# PEROVSKITE

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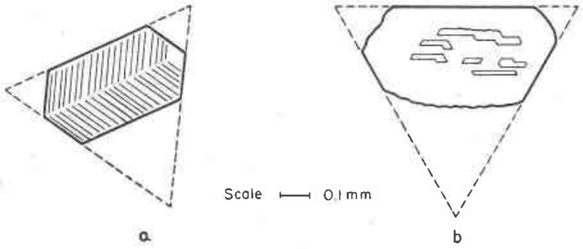
## ABSTRACT

Optical and $x$-ray study of perovskite from two new localities in California, and from Magnet Cove, Arkansas, and Vogtsburg, Germany, shows a unit cell edge double the current value. The new figure is: $a_0 = 15.26 \pm .01$ Å for the more ordinary perovskite, and somewhat greater for the variety dysanalyte: $a_0 = 15.39 \pm .01$ Å. All specimens showed multiple twin lamellae, parallel to the cube edge and also to the dodecahedron.

## CRESTMORE—1

Recently, one of the author's students found on the 910 level of the Commercial quarry at Crestmore, Riverside County, California, some fragments which contained scattered small octahedral crystals, amber to yellow in color. An examination of these proved them to be perovskite, and this, the first record of this mineral for California, was reported at the El Paso Meeting of the Mineralogical Society of America (1). The mineral occurs in the contact zone of the deposit, associated with nearly black octahedra of spinel, and an unidentified soft fibrous white mineral, probably a calcium silicate, interstitial to coarsely crystalline calcite. The perovskite is essentially normal calcium titanate, but with a perceptible amount of Zr, suggesting relationship to the mineral uhligite. Spectroscope analysis yields the following information: Large amount, Ca, Ti; % in units, Zr, Fe, Si (probably as impurity); % in tenths, Mg, Al; trace, Na, Sr, Mn. The presence of ordinary perovskite in a contact metamorphic deposit has not hitherto been reported, although dyasnalyte is known under these conditions. The perovskite crystals range from a few tenths of a millimeter up to one or even two millimeters in diameter. In habit they are essentially octahedra, with sometimes small modifying cube faces. The octahedron faces are in general of very good quality, and measurement on the goniometer of selected crystals showed very close correspondence in position with the true isometric form. In four good measured crystals the rho angle varied from the theoretical by a maximum of 21′, and in most cases much less than this. The phi angle was even closer, with a maximum variation of 14′, and in one crystal the theoretical value was recorded, within limit of reading error, for all four faces of the measured half of the crystal. In none of these variations was there indication of a systematic deviation, such as Zedlitz (2) p. 268, reported for minute synthetic crystals. The cube faces were not in general of such good quality, but their position was in reasonable agreement with the theoretical.

Many of the crystals are equidimensional, but not infrequently some are flattened perpendicular to an octahedral axis. Such crystals, observed under the microscope, show multiple twin lamellae, with the junction lines running usually in two, and occasionally in three directions, at 60° to each other. Sometimes these directions bisect the angles of the octahedral face, indicating twinning on {110}. At other times the lines run parallel to the edges of the face, which could mean twining either on {110} or {100}. In this case it would be possible to distinguish between the two possibilities by means of the universal stage. Some of the crystal faces, with proper illumination show a pattern of lines indicating twin lamellae, and one showed geometrically outlined "plateaus" on the surface. These are illustrated in the accompanying sketch (Fig. 1).



Natural crystal faces. a- striations b-"plateaus"

FIG. 1

A few crystals were ground down to thin sections, some parallel to the cube, some to the octahedron. Those on the cube face showed twin-lamellae parallel to the cube edge, as well as some diagonal ones. The cubic twin lamellae show at times a nearly centered optic axis figure with 2V about 90°. Dispersion is prominent. Occasionally, as on some cube faces, a negative uniaxial figure was observed, not perpendicular to the cube, but with the center just at the edge of the microscope field. This effect may be produced by multiple cross lamellae, as suggested by Mallard (3) p. 149, as it appears in areas which do not show entire uniformity of optical direction, but have a wavy or vague extinction, clearly produced by several lamellae in the field of view. Bowman (4) p. 160 finds similar anomalies in crystals from the Tirol, and reports a positive acute bisectrix of small angle on the cube face.

## CRESTMORE—2

More recently the author found another occurrence of perovskite at Crestmore. This also comes from the 910 level, Commercial quarry, but differs in association and appearance from the first. The crystals are dark brown in color, not in general so well developed, although some octahedron faces and an occasional cube face were observed. They are closely associated with calcite, abundant pale greenish xanthophyllite and a light amber monticellite, and apparently crystallized earlier than these minerals.

### SAN BENITO COUNTY

At the time the Crestmore occurrence was reported, the author was informed of a second California locality, near the headwaters of the San Benito River, near the benitoite Gem Mine, in San Benito County. The perovskite was found here by Mr. David Grigsby of Berkeley, who very kindly supplied the writer with material for study, as well as providing information regarding the occurrence. The mineral is found as black, highly lustrous cubic crystals, sometimes rather highly modified, and ranging in size from under a millimeter up to at least 0.5 cm. across. It is associated with black dodecahedral crystals of melanite garnet, in a greenish chloritic schist. One of the crystals, measured on the goniometer, showed, besides the cube, which roughly determines the outline, the following forms: $\{210\}$, $\{320\}$, $\{430\}$, $\{540\}$, $\{111\}$, $\{311\}$, and more doubtfully $\{14.1.0\}$, $\{13.1.0\}$, $\{310\}$. The shiny black aspect is purely superficial, for on crushing, the mineral is seen to be nearly colorless and transparent. Fragments and sections show typical multiple twin lamellae, with the twinning usually but not invariably parallel to the cube edge. Some of the broader lamellae show extremely fine, barely visible lamellae parallel to the larger ones. The lamellae show extinction parallel to the cube edge, and a nearly centered optic axis figure with $2V = 90° \pm$. Dispersion is pronounced, with the red brush showing more curvature than the blue, indicating a negative optical character with $r < v$.

Spectroscopic analysis is essentially parallel with that of the Crestmore mineral in spite of the wide difference in color and habit. The following is reported: Large amount, Ca, Ti; % in units, Zr, Fe; % in tenths, Mg, Al, Mn, Si; trace, Na, Sr.

### DIMENSIONS OF THE UNIT CELL

The validity of the current value for the unit cell edge ($a_0 = 7.55$ Å) was brought in question by examination of an $x$-ray powder photograph of the Crestmore perovskite taken by Professor W. J. McCaughey of the Ohio State University. This was made for purposes of identification and the film kindly given the writer by Dr. McCaughey. He noted on this film several faint lines which could not be indexed as pseudo-cubic, using the old value $a_0=3.83$ Å. Barth (8) p. 204, 210, finds $a_0=3.795$ Å for perovskite, and $a_0=3.826$ Å for dysanalyte. The writer tried indexing these with the doubled value found by Levi and Natta (5) and Zedlitz (2) p. 259, but still could not get agreement. Accordingly a new photograph was taken of the Crestmore—1 material. This photograph showed many more lines than the previous one, and on trial it was found possible to index practically all of these on a cubic basis by using a still further doubled value of $a_0$. Crestmore—2 showed essentially the same lines as Crestmore—1. In consequence of this discovery a powder photograph of the San Benito perovskite was made, and proved to be practically identical in pattern and spacing with that from Crestmore. This agreement confirms the validity of the fainter lines of the pattern, since impurities in two such widely different occurrences would probably not be the same. In addition, both samples were very carefully selected under the binocular and almost completely free from foreign matter. The spectroscopic analyses also show the essential similarity of the two, and the agreement in *x*-ray patterns could have been predicted from this.

After this confirmation of the more complex character of the perovskite structure, it was thought desirable to see what differences in the pattern were present with important variation in composition. Accordingly, through the courtesy of the U. S. National Museum, specimens of dysanalyte were obtained from Magnet Cove, Arkansas, and from the Kaiserstuhl, Baden, Germany. The Magnet Cove mineral (U.S.N.M. 80431) presumably carries about 10% $Ta_2O_5$ plus $Cb_2O_5$, if as is probable it corresponds to the analyzed material from that locality. The German specimen (U.S.N.M. R-5029) may be somewhat different, as published analyses vary rather widely in the $Cb_2O_5$ content although all show absence of $Ta_2O_5$. Analyses of these two occurrences are listed in the following table.

These two specimens were crushed, hand-picked for purity, and similarly photographed and measured. Both showed essentially the same lines as the earlier ones, with comparable intensities, but with slightly different spacings. The German mineral showed considerable alteration to a black powdery substance, which could not be entirely separated from the clear material. This diminished the quality of the *x*-ray picture, but introduced no new lines.

The Magnet Cove specimen was black, somewhat corroded and pitted, and full of small white apatite prisms, which also appear in the lining of some of the cavities. Only the perfectly fresh material was picked out for the powder photograph. Unaltered parts of the crystal were transparent in very thin section, showing anisotropism and poorly defined twinning lamellae parallel to the cube edge; no interference figure could

| | *Magnet Cove, Ark.* | *Vogtsburg, Kaiserstuhl, Baden* | | |
|---|---|---|---|---|
| | 1 | 2 | 3 | 4 |
| CaO | 33.22 | 25.60 | 21.63 | 23.51 |
| MgO | 0.74 | — | 0.02 | — |
| (Y, Er, Tr)$_2$O$_3$ | 5.42 | — | — | — |
| (Ce, La)$_2$O$_3$ | 0.10 | 2.80 | 3.32 | 3.08 |
| $Na_2O$ | — | 4.37 | 4.20 | — |
| $K_2O$ | — | — | 0.39 | 0.44 |
| $SiO_2$ | 0.08 | 2.21 | 0.29 | 0.33 |
| $TiO_2$ | 44.12 | 50.93 | 48.31 | 38.70 |
| $Cb_2O_5$ | 4.38 | 4.86 | 16.12 | 25.99 |
| $Ta_2O_5$ | 5.08 | — | — | — |
| MnO | — | — | 0.23 | — |
| $Fe_3O_4$ | 0.73 | — | — | — |
| $Fe_2O_3$ | 5.66 | — | — | — |
| FeO | — | 9.22 | 5.35 | 5.69 |
| $Al_2O_3$ | — | — | — | 1.25 |
| | 99.53 | 100.22 | 100.88 | 100.28 |

1. F. W. Mar, *Am. J. Sci.*, **40,** 403–405 (1890); 2. Hauser, *Z. anorg. chem.*, **60,** 237 (1908); 3. & 4. Meigen & Hugel, *Z. anorg. chem.*, **82,** 242 (1913).

be seen. The Kaiserstuhl mineral, in its clear portions, also showed double refraction and poorly observable twinning lamellae. Hauser (6) called the mineral isotropic and believed that the Cb and Ce were present in mechanical impurities. It is interesting to note that Williams (7) p. 140 found minute (.05—.003 mm.) octahedra of perovskite in serpentine, and states that they are isotropic.

All powder photographs were taken with a North American Philips $x$-ray apparatus, using a camera of 57.3 mm. radius, Copper $K_\alpha$ radiation with Ni filter using exposures of 8 hrs. at 28 KVP and 8 MA. Each film was calibrated from back reflections and measured to the nearest .05 mm. Spacings have been calculated in Å units. The value of $a_0$ has been averaged from the measurements of a number of spacings both large and small and should for that reason be accurate to .01± Å units. The values of $a_0$ for the four localities are as follows:

| | | | |
|---|---|---|---|
| Crestmore—1. | 15.27 Å | Magnet Cove | 15.38 Å |
| Crestmore—2. | 15.29 Å | Kaiserstuhl | 15.41 Å |
| San Benito | 15.25 Å | | |

Study of the powder photographs shows very close correspondence with cubic spacings, although of course, since the mineral is anisotropic, it must be only pseudo-cubic. The deviation of the cell from a cube must be very small indeed, as in only two lines is there a suggestion of doublets, whose presence would be a very delicate indication of differences in the lengths of the cell edge. These appear at spacings 1.56–1.55, Å (448), with intensity 7 and 7, and at 1.018–1.023, Å (4.8.12) with intensities 4 and 1, respectively. The latter was noted by Zedlitz (2) p. 259 as diffused, with equal intensities (10–10), indexed as (246).

The following table gives the lists of spacings and estimated intensities of the lines for each locality. *(See next page.)*

## CONCLUSIONS

From the data at hand, the similarity of pattern for all occurrences and the close agreement with a pseudo-cubic structure, it seems most probable, as has been suggested, that perovskite crystallizes in truly isometric form, but inverts with lowering temperature to the observed structure, whose true symmetry remains uncertain, but is clearly non-isometric optically, though it appears to be practically cubic structurally. The pseudo-cubic unit cell increases in size with the increase in Ta and Cb content, ranging as shown from 15.25 to 15.41 Å units. No attempt has been made to determine the distribution of atoms in this structure, owing to its complexity and the apparent improbability of getting a single crystal for *x*-ray study.

## ACKNOWLEDGMENTS

The author wishes to express thanks to the following for assistance in the preparation of this paper: Professor George Tunell, Department of Geology, University of California at Los Angeles, for use of *x*-ray equipment, and very valuable assistance in discussing the powder photographs; Professor W. J. McCaughey of the Ohio State University for the initial *x*-ray film which started the investigation; Drs. W. F. Foshag and George Switzer of the U. S. National Museum for the generous gift of specimens of dysanalyte from Magnet Cove and from Germany; Mr. David Grigsby, of Berkeley, California, for specimens from the benitoite mine locality; the Research Fund of the University of California for making possible the spectroscopic analyses.

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Table 2. Powder Photograph Data on Perovskite

Copper radiation, $d/n$ in Å units

| No. | Indices | San Benito | | Crestmore-1 | | Crestmore-2 | | Magnet Cove | | Kaiserstuhl | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $d/n$ | $I$ | $d/n$ | $I$ | $d/n$ | $I$ | $d/n$ | $I$ | $d/n$ | $I$ |
| 1 | 004 | 3.81 | 4 | 3.82 | 3 | 3.81 | 2 | 3.84 | 4 | 3.84 | 3 |
| 2 | 024 | 3.41 | 1 | 3.42 | 1 | 3.42 | ½ | 3.43 | ½ | 3.54?<br>2.30? | 1<br>1 |
| 3 | 015, 134 | 2.98 | 1 | 2.99 | 1 | 3.01 | ½ | 3.00 | ½ | 3.01 | 1 |
| 4 | 044 | 2.70 | 10 | 2.70 | 10 | 2.70 | 10 | 2.72 | 10 | 2.72 | 10 |
| 5 | 006 | 2.54 | ½ | 2.56 | ½ | 2.56? | ½ | 2.58 | ½ | 2.54 | ½ |
| 6 | 026 | 2.41 | 1 | 2.41 | 1 | 2.42 | ½ | 2.44 | ½ | 2.43 | ½ |
| 7 | 226 | 2.30 | 3 | 2.30 | 1 | 2.30 | 1 | 2.32 | 2 | 2.32 | ½ |
| 8 | 444 | 2.20 | 3 | 2.21 | 2 | 2.21 | 1 | 2.24 | ½ | 2.22 | 1 |
| 9 | 046 | 2.12 | 2 | 2.12 | 1 | 2.12? | ½ | 2.14 | ½ | 2.14 | ½ |
| 10 | 246 | 2.04 | ½ | 2.04 | ½ | 2.05 | ½ | 2.06 | ½ | 2.11 | ½ |
| 11 | 008 | 1.91 | 9 | 1.91 | 9 | 1.91 | 7 | 1.93 | 8 | 1.93 | 9 |
| 12 | 028, 446 | 1.85 | ½ | 1.86 | 1 | 1.86 | ½ | 1.88 | ½ | 1.87 | ½ |
| 13 | 048 | 1.71 | 1 | 1.71 | 1 | 1.72 | ½ | 1.73 | 1 | 1.73 | 1 |
| 14 | 119, 357 | 1.67 | 1 | 1.67 | 1 | 1.68 | ½ | 1.69 | ½ | 1.69<br>1.67 | ½<br>½ |
| 15 | 139 | 1.56 | 7 | 1.56 | 7 | 1.57 | 5 | 1.57 | 6 | 1.57 | 5 |
| 16 | 448 | 1.55 | 7 | | | | | | | | |
| 17 | 359 | 1.42 | ½ | 1.43 | ½ | — | | — | | — | |
| 18 | 369, 1.2.11, 1.5.10 | 1.356 | ½ | — | | — | | — | | — | |
| 19 | 088 | 1.349 | 6 | 1.35 | 5 | 1.35 | 3 | 1.36 | 3 | 1.36 | 3 |
| 20 | 2.3.11, 279, 3.5.10, 677 | 1.32 | ½ | — | | — | | — | | — | |
| 21 | 0.4.11, 1.6.10, 388 | 1.30 | ½ | — | | — | | — | | — | |
| 22 | 2.6.10 | 1.29 | ½ | 1.29 | ½ | — | | — | | — | |
| 23 | 0.4.12 | 1.21 | 5 | 1.21 | 4 | 1.21 | 2 | 1.22 | 3 | 1.22 | 3 |
| 24 | 199 | 1.19 | ½ | — | | — | | — | | — | |
| 25 | 0.2.13, 2.5.12, 3.8.10, 4.6.11 | 1.16 | ½ | — | | 1.147? | ½ | — | | — | |
| 26 | 1.3.13, 779, 3.7.11 | 1.14 | ½ | 1.14 | ½ | — | | — | | — | |
| 27 | 3.9.10 | 1.11 | 1 | 1.11 | 1 | 1.12 | ½ | 1.12 | 1 | 1.12 | ½ |
| 28 | 0.7.12, 6.6.11 | 1.01 | 1 | 1.01 | 1 | 1.11 | ½ | 1.11 | 1 | 1.11 | ½ |
| 29 | 0.2.14, 0.10.10, 6.8.10 | 1.08 | ½ | — | | — | | — | | — | |
| 30 | 1.9.11, 3.5.13 | 1.07 | ½ | — | | — | | — | | — | |
| 31 | 1.8.12, 2.3.14, 2.6.13, 3.10.10, 4.7.12, 889 | 1.06 | ½ | — | | — | | — | | — | |
| 32 | 1.5.14, 1.10.11, 2.7.13 | 1.023 | 1 | 1.024 | 1 | | | 1.035 | ½ | 1.035 | ½ |
| 33 | 4.8.12, 0.0.15, 0.9.12, 2.5.14, 2.10.11, 5.10.10 | 1.018 | 4 | 1.019 | 3 | 1.021 | 2 | 1.027 | 2 | 1.026 | 1 |
| 34 | 0.0.16, 2.5.15, 2.9.13, 3.7.14, 6.7.13 | .9554 | 1 | .9563 | ½ | .956 | ½ | .9643 | ½ | .9638 | ½ |
| 35 | 0.3.16, 0.11.12, 2.6.15 | .9362 | ½ | — | | — | | — | | — | |
| 36 | | .9312 | ½ | — | | — | | — | | — | |
| 37 | | .9069 | ½ | — | | — | | — | | — | |
| 38 | | .9043 | ½ | — | | — | | — | | — | |
| 39 | | .9011 | 4 | .9005 | 2 | .9012 | 2 | .9070 | 2 | .9078 | 2 |
| 40 | | .8549 | 2 | .8560 | 2 | .8557 | 1 | .8623 | 2 | .8601 | ½ |
| 41 | | .8525 | 1 | .8536 | 1 | .8527 | 1 | — | | .8588 | ½ |
| 42 | | — | | — | | — | | — | | .8258 | ½ |
| 43 | | .8188 | ½ | .8188 | ½ | — | | — | | .8186 | ½ |
| 44 | | — | | — | | — | | — | | .8258 | ½ |
| 45 | | .8129 | 2 | .8134 | 2 | .8126 | 1 | .8190 | 2 | .8185 | ½ |
| 46 | | .8108 | 1 | .8118 | 1 | — | | — | | — | |
| 47 | | .7841 | 1 | .7849 | 1 | — | | — | | — | |
| 48 | | .7822 | 1 | .7824 | 1 | .7826 | ½ | .7841 | ½ | — | |
| 49 | | .7787 | ½ | .7790 | ½ | — | | — | | — | |
| 50 | | — | | .7768 | ½ | — | | — | | — | |
| 51 | | — | | — | | — | | .7753 | ½ | — | |
| 52 | | — | | — | | — | | .7747 | ½ | | |

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*Manuscript received Aug. 28, 1950*