

On the Relations Between Structure and Morphology of Crystals. III

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The morphology of barite is deduced from the structure. It is found that there are six *F*-forms, namely {001}, {010}, {211}, {210}, {101} and {100}. An estimate of the relative importance of these faces is obtained by approximate calculations of the attachment energies. The results are in satisfactory agreement with observations.

The form {011} is found to be a *K*-face. Its relatively high morphological importance is explained in terms of dehydration and impurity effects.

All other forms of some importance appear to be *S*-forms. Crystals of some compounds isotype with barite, grown from pure aqueous solutions, show only the six *F*-forms, and {011} due to the dehydration effect. This suggests the assumption that the occurrence of *S*- and *K*-forms on minerals is due to a period of dissolution followed by growth in an impure environment.

1. Introduction

In Parts I and II (Hartman & Perdok, 1955*a, b*) it was shown, by means of theoretical considerations, how the morphology of crystals can be deduced from the structure. In the present article the results obtained are applied to the structure of barite.

Barite has space group *Pnma* with $a = 8.8625$, $b = 5.4412$, $c = 7.1401$ Å. The positions of the barium and sulfur atoms are given in Table 1. In the following

Table 1. Positions of barium and sulfur atoms in the structure of barite

Atom	<i>x</i>	<i>y</i>	<i>z</i>	Atom	<i>x</i>	<i>y</i>	<i>z</i>
Ba(1)	0.182	$\frac{1}{2}$	0.161	S(1)	0.068	$\frac{1}{2}$	0.695
Ba(2)	0.318	$\frac{3}{4}$	0.661	S(2)	0.432	$\frac{3}{4}$	0.195
Ba(3)	0.682	$\frac{1}{4}$	0.339	S(3)	0.568	$\frac{1}{4}$	0.805
Ba(4)	0.818	$\frac{3}{4}$	0.839	S(4)	0.932	$\frac{3}{4}$	0.305

the sulfate ions as well as the barium ions are considered as point charges.

2. Bonds and P.B.C. vectors

High-energy bonds are found between Ba⁺⁺ ions and SO₄⁻ ions belonging to the first coordination sphere. Five types of bonds can be distinguished: every ion is surrounded by seven ions of the opposite sign, making with it two bonds *a*, two bonds *a'* and one of *b*, *c* and *d* each (see Fig. 1 and Table 2). The energy

Table 2. High-energy bonds in the barite structure

Bond	Between ions*	'Energy', 1/ <i>r</i> (Å ⁻¹)
<i>a</i>	S(1) and Ba(2)	0.284
<i>a'</i>	S(1) and Ba(4,100)	0.273
<i>b</i>	S(1) and Ba(1,001)	0.287
<i>c</i>	S(1) and Ba(1)	0.254
<i>d</i>	S(1) and Ba(3,100)	0.235

* The notation Ba(4,100) is used to denote the barium atom at a distance [100] from the barium atom Ba(4).

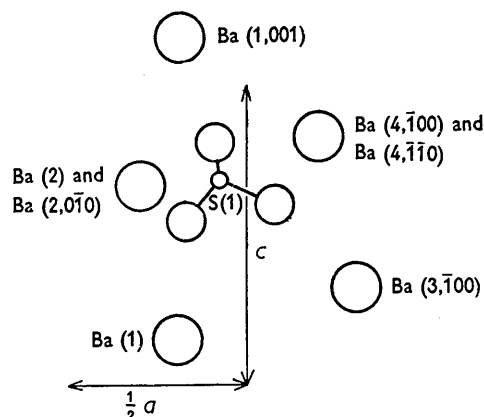


Fig. 1. Sulfate ion surrounded by seven barium ions in the structure of barite. The figure represents a projection on (010). Circles of intermediate size represent oxygen atoms, which are not shown in the other figures (cf. also Table 2 and Fig. 3(b)).

of these bonds, expressed in arbitrary units, is $1/r$, where r is the distance in Å between two ions.

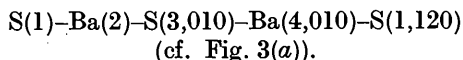
By combining these bonds, periodic bond chains can be constructed; for example, combination of bond

Table 3. P.B.C. vectors of the barite structure

P.B.C. vector	Atoms that form part of one period of a chain	Bonds per period
<i>A</i>	[$\frac{1}{2}$, 1, 0] S(1)-Ba(2)-S(3,010)	$a + a'$
<i>B</i>	[0, 1, 0] S(1)-Ba(2)-S(1,010)	$a + a$
<i>C</i>	[$\frac{1}{2}$, 0, 0] S(1)-Ba(2)-S(3)	$a + a'$
<i>D</i>	[0, 0, 1] Ba(1)-S(1)-Ba(1,001)	$c + b$
<i>E</i>	[1, 0, 1] Ba(1,100)-S(1,001)-Ba(3)-S(3)-Ba(1,001)	$c + d + b + d$
<i>F</i>	[$\bar{1}$, 1, 1] Ba(1,100)-S(4)-Ba(4)-S(3,010)-Ba(1,011)	$a' + c + a + d$
<i>G</i>	[1, 1, 0] S(1)-Ba(1,001)-S(2,001)-Ba(4)-S(1,110)	$b + a + d + a'$
<i>H</i>	[0, $\frac{1}{2}$, $\frac{1}{2}$] S(4)-Ba(3)-S(3) or S(4)-Ba(4)-S(3)	$a + b$ $c + a$

b with bond c gives the P.B.C. vector $[001]$. In Table 3 eight P.B.C. vectors are given.

The periods of the vectors do not always agree with the lattice periods. This is demonstrated clearly by the bond chain parallel to $[120]$. This chain is composed of bonds a and a' and runs



This part of the chain covers a structural period. Now the second half of the chain (from $S(3,010)$ to $S(1,120)$) can be obtained from the first half by the action of the glide plane a , parallel to (001) at height $\frac{3}{4}$. Therefore the period referred to bond energy is half the structural period. In the same way the energy period of the vector C is $[\frac{1}{2}, 0, 0]$ instead of $[100]$. The energy period of the vector H is half the structural period, owing to the action of the glide plane n , parallel to (100) .

3. F -forms

The eight P.B.C. vectors define twelve possible F -forms; seven of them appear to have F -character, the others being S -forms. The F -forms are $\{001\}$, $\{011\}$, $\{010\}$, $\{211\}$, $\{210\}$, $\{101\}$ and $\{100\}$ (cf. Fig. 2). Because F -forms contain two or more P.B.C. vectors, it must be possible to divide the whole structure into slices with stoichiometric composition parallel to the F -faces. For the F -faces (100) , (210) and (010) slices are shown in Fig. 3(a), which represents a projection of the structure on (001) . The elements of the F -faces are indicated in the figure; the period of an element can be characterized by a P.B.C. vector lying in it. One element of (210) can be characterized by the vector $[\frac{1}{2}, \bar{1}, 0]$ and one element of (010) can be characterized by the vector $[\frac{1}{2}, 0, 0]$. In the figure also a slice of the face (110) is shown. It is seen that the profile of this slice consists actually of alternating elements of (210) and (010) . Therefore (110) is not an F -face but an S_1 -face in the zone $[001]$. With the aid of a structure

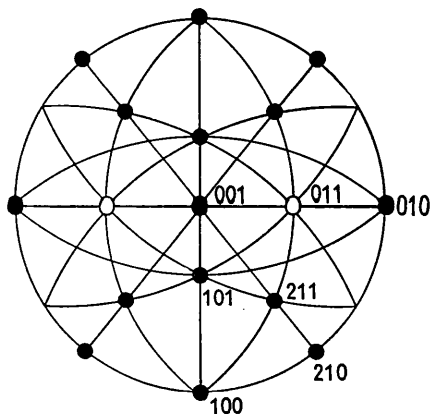


Fig. 2. P.B.C. vectors and F -forms of barite in stereographic projection. The P.B.C. vectors are represented by the corresponding zone circles. The faces of the particular K -form $\{011\}$ are indicated by open circles.

model it was found that also the forms $\{121\}$, $\{111\}$, $\{213\}$ and $\{212\}$ are S -forms.

The relative importance of F -forms is determined by the attachment energies. These energies have been calculated, taking into account only the bond energies given in Table 2. The results are summarized in Table 4, which also gives the attachment energies for each separate place of attachment.

As an example of the manner in which these quantities have been calculated $\{001\}$ and $\{101\}$ may be taken. In Fig. 3(b) two slices of (001) are shown. Suppose that ions of the upper slice attach to the lower one. The ion $Ba(1,003)$ forms bonds $b+d$ with the sulfate ions of the lower slice. $Ba(3,003)$ forms one bond c ; $S(2,003)$ forms bonds $c+d$, while $S(4,003)$ forms one bond b . Thus, the number of bonds formed per ion is: $(2b+2c+2d)/4$. The energy of a bond is taken (in very rough approximation) as $4e^2/r$, where r is the distance between two ions. These 'energies' are given in Table 2. Substitution of these energies in the expression $(2b+2c+2d)/4$ gives $0.388 \times 4 e^2 \cdot \text{\AA}^{-1}$ as the mean attachment energy per ion.

In the same way this quantity is calculated for $\{101\}$.

Table 4. Attachment energies of F -faces

Face	Bonds formed when an ion attaches to the surface	Energy	Mean attachment energy per ion in units $4 e^2 \cdot \text{\AA}^{-1}$
(001)	$b+d$	0.522	$(2b+2c+2d)/4 = 0.388$
	$c+d$	0.489	
	b	0.287	
	c	0.254	
(210)	a	0.284	$(2a+2a'+2d)/4 = 0.396$
	a'	0.273	
	$a+d$	0.519	
	$a'+d$	0.508	
(101)	b	0.287	$(4a'+2b+2c)/5 = 0.435$
	$2a'$	0.546	
	$2a'+c$	0.800	
	c	0.254	
	b	0.287	
(211)	a	0.284	$(4a+4a'+2b+2c+2d)/8 = 0.472$
	a'	0.273	
	$a+d$	0.519	
	$a'+d$	0.508	
	$a+b$	0.571	
	$a+c$	0.538	
	$a'+b$	0.560	
$a'+c$	0.527		
(100)	$2a'$	0.546	$(4a'+2d)/3 = 0.521$
	$2a'+d$	0.781	
	d	0.235	
(010)	$a+a'$	0.557	$a+a' = 0.557$
(011)	$a+a'+b$	0.844	$(4a+4a'+2b+2c+2d)/4 = 0.945$
	$a+a'+c$	0.811	
	$a+a'+b+d$	1.079	
	$a+a'+c+d$	1.046	

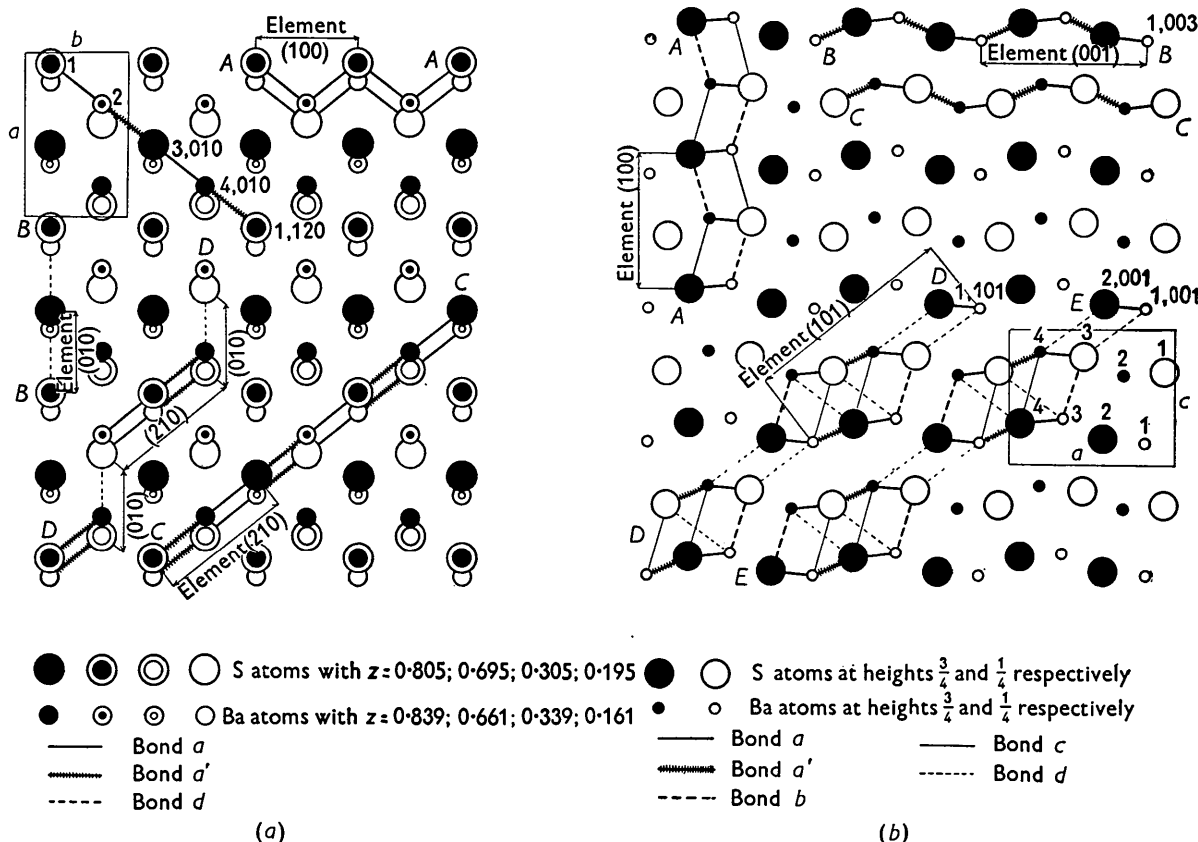


Fig. 3. (a) Projection of the structure of barite on (001). A-A is a slice of (100); B-B is a slice of (010); C-C is a slice of (210); D-D is a slice of (110), showing its S-character. The unit cell is outlined. (b) Projection of the structure of barite on (010). A-A is a slice of (100); B-B and C-C are slices of (001); D-D and E-E are slices of (101). The unit cell is outlined.

Suppose again that ions of the upper slice of (101) in Fig. 3(b) attach to the lower slice. Ba(1,101) forms bond b with the sulfate ions of the lower slice. Ba(3,100) forms bonds $c+2a'$; S(2,101) forms one bond c ; S(3,100) forms $2a'$; S(4,100) forms b . The ions Ba(2,200), Ba(4,100) and S(1,200) do not form bonds in the first coordination sphere with the ions of the lower slice, so that they cannot be attached to it. Hence the number of bonds formed per ion is $(4a'+2b+2c)/5$, which gives $0.435 \times 4 e^2 \cdot \text{\AA}^{-1}$ as the mean attachment energy per ion.

The attachment energies of the other faces have been calculated in the same way (Table 4). In Table 5 the order of the F -faces, obtained in this way, is compared with the observed order (P - and F -values have been taken from Braun, 1932), and with the order given by the law of Donnay & Harker (1937).

For the F -faces in the zones [001] and [120], the attachment energies have been calculated more precisely. To obtain these, the electrostatic potential of an ion with respect to a periodic bond chain was calculated for various chains parallel to the zones [001] and [120], by means of the method of Kleber (1940). The results are given in the following scheme:

Zone [001]; electrostatic potential of the sulfate ion S(1) with respect to chains of ions going through the ions indicated

	S(3,100)	
	0.217	
	Ba(4,100)	Ba(4,100)
	-0.054	-0.054
S(1,010)	S(1)	S(1,010)
-0.038	-	-0.038
	Ba(2,010)	Ba(2)
	0.302	0.302
	S(3)	
	-0.250	

Zone [001]; electrostatic potential of the barium ion Ba(1) with respect to chains of ions going through the ions indicated

	Ba(3,100)	
	-0.238	
	S(4,100)	S(4,100)
	0.264	0.264
Ba(1,010)	Ba(1)	Ba(1,010)
-0.038	-	-0.038
	S(2,010)	S(2)
	0.001	0.001
	Ba(3)	
	0.228	

Table 5. Comparison between observed and calculated order of importance

Face	P	F	$(P+F)/2$	Attachment energy (Table 4)	Attachment energy (electrostatic potential)	Donnay-Harker relative order
(001)	97.8	94.8	96.3	0.388	0.058	4
(210)	91.9	91.3	91.6	0.396	0.079; 0.072	5
(101)	86.4	88.1	87.2	0.435	—	1
(011)	85.9	82.5	84.2	0.945	—	3
(211)	69.2	59.9	64.5	0.472	0.134	6
(010)	70.8	54.0	62.4	0.557	0.218	7
(100)	61.1	50.0	55.5	0.521	0.261	2

Zone $[\bar{1}20]$; electrostatic potential of the sulfate ion S(2) with respect to chains of ions going through the ions indicated

S(1)	Ba(2)	S(3,010)
-0.020	0.218	-0.036
Ba(1)	S(2)	Ba(3,010)
0.084	—	0.126
S(1,00 $\bar{1}$)	Ba(2,00 $\bar{1}$)	S(3,01 $\bar{1}$)
-0.033	-0.028	0.000

Zone $[\bar{1}20]$; electrostatic potential of the barium ion Ba(1) with respect to chains of ions going through the ions indicated

Ba(4, $\bar{1}\bar{1}0$)	S(1)	Ba(2)
-0.088	0.093	0.008
S(4, $\bar{1}\bar{1}0$)	Ba(1)	S(2)
0.140	—	0.106
Ba(4, $\bar{1}\bar{1}\bar{1}$)	S(1,00 $\bar{1}$)	Ba(2,00 $\bar{1}$)
0.060	0.117	-0.060

In this scheme the chains are grouped around the central ion in such a way that they form a projection, as it were, on (001) and on (2 $\bar{1}0$). The potential energies are expressed in units $e \cdot 2 \text{ \AA}^{-1}$.

The potential energies of the chains going through the central ions were also calculated and found to be 3.079 for the zone $[\bar{1}20]$ and 2.945 for the zone [001], both per molecule BaSO_4 . The lattice energies then become 3.766 and 3.776 respectively, based on the calculations starting with the zones $[\bar{1}20]$ and [001] respectively.

The attachment energies for the F -faces in the two zones can be calculated by taking the mean of the potentials at various places of attachment. In the case of (001), for example, the attachment energy is the mean of $(-0.088+0.093+0.008)$, $(0.060+0.117-0.060)$, $(-0.020+0.218-0.036)$ and $(-0.033-0.028+0.000)$. The face (210) lies in both zones; in the zone [001] the attachment energy is 0.079, while in the zone $[\bar{1}20]$ it is 0.072. The agreement is satisfactory.

From Table 5 it appears that the order given by the attachment energies agrees well with the experimental order. The only serious deviation is the face (011). The attachment energy is half the total energy $(2a+2a'+b+c+d)$, so that the face (011) must be regarded as a kinked face. The outermost layer consists of ions of the same sign only and the face can therefore be compared with the octahedron face of rock salt. According to Stranski (1928) the surface

of the octahedron consists of steps of cube faces. With barite the surface of (011) must then be built up from flat parts of (001), (210) and (2 $\bar{1}0$); that means in our terminology that it is a K -face (see also Buckley, 1951, p. 199). The question arises why a K -face can have such high F - and P -values. The answer must be sought in the influence of impurities, which enhance (011). Buckley (1935) found that the habit of KClO_4 crystals, which have the same structure as barite, is modified by inorganic and organic impurities, the faces enhanced being (101) and (011) in most cases. From the experiments of Kern (1953) on rock salt it may be expected, moreover, that KClO_4 crystals grown slowly will not show (011), whereas this face will appear when growth is rapid.

4. S-forms

The development of the S -forms in the zone [001] can be read off from Fig. 3(a). The first S -face between (100) and (210) is obtained by taking one element of each F -face. An element of (100) is characterized by the P.B.C. vector [010] and an element of (210) is characterized by the P.B.C. vector $[\frac{1}{2}, 1, 0]$; the sum-vector is $[\frac{1}{2}, 2, 0]$, so that the S_1 -face is (410). In the same way it is found that the first S -face between (210) and (010) is (110). The addition scheme of indices is:

Zone [001]					
200		210	210	010.....	F -faces
	410			220 S_1 -faces
610	620		430	230 S_2 -faces

The development of the other zones was studied with the aid of a structure model. The addition schemes of indices are:

Zone [010]					
100		101	101		001
	201			102	
301	302		203	103	
Zone $[\bar{1}20]$					
001		211	211		210
	212			421	
213	423		632	631	

Zone $[\bar{1}01]$	
101	010
111	
212	121
Zone $[\bar{1}11]$	
101	211
312	
413	523
Zone $[01\bar{1}]$	
211	100
311	
522	411

Zone $[110]$ contains one F -face only and hence no S -faces can occur in this zone.

Table 6. Comparison between observed morphological importance of barite forms, their F -, S - or K -character and the order according to the law of Donnay & Harker

Form	P value	Character	Donnay-Harker
{001}	97.8	F	6
{210}	91.9	F	7
{101}	86.4	F	1
{011}	85.9	K	3
{010}	70.8	F	12
{211}	69.2	F	9
{100}	61.1	F	2
{410}	38.9	S_1 [001]	26
{102}	37.3	S_1 [010]	8
{111}	26.5	S_1 [101]	4
{213}	25.9	S_2 [120]	28
{230}	25.9	S_2 [001]	>29
{201}	24.4	S_1 [010]	5
{214}	16.7	S_3 [120]	>29
{212}	15.7	S_1 [120]	13
{310}	14.6	S_2 [001]	>29
{110}	11.4	S_1 [001]	16

5. Survey

In Table 6 all forms of barite with a P value higher than 10 have been tabulated (Braun, 1932). The dominant position of the F -forms is clear. The anomaly of {011} can be explained by the particular surface structure. As a consequence of {011} being a K -form, all forms $\{0kl\}$ will also have K character.

S -forms of higher order occur only in the zones [001] and [120], the most important zones of barite. The potential energy of the periodic bond chains corresponding with these zones must be higher than that of the other zones, because these chains deviate less from a straight line than the other chains (cf., for example, the potential energies of the zones [100] and [110] for NaCl, which are respectively 2.773 and 2.126 units, according to Kleber, 1940).

Outside the naturally occurring crystals there are a number of laboratory products that are isotype with

barite. The morphology of some of these (the perchlorates of K, Rb, Cs, Tl and NH_4 and potassium permanganate) is described by Groth (1906–1919, vol. 2, pp. 167 *et seq.*). The forms observed on these compounds appear to be the six F -forms and the K -form {011}. Their frequencies are:

Observed on 6 compounds: {001}, {210} and {101}.

Observed on 5 compounds: {211}.

Observed on 4 compounds: {011} and {010}.

Observed on 3 compounds: {100}.

The three forms of barite with the highest P -values have also here the highest frequencies.

There is a striking difference between the mineral barite and the isotype laboratory products. The latter show only F -forms (and in this case the particular K -form {011}), while barite shows also a large number of S - and K -forms. This difference in number of forms between a mineral and a laboratory product appears to be rather general (unpublished investigations). The occurrence of S - and K -forms requires a big seed (Hartman & Perdok, 1955a) which might be formed during a period of dissolution. During renewed growth the S - and K -forms are then eventually stabilized through the influence of impurities, which are always present in the liquid from which a mineral crystallizes. Thus the assumption is made that the occurrence of S - and K -forms on minerals is due to alternating periods of dissolution and growth in an impure environment.

It is evident from the last column of Table 6 that the morphology of barite does not obey the law of Donnay & Harker at all. We were unable to find an appropriate pseudo-structure which should give {001}, {210} and {101} as the most important forms. The question why the law of Donnay & Harker is not obeyed will be discussed elsewhere.

References

- BRAUN, F. (1932). *N. Jb. Min. Geol. Paläont.* Beil.-Bd. A, **65**, 173.
 BUCKLEY, H. E. (1935). *Z. Kristallogr.* **91**, 375.
 BUCKLEY, H. E. (1951). *Crystal Growth*. London: Chapman and Hall.
 DONNAY, J. D. H. & HARKER, D. (1937). *Amer. Min.* **22**, 446.
 GROTH, P. (1906–1919). *Chemische Kristallographie*. Leipzig: Engelmann.
 HARTMAN, P. & PERDOK, W. G. (1955a). *Acta Cryst.* **8**, 49.
 HARTMAN, P. & PERDOK, W. G. (1955b). *Acta Cryst.* **8**, 521.
 KERN, R. (1953). *Bull. Soc. franç. Minér. Crist.* **76**, 325.
 KLEBER, W. (1940). *N. Jb. Min. Geol. Paläont.* Beil.-Bd. A, **75**, 72.
 STRANSKI, I. N. (1928). *Z. phys. Chem.* **136**, 259.