

NOTES AND NEWS

PRECISION MEASUREMENTS OF THE CELL EDGE OF SYNTHETIC PYRITE

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In the course of an experimental investigation of the stability ranges of certain iron minerals, a number of synthetic pyrite specimens were produced from chemically pure materials at controlled temperatures. These specimens seemed ideal for an investigation of a possible relation between the cell edge of pyrite and its temperature of formation. Precision measurements were, accordingly, made on three of the specimens representing a range of 340° C. in temperature of formation.

Smith (1942) carried out extensive studies on the physical properties, and more specifically the electrical conductivity of pyrite. He was able to correlate variations in some of these properties with temperature of formation, and it is partly as a result of his work that the present study was undertaken. Peacock and Smith (1941) previously conducted a limited investigation of a possible relation between the temperature of formation and the cell edge of pyrite. They measured two specimens representing the extreme electrical conductivity and hence temperature of formation range, but their measurements failed to show an appreciable variation in the two cell edges.

The present measurements were made on photographs taken with a Picker camera of 10.78 cm. radius using iron radiation. The camera was loaded by the Straumanis method. A reader equipped with magnifier and designed to read directly to 0.005 cm. was used to measure the films. All lines were measured, but only the high θ doublets were used for parameter determinations. The final results were plotted against $\cos^2 \theta$ and extrapolated to $\cos^2 \theta = 0$ according to the method of Bradley and Jay.

The following specimens were used in this study:

No. L-55—prepared by heating at 540° C., stoichiometric quantities of iron and sulfur powders in a sealed pyrex tube from which the air had been displaced by carbon dioxide.

No. L-51—prepared by passing hydrogen sulfide over synthetic siderite at 350° C. Product contained some pyrrhotite.

No. L-27—prepared by passing hydrogen sulfide over $\text{FeCl}_2 \cdot 6\text{H}_2\text{O}$ at 200° C. Product contained some pyrrhotite.

The results of the measurements are compared with published precision cell edge values for natural pyrite in Table 1. For comparison all measurements have been recorded in kX units. Wasserstein (1949) recalculated the Peacock and Smith and the Kerr measurements to these

units, and the writer converted Gordon's measurement from angstrom to kX units.

TABLE 1. COMPARISON OF PYRITE CELL EDGE MEASUREMENTS

<i>Pyrite, Leadville</i>	
Peacock and Smith (analysis $\text{FeS}_{2.0}$)	$d_0 = 5.4066 \pm 0.0003$ kX units
Kerr, Holmes and Knox	$d_0 = 5.4067 \pm 0.0001$ kX units
Gordon	$d_0 = 5.4070 \pm 0.0003$ kX units
<i>Pyrite, Elba</i>	
Peacock and Smith (analysis $\text{FeS}_{1.98}$)	$d_0 = 5.4050 \pm 0.0003$ kX units
<i>Pyrite, Synthetic</i>	
L-55 (probably $\text{FeS}_{2.0}$)	$d_0 = 5.4066 \pm 0.0003$ kX units
L-51	$d_0 = 5.4055 \pm 0.0007$ kX units
L-27	$d_0 = 5.4053 \pm 0.0007$ kX units

The values presented above show that there is a measurable difference in the unit cell dimensions of various pyrite specimens. The close correspondences between the three values for Leadville pyrite and that for specimen L-55 are noteworthy. Peacock and Smith (1941) found by chemical analysis and physical tests that their Leadville specimen had a composition of $\text{FeS}_{2.0}$. Since L-55 was formed by heating carefully weighed molar quantities of pure iron and sulfur powders in a sealed tube its composition must have been close to the theoretical $\text{FeS}_{2.0}$.

Specimens L-51 and L-27 gave smaller unit parameters than L-55 but their limits of error covered a broader range. The former specimens were prepared by a different method than L-55 and hence one can not conclude from these measurements that the cell dimensions vary with temperature of formation. Peacock and Smith's Elba specimen was found by analysis to be slightly sulfur deficient, and specimens L-51 and L-27 may have been somewhat low in sulfur as indicated by their small pyrrhotite contents. The smaller cell edge values in these specimens may therefore be due to a sulfur deficiency.

Acknowledgments: This study constitutes part of a Ph.D. thesis submitted by the writer to the graduate faculty of the University of Minnesota. The interest and aid of Drs. J. W. Gruner and G. Bitsianes are gratefully acknowledged.

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BORON IN TETRAHEDRA OF BORATES AND BOROSILICATES

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Conditions of co-existence and types of condensation of boron and silicon tetrahedra are examined.

It was formerly believed that boron occurred in natural compounds chiefly surrounded by oxygen in triangular co-ordination. Fourfold tetrahedral co-ordination, as determined by Dunbar and Machatschki (1) in danburite, was supposed to be exceptional. More recently, new examples of boron in tetrahedra have been determined, and it seems now that this type of co-ordination is relatively frequent.

Four is an enhanced number of co-ordination of boron towards oxygen, and thus, as was shown by the author in a previous note (2), compounds with boron in tetrahedra can not generally be expected to conform strictly to the Pauling electrostatic valence rule. This had been, in fact, already observed by Berger (3) in the structure of B_2O_3 . While the unfavorable radius ratio makes oxygen bridges between aluminum tetrahedra generally unstable, and hence no such bridges occur in any of the structures of Al_2O_3 , the favorable radius ratio permits boron tetrahedra in B_2O_3 to be linked to each other in such a way that corners are shared by two and even by three tetrahedra.

The maximum number of tetrahedra which can share one corner without sharing edges is four, since the resulting oxygen configuration is cubic close-packed in the ideal case: one central ion is surrounded by twelve others situated at the centers of the edges of a cube. Four cations are tetrahedrally distributed around the strongly polarized central anion. Such a structure occurs in the well-known basic beryllium acetate, $Be_4O(CH_3CO_2)_6$. A similar configuration, with four boron tetrahedra sharing one corner, was found by Ito, Norimoto and Sadanaga (4) in boracite. The Pauling electrostatic valence rule is fulfilled if a bond-strength as low as $\frac{1}{2}$ is attributed to the boron oxygen bond in this particular case. It may reasonably be expected that also the tetraborate ion has a similar structure, and hence in its completely hydrated form has the composition $[B_4O(OH)_{12}]^{2-}$ or $[B_4O_7 \cdot 6H_2O]^{2-}$. Sharing of corners by the oxygen polyhedra which surround the central oxygen ion should lead to the less hydrated forms of sodium borate.

Boron tetrahedra not only can share corners with each other, but also