ARTIFICIAL PYRRHOTITE

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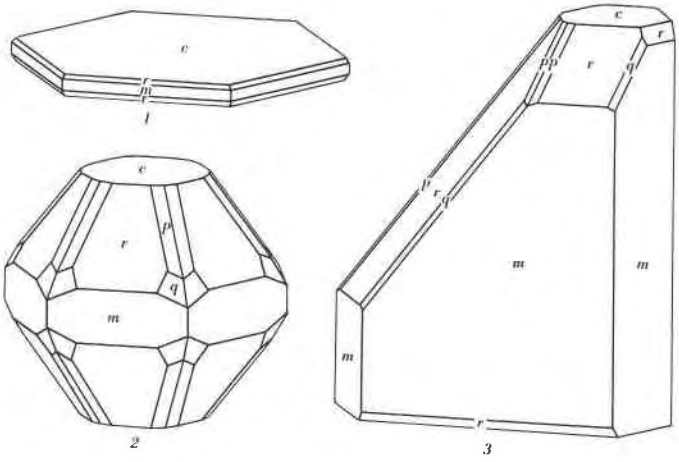
Well-developed crystals of non-magnetic artificial pyrrhotite displaying two new crystallographic forms appeared in the products of certain experiments designed primarily for the synthesis of lead-bismuth sulphides from strongly alkaline sodium sulphide solutions. These solutions, held in a bomb at about 1200 bars and 400° C., attacked the steel walls and, after cooling, were found to have precipitated part of the iron in combination with the sulphur of the charges as lustrous bronze-brown crystals of pyrrhotite. Various habits, platy, equidimensional, columnar, and fibrous, were displayed by individuals sometimes reaching a greatest dimension of two or three millimetres. The perfection and excellent development of these crystals, as well as the rarity of good crystals of pyrrhotite in nature, made worthwhile a goniometric and *x*-ray study.



Portraits of typical habits are shown in Figs. 1 and 3; Fig. 2 shows ideal development of all the observed forms: the basal pinakoid $c(0001)$, the hexagonal prism $m(10\bar{1}0)$, the hexagonal dipyramid $r(10\bar{1}1)$, and the two new forms, dihexagonal dipyramids, $p(21\bar{3}3)$, and $q(31\bar{4}3)$. Several crystals are tabular on m, with dominant development of a zone of the type $[(01\bar{1}1)(10\bar{1}0)]$, large r faces and narrow p and q facets (Fig. 3). Ordinarily, only one termination is well-developed; the other usually displays a large basal pinkaoid modified by one or two narrow pyramidal faces, suggesting the hemimorphic class $6mm$.

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Excellent signals were obtained on the reflecting goniometer from *c*, *m*, and *r*, permitting the calculation of an accurate morphological axial ratio

$$a':c' = 1:1.6918$$

The signals from *p* and *q* were weak and blurred. Table 1 gives the observed and calculated angles from the fourteen crystals examined.

TABLE 1. ARTIFICIAL PYRRHOTITE. TWO-CIRCLE ANGLES

$a':c' = 1:1.6918$; $p_0:r_0 = 1.9535:1$

Form	No. of Faces	Observed Range ϕ	Observed Range ρ	Observed Mean ϕ	Observed Mean ρ	Calculated ϕ	Calculated ρ
m (10$\bar{1}$0)	49	29° 40′–30° 20′	—	30° 00′	90° 00′	30° 00′	90° 00′
r (10$\bar{1}$1)	40	29 56 –30 02	62° 35′–63° 04′	30 00	62 53½	30 00	62 53½
p (21$\bar{3}$3)	16	11 55 –13 56	59 29 –60 07	12 57	59 55	10 53½	59 50½
q (31$\bar{4}$3)	8	15 43 –18 15	66 31 –66 58	17 32	66 40	16 06	66 56

Laue photographs with the beam perpendicular to the *c*-axis showed no lack of reflection symmetry across (0001), and indeed none could be expected unless pyrrhotite should afford an exception to Friedel's law, like zinckenite (Nuffield, 1946).

Rotation and Weissenberg films about the *c*- and *a*-axes showed the symmetry of the space group $C6/mmc$, and strong diffractions defining a pseudo-cell

$$a' = 3.435,\ c' = 5.811 \text{ kX};^2\ c'/a' = 1.692$$

Weak layer lines on the rotation films about the *a*- and *c*-axes gave evidence of a superstructure with $a = 3a'$, $c = 2c'$. On the gnomonic projection of the forms, a partial influence of the superstructure on the morphology is shown by the position of the *p* and *q* face-nodes thirding the p_0 dimension, corresponding to tripling of the *a* axis.

Representative recent measurements of the cell dimensions of artificial and natural crystals of $Fe_{2-x}S_2$ are collected in Table 2. All the examples, except the pyrrhotite from Kuså, are hexagonal, with the small cell $a'c'$ containing $Fe_{2-x}S_2$, and in some cases hexagonal superstructures ac. The data for Kuså fairly represent ten sets of similar values for monoclinic (nearly orthohexagonal) pyrrhotite from Sweden. It will be seen that a' is nearly constant while c', and hence c'/a', decreases with increasing shortage of Fe. Thus the new artificial crystals are apparently only slightly deficient in Fe. However the marked shrinkage of c' from the hexagonal to the monoclinic types with similar composition, appears to

[2] Using Cu$K\alpha_1$, $\lambda = 1.5374$ kX.

TABLE 2. CELL DIMENSIONS[3] OF MEMBERS OF THE SERIES $Fe_{2-x}S_2$

		a'	c'	c'/a'	a	c	
Artificial	$Fe_{2.00}S_2$	3.433	5.860	1.707	$\sqrt{3}a'$	$2c'$	(1)
Artificial	—	3.435	5.811	1.692	$3a'$	$2c'$	(2)
Artificial	$Fe_{1.83}S_2$	3.437	5.746	1.672	a'	c'	(3)
Boliden	$Fe_{1.85}S_2$	3.437	5.722	1.665	a'	c'	(4)
Lavergruvan	$Fe_{1.76}S_2$	3.434	5.714	1.664	a'	c'	(4)
Kuså	$Fe_{1.82}S_2$	b 3.428	c 5.677	c/b 1.656	a 5.937	β 89.60°	(4)
Schneeberg Morro Velho	—	3.435	5.68	1.65	$2a'$	$4c'$	(5)

(1) Hägg & Sucksdorff (1933). (2) A. R. G. (3) Haraldsen (1937). (4) Byström (1945). (5) Buerger (1947).

be due to a transformation discussed by Byström (1945). There is no agreement in the dimensions of the superstructures noted on these materials.

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[3] The previous values are all given as Å, but they are presumably all in kX.