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New data on georgiadesite

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ABSTRACT. The chemistry and crystallography of type georgiadesite from Laurion, Greece, have been re-examined using electron microprobe analysis along with powder and single-crystal X-ray diffraction. Georgiadesite is monoclinic, $P2_1/c$, with $a = 13.803(10)$, $b = 7.910(2)$, $c = 10.812(4)$ Å, and $\beta = 102.68(3)°$. No twinning was observed. The probable chemical formula is either $Pb_{16}(AsO_4)_4Cl_{14}O_2(OH)_2$ or $Pb_{16}(AsO_4)_4Cl_{14}(OH)_6$. The calculated densities for these formulae are 6.39 and 6.44 g/cm^3, respectively, compared to a measured value of 6.3 ± 0.3 g/cm^3.

THE mines and associated slag deposits at Laurion, Attike, Greece, are renowned for their production of rare and exotic mineral species, some of which are unique to that locality (Kohlberger, 1976). One of the rarest of these is georgiadesite, whose existence was discovered by Lacroix and de Schulten (1907, 1908) on what was, until recently, a unique specimen. The new mineral was described as being a lead arsenate chloride of probable formula $Pb_3(AsO_4)Cl_3$ and orthorhombic–pseudohexagonal symmetry. The original morphological data were subsequently reinterpreted by Palache (Palache *et al.*, 1951), who considered the crystals to be monoclinic but composed of 'polysynthetic lamellar twins'.

In the last three years additional specimens of georgiadesite having a provenance similar to that of the type specimen have come to light. Dunn and Rouse (1980) and Schnorrer-Köhler *et al.* (1981) have reported georgiadesite occurring with one or more of the minerals nealite, laurionite, and phosgenite lining cavities in specimens of slag from Laurion. In the present report we re-examine the chemistry and crystallography of georgiadesite using crystals from a portion of the type specimen, which had been presented to the American Museum of Natural History (AMNH no. 28427) by Professor Claude Guillemin. We also present the first published set of powder X-ray diffraction data for georgiadesite, which should facilitate the discovery of new occurrences of this previously obscure mineral.

Experimental methods and results. Georgiadesite was chemically analysed with an ARL-SEMQ electron microprobe using an operating voltage of 15 kV and a beam current of 0.15 μA. The standards used were synthetic PbO for lead, $Cu_2(AsO_4)OH$ for arsenic, and NaCl for chlorine. No additional elements of atomic number nine or greater were detected. The intensity data were corrected by the computer program MAGIC-4 and the resulting quantitative analysis, together with the original analysis of Lacroix and de Schulten (1907, 1908), appears in Table I.

Fragments of a georgiadesite crystal identical in appearance to the drawing in Lacroix and de Schulten (1908) were examined by the precession and rotating crystal methods. The mineral proved to be monoclinic, $P2_1/c$, with unit-cell parameters $a = 13.803(10)$, $b = 7.910(2)$, $c = 10.812(4)$ Å, and $\beta = 102.68(3)°$. The parameters were refined by

TABLE I. *Chemical analyses and unit-cell contents of georgiadesite*

	Present study		Previous work*		Theory†
	wt. %	atoms/cell	wt. %	atoms/cell	wt. %
PbO	81.3	15.7	78.05	15.3	80.55
As_2O_5	11.2	4.2	12.49	4.7	10.37
Cl	11.3	13.8	12.47	15.3	11.20
H_2O	—		—		0.41
O = Cl	2.6		2.81		2.53
Total	101.2		100.20		100.00

* Lacroix and de Schulten (1907, 1908). Analysis recalculated to conform to conventional presentation.

† For $Pb_{16}(AsO_4)_4Cl_{14}O_2(OH)_2$.

Accuracy of electron microprobe data is ±5% of amount present.

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least-squares from the powder diffraction data, which had been corrected with an NBS silicon internal standard ($a = 5.43088$ Å) and indexed with the aid of the single-crystal photographs. The full set of powder data appears in Table II. Georgiadesite is, in fact, monoclinic as suggested by Palache, but no twinning relationship could be recognized on the precession photographs. Each crystal fragment was, however, composed of several individuals, apparently in parallel alignment.

TABLE II. *X-ray powder diffraction data for georgiadesite**

I	d_{meas}	d_{calc}	hkl	I	d_{meas}	d_{calc}	hkl
3	6.33	6.33	011			2.463	412
2	5.47	5.46	111	1b	2.456	2.455	230
3	5.30	5.32	$10\bar{2}$			2.450	$32\bar{3}$
		5.27	002	< 1	2.393	2.395	313
< 1	4.951	4.948	$21\bar{1}$	< 1	2.354	2.350	231
2	4.679	4.681	$20\bar{2}$	< 1	2.299	2.304	$51\bar{3}$
< 1	4.411	4.417	$11\bar{2}$			2.297	$23\bar{2}$
3	4.031	4.028	$21\bar{2}$	< 1	2.230	2.231	$12\bar{4}$
5	3.955	3.964	112			2.266	520
		3.955	020	< 1	2.207	2.210	502
2	3.862	3.862	$30\bar{2}$			2.208	$22\bar{4}$
3	3.773	3.770	202	< 1	2.160	2.161	232
< 1	3.471	3.471	$31\bar{2}$	2	2.131	2.133	$50\bar{4}$
2	3.414	3.410	220			2.131	$32\bar{4}$
		3.403	212	< 1	2.083	2.083	304
5	3.164	3.164	022	< 1	2.052		
10	3.096	3.099	302	3b	2.012		
		3.098	410	< 1	1.933		
< 1	3.015	3.021	$22\bar{2}$	2	1.889		
3	2.967	2.971	$32\bar{1}$	3	1.861		
		2.967	320	2	1.847		
< 1	2.900	2.903	$31\bar{3}$	< 1b	1.804		
2	2.759	2.763	$32\bar{2}$	< 1	1.772		
		2.754	321	1	1.748		
1	2.730	2.729	222	< 1	1.706		
		2.702	$10\bar{4}$	1	1.678		
3	2.698	2.697	213	< 1	1.658		
		2.693	500	< 1	1.634		
< 1	2.639	2.645	$50\bar{2}$	1	1.548		
		2.637	004	< 1	1.520		
3	2.587	2.592	$42\bar{1}$	< 1	1.496		
		2.589	130	< 1	1.482		
3	2.556	2.557	$11\bar{4}$	< 1	1.468		
< 1	2.504	2.509	$51\bar{2}$	< 1	1.426		
		2.503	123	< 1	1.410		

* 114.6 mm Gandolfi camera, Si internal standard, Cu-$K\alpha$ radiation, polycrystalline specimen, visually estimated intensities, b = broadened line.

A new determination of the density of georgiadesite, made with a Berman balance and a temperature correction, gave 6.3 ± 0.3 g/cm^3. This is considerably lower than the 7.1 g/cm^3 reported by Lacroix and de Schulten.

Discussion. The unit-cell contents of georgiadesite, as calculated from the new chemical analysis (recalculated to 100%), density, and cell volume, are $Pb_{15.7}(AsO_4)_{4.2}Cl_{13.8}O_{2.5}$, which may be idealized as $Pb_{16}(AsO_4)_4Cl_{14}O_2$ (or O_3). Assuming two oxygen atoms leads to an imbalance in the valence sums and assuming three oxygens gives a formula inconsistent with the equipoint multiplicities (twofold and fourfold) of space group $P2_1/c$. However, no water determination could be made by us and none was reported by Lacroix and de Schulten. If hydroxyl ion is present, two formulae are possible, both of them consistent with the observed space group and density (6.3 g/cm^3). These are $Pb_{16}(AsO_4)_4Cl_{14}O_2(OH)_2$ and $Pb_{16}(AsO_4)_4Cl_{14}(OH)_6$, which yield calculated densities of 6.39 and 6.44 g/cm^3, respectively. Other formulae are possible if Pb^{4+} or $(AsO_3)^{3-}$ are present, but this seems unlikely in view of the rarity of these ions in minerals generally and the fact that all of the lead-bearing species associated with georgiadesite, namely nealite, fiedlerite, laurionite, phosgenite, and matlockite, contain only divalent lead.

There remains the question of why the density and simple formula $Pb_3(AsO_4)Cl_3$ proposed by Lacroix and de Schulten are not in good agreement with our results on crystals from the same specimen. A possible explanation of the discrepancy may be found in the minute amount of material (0.1249 g) used by Lacroix and de Schulten for the original chemical analysis. This suggests the probability of substantial errors in their results and the formula derived from them (M. H. Hey, pers. comm.). Moreover, if this same small quantity had been previously used for a pycnometric density determination (the method was not specified), that quantity may also be substantially in error. We believe that the new density and chemical data, which were determined by modern microanalytical methods, more correctly represent the true values for georgiadesite.

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