

COMMUNICATIONS FROM THE OXFORD MINERALOGICAL
LABORATORY. No. XVI.

*Contributions to the study of parallel growths of
different substances.*

By STEFAN KREUTZ, Ph.D.

[Communicated by Principal Miers, and read January 26, 1909.]

1. *Parallel Growth on Barytocalcite.*

MR. T. V. BARKER¹ has lately shown that the parallel growth of isostructural substances upon one another is conditioned by similarity of molecular volume. This very important conclusion invites further investigation from this new point of view, and Professor H. A. Miers suggested to me, while working in his laboratory last summer, that I should make experiments on the parallel growth of sodium nitrate on the pseudo-rhombohedral mineral barytocalcite.

The first experiments, which were made on crystals of barytocalcite in the Oxford collection, were unsuccessful, the crystals employed being small and somewhat impure.² Later, I received, from the Museum of Practical Geology in London, some very good and perfectly pure crystals of barytocalcite from Blagill, near Alston, in Cumberland. With these crystals I succeeded in obtaining parallel growths of sodium nitrate on all the cleavage-faces—*m* (110) and *c* (001)—just like those of sodium nitrate on calcite.

¹ Mr. Barker's papers are :—

- (1) 'Contributions to the theory of isomorphism based on experiments on the regular growth of crystals of one substance on those of another.' Journ. Chem. Soc., 1906, vol. lxxxix, pp. 1120-1158.
- (2) 'On the regular growth of soluble salts on each other.' Min. Mag., 1907, vol. xiv, pp. 235-257.
- (3) 'The question of a relation between parallel growths of crystals and isomorphous miscibility, and the bearing of parallel growths on questions of isomorphism.' Min. Mag., 1908, vol. xv, pp. 42-53.

See also Zeits. Kryst. Min., 1908, vol. xiv, pp. 1-59.

² It is probably the same material which yielded negative results to Mr. Barker.

On the cleavage-face c (001) the rhombohedra of sodium nitrate are so orientated that they extinguish simultaneously with the barytocalcite; and on m (110) the rhombohedral edges of the sodium nitrate are parallel to the prism-edges of the barytocalcite. To obtain this result it is necessary to use very pure crystals and fresh cleavage-faces. The best method is to immerse the cleaved crystal in a warm, saturated solution of sodium nitrate for only a short time, according to the method recommended by Mr. Barker for calcite.

In this way it is possible to obtain on the same crystal of barytocalcite three cleavage-faces covered with microscopic rhombohedra of sodium nitrate in parallel position. The parallel growth seemed to be more perfect and easy to obtain on the faces (110) than on (001), but the difference is not great. If the solution of sodium nitrate is very strong, the regular deposit of crystals forms a crust, as in a zoned crystal. In none of my experiments have the rhombohedra of sodium nitrate been obtained in twinned position (twin-plane (110)), and in this respect barytocalcite differs from calcite.

Barytocalcite is almost isostructural with the rhombohedral sodium nitrate and calcite. There are two perfect cleavages parallel to the prism m {110}, and that parallel to the base c {001} is almost as perfect. On (001) there may sometimes be distinguished a fine striation parallel to the edge [010], like that which is produced on calcite by gliding parallel to (110). This indicates that there is only one glide-plane, viz., that parallel to (100).

The optical properties, and especially the position of the principal directions of vibration, are very similar in both barytocalcite and calcite, as has been shown by Mallard,¹ who called attention to the resemblance between these two minerals.

It is therefore possible to compare the topic parameters of barytocalcite and of sodium nitrate and calcite.² For purposes of comparison we can regard the cleavage rhombohedra of calcite and sodium nitrate as rhombic prisms with an oblique basal plane. The topic parameters are then χ , ψ , ω , where $\chi = \psi$, and ω is only different from them in barytocalcite. In the table below, ξ and η are the dimensions of the structural units along the long and short diagonals of the rhombic meshes. In

¹ E. Mallard, 'Sur l'alstonite et le barytocalcite.' (Note posthume.) Bull. Soc. franç. Min., 1895, vol. xviii, pp. 7-12.

² W. Haidinger ('Handbuch der Mineralogie,' 1845, p. 279) described the regular intergrowth of crystals of barytocalcite and calcite. See also F. Wallerant, Bull. Soc. franç. Min., 1902, vol. xxv, pp. 183, 210.

barytocalcite the values for the basal and prismatic planes are distinguished as ξ_b and ξ_p respectively. The topic mesh area¹ of the plane (hkl) is denoted by $\mathfrak{S}_{(hkl)}$.

Barytocalcite.	Sodium nitrate.	Calcite.
$\frac{1}{2}$ Mol. Vol. = 41.47	Mol. Vol. = 37.8	Mol. Vol. = 36.8
$a:b:c = 0.7717:1:0.6254$	$a:b:c = 0.79956:1:0.64017$	$a:b:c = 0.81100:1:0.64376$
$\beta = 106^\circ 8'$	$\beta = 110^\circ 46'$	$\beta = 109^\circ 8'$
$\chi = \psi = 3.560$	$\chi = \psi = \omega = 3.460$	$\chi = \psi = \omega = 3.413$
$\omega = 3.524$		
$\xi_b = 4.348, \eta_b = 5.635$	$\xi = 4.322, \eta = 5.405$	$\xi = 4.300, \eta = 5.302$
$\xi_p = 4.453, \eta_p = 5.509$		
$\mathfrak{S}_{(001)} = 12.259$	$\mathfrak{S}_{(100)} = 11.679$	$\mathfrak{S}_{(100)} = 11.408$
$\mathfrak{S}_{(110)} = 12.266$		
$[1\bar{1}0][110] = \alpha' = 104^\circ 41'$	$\alpha = 102^\circ 42\frac{1}{2}'$	$\alpha = 101^\circ 55'$
$[1\bar{1}0][00\bar{1}] = \alpha'' = 102^\circ 7'$		

The values for χ , ξ , &c., and \mathfrak{S} show a very close agreement. It would perhaps be more correct to double the molecular volume of sodium nitrate, in order to make it comparable with that of barytocalcite (82.94). This agrees with the view of Tschermak, who writes the formula of calcite as $\text{Ca}_2\text{C}_2\text{O}_6$, to make intelligible the isomorphism with dolomite, CaMgC_2O_6 . The topic parameters would then be: for barytocalcite, $\chi = \psi = 4.485$, $\omega = 4.440$; for sodium nitrate, $\chi = \psi = \omega = 4.319$; and for calcite, $\chi = \psi = \omega = 4.301$. These also are very similar.

According to the view of Groth, barytocalcite is a double salt, BaCO_3 , CaCO_3 , and this is confirmed by Becker's chemical analyses of the mineral. In agreement with this view is also the constancy of the angles measured on different crystals. I found $mm = 73^\circ 9'$ and $mc = 77^\circ 11'$, whilst Brooke gave the values $mm = 73^\circ 6'$ and $mc = 77^\circ 6'$.

The specific gravity of barytocalcite was determined, on about 2.2 grams of material in a pycnometer, as 3.71 at 20°C . If we calculate the specific gravity of an isomorphous mixture of similar composition, containing 57.7% by volume of witherite and 42.3% by volume of aragonite, we get 3.696. The value found is a little higher, as is often the case in double salts. Thus, dolomite has a density of 2.87, while the value calculated for an isomorphous mixture is 2.843 (Retgers).

¹ Compare E. Sommerfeldt, 'Physikalische Kristallographie,' 1907, p. 106.

The observed indices of refraction are also higher (except α)¹ than those calculated for an isomorphous mixture of aragonite and witherite. Mallard (loc. cit.) has measured the indices of refraction of witherite, barytocalcite, and alstonite; he found for barytocalcite the values $\alpha = 1.525$, $\beta = 1.684$, $\gamma = 1.686$. On calculating the indices of a mixture as the average of those for aragonite and witherite (the molecular ratio in barytocalcite being 1:1), he obtained $\alpha = 1.529$, $\beta = 1.679$, $\gamma = 1.681$. If, however, we take the indices of refraction of a mixed crystal as proportional to the percentages by volume of its components,² we get $\alpha = 1.529$, $\beta = 1.678$, $\gamma = 1.681$.

On ignition in a platinum crucible, barytocalcite loses easily 15.4–15.7 % of its weight, and afterwards the loss is very slow. Since the total amount of carbon dioxide theoretically present is 29.6 %, the half that is more readily lost must be combined with the calcium (barium carbonate remaining practically unaltered at a red-heat).

The resistance to solution offered by the faces of the two forms {110} and {001} of barytocalcite is different, as shown by the treatment of a crystal with a dilute solution of citric acid: the face (001) is at once roughened, while the faces (110) remain smooth.

The Meigen reaction for aragonite is also shown very strongly by barytocalcite.

2. *Parallel Growths on Rhodochrosite and Chalybite.*

Mr. Barker has drawn attention to the fact that sodium nitrate gives only irregular deposits on cleavage-surfaces of the rhombohedral carbonates isomorphous with calcite, namely chalybite, rhodochrosite, breunnerite, &c. I have therefore attempted to obtain regular growths of another soluble salt upon these minerals.

The rhombohedral modification of lithium nitrate (LiNO_3) is isostructural with calcite, and has nearly the same molecular volume as chalybite and rhodochrosite. But since this modification is unstable at the ordinary temperature (20° C.), experiments with it present some difficulty. A cleavage-fragment of rhodochrosite³ or of chalybite was suspended by a

¹ This comparison is not altogether satisfactory, and I hope to return to the discussion of the optical properties of barytocalcite and alstonite.

² In some cases neither method is exact, according to G. Wulff, *Zeits. Kryst. Min.*, 1907, vol. xlii, p. 558.

³ Rhodochrosite from the John Reed mine, Alicante, Colorado.

thread in a hot, saturated solution of lithium nitrate, and after removal from the solution it was kept warm; it was thus possible to obtain rhombohedral crystals of lithium nitrate on the surface of the rhodochrosite and chalybite. The edges of the microscopic crystals are almost parallel to the rhombohedral edges of the rhodochrosite or chalybite, like those of sodium nitrate on calcite. These crystals being deliquescent, it is, unfortunately, not possible to preserve them for more than a few minutes, but they may be kept for a longer time in oil or Canada-balsam.

Troost,¹ who obtained the rhombohedral phase of lithium nitrate at 15° C., determined its geometrical properties, and this was also done later by Retgers. The points of equilibrium of the different phases of $\text{LiNO}_3 + n\text{Aq}$ have been determined by Donnan and Burt,² who found that above 61.1° C. the stable phase is LiNO_3 ; between 61.1° and 29.6° C., $\text{LiNO}_3 + \frac{1}{2}\text{Aq}$.; and below 29.6° C., $\text{LiNO}_3 + 3\text{Aq}$.

The molecular volumes and topic parameters are approximately as follows:—

	Mol. Vol.	χ	$\mathfrak{F}_{(100)}$	α	$c : a$
Lithium nitrate (LiNO_3) ...	29.59	3.181	9.887	$102^\circ 16\frac{1}{2}'$	0.843
Rhodochrosite (MnCO_3) ...	31.19	3.247	10.275	102 50	0.818
Chalybite (FeCO_3) ...	29.35	3.204	10.000	103 $4\frac{1}{2}$	0.819

The values for rhodochrosite are those given by Groth;³ and the specific gravity (3.949) of pure chalybite is calculated, according to Retgers's rule, from the value (3.937) determined by Hutchinson⁴ on analysed Cornish crystals (assuming the specific gravities CaCO_3 2.72, MnCO_3 3.65, and MgCO_3 3.0).

I was unable to obtain a regular growth of lithium nitrate on calcite, although its angles show a closer correspondence than those of rhodochrosite (the rhombohedral angle of lithium nitrate being $105^\circ 40'$, and of calcite $105^\circ 5'$). An attempt to obtain regular growths of lithium nitrate on fresh cleavage-flakes of mica was also unsuccessful, although the basal plane occurs upon its rhombohedral crystals.

The experiments described above are concordant with the results

¹ L. Troost, *Ann. Chim. Phys.*, 1856, ser. 3, vol. li, p. 134.

² F. G. Donnan and B. C. Burt, *Journ. Chem. Soc.*, 1903, vol. lxxxiii, p. 335.

³ P. Groth, '*Chemische Kristallographie*,' 1908, Teil ii, p. 207.

⁴ A. Hutchinson, *Min. Mag.*, 1903, vol. xiii, p. 210.

obtained by Mr. Barker, and with the views now held as to the structure and growth of crystals.¹

I take this opportunity of expressing my thanks to Professor Miers, who allowed me to work in his laboratory, for his suggestions and advice, as well as to Dr. J. J. H. Teall for the loan of material from the Museum of Practical Geology, without which this work could not have been carried out.

Cracow, Austria.

¹ Compare H. A. Miers, 'Some recent research upon the birth and affinities of crystals.' *Science Progress*, 1907, vol. ii, pp. 121-134.
