Legrandite, a new zinc arsenate.

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With X-ray measurements by F. A. BANNISTER,[1] M.A.

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AMONG a number of specimens which the senior author (J. Drugman) obtained some years ago from the widow of a mine manager, Mr. Legrand, of Belgian nationality, was one of massive blende from the Flor de Peña mine,[2] Lampazos, Nuevo Leon, Mexico, which carried a small quantity of a bright yellow, transparent substance that could not be identified with any known mineral. Goniometric and optical examination showed it to be monoclinic, but the material was mainly massive radiating-prismatic, and the few freely developed crystals gave only very approximate measurements (see table II). A chemical analysis by the junior author showed it to be indeed a new mineral, a basic zinc arsenate, and the name 'legrandite' is proposed for it in recognition of the collector. The larger part of what remains after investigation of the small specimen has been presented to the British Museum for preservation in the mineral collection.

The results of the chemical analysis are given in table I, and the molecular ratios (column 4) at first suggested the formula $Zn_3As_2O_8 . 3H_2O$, to which they offer a fair approximation. But the X-ray examination showed that this formula is impossible. The specific gravity[3] (determined by flotation in Clerici solution) is $4{\cdot}01 \pm 0{\cdot}05$, and together with the measured cell-size, this leads to a cell-content of 4·54 molecules of the above formula, which is clearly out of the question. Computing instead the actual atomic cell-contents from the specific gravity, cell-size, and chemical analysis, the figures given in column 5 are obtained; allowing for the fact that the determined

[1] Assistant-Keepers in the Mineral Department of the British Museum of Natural History.

[2] Stated by Mr. Legrand to be a 'mine with complex zinc and lead minerals, unfortunately very rich in arsenic, which renders it unworkable'.

[3] Two determinations were made and gave sp. gr. 3·98 and 4·04.

amount of ferric oxide may include a little arsenic pentoxide, these agree well with the formula $Zn_{14}(AsO_4)_9OH.12H_2O$, which is therefore proposed for the mineral.[1] As columns 2 and 3 of table I show, the composition calculated from this formula agrees distinctly better with the analysis than does the calculated composition for $Zn_3As_2O_8 \cdot 3H_2O$. There is a small degree of replacement of zinc by iron and a trace of manganese.

TABLE I. Chemical analysis and molecular ratios of legrandite; also the atomic cell-contents calculated from the analysis, specific gravity, and X-ray data.

		Calculated for:			
	Analysis.	$Zn_3As_2O_8.3H_2O$.	$Zn_{14}(AsO_4)_9OH.12H_2O$.	Molecular ratios.	Atomic cell-contents.
As_2O_5 ...	42·02 %	43·53 %	43·11 %	1·000	As 8·80
ZnO ...	46·68	46·23	47·49	3·138	Zn 13·79
Fe_2O_3 ...	2·14	—	—	0·073	Fe 0·64 } 14·45
MnO ...	0·05	—	—	0·003	Mn 0·02
H_2O ...	9·36	10·24	9·40	2·842	H 24·98
Total ...	100·25	100·00	100·00	—	—
Oxygen ...	32·69 %	33·30 %	32·68 %	11·176	O 49·01

Weight of material used for the analysis 0·2190 gram. The arsenic was precipitated as sulphide and weighed as magnesium pyroarsenate. The zinc was precipitated as sulphide and weighed as pyrophosphate. Manganese was determined colorimetrically, and the total iron was estimated as Fe_2O_3. Calcium, magnesium, and cadmium were tested for and found to be absent. Owing to the small amount of material available, the water could only be obtained as loss on ignition; qualitative tests show that carbonates are absent, but fluorine or chlorine might possibly be present and would be included with the water.

The colour of the mineral as observed on the specimen is canary-yellow, but closer examination shows that it is not uniform—in places the mineral is almost, if not quite, colourless. It is possible that the iron shown by the analysis was originally present in the mineral in the ferrous state, and that the yellow colour is due to local oxidation of the iron, corresponding to an isomorphous admixture of $Zn_{13}(AsO_4)_9FeO.12H_2O$ instead of $Zn_{13}(AsO_4)_9FeOH.12H_2O$, but the quantity of material was insufficient to test this point, or to determine the state of oxidation of the iron. The pleochroism mentioned below suggests that the colour, although non-uniform, is not due to inclusions of limonite. Moreover, the crystals were all perfectly clear.

[1] The comparative complexity of the formula as shown by the X-ray data suggests that the simple formulae usually given to some other arsenates and phosphates may require revision.

The refractive indices of the mineral were measured by the immersion method, which gave α 1·675, β 1·690, and γ 1·735 for sodium-light (all $\pm$0·005), and (very approximately) by the prism method on a small, natural prism (110) : (1$\bar{1}$0). Owing to multiple reflections from the prism-faces, the angle of the refracting prism could not be exactly fixed; hence the values found probably give a fairly accurate measure of the birefringence and dispersion, but only

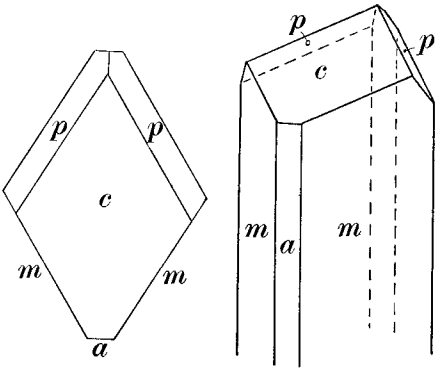

FIG. 1. Crystal of legrandite (plan and clinographic drawing).

a very approximate one of the actual indices. The values found by the prism method were : α 1·702 (red light), 1·709 (yellow), and 1·717 (blue); γ'(vibrations parallel to the *c*-axis) 1·721 (red), 1·724 (yellow), and 1·753 (blue). Approximate determinations of the birefringence, under the microscope, gave $\beta - \alpha$ 0·015 and $\gamma - \alpha$ 0·07. The optical orientation, determined on cleavage fragments under the microscope, is $Bx_o(\alpha) \perp$ b (010), $Bx_a(\gamma)$ at 36–40° to the *c*-axis in the acute angle β. The mineral is optically positive, and the optic axial angle, 2E, was measured approximately under the microscope, and found to be 65° $\pm$ 5°, with $\rho < v$ distinct, and a slight horizontal dispersion of the acute bisectrix. The more deeply coloured parts of the mineral are distinctly pleochroic, the yellow colour of fragments lying on *b* (010) being more intense for vibrations parallel to the acute bisectrix than for those parallel to the third mean line.

An X-ray examination confirmed the monoclinic symmetry of the mineral, and gave the unit-cell dimensions : *a* 12·70, *b* 7·90, *c* 10·18 Å., β = 75° 35′ $\pm$ 5′. The atomic contents of the unit cell are discussed above. Time did not permit of a determination of the space-group,

but a short study of the Lauegram suggests that the lattice is the simple monoclinic. The axial ratio, calculated from the X-ray measurements, is $a : b : c = 1{\cdot}6075 : 1 : 1{\cdot}2886$, which will be seen to agree reasonably well with the approximate goniometric measurements (table II).

The only crystals suitable for goniometric measurement were three very tiny prisms, 1–2 by 0·1–0·2 mm., found in a cavity; they show the forms $a(100)$, $m(110)$, $c(001)$, and $p(\bar{1}11)$, but all the faces are poorly developed and give multiple reflections, those given by a and m being spread out in the zone [001], those given by c in [010], and those given by p in [110]. On m there are striations at 54° to the c-axis, parallel to the zone-axis $[\bar{1}11]$ (calculated angle $[001] : [\bar{1}11] = 50° 56'$). The goniometric measurements are given in table II, the calculated values being derived from the more accurate X-ray data.

TABLE II. Goniometric measurements of legrandite, with calculated values from the X-ray data. ($a : b : c = 1{\cdot}6075 : 1 : 1{\cdot}2886$; $\beta = 75° 35'$.)

Interfacial angles:	Measured.	Limits and no. of angles.	Calculated.
$am(100) : (110)$ ...	57° 13′	56° 7′–60° 13′ (14)	57° 17′
$ac(100) : (001)$ ...	75 25	71 36 –78 22 (4)	75 35
$mc(110) : (001)$ ...	82 1	81 30 –82 22 (4)	82 16
$pc(\bar{1}11) : (001)$ ...	60 58	59 17 –62 26 (4)	61 25
Interzonal angle:			
$[ca] : [cpm] = [010] : [110]$	57 46	55 18 –60 31 (8)	58 7

The original measurements were made by the senior author on a two-circle goniometer with the zone [001] in zone-adjustment, and have been in part re-computed for convenience of presentation. The setting is in agreement with the conventions suggested by Dr. T. V. Barker (Systematic crystallography, London, 1930), and the classification angles are: $cr(001) : (101) = 32° 54'$, $ar(100) : (101) = 42° 40'$, $am(100) : (110) = 57° 17'$, $bq(010) : (011) = 38° 42'$.

The specimen consists mainly of reddish-brown blende, and carries, besides the legrandite, occasional minute crystals of pyrite, and in numerous minute cavities there are tiny whitish hexagonal crystals, perhaps mimetite, and lenticular crystals resembling chalybite.