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A Re-appraisal of the Chemical Formula of Nealite, $Pb_4Fe(AsO_3)_2Cl_4 . 2H_2O$, on the Basis of a Crystal Structure Determination

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With 1 Figure

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Summary

A crystal structure determination of the mineral nealite, $Pb_4Fe(AsO_3)_2Cl_4 . 2H_2O$, (a = 6.548(4), b = 10.243(8), c = 5.587(3) [Å]; α = 96.2(1), β = 89.6(1), γ = 97.7(1) [°]; Z = 1; space group $P\bar{1}$-$C_i{}^1$) was performed using single crystal X-ray data and a direct method strategy; the structural parameters were fitted by least squares techniques. The structure is characterized by isolated $FeO_2Cl_2(H_2O)_2$ octahedra (Fe-O: 2.08 Å, 2x, and 2.12 Å, 2x, Fe-Cl: 2.60 Å, 2x) and AsO_3 pyramids (As-O from 1.79 to 1.89 Å) which are connected by PbO_4Cl_4 and PbO_5Cl_4 polyhedra to a framework (with Pb-O distances from 2.22 to 3.34 Å, Pb-Cl distances from 3.10 to 3.54 Å). Oscillation photographs, exposed for 20 h, show very faint streaks indicating a doubling of c, probably caused by a partial ordering of a "split" lead atom position. Nealite is the first mineral found to contain a divalent iron atom coordinated to oxygen and chlorine atoms simultaneously.

Zusammenfassung

Änderung der chemischen Formel des Nealits, $Pb_4Fe(AsO_3)_2Cl_4 . 2H_2O$, *basierend auf der Kristallstrukturbestimmung*

Die Kristallstrukturbestimmung des Minerals Nealit, $Pb_4Fe(AsO_3)_2Cl_4 . 2H_2O$, (a = 6.548(4), b = 10.243(8), c = 5.587(3) [Å]; α = 96.2(1), β = 89.6(1), γ = 97.7(1) [°]; Z = 1; Raumgruppe $P\bar{1}$-$C_i{}^1$) wurde anhand von röntgenographischen Einkristalldaten mit direkten Methoden durchgeführt und die Strukturparameter nach der Methode der kleinsten Quadrate verfeinert. Die Kristallstruktur ist charakterisiert durch isolierte $FeO_2Cl_2(H_2O)_2$-Oktaeder (Fe-O: 2.08 Å, 2x, und 2.12 Å, 2x, Fe-Cl: 2.60 Å, 2x) und

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Dedicated to Prof. Dr. Josef Zemann (Vienna) on the occasion of his 70th birthday

AsO_3-Pyramiden (As-O von 1.79 Å bis 1.89 Å), welche durch PbO_4Cl_4- und PbO_5Cl_4-Polyeder zu einem Gerüst verknüpft sind (Pb-O von 2.22 bis 3.34 Å und Pb-Cl von 3.10 bis 3.54 Å). Schwenkaufnahmen, etwa 20 h belichtet, zeigen sehr feine Schwärzungsstreifen, die auf eine Verdopplung von c hinweisen, möglicherweise durch eine teilweise Ordnung einer aufgespaltenen Position eines Bleiatoms hervorgerufen. Nealit ist das erste Mineral, in dem ein zweiwertiges Eisenatom gleichzeitig an Sauerstoff- und Chloratome gebunden ist.

Introduction

Nealite was described by *Dunn* and *Rouse* (1980) as a new mineral species from Laurion, Greece. It occurs as bright orange, transparent, bladed crystals, tabular on {010} and forming radial groups. The crystals are always twinned with the two-fold twin axis in [001]. These authors also report details regarding the paragenesis, the physical properties and chemical composition (layed upon electron microprobe analyses) recalculated to give a formula of $Pb_4Fe^{2+}(AsO_4)_2Cl_4$. The oxydation state of iron was determined by these authors using a microchemical test.

The extreme paucity of material available for study precluded the accurate determination of the valence state of arsenic and, in addition, the possible presence of hydrogen (either as water molecules or hydroxyl groups) was uncertain. To solve such problems, a single crystal structure determination is the best method. One of the first papers to use this approuch was the X-ray work undertaken on the mineral teineite by *Zemann* and *Zemann* (1962).

Table 1. *Crystal data, intensity measurements and refinement parameters for nealite*

Space group	$P\bar{1}$-C_i^1	Range of hkl	±h, ±k, ±l
a [Å]	6.548(4)	Total data	4514
b [Å]	10.243(8)	Total unique data	2150
c [Å]	5.587(3)	Internal consistency	0.062
α [°]	96.2(1)	Observed data ($I > 6\sigma_I$)	1188
β [°]	89.6(1)	Empirical absorption	
γ [°]	97.7(1)	correction	
Volume [Å^3]; Z	369.2; 1	min/max	0.043/0.070
μ (Mokα)[cm^{-1}]	497.7	Number of variables	69
ρ calc [g.cm^{-3}]	5.89	Extinction parameter	$1.2(3).10^{-6}$
$2\theta/\omega$ scan mode with		Final least-squares	
Step width [°]	0.03	shift/error	$< 10^{-3}$
Steps reflection +		Final difference Fourier	
(α_1,α_2)-splitting	50	($\Delta\rho$) max/($\Delta\rho$) min	1.13/1.060
Time/step [s]	0.5–1.5	Final R/R_w	0.139/0.139
Range of data,		Crystal	yellow cut
2θmax [°]	60	shape	plate
		and size [mm]	0.10 × 0.02 × 0.05

The data were collected on a Stoe four-circle diffractometer AED2, and graphite monochromatized MoK radiation, $\lambda = 0.7107$ Å at room temperature. All calculations were performed with the program system STRUCSY (1984) on an Eclipse S 140. The scattering functions for neutral atoms are from the International Tables for X-ray Crystallography (1974)

Table 2. *Atomic coordinates and anisotropic displacement factors*

	x	y	z	U_{11}/U_{iso}	Cl_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pb(1)	0.2014(4)	0.4519(3)	0.2450(6)	185(13)	343(17)	174(13)	14(11)	−46(9)	19(11)
Pb(2)	0.0689(5)	0.8204(4)	0.2842(12)	180(17)	343(22)	1527(58)	−6(15)	231(23)	−13(28)
Fe	0.5	0.0	0.0	133(61)	223(73)	347(83)	−34(54)	−10(57)	35(64)
As	0.3059(11)	0.6849(8)	0.7892(14)	178(33)	310(42)	232(37)	−8(30)	−13(28)	5(33)
Cl(1)	0.352(3)	0.368(2)	0.723(4)	0.30(8)					
Cl(2)	0.203(3)	0.128(2)	0.171(4)	0.34(8)					
O(1)	0.131(8)	0.634(6)	0.533(9)	0.27(12)					
O(2)	0.122(9)	0.643(6)	0.039(9)	0.31(12)					
O(3)	0.276(9)	0.856(7)	0.836(9)	0.48(17)					
O(4)	0.460(9)	0.902(7)	0.314(9)	0.43(16)					

(for atoms Pb, Fe, and As) defined as

$$\exp\left(-2\pi^2 \sum_{i=1}^{3} \sum_{j=1}^{3} U_{ij} h_i h_j a_i^* a_j^*\right) [\mathrm{pm}^2]$$

as well as isotropic displacement factores (for atoms O and Cl) defined as $\exp(-8\pi^2 u^2 \sin^2 \vartheta/\lambda^2)$ [nm^2]. Estimated standard deviations in parentheses

The present paper is also a contribution to a series of investigations on the crystal chemistry of natural arsenic chalcogenides initiated by *Josef Zemann* with studies of trippkeite, $CuAs_2O_4$ (*Zemann*, 1951) and lorandite, $TlAsS_2$ (*Zemann* and *Zemann*, 1959) and continued at the Institut für Mineralogie und Kristallographie der Universität Wien with structure investigations on freedite, $Pb_8Cu(AsO_3)_2O_3Cl_5$ (*Pertlik*, 1987) and bernardite, $TlAs_5S_8$ (*Pašava* et al., 1989).

Nealite crystals for the present structure determination were collected by *K.* and *L. Standfuss* at Laurion, Greece (cf. *Schnorrer-Köhler* et al., 1981).

Experimental

Preliminary single crystal X-ray investigations on a cut crystal chip (to obtain an untwinned fragment of nealite) were carried out by oscillation and Weissenberg film methods. The cell parameters given by *Dunn* and *Rouse* (1980) were confirmed within limits of error. Crystal data, details on intensity measurements and structure determination are compiled in Table 1. The measured X-ray data were corrected for Lorentz- and polarization effects as well as for absorption (empirical ψ scan-data).

The positions of the lead atoms were determined by direct method strategy, the positions of the other atoms (except hydrogen) determined by subsequent Fourier-summations. The structure parameters were fitted using least-squares techniques: results are listed in Table 2. Some relevant interatomic distances and bond angles are given in Table 3. Figure 1 shows the structure of nealite as a projection onto (001). A ($|F_0| - |F_c|$) list was deposited at the Institut für Mineralogie und Kristallographie der Universität Wien, Austria.

Rotation photographs of approximately one dozen crystals with [001] as the rotation axis, each exposed for at least 20 h to X-ray radiation (CuKα,β), show very faint streaks, which are never resolved into single spots, indicating that the true

Table 3. *Selected interatomic distances (Å) and bond angles (°) in nealite (estimated standard deviations in parentheses)*

Pb(1) – Cl(1) = 3.10(2)	Pb(2) – Cl(1) = 3.14(2)
– Cl(1′) = 3.14(2)	– Cl(2) = 3.29(2)
– Cl(1″) = 3.24(2)	– Cl(2′) = 3.54(2)
– Cl(2) = 3.30(2)	– Cl(2″) = 3.24(2)
– O(1) = 2.42(6)	– O(1) = 2.56(6)
– O(1′) = 2.59(6)	– O(2) = 2.22(6)
– O(2) = 2.49(6)	– O(3) = 3.34(6)
– O(2′) = 2.67(6)	– O(3′) = 2.88(6)
	– O(4) = 2.59(6)
Fe – Cl(2) = 2.60(2) × 2	As – O(1) = 1.83(7)
– O(3) = 2.08(7) × 2	– O(2) = 1.89(7)
– O(4) = 2.12(7) × 2	– O(3′) = 1.79(7)
O(1) – As – O(2) = 99(2)	
– O(3) = 99(2)	
O(2) – As – O(3) = 92(2)	

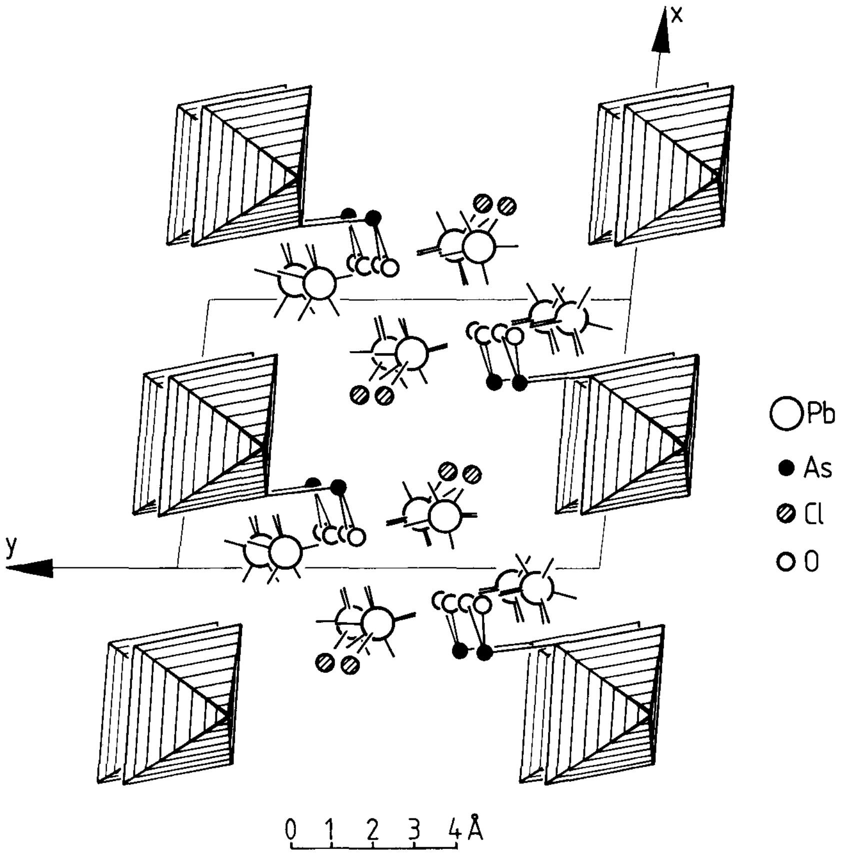

Fig. 1. Projection of the crystal structure of nealite onto (001). The $FeO_2Cl_2(H_2O)_2$ octahedra are hatched

lattice constant c of nealite is 11.174 Å. A possible explanation for this doubling by partial ordering of one split lead atom position is discussed later in this paper.

The neglected X-ray diffraction intensities of the interlayer streaks and the small volume of the crystal used for data collection only allow an inaccurate structure refinement. Although it was impossible to determine accurate structural details, the structure-type of nealite could be determined, which enabled us to revise the chemical formula on the basis of crystal chemical considerations. Besides a change in the oxidation state of arsenic (from pentavalent arsenic to trivalent arsenic), there was evidence, that nealite contains two water molecules per formula unit. To verify this, hydrogen analysis was performed using an organic microchemistry method. Although there is a great difference between the calculated hydrogen content of 0.31 wt% against the determined 0.22 wt%, the two water molecules per formula unit must be regarded as correct. The difference is caused by large analytical error; due to lack of material, only one run with ~2 mg nealite could be performed.

Discussion

The two crystallographically independent lead atoms in nealite are coordinated to four or to five oxygen atoms (Pb-O from 2.22 to 3.34 Å), respectively, and to four chlorine atoms (Pb-Cl from 3.10 to 3.54 Å). The average values for these distances for the atom Pb(l): are ⟨Pb(1)-O⟩ = 2.54 Å, ⟨Pb(1)-Cl = 3.20 Å and for Pb(2): ⟨Pb(2)-O⟩ = 2.72 Å, ⟨Pb(2)-Cl⟩ = 3.30 Å. Distances to the next atom neighbours are > 4.0 Å.

The coordination chemistry of Pb(II)O_xCl_y polyhedra, [without (OH) or (H_2O) ligands] has been investigated by *Pertlik* (1988) using twenty five examples of lead atoms in sixteen different crystal structures. Mean ⟨Pb-O⟩ bond lengths were calculated as 2.50(19) Å, mean ⟨Pb-Cl⟩ distances as 3.18(15) Å. On the basis of the available data, no dependence of the average bond lengths on the number of ligands or the ratio x:y (=O:Cl) were found.

In nealite, the values found for ⟨Pb(1)-σ⟩ and ⟨Pb(1)-Cl⟩ compare well with the values given by *Pertlik* (1988), whereas the values for ⟨Pb(2)-O⟩ and ⟨Pb(2)-Cl⟩ are unusually large. In addition, the Pb(2) atom clearly shows larger anisotropic displacement parameters in comparison with the Pb(1) atom. The root-mean-square amplitudes for Pb(1) range from 0.19 Å to 0.12 Å, but they are 0.40 Å, 0.19 Å and 0.12 Å for Pb(2). The direction of the greatest elongation of the elipsoid deviates by approximately ten degrees from [001]. A plausible explanation for this elongation is the splitting of atom position Pb(2) into two positions, separated in [001] by some tenths of an Ångstrom. This splitting into two positions reduces the mean values ⟨Pb(2)-O⟩ and ⟨Pb(2)-Cl⟩ simultaneously, and reduces the "coordination number". The interatomic distances between the atoms Pb(1) and Pb(2) and their neighbouring atoms then become comparable. A partial ordering of the atom position Pb(2) in [001] is probably indicated by the weak streaks observed on the oscillation photographs.

The iron atom in nealite (point symmetry $\bar{1}$) is six coordinated by chlorine and oxygen atoms, forming a $[FeO_2Cl_2(H_2O)_2]$ octahedron. Crystal structures in which Fe(II) atoms are simultaneously coordinated to O and Cl atoms are rare and, up until now, unknown in minerals. Similar coordination geometries have been determined for the $[FeCl_2(H_2O)_4]$ octahedron in $FeCl_2 . 4H_2O$ (*Penfold* and *Grigor*, 1959; *Meunier-Piret* and *van Meersche*, 1972) and the $[FeCl_4(H_2O)_2]$ octahedron in $FeCl_2 . 2H_2O$ (*Morosin* and *Graeber*, 1965; *Schneider* and *Weitzel*, 1976). The Fe(II)-Cl bond distances in these compounds with formally divalent iron atoms vary from 2.49 Å to 2.60 Å, and the Fe-O distances from 2.08 Å to 2.12 Å. The $FeCl_2(H_2O)_4$ octahedra are isolated in $FeCl_2 . 4H_2O$ and in nealite, in $FeCl_2 . 2H_2O$ they are combined via common Cl-Cl edges. The As atom is coordinated to three O atoms forming a trigonal pyramid with the As atom at the apex, as is characteristic for trivalent arsenic (cf. *Pertlik*, 1978, 1979). The ⟨As-O⟩ distance of 1.84 Å and the ⟨O-As-O⟩ angle with 97 ° are further indications of trivalent arsenic. Pentavalent arsenic requires a tetrahedral environment and an ⟨As-O⟩ bond length of 1.63 Å (*Shannon* and *Calvo*, 1973).

According to the bond valences of the individual atoms, there is no doubt that O(4) is part of a water molecule. This atom has one oxygen and one chlorine atom neighbour, both in different iron octahedra. The distances to these atoms are O(4)...O(4′) = 2.73 Å and O(4)...Cl(1) = 3.16 Å the angle O(4′) – O(4)-Cl is 124 °. Therefore, it can be assumed that Cl(1) is an acceptor atom of one hydrogen bridge, and O(4) is both acceptor and donor atom for hydrogen bridges. It is worth noting that in a compilation of Cl..H-O bond lengths, determined by X-ray or neutron diffraction data for the crystal structures of about ten compounds, the

Table 4. *Bond valences* (v_{ij}) *in nealite*

	Cl_1	Cl_2	O_1	O_2	O_3	O_4	$\sum V$
Pb(1)	0.557	0.125	0.713	0.585			1.980
Pb(2)	0.191	0.340	0.297	0.755	0.164	0.287	2.034
As			0.902	0.765	1.027		2.694
Fe		0.460			0.783	0.714	1.957
$\sum V$	0.748	0.925	1.912	2.105	1.974	1.001	

Note: The bond-valence parameters for the equations $v_{ij} = \exp[(R_{ij} - d_{ij})/0.37]$ according to *Brese* and *O'Keeffe* (1991) are: Pb-O: 2.112; Pb-Cl: 2.53; As-O: 1.789; Fe-Cl: 2.06; Fe-O: 1.734

distances from the acceptor Cl atoms to the donor O atoms are all within the range of 2.9 Å to 3.2 Å (*Brown* and *Altermatt*, 1985; *Pertlik* and *Dunn*, 1989).

The coordination polyhedra and the bond valence calculations (Table 4) require a formula, which differs slightly from that provided with the first description of nealite (*Dunn* and *Rouse*, 1980); namely $Pb_4Fe(AsO_3)_2Cl_4.2H_2O$ instead of $Pb_4Fe(AsO_4)_2Cl_4$. The differences between the two formulae lie in the valence state of the arsenic atom and in the water content. The valence state of the iron atom, determined by microchemical tests carried out by the first investigators now have been confirmed by bond valence calculations on the basis of the crystal structure.

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