

COMMUNICATIONS FROM THE OXFORD MINERALOGICAL
LABORATORY. NO. XXVI.*Litharge from Zarshuran, Persia.*

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THE specimen to which this paper refers, is one of a number of minerals from Kurdistan, presented to the Hunterian Museum, in Glasgow University, by Mr. D. Ferguson, to whom I am indebted for the following particulars of the occurrence. The exact locality is the Zarshuran River, in Kurdistan, where a large mineral vein, which has been worked for centuries for orpiment, is found. The country-rock is red sandstone, overlying, unconformably, altered slates and schists, which are intruded by a boss of felspathic granite or syenite. Near the surface the vein-stone is chiefly a kind of calc-sinter, but this disappears as the depth increases and calcite becomes the predominant mineral in the gangue, being associated with some quartz and fluorspar. The metalliferous minerals present, in addition to orpiment, include realgar, stibnite, a complex sulphide of antimony, lead, zinc, and iron, and the litharge which is to be described.

The specimen, which is about five inches in length and two in thickness, is coated with a white decomposition product which seems to be cerussite. One half of the material is composed of lustrous, red, mica-like flakes which are obviously crystalline, while the remainder, which is dull red in colour, appears to be massive. The streak is yellowish-brown and the hardness between 2 and 3. The weathered surface of the crystalline portion has a peculiar ribbed appearance, which is apparently connected with the sheaf-like arrangement of the thin flakes. There is no sharp line of demarcation between the two varieties, the laminated form gradually passing into the massive.

Under the microscope the laminae are seen to be translucent, the

colour being red in thick flakes, and yellow to yellowish-green in thin ones. There are two well-developed cleavages, perpendicular to each other, as well as several subsidiary sets of lines which appear to be glide-planes. One set of the latter is inclined to one of the cleavages at an angle of 18° – 22° and another at 54° – 58° . Measurements on a large number of fragments show these angles to be fairly constant within the limits mentioned. In thin sections the extinction is always straight with respect to the cleavages, and the mean refractive index, as determined by immersion in diluted methylene iodide, is 1.735 ± 0.005 . The double refraction is fairly low and is probably somewhat less than 0.01, as 'yellow' sections show first order green and red interference-colours between crossed nicols and thinner ones first order yellow. In convergent light, these thin plates show a biaxial figure with a moderately wide angle, the optic axial plane being parallel to a cleavage, and the optical sign negative. There is no apparent pleochroism and the dispersion is fairly low. So far as the optical evidence goes, the mineral appears to be orthorhombic.

Some of the sections, which are sufficiently thick to appear red by transmitted light, appear to have different optical properties, being isotropic, or nearly so, between crossed nicols and giving, in convergent light, a figure which is either uniaxial, or biaxial with a very small angle. This phenomenon appears to resemble that obtained by Nörremberg¹ by the superposition of exceedingly thin plates of mica in such a way that their principal sections coincided. Such a combination behaves optically in the same way as a section of a uniaxial crystal cut perpendicular to the optic axis.

In the case of the litharge, the plates which are translucent are exceedingly thin, and can only be examined in minute fragments. Further, in some fragments, which are partly isotropic and partly doubly-refracting, the division between the two parts is generally a cleavage-plane, while the fact that the cleavages are parallel throughout indicates that the superposition, if such there be, cannot be oblique. Hence the most plausible explanation of the anomalous optical behaviour of these thicker plates is that it is due to overlapping, in some form or other, of very thin cleavage-flakes.

Some of the crystalline substance was picked out under a lens and an analysis, partly in duplicate, made of the material thus obtained, after allowing it to remain over sulphuric acid till it reached a constant weight. The results obtained were as follows:

¹ Cf. P. Groth, 'Physikalische Krystallographie,' 4^{te} Aufl., 1905, p. 149.

		(a)		(b)		Mean.
PbO	...	97.04	...	97.30	...	97.17
CuO	...	2.70	...	2.53	...	2.61
Sb ₂ O ₃	...	0.30	...	—	...	0.30
P ₂ O ₅	...	trace	...	—	...	trace
CO ₂	...	trace	...	—	—	trace
		<u>100.04</u>				<u>100.08</u>

Qualitative tests for lead peroxide, PbO₂, were made, but none was found. Iron oxide was also proved to be absent. The analyses show the mineral to be nearly pure litharge. The specific gravity is 8.61.

Occasionally, plates, which are obviously unaltered by weathering, show under the microscope minute dendritic growths of black material in the midst of the yellow crystalline substance. These skeletal growths bear a remarkable resemblance to the crystallites which commonly occur in metallic alloys, and particularly to those which form in eutectiferous mixtures where one constituent is in excess. It therefore seems probable that the crystallites represent either the excess of copper oxide which the lead oxide is incapable of taking up in solid solution, or else the excess of copper oxide over the eutectic mixture of the two oxides. Of these, the former explanation is the more probable.

Hintze¹ states that lead oxide is not known to occur in a crystalline state in nature, but is found in scaly, granular, and earthy forms. The only analyses in the literature are two by Pugh² of rather impure material from Mexico. Several occurrences in Mexico have been recorded, but the crystalline nature of the material in all cases is somewhat doubtful.

Two crystalline modifications have been prepared synthetically, but their conditions of equilibrium have not been definitely determined, while there is also some doubt regarding the optical properties. The two varieties can be prepared by dissolving lead oxide in molten potassium hydroxide, yellow crystals being obtained with rapid cooling and red ones with slow cooling. This would point to the latter modification being the stable one at ordinary temperatures. Luedecke³ found that

¹ C. Hintze, 'Handbuch der Mineralogie,' 1910, vol. i, p. 1934.

² E. Pugh, Inaug.-Diss., Göttingen, 1856; quoted in Hintze, loc. cit. An early analysis by J. F. John (1812) is quoted in Dana's 'System of Mineralogy,' 5th edition.

³ O. Luedecke, Zeits. Kryst. Min., 1884, vol. viii, pp. 82-83. Numerous references to previous literature are given.

the red variety was tetragonal, while the yellow one was orthorhombic. Termier¹ investigated the orthorhombic form in some detail and found that it was pseudo-cubic with a refractive index above 1.8, strong double refraction, and sensible pleochroism. The tetragonal form has not, so far, been investigated further.

As there seems to be some confusion regarding the two forms, an examination was made of some synthetic crystals of the red variety. These were bright red under a lens, but under the microscope thin sections appeared yellow. Two good cleavages were visible and extinction was straight with regard to them. In convergent light a decidedly biaxial figure was obtained, the optical sign being negative. This material, therefore, is very similar to the natural mineral from Persia, save that the glide-planes and optical anomalies are absent. Some of the red crystals were melted and allowed to cool fairly quickly. A very fine-grained yellow crystalline product resulted, and this, under the microscope, appeared greenish. The crystals, however, were too minute for further examination.

The Persian mineral seems to be crystalline litharge, and its optical properties are in agreement with those of the red synthetic variety which was examined. As previous investigators simply describe the red form as tetragonal without any mention of it being yellow by transmitted light in thin section, there is obviously some confusion as to the nature of the two varieties. The whole question of the polymorphism of lead oxide requires a thorough re-investigation before our knowledge of it can be regarded as satisfactory.

Under these circumstances it is somewhat difficult to give any satisfactory explanation of the origin of the mineral. It was most probably derived from the oxidation of the lead-bearing sulphides which are common in the vein; but it is impossible to give any account of how this oxidation could be brought about.

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¹ P. Termier, *Bull. Soc. franç. Min.*, 1895, vol. xviii, pp. 367-380.
