, and trona, $\text{Na}_3\text{H}(\text{CO}_3)_2 \cdot 2\text{H}_2\text{O}$. The structures of these minerals are known and only natrite does not contain hydrogen atoms, a peculiarity which allows to consider this mineral as an endogenous high temperature species.

In spite of its relatively simple chemical composition and the availability of large size crystals (1 cm and more), the crystal structure of natrite was not studied so far mainly because of polysynthetic twinning. By comparison with the XRD powder pattern of synthetic $\gamma\text{-Na}_2\text{CO}_3$ (BROUNS et al. 1964), KHOMEYAKOV (1982) assigned to natrite the following monoclinic unit cell: $a = 8.906(1)$, $b = 5.238(1)$, $c = 6.045(1)$ Å, $\beta = 101.21(1)^\circ$, $Z = 4$. However, several reflections in the XRD powder patterns of both natrite and synthetic $\gamma\text{-Na}_2\text{CO}_3$ are not indexed with this cell.

The structures of three synthetic polymorphs of Na_2CO_3 are known: two monoclinic (β and γ) and one hexagonal (α); they are stable in different temperature ranges (BROUNS et al. 1964) and their cell parameters are given in Table 1. At room temperature the diffraction pattern of $\gamma\text{-Na}_2\text{CO}_3$, which is stable below 360°C , contains satellite reflections typical of incommensurate modulated structure. The average structure of this phase was refined to R 0.128 for 313 reflections by DUBBELDAM & DE WOLFF (1969). Later on, VAN AALST et al. (1976) characterised the modulation using 758 main reflections and 1152 first-order satellites with final $R = 0.108$. At 360°C $\gamma\text{-Na}_2\text{CO}_3$ transforms into $\beta\text{-Na}_2\text{CO}_3$ which is stable up to 489°C . This transition is accompanied by a continuous weakening of the satellite reflections; according to DE PATER (1979) the structure of $\beta\text{-Na}_2\text{CO}_3$ is identical to the basic structure of the γ -phase. The $\gamma \rightarrow \beta$ transition is followed by the hexag-

Table 1. Crystal data for natrite, gregoryite and their synthetic polymorphs.

Compound	a (Å)	b (Å)	c (Å)	β (°)	Symmetry	References
$\gamma\text{-Na}_2\text{CO}_3$	8.904(3)	5.239(2)	6.042(2)	101.35(2)	$C2/m$	VAN AALST et al. 1976
$\beta\text{-Na}_2\text{CO}_3$	9.013(2)	5.237(2)	6.321(2)	96.83(2)	$C2/m$	DE PATER 1979
$\alpha\text{-Na}_2\text{CO}_3$	5.20	5.20	6.50		$P6_3mc$	BROUNS et al. 1964
Gregoryite	5.22	5.22	6.58		$P6_3mc$	CHURCH & JONES 1995
Natrite	8.905(4)	5.237(3)	6.045(2)	101.32(3)	$C2/m$	This work

onal α -form which appears at 489 °C without discontinuities in the cell parameters (DUBBELDAM & DE WOLFF 1969). Due to these transitions, the polysynthetic twinning observed in natrite is considered as an indication of a possible monoclinic \leftarrow hexagonal transformation of the original mineral (KHOMYAKOV 1982). Gregoryite, $(\text{Na},\text{K},\text{Ca})_2\text{CO}_3$, is a poorly characterised natural analogue of α - Na_2CO_3 reported from carbonatites in northern Tanzania (CHURCH & JONES 1995, GITTINS & MCKIE 1980).

Recently a new occurrence of natrite has been discovered in a hyperalkaline pegmatite at Mt. Koashva (south-eastern part of Khibiny massif). The good quality of the crystals occurring in the new locality allowed us to improve the mineralogical and structural characterisation of this mineral. The results of this work are reported below.

Occurrence

Zonal irregular lenses, about 1 m thick, of pegmatite occur at the contact between urtite and apatite–nepheline rocks at Mt. Koashva. In their outer zones these lenses contain major light-green orthoclase, grey nepheline, amphibole, dark-green aegirine–salite and minor sodalite, eudialyte, titanite, rinkite and lamprophyllite. The core of the lenses mainly consists of green fibrous aegirine with minor microcline, sodalite, pectolite, villiaumite and natrite. For the latter mineral this is the richest occurrence ever found: monomineral natrite lenses can be larger than 20 cm. Crystals of lomonosovite and pectolite, grains of villiaumite and rare tabular microcline and rhombododecahedral sodalite are found within the massive coarse-grained natrite. Besides, sphalerite, fluorcaphite and thermonatrite partially replace natrite.

Natrite from Mt. Koashva is colourless and transparent with vitreous lustre and a calcite-like aspect. In humid air, the surface of natrite quickly transforms into thermonatrite. Also the present natrite crystals show the same system of three cleavages which are parallel to the directions of lamellar polysynthetic twinning as reported by KHOMYAKOV (1982). However, in our case the lamellae are thicker than 0.1 mm and a single crystal suitable for XRD study could be extracted.

Experimental

Electron probe microanalyses (Institute of Mineralogy, Geochemistry and Crystal Chemistry of Rare Elements RAS, Moscow; "Camebax micro

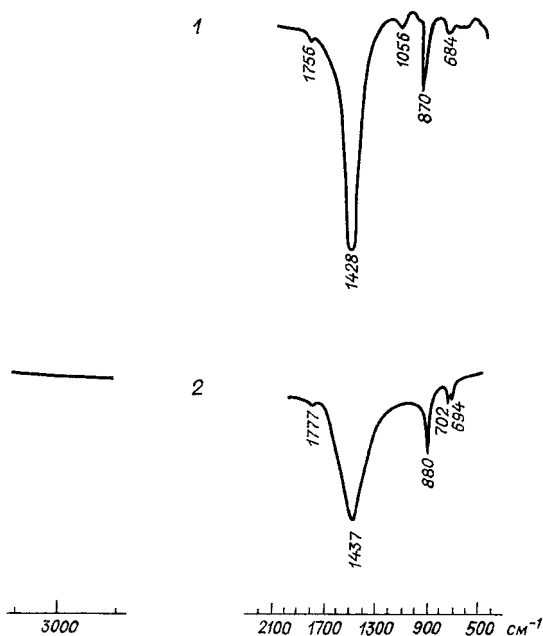


Fig. 1. IR-spectra for the holotype sample of natrite (KHOMYAKOV 1982) (1) and for natrite studied in the present work (2).

beam" electron probe) proved the presence of Na as a main element and about 0.1–0.2% of K_2O .

Optical properties of natrite from Mt. Koashva practically correspond to those reported by KHOMYAKOV (1982). The IR spectrum (spectrophotometer Specord 75 IR; KBr pellet; polystirol and gaseous NH_3 as standards) contains five absorption bands at 1777, 1437, 880, 702, and 694 cm^{-1} (Fig. 1). The non-degenerate band at 880 cm^{-1} corresponds to the out-of-plane bending vibration of the $(\text{CO}_3)^{2-}$ -group; it is not split because in the structure there is only one crystallographically independent carbonate anion. The absence of the non-degenerate C–O–stretching vibrations in the region 1000–1100 cm^{-1} indicates a local axial symmetry of the planar $(\text{CO}_3)^{2-}$ -groups. The bands at 702 and 694 cm^{-1} correspond to the splitting of the degenerate in-plane bending vibrations of the $(\text{CO}_3)^{2-}$ -group as a result of the long-range resonance interactions between these groups. The IR-spectrum of the holotype natrite (KHOMYAKOV 1982) contains an additional absorp-

Table 2. Data collection and structure refinement parameters for natrite.

Chemical formula	Na_2CO_3
Unit formula weight	423.96
Absorption coefficient μ , mm^{-1}	0.49
Radiation and wavelength, \AA	$\text{MoK}\alpha$, 0.71069
Space group; Z	$C2/m$, 4
Unit cell dimensions (\AA) and angle ($^\circ$)	$a = 8.905(4)$, $b = 5.237(3)$, $c = 6.045(2)$ $\beta = 101.32(3)^\circ$
Unit cell volume, \AA^3	276.4(2)
$F(000)$	208.0
Density (calc.), g/cm^3	2.55
Density (obs.), g/cm^3	2.54
Crystal size, mm	$0.35 \times 0.25 \times 0.2$
Diffractometer	Siemens P4
Index ranges	$-14 \leq h \leq 0$, $-8 \leq k \leq 8$, $-9 \leq l \leq 9$
Standard reflection	Every 50 reflections
Collected reflections	1290
Independent reflections	669; $R_{\text{merge}} = 0.02$
Reflections with $I > 2\sigma(I)$	620
Refinement method	Full-matrix least-squares on F^2

tion band at 1056 cm^{-1} which might be due either to the presence of some impurities or to the deviation of the $(\text{CO}_3)^{2-}$ -group from planarity.

Single-crystal X-ray diffraction data were collected (Table 2) and the following unit cell parameters were obtained by Least-Squares refinement of 18 reflections ($15^\circ \leq 2\theta \leq 30^\circ$): $a = 8.905(4)$, $b = 5.237(3)$, $c = 6.045(2)\text{ \AA}$, $\beta = 101.32(3)^\circ$; $V = 276.4(2)\text{ \AA}^3$. Absorption correction by the semi-empirical ψ -scan method of NORTH et al. (1968) was applied. Satellite reflections revealing that the real structure of natrite is modulated have been detected on oscillation photographs but were not collected.

The average crystal structure of natrite was determined by direct methods (SHELX-97; SHELDRIK 1997) and refined [SHELX-97 and JANA98 (PETRICEK & DUSEK 1998)] in the space group $C2/m$, $Z = 4$. The average structure with unsplit atomic positions and with relatively high values of equivalent thermal displacement parameters converged to $R_{\text{aniso}} = 0.106$ for 620 reflections with $I > 2\sigma(I)$. The largest residues of electron density were 1.21 e/\AA^3 at 0.47 \AA from O(1) and -1.36 e/\AA^3 at 0.78 \AA from Na(2). In order to approximate the average structure to the real modulated structure

Table 3. Atom coordinates (1st line) and *B* isotropic equivalent displacements (Å², 2nd line) for natrite (for the models see text).

Atoms	Model I			Model II		
Na (1)	0	0.356 (2)	0	0	0	0
		1.62 (2)			2.27 (2)	
Na (2)	0	0.425 (1)	½	0	0	1/2
		1.53 (2)			2.46 (2)	
Na (3)	0.17050 (5)	0.54531 (8)	0.74786 (8)	0.17047 (6)	1/2	0.7478 (1)
		2.16 (1)			3.22 (2)	
C	0.16394 (9)	0.4623 (2)	0.2491 (1)	0.1645 (2)	1/2	0.2497 (2)
		1.21 (3)			1.85 (5)	
O (1)	0.1237 (1)	0.2438 (2)	0.3089 (2)	0.1023 (1)	0.2944 (2)	0.2859 (1)
		2.89 (2)			4.58 (3)	
O (2)	0.28979 (7)	0.492 (2)	0.1775 (1)	0.2894 (1)	1/2	0.1781 (1)
		2.00 (3)			1.81 (2)	
O (3)	0.0800 (1)	0.6573 (2)	0.2622 (2)			–
		2.83 (2)				

of synthetic γ -Na₂CO₃ (VAN AALST et al. 1976), the following procedures of refinement were adopted: (i) all atomic positions were split (Table 3) according to the model I adopted by DUBBELDAM & DE WOLFF (1969) for synthetic γ -Na₂CO₃; (ii) anharmonic thermal displacement parameters [Gram-Charlier expansion of the tensor F(ijklmn)] were applied to unsplit atoms [model II]. The split model converged to $R = 0.036$ for the 620 reflections with $I > 2\sigma(I)$ and anisotropic displacement parameters for all atoms. The largest residues of electron density were $0.43 \text{ e}/\text{\AA}^3$ at 0.52 \AA from O(3) and $-0.21 \text{ e}/\text{\AA}^3$ at 0.46 \AA from Na(2). The introduction of the anharmonic thermal displacement factors for all atoms led to $R = 0.029$ for the same 620 reflections and the largest residues of electron density were $0.28 \text{ e}/\text{\AA}^3$ at 1.09 \AA from C and $-0.19 \text{ e}/\text{\AA}^3$ at 1.04 \AA from Na(1). Results of the refinements of atomic coordinates in both models and the interatomic distances for model II are summarised in Table 3 and 4, respectively. Intensity calculations (YVON et al. 1977) for Koashva natrite (Table 5) demonstrated an agreement with powder diffraction data despite some discrepancies between I_{obs} and I_{calc} presumably due to preferred orientation effects related to the

Table 4. Selected bond lengths (Å) and angles (°) in the average structure of natrite (nonsplit model) and in the modulated structure of γ -Na₂CO₃ (VAN AALST et al. 1976).

Natrite		γ -Na ₂ CO ₃		
			Min	Max
Na(1)–O(2)	2.339 (1) × 2	Na(1)–O(2)	2.33 × 2	2.34 × 2
–O(1)	2.361 (1) × 4	–O(1)	2.34 × 4	2.45 × 4
Na(2)–O(1)	2.312 (2) × 4	Na(2)–O(1)	2.31 × 4	2.36 × 4
–O(2)	2.423 (1) × 2	–O(2)	2.42 × 2	2.44 × 2
Na(3)–O(1)	2.584 (1) × 2	Na(3)–O(1)	2.39 × 2	2.80 × 2
–O(2)	2.609 (1)	–O(2)	2.60	2.62
–O(1)	2.628 (1) × 2	–O(1)	2.34 × 2	2.92 × 2
–O(2)	2.669 (1) × 2	–O(2)	2.42 × 2	2.93 × 2
–O(1)	2.942 (1) × 2	–O(1)	2.65 × 2	3.25 × 2
C–O(1)	1.250 (1) × 2	C–O(1)	1.25 × 2	1.31 × 2
–O(2)	1.270 (2)	–O(2)	1.28	1.29

easy cleavages of natrite. In contrast to XRD powder diagram given by KHOMEYAKOV (1982) all reflections with $I > 1\%$ were indexed.

The figures were obtained with the use of the program ATOMS (DOWTY 1995).

Discussion

The average structure of natrite (Fig. 2) differs from the modulated structure of γ -Na₂CO₃ reported by VAN AALST et al. (1976) only in details which are discussed below. The main common elements of their mixed polyhedral framework are [001] columns formed by alternating Na(1) and Na(2) octahedra. These octahedra share a face and the columns are connected by CO₃ triangles along [010] and [100]. Both in the average and modulated structure of VAN AALST et al. (1976), Na(1) and Na(2) have quite regular octahedral coordination (Table 4) with Na–O distances in the range 2.339(1) – 2.361(1) Å and 2.312(2) – 2.423(1) Å respectively. Instead, similarly to the modulated structure of γ -Na₂CO₃, where Na(3) occupies a larger site and is surrounded by nine oxygen atoms with Na–O distances in the range 2.60–2.95 Å (VAN AALST et al. 1976), in natrite this cation has

Table 5. X-ray powder data* for natrite from Mt. Koashva, Khibiny.

I_{obs}	I_{calc}	$d_{\text{obs}}, \text{\AA}$	$d_{\text{calc}}, \text{\AA}$	h	k	l
1	2	3.892	3.900	2	0	-1
3	11	3.401	3.417	1	1	1
5	15	3.215	3.226	2	0	1
100	76	2.950	2.964	0	0	2
3	14	2.702	2.712	2	0	-2
5	44	2.614	2.619	0	2	0
7	43	2.589	2.597	1	1	-2
8	80	2.539	2.544	3	1	0
22	100	2.359	2.366	1	1	2
18	47	2.249	2.255	2	0	2
6	28	2.188	2.193	4	0	-1
9	36	2.173	2.174	2	2	-1
2	15	2.029	2.033	2	2	1
6	26	1.947	1.950	4	0	-2
5	37	1.882	1.884	2	2	-2
6	16	1.707	1.709	2	2	2
2	8	1.677	1.677	4	2	0
1	9	1.631	1.633	4	0	-3
2	7	1.610	1.613	4	0	2
2	4	1.575	1.577	0	2	3
	4		1.577	5	1	-2
2	5	1.563	1.564	4	2	-2
	6		1.564	2	2	-3
1	3	1.525	1.524	5	1	1
1	5	1.494	1.497	3	3	0
	4		1.495	2	0	-4
4	5	1.480	1.482	6	0	-1
	11		1.482	0	0	4
1	4	1.455	1.458	1	3	2
	4		1.455	6	0	0
1	2	1.415	1.418	3	3	1
1	7	1.388	1.388	3	1	-4

* DRON UM-1 diffractometer (CuK $_{\alpha}$ -radiation, Ni-filter).

7+2-fold coordination with 7 Na–O distances in the range 2.584(1) – 2.669(1) Å and two elongated Na–O distances 2.942(1) Å (Table 4). The CO₃ group is almost regular (Table 4) and well agrees with the average val-

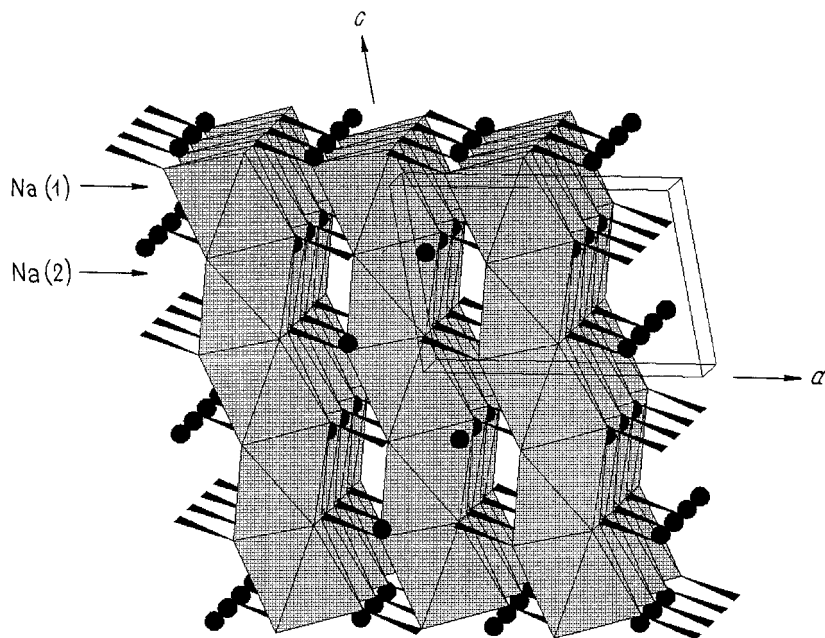


Fig. 2. Perspective view of the average structure of natrite. Black circles represent Na(3) sites.

ues $C-O = 1.284 \text{ \AA}$, $O-C-O = 120.0^\circ$ reported by ZEMANN (1981). According to the classification of LIMA-DE-FARIA (1994) the structure of natrite can be considered as a group structure.

Apart from the average structures of natrite (this study) and $\gamma\text{-Na}_2\text{CO}_3$ (DUBBELDAM & DE WOLFF 1969), VAN AALST et al. (1976) revealed that the supercell of modulated $\gamma\text{-Na}_2\text{CO}_3$ contains 22 unit subcells. All Na and carbon atoms exhibit an overall sinusoidal modulation with an amplitude close to 0.33 \AA along $[010]$. The modulation vector is perpendicular to the plane of the CO_3 groups and the orientational modulation of CO_3 anions is out of phase with the overall modulation.

Projections of both unsplit and split structures of natrite are shown in Fig. 3 together with a projection of the $\beta\text{-Na}_2\text{CO}_3$ structure. Also this latter structure has been described (DE PATER 1979) by using both an average ($R = 0.15$) and a split ($R = 0.07$) model. The pattern of splitting differs substantially in the natrite and $\beta\text{-Na}_2\text{CO}_3$ structures. In both structures the space

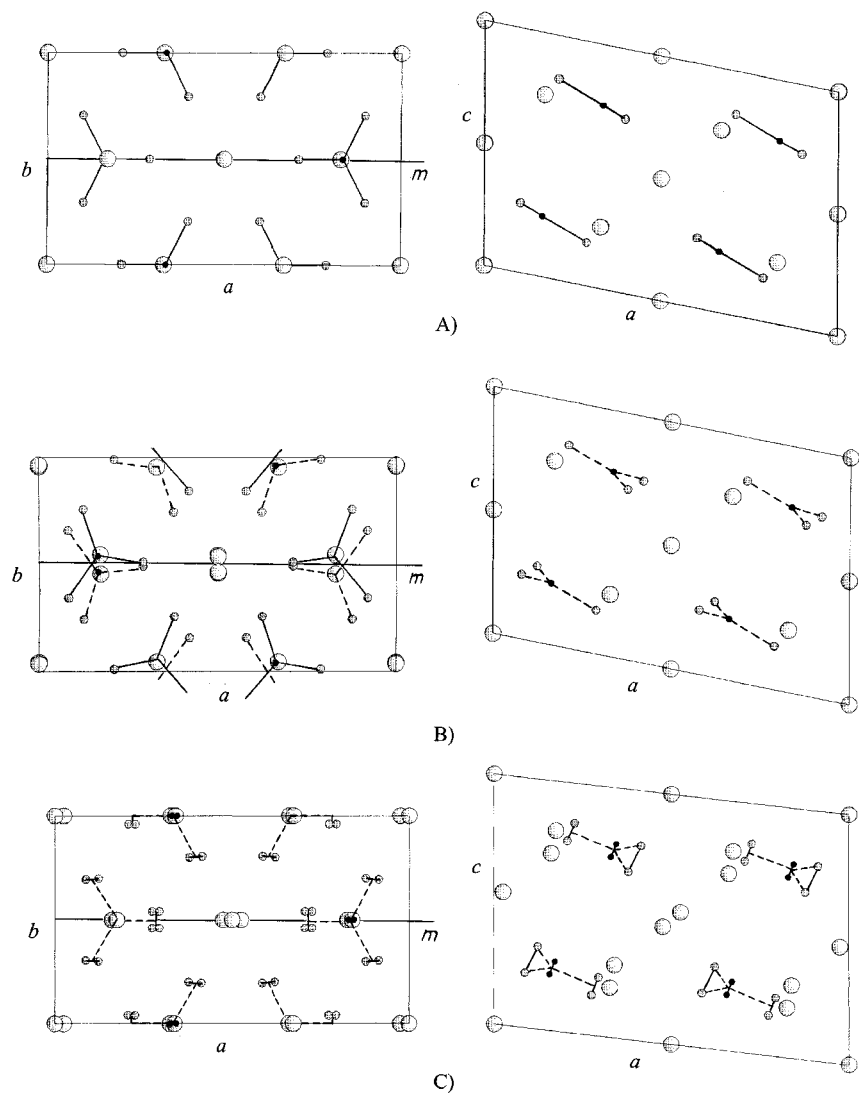


Fig. 3. Projections on (001) and (010) of the structure of synthetic γ -Na₂CO₃ model II (A) and model I (B) and of synthetic β -Na₂CO₃ (C). Large and small blank circles represent Na and O respectively; small filled circles represent C.

group $C2/m$ allows two types of splitting for the atoms that lie on the mirror plane: the splitting can be either perpendicular or parallel to the mirror plane. In β - Na_2CO_3 only one oxygen atom splits up perpendicularly to the mirror plane; the splitting of the other atoms occurs instead mainly in the mirror plane. In natrite the splitting of the atoms revealed in model I is mostly observed perpendicular to the mirror plane.

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