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New Data on Fiedlerite-1*A* from Ancient Slags of Lavrion, Greece: Crystal Structure and Hydrogen Bonding

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Abstract—The crystal structure (R = 0.0750) of fiedlerite-1*A* $Pb_3Cl_4F(OH) \cdot H_2O$ from ancient slags of Lavrion (Greece) was studied on a single crystal. The mineral is triclinic, a = 8.5741 (7) Å, b = 8.0480 (5) Å, c = 7.2695 (4) Å, α = 90.087 (5), β = 102.126 (6), γ = 103.424 (6)°, V = 476.37 (6) Å^3, Z = 2. The Pb^{2+} cations center the $Pb(1)F(H_2O)Cl_6$, $Pb(2)(OH)_2FCl_5$, and $Pb(3)(OH)F_2Cl_5$ bicapped trigonal prisms. In the structure there is an additional position Pb', filled by 10% with Pb^{2+}. There are two main structural fragments alternating along the a axis: (100) layers of Pb(2)- and Pb(3)-centred polyhedra and zigzag chains, stretched along the b axis formed by Pb(1)-centred polyhedra sharing common edges. The IR spectrum of fiederlite-1*A* is given.

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The area around the city of Lavrion (Peninsula of Attica, Greece) is known for deposits of polymetallic ores, mined, with some interruptions, for about 5000 years [1]. The most active exploitation of the Lavrion ore deposits took place during two periods: the sixth through third centuries BC and from the end of the nineteenth century to the 1970s. In ancient times, ore was mined mainly for silver (lead was extracted in a subordinate amount), while slag containing other components (residual Pb, as well as Zn, Cu, As, Sb) was mainly buried in the sea. The interaction of various slag components with seawater for more than two thousand years has formed a large number of new mineral phases. To date, their diversity in the ancient Lavrion slag has exceeded one hundred, and this number includes many rare and endemic mineral species, mainly belonging to chlorides, hydroxides, arsenates, arsenites, and Pb, Cu, Fe, Zn, and Ag sulfates.

Knowledge of the forms of sequestration of toxic elements (Pb, As, Cu, etc.) in various conditions is important from the point of view of the problem of their immobilization in industrial waste. Earlier, some chlorarsenites, $Pb_5(As^{3+}O_3)Cl_7$, $Pb_2(As^{3+}O_2OH)Cl_2$, and $Pb_6Cu^+(As^{3+}O_3)_2Cl_7$ [2–4] were described in the Lavrion slags. These compounds contain arsenic and copper in low-charge states, which are not quite common for minerals from the hypergene zone of ore deposits, which unequivocally implies the reducing conditions of crystallization in the system "metallurgical slag—seawater." This paper presents new data on fiedlerite-1*A* from ancient slag dumps buried in the sea near Pacha Limani.

Fiedlerite ($Pb_3Cl_4F(OH) \cdot H_2O$) is a rare mineral mainly of anthropogenic origin: it is mainly formed as a secondary phase of metallurgical slags [1, 5–7]. Earlier, fiedlerite-2*M* was studied from antique slags of Lavrion, and in some of its crystals, the presence of ingrowths of polytype 1*A* was noted (disordered mixed-layer intergrowths with the prevailing polytype 2*M*) [8]. The finding of single crystals of the fiedlerite-1*A* in the slag from Paha Limani allowed to refine its crystal structure, to obtain a high-quality IR spectrum, and to reveal a type of hydrogen bonds. Fiedlerite-1*A* forms colorless tabular crystals with a size up to 0.1 × 0.3 × 0.5 mm in caverns (gas bubbles) of predominantly silicate slag in close association with light yellow thick—lath and isometric crystals of phosgenite $Pb_2(CO_3)Cl_2$.

The fidlerite-1*A* chemical composition was studied by the method of local X-ray spectral analysis using a Tescan Vega II XMU scanning electron microscope with INCAx–sight energy dispersive spectrometer (accelerating voltage 15.7 kV, probe current 0.5 nA). The composition was determined (average of three

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Table 1. Atom coordinates (x, y, z) their thermal displacement parameters (U_{eq}, Å^2) and site occupancy factors (s.o.f.) in the fiedlerite-1*A* structure

Position	x	y	z	U_{eq}	s.o.f.
Pb(1)	0.37024(11)	0.21458(12)	0.32535(13)	0.0208(4)	$Pb_{0.903(5)}$
Pb'	0.3705(9)	−0.2762(10)	0.3233(13)	0.018(3)	$Pb_{0.097(5)}$
Pb(2)	0.89593(10)	0.35231(10)	0.27289(12)	0.0210(5)	1
Pb(3)	0.90088(10)	0.84639(10)	0.25981(12)	0.0211(5)	1
Cl(1)	0.1925(7)	0.4209(8)	0.0843(8)	0.0248(13)	1
Cl(2)	0.3448(7)	0.4595(8)	0.6354(10)	0.0257(12)	1
Cl(3)	0.1951(7)	0.9226(8)	0.0913(8)	0.0261(13)	1
Cl(4)	0.3496(8)	0.9658(8)	0.6343(11)	0.0280(13)	1
F	0.9289(18)	0.8595(19)	0.612(2)	0.029(3)	$F_{0.90}(OH)_{0.10}$
O = OH	0.945(2)	0.364(2)	0.614(2)	0.020(3)	$(OH)_{0.90}F_{0.10}$
Ow = H_2O	0.5019(19)	0.7526(16)	0.9959(17)	0.029(5)	1

measurements, wt %): Pb 76.46, Cl 17.34, F 2.24, total 96.04. The H_2O was not determined due to an insufficient amount of samples. The empirical formula calculated for 3 Pb atoms taking into account the charge balance and X-ray analysis results (see below) is $Pb_{3.00}Cl_{3.98}F_{0.96}(OH)_{1.06} \cdot H_2O$. The crystal structure of fiedlerite-1*A* was studied for a single crystal of 0.04 × 0.09 × 0.28 mm size. A three-dimensional set of diffraction data was obtained at room temperature using a single-crystal diffractometer Xcalibur S CCD with MoK_α radiation (λ = 0.71073 Å) for a full sphere of reciprocal space for an angular interval of θ = 2.61°–26.37°. The experimental data were processed using the CrysAlis v. 1.171.37.34 software. The parameters of the triclinic unit cell, refined using 4380 reflections, are the following: a = 8.5741 (7) Å, b = 8.0480 (5) Å, c = 7.2695 (4) Å, α = 90.087 (5)°, β = 102.126 (6)°, γ = 103.424 (6)°, V = 476.37 (6) Å^3, Z = 2. The structure was determined by direct methods in the space group P-1 and refined in anisotropic approximation of atomic thermal displacement parameters using the SHELX-97 program package [9]. The final divergence factor R = 0.0750 for 1723 independent reflections with $I > 2\sigma(I)$. The coordinates of atoms and their thermal displacement parameters are given in Table 1.

The structure of fiedleriite-1*A* from Lavrion is close to the previously studied structure of this polytype from ancient iron ore slags of the Etruscan period from the coast of the Baratti Gulf in Tuscany, Italy [8]. Pb^{2+} cations in three main crystallographically nonequivalent positions center bicapped trigonal prisms (coordination number = 8) $Pb(1)F(H_2O)Cl_6$, $Pb(2)(OH)_2FCl_5$, and $Pb(3)(OH)F_2Cl_5$. The main difference in the sample studied by us from the Italian fiedlerite-1*A* is the presence of an additional position (Pb'), partially filled (by 10%) with Pb^{2+} cations. This position is located at a distance of 2.97 Å from Pb(1), which prohibits their simultaneous occupancy. Refinement of the Pb(1) occupancy coefficient showed that this position is by 90% occupied with Pb^{2+} cations. Pb' also centers the $Pb'(OH)(H_2O)Cl_6$ bicapped trigonal prism. The interatomic distances of the fiedlerite-1*A* structure are shown in Table 2. The structure has two main fragments alternating along the *a* axis: (100) layers of alternating Pb(2)- and Pb(3)-centered polyhedra (Fig. 1a) and elongated along the *b* axis zigzag chains of Pb(1) polyhedra interconnected through common edges [polyhedra centered with a weakly occupied Pb' position form topologically identical chains “nested” in Pb(1) chains (Fig. 1b)]. The structure of fiedlerite-1*A* is shown in Fig 1c. The positions of the F^- and OH^- anions are located according

Table 2. Interatomic distances (Å) in the fiedlerite-1*A* structure

Pb(1)	– F	2.632(13)	Pb(1)	– O	2.444(17)
	– Ow	2.769(13)		– F	2.517(16)
	– Cl(3)	2.819(6)		– F	2.535(16)
	– Cl(1)	2.865(6)		– Cl(3)	2.970(6)
	– Cl(4)	3.016(6)		– Cl(2)	3.058(6)
	– Cl(4)	3.048(6)		– Cl(4)	3.113(6)
	– Cl(2)	3.067(6)		– Cl(1)	3.141(7)
	– Cl(2)	3.108(6)		– Cl(3)	3.239(6)
Pb(2)	– O	2.415(16)	Pb'	– O	2.767(17)
	– O	2.427(17)		– Cl(3)	2.780(10)
	– F	2.555(14)		– Ow	2.827(16)
	– Cl(2)	3.004(6)		– Cl(1)	2.905(11)
	– Cl(1)	3.077(6)		– Cl(4)	2.999(10)
	– Cl(4)	3.089(6)		– Cl(4)	3.042(11)
	– Cl(1)	3.237(6)		– Cl(2)	3.096(9)
	– Cl(3)	3.290(6)		– Cl(2)	3.118(10)

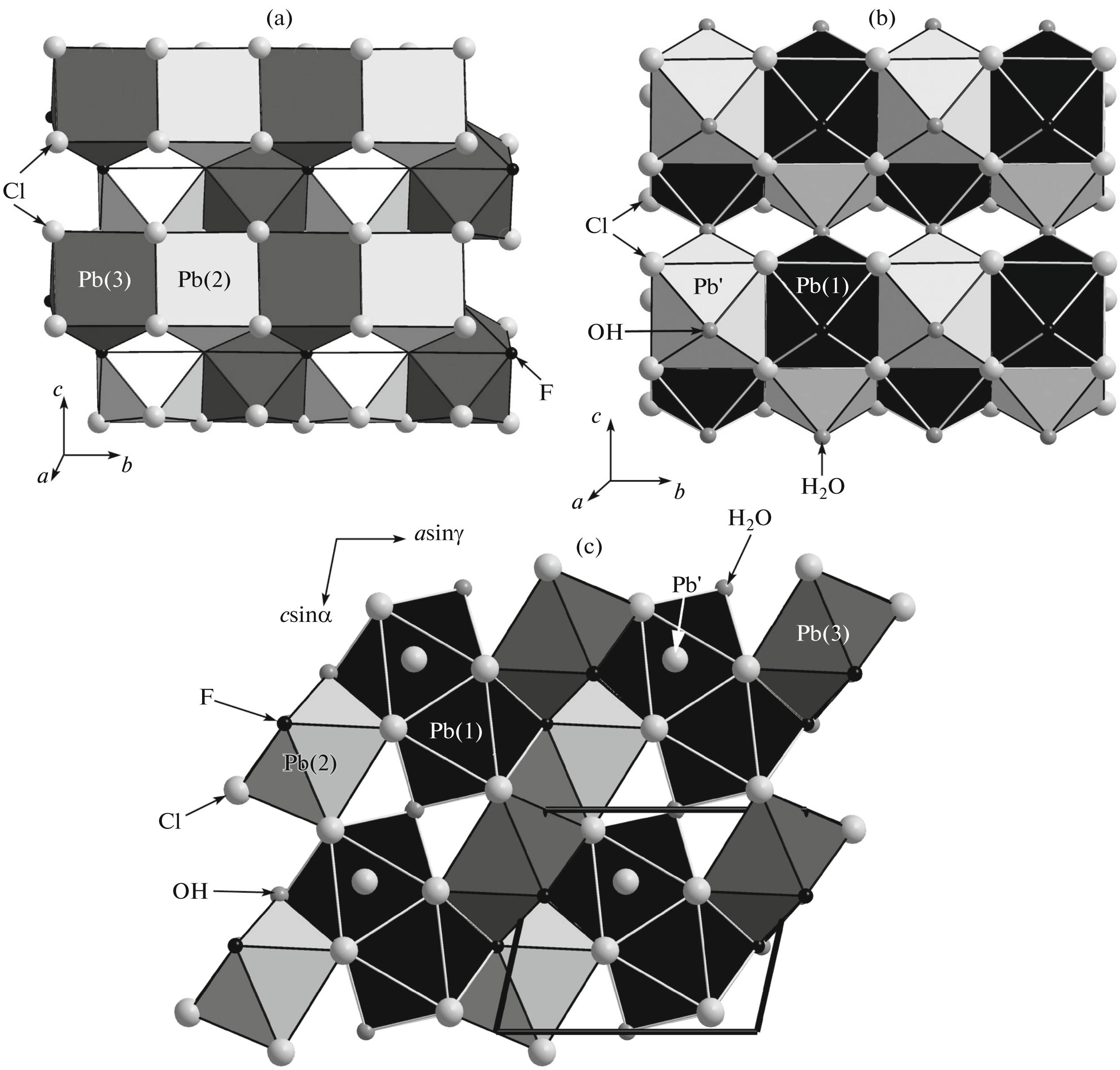

Fig. 1. Layer formed by Pb(2)- and Pb(3)-centered polyhedra (a), the layer formed by Pb(1)- and Pb'-centered polyhedra (b) and alteration of these layers in the structure of fiedlerite-1*A* (projected along *b*) (c) (Pb' sites are light gray circles).

to the principle proposed in [8]: a position tetrahedrally coordinated by four Pb^{2+} cations, is occupied by a fluorine atom, while a position neighbored by three lead atoms on one side is occupied by an oxygen atom of OH group (with the hydrogen atom possibly located on the side opposite to the triangle of Pb atoms). The site partially (by 10%) occupied by the Pb' position is located in such a way that it completes to a tetrahedron the triangular coordination of the position of the oxygen atom of an OH group. Thus, in our case, this anionic position is occupied with oxygen by 90% with and fluorine by 10%. The occurrence of fluorine in the OH position is realized when the Pb' position is filled. For the position of F, the situation is similar: its population with F atoms is 90%, which corresponds to the situation when the Pb(1) position is occupied, and 10% of this position is occupied by OH–oxygen atoms (in the case of filling the Pb' position and a vacancy in the Pb(1) position).

The infrared spectrum of powdered fiedlerite-1*A*, pressed into a tablet with KBr (Fig. 2), was taken employing an ALPHA FTIR Fourier spectrometer (Bruker Optics, Germany) in the range of wave numbers 360–3800 cm^{-1}, at a resolution of 4 cm^{-1} and 16 scans. A similar tablet of pure KBr was used as a comparison sample. The wave numbers of the absorption bands (cm^{-1}; s, strong band; w, weak band) and

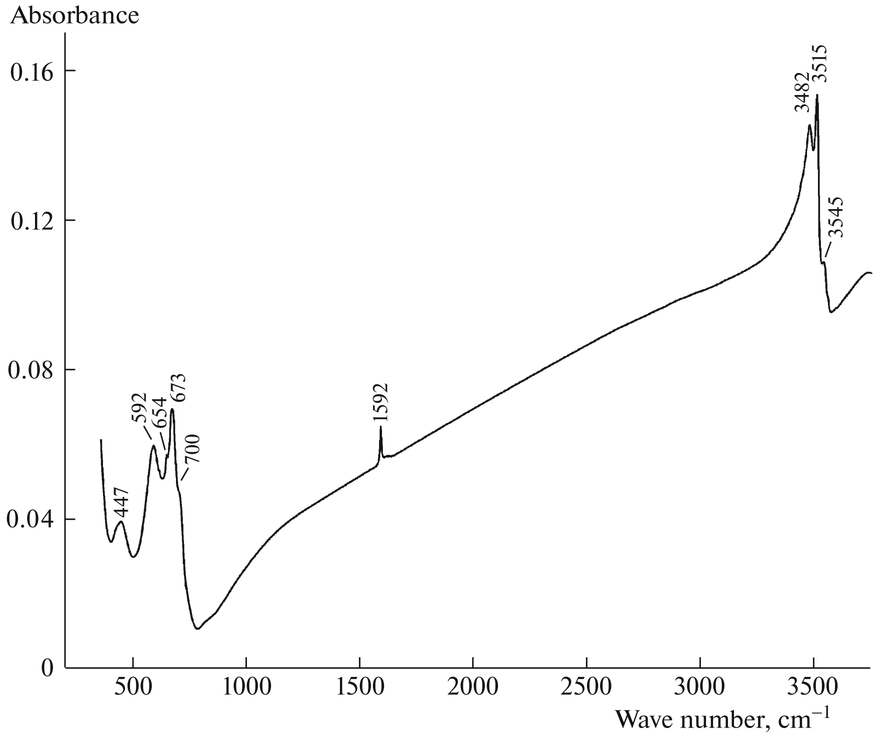

Fig. 2. IR spectrum of fiedlerite-1*A*.

their assignments are as follows: 3545w, 3515s, 3482s (O–H stretching vibrations of H_2O molecules and OH groups), 1592w (deformation vibrations of H_2O molecules), 700 (shoulder), 673s, 654, 592s (deformation vibrations of Pb···O–H), 447 (liberation vibrations of water molecules).

According to the well-known correlation between the position of the band of O–H valence vibration in the IR spectrum and the O···O distance between the oxygen atoms of the donor group of the hydrogen bond and its acceptor [10], the band at 3482 cm^{-1} corresponds to O···O equal to 2.87 Å. The OH···OH distance of 2.83 (3) Å agrees well with this value. The weak band at 3545 cm^{-1} corresponds to the OH···OH distance of 2.98 Å. The low intensity of this band suggests that it can be attributed to extrinsic OH groups in the F position: the OH···OHF distance is 2.95 (2) Å. Thus, the most intense O–H valent vibration band at 3515 cm^{-1} should be assigned to H_2O molecules, which form weak hydrogen bonds with Cl^- ions.

Each OH group has two degrees of freedom associated with the deformation vibrations of Pb···O–H. Considering this fact, the strong bands at 592 and 673 cm^{-1} are attributed to vibrations of the hydroxyl groups in the OH position, and the weak bands at 654 and 700 cm^{-1}, to vibrations of extrinsic OH groups in the F position.

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